Stellingen

behorende bij het proefschrift:

Laser Ablation and Deposition of Alloys

door

R.P. van Ingen

(1) De stellingname dat laserablatie en depositie (LAD) van vaste stoffen eenvoudig is doet de fysica en technologie van LAD sterk tekort.

Dit proefschrift.

(2) Doordat de laserablatiedepositietechniek (LAD) zich onderscheidt van andere fysische dampdepositietechnieken met name door de hoge instantane groeisnelheid van de te produceren laag vaste stof, terwijl de kinetische energieën van de deeltjes die neerslaan tenminste even groot zijn, biedt LAD, in vergelijking met de gebruikelijkere technieken, betere mogelijkheden om relatief eenvoudig bij kamertemperatuur dunne films te groeien met een metastabiele microstructuur.

Dit proefschrift: de Hoofdstukken 7 en 8.

(3) Voor een studie van fundamentele desorptiemechanismen met behulp van vluchtijdsspectrometrie c.q. vluchtijdspectroscopie van gedesorbeerde deeltjes is het van essentieel belang dat de vluchtijdverdelingen van de deeltjes in een zeer vroeg stadium na de desorptie gemeten worden en dat tegelijkertijd de interne-energieetoestand van de deeltjes gemeten wordt. Derhalve is lasergeïnduceerde-fluorescentiespectroscopie meer geschikt voor de bestudering van fundamentele laserablatiemechanismen dan quadrupoolmassaspectrometrie.

Dit proefschrift: de Hoofdstukken 3, 4, 5 en 6.
Het is kortzichtig om aan te nemen dat gassen die niet in thermodynamisch evenwicht verkeren met alleen statistische mechanica beschreven zouden kunnen worden.


Gezien de twijfelachtige kwaliteit en originaliteit van een grote fractie van het aantal wetenschappelijke publicaties, is het wenselijk dat voor publicatie in de wetenschappelijke literatuur een strengere censuur toegepast wordt. Hierdoor zal bij een gelijkblijvend aanbod relevante informatie de stroom publicaties sterk ingedamd worden.

Een goede relatie met de baas is niet essentieel om effectief te zijn in het werk.


Gezien de leidinggevende, organiserende en vertegenwoordigende taken die vele academici gedurende hun carrière toebedeeld krijgen dient per universitaire faculteit in de doctoraalprogramma's een vak "management" opgenomen te worden.

Het is redelijkerwijs niet te verifiëren of een promovendus de stellingen behorende bij zijn/haar proefschrift ontleent heeft aan zijn/haar wetenschappelijke kennis, dan wel aan zijn/haar wetenschappelijke kennis. Mede daarom dient de verplichting om aan een proefschrift stellingen toe te voegen afgeschaft te worden.

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Chapter 4  R.P. van Ingen, *Angle-resolved time-of-flight spectrometry of neutrals laser ablated from Nd$_{1.85}$Ce$_{0.15}$CuO$_4$*, submitted for publication in *J. Appl. Phys.*.

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Chapter 6  R.P. van Ingen and J.C.S. Kools, *Detection of electric-field ionized Rydberg atoms originating from laser ablation of Si*, submitted for publication in *J. Appl. Phys.*.

Chapter 7  R.P. van Ingen, R.H.J. Fastenau and E.J. Mittemeijer, *Formation of crystalline Ag$_x$Ni$_{1-x}$ solid solutions of unusually high supersaturation by laser ablation deposition*, submitted for publication in *Phys. Rev. Lett.*.

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Chapter 1
General introduction

1.1 Introduction

Since the operation of a ruby laser was first demonstrated in 1960 [1], lasers have been widely used as powerful tools for diagnostics, for example spectroscopy [2,3], and for materials processing [2,4,5]. The field of laser processing of materials encompasses a great variety of applications ranging from drilling and cutting to heat treatment and microsurgery [2,4]. Many of these applications rely on the ability of lasers to deliver high-power electromagnetic radiation to a workpiece, in a spatially and temporally confined way; that laser radiation is both monochromatic and highly coherent is of minor importance here. (See for background knowledge: reviews on the physics pertaining to lasers [6-8], on the technology of laser instrumentation [6-8] and on laser application [2,4,5].)

Lasers can be utilized to grow thin solid films, for example in laser-induced chemical vapour deposition [8,10] and in laser-induced physical vapour deposition (PVD). In nowadays technology thin films are frequently used for applications of electrical, optical, mechanical and chemical nature [11-13]. In addition, thin films offer the possibility to produce and study materials that have interesting (anomalous) properties from a scientific point of view. These properties can (artificially) be induced, because vapour deposition conditions can be chosen such that the film growth proceeds far from thermodynamic equilibrium. For example, thus films incorporating non-equilibrium phases can be formed. A PVD technique that is inherently of such non-equilibrium nature is laser ablation deposition (LAD).

1.2 Laser ablation and deposition

The principle of LAD is as follows. A target is irradiated by a pulsed, high-power laser beam; the duration and the irradiance of the laser pulses range typically from 10 to 1000 ns and from $10^8$ to $10^9$ W cm$^{-2}$, respectively. The target material is thereby transiently and locally heated. At sufficiently high temperatures the material melts and evaporates in an explosive way; a plasma is formed. This part of the LAD process is referred to as laser ablation; it has been described in detail in several reviews [4,5]. The last part of the process involves the deposition of species from the plasma onto a substrate, thereby growing a thin solid film.
LAD has been used to grow a great variety of materials since the mid 1960s [14,15]. However, only after the recent successful preparation of high-$T_c$ superconducting YBa$_2$Cu$_3$O$_{6+\delta}$ thin films using LAD [16] the technique became widely recognized as an alternative for the more conventional PVD techniques, such as evaporation and sputtering. This initiated a considerable amount of research on laser ablation and deposition [17-21].

The advantages of LAD are the following. Firstly, under high-power laser irradiation almost any material can be ablated [15]. This is independent of the material's basic optical properties, because optical breakdown due to high-irradiance laser irradiation passes nearly any material into an optically opaque state [2,4,5]; this will be explained in Chapter 2. Secondly, ablation of alloys proceeds congruently regardless possible differences between the partial evaporation enthalpies of the constituent elements, that is, the composition of the laser-produced plasmas is equal to the composition of the target [5,15]; this is also discussed in Chapter 2. As targets of a desired composition can be prepared relatively easily, for this reason, thin films of a desired composition may be grown by LAD in a less laborious and costly way than with conventional PVD techniques. Finally, LAD is associated with very high quenching rates and very high instantaneous deposition rates. The quenching rate is of the same order of magnitude as in the case of sputter deposition ($\sim10^6$ K s$^{-1}$ [22]), because the kinetic energies of laser ablated particles ($\sim$1-25 eV [4,5,15,18-21]; see also the Chapters 4 and 5) are of the same order of magnitude as those of ion-sputtered particles [22]. The instantaneous growth rate ($\sim10^{-2}$-1 nm per laser pulse [15] (see Chapter 8), corresponding to $\sim10^3$-$10^5$ nm s$^{-1}$ [15] (see also Chapter 8)), however, is substantially higher than the growth rate during sputter deposition ($\sim$10 nm s$^{-1}$ [22]). These properties enable, for example, to grow films of highly metastable nature exhibiting anomalous properties (see Chapters 7 and 8).

A major drawback, inherent to LAD is that, apart from small species (atoms, ions, etc.), a substantial number of particulates of sizes of up to a few micrometres is ablated. The incorporation of these particulates in thin films is in general undesired.

1.3 Scope of this thesis

This thesis concerns (1) the physics of laser ablation and (2) the materials science of thin films grown by LAD. The basic ablation mechanisms play an important role in determining the properties of thin films grown by LAD. Laser ablation and deposition mechanisms can roughly be separated into three categories: category 1 involves the mechanisms associated with the interaction between laser pulses and a target, category 2 involves the mechanisms associated with the interaction between laser pulses and ablated species and the interactions among the latter, and category 3 involves the mechanisms associated with the interaction between ablated species and a substrate (and the target).
General introduction

The mechanisms of category 1 are fairly well understood, especially due to studies on laser machining of metals [2,4,5] and laser annealing and alloying of semiconductors [23-25]. It appears that laser ablation proceeds as follows. Laser radiation is locally absorbed by electrons in the surface region of a target. Consequently, the target surface is heated. As the heating takes place very locally and in a very short lapse of time, material is melted and evaporated in an explosive way [4,5]. These mechanisms are dealt with in more detail in Chapter 2.

When the present research program on laser ablation and deposition was started much less was known about the mechanisms of category 2. Though laser-produced vapours and plasmas have been the subject of many studies [4,26-28], no models exist that combine all phenomena involved, as collisional interaction, excitation, ionization, recombination and plasma expansion, in one comprehensive theory. Hence, the mechanisms of these phenomena were the subject of part of our research program.

The majority of the species in a laser ablation-produced plasma are neutrals and positively charged ions, which are mono- or polyatomic. For the present work angle-resolved time-of-flight (ARTOF) spectrometry, utilizing a quadrupole mass spectrometer, was employed to characterize these species. This technique provided time-of-flight (TOF) distributions of species originating from laser ablation of alloys, selected on mass, but regardless their internal energy state, as a function of the detection angle. In addition, from these TOF distributions the yields of ablated species detected as a function of the detection angle, the so-called angle-resolved yield (ARY) distributions, were obtained. The alloys provided the possibility to study possible dependencies of the ARTOF and ARY distributions on the mass of the constituent species. On the basis of these TOF and ARY distributions much information about the mechanisms of formation and expansion of laser-ablation-produced plasmas was obtained. The laboratory-built experimental set-up and associated procedures used to conduct these experiments are described in some detail in Chapter 3.

TOF and ARY distributions of neutral atoms and diatomic molecules that arose from laser ablation of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ are presented and discussed in Chapter 4. The results are discussed in terms of pressure-gradient-induced expansion of laser-produced plasmas.

TOF and ARY distributions of positive ions originating from plasmas produced by laser ablation of Si and Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ and the degrees of ionization of those plasmas are the subject of Chapter 5. The results obtained are explained on the basis of ambipolar diffusion of electrons and ions from a plasma.

The observation and explanation of 'obscure' contributions in TOF and ARY distributions of neutrals and ions are dealt with in Chapter 6. For the sake of simplicity the experiments have been conducted using a Si model system. The said contributions are ascribed to electronically highly excited neutral species, so-called Rydberg species.
Relatively little is known about the mechanisms of category 3. In particular, it is desired to predict and control the composition and microstructure of the thin films obtained by deposition of the plasma species onto the substrate. LAD of especially metal alloy films seems not to have been investigated in a significant way. Hence, part of the present work was devoted to the analysis of the composition and microstructure of such films produced by LAD.

By choosing appropriate model systems some specific features of LAD can be explored; for example, the potential of LAD to obtain non-equilibrium phases. The model systems chosen were the binary alloys Cu-Ni and Ag-Ni. These systems have similar optical and thermophysical properties. However, both in the liquid and the solid state these alloys show contrasting mixing behaviour: Cu and Ni can form solid solutions over the entire composition range [29], whereas Ag and Ni are not soluble into each other at all [29]. The laboratory-built experimental set-up and associated procedures that were used to grow the Cu-Ni and Ag-Ni thin films is described in some detail in Chapter 3. The growth and microstructural properties of highly metastable Ag$_{x}$Ni$_{1-x}$ solid solutions, which showed anomalously high supersaturation, are discussed in Chapter 7. Finally, in Chapter 8 the results are presented of an elaborate comparative study of the compositional and microstructural properties of the said Cu-Ni and Ag-Ni films.

References

General introduction


Chapter 2

Basic physics of laser ablation

A brief phenomenological survey of the physics underlying laser ablation of metals, semiconductors and dielectrics is presented. Firstly, photon absorption by these materials and the conversion of the absorbed photon energy first into electronic energy and subsequently into mainly thermal energy are dealt with. Then, laser ablation, plasma formation and plasma expansion are discussed in some more detail, because the associated mechanisms are of major importance for the discussion of the results that are presented in the rest of this thesis.

2.1 Introduction

The field of laser ablation and deposition is inherently multidisciplinary. Insight in the basic ablation mechanisms requires knowledge of several branches of science, such as laser physics, plasma physics and materials science. In this chapter the reader is introduced into the physics underlying laser ablation, in order to enable him or her to get some insight in the results and the discussion of the experimental study of laser ablation and deposition that is the subject of this thesis.

Due to the interaction of an intense, pulsed laser beam with a target a manifold of physical mechanisms is operative. For the sake of brevity, only the major mechanisms will be dealt with in this chapter. We discuss the following sequence of events involved in laser ablation of metals, semiconductors and dielectrics: (1) photon absorption at the surface of the said targets, resulting in energetic charge carriers, (2) thermal relaxation of the energetic charge carriers, resulting in 'cold' carriers and a 'hot' target lattice, (3) heat diffusion from the surface into the bulk of the targets, and (4) laser ablation of the target surfaces and the ignition of a plasma in the ablation-produced vapour. For more background knowledge, the reader is referred to more extensive treatments on laser-solid interaction and heat production [1-4] and on laser ablation and plasma formation [1,3,5-7].

The knowledge required to have some insight in the properties of the laser-ablation-produced deposit is dependent on the nature of that deposit [8-11]; it can be obtained from various branches of science, such as materials science and solid state physics. To date, it would only be speculative to ascribe certain properties of thin solid films to the particular properties of the laser ablation and deposition process.
Therefore the impact of the basic physics of laser ablation on the properties of the thin films is not discussed in this chapter.

### 2.2 Laser-photon absorption and heat production

Photons in a laser pulse must first be absorbed by a target to cause any effect on it. The dominant physical effect of laser photon absorption on a target is heating of its surface. The nature of the laser-target interaction depends on many parameters, such as the wavelength of the photons, the duration of the laser pulses, the laser irradiance at the target surface and the optical and thermophysical properties of the target’s near-surface regions.

Photons are associated with electromagnetic radiation with wavelengths in the electromagnetic spectrum ranging from the ultraviolet (UV) regions to the infrared regions, that is, from about 100 nm up to about 10 μm. Radiation of such wavelengths interacts almost exclusively with the free electrons in metals and with the valence electrons, either bound or free, in semiconductors and dielectrics. The frequencies corresponding to such wavelengths, being higher than $3 \times 10^{13}$ Hz, are too high for the relatively heavy nuclei of the atoms in a target to significantly respond to. On the other hand, these frequencies are too low to have any significant effect on the atoms’ core electrons.

As the said wavelengths are long compared to the interatomic distances, the response of a homogeneous material can be described in terms of averaged macroscopic quantities.

#### 2.2.1 Metals

The optical appearance of a metal is basically separated in two regimes by the plasma frequency, which is of the order of $10^{15}$ Hz [3,12]. For photon frequencies lower and higher than the metal’s plasma frequency the optical reflectance and the optical absorption coefficient are high and low, respectively. According to the free-electron-gas theory [12] photons interact only strongly with the metal’s conduction electrons close to the Fermi energy level, the so-called free electrons. Hence, the basic optical properties of a metallic target are predominantly determined by the number density and the energy state of these free electrons. Photon absorption by a free electron proceeds by the inverse Bremsstrahlung mechanism: a free electron absorbs a photon, thereby gaining kinetic energy, during interaction with a heavy neutral or ionized particle in order that momentum is conserved [13]; when the electron reradiates its kinetic energy, the resulting photons are said to be reflected. The cross section for absorption involving electron-ion interaction is larger than the one involving electron-neutral interaction [1,7]. Clearly, upon photon absorption the number of free carriers in a metallic target is conserved. Because the number density
of free electrons in a metal is generally high, the optical absorption length of a metal is short, that is, typically of the order of 10 nm [3]. Hence, the photons are absorbed at the surface rather than in the bulk.

Actually, the optical appearance of metals is not fully described by the free-electron-gas model [1,3,12]. Especially under irradiation of photons with a wavelength in the visible and UV spectral regions bound, inner-shell electronic transitions contribute to absorption, resulting in a significant decrease of the reflectance. Moreover, the surface of a metal in which photons are absorbed usually has a lower reflectance than the bulk, due to contamination and macroscopic defects at the surface. Therefore, laser processing of most metals presents no particular difficulties for laser beams with photon wavelengths in the visible and UV parts of the electromagnetic spectrum.

2.2.2 Semiconductors and dielectrics

The most likely and efficient mechanism for photon absorption in semiconductors and dielectrics is simple electronic interband absorption. This mechanism involves photon-induced excitation of an electron from the valence band to the conduction band, thereby leaving a hole in the valence band [2-4,12]. To induce such a transition the photon energy must at be least equal to the band-gap energy. The excess photon energy is initially shared by the electron-hole pair as kinetic energy. Absorption of photons with an energy approximately equal to the band-gap energy in indirect band-gap materials, such as Si, requires the simultaneous absorption or emission of a phonon providing extra crystal momentum; this is not the case for direct band materials. Photons with energies lower than the band-gap energy only can induce intraband transitions [2-4,12]. In addition, substantial number densities of free carriers can also be created by thermal electron excitation. However, the latter two mechanisms are far less efficient than the interband photon-absorption mechanism.

The fore-mentioned simple picture only applies to a homogeneous target. The optical appearance of a target that is inhomogeneous on a scale of one photon wavelength or more is modified by the presence of defects, such as grain boundaries and impurities. These defects may absorb the incident photons and, additionally, due to scattering of those photons at these defects, the effective photon range and thereby the photon-absorption probability within the target may increase. Thus, even a material that would be intrinsically transparent, such as a ceramic, can be photon absorbing. Moreover, even in homogeneous materials for which the photon energy is lower than the band-gap energy free-carrier generation can be induced either by multiphoton excitation or by impact ionization. The laser irradiance required to induce these phenomena is high, usually in excess of about 10^7 W cm^-2 [3].

In a multiphoton interband transition \( n \) photons of which the combined energy exceeds the band-gap energy are absorbed simultaneously. According to the
uncertainty principle the simultaneous absorption of \( n \) photons requires that those photons are incident upon the absorbing cross-sectional area within a time interval of one period. The probability of such an event is proportional to the photon flux raised to the power \( n \) [7]. Because the cross sections become increasingly small for higher \( n \), the contribution of multiphoton ionization to free-carrier production is of practical relevance only for low values of \( n \). Therefore, the contribution of this mechanism to free-carrier production is only significant for short photon wavelengths.

Impact ionization is the inverse of Auger recombination [14-16]. Upon colliding with an atom in the target an energetic carrier is slowed down while creating an additional low-energy electron-hole pair. These new free carriers are accelerated by the photoelectromagnetic field until the mechanism of impact ionization repeats and a free carrier avalanche develops. At each stage the number of electrons is doubled, except for losses of electrons due to diffusion and recombination. When the electron number density exceeds about \( 10^{18} \) cm\(^{-3} \) the target will become essentially optically opaque. This phenomenon is known as avalanche breakdown and optical breakdown.

Once the free-carrier number densities in a semiconducting or dielectric target become sufficiently high, the target’s optical appearance becomes metallic and additional photon absorption proceeds similarly as in a metal.

2.2.3 Modified optical properties

The basic optical properties of targets as outlined in the preceding sections apply only when the photon irradiance at the target surface is so low that the energy states of the electrons and the atoms present are not substantially disturbed. The optical properties, however, can be modified under powerful laser irradiation as in the case of laser ablation. Then, the number of photons absorbed in a target may turn out to be different from the one expected from the basic optical properties. The following three photon-induced mechanisms, roughly in order of increasing irradiance, can be responsible for this: (1) heat production and resulting changes in the density or the electronic properties of the material, (2) free-carrier generation in semiconductors and dielectrics by interband absorption or impact ionization and (3) non-linear distortion of electron orbitals by the photoelectromagnetic field, for example resulting in a non-linear phenomenon such as multiphoton absorption.

Apart from these intrinsic effects, photon-target coupling also tends to be affected by photon-induced changes in the shape of the material, usually due to melting and evaporation. For example, melting of a surface by laser radiation typically leaves a trace in the from of corrugations and stalagmite-like features, which are often unrelated to the beam profile and appear even if the incident beam has a homogeneous energy distribution. Moreover, dense vapours can scatter and absorb incident photons, thereby attenuating the incident laser beam.
2.2.4 Thermalization and heat transport

After the electrons in the target surface have absorbed a quantum of photon energy their motion randomizes spatially and temporally by collisional interaction within about $10^{-14}$ s \cite{15}. Subsequently, equipartition of the electron energy takes place. The transfer of energy from the electrons to the atoms in the target lattice can proceed by several mechanisms, for example in semiconductors, dielectrics and metals by electron-atom collisions and in semiconductors and dielectrics by electron-hole recombination. The dominant recombination mechanisms is Auger recombination in which the energy released by recombination is transferred to a third carrier (an electron or a hole), on a time scale of $10^{-11}$ s \cite{14-16}. In general, the said mechanisms do not involve the lattice. The energetic electrons undergo intraband relaxation on a picosecond time scale to come into thermal equilibrium with the lattice \cite{3,15}. As the temperature increases, carrier diffusion lengths decrease; the resulting spatial localization of energetic carriers can lead to a further increase of the temperature. This relaxation proceeds so fast and the electron mean-free paths are so short that for a laser pulse with a durations of a few nanoseconds, as considered in laser ablation and deposition, the heat can be considered to be produced instantaneously in the volume where the photons were absorbed.

Once the heat is produced locally at the target surface it will diffuse into the bulk. The balance between the rate at which the heat is produced and the rate at which it is removed determines the resulting spatial and temporal temperature distribution. The mathematical theory of heat conduction is based on the assumption that the heat flux across a plane is proportional to the local temperature gradient. This assumption has resulted in the so-called heat-flow equations \cite{1,17-19}. The problem of calculating the spatial-temporal temperature profiles due to laser irradiation has been examined extensively with regard to laser processing of metals \cite{1} and especially of semiconductors \cite{17,19}. For many cases of practical interest, the problem can be regarded as being one-dimensional: the transverse dimensions of the laser beam are large compared to the depth to which heat is conducted. Nevertheless, accurate temperature distributions must be calculated numerically \cite{18}, because the thermophysical properties of a material, such as thermal conductivities, heat capacity, etc., are dependent on temperature. For example, due to electron-phonon interactions the gap energy of semiconductors and the reflectance of materials decrease with temperature and some semiconducting materials, including Si, become metallic upon melting \cite{2,3}.

From these heat flow calculations the heating and cooling rates and temperature gradients in a target surface under high-power laser irradiation are estimated to be of the order of $10^9$ K s$^{-1}$ and $10^7$ K cm$^{-1}$, respectively. When the temperature becomes sufficiently high, locally the target surface starts melting. The heating and cooling cycles for nanosecond irradiation are very short compared to the
times required for the constituent elements in alloys to diffuse substantially out of the heated region [3,6]. Therefore, in first order approximation the composition of the laser-produced melt will be equal to the composition of the alloy, which can be advantageous for the application of LAD.

2.3 Ablation

When the laser irradiance at the target surface becomes sufficiently high, locally the target does not only melt, but also starts to evaporate in an explosive way. This is called laser ablation. The ablated species can acquire high kinetic energies, that is, of the order of a few electronvolts or more. The minimum irradiance required for ablation of a metal can be estimated to be of the order of $10^8 \text{ W cm}^{-2}$ [20]. For a semiconductor or a dielectric a significantly lower irradiance is sufficient, due to the fact that these materials have a lower reflectance than a metal. As far as kinetics is concerned, laser ablation is thought to proceed via two distinct modes [3]: either via surface evaporation or via volume evaporation. We now present a brief phenomenological description of both mechanisms.

Surface evaporation is the normal case for media with a short photon-absorption length, such as metals. Such media melt upon high-power pulsed laser irradiation at the open surface. When the temperature of the melt becomes sufficiently high particles start evaporating from that melt. The evaporated particles constitute a Maxwell-Boltzmann kinetic-energy distribution associated to the local surface temperature; the particles’ angular distribution with respect to the target-surface normal is cosine-like. If the number density of evaporated particles is sufficiently low, those particles have a mean free path that is sufficiently long so as to travel from the melt without, or with negligible, mutual collisional interaction. However, for evaporation rates exceeding about a few tenths of a monolayer per 10 ns the mean free path is thus short that collisions amongst the particles take place [21-23]. The region in which such collisions take place will be referred to as the collisional region. (In some literature this region of gas-dynamic discontinuity is also called the Knudsen layer.) Within this region a new thermodynamic quasi-equilibrium is reached, associated to a temperature different from the temperature of the melt from which the vapour evolved; associated vapour pressures can be of the order of $10^6 \text{ Pa}$. When the pressure in the collisional region is high enough, upon equilibration the region becomes an isolated system flowing along the target surface normal. It dissolves by pressure-gradient-induced expansion; a simple assumption, often made, is that the expansion proceeds adiabatically. Upon expansion the temperature and the pressure within the collisional region decrease rapidly, while the kinetic energies of the constituent particles increase. A detailed discussion on vapour expansion can be found in literature [24,25]. Monte-Carlo simulations [21-23] and analytical calculations [26,27] have shown that the said mechanisms cause the nascent kinetic
energy and angular distributions to be modified: particles emitted at low angles with respect to the target-surface normal acquire higher kinetic energies and their number densities increase at the expense of those emitted at high angles. Hence, the expansion of pulsed-laser-produced vapours appears to resemble the expansion of continuum free jets [26-28]. The said modifications could be caused by as few as about three collisions on average [22], but the higher the average number of collisions involved, the more pronounced the modifications are. As in a non-spherical collisional region the pressure gradients in the direction of the region’s smallest dimension are higher than in the other direction, the said effects in the former direction are also more pronounced than in the latter direction [29].

Volume evaporation may play a role in media with a relatively long photon absorption length, such as dielectrics. Upon high-power laser irradiation in such materials a relatively thick volume at the surface is heated. As initially the evaporating species extract thermal energy, of the order of the binding energy plus some excess energy, only from the surface the temperature beneath the surface can exceed the temperature at the surface. As a result volume evaporation may take place. Relatively high subsurface temperatures favour subsurface superheating and explosive volume evaporation. A liquid is superheated if the actual pressure in a liquid at a temperature is less than might have been expected thermodynamically at that temperature. Superheated liquids can exist as a metastable state if the vapour pressure is below that necessary for the nucleation and growth of vapour bubbles from atomic-scale voids [30]. However, at some critical temperature the liquid can no longer sustain the tensile forces present and statistical pressure fluctuations initiate explosive nucleation and growth of vapour bubbles; associated vapour pressures are of the order of $10^8$ Pa. As a large change in density is associated with vapour nucleation, the strong increase in the nucleation rate above the nucleation temperature causes violent expansion of the superheated liquid, thereby removing intervening (condensed) material from the target surface. This is called a vapour explosion.

In the preceding section it has been argued that for laser ablation of alloys the composition of the melt is almost equal to the local target composition. Moreover, upon ablation the atoms can acquire thermal energies far in excess of their binding energies, so that differences in the partial evaporation enthalpies of the species become unimportant. Thus, alloys are congruently ablated, that is, the vapour also has the same composition as the target. Due to its ability to preserve the target composition in the vapour, laser ablation is used amongst others for the deposition of thin films.

Violent boiling may result in the emission of particulates and droplets of liquid material. However, the emission of the said species can also be caused otherwise. The said evolving vapours exert recoil forces to the target surface. In general, the primary target of the vapour recoil is the melt from which particles evaporate. The recoil
forces result in displacement of the liquid melt. This can result in the emission of droplets of material. Moreover, resolidification of the melt results in the formation of corrugations and stalagmite-like features at the ablated spot. As a result, upon subsequent ablation small particles of molten and resolidified material may break off and be carried along with the vapour flowing away from the surface. This results in droplet deposition onto a substrate, which is one of the major drawbacks of LAD.

2.4 Plasma formation

For the irradiances employed in laser ablation, that is, of the order of $10^8$ W cm$^{-2}$ or higher, the laser-produced vapour becomes a plasma. Laser-induced plasmas have been the subject of many extensive studies [1,5,7,20]. Nevertheless, due to the complexity of plasmas, involving processes such as photon absorption, excitation, plasma expansion, to date there are no models that combine all these phenomena in one comprehensive theory. The ignition of a plasma basically starts in a hot target vapour by thermal excitation and in a cold gas by high-irradiance-induced optical breakdown.

The hot vapour represents an easily ionizable medium, due to thermal excitation of the atoms. With increasing irradiance the thermal and internal energies of the species in the vapour increase. Hence, photon absorption further heats the vapour, which in turn leads to even more absorption. This positive feedback favours the creation of a plasma in front of an evaporating target even at irradiances far below the threshold for breakdown in a cold gas.

Laser-induced gas breakdown involves the same fore-mentioned high-irradiance-induced mechanisms as avalanche breakdown in semiconductors and dielectrics [1]. Ionization for photon energies lower than the ionization energies can occur by multiphoton absorption or by avalanche (impact) ionization. Both mechanisms require laser irradiances in excess of about $10^8$ W cm$^{-2}$. Multiphoton ionization (bound-free transitions) will only contribute for short photon wavelengths. Avalanche breakdown requires the presence of some nascent free electrons. A key difference between the breakdown in semiconductors and dielectrics and in cold gases is that priming electrons are very much scarcer in the latter case. The first electrons of the avalanche have to be delivered either by thermionic electron emission from the heated target or by impurities with a low-ionization potential, like dust particles, or by multiphoton ionization of gas atoms. In addition, thermionic emission of positive ions from the heated target can contribute to the number of ions present in the plasma.

Further excitation and ionization generally commences via electron-neutral inverse Bremsstrahlung (free-free transitions), but when sufficient electrons are generated, the dominant photon absorption mechanism makes a transition to electron-ion inverse Bremsstrahlung. This is due to the fact that the number density of neutrals
decreases, whereas the number density of ions increases, while the absorption coefficient associated to the latter mechanism is about three orders of magnitude higher than for the former one. Once the gas is fully ionized, light absorption is dominated by inverse Bremsstrahlung absorption. Above the cutoff density (~10^{21} \text{ cm}^{-3}), where the plasma frequency exceeds the laser frequency, the plasma behaves essentially like a metal.

References

Chapter 3

Experimental set-ups and procedures for laser ablation deposition and time-of-flight spectrometry

For the basic work described in this thesis two laboratory-designed and constructed ultrahigh vacuum systems were used: one for laser ablation of solids and deposition of thin solid films, and one for laser ablation of solids and angle-resolved time-of-flight quadrupole mass spectrometry of ablated species. Here, the set-ups and associated procedures are described in some detail.

3.1 Introduction

The initial goal of the research program of which the main results are discussed in this thesis was three-fold: (1) to investigate the basic mechanisms of laser ablation and deposition, (2) to explore the technological applications of laser ablation deposition (LAD) and (3) to produce (high-$T_c$) superconducting thin films using LAD and to study their physical properties. In the course of time we directed our attention to the growth of metallic alloy thin films with LAD and the analysis of the physical and metallurgical properties of those films. As the ultrahigh vacuum systems that were required for the basic work of this research program could not be purchased as a whole, they were laboratory-designed and built.

For the study of the basic laser ablation mechanisms, in particular those involved in the formation and the expansion of the laser-ablation-produced plasmas, angle-resolved time-of-flight (ARTOF) quadrupole mass spectrometry was employed. This technique was chosen, because it enables to measure the time-of-flight (TOF) distributions of neutral species and of ionized species, selected on their mass-to-charge ratio, but in general regardless of their momenta and regardless of their internal energy state [1]. (See for a review of some methods for plasma diagnostics: [2].)
3.2 The Laser Ablation Deposition Investigation and Etching System

The basic set-up that was used for laser ablation and deposition is shown schematically in Fig. 3.1; it was called the Laser Ablation Deposition Investigation and Etching System (LADIES). The stainless steel ultrahigh vacuum system comprised a processing chamber and a load-lock chamber (see for background information on vacuum technology: [3,4]). The processing chamber was pumped by a turbomolecular pump with a pumping speed of 2.20 m$^3$ s$^{-1}$. The pump was lubricated with perfluoropolyether oil, which is resistant to reactive gases, to enable it to pump pure oxygen at high rate. The turbo pump was back-pumped by a perfluoropolyether-filled rotary pump. The chamber and the turbo pump were separated by a control gate valve with a stepping motor drive for regulating the effective pumping speed with which the chamber was to be pumped. With feedback from a pressure gauge the valve controller could be programmed to maintain a particular ambient pressure in the chamber. This type of turbo pump and valve were utilized in this set-up to be able to maintain pressures in the processing chamber constant and to sustain pressure rises caused by the inlet of oxygen from a gas inlet, an ion source or a plasma source. Oxygen flows would have been used if thin films of oxific materials, such as high-$T_c$ superconductors, were to be grown, which initially was the goal of our research program. The base pressure in the processing chamber without baking it was about 5×10$^{-7}$ Pa; after baking the chamber a base pressure of about 5×10$^{-8}$ Pa was obtained. Residual gas analysis, using a quadrupole mass spectrometer, showed that the main residual gases were H$_2$O and CO.

To replace substrates that were attached to a manipulator in the processing chamber without breaking the vacuum of that chamber a load-lock chamber was used. This chamber was separated from the processing chamber by an electropneumatic valve, which could not be closed upon an electric failure in order to protect a transfer rod from damage. The load-lock chamber was pumped by a turbomolecular pump with a pumping speed of 0.15 m$^3$ s$^{-1}$. As this chamber had a small inner surface area, it could be pumped down to a pressure of about 2×10$^{-5}$ Pa within only about one hour. Then, by means of a magnetic transfer rod a substrate clamped on a substrate holder could be transferred from the load-lock chamber to the manipulator in the processing chamber or vice versa. A bayonet fitting mechanism at the front of the rod allowed for simple attachment of the holder to the rod and easy release once the holder was plugged into the manipulator. Attachment and release was achieved simply by clockwise and anti-clockwise rotation of the rod, respectively. When a substrate was replaced the relatively high pressure in the load-lock chamber caused the pressure in the processing chamber to rise from about 5×10$^{-7}$ Pa up to about 2×10$^{-6}$ Pa, but the pressure in the processing chamber dropped to its initial value within several minutes.

The vacuum equipment was controlled by a programmable logic counter (PLC). Using electrical feedback from the equipment, such as pumps, valves and
Fig. 3.1. Scheme of the Laser Ablation Deposition Investigation and Etching System (LADIES), the experimental set-up used for laser ablation of solids and deposition of thin solid films.

pressure gauges, it controlled the start-up, the running and the shut-down of the processing part and/or load-lock part of the system. In the case of malfunctioning it stopped a particular part of the set-up in order to minimize damage to the equipment and make it possible to continue to work as soon as possible.

In the processing chamber a carrousel target holder was mounted that could hold up to six targets to be used for laser ablation and deposition. This made prolonged experiments and growth of multilayers of ablated material possible. The carrousel was mounted on a linear transfer mechanism, so that the distance between a target and a substrate, attached to the said manipulator opposite of the target, could be varied. A shield in front of five targets prevented those targets to be contaminated by redeposition of material laser ablated from the target that was left open for laser
ablation. During laser irradiation the targets rotated around their surface normal to limit target-surface degradation by prolonged ablation. Moreover, the targets were regularly refreshed. Thus, physical and chemical effects that could have been disadvantaged for the laser ablation and deposition process, such as plasma-cone narrowing and flake formation at the target surface, were be limited.

Another way to minimize target-surface degradation was to scan the ablating laser beam systematically over the target surface by moving a mirror or a lens in a scanning mode, so that the entire surface was uniformly ablated and remained relatively smooth. However, by scanning the beam, which was incident upon the target surface at 45°, the laser spot size, and thereby the fluence at the target surface, varied slightly over the surface. This induced undesired variations in physical and chemical ablation parameters, which affected the quality of the results. A better way to achieve uniform ablation would have been translating the target in a scanning fashion under the incident laser beam. In addition, to limit the growth of flakes at the target surface, the target should have been rotated simultaneously. When this set-up was built, however, there where no financial means to buy or construct a device to move the target in the said scanning mode.

In the processing chamber a substrate was clamped on a substrate holder that was mounted on the fore-mentioned manipulator. The substrate could have a maximum size of about 12×12 mm². The holder had provisions for heating the substrate. A molybdenum block carrying the substrate could be heated by radiant heat from a filament. The substrate temperatures could be measured with an infrared pyrometer or with a thermocouple embedded in the Mo block. The maximum attainable temperature was about 1100 K. Depending on the deposition conditions other types of substrate holders could have been used; for example, for the growth of thin films at a high temperature in a high-pressure oxygen ambient an oxygen resistant aluminum nitride substrate holder wound by platinum wire for resistive heating was available, and for laser ablation of condensed gases a substrate holder was available that could be cooled down to about 77 K. The temperature of the substrate holders could be controlled by a PID that used the feedback from the pyrometer.

The manipulator enabled the substrate to translate in three orthogonal directions and to rotate its surface normal. These translations and rotation were operated by DC motors and controlled by a computer. Translating the substrate parallel to the target surface through a laser-produced plasma made it possible to deposit material from the plasma uniformly onto the substrate in order to obtain thin films that were uniform in thickness. Uniform deposition by the fore-mentioned scanning movement a mirror or a lens was less favourable, because of the associated fore-mentioned reasons.

Geometrically, the processing chamber was prepared for miscellaneous facilities, for example an oxygen ion source for ion-beam-assisted LAD of oxidic thin
films, an Auger electron spectroscope (AES) for in-situ analysis of LAD-grown thin films, and optics for laser-induced fluorescence spectroscopy of laser ablated species. We had the intension to extend this set-up with a differentially pumped quadrupole mass spectrometer (QMS) to conduct ARTOF spectrometry on species that were ablated under LAD conditions. Almost each part necessary for such a facility was designed, constructed, purchased and available. Lack of money, however, omitted the purchase of the required quadrupole mass spectrometer. Therefore, another set-up was used to conduct the ARTOF experiments.

3.3 The system for angle-resolved time-of-flight spectrometry

The set-up that was used for ARTOF spectrometry of laser ablated species is shown schematically in Fig. 3.2. The stainless steel ultrahigh vacuum system comprised a processing chamber and a detector chamber. As for LADIES, which has been described in the preceding section, this set-up was controlled by a PLC. The detector chamber was divided in two stages. The first stage and the processing chamber were separated by an aperture with a diameter of 6 mm; the first stage and the second stage were separated by an aperture that had a diameter of 4 mm. The processing chamber was pumped by an oil diffusion pump with a pumping speed of 2.00 m³ s⁻¹, which was back-pumped by a rotary pump. On top of the diffusion pump a baffle was mounted. It had a pumping capacity of 1.00 m³ s⁻¹ when it was filled with liquid nitrogen to prevent the oil from the diffusion pump to contaminate the chamber. Thus, the base pressure of this chamber was about 5×10⁻⁷ Pa after baking it. The first and the second stage of the detector chamber were pumped by turbomolecular pumps with pumping speeds of 0.05 and 0.15 m³ s⁻¹, respectively. The base pressure of the second stage was about 5×10⁻⁸ Pa after baking the entire detector chamber. Because the detector chamber was pumped differentially, this base pressure could sustain pressures in the processing chamber of up to about 1×10⁻³ Pa and thus an ultrahigh vacuum was guaranteed.

In the second stage of the detector chamber a quadrupole mass spectrometer [4] was mounted. Just beyond the entrance of the spectrometer an axial electron impact ionizer was placed. It enabled neutral species entering the ionization volume to be ionized by a 1-mA current of 60-eV electrons with an efficiency of 10⁻⁴-10⁻⁶ for species moving at (thermal) kinetic energies of the order of 3×10⁻² eV. The number of neutrals ionized was proportional to the number densities of the neutrals. The ionization probability was inversely proportional to the velocity of the neutrals. Resulting positively charged ions were extracted by a potential of -21 V towards ion optics, thereby acquiring 21 eV additional kinetic energy. By means of the ion optics, an ion flux was optimized for mass selection and detection. The electric fields generated by a set of quadrupole rods, enabled to select ions, traversing the quadrupole space, on a m/q ratio of up to 1000 amu e⁻¹ with a resolution, m/Δm, of
up to approximately 200. The selection depended on the kinetic energies of ions and was optimal for ions traversing the quadrupole space with a kinetic energy of about 21 eV. Selected ions could be detected by a channel electron multiplier that was mounted off-axis, out of sight of species entering the spectrometer, to prevent (direct) detection of neutrals and photons. Ions were accelerated to the channeltron’s front cone, which was set at a potential of -2600 V with respect to earth, and were detected. The maximum count rate of ions was 1 per 5 μs; for higher count rates the multiplier got saturated. The multipliers quantum efficiency was about 10% and its multiplication factor was about $10^8$.

The electric fields of the ionizer, ion optics and quadrupole rods could affect the trajectories of ions traversing the mass spectrometer with kinetic energies much higher than the fore-mentioned 21 eV; the degree in which the trajectories were affected was dependent on the kinetic energy of the ions. As the nascent ions emitted

![Diagram of experimental set-up](image)

*Fig. 3.2. Scheme of the experimental set-up used for laser ablation of solid and angle-resolved time-of-flight spectrometry of ablated species.*
from laser-produced plasmas could have had kinetic energies of up to several tens of eV, their TOF distributions were measured while the said parts of the mass spectrometer were grounded, in order to circumvent the trajectories of the ions to be affected. Consequently, however, these ions were not selected on mass. The number of nascent ions that was detected was proportional to the flux of these ions.

In front of the detector’s entrance aperture two parallel deflection plates were mounted along the flight path. The distance, \( d_p \), between them was 7.5 mm, their length, \( l_d \), was 30 mm and their width was 10 mm. By applying a sufficiently high DC potential, \( V_d \), with respect to earth over the plates an electric field could be applied that prevented ions from entering the detector. The experimentally permitted maximum value of \( V_d \) was 3 kV. These potentials also enabled to field ionize highly excited neutral species and to deflect the resulting ions. The deflection angle with respect to the flight path, \( \theta_d \), for ionized species with a kinetic energy \( E_k \) is given by:

\[
\theta_d = \arctan \left( \frac{2el_dV_d}{E_kd_d} \right),
\]

where \( e \) is the elementary charge. The minimum angle to deflect ions from entering the detector was approximately 2.5°.

In the centre of the processing chamber, in sight of the detector, a target was clamped onto a target holder on a manipulator. The distance from the target to the 6-mm- and 4-mm-diameter apertures were 205 and 300 mm, respectively. Thus, the solid detection angle was approximately 1.4×10⁴ sr. The length of the field-free flight path for neutral species, that is, the distance from the target to the ionizer, was 313 mm. The length of the field-free flight path for nascent ions, that is, the distance from the target to the channeltron, was 577 mm. The distance from the target to the deflection plates was about 140 mm.

The manipulator enabled the target to translate in three orthogonal directions and to rotate it around its vertical axis to align the target to the detector, and to select a fresh target-surface spot to be ablated. In addition, the target could also be rotated so that its surface normal rotated over an angle, \( \phi \), around the length axis of a laser beam incident at an angle, \( \psi \), with respect to the normal; this rotation was operated by a DC motor and controlled by a computer. Thus, the angle between the normal and the length axis of the detector, that is, the detection angle, \( \theta \), could be varied while keeping \( \psi \), and thus the incident laser flux, constant \([5]\). The geometry described is shown schematically in Fig. 3.3. The interval over which \( \theta \) could be varied is given by:

\[
\theta = \arccos(\cos^2 \psi + \sin^2 \psi \cos \phi).
\]

Obviously, \( \theta \) could be varied between 0° and 2\( \psi \), which in our set-up was 90°.
At any detection angle the detector viewed the entire laser-irradiated target-surface area. Thus, a cos\(\theta\)-like angular distribution of laser ablated species was measured as such. If the detector would have viewed only part of the laser-irradiated area that part would have increased with \(\theta\) as cos\(\theta\). Then, a cos\(\theta\)-like angular distribution of laser ablated species would have been measured as if it were a distribution independent of \(\theta\).

A computer triggered simultaneously a laser, which supplied the laser pulses to ablate the target, and a multichannel analyzer. Species ablated from the target by a laser pulse were time-resolved detected by the electron multiplier. Ion-impact-induced electric pulses from this channeltron were fed into the multichannel analyzer, via a preamplifier, and counted as a function of time in 1024 intervals of 5 \(\mu\)s. The data in the multichannel analyzer were read out and evaluated using the computer. Thus, a raw TOF spectrum per laser pulse was recorded. Depending on the species’ count rate, sequences of several hundreds or thousands of such spectra were added to obtain a spectrum with acceptable statistics. The maximum times-of-flight of laser-ablated species and the repetition rate of the laser pulses were sufficiently low so that the raw TOF spectra per laser pulse did not overlap; on the other hand, the times-of-flight of the species were sufficiently long so that the time resolution of the TOF spectra was relatively high.

To present TOF spectra in which the flight times were the times needed for species to travel the field-free flight path, the measured times for nascent neutrals to travel from a target to the channeltron were corrected for the flight time after electron impact ionization in the ionizer and subsequent acceleration by the extraction potential of -21 V. For nascent ions the flight times needed to travel the field-free path were the times-of-flight as measured. Thus, the spectra that are presented and discussed in
the Chapters 4, 5 and 6 were obtained. When possible, these spectra were fitted with theoretical distributions, normalized to the maximum (partial) yield per TOF interval, by eye using a trial-and-error approach.

By summing the total number of counts constituting a TOF spectrum, the total yield of species detected at \( \theta \), \( Y_{\theta} \), was obtained. By determining \( Y_{\theta} \) for various angles, while keeping other experimental parameters constant, angle-resolved yield distributions were obtained.

### 3.4 Laser and optics

For ablation of material an excimer laser [6,7] was used. This is a relatively new promising type of high-power, pulsed laser that emits radiation with a wavelength in the ultraviolet spectral region, which is a great advantage as far as photon absorption in metals, semiconductors and dielectrics is concerned. The excimer laser, operating with an \( \text{Ar/F}_2/\text{He} \) gas mixture, supplied pulses with a wavelength of 193 nm and with a duration of 15 ns (full width at half maximum). Henceforth, a train of pulses will be referred to as a laser beam. Unstable optics was used to obtain a beam profile that had approximately a uniform energy flux. The beam profile was roughly a flattened top in its long, horizontal direction and gaussian in its short, vertical direction. To select a homogeneous part of the laser beam, a diaphragm was inserted into the beam. Biconvex fused silica lenses with a focal length of 500 mm for light in the visible spectral region were used to focus the beam on the targets through fused silica viewports in either processing chamber. Both lenses and viewports had a transmittance of approximately 92%. To maintain the transmittance of the latter more or less constant, the viewports were kept clean by regularly removing laser-ablation-produced contamination, which attenuated the transmitting laser beam.

The laser fluence, \( F \), at a target surface was determined from the ratio of (1) the laser-beam power just in front of either viewport, correcting it for the transmission of the viewport and (2) the area of a spot etched by 50 laser pulses in the surface of a 10-\( \mu \)m-thick, photo-sensitive polymethyl methacrylate coating on a Si substrate. The uncertainty in the thus determined fluences was estimated to be 20\%. The major sources of the uncertainty were the blurred edges of the etched spots and the inhomogeneous energy flux distribution of the laser beam. Neutral density filters were used to attenuate the laser beam so as to obtain fractions of the set constant fluence. Thus, the relative values of \( F \) were more reliable than the absolute values. Because varying the laser’s discharge voltage resulted in varying the lasers beam profile, the fluence was not moderated by changing the discharge voltage.

To study the influence of the morphology of a target-surface spot being ablated, the spot’s relative reflectivity was measured as a function of the number of
laser pulses. For this purpose a beam from a HeNe laser, frequency stabilized at a wavelength of 633 nm and supplying a continuous output power of 1 mW, was focused on the said spot under an angle of incidence of 45°. The specular reflected beam, which would become increasingly diffuse with increasing target roughness, was detected by a fast photodiode and displayed on a digitizing oscilloscope with a time resolution of 4 ns.

This set-up might also have made it possible to calibrate the fluence to the fluence, $F_m$, required as a minimum to melt a thin surface layer of a fresh, oxide-free silicon target. $F_m$ would have been set by varying the beam power and probing the reflectivity of the target-surface spot being irradiated as a function of time so as to find the minimum power inducing the low-high-low reflectivity transition associated to the semiconductor-metal transition, which in turn is associated to the solid-liquid transition of the silicon target surface. Though $F$ would not have been known much more accurately, as for laser pulses with a wavelength of 193 nm and a duration of 15 ns the reported values of $F_m$ range from 0.13 [8] to 0.65 J cm$^{-2}$ [9], it would have been more accurately defined and could have been expressed in units of $F_m$. Due to severe electromagnetic disturbances of the Ar/F$_2$/He-filled laser, however, the said slight, nanosecond-during transition could not be to be distinguished from the noise.

References

Chapter 4

Angle-resolved
time-of-flight spectrometry of neutrals laser ablated from Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4}

Angle-resolved time-of-flight (ARTOF) distributions of O, Cu and Nd atoms and of NdO molecules ablated from the alloy Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} were measured with a quadrupole mass spectrometer. From these distributions angle-resolved yield (ARY) distributions of the neutrals were obtained. The most probable kinetic energy was irrespective of the type of neutral approximately 2.3 eV. The experimental ARTOF spectra were fitted quite well with theoretical Maxwell-Boltzmann (FMB) distributions superimposed onto angle-dependent flow-velocity contributions. The temperatures and Mach numbers associated with these fits were about $1.20 \times 10^3$ K and 4.9, respectively, irrespective of the type of atom considered. The experimental ARY distributions were fitted with $\cos^p \theta$ distributions, where $p \approx 6$. This $p$ value was much lower than expected from the FMB distributions. The results are discussed in terms of explosive surface evaporation followed by collisional modification in the ablation-induced plasmas of the nascent ARTOF and ARY distributions and in terms of explosive volume evaporation. Additional contributions to the experimental ARTOF and ARY distributions with respect to the fits are ascribed to additional thermal mechanisms.

4.1 Introduction

Laser ablation deposition (LAD) emerged a few decades ago as a physical vapour deposition (PVD) technique for the growth of thin films of a great variety of materials [1], particularly non-metallic alloys. For example, already a decade ago it was used to grow oxidic, superconducting thin films [2]. However, only after the successful preparation of high-$T_c$ superconducting YBa$_2$Cu$_3$O$_{6+\delta}$ thin films with LAD was first reported in the late 1980s [3], LAD has become widely recognized as a promising, versatile technique for small-scale thin-film growth, in addition to relatively conventional PVD techniques, such as evaporation and sputtering. Since then it has been used often to grow thin films of oxidic alloys with potential technological applications [4-7], for example YBa$_2$Cu$_3$O$_{5+\delta}$ for its said high-$T_c$ superconducting properties and PbZr$_{1-x}$Ti$_x$O$_3$ for its ferroelectric properties. The main
impetus to use LAD to grow thin films of these alloys is the following. Laser ablation proceeds congruently [1,8], so that the composition of the laser-produced plasmas is equal to that of the target. Hence, in the case of the said oxidic alloys deposition of thin films with a composition equal to that of the (relatively easily preparable) target can be obtained in a less laborious and costly way than with the other PVD techniques; for other alloys this is not necessarily the case [9] (see Chapter 8). However, the application of LAD is ahead of its comprehension: thus far many results have been obtained by a trial-and-error approach.

Since LAD was first employed effort has been made, albeit modest, to elucidate its basic mechanisms in order to reduce its process development time and to improve the quality of the thin films to be grown (see for a historical overview: [10,11]). Large-scale research and development endeavour on the subject, however, was initiated only recently after the said preparation of superconducting YBa$_2$Cu$_3$O$_{6.5}$ thin films with LAD [3]. Despite the considerable research efforts made, to date the basic laser ablation and deposition mechanisms are poorly understood. Therefore, studies on the subject are ongoing in an attempt to clarify those mechanisms.

Small (poly)atomic neutrals constitute the majority of species in a laser-ablation-induced plasma [1]. Hence, angle-resolved time-of-flight (ARToF) spectra of these species can supply a lot of information about the dynamics involved in laser ablation, in particular about the expansion of the ablation-induced plasmas. In the present chapter such spectra of atoms and diatomic molecules originating from laser ablation of the alloy Nd$_{1.85}$Ce$_{0.15}$CuO$_4$, measured with a quadrupole mass spectrometer, are presented and discussed. In addition, the angle-resolved yield (ARY) distributions of the said species, which were obtained from the ARToF spectra, are discussed. The results presented here can be compared with the results obtained positive ions emitted from the same laser-produced plasmas, which may be helpful in elucidating the mechanisms underlying the formation and expansion of the said plasmas.

Because of the interest in fore-mentioned oxides, many studies have used those materials as a model system. We used Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ used as a target. This alloy is a high-$T_c$ superconductor with a $T_c$ of only about 24 K. Hence, it is not interesting from the technological point of view. From the fundamental point of view, however, it can be interesting [12], because its electric charge carriers might be electrons [13] instead of holes as in the case for most other high-$T_c$ superconducting cuprates. A study of the superconducting properties of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ may provide crucial information about the basic mechanisms of high-$T_c$ superconductivity. Therefore, work has been performed to grow thin Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ films and to render those films in a superconducting state [14,15]. Following that work Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ was also used as a model system in the present experiments, because it suited our wishes with regard to a target. It is an alloy composed of various elements with very different atomic masses, which enabled to study possible mass dependencies of the
Angle-resolved time-of-flight spectrometry of neutrals...  29

AR TOF and ARY distributions. In addition, its structure, optical and thermophysical
properties are similar to those of the fore-mentioned cuprates that may have
technological applications and therefore have been the subject of many studies on
LAD [4-7], so that a fair comparison with data of others could be made.

4.2 Experimental

Although the experimental set-up and procedures have been described in detail
in Chapter 3, for the sake of completeness they are briefly reviewed here. In addition,
some supplementary information is given.

The ultrahigh vacuum system used comprised a processing chamber and a two-
stage, differentially pumped detector chamber. The base pressure of the former was
about 1×10^{-6} Pa and that of the second stage of the latter was about 5×10^{-8} Pa. A
quadrupole mass spectrometer was mounted in the said second stage. Neutral species
entering the spectrometer’s ionizer could be ionized by the impact of 60-eV electrons.
The number of neutrals ionized was proportional to the neutrals’ number densities;
the ionization probability was inversely proportional to the neutrals’ velocities. The
positive ions thus formed were extracted by a potential of -21 eV from the ionizer,
selected on a desired mass-to-charge ratio by the electric quadrupole fields and
detected by a channeltron, which was set at -2600 V with respect to ground.

Ions and highly excited neutrals could be prevented from entering the
spectrometer by applying a deflection potential, V_{dp}, over a pair of parallel deflection
plates mounted in front of the spectrometer’s entrance aperture.

The targets were attached to the holder of a manipulator in the centre of the
processing chamber in sight of the mass spectrometer. The field-free flight path, L,
for the neutrals from the target to the ionizer was 313 mm. The solid detection angle
was about 1.4×10^{-4} sr. By rotating the target normal around the laser beam irradiating
the target surface at 45° incidence, the angle between that normal and the length axis
of the spectrometer, the detection angle θ, could be varied from 0° up to 90°, while
keeping the laser fluence at the target surface constant. At any detection angle the
spectrometer viewed the entire 0.6-mm²-large laser-irradiated target-surface spot, so
that \cosθ-like angular distributions could measured as such.

The ionized neutrals were detected as a function of time to obtain the time-of-
flight (TOF) spectra; the time-of-flight as displayed in the TOF spectra was the time
needed for neutrals to travel the 313-mm-long field-free flight path. TOF spectra were
recorded at various detection angles. These spectra were fitted with theoretical TOF
distributions, normalized to the maximum (partial) yield per TOF interval, by eye by
a trial-and-error approach. By summing the total number of counts constituting a TOF
spectrum at a detection angle, the associated yield, Y_φ, was obtained. By repeating this
procedure for various values of θ, ARY distributions were obtained.
The targets were ablated by laser pulses with a wavelength of 193 nm and a duration of 15 ns from an ArF<sub>2</sub>/He-filled excimer laser operating at 10 Hz. The fluence, \( F \), of the laser pulses focused at the target surface was estimated from the area ablated in the surface of a PMMA-coated Si sample and the associated laser beam power. Neutral density filters were used to attenuate the beam of constant power so that \( F \) values of about 0.6, 0.9 and 1.2 J cm\(^{-2}\) were obtained. For \( F > 0.6 \) J cm\(^{-2}\) photon emission from the ablation-induced plasmas, increasing in intensity with \( F \), was observed by the naked eye. The target-surface areas to be ablated were regularly refreshed, so as to avoid possible effects of target degradation on the results to be obtained.

The targets were Nd<sub>1.85</sub>Ce<sub>0.15</sub>CuO<sub>4</sub> powder-pressed pellets that were prepared as follows. A mixture of appropriate amounts of Nd<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and CuO powders was pre-fired at 1125 K for 10 hours in air, subsequently pulverized and fired again at 1775 K in air. Thus, Nd<sub>1.85</sub>Ce<sub>0.15</sub>CuO<sub>4</sub> was obtained, which appeared to be composed of a single phase, according to X-ray powder diffraction analysis. Then, the mixture was pulverized again and pressed isostatically at 0.2 MPa in pellets that were sintered at 1275 K for 16 hours in an oxygen ambient. (In order to render the pellets in a superconducting state below about 22 K, the pellets were annealed at 1175 K for 16 hours in a reducing N<sub>2</sub> atmosphere.)

The ARTOF spectra of the neutrals that were measured while a deflection potential of about 25 V was applied, which was sufficient to deflect the ablation-

![TOF distribution](image)

**Fig. 4.1.** A TOF distribution of Nd atoms with a contribution due to highly excited neutrals (left) measured with \( V_d = 0 \) V; the contribution was extinguished for \( V_d = 2.5 \) kV (cf. Fig. 4.2c).
produced positive ions [16] (cf. Chapter 5), displayed two contributions. These contributions were comparable in magnitude. An example of such a spectrum is shown in Fig. 4.1. The contribution at the relatively long times-of-flight could be observed only when the electron impact ionizer was in operation. Hence, this contribution was due to neutrals (cf. Fig. 4.2c). The contribution at relatively short times-of-flight, however, was detectable whether the ionizer was in operation or not. The yield of the species constituting this contribution gradually decreased with increasing $V_d$ and became relatively negligible for $V_d \geq 2500$ V. Hence, this contribution was ascribed to highly excited neutrals that were electric-field-ionized either between the deflection plates or near the channeltron. The nature of these neutrals will be discussed in detail elsewhere [17] (see Chapter 6). Here, to obtain spectra with negligible interference of these contributions all further spectra of neutrals were measured with $V_d=2500$ V.

### 4.3 Results and discussion

Neutral species that were ionized in the mass spectrometer's ionizer could be detected at mass-over-charge setting, $m/q=16$, 63, 140, 144, 156 and 160 amu e$^{-1}$. These species were identified as O, Cu, Ce and Nd atoms and as CeO and NdO molecules, respectively, assuming single ionization. Metal atoms and metal-oxide diatomic molecules were detected before after laser ablation of a cuprates, like YBa$_2$CuO$_{4+\delta}$, employing photon emission spectroscopy [18,19], photon absorption spectroscopy [20] and quadrupole mass spectrometry [21]. We did not detect species other small species, such as Cu$_2$ and Cu molecules, and have made no attempts to detect other species with an $m/q$ ratio of up to the experimentally maximum attainable value of 1000 amu e$^{-1}$ (see Chapter 3), such as Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ molecules. CuO molecules could not be detected either in a laser-induced fluorescence study of species ablated from Cu, YBa$_2$CuO$_{4+\delta}$ and CuO also by laser pulses with a wavelength of 193 nm [22]. This can be explained by dissociation of nascent CuO molecules, having a dissociation energy of about 2.7 eV, by the ablating 193-nm photons, having an energy of 6.3 eV. Similarly, as Cu$_2$ molecules have a dissociation energy of about 2 eV, these molecules could have been photodissociated as well.

The ARTOF spectra of the Ce atoms and the CeO molecules and those of the Nd atoms and NdO molecules were alike, respectively, due to the species' mass resemblance. Because the targets contained substantially more Nd than Ce, substantially more Nd atoms and NdO molecules than Ce atoms and CeO molecules were detected. For these reasons, only ARTOF spectra of Nd atoms and NdO molecules were measured in all further experiments. In order to obtain a higher signal-to-noise ratio these experiments were conducted employing a slightly reduced mass resolution; some overlap between signals at $m/q=144$ and 140 amu e$^{-1}$ and between signals at $m/q=160$ and 156 amu e$^{-1}$ can therefore not be excluded.
4.3.1 Experimental ARTOF distributions

Some TOF spectra of laser ablated O, Cu and Nd atoms and NdO molecules are shown in Figs. 4.2a-d; the spectra were recorded at θ=0° employing F=1.2 J cm⁻². The spectra of the species with a relatively high mass were shifted to relatively long times-of-flight with respect to the spectra of the species with a relatively low mass. The most probable time-of-flight, \( TOF_p \), of the four types of species under investigation scaled inversely proportional to the square of the species’ mass. Hence, the values of the most probable kinetic energy, \( E_{kp} \), of the four types of species were approximately equal (cf. Table 4.1). Moreover, the said shifts were inversely proportional to the square of species’ mass. This indicates that even the kinetic-energy (KE) distributions of the four types of species were similar.

It has been shown that ultraviolet radiation can induce substantial fragmentation of laser ablated molecules [23]. Hence, the trailing edges of the present laser pulses, having a wavelength of 193 nm, could have induced some fragmentation of molecules that could have been ablated from the Nd₁₈₅Ce₀₁₅CuO₄ targets. However, the fact that the KE distributions and not the TOF distributions of the neutrals were similar indicated that the vast majority of the detected neutrals were nascent ejecta and not products of fragmentation of larger molecules.

The four types of species had equal values of \( E_{kp} \) rather than equal values of \( TOF_p \) (cf. Table 4.1). These results contrast results obtained with quadrupole mass

![Fig. 4.2a. A TOF distribution of O atoms measured at θ=0°; the atoms were ablated applying F=1.2 J cm⁻². The solid curve is a theoretical FMB distribution, given by Eq. 4.2 with T=1.60×10³ K and u=5.00×10³ m s⁻¹, fit to the experimental data.](image)
**Fig. 4.2b.** A TOF distribution of Cu atoms measured at $\theta=0^\circ$; the atoms were ablated applying $F=1.2$ J cm$^2$. The solid curve is a theoretical FMB distribution, given by Eq. 4.2 with $T=1.40 \times 10^5$ K and $u=2.40 \times 10^4$ m s$^{-1}$, fit to the experimental data.

**Fig. 4.2c.** A TOF distribution of Nd atoms measured at $\theta=0^\circ$; the atoms were ablated applying $F=1.2$ J cm$^2$. The solid curve is a theoretical FMB distribution, given by Eq. 4.2 with $T=1.25 \times 10^5$ K and $u=1.55 \times 10^3$ m s$^{-1}$, fit to the experimental data.
spectrometry that appeared to show that products with different masses laser-sputtered from chlorinated copper had similar $TOF_p$ values [24]. However, those results were probably due to cracking of $\text{Cu}_2\text{Cl}_3$ molecules in the mass spectrometer's ionizer. On the other hand, the observation that after laser ablation of $\text{YBa}_2\text{CuO}_{6+\delta}$ the TOF spectrum of BaO molecules peaked at about the same flight time as the Cu one [25] was probably due to a substantial number of highly excited BaO$^+$ molecules that contributed to the leading edge of the overall TOF spectrum of BaO molecules; it has been shown that such highly excited neutrals have significantly shorter flight times than neutrals in non- or lowly excited states [17,20,26] (see also Chapter 6). Hence, the assumption in theoretical treatments of high-rate material desorption that all species, irrespective of their mass, tend to move with similar most probable velocities [27,28] is not justified. Those treatments erroneously applied theories of continuum free jet expansion to pulsed-vapour expansion [29-31]. In continuum free jets of a binary gas mixture the velocity distributions of both types of species are identical; the behaviour of the jet is similar to that of a pure gas with a mass and a specific heat ratio equal to the average of the gas mixture. By this so-called seeded beam technique heavy atoms can be accelerated by adding light atoms to the jet. In transient, pulsed vapour expansion, however, species moving at a high velocity are not continuously hindered by preceding species moving at a lower velocity and thus can move freely into the vacuum as soon as they have passed those slower species.
Fig. 4.3a. TOF distributions of Nd atoms measured at θ=0° (●) and θ=40° (○); the atoms were ablated applying \( F=1.2 \, \text{J cm}^{-2} \). The solid curve is a theoretical FMB distribution, given by Eq. 4.2 with \( T=1.25\times10^5 \, \text{K} \), \( u=1.55\times10^4 \, \text{m s}^{-1} \) and \( \theta=40° \), fit to the experimental data.

Fig. 4.3b. \( E_{np} \) for Nd atoms as a function of \( \theta \); the atoms were ablated applying \( F=1.2 \, \text{J cm}^{-2} \). The solid curve is obtained from theoretical FMB distributions, given by Eq. 4.2 with \( T=1.25\times10^5 \, \text{K} \) and \( u=1.55\times10^4 \, \text{m s}^{-1} \), fit to the experimental data.
Fig. 4.4a. TOF distributions of Nd atoms ablated applying $F=1.2$ (●) and 0.6 $J \ cm^{-2}$ (○) measured at $\theta=0^\circ$. The solid curve is a theoretical FMB distribution, given by Eq. 4.2 with $T=1.08\times10^3 \ K$ and $u=1.35\times10^3 \ m \ s^{-1}$, fit to the experimental data for $F=0.6 \ J \ cm^{-2}$.

Fig. 4.4b. $E_{ip}$ for Nd atoms measured at $\theta=0^\circ$ as a function of $F$.

By increasing the detection angle, $\theta$, the TOF spectra of the species shifted to longer times-of-flight, as is illustrated for the case of the Nd atoms in Fig. 4.3a. Correspondingly, the KE distributions shifted to lower kinetic energies. Similar
observations were made in other studies of transient, pulsed, high-rate-desorbed species [26,32-40]. The decrease of $E_{kp}$ with increasing $\theta$ is shown in Fig. 4.3b. The ARTOF spectra of the O, Cu and NdO species changed with $\theta$ similar to those of the Nd atoms. Thus, also at higher detection angles the KE distributions of the four types of species were similar.

The TOF spectra shifted also to shorter flight times, albeit only slightly, by increasing the laser fluence, $F$; for the Nd atoms this is illustrated in Fig. 4.4a. For $F>0.6 \text{ J cm}^{-2}$ an increase of $F$ by a factor of two resulted on average in a decrease of $E_{kp}$ by a factor of approximately 1.3; a change of $F$ had a similar slight effect on the $E_{kp}$ values of particles that were laser ablated from other oxides [18] and metals [26,40]. An increase of $F$ from about 0.3 to 0.6 J cm$^{-2}$ resulted in a more pronounced increase of $E_{kp}$. This might indicate that a transition from plain laser evaporation to laser ablation for Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ took place between the two said values of $F$. The ARTOF spectra of the other types of species behaved similarly; the values of $E_{kp}$ for those species as a function of $F$ are shown in Table 4.1. Clearly, also for other values of $F$ the KE distributions of the four types of species were similar.

4.3.2 Comparison with theoretical ARTOF distributions

A basic mechanism of desorption of species in the process of laser ablation is evaporation [8] (see also Chapter 2). Therefore, attempts were made to fit the experimental ARTOF spectra with Maxwell-Boltzmann (MB) ARTOF distributions. These attempts were unsuccessful. MB distributions with a value of $TOF_p$ in agreement with the data were too broad compared with the experimental distributions; on the other hand, MB distributions with a width in agreement with experimental distribution had a $TOF_p$ value that was too low compared with that of the data. Similar observations were made for TOF spectra of neutrals ablated from other oxides [18-20], metals [26,40] and various other materials [37,38,41]. Most of these spectra were fitted fairly well with MB distributions superimposed onto flow velocities. Some angular TOF spectra could only be fitted with MB distributions superimposed onto flow velocities if the fitting parameters temperature and flow velocity varied with the detection angle [37]. An angle-dependent 'temperature', however, is not physical; a scalar thermodynamic quantity, such as temperature, cannot be angle-dependent. To circumvent variation of the said fitting parameters with the detection angle, so-called ellipsoidal MB (EMB) distributions were applied successfully to fit both simulated [35,36] and experimental [26,38,40] ARTOF spectra of transient, pulsed, high-rate-desorbed species. EMB velocity distributions were introduced [42], and henceforth often used, to describe the expansion of continuum free jets [43]. In spherical coordinates the EMB velocity distribution has the form:
\[
\frac{d^3n_{Qv}}{d\Omega dv} = C v^2 \exp \left\{ -\frac{mv^2\sin^2\theta}{2kT_{xy}} - \frac{m[v\cos\theta - u]^2}{2kT_z} \right\} d\Omega dv,
\] (4.1a)

with:

\[
T_{xy} = \frac{\sin^2\phi}{T_x} + \frac{\cos^2\phi}{T_y},
\]

where \(d^3n_{Qv}\) is the number density of species detected per solid detection angle interval, \(d\Omega\), and per velocity interval, \(dv\), \(v\) is a velocity of the species, \(m\) is the mass of the species, \(\theta\) and \(\phi\) are the polar and azimuthal detection angles, respectively, \(k\) is the Boltzmann constant, \(T_{xy}\) and \(T_z\) are the transversal and longitudinal 'temperatures', respectively, \(u\) is a longitudinal flow velocity and \(C\) is a normalization constant; the said angles and directions are defined with respect to the normal of the target. The 'temperatures' \(T_{xy}\) and \(T_z\) are measures of the thermal velocities in the coordinate system flowing with a velocity \(u\) rather than true temperatures in the sense of the thermodynamic quantity temperature.

Recognizing that a neutral's ionization probability is inversely proportional to its velocity, transformation of the EMB velocity distribution (Eq. 4.1a) to an EMB TOF distribution results in:

\[
\frac{d^3n_{Qt}}{d\Omega dt} = C \frac{1}{t^3} \exp \left\{ -\frac{m(L/t)^2\sin^2\theta}{2kT_{xy}} - \frac{m[(L/t)\cos\theta - u]^2}{2kT_z} \right\} d\Omega dt,
\] (4.1b)

where \(d^3n_{Qt}\) is the number density of species measured per solid detection angle interval and per time-of-flight interval, \(dt\), \(t\) is a time-of-flight of the species and \(L\) is the field-free flight path for the neutrals. Note that for \(\theta=0^\circ\) Eq. 4.1 reduces to a normal MB distribution superimposed onto a flow velocity, which has been used often to fit experimental TOF spectra of ablated neutrals [18-20,41].

The EMB distributions fitted the experimental ARTOF spectra of the ablated O, Cu and Nd atoms and NdO molecules quite well; this can be seen from the Figs. 4.2a-d, 4.3a and 4.4a. The peak of the fits was normalized to the peak of the experimental spectra. The fitting parameters that were used are listed in Table 4.1. \(T_{xy}\) and \(T_z\) were found to be equal and are henceforth referred to as \(T\); the equality \(T_{xy}=T_z\) contrasts the results obtained from other studies using EMB distributions to fit TOF data of transient, pulsed, high-rate desorption of species [35,36,38,40]. Here, \(T\) can be viewed as being a real measure of temperature.

The fitting parameters \(T\) and \(u\) did not change with the detection angle, \(\theta\). So, the ARTOF distributions were described by only a single set of angle-independent
Table 4.1. The values of (a) \(E_{k_p}\) of ablated O, Cu and Nd atoms and NdO molecules, (b) the fitting parameters \(T\) and \(u\) of theoretical FMB distributions fit to the experimental ARTOF distributions of the said species and (c) \(M\) for flows of the said species, as a function of \(F\) for \(\theta=0^\circ\).

<table>
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<tr>
<th>species</th>
<th>(F) (J cm(^{-2}))</th>
<th>(E_{k_p}) (eV)</th>
<th>(T) (10(^3) K)</th>
<th>(u) (10(^2) m s(^{-1}))</th>
<th>(M)</th>
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</table>

(a) The accuracy of the determination of the TOF interval in which the ARTOF distribution peaked was limited by the width of the TOF intervals, which were relatively broad compared to the times-of-flight. The estimated errors in the values of \(E_{k_p}\), \(T\) and \(u\) and \(M\) were 0.5 eV, 4\(\times\)10\(^2\) K, 1\(\times\)10\(^3\) m s\(^{-1}\) and 0.3, respectively.

(b) The estimated errors in the values of \(E_{k_p}\), \(T\), \(u\) and \(M\) were 0.2 eV, 1\(\times\)10\(^2\) K, 5\(\times\)10\(^3\) m s\(^{-1}\) and 0.3, respectively.

(c) The estimated errors in the values of \(E_{k_p}\), \(T\), \(u\) and \(M\) were 0.1 eV, 1\(\times\)10\(^2\) K, 2\(\times\)10\(^4\) ms\(^{-1}\) and 0.3, respectively.

parameters, which is satisfactory from a physical point of view. The value of \(T\) was about equal for the Cu, Nd and NdO species, but for the O atoms it was significantly higher. On the other hand, the value of \(u\) was about inversely proportional to \(m_k^{1/2}\), this appeared also to be the case for laser-ablated Cu\(_3\)Cl\(_2\) species [38]. Obviously, the kinetic flow energies, \(\sqrt{2mu}\), of the flows of the four types of species were approximately equal. These observations hold for fluences at least down to 0.6 J cm\(^{-2}\). Clearly, these results show that the assumption that species desorbing in pulses at high rate tend to acquire equal flow velocities [27,28] cannot be justified.
Upon decreasing de fluence, \( F, T \) and \( u \) fell only slightly (cf. Table 4.1); a change of \( F \) had more effect on \( u \) than on \( T \). When \( F \) decreased to well below 0.3 J cm\(^{-2} \) \( u \) reduced to approximately zero and the fit became a simple thermal MB distribution. Clearly, at such low values of \( F \) the species desorbed from the target surface by plain evaporation. Because under these conditions \( F \) was ill-defined and the signal-to-noise ratio was poor, no further effort was made to study the desorption of the species at these low values of \( F \). Research on laser ablation with values of \( F \) well below the threshold values for clear ablation could, however, contribute substantially to the clarification of the basic ablation mechanisms.

The EMB distributions, given Eq. 4.1b, employed only a single value for \( T \) to fit the experimental data. Thus, the EMB distributions became equivalent to distributions given by:

\[
\frac{d^3n_{\Omega}}{d\Omega dt} = C_1 \frac{1}{t^3} \exp \left\{ - \frac{m[(L/t) - u \cos \theta]^2}{2kT} \right\} d\Omega dt, \tag{4.2}
\]

where:

\[ C_1 = C \exp \left\{ - \frac{mu^2 \sin^2 \theta}{2kT} \right\}, \]

which from this point will be called flowing MB (FMB) distributions. The angle dependence of these distributions is no longer due to the angle-dependent contributions of two orthogonal 'temperature' components. Now it is only due to the angle-dependent contribution of the longitudinal flow velocity to a thermal velocity, \( L/t \), in the direction of \( \theta \), that is, the projection of \( u \) in the direction given by \( \theta \).

When describing dynamic gas flows, one often supplies the local Mach number, \( M \). This is a measure of the randomness of the particle motion; it is defined as the ratio of the flow velocity to the local sound velocity. As an expanding gas flow as induced by laser ablation is a non-equilibrium state, a definition of a local speed of sound in the flow is rather ad hoc. Nevertheless, we defined:

\[
M = \frac{u}{\sqrt{\gamma kT/m}}, \tag{4.3}
\]

where \( \gamma \) is the ratio of the specific heat at constant pressure to the specific heat at constant volume. For perfect gases this ratio is given by:
\[ \gamma = \frac{j+5}{j+3}, \]

where \( j \) is the number of internal, rotational and vibrational, degrees of freedom accessible to the gas phase particle considered; for an atom \( j = 0 \), for a diatomic molecule that can rotate \( j = 2 \), and for a diatomic molecule that can rotate and vibrate \( j = 4 \). When electronic degrees of freedom are accounted for \( \gamma = 1.2 \text{ to } 1.3 \) [44]. The temperature \( T \) in Eq. 4.3 is equal to the mean temperature \( T = \frac{1}{3}(T_x + T_y + T_z) \) [45].

For the ARTOF distributions the values of \( M \) were calculated using the local velocities of sound in the partial O, Cu, Nd and NdO flows and \( \gamma = 1.3 \) for all four types of species; the results are shown also in Table 4.1. Of course \( M \) was independent of the detection angle \( \theta \), because both \( T \) and \( u \) were independent of \( \theta \). In addition, due to the fore-mentioned relations between \( T, m \) and \( u \) for the different types of species, \( M \) appeared to be approximately equal for all three partial flows of atoms, irrespective of the atoms’ mass. \( M \) decreased only slightly with decreasing the fluence, because correspondingly \( u \) decreased more than \( T \) did.

4.3.3 Additional contributions to theoretical ARTOF distributions

The FMB distributions (Eq. 4.2) fitted the experimental ARTOF spectra only up to flight times where the trailing part of the experimental distributions fell below approximately 10% to 20% of the experimental ARTOF spectra’s (partial) yield at the peak; this can be seen in Figs. 4.2a-d, 4.3a and 4.4a. Thereafter, the experimental data displayed an additional contribution with respect to the fit. Note that this effect was more pronounced for the O atoms than for the other species. Such relatively slow, low yield contributions to the TOF spectra of laser-ablated species have been observed before [19,20,41]. Thus far, no satisfactory explanation for their origin has been given.

The magnitude of these contributions decreased with increasing the detection angle \( \theta \), but relative to the FMB-like part of the experimental TOF spectra their magnitude increased with increasing \( \theta \); this was also the case for decreasing the fluence. The additional contributions could be separated from the overall ARTOF spectra by subtracting the fits from the experimental data. The contributions that remained could not be fitted simply with other FMB distributions. The origin of these contributions was investigated in more detail in the study of the ARY distributions of neutrals.
4.3.4 Experimental ARY distributions

From the ARTOF distributions of the neutrals the corresponding ARY distributions were obtained. An example for the case of Nd atoms, laser ablated with $F \approx 1.2$ J cm$^{-2}$, is shown in Fig. 4.5. Similar distributions were also obtained for the other types of species under investigation; the values of the relative overall yield at $\theta = 0^\circ$, $Y_{\theta}$, are shown in Table 4.2. (Note that these values only reflect the relative yields of detected species and not those of ablated species. The former can not be obtained simply from the latter, because amongst other things the ionization cross sections of the considered neutrals under the experimental conditions are unknown.) The spread in the values of $Y_{\theta}$ was higher than could have been expected statistically, that is, higher than the square root of the associated number of counts. This may be explained by fluctuations in the performance of the laser and the electronics of the mass spectrometer during the prolonged measurements; in addition, also the granular structure of the targets might have played an important role in determining the spread in the data.

The ARY distributions were quite strongly peaked along the target normal; this is illustrated by the ARY distribution of Nd atoms in Fig. 4.5. Attempts were made to fit the experimental data with distributions of the form:

$$Y_{\theta} \cos \theta \, d\Omega = Y_{\theta_0} \cos \theta \, d\Omega,$$

employing the least-squares fitting method. The fore-mentioned ARY distribution of Nd atoms was fitted quite well with such a distribution for $Y_{\theta_0} = 1.0$ and $p = 6.4$ (cf. Fig. 4.5). The other experimental ARY distributions were fitted with similar fits; the fitting parameters are listed in Table 4.2. In some cases for $\theta = 40^\circ$ or even already for $\theta = 30^\circ$, $Y_{\theta}$ was higher than was expected from the trend of $Y_{\theta}$ at lower values of $\theta$. Those deviating data were not considered in the fitting procedure. For all the ARY distributions $p$ was substantially higher than one: the distributions were more peaked along the target normal than a $\cos \theta$ distribution is; this is also in qualitative agreement with other reports on studies of transient, pulsed, high-rate desorption of species [26,32-40].

From Table 4.2 it is seen that $Y_{\theta}$ fell upon decreasing the fluence, $F$. Qualitatively, this was to be expected considering the fact that in the present fluence regime the ablation rate of, for example, YBa$_2$Cu$_3$O$_{6+\delta}$ decreases upon lowering $F$ [46]. Further, two trends, albeit subtle, can be discerned from the table. Firstly, $p$ tended to decrease when $F$ decreased from 1.2 down to 0.6 J cm$^{-2}$; it decreased substantially upon decreasing $F$ from 0.6 down to 0.3 J cm$^{-2}$. Qualitatively similar effects have been observed before in the case of laser ablation [34]. Secondly, the fits regularly failed to fit the experimental data for $\theta = 40^\circ$ and sometimes even for $\theta = 30^\circ$ and $40^\circ$. These results resemble the results obtained from thickness profiles of laser ablation deposited thin YBa$_2$Cu$_3$O$_{6+\delta}$ films [47]. The ARY distributions did not
Fig. 4.5. An ARY distribution of Nd atoms; the atoms were ablated applying \( F=1.2 \) J cm\(^2\). The solid curve is a \( \cos^p\theta \) distribution, given by Eq. 4.4 with \( p=6.4 \), fit to the experimental data.

depend significantly on the species' mass, which is in agreement with other studies of pulsed, high-rate desorption of species [36,38].

### 4.3.5 Comparison with theoretical ARY distributions

By integration of the FMB distribution (Eq. 4.1b) over all positive times-of-flight, it can be shown that the yield of species emitted in the direction given by a detection angle \( \theta \) is given by:

\[
Y_\theta = \frac{\exp(-c)}{2a\sqrt{\pi}} \left[ \sqrt{\pi} \left( \frac{b^2}{4a} + \frac{1}{2} \right) \exp \left( \frac{b^2}{4a} \right) \text{erfc} \left( \frac{b}{2\sqrt{a}} \right) - \frac{b}{2\sqrt{a}} \right],
\]

where:

\[
a = \frac{m}{2kT},
\]

\[
b = \frac{-m \cos \theta}{kT},
\]

and:
Table 4.2. The values of (a) $Y_{\phi}$ of ablated O, Cu and Nd atoms and NdO molecules, (b) $p_\phi$ of cos$^2\theta$ distributions fit to the experimental ARY distributions and (c) $p_{FMB}$ of cos$^2\theta$ distributions fit to the theoretical ARY distributions, given by Eq. 4.5 with the corresponding parameters from Table 4.1, as a function of $F$.

<table>
<thead>
<tr>
<th>species</th>
<th>$F$ (J cm$^{-2}$)</th>
<th>$Y_{\phi}$ (arb. units)</th>
<th>$p_\phi$</th>
<th>$p_{FMB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O*</td>
<td>0.3</td>
<td>0.11</td>
<td>5.0</td>
<td>15.5</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.46</td>
<td>6.4</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.96</td>
<td>6.4</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>2.02</td>
<td>6.6</td>
<td>31.3</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>0.3</td>
<td>0.01</td>
<td>4.5</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.14</td>
<td>6.3</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.24</td>
<td>6.1</td>
<td>30.1</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>0.52</td>
<td>6.4</td>
<td>32.4</td>
</tr>
<tr>
<td>Nd$^+$</td>
<td>0.3</td>
<td>0.04</td>
<td>4.8</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.26</td>
<td>6.0</td>
<td>30.6</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.48</td>
<td>6.2</td>
<td>32.2</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.00</td>
<td>6.4</td>
<td>34.5</td>
</tr>
<tr>
<td>NdO$^+$</td>
<td>0.3</td>
<td>0.04</td>
<td>4.6</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.27</td>
<td>6.2</td>
<td>46.9</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.60</td>
<td>6.4</td>
<td>43.5</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.12</td>
<td>6.2</td>
<td>44.5</td>
</tr>
</tbody>
</table>

$$c = \frac{mu^2 \cos^2 \theta}{2kT}.$$  

The theoretical ARY distributions obtained from Eq. 4.5 and the required fitting parameters were fitted with functions of the form of Eq. 4.4 by the least-squares fitting method. Thus, a theoretical ARY distribution of Nd atoms, ablated with $F \approx 1.2$ J cm$^{-2}$, obtained by using $T = 1.25 \times 10^3$ K and $u = 1.55 \times 10^3$ m s$^{-1}$ was shown to be cos$^2\theta$-like. The applied $p$ value was much higher than the one obtained from fitting of the corresponding experimental ARY distribution (see Fig. 4.5). The values of $p$ obtained from fitting of the theoretical ARY distributions of the O and Cu atoms were similar to the value for Nd atoms, irrespective of the species’ mass (see Table 4.2); they all decreased similarly with the fluence. The values for the NdO molecules were substantially higher. Although the FMB distributions fitted well to the experimental ARTOF spectra, the corresponding ARY distributions failed to fit the experimental ones. The reason for this is thus far unknown.
A simple quasi-empirical relationship between \( p, m, T \) and \( u \) that has been claimed to describe the theoretical ARY distributions obtained from the theoretical EMB distributions [38] did not hold for our case. Systematic variation of the said parameters showed that that relationship only holds in a very limited range of \( m/T \) and \( m/u \) ratios. Therefore, that relation should be employed only with great care.

A theory, based on continuum free-jet-expansion theory, put forward to describe pulsed sputtering phenomena, predicts the maximum (partial) yield per TOF interval in a TOF spectrum to be proportional to \( \cos^p \theta \), where for atoms \( p \approx (1+M)^{2.1} \) (and \( M \) is the local Mach number) [28]. Because the present TOF spectra became broader with increasing \( \theta \), the overall yield of a certain type of species measured at \( \theta = 0^\circ \), normalized to the corresponding maximum (partial) yield per TOF interval, increased with approximately 20\% when \( \theta \) was increased from 0\(^\circ\) to 40\(^\circ\). Thus, the \( p \) values obtained from the maximum (partial) yield per TOF interval as a function of \( \theta \) were approximately 7 instead of 6, as has been reported in the preceding section. Nevertheless, the \( p \) values obtained from the said theory, using the values of \( M \) from Table 5.1, did not agree with the experimental \( p \) values either. Qualitatively, the former displayed trends similar to those displayed by the \( p \) values obtained from Eq. 4.5. As the flows of the different types of species had about equal values of \( M \), according to the fore-mentioned theory they also had similar \( p \) values, which is in agreement with our experimental observations. Quantitatively, however, the theoretical \( p \) values were several times higher than the experimental ones; they were approximately 1.3 times as high as the values that were obtained from Eq. 4.5. Clearly, the relation \( p \approx (1+M)^{2.1} \) does not adequately describe the experimental ARY distributions of the neutrals either.

### 4.3.6 Additional contributions to theoretical ARY distributions

By subtracting the FMB fits from the corresponding experimental ARTOF spectra and determining the remaining overall yields, the ARY distributions of the fore-mentioned slow, low-yield contributions were obtained. The estimated spread of the data of these so-called ARY contributions was considerable. These ARY contributions were also fitted with distributions of the form of Eq. 4.4. An example obtained from the slow, low-yield TOF contribution to the TOF spectra of Nd atoms, ablated with \( F \approx 1.2 \text{ J cm}^{-2} \), is depicted in Fig. 4.6; similar distributions were obtained for the other types of species, as well as for other fluences. As expected from the increase of the contribution relative to FMB-like part of the experimental ARTOF spectra for higher detection angles, \( \theta \), and from the observation that the fits of the form of Eq. 4.4 regularly failed to fit the ARY data for higher values of \( \theta \), the said ARY contributions were less peaked along the target normal than the overall ARY distributions.

To investigate whether or not the edges of the laser-irradiated target-surface spot affected the slow contribution, in a separate experiment the effective size of this
edge was varied by varying the spot size, while the fluence was held constant. No significant alteration in the ARY contribution was observed. In order to investigate the influence of fragmentation of desorbed particle clusters and droplets by the latter part of the ablating laser pulses on the said contributions, in yet another separate experiment a target with a substantially lower mass density and thereby poorer thermal contact between individual powder particulates was used; ablation of such a target has been shown to result in a higher number of particulates than for a target with higher density [9,48] (see Chapter 8). Once again, no significant change in the ARY contributions was observed. Hence, neither the edge size nor fragmentation of particulates could account for the ARY contributions associated with the slow, low-yield contributions in the experimental ARTOF spectra of the neutrals.

4.3.7 Basic ablation mechanisms

It has been observed that the most probable kinetic energies of the laser ablated neutrals were independent of the species’ mass (cf. Section 4.3.1). Moreover, they decreased with increasing detection angle $\theta$ (cf. Section 4.3.1). In addition, the ARY distributions of the neutrals were $\cos^p\theta$-like with $p$ substantially higher than one (cf. Section 4.3.4). These observations can be explained qualitatively in terms of two mechanisms involved in the laser ablation process: (1) explosive surface evaporation of neutrals followed by collisional interaction amongst those neutrals on
the one hand and (2) explosive volume evaporation of neutrals on the other hand [8]. We now give a brief phenomenological description of both mechanisms.

It has been recognized for a long time that collisional interaction between species, which have been evaporated from the surface of a target, in a gas-phase collisional region just above the target surface and subsequent expansion of that region affect both the ARTOF and ARY distributions of the species [32]. If the species desorb and their number density is sufficiently low, their mean free path will be sufficiently long to travel from the target surface without, or with negligible, mutual collisional interaction. If the desorption mechanism is plain evaporation simple Maxwellian ARTOF distributions and cosθ-like ARY distributions can be expected. This was the case in the present experiments for fluences much lower than 0.3 J cm⁻². For desorption rates exceeding about a few tenths of a monolayer per 10 ns [35,36,39], however, the mean free path of the desorbed species is so short that collisions amongst the species take place. The volume in which those collisions take place will be referred to as the collisional region. This region dissolves by pressure-gradient-induced expansion. Monte-Carlo simulations [35,36,39] and analytical calculations [27,28] showed that these effects cause a redistribution of both kinetic energy and yield in a certain direction: species at low angles with respect to the target normal acquire more kinetic energy and their yield increase at the expense of the species at high angles. These effects are more pronounced for higher average numbers of collisions [27,28,36,39]; they could be caused by as few as about three collisions on average [35]. Hence, the anisotropies shown in the Figs. 4.3b and 4.5 and in the Tables 4.1 and 4.2 can be explained by the fore-mentioned collisional effects. Because collisional modification can alter non-thermal TOF distributions also into MB-like distributions [39], little can be said about the initial desorption mechanism.

Instead of being determined by post-desorption gas-phase dynamics, the ARTOF and ARY distributions may also have been determined by the initial desorption dynamics of volume evaporation [8]. Amongst other things, heat flow calculations [49] have led to the following picture based on the concept of volume evaporation, which gains increasingly interest [50-52]. When in a surface, being subjected to high-power laser pulses, sufficient photon energy is converted into thermal energy, it melts and subsequently vaporizes. Due to the latent heat of vaporization thermal energy is removed from the target surface. If the removal of energy does not proceed rapidly enough, the subsurface regions may reach temperatures that are substantially higher than the surface temperature. This can particularly be the case for materials with a relatively long photon absorption length [8,49,51], such as Nd₁₈G₃Ce₀₁₅CuO₄. Superheating of a subsurface melt can occur, that is, the local pressure is lower than the equilibrium pressure corresponding to the local subsurface temperature. If, subsequently, the subsurface temperature becomes so high that nucleation and growth of gas phase bubbles takes place, that is,
the liquid starts to boil, the local pressure becomes so high that explosive subsurface
gas phase expansion initiates material ejection, thereby removing intervening material.

For both of the proposed mechanisms neutrals evaporate from a hot spot. The
flow of the neutrals imparts momentum to the target and in the flow the neutrals
equilibrate. Thereby the flow acquires a flow velocity $u$. Because of symmetry, $u$
is directed along the normal of the target surface. Thus, the TOF distributions of the
species are MB-like and superimposed onto the said flow velocity, as has been shown
in Section 4.3.2. In the case of surface evaporation, the temperature in the flow would
have been determined by the degree of equilibration in the collisional region where
the species experience only a limited number of collisions. In the case of volume
evaporation, the said temperature would have been approximately equal to the
subsurface boiling temperature. Because the temperatures of the O, Cu and Nd flows,
as shown in Table 4.1, were not exactly the same, this suggests the temperatures of
the ARTOF distributions were determined mainly by partial equilibration of the
ablated species in a collisional region. The partition of kinetic energy over
temperature and flow velocity was, at least for the observed atoms, determined by the
observed tendencies of both the Mach numbers and the kinetic flow velocity to be the
same for flows of atoms with different masses. The reasons for these tendencies are
as yet not known.

Both mechanisms might also have been responsible for the peaking of the
ARY distributions along the target-surface normal. Hence, on the basis of the ARY
distributions it cannot be ruled out either which ablation mechanism was operative.

Even under the near-threshold ablation conditions applied the neutrals acquired
considerable kinetic energies. For surface evaporation followed by collisional effects
it has been shown that the kinetic energy of species detected at $\theta=40^\circ$-$50^\circ$ is
characteristic for the surface temperature at which the species were evaporated [39].
Thus, as for $F=1.2 \text{ J cm}^{-2}$ the most probable kinetic energies, $E_{kp}$, at these angles were
about 1.4 eV (cf. Fig. 4.3b), the temperatures of the spots from which the neutrals
were ablated should have been about $10.8\times10^3$ K. The temperatures reached for lower
fluences are in reasonable agreement with solutions of the one-dimensional heat flow
equations in which the temperatures reached a maximum at [53] as well as below the
surface [50]; one should bear in mind that the heat flow calculations rely on optical
and thermodynamic material characteristics that probably do not hold under ablation
circumstances. Thus, the values of $E_{kp}$ also do not rule out either which ablation
mechanism was operative.

The change of the data as a result from a change in the fluence, $F$, can also
be explained on the basis of both mechanisms. Qualitatively, by decreasing $F$, the
amount of energy coupled into the target surface decreases. Thus, the maximum
temperature at or below the surface is reduced. As a consequence, fewer species are
ablated and those species acquired less kinetic energy. Thus, in the case of surface
evaporation fewer collisions can take place, the extent of expansion decreases and
consequently, the forward peaking of both kinetic energy and yield decreases in
agreement with simulations on the subject [35,36,39]. In the case of volume evaporation, apart from lower temperatures, the pressures build up inside the subsurface gas bubbles are lower. As a result the explosive evaporation proceeds less violently, resulting in the same fore-mentioned effects. The qualitative origin of the dependence of $E_{kp}$ on $F$ is as yet not clear.

Hence, as far as the prime ablation mechanism is concerned, on the basis of the present results no distinction can be made between surface evaporation and volume evaporation. This is also the case for results obtained with other techniques that rely on the characterization of the ablated species, such as photon emission spectroscopy and laser-induced fluorescence. The present results, however, do present quite a number of (quantitative) data that can be used in models for laser ablation to be developed.

4.3.8 Additional contributions

The additional component in the ARTOF and ARY distributions can be explained to some extent by the two fore-mentioned mechanisms. As evaporation depends exponentially on the temperature, most neutrals are evaporated at about the maximum temperature reached at or below the target surface. However, because the temperature of the heated regions of materials with a low thermal conductivity, such as $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, drops to and remains at a temperature plateau at the melting point for a considerable length of time [53], significant evaporation persists at lower temperatures. Thus, as in the case of decreasing fluences, the effects causing the anisotropy in both kinetic energy and yield are less pronounced, just like for the slow contributions. The contributions become relatively more significant as the fluence is decreased, because then the relative temperature drop decreases. Moreover, they will also be more pronounced for volatile species, which explains the observation that the contributions for the O atoms were relatively more pronounced than those for the other neutrals (cf. Section 4.3.3). In materials with a high thermal conductivity the temperature dwell after high-irradiance laser irradiation will be very short. As a consequence, ARTOF and ARY distributions of neutrals ablated from such materials will not display significant slow, less peaked contributions, which is in agreement with, for example, the thickness profiles of Cu-Ni and Ag-Ni films grown by LAD [9] (see Chapter 8). The fact that the additional ARTOF contributions could not be fitted with simple MB-like distributions could be attributed to the fact that species were evaporated during a stage in which the temperature continued to decrease significantly. The contribution of the trailing edges of laser pulses to the heating of the target and to the effects observed was in all probability relatively insignificant.
4.4 Impact of results on deposition

In general, the impact of particles with kinetic energies of the order of several eVs, can be beneficial for the physical and metallurgical properties of the thin film [54,55]. For example, as particles can employ their kinetic energy to be mobile at the film surface upon incidence, thin films with a desired microstructure may be grown at lower substrate temperatures than would be possible if the incident particles carried along less kinetic energy. Thus, less undesired physical and chemical reactions in the film-substrate assembly may take place.

The particle energies, however, should not exceed a certain threshold so as to circumvent sputtering of species from the growing film. Recognizing that in order to demonstrate the said effects for the neutrals, ions and other species have to be removed from the flux of laser-ablated neutrals to deposited, to our knowledge these effects have not been experimentally demonstrated yet.

Because the species have approximately equal kinetic energies, they arrive at a substrate in order of increasing mass. This may be unfavourable for uniform sticking of the species to the substrate. For example, in the case of laser ablation deposition of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ or a comparable oxide, O atoms will be the first to arrive at the substrate. If the atoms do not form volatile O$_2$ molecules and evaporate, especially at the high substrate temperatures applied [3,15], they are likely to be sputtered by the species having a higher mass, which arrive at the substrate in a later stage. In addition to preferential evaporation of oxygen from the target and the heated film, these effects may contribute substantially to the oxygen deficiency observed [3] in laser-ablation-deposited metal-oxide films.

The ARY distributions, which were cos$^p\theta$-like with $p \approx 6$, will be reflected in the thickness distributions of LAD-grown thin films. For a non-spherical laser-produced plasma the pressure gradients in the direction of the smallest dimension will be the highest [56]. Therefore, the extent of expansion in that direction will be the highest. Hence, when the laser-ablated spot at a target surface is rectangular or elliptic, the ratio of the $p$ values for the angular distributions parallel and perpendicular to the spot's length axis are about inversely proportional to its aspect ratios. Indeed, for example for a Ag-Ni film grown by LAD on a stationary substrate it was measured with electron probe microanalysis (EPMA) that the thickness profile along the film axis that was parallel to the long axis of the laser spot was narrower than the one that was perpendicular to it [9] (cf. Chapter 8). The data points of the thickness profiles parallel and perpendicular to the spot's long axis could be fitted well with cos$^{5.4}\theta$ and cos$^{9.4}\theta$ distributions, respectively. The thickness profiles of Ag-Ni film did not contain additional less peaked contributions in accordance with the high thermal conductivity of this metallic alloy (see Section 4.3.8). To obtain the associated ARY distributions two corrections should be made. Firstly, as EPMA measured the number density of species deposited in a plane, the thickness profiles are to be corrected with a geometric factor of cos$^2\theta$ to account for the decrease of
depositing flux with an increase of the distance from the ablated spot during deposition. In addition, a $\cos^4 \theta$ factor is to be introduced to correct for the inclination of the probed volume with respect to local angle of incidence of ablated species. Hence, the ARY distributions associated to the $\cos^5 \theta$ and $\cos^9 \theta$ distributions were $\cos^2 \theta$ and $\cos^4 \theta$ distributions, respectively. As in the present experimental configuration the ARY distributions were measured (in particular) with respect to the long axis of the laser spot at the target surface, the said $\cos^6 \theta$ distribution is in fair agreement with the present $\cos^9 \theta$-like ARY distributions. However, as the sticking probability of species depends on the nature of the species, their kinetic energy and their angle of incidence the angular distributions deduced from the thin films grown will in all probability not be the same as the ARY distributions determined from ARTOF measurements.

4.5 Summary and conclusions

TOF distributions of O, Cu and Nd atoms and of NdO molecules laser ablated from Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ were measured as a function of the detection angle $\theta$. From these distributions ARY distributions of ablated species were obtained.

The most probable kinetic energies, $E_{kp}$ (~2.3 eV) of the said four types of species, obtained from the TOF distributions, were equal. Moreover, the TOF distributions indicated that the KE distributions of laser ablated neutrals were similar regardless of the species' mass, $m$, and regardless of $\theta$.

The TOF distributions of a type of neutrals were fitted with normalized FMB distributions using only one value of $T$ and of $u$, regardless of $\theta$. The values of $T$ and $\frac{1}{2}mu^2$ were similar for the four types of species.

The ARY distributions were fitted with $\cos^p \theta$ distributions with $p \approx 6.4$. The values of $p$ obtained from the FMB distributions fitting the TOF distributions were several times as high as the experimental values.

Qualitatively, the results can be due to two mechanisms: (1) laser ablation of neutrals from the target surface followed by collisional interaction between those species in plasmas near the target surface and jet-like expansion of those plasmas, and (2) jet-like laser ablation of neutrals from gas bubbles below the target surface. Quantitatively, the results are not in agreement with any laser-ablation theory put forward thus far. On the basis of the present results a choice for mechanism or the other would only be speculative, because on the basis of ARTOF and ARY distributions of ablated neutrals alone a distinction between the two cannot be made.

Finally, the contributions of neutrals that constituted TOF distributions slower than the fore-mentioned and ARY distributions less peaked along the target normal than the fore-mentioned were ascribed to laser evaporation of the neutrals from laser-ablated target-surface spots that cooled down.
References

[15] R.P. van Ingen, unpublished (concerned laser ablation deposition of Nd_{1.85}Ce_{0.15}CuO_{4} thin films).
Angle-resolved time-of-flight spectrometry of neutrals...

Chapter 5

Ejection of positive ions from plasmas induced by laser ablation of Si and Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4}

Angle-resolved time-of-flight distributions of Si\textsuperscript{+} ions and of O\textsuperscript{+}, Cu\textsuperscript{+} and Nd\textsuperscript{+} ions originating from laser ablation of Si and Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4}, respectively, were measured using a quadrupole mass spectrometer. From these distributions angle-resolved yield distributions of the ions were obtained. The time-of-flight distributions did not change with the detection angle; consequently, neither did the associated yields. The degrees of ionization of the laser-induced plasmas appeared to be about 5\times10\textsuperscript{-7}. However, it is argued that only a fraction of the order of 5\times10\textsuperscript{-4} of the total number of ions could have been be detected and that thus the actual degrees of ionization were of the order of 1\times10\textsuperscript{-3}. All these observations are explained in terms of ambipolar diffusion of the ions (and electrons) from the skins, with thicknesses of the Debye shielding distance, of the laser-induced plasmas in their initial stages. The results obtained indicate that in the case of the Si\textsuperscript{+} ions the main ionization mechanisms were collisional ionization and multiphoton ionization.

5.1 Introduction

A manifold of reasons has been put forward to motivate the usage of laser ablation deposition (LAD) instead of other physical vapour deposition (PVD) techniques for the growth of thin films [1]. One of those reasons is that the ablated species to be deposited have substantial kinetic energies. The kinetic energies of atoms and small polyatomic molecules, constituting the majority of species in laser-produced plasmas, can range from a few eV [2,3] (cf. Chapter 4) up to a few tens of eV [4,5]. Moreover, it has been reported that the positive ions in the ablation-induced plasmas can acquire kinetic energies of up to several tens of eV [6-9] or even (far) in excess of 100 eV [1,10-12]. If those ions would be present in the plasmas in sufficiently high number densities, then LAD would resemble an (inherently) ion-beam-assisted PVD technique. Simultaneous irradiation of a thin film during vapour deposition of low-energetic species by ions having such high kinetic energies can be useful in modifying the film's growth kinetics and thus its physical and metallurgical
properties [13]. For example, it has been shown that LAD-grown films were single crystalline when the energetic ions from the laser-produced plasma were incident upon the film, whereas the films were polycrystalline when the ions were deflected from incidence [14]. In order to control the depositing fluxes of ions during LAD and the quality of the thin films to be grown elucidation of the basic ablation mechanisms may be helpful. This is one of the reasons why considerable research on LAD has been devoted to the study of the kinetic energies and number densities of positive ions emitted from laser-ablation-produced plasmas.

In the present chapter experimental angle-resolved time-of-flight (ARTOF) and associated angle-resolved yield (ARY) distributions of positive ions arising from laser ablation of Si and Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} are discussed. The results for Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} can directly be compared with the ARTOF and ARY distributions of atoms and diatomic molecules arising from the same ablation events [2] (see Chapter 4), which may be useful for comprehension of the mechanisms underlying laser ablation and deposition, in particular the mechanisms of plasma formation and plasma expansion.

Silicon was taken as a target, because of its importance as a semiconductor material. Moreover, its basic optical and thermophysical properties are fairly well established and much is known about the interaction of (high-irradiance) laser pulses with Si, because of prolonged studies of pulsed laser annealing [15-17]. In the present experiments an Ar\textsuperscript{+} excimer laser was used, which supplied pulses with a wavelength of 193 nm, a duration 15 ns and fluences of 0.6 up to 1.2 J cm\textsuperscript{-2}. Thus the conditions were similar to those used in near-threshold LAD of Si thin films [6,7].

Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} was used as a model system for mainly two reasons. Firstly, it is an alloy composed of various elements with very different atomic masses, which enables to study possible mass dependencies of the ARTOF and ARY distributions. Secondly, it resembles copper oxides that may have technological applications, such as high-$T_c$ superconductors, ferroelectrics and dielectrics, and therefore have been the subject of many studies on laser ablation [18-21]. The conditions applied were chosen similar to the conditions used for near-threshold vacuum deposition of Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} thin film employing laser ablation [22].

### 5.2 Experimental

Although the experimental set-up and associated procedures have been described in detail in Chapter 3, for the sake of completeness they are briefly reviewed here. In addition, some supplementary information is given.

The ultrahigh vacuum system used comprised a processing chamber and a two-stage, differentially pumped detector chamber. The base pressure of the former was about 1×10\textsuperscript{-6} Pa; that of the second stage of the latter was about 5×10\textsuperscript{-8} Pa. The detector, a quadrupole mass spectrometer, was mounted in the said second stage. For
good performance of the spectrometer, ions traversing it should have kinetic energies of the order of 21 eV. As the nascent ions arising from laser ablation might have had substantial higher kinetic energies, the electric fields of the ionizer, ion optics and quadrupole rods might have affected the trajectories of the ions. In order to provide the ions traversing the spectrometer a field-free flight path, these components were grounded. To detect the ions only the channeltron, set at -2600 V with respect to ground, was operative; its quantum efficiency was about 10%. As the channeltron samples ions two-dimensionally, fluxes of ions were measured.

Nascent ions could be prevented from entering the mass spectrometer by applying a deflection potential, $V_d$, over a set of two parallel deflection plates mounted before the spectrometer’s entrance aperture. The distance, $d_d$, between them was 7.5 mm, their length, $l_d$ was 30 mm and their width was 10 mm. The deflection angle with respect to the flight path, $\theta_d$, for ionized species with a kinetic energy $E_k$ is given by:

$$\theta_d = \arctan \left( \frac{2el_d V_d}{E_k d_d} \right),$$

(5.1)

where $e$ is the elementary charge. The minimum angle to deflect ions from entering the detector was approximately 2.5°.

The targets were attached to the holder of a manipulator in the centre of the processing chamber in sight of the spectrometer. The field-free flight path, $L$, from a target to the channeltron was 577 mm. The solid detection angle was approximately $1.4 \times 10^{-4}$ sr. By rotating the target normal around the laser beam incident at 45°, the angle between that normal and the longitudinal axis of the spectrometer, the detection angle $\theta$, could be varied from 0° up to 90°. As the detector viewed the entire laser-irradiated target-surface spot, a $\cos \theta$ could have been measured as such.

The nascent positive ions arising from ablation were detected as a function of time to obtain the time-of-flight (TOF) spectra desired. This was done at various detection angles. When possible the experimental spectra were fitted by normalized, theoretical distributions. By summing the total number of counts constituting a TOF spectrum at a detection angle, the associated yield, $Y_\theta$, was obtained. By repeating this procedure for various values of $\theta$, ARY distributions were obtained.

The targets were ablated by laser pulses with a wavelength of 193 nm and a duration of 15 ns supplied from an Ar/F\textsubscript{2}/He-filled excimer laser operating at 10 Hz. Some additional experiments were conducted using a Xe/Cl\textsubscript{2}/He-filled excimer laser, supplying 308-nm pulses of 28-ns duration, also operating at 10 Hz. The laser fluence, $F$, at the target surface was estimated from the area ablated in the surface of a PMMA-coated Si sample and the beam power used at that surface. Neutral density filters were used to reduce the $F$ values to about 0.6, 0.9 and 1.2 J cm\textsuperscript{-2}. The
ellipsoidal ablated areas at the target surfaces were approximately 0.5×0.3 mm². As soon as these areas showed significant degradation, fresh spots were used.

Si and Nd₃Ce₀.₁₅CuO₄ were used as targets. The Si targets were commercial boron doped (100)-oriented samples (ρ=1-50 Ω cm⁻¹) from which the native oxide layers were stripped by a dip in a solution of 5 vol.% HF in water. The Nd₃Ce₀.₁₅CuO₄ targets were powder-pressed pellets, which were prepared as follows. A mixture of appropriate amounts of Nd₂O₃, CeO₂ and CuO powders was presintered in air at 1125 K for 10 hours, subsequently pulverized and fired again in air at 1775 K. Thus, Nd₃Ce₀.₁₅CuO₄ was obtained that, according to X-ray powder diffraction analysis, appeared to be composed of a single phase. Then the mixture was pulverized again and pressed isostatically at 0.2 MPa in pellets that were sintered at 1275 K for 16 hours in an oxygen ambient.

It has been argued that the TOF distributions of laser ablated neutrals contained significant contributions of highly excited neutrals, when the deflection potential was only about 25 V [2] (cf. Chapter 4). ARTOF distributions with negligible contributions of these excited neutrals were obtained by applying \( V_\text{d}=2500 \) V; thus, the excited neutrals were ionized by the electric field between the deflection plates and thereby deflected. However, as the ion distributions had to be measured without applying a deflection potential, these distributions always contained contributions of excited neutrals. Fortunately, these contributions, which could be separated from the ion distributions, interfered only negligibly with the ion distributions and were therefore further ignored in the experiments that are described in this chapter.

In the case of the Si⁺ ions, the yields increased roughly linearly with the number of laser pulses incident on a fresh target until a steady state was reached. To avoid the influence of this starting effect the ARTOF spectra that are presented here were measured in steady state. For \( P=1.2 \) J cm⁻² this state was reached after about \( 3.0\times10^3 \) pulses. To study the influence of the morphology of a target surface spot being ablated, the spot’s relative reflectivity was measured as a function of the number of laser pulses. For this purpose a beam from a HeNe laser was focused on the said spot. The reflected light, which would become increasingly diffuse with increasing target roughness, was detected by a photodiode and displayed on a digitizing oscilloscope.

5.3 Results and discussion

A typical TOF spectrum of species originating from laser ablation of Si measured while \( V_\text{d}=0 \) V is shown in Fig. 5.1a; it was measured in a steady state at \( \theta=0^\circ \) employing \( P=1.2 \) J cm⁻². The species constituting this spectrum had a most
probable time-of-flight, $TOF_p$, of approximately 90 μs. (Species ablated from a target before a steady state was reached had the same value of $TOF_p$; their TOF distribution, however, was narrower than the one shown in Fig. 5.1a. The reason for this is not clear.) Upon increasing $V_d$ to approximately 10 V roughly 90% of the number of species constituting the spectra, such as shown in Fig. 5.1a, was deflected. The species that were still detectable constituted a low-yield, relatively broad TOF distribution; the $TOF_p$ value of the said species was about 140 μs. It was concluded that the species that were deflectable by an electric field as low as 10/0.75 V cm$^{-1}$ were positive ions and the species that appeared to be unaffected by such a low field were highly excited neutrals; the nature and the ARTOF and ARY distributions of these neutrals are discussed in more detail in Chapter 6.

In some separate experiments it was found that ablation with laser pulses with a wavelength of 308 nm yielded much less positive ions than ablation with the laser pulses of 193-nm wavelength did, even when the irradiance of the 308-nm beam at the target surface was higher than that of the 193-nm beam. For both wavelengths, however, the ARTOF and ARY distributions displayed similar trends. Therefore, further discussion of the results on Si ablation by 308-nm laser pulses is omitted, unless stated otherwise.

By activating the quadrupole rods, the said ions could be observed only at a mass-over-charge setting, $m/q=28$ amu e$^{-1}$. Recognizing that Si$^{q+}$ ions with $q=2$, 3, etc., are unstable, the ions must have been Si$^+$ ones. Indeed, this conclusion

![Graph showing TOF distribution](image)

**Fig. 5.1a.** A TOF distribution of Si$^+$ ions measured at $\theta=0^\circ$; the ions were emitted applying $F=1.2$ J cm$^{-2}$. The solid curve is a theoretical (angle-independent) MB-like distribution, given by Eq. 5.2 with $T=18.00\times10^3$ K and $u=3.40\times10^3$ m s$^{-1}$, fit to the experimental data.
was also drawn from analysis of plasmas produced by laser ablation of Si employing photon emission spectroscopy [6,23] and X-ray absorption spectroscopy [24]; with these techniques species can be identified with greater certainty than with quadrupole mass spectrometry. Further, no other ions, such as Si$^{2+}$ ions, were detected. Multiply ionized Si ions, however, could have been expected when considerably higher laser fluences would have been applied [6,23,24].

A typical TOF spectrum of species originating from laser ablation of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ measured while $V_d=0$ V is shown in Fig. 5.1b; it was also measured at $\theta=0^\circ$ employing $F=1.2$ J cm$^{-2}$. It comprised three partially overlapping contributions. By slightly raising $V_d$ from 0 V up to approximately 12 V the yield associated with these contributions decreased similarly for all three contributions. It was observed that the (partial) yield per TOF interval of the contribution at relatively long times-of-flight, which to a large extent was distinguishable from the other two contributions, fell quicker at the contribution’s trailing edge than at its leading edge; this appeared also to be the case for the other two contributions. At $V_d=12$ V all three contributions disappeared completely. For this reason it was concluded that the contributions were made up by three types of easily deflectable positive ions that had similar kinetic-energy (KE) distributions, irrespective of the ions’ mass, $m$. As the three types of ions had similar KE distributions, but different TOF distributions, the
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$TOF_p$ values corresponding with the three TOF contributions were recognized as a measure of $m/q$ for the ions they were associated with. By applying Eq. 5.1, using the potential of approximately 12 V at which the ion contributions vanished and the $TOF_p$ values associated with the three contributions, it was calculated that the $m/q$ values of the ions constituting the contributions at relatively short, intermediate and long flight times were about 16, 63 and 144 amu e$^{-1}$, respectively.

By activating the quadrupole rods, the three contributions could be measured separately. The separate TOF distributions hardly differed from the corresponding parts that were visible in the overall distributions measured under field-free conditions. The contributions at the relatively short, intermediate and long times-of-flight were indeed only visible at the said $m/q$ settings. Hence, the ions were identified as O$_2^+$, Cu$_2^+$ and Nd$_3^+$ ions of which the O$^+$, Cu$^+$ and Nd$^+$ ones were by far the most probable. Further, no other ions, like doubly charged ions or NdO$^+$ ions, were observed.

5.3.1 ARTOF distributions

The Si$^+$ ions constituting the TOF spectrum shown in Fig. 5.1a had a $TOF_p$ value of approximately 90 μs. Given the field-free flight path of 557 mm (see Section 5.2 and Chapter 3), this value corresponded to a most probable kinetic energy, $E_{kp}$, of approximately 6.1 eV. Similarly, the $TOF_p$ values of the O$^+$, Cu$^+$ and Nd$^+$ ions constituting the TOF spectrum shown in Fig. 5.1b, corresponded to $E_{kp}$ values of about 9.8, 10.0 and 9.8 eV, respectively. Thus, for various types of equally charged ions emitted from a plasma produced by laser ablation of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ $E_{kp}$ was independent of the masses of those ions. This is in good agreement with the fore-mentioned conclusion that the KE distributions of those ions were alike.

Neither the TOF distributions of the Si$^+$ ions nor those of the O$^+$, Cu$^+$ and Nd$^+$ ions changed significantly with the detection angle, $\theta$. This contrasts the behaviour of the TOF spectra of the neutrals emitted from the same plasmas [2] (cf. Chapter 4): upon increasing $\theta$ those spectra shifted to longer times-of-flight and decreased in yield. Clearly, the mechanisms that were responsible for the emission of the positive ions during laser ablation were different from those responsible for the emission of the neutrals.

The TOF distributions of the Si$^+$ ions did not change significantly with the laser fluence, $F$, either; this has also been observed for Si$^+$ ions [6], Ag$^+$ ions [25] and Al$^+$ ions [26] arising from ablation of Si, Ag and Al, respectively. As the surface or subsurface temperatures associated with laser ablation depend on $F$, it was concluded that in a first order approximation the emission of the Si$^+$ was not the result of a temperature-dependent ablation mechanism, such as explosive surface evaporation or volume evaporation [27]. However, for higher values of $F$ the TOF distributions due to the O$^+$, Cu$^+$, Nd$^+$ ions were shifted to shorter times-of-flight. Hence, in this case temperature-determined ablation mechanism could not be excluded.
The ARTOF spectra of laser ablated neutrals have been fitted successfully with Maxwell-Boltzmann (MB) TOF distributions superimposed onto longitudinal flow velocities [2] (cf. Chapter 4). These fits gave valuable information about the mechanisms involved in laser ablation of neutrals from a target. Therefore, such MB distributions were also tried to fit the TOF spectra of the ions. Note, that in the case of ions TOF flux distributions were measured, whereas in the case of the neutrals TOF number-density distributions were measured (see Section 5.2 and Chapter 3). Therefore, MB TOF flux distributions had to be applied to fit the experimental TOF spectra of the ions. As the latter did not change with the detection angle, $\theta$, the MB fits were not to change with $\theta$ either. Hence, any angle dependence in a distribution (as described by Eq. 4.2 (cf. Chapter 4)) had to be omitted. This resulted in:

$$d^3 f_{\Omega t} = C \frac{1}{t^4} \exp \left\{ - \frac{m[(L/t) - u]^2}{2kT} \right\} \, d\Omega \, dt,$$

(5.2)

where $d^3 f_{\Omega t}$ is the species' flux detected per solid detection angle interval, $d\Omega$, and per TOF interval, $dt$, $t$ is a time-of-flight of the species, $m$ is the mass of the species, $L$ is the flight path, $u$ is a longitudinal flow velocity, $k$ is the Boltzmann constant, $T$ is a temperature and $C$ is a normalization constant. (With respect to the MB number-density distribution given by Eq. 4.2 (cf. Chapter 4) in Eq. 5.2 an extra prefactor $t^4$ has appeared to neglect the velocity dependence of the ionization probability involved in the number-density measurements of neutrals (see Chapter 3)).

*Fig. 5.2. The fitting parameters $T$ and $u$ of theoretical (angle-independent) MB-like distributions fit to the experimental TOF distributions of Si$^+$ ions, as a function of $\theta$; the ions were emitted applying $F=1.2$ J cm$^{-2}$. 
The TOF spectrum of Si$^+$ ions shown in Fig. 5.1a was fitted well with a
distribution described by Eq. 5.2 utilizing the fitting parameters $m=28$ amu,
$T=18.00\times10^3$ K and $u=3.40\times10^3$ m s$^{-1}$; this fit is shown as a solid curve in Fig. 5.1a.
Because the Si$^+$ TOF distributions did not change with $\theta$, neither did $T$ and $u$; this is
illustrated by Fig. 5.2. To our knowledge, this is the first time that a TOF distribution
of ions originating from laser ablation was successfully fitted with an MB distribution superimposed onto a flow velocity.

Also the separate O$^+$, Cu$^+$ and Nd$^+$ TOF distributions measured with the
quadrupole rods in operation were fitted quite well with distributions as given by
Eq. 5.2; for this the fitting parameters $m=16$, 63 and 144 amu, $T=12.50\times10^3$, $10.00\times10^3$ and $4.90\times10^3$ K and $u=8.40\times10^3$, $5.00\times10^3$ and $3.45\times10^3$ m s$^{-1}$ were
applied, respectively. The corresponding TOF spectrum that was measured under
field-free conditions was fitted with a summation of those individual fits weighted to
the associated relative yields. This three-component fit is shown in Fig. 5.1b as a
solid curve. Though the trend that both the $T$ and $u$ values fell with an increasing ion
mass was observed, thus-far, we have not been able to come up with a (qualitative)
relation between that mass and those two MB fitting parameters.

### 5.3.2 ARY distributions

From the ARTOF distributions of the ions ARY distributions were obtained.
ARY distributions of Si$^+$ and Nd$^+$ ions emitted upon laser ablation with $F\approx0.6$, 0.9

![Graph](image)

**Fig. 5.3a.** An ARY distribution of Si$^+$ ions; the ions were emitted applying $F\approx1.2$ (●), 0.9 (○) and 0.6 J cm$^{-2}$ (■).
and 1.2 J cm\(^{-2}\) are shown in Fig. 5.3a and b, respectively; the ARY distributions of the O\(^{+}\) and Cu\(^{+}\) ions were similar to the Nd\(^{+}\) ones. Because the separate contributions of the O\(^{+}\), Cu\(^{+}\) and Nd\(^{+}\) ions in the TOF spectra, such as shown in Fig. 5.1b, partially overlapped, the yields of those three types of ions were obtained using the separate TOF distributions of those ions measured with the mass spectrometer’s quadrupole rods activated; the yields obtained were normalized to the peak of the corresponding contributions in the three-component TOF distribution to yield the data to be desired.

The spread in the data in the Figs. 5.3a and b was about 15\%. This was higher than the square root of the number of counts involved, which could have been expected statistically. This might have been due to surface roughness and/or to instable performance of the laser and the electronics of the mass spectrometer by prolonged measuring.

Within the experimental spread of the data both the Si\(^{+}\) and Nd\(^{+}\) yields remained about constant up to \(\theta=80^\circ\). It was concluded that the emission of the ions originating from laser ablation of a target is isotropic, at least up to \(\theta=80^\circ\). Angular distributions of ions emitted from laser-produced plasmas that were isotropic up to lower detection angles have been reported before [28,29]. These ARY distributions were quite different from the \(\cos^6\theta\)-like ARY distributions of the neutrals emitted from same plasmas [2] (cf. Chapter 4). This indicates that the mechanisms that were responsible for the emission of the positive ions due to laser ablation of material were not the same as those responsible for the emission of the neutrals, as was concluded before in relation with the ARTOF spectra.
In the case of the Si\(^{+}\) ions, the yields increased roughly linearly with the number of laser pulses incident on a fresh target until a steady state was reached. This starting effect did not influence the fore-mentioned isotropy of the ion emission: the ion yields that were obtained from the first several tens of ablative pulses of fresh target surface areas, which were refreshed every time a new detection angle was employed, also remained constant with \(\theta\). It was expected that this starting effects was associated with the roughness of the target-surface spot that was being ablated. Therefore, during the experiments the reflectivity of that spot was monitored (see Section 5.2). Until the steady state was reached the intensity of the reflected 633-nm laser beam faded: the reflected beam became increasingly diffuse due to surface roughening. This was verified by scanning electron microscopy (SEM) analysis of Si targets before the steady state was reached. So, the ion yield increased with increasing surface roughness. This was also the case for Si\(^{+}\) ions that were photo-emitted from Si for fluences, \(F\), well below the melting and ablation threshold of Si [30]. Comparison with that experiment, however, should be made with caution, because for such low values of \(F\) the ion emission mechanisms are likely to be different from those operative for the relatively high values of \(F\) that were applied in the present experiments.

5.3.3 Preliminary degrees of ionization

The degree of ionization, \(\alpha\), of a plasma is defined as the number of ions per original atom present in the plasma [31]. The numbers of ions in the plasmas produced by ablation of Si and Nd\(_{1.85}\)Ce\(_{0.15}\)CuO\(_4\) were estimated from the ARTOF and ARY distributions of the ions. Accounting for the channeltron’s quantum efficiency of approximately 10\%, the average numbers of Si\(^{+}\) and of O\(^{+}\), Cu\(^{+}\) and Nd\(^{+}\) ions detected within a solid detection angle of 1.4\times10\(^4\) sr were about 36 and 124 per laser pulse, respectively, for \(F=1.2\) J cm\(^{-2}\). Thus, the respective numbers of ions emitted into vacuum into a solid angle of 2\(\pi\) sr were about 1.6\times10\(^6\) and 5.6\times10\(^6\) per pulse. From SEM analysis of the ablated target surfaces the respective numbers of ablated Si and O, Cu and Nd atoms, present in the laser-induced plasmas, were estimated to be 4.5\times10\(^{12}\) and 3.2\times10\(^{13}\) per laser pulse, respectively. Thus, for the plasmas produced by laser ablation of Si and Nd\(_{1.85}\)Ce\(_{0.15}\)CuO\(_4\), as determined from the number of ions detected at 577 mm from the targets, \(\alpha\) appeared to be of the order of 3.6\times10\(^{-7}\) and 1.8\times10\(^{-7}\), respectively; in Section 5.3.5 it will be shown that these preliminary values were underestimates actually.

These preliminary values are in fair agreement with similarly obtained values for similarly produced plasmas [29,32], whereas also values have been reported that were of the order of a tenth of a percent [6,33], several percent [12,34] or even much higher [7-9]. Most of these results were obtained making use of an electric (Langmuir) probe for the detection of the ions. However, from the surface of this kind of probe secondary electrons can be liberated upon the impact of species that
had kinetic and/or internal energies greater than the work function of that surface [35,36]. Therefore, the relative high values of \( \alpha \) that were obtained from experiments in which the impact of a positive ion on a probe could not have been distinguished from the emission of a secondary electron from the probe [6-9,12] have been considered to be overestimated due to neglect of the said secondary electron emission effect [29,37].

However, laser-induced fluorescence (LIF) analysis of plasmas originating from laser ablation of Cu using near-threshold laser fluences indicated that for those plasmas \( \alpha \) was of the order of a few tenths of a percent [33]. Though accurate quantitative number densities of selected species in a plasma cannot be obtained from LIF analysis, orders of magnitude of those number densities can. So, the values of \( \alpha \) obtained from the LIF data [33] appeared to disagree with the said values of about \( 10^{-7} \) as well. Note, however, that the former values were obtained from the numbers of ions within the plasmas, whereas the latter values were obtained from the numbers of ions far from the plasmas. Therefore, the latter values are to be corrected for effects due to ambipolar diffusion (AD) of ions and electrons from the plasmas to estimate the actual values of \( \alpha \). This was omitted in other reports [29,32], but will be demonstrated in Section 5.3.5.

5.3.4 Ambipolar diffusion

Several observations made on the behaviour of positive ions and electrons originating from laser ablation of materials, which have been presented in the preceding sections and in literature [6,24,28,29,33,38-40], have led us to the following conclusion: the emission of positive ions and electrons from laser-induced plasmas are due to AD. The action of AD in plasmas is well known in the field of plasma physics [31,41]. However, in the field of physics of laser ablation (and deposition) it appears not to be common [3,6,24,25,29,32,39,40,42], although it has been recognized to be operative in laser-produced plasmas as well [10,11,43]. Hence, for the sake of completeness a brief, qualitative description of this phenomenon will be given first, before the effects of AD will be discussed in relation to the fore-mentioned observations; a more detailed treatise of AD can be found in literature on plasma physics [31,41].

In a plasma that contains considerable number densities of species with substantial kinetic energies, like a laser-induced plasma, the pressure is high. When the ambient pressure is lower, the plasma will expand, that is, its constituent species tend to diffuse out of it. When the number densities of positive ions and of electrons are similar, the diffusion of the ions and electrons proceeds ambipolar, that is, the ions and electrons diffuse together in a coupled fashion out of the plasma. As the electrons are very small and have a very small mass, they have a long mean free path, acquire high velocities and tend to leave the plasma much faster than the ions do. In this way the plasma tends to become electron-depleted. However, the remainder of
ions and electrons in the plasma constitutes a net positive space charge. The effected space-charge separation creates an electric field, which retards the electrons and accelerates positive ions diffusing out of the plasma. Thus, it limits the number of electrons leaving the plasma and establishes quasi-macrosopic charge neutrality within the plasma. As a result, the electron depletion is confined to a skin of the plasma. Consequently, only the ions within this skin are accelerated by the electric field, whereas the ions within the interior of the plasma are shielded from it.

Several observations made on the behaviour of positive ions and electrons originating from laser ablation of materials can be explained on the basis of AD. We observed that the TOF distributions of the positive ions emitted from plasmas originating from laser ablation of Si and Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ did not change with the detection angle, $\theta$; correspondingly, the yield of those ions did not change with $\theta$ either. This isotropic AD is initiated by isotropic electron emission from laser-induced plasmas; it has been observed that when a solid is irradiated by a pulsed laser beam, where the applied fluences were too low to form plasmas, the electron emission was highly anisotropic, directed along the target-surface normal, whereas it became isotropic as the fluence was raised above the threshold for plasma formation [38]. This indicates that the plasmas considered were spherical.

We also observed that the degrees of ionization, $\alpha$, that have been obtained in Section 5.3.3 from the numbers of ions detected far from the ablation-induced plasmas were several orders of magnitude lower than those obtained from the numbers of ions within or near the plasmas [33]. Clearly, this can be explained by the fact that of the number of ions present in the plasmas only the fractions present within the fore-mentioned plasma skin can be extracted due to AD; quantitative estimates for the said fractions will be presented in the following section.

It has also been observed that for ions the most probable kinetic energy, $E_{kp}$, was substantially higher than for the neutrals emitted from the same plasmas. Moreover, $E_{kp}$ was independent of the ions' mass. These observations can be explained as follows. As a result of pressure gradient-induced diffusion the ions and neutrals in the plasmas have similar kinetic energies, which are independent of the species' mass. In addition to these energies, due to AD, the ions acquire additional quantities of kinetic energy that are independent of the ions' mass, whereas the neutrals do not.

One of the said several unsatisfactory explained observations made by others was that the TOF spectra of positive ions and of electrons, which were also measured far outside the laser-produced plasmas, were alike [39,44]. This was probably a result of the said coupled motion of the ions and electrons that participate in AD.

Finally, it has been observed that the most probable time-of-flight, $TOF_p$, of the positive ions outside ablation-produced plasmas were about inversely proportional to the charges of those ions [6,34,40]. This can be explained by the fact that in the AD-induced electric fields the kinetic energies that ions can acquire increase with the
charges of those ions; note, however, that it might have been expected that $E_{kp}$, instead of $TOF_p$, was inversely proportional to the charges of the ions.

The mechanism of AD took place in the initial stages of the plasmas that arose from laser ablation of Si and of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$. Here this will only be shown for the case of Si, but similarly it can be shown for the case of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$. Laser-produced plasmas in a relatively low-pressure ambient expand (see Chapters 2 and 4). The majority of the species from these plasmas, being neutral, constitute MB ARTOF distributions superimposed on flow velocities directed along the target-surface normal. This indicates that the plasmas detached from the target surface and equilibrated in flowing systems. If the detected Si$^+$ ions would have been emitted from a system flowing at a flow velocity $u$, their most probable velocity, $v_\theta$, in a direction associated with a detection angle $\theta$ would have been given by:

$$v_\theta = \sqrt{\left([v_{AD} - u] \cos \theta + u \cos \theta \right)^2 + \left[v_{AD} - u \right]^2},$$

(5.3)

where $v_{AD}$ is the velocity that the ions acquired by AD. Knowing that the most probable velocity of the Si$^+$ was approximately $6.4 \times 10^3$ m s$^{-1}$ and assuming that for the flowing system $u$ was typically $2.0 \times 10^3$ m s$^{-1}$ (cf. Chapter 4), the corresponding value of $v_{AD}$ would have been about $4.4 \times 10^3$ m s$^{-1}$. Applying Eq. 5.3 with these parameters results in $v_{90^o}=6.4 \times 10^3$ m s$^{-1}$ and $v_{80^o}=4.5 \times 10^3$ m s$^{-1}$. The corresponding values of $TOF_p$ necessary to travel the 577-mm-long flight path would have been approximately 130 and 90 $\mu$s, respectively. As the experimentally obtained value of $v_{80^o}$ was also about $6.4 \times 10^3$ m s$^{-1}$, it is concluded that the Si$^+$ ions were expelled from the plasmas before the plasmas detached from the target surface and acquired a flow velocity. In those initial stages of the plasmas the number densities of ions and electrons present, the potential energies to expel those ions and electrons and, consequently, the action of AD were at a maximum.

5.3.5 Degrees of ionization

The dynamics of AD can be modelled pseudo-analytically [31,41]. Primary input parameters for the model are a plasma temperature, mobilities of the ions and the electrons, and the number density distributions of the ions and electrons. The analytical equations in the model have to be solved numerically. For the sake simplicity, however, here only an estimate of the degree of ionization, $\alpha$, of the plasmas produced by laser ablation of Si taking AD into account are presented; subsequently, some estimates of the kinetic energies that the ions emitted from these plasmas could have acquired by AD are presented. Similar estimates for the case of laser ablation of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ yielded similar results.

To obtain the said values of $\alpha$, firstly, the number density of the Si atoms in the laser-induced plasmas will be evaluated. Assuming the Si atoms to have had an
(average) $E_{kp}$ value of typically 1.5 eV [2] (cf. Chapter 4), during a 15-ns-during laser pulse a plasma of about 48 $\mu$m thickness would have been developed; the length and breadth of the plasma are assumed to have been 0.5 and 0.3 mm, respectively, which dimensions stem from those of the laser-ablated target-surface area. Considering the estimated Si ablation rate of several monolayers per incident laser pulse (cf. Section 5.3.3), the number density of Si atoms in a plasma is assessed to have been $4.8\times10^{14}$ mm$^{-3}$. Secondly, the number density of ions in the plasmas will be evaluated. For this the depth of the plasma skin to which the AD-induced electric field can be operative is to be assessed. This depth was of the order of the Debye shielding distance, $\lambda_D$, which is given by [31]:

$$\lambda_D = \left( \frac{e_0 kT}{2n_i e^2} \right)^{1/2},$$

(5.4)

where $e_0$ is the permittivity in vacuum, $n_i$ is the number density of free positive ions and electrons, and $e$ is the elementary charge. (This shielding distance is quite appropriate for stationary singly charged species; in dynamical situations, however, the ions and electrons contribute to a different extent to the shielding of the electric field [31].) Applying the fore-mentioned LIF data [33] to this case, for the plasma considered $n_i$ is stipulated to have been 0.2% of the number density of the Si atoms; note that thus the plasma’s initial value of $\alpha$ is stipulated to have been 0.2%. A typical (average) value of $E_{kp}$ for neutrals of about 1.5 eV [2] (cf. Chapter 4) indicates that the initial plasma temperature was about $11.8\times10^3$ K. Then, applying Eq. 5.4, $\lambda_D$ would have been about 0.1 $\mu$m. Thus, the volume of the said plasma skin constituted only a fraction of 0.3% of the entire plasma volume. Consequently, only about 0.3% of the total number of ions was detected. Applying this result to the experimentally studied plasmas originating from laser ablation of Si, the number density of the $Si^+$ ions in those plasmas were about $7.5\times10^{10}$ mm$^{-3}$. As a result, for those plasmas $\alpha$ was about $1.6\times10^4$.

An additional correction on the obtained value of $\alpha$ can be made. Analysis of laser-induced plasmas by photon emission spectroscopy [4,26] and by photon absorption spectroscopy [5] showed that the number of (excited) positive ions fell rapidly beyond about 1 mm from the target surface. These results can be ascribed to pronounced electron-ion recombination, which takes place as soon as the plasma expands (three dimensionally); far beyond several millimetres from the target surface the number densities of the ions and electrons fall such that the probability for further recombination becomes negligible. As for the said LIF analysis the number densities of ions at 5 mm and further from the target surface were probed, the resulting data are an underestimate of the number density of the ions in the plasmas in their initial stages. Hence, the initial value of $\alpha$ of 0.2% that was applied in the foregoing calculation should have been higher. Consequently, the obtained value of $\alpha$ should have been higher.
Though the values of some parameters have been estimated in the foregoing calculations, it is obvious that by taking AD into account the value of $\alpha$ approaches those obtained from the fore-mentioned LIF data [33] quite well.

5.3.6 Kinetic energies of ejected ions

Now some estimates of the kinetic energies that the Si$^+$ ions acquired from AD from the plasmas arising from laser ablation of Si will be presented. For the sake of simplicity some properties of laser-induced plasmas will be simplified. Because it has been observed that the emission of the ions was isotropic, the plasma will be assumed to be half a sphere, with a radius $R$, that is attached by its section to the target surface. (At first sight this assumption may seem to be rough. Note, however, that due to the Gaussian intensity profile of the laser beam the plasmas probably indeed were spherical rather than disk-like. This assumption does hardly affect the degree of ionization, $\alpha$, that was calculated in the preceding section.) The plasma skin from which ions and electrons diffuse ambipolarly has a thickness of $d_s$. This skin contains gross $N_i$ and net $N_n$ homogeneously distributed positive ions. When the electrons outside the plasmas are neglected and AD is assumed to proceed collisionless, the average potential (electric) energy $U_i$ available per ion is given by (see Appendix 5.A):

$$U_i = \frac{3N_n^2e^2}{20\pi \varepsilon_0 N_i} \left[ \frac{1}{R} - \frac{(R - d_s)^5}{6R^6} \right],$$  \hspace{1cm} (5.5)

The maximum and the minimum values of $d_s$ are $R$ and 0, respectively. Hence, the maximum and minimum values of the factor $(1/R)-(R-d_s)^5/6R^6$ in Eq. 5.5 are $1/R$ and $5/6R$, respectively. These values associated with Eq. 5.5 indicate that the influence of the value $d_s$ on the available potential energy is small compared with the influence of the value of $R$ on that energy. Obviously, for constant values of $N_i$ and of $N_n$, with a change of the value of $d_s$ the corresponding change of the action of the net number of ions contributing to the potential energy is almost fully compensated by the change in action of the net number density of those ions.

The kinetic energy of the ions that were expelled from the said plasma skin can be estimated by applying Eq. 5.5, because those ions obtained their kinetic energy from the AD-produced potential energy. It has been shown that the value of $N_i$ was about $1.6 \times 10^6$ (cf. Section 5.3.3). For simplicity the value of $N_n$ is taken equal to the said value of $N_i$. $R$ is assessed to have been 0.13 mm, stemming from the initial plasma dimensions. The value of $d_s$ is taken equal to about 0.1 $\mu$m, the value of $\lambda_D$ that has been calculated in Section 5.3.5. Applying Eq. 5.5 and using these parameters results in a potential energy of 9.2 eV. This is the maximum kinetic energy that the Si$^+$ ions could have acquired according to this simple model. If the skin of the Si plasmas would have contained a substantial number of electrons, in
addition to the positive ions contained, the available amount of potential energy would have been less than the obtained value. Clearly, this simple calculation yields a value for a kinetic energy that is in reasonable agreement with the experimentally obtained value of 6.2 eV.

It has been shown that the most probable kinetic energy of the neutrals originating from Nd_{1.85}Ce_{0.15}CuO_{4} from the same ablation events as the O^{+}, Cu^{+} and Nd^{+} ions were approximately 1.5 eV. Hence, if the free electrons also would have had a kinetic energy of about 1.5 eV [2] (cf. Chapter 4), about seven of them would have been required to accelerate the said ions so that these would acquire their most probable kinetic energy of about 10 eV (cf. Section 5.3.1). This mechanism is not very likely. Therefore it can be concluded that in the initial plasma stages, in which AD took place (cf. Section 5.3.4), the kinetic energies of the electrons were substantially higher than the said 1.5 eV. This was probably a result of the inverse Bremsstrahlung (IB) mechanism, in which a free electron during collisional interaction with a neutral or an ion gains kinetic energy by absorption of a photon from the trailing edge of the ablating laser pulse.

### 5.3.7 Ionization mechanisms

During the process of laser ablation of material several mechanisms can contribute to the excitation and ionization of (excited) neutrals in the laser-produced plasma. Amongst others, those neutrals can get excited and ionized by (1) collisions with other neutrals, ions and (free) electrons and (2) absorption of photons. Ions may also be emitted from a target surface by photoelectron-induced electric-field emission [30]. Each mechanism will be discussed briefly.

As the 193-nm photon energy is 6.3 eV and the work function of a Si surface is approximately 4.3 eV, photoelectrons with a binding energy of up to approximately 2.3 eV can be emitted from a Si-target surface. Thus, an electric field between the emitted electrons and the target surface is induced. This field impedes the emission of electrons and accelerated positive ions from the surface to reestablish space-charge neutrality. This mechanism can explain the observations that for ions $E_{kp}$ was independent of the ion mass, but increased with the ion charge, and that electrons and ions acquired more or less equal velocities. The fact that the TOF and associated yields did not change with the detection angle, however, cannot be explained on the basis of this mechanism. As photoelectrons are emitted along the normal of a target surface, the said electric field would have been directed along that normal. Thus, ions would have been accelerated from the target surface only under small angles, as was observed for Si^{+} ions originating from a surface that was irradiated with 193-nm photons well below the Si melting and ablation threshold [30]. Hence, photoemission of electrons did not play a significant role in the present experiments.

In an isolated (laser-induced) plasma, the neutrals, free ions and free electrons tend to attain and maintain a local thermodynamic equilibrium by mutual collisional
interaction; the photons are not involved in this equilibration. (Note, that strictly speaking the laser-induced plasma cannot attain thermodynamic equilibrium due to the non-equilibrium nature of laser ablation.) The number densities of the ions and electrons decrease when the temperature of the plasma decreases. As a laser-produced plasma expands (see Chapter 2 and 4) the initial thermal energy of the plasma is converted into kinetic energy of the particles that diffuse out of the plasma. Moreover, as the plasma tends to equilibrate in a flowing system, the initial thermal energy is divided over the thermal energy and the kinetic flow energy of the flowing plasma (see Chapter 4). As a result, the plasma attains a new state in which the equilibrium plasma temperature and following electron-ion recombination, the corresponding number densities of the ions and electrons are lower than in its initial state.

In an isolated plasma, the number densities of the said particles at equilibrium are given by the Saha equation [31,36,45]:

\[
\frac{n_p n_e}{n} = 2 \frac{g_i}{g} \left( \frac{2 \pi m_e kT}{\hbar^2} \right)^{3/2} \exp \left( - \frac{E_0}{kT} \right), \tag{5.6a}
\]

where \(n_p, n_e,\) and \(n\) are the number densities of the singly charged ions, the electrons and the atoms, respectively, \(g_i\) and \(g\) are the degeneracies of the ground level of the ions and atoms, respectively, \(m_e\) is the electron mass, \(\hbar\) is the Planck constant and \(E_0\) is the first ionization potential for isolated atoms. For the sake of simplicity, the plasma temperature \(T\) is taken equal to the heavy-particle temperature and the electron temperature in the plasma; as has been argued in the preceding section, however, this was probably not the case in the present experiments. If, in addition, the rates of formation of the particles in the plasma are assumed to be in equilibrium with the rate of thermonic electron emission from the target surface, the latter being described by the Richardson-Dushman equation [35,46], the degree of singly ionization can be estimated using the Saha-Langmuir equation [47]:

\[
\frac{n_i}{n} = \frac{g_i}{g} \exp \left( - \frac{E_0 - \Phi}{kT} \right), \tag{5.6b}
\]

where \(\Phi\) is the work function of the surface. Note that the ratio \(n/n\) is not equal to the degree of ionization, which has been defined as \(n/(n+n_i)\).

To estimate the degree of the number of Si atoms that were singly ionized under the experimental conditions used both Eq. 5.6a and b will be applied. For simplicity, \(g_i/g_0\) is taken unity and the number densities of free ions and of free electrons are taken equal. Further, for Si atoms \(E_0\) is approximately 8.15 eV [48] and for Si that has been molten by the incident laser irradiation \(\Phi\) is approximately 4.3 eV [49]. The typical (average) \(E_{kp}\) value for neutrals of about 1.5 eV [2] (cf. Section 4.3.1) indicates that the plasma temperature was about 11.3×10^3 K. Applying
Eq. 5.6a and 5.6b and using these parameters results in values of $\alpha$ that were 8.3\% and 1.8\%, respectively. These values are only an order of magnitude higher than the values that were obtained in Section 5.3.5 for the Si plasmas in their initial stage. Note, however, that for collisional ionization $\alpha$ changes exponentially as a function of the plasma temperature (cf. Eqs. 5.6a and b). This plasma temperature has been estimated for the foregoing calculation. Hence, though it is likely that collisional excitation played an important role as a ionization mechanisms during the present experiments, accurate determination of the initial plasma temperature is required to determine whether or not collisional ionization was playing a major role in formation of Si$^+$ ions in the plasmas produced by laser ablation of Si.

It is known that species are able to desorb within a nanosecond after the impact at the target surface of photons from the leading edge of a laser pulse. Hence, in the present experiments the 15-ns-long laser pulses intersected the ablation-produced plasmas. Thus, by IB, free electrons can gain kinetic energy by absorption of photons during interaction with neutrals and ions, and subsequently excite and ionize neutrals. The absorption coefficient for electron-ion IB is higher than the one for electron-neutral IB. The coefficient increases with increasing excitation wavelength. As for ablation by 308-nm pulses $\alpha$ turned out to be significantly lower than for ablation by 193-nm pulses, it is concluded that, though in the experiments a significant number of Si$^+$ ions was formed in the initial plasma stages, IB probably did not play a dominant role in further ion formation.

However, intersection of a plasma by a laser pulse also enables multiphoton ionization. As the ionization energy of an isolated Si atom in the plasma is 8.15 eV and the 193-nm photon energy is 6.3 eV, atoms in the ground state can be ionized by absorption of two photons and atoms that already have an energy of 1.85 eV or more with respect to the ground state can be ionized by absorption of a single photon. The absorption cross sections for such mechanisms are significant. The absorption cross sections for 308-nm photons with an energy of only 4.0 eV are significantly lower. Consequently, for 308-nm ablation $\alpha$ should be lower than for 193-nm ablation, which is in agreement with the preliminary observations. Hence, multiphoton ionization probably played a dominant role in ionization of desorbed Si atoms.

### 5.4 Summary and conclusions

TOF distributions of Si$^+$ ions and of O$^+$, Cu$^+$ and Nd$^+$ ions emitted from plasmas produced by laser ablation of Si and Nd$_{1.85}$Ce$_{0.15}$CuO$_4$, respectively, were measured as a function of the detection angle, $\theta$. From these distributions ARY distributions of the said ions were obtained.

The most probable kinetic energies ($\sim$10 eV) of the O$^+$, Cu$^+$ and Nd$^+$ ions obtained from the TOF distributions were equal, but higher than those of the laser ablated neutrals. Moreover, the TOF distributions indicated that the KE distributions
of ions emitted from laser-induced plasmas are similar regardless of the ions’ mass and regardless of $\theta$.

The TOF distributions did not change with $\theta$; consequently neither did the yields.

These results (and many thus far poorly explained results of others) can be explained by AD of electrons and positive ions from laser-produced plasmas in their initial stages. The degrees of ionization, $\alpha$, of the plasmas, corrected for the fact that the ions were emitted only from a thin skin of the plasmas, were several tenths of a percent. Because only a small fraction of the ions present in the plasmas was characterized, little can be said about the impact of ions on the properties of LAD-grown films.

The present results indicate that collisional ionization and multiphoton ionization were the prime mechanisms for the formation of the ions.

5.A Appendix: The kinetic energy of ambipolar diffusing ions

Consider a static, spherical plasma with radius $R$. Within a sphere with radius $R-d_s$, where $d_s$ is a skin depth, equal number densities of homogeneously distributed positively charged ions and electrons is present. Consequently, macroscopically this sphere is electrically neutral. Due to AD, however, within the spherical plasma skin, with depth $d_s$, the number of positive ions, $N_p$, exceeds the number of electrons, $N_e$; both ions and electrons are also distributed homogeneously within the skin. Thus, the net space charge within the skin is $N_p e$, where $N_p = N_p - N_e$ is the net number of charges and $e$ is the elementary charge. Applying the Gauss equation $\nabla \cdot E = \rho_n / \varepsilon_0$, where $E$ is an electric field and $\rho_n$ is the net charge density, results in an electric field $E$:

\[
E = \frac{eN_p}{4\pi \varepsilon_0 R^3} \quad \text{for} \quad R - d_s \leq r \leq R
\]  
(5.A1a)

\[
E = \frac{N_p e}{4\pi \varepsilon_0 r^2} \quad \text{for} \quad r \geq R,
\]  
(5.A1b)

where $r$ is the distance to the centre of the spherical plasma. The average potential energy, $U_s$, available in the plasma skin is calculated using:

\[
U_s = \frac{1}{2} \varepsilon_0 \int_{R-d_s}^{R} E^2 \, d^3r,
\]  
(5.A2)

Substitution of Eq. 5.A1a and 5.A1b in Eq. 5.A2 results in:
\[ U_s = \frac{3N_n^2e^2}{20\pi\varepsilon_0} \left( \frac{1}{R} - \frac{(R - d_s)^5}{6R^6} \right). \]  

(5.A3)

Hence, the potential energy, \( U_p \), available for the kinetic energy of a single positive ion is:

\[ U_i = \frac{U_s}{N_i}. \]  

(5.A4)

References


[22] R.P. van Ingen, unpublished (concerned the growth of Nd$_{1.45}$Ce$_{0.15}$CuO$_x$ thin films).


Chapter 6

Detection of electric-field-ionized Rydberg atoms originating from laser ablation of Si

Angle-resolved time-of-flight distributions of \( \text{Si}^+ \) Rydberg atoms originating from laser ablation of Si were measured, employing a pair of deflection plates for electric-field ionization of the atoms and a quadrupole mass spectrometer. The atoms had a principle quantum number of up to approximately 60. From the said distributions angle-resolved yield distributions were obtained. Both the most probable time-of-flight and the yield of the \( \text{Si}^+ \) atoms decreased with an increasing detection angle. Further, the atoms' most probable time-of-flight decreased with increasing target surface roughness, while their yield increased. On the basis of the present results it cannot be ruled out which of the many possible mechanisms were responsible for the formation and emission of the Rydberg atoms.

6.1 Introduction

Laser ablation deposition (LAD) is a promising, versatile technique for the production of thin films of a wide variety of materials [1]. However, its development is retarded, because little is known about the fundamental ablation mechanisms. Therefore, a considerable amount of research is conducted to comprehend the dynamics of laser ablation. Particularly the time-of-flight (TOF) distributions of the ablated species to be deposited are of interest. To measure these photon emission spectroscopy or quadrupole mass spectrometry can be employed. The latter technique is often preferred to the latter, because in contrast to the latter technique it enables to detected species regardless of their internal energy state. However, in this chapter it will be shown that this need not always be the case.

It is known that highly excited neutral species may liberate secondary electrons upon impact at the surface of a solid target [2,3]. If the target is an electric probe the emission of those electrons can be ascribed to the impact of positive ions, which may lead to erroneous conclusions. Therefore, usually in a quadrupole mass spectrometer the electron multiplier is mounted in such a geometry that it cannot be irradiated by high-energetic neutrals and photons entering the spectrometer. However, even then
'obscure' high-energetic species originating from laser-produced plasmas can be detected [4,5] (see Chapters 4 and 5). As these species can contribute substantially to the TOF spectra of neutrals and positive ions arising from the same plasmas one should be aware of their presence in the laser-induced plasmas and interpret the said spectra with great care.

This chapter reports the identification of the said species arising from laser ablation of Si. Si was used as a target, because contributions of the species under investigation have been observed in TOF distributions of Si$^+$ ions [5] (cf. Chapter 5) and the species might be identified more easily than in the case of, for example, an alloy. Also some preliminary angle-resolved time-of-flight (ARToF) spectra and associated angle-resolved yield (ARY) distributions of the species are presented and discussed as a first step for further study of the species.

6.2 Experimental

The experimental equipment used and the procedures applied have been described in detail in Chapter 3. For the sake of completeness, however, they are briefly reviewed here. Additionally, some supplementary information is given.

The ultrahigh vacuum system utilized comprised a processing chamber and a two-stage, differentially pumped detector chamber. The base pressure of the former was about $1\times10^{-6}$ Pa and that of the second stage of the latter was about $5\times10^{-8}$ Pa. In the second stage a quadrupole mass spectrometer for detection of the Rydberg atoms was mounted. To provide the atoms to be detected a field-free flight path, the spectrometer's ionizer, ion optics and quadrupole rods were grounded. Only the channeltron, set at -2600 V with respect to ground, was in operation; the channeltron's quantum efficiency was about 10%. As the ionizer was out of operation fluxes of Rydberg atoms were measured, instead of number densities. The number of Rydberg atoms entering the mass spectrometer could be reduced by increasing the deflection potential, $V_d$, over a pair of parallel deflection plates mounted before the spectrometer's entrance aperture.

The targets were attached to the holder of a manipulator in the processing chamber in sight of the mass spectrometer. The distance from a target to the channeltron, the flight path $L$, was 577 mm. The solid detection angle was about $1.4\times10^{-4}$ sr. By rotating the target around the laser beam, incident at $45^\circ$, the angle between the target-surface normal and the length axis of the spectrometer, the detection angle $\theta$, could be varied from $0^\circ$ up to $90^\circ$.

An ArF$^*$ excimer laser, operating at 10 Hz, supplied 193-nm wavelength pulses of 15-ns duration to ablate the targets. The laser fluence, $F$, at the target surface was estimated from the beam power at that surface and the resulting area ablated in a PMMA-coated Si sample. Neutral density filters were utilized to reduce the beam
power so as to obtain $F$ values at the target surface of about 0.6, 0.9 and 1.2 J cm$^{-2}$. The ellipsoidal laser-irradiated areas at the target surfaces were about 0.6 mm$^2$.

The TOF spectra were measured by detecting the Rydberg atoms as a function of time; this was done at various detection angles. By summing the total number of counts constituting a TOF spectrum at a detection angle, $\theta$, the associated yield, $Y_p$, was obtained. This procedure was repeated for various values of $\theta$, so as to obtain the ARY distributions.

The Si targets used were commercial boron-doped (100)-oriented slabs from which the native oxide layers were stripped by a dip in a solution of 5 vol.\% HF in water. In general, the targets were regularly refreshed, so as to avoid effects of target degradation on the ARTOF measurements.

6.3 Results and discussion

A TOF distribution of species originating from laser ablation of Si that was measured with $V_d=0$ V is shown in Fig. 6.1a; it was measured at $\theta=0^\circ$ employing $F\approx1.2$ J cm$^{-2}$. The species constituting it had a most probable time-of-flight, $TOF_p$, of approximately 90 $\mu$s. For $V_d=10$ V about 90$\%$ of the number of species constituting a spectrum as shown in Fig. 6.1a was deflected. The non-deflected species constituted a relatively low-yield, broad TOF distribution, of which an example is shown in Fig. 6.1b, and had a value of $TOF_p$ of about 140 $\mu$s. Hence, the distribution measured with $V_d=0$ V can be considered as consisting of two distinct contributions. It has been shown that the major, 90$\%$-contribution was due to Si$^+$ ions [5] (see Chapter 5), which were deflectable by an electric field of only 10/0.75 V cm$^{-1}$. The contribution shown in Fig. 6.1b has been ascribed to neutral species, which appeared to be unaffected by such a low field. In this chapter the nature of the species constituting the latter contribution is identified and of characteristics of the species’ ARTOF and ARY distributions are discussed.

The species appeared to be unaffected by the electric field of 10/0.75 V cm$^{-1}$, yet on average had longer times-of-flight than the Si$^+$ ions. Many more of these species were detected with activated quadrupole rods at a mass-over-charge ratio $m/q=28$ amu e$^{-1}$. It was concluded that the species were neutral when passing the deflection plates, because ions with a value of $m/q$ similar to that of the fore-mentioned Si$^+$ ions, but on average having longer times-of-flight than the ions would have been deflected at $V_d=10$ V. As during these experiments the mass spectrometer’s ionizer was not in operation and only positive ions could be detected by the channeltron, the neutrals under investigation were obviously ionized after passing the deflection plates.

With raising $V_d$ to 80 V and higher the number of the said neutrals that was detected fell substantially. Evidently, they were ionized upon passing the deflection plates and subsequently deflected from their way to the detector. So, an electric field
Fig. 6.1a. A TOF distribution of Si⁺ ions and Si⁺ atoms measured with \( V_g = 0 \) V at \( \theta = 0^\circ \); the species were emitted applying \( F = 1.2 \) J cm\(^{-2} \). The solid curve is a theoretical MB-like distribution, given by Eq. 6.1 with \( T = 18.00 \times 10^5 \) K and \( u = 3.40 \times 10^4 \) m s\(^{-1} \), fit to the experimental data.

Fig. 6.1b. A TOF distribution of Si⁺ atoms measured with \( V_g = 10 \) V at \( \theta = 0^\circ \); the atoms were emitted applying \( F = 1.2 \) J cm\(^{-2} \). The solid curve is a theoretical MB distribution, given by Eq. 6.1 with \( T = 15.00 \times 10^5 \) K (and \( u = 0 \) m s\(^{-1} \)), fit to the experimental data.
strength as low as 80/0.75 V cm\(^{-1}\) was sufficient to ionize them. This indicated that these neutral species were in highly excited states and therefore easily ionizable. The neutrals that passed the deflection plates without being ionized could be ionized by the electric field near the cone of the channeltron, set at -2600 V with respect to ground, and therefore be detected.

As has been said above, upon activating the quadrupole rods more neutrals were detected at a mass setting \(m/q=28\) amu e\(^{-1}\). Recognizing that \(\text{Si}_q^+\) species, ionized to \(\text{Si}_{q+}\) ions, for \(q=2, 3, \text{etc.}\), are unstable, the species must have been \(\text{Si}^+\) atoms; this conclusion was affirmed by spectroscopy data of radiative decay of excited Si species that arose from laser ablation of Si [6-8]. The fact that the number of detected \(\text{Si}^+\) atoms changed by tuning the quadrupole’s mass-to-charge setting showed that the atoms could also be ionized by the electric quadrupole fields. As these fields thus affected the TOF distributions of the \(\text{Si}^+\) atoms, the ARTOF distributions were measured with only the mass spectrometer’s channeltron in operation (cf. Section 6.2 and Chapter 3), so as not to draw any erroneous conclusion. Note, that the \(\text{Si}^+\) signal could not be extinguished by tuning the mass setting off from \(m/q=28\) amu e\(^{-1}\), because most atoms remained neutral during their flight through the spectrometer.

### 6.3.1 ARTOF distributions

The \(\text{Si}^+\) atoms constituting the TOF distribution shown in Fig. 6.1b had a \(\text{TOF}_{p}\) value of about 140 \(\mu\)s. Given the field-free flight path of 557 mm, this value corresponds with a most probable kinetic energy, \(E_{kp}\), of approximately 2.5 eV. This is considerably less than the \(E_{kp}\) value of 6.1 eV corresponding with the \(\text{TOF}_{p}\) value of 90 \(\mu\)s for the \(\text{Si}^+\) ions that originated from the same laser ablation events [5] (cf. Fig. 6.1a).

For an increasing detection angle, \(\theta\), the yield of the \(\text{Si}^+\) atoms decreased substantially, while the TOF distributions if the species shifted to longer times-of-flight. Qualitatively, this was similar to the case of the laser ablated neutrals [4] (cf. Chapter 4). The ARTOF spectra of the neutrals were fitted well with Maxwell-Boltzmann distributions superimposed onto angle-dependent flow velocity contributions. These fits were helpful in determining the mechanisms operative during laser ablation of neutrals. Hence, to clarify the mechanism responsible for the presence and determining the TOF distributions of the \(\text{Si}^+\) atoms originating from laser ablation of Si, attempts were made to fit the experimental ARTOF spectra of the \(\text{Si}^+\) atoms also with Maxwell-Boltzmann (MB) like distributions. Note that in the case of the \(\text{Si}^+\) atoms TOF flux distributions were measured, whereas in the case of the neutrals TOF number-density distributions were measured (see Section 6.2 and Chapter 3). Therefore, the distributions that were tried to fit the data were of the form:
Fig. 6.2. The fitting parameter $T$ of theoretical MB distributions (Eq. 6.1) fit to the experimental ARTOF distributions of Si$^+$ atoms, as a function of $\theta$; the atoms were emitted applying $F=1.2$ J cm$^2$.

\[
d^3f_{\Omega,t} = C \frac{1}{t^4} \exp\left\{-\frac{m[(L/t)\cos\theta - u]^2}{2kT}\right\} \, d\Omega \, dt,
\]

(6.1)

where $d^3f_{\Omega,t}$ is the flux of species detected per solid angle interval, $d\Omega$, and per TOF interval, $dt$, $m$ is the mass of the species, $t$ is a time-of-flight of the species, $L$ is the field-free flight path, $\theta$ is the polar detection angle, $u$ is a longitudinal flow velocity, $k$ is the Boltzmann constant, $T$ is a temperature and $C$ is a normalization constant. The distribution fitting the experimental data in Fig. 6.1b is an MB distribution with $m=28$ amu and $T=15.00 \times 10^3$ K; a flow velocity, which narrows an MB distribution, was discarded in this case. The fit was narrower than the experimental spectrum; this was also the case for all the other spectra measured with $V_d=10$ V. Nevertheless, the data were fitted with MB distributions as good as possible, in order to characterize the experimental data better than by just a single value of $TOF_{r'}$.

The temperature, $T$, used in the fits to the experimental spectra is shown in Fig. 6.2 as a function of $\theta$. Clearly, it fell slightly with increasing $\theta$, corresponding to a decrease of $E_{kp}$ with increasing $\theta$, analogously to the case of the laser ablated neutrals [4] (cf. Chapter 4).
Fig. 6.3. ARY distributions of Si\textsuperscript* atoms; the atoms were emitted applying $F=1.2$ (●), 0.9 (○) and 0.6 $J \text{cm}^2$ (▲). The solid curves are $\cos^{16} \theta$ distributions fit to the experimental data.

6.3.2 ARY distributions

From the ARTOF distributions of the Si\textsuperscript* atoms ARY distributions were obtained; examples for $F=0.6$, 0.9, and 1.2 $J \text{cm}^2$ are shown in Fig. 6.3. Assuming that the atoms were ionized by the electric field of the channeltron with an efficiency of 100% and accounting for the channeltron's quantum efficiency of about 10%, the average number of Si\textsuperscript* atoms detected within the solid detection angle of $1.4 \times 10^{-4}$ sr was about 4.3 per laser pulse at $\theta=0^\circ$ for $F=1.2$ $J \text{cm}^2$.

The ARY distributions were fitted quite well with normalized $\cos^{16} \theta$ distributions, irrespective of the fluence. Just as for the fore-mentioned angular dependence of the temperature of the fitting MB distributions, qualitatively this behaviour more or less resembles that of laser ablated neutrals [4] (cf. Chapter 4). The ARY distributions of the Si\textsuperscript* atoms, however, were substantially less peaked along the target-surface normal that those of the neutrals.

6.3.3 Si\textsuperscript* Rydberg atoms

In this section it will be shown that the Si\textsuperscript* atoms were Rydberg atoms. A Rydberg atom is an atom populating an energy level corresponding with a principal quantum number, $n$, higher than 10 [9]; the radiative lifetimes if these instable atoms increase from a few $\mu$s for atoms populating a low $n$ level, up to a few hundred $\mu$s for atoms populating a high $n$ level [9,10]. When $n$ exceeds a critical level $n_c$ the
Fig. 6.4a. TOF distributions of Si\(^+\) atoms measured with \(V_d=0\) (\(\bullet\)), 80 (\(\circ\)) and 640 \(V\) (\(\square\)) at \(\theta=0^\circ\); the atoms were emitted applying \(F\approx1.2\) J cm\(^{-2}\).

Fig. 6.4b. TOF distributions of Si\(^+\) atoms measured with \(V_d=0\) (\(\bullet\)) and 1280 \(V\) (\(\circ\)) at \(\theta=0^\circ\); the atoms were emitted applying \(F\approx1.2\) J cm\(^{-2}\).

Rydberg atom can be ionized by a minimum critical electric field with strength \(E_c\), which satisfies Eq. 6.A1 (see Appendix 6.A). In the present experimental set-up \(E_c\)
was equal to \( V_d = 0.75 \) V cm\(^{-1}\). Hence, for Rydberg atoms an increase of \( V_d \) would have resulted in a decrease of the threshold for being ionized by the electric field, that is, the value of \( n_c \) for those Rydberg atoms would have decreased. As a consequence, the Rydberg atoms populating energy levels higher than those corresponding to \( n_c \) could not have passed the deflection plates without being ionized and deflected, and the number of Rydberg atoms that could have been detected would have decreased. In Fig. 6.4a it is shown that the yield associated with ARTOF spectra measured with \( V_d = 10, 80 \) and 160 V decreased substantially upon raising \( V_d \). Therefore, it was concluded that the Si* were electronically excited to high Rydberg states.

Apart from relatively low thresholds for electric-field ionization, species in relatively high Rydberg states also have relatively long radiative lifetimes (cf. Eq. 6.3 in the appendix). Hence, due to ionization and deflection of such highly excited atoms for higher values of \( V_d \) a decrease of the yield in an TOF spectrum would be more pronounced at the spectrum’s trailing edge than at its leading edge. From Fig. 6.4b it can be seen this was the case for the TOF spectrum of Si* atoms measured with \( V_d = 10 \) V, in comparison with the one measured with \( V_d = 1280 \) V; the peak of the latter distribution was normalized to the one of the former distribution. Therefore, also Fig. 6.4b affirms that the ARTOF distributions that are considered in this chapter were due to atoms in high Rydberg states.

The yield, \( Y_\theta \), of the Si* atoms as a function of \( V_d \) is shown in Fig. 6.5a; the Si* atoms were measured at \( \theta = 0^\circ \) and \( 20^\circ \) and originated from ablation with \( P \approx 1.2 \) J cm\(^{-2}\). Apart from the relative values of \( Y_\theta \), both sets of data display similar trends. \( Y_\theta \) decreased only slightly when \( V_d \) was raised up to approximately 40 V. For higher values of \( V_d \), \( Y_\theta \) fell more rapidly. These trends were also observed for the other sets of data that were measured; the values of \( Y_\theta \) at \( V_d = 10 \) V of those sets of data can be obtained from Fig. 6.3. For \( V_d > 40 \) V \( Y_\theta \) was proportional to \( V_d^{-0.95} \). This proportion and Eq. 6.4 (see Appendix 6.A) were employed to calculate the population per level \( n \), \( Y_n \) for the Si* atoms at the channeltron. The results are shown in Fig. 6.5b. (Using only the rough data, resulted in a population distribution that consisted of only six data points that enclosed seven to ten \( n \) levels; that distribution did not show a clear trend like the one shown in Fig. 6.5b.) It can be seen from Fig. 6.5b that the highest Rydberg state in which the Si* atoms were detected corresponded to \( n = 60 \). This does not imply that Si* atoms in higher Rydberg states were not formed in the ablation process. As these atoms would have needed only a few meV of energy to be ionized, they could already have been ionized, for example by thermal background radiation and, as a result, have been deflected before arriving at the channeltron.

The number of Si* atoms, \( Y_n \), populating the energy levels corresponding to a certain level \( n \) was proportional to \( n_c^{2.8} \). This can be obtained from Fig. 6.5b. It can also be shown by employing \( Y_\theta \propto V_d^{-0.95} \) and Eq. 6.4, which results in \( Y_\theta \propto n_c^{3.8} \), and by subsequently applying Eq. 6.4A3, which implies that \( Y_\theta \) is the derivative of \( Y_\theta \) to
Fig. 6.5a. $Y_\theta$ for Si$^+$ atoms as a function of $V_d$ measured at $\theta=0^\circ$ (●) and 20$^\circ$ (○); the atoms were emitted applying $F=1.2$ J cm$^{-2}$.

Fig. 6.5b. $Y_\theta$ for Si$^+$ atoms as a function of $n$ measured at $\theta=0^\circ$; the atoms were emitted applying $F=1.2$ J cm$^{-2}$.

$n_c$. This observation may be attributed to the fact that the lifetimes of atoms in a high Rydberg state are longer than the lifetimes of atoms in lower Rydberg states (cf.
Eq. 6.A3). To date, similar experiments during laser ablation have not been conducted.

6.3.4 Target degradation

The results of the fore-mentioned experiments were reproducible until the initially fresh Si target was ablated by a certain number of laser pulses; for $F \approx 1.2$ J cm$^{-2}$ this number was about $8 \times 10^3$. Hereafter, the measuring conditions became ill-defined: the yield of Si$^+$ atoms detected per laser pulse increased and the TOF distributions of the atoms shifted to shorter times-of-flight. These effects are illustrated in Fig. 6.6. The TOF distributions shown in this figure were measured after $5 \times 10^3$, $15 \times 10^3$ and $25 \times 10^3$ laser pulses. Clearly, after $15 \times 10^3$ pulses the said effects became drastic. After $25 \times 10^3$ pulses the number of Si$^+$ atoms detected saturated the channeltron. Therefore, it could not be examined whether the TOF distributions would continue to change or not.

Scanning electron microscopy (SEM) analysis of the ablated Si targets indicated that the fore-mentioned effects were associated to the development of pronounced target-surface roughness with an increasing number of incident laser pulses. The target was not ablated smoothly; it displayed stalagmite-like features that, probably due to shadowing of the incident laser pulses, were directed towards the incident laser beam during ablation.

![Graph](image)

**Fig. 6.6.** TOF distributions of Si$^+$ atoms measured after $25 \times 10^3$ (●), $15 \times 10^3$ (○) and $5 \times 10^3$ (■) laser pulses with $V_a = 0$ V at $\theta = 0^\circ$; the atoms were emitted applying $F \approx 1.2$ J cm$^{-2}$. 
6.3.5 Si⁺ formation and emission mechanisms

Rydberg atoms can be formed from positive ions by electron-ion recombination and from neutrals by collisional excitation and photon excitation [2,9]; these mechanisms produce Rydberg atoms in a manifold of Rydberg states. Many of these mechanisms can be operative in laser-ablation-produced plasmas.

Electron-ion recombination involves the capture of an electron by a positive ion into a Rydberg state. If the ion is monoatomic, the recombination proceeds radiatively; it results in a Rydberg atom and a photon. If the ion is diatomic, the recombination proceeds dissociatively; it results either in two Rydberg atoms or in one Rydberg atom, a positive ion and an electron.

In collisional excitation and photon excitation an electron of a neutral particle is raised to a higher energy level by the impact of particles or photons, respectively; there exist many variants of these excitation mechanisms, for example excitation via an intermediate state.

All these mechanisms could have been operative during laser ablation of Si. For example, during laser irradiation of a Si target, 193-nm laser photons, having an energy of 6.3 eV, can be absorbed by the species in the ablation-produced plasmas resulting in massive photon excitation or even multiphoton ionization; upon ending of the laser pulse massive recombination of electrons and photon-ionized ions will occur. Massive (net) electron-ion recombination can also take place during the expansion of a laser-produced plasma. Then, the pressure in and the temperature of the plasma fall; the thermal energy is converted into kinetic energy of particles diffusing out of the plasma. Consequently, less collisional excitation and relatively more electron-ion recombination can take place.

It has been observed that the ARY distributions of the Si⁺ atoms resembled those of ablated neutrals. Therefore, it may be tempting to conclude that the mechanisms using neutral precursors to populate the Rydberg states dominated the formation of the Si⁺ atoms. However, the ARY distributions of the Rydberg atoms were cos^{16}θ-like, whereas those of the neutrals were cos^{6}θ-like. Moreover, it has been observed that the leading edges of TOF spectra of atoms in highly excited states did not coincide with those of TOF distributions of species in non- and lowly-excited states. [11,12]. Hence, at first sight these observations may indicate that the Rydberg atoms were not formed from neutrals. However, the latter observation might be explained as follows. During the plasma expansion, only the few neutrals that preceded the ones constituting the leading edges of the TOF distributions have sufficient kinetic energy to excite each other by collisional interaction into Rydberg states. Consequently, the few Rydberg atoms that can be observed have higher kinetic energies than the neutrals that are clearly visible in the leading edges of the TOF spectra of neutrals. This would imply that the precursors of the Rydberg atoms were neutrals.
Whatever the parents of Si\textsuperscript{+} atoms might have been, the increase of $Y_\theta$ per laser pulse and associated shift of the TOF distributions to shorter times-of-flight can be explained qualitatively by the development of stalagmite-like features at the Si target surface by ablation. These features have inferior thermal contact with their surroundings compared with similar amounts of mass that are fully in contact with their surroundings. As a result the temperatures reached in the former are higher than the temperatures reached in the latter. In addition, multiple scattering of the incident laser photons between the columnar features will further increase the coupling between those photons and the target, resulting in even higher temperatures. At those higher target temperatures the number of ablated species is higher. Moreover, at the stalagmite-like features the effective target surface available for ablation is higher, resulting in higher ablation rates.

The said effects were probably also responsible for the shift of the TOF distributions of the Si\textsuperscript{+} atoms to shorter times-of-flights. Due to the increase of the ablation rates more collisions between ablated species can take place, which can result in the said shift [13]. Moreover, between the columnar features more collisions can take place than above a flat, open target surface. Thus, the collisional effect can be even more pronounced.

6.4 Summary and conclusions

TOF distributions of field-ionized Si\textsuperscript{*} Rydberg atoms emitted from plasmas produced by laser ablation of Si were measured as a function of the detection angle, $\theta$. From these distributions ARY distributions were obtained. Both the most probable time-of-flight and the yield decreased with increasing $\theta$. TOF distributions of the Si\textsuperscript{+} atoms were also measured as a function of the electric fields that ionized and deflected the atoms.

Rydberg atoms can be detected due to electric-field ionization by the channeltron of a quadrupole mass spectrometer, whether or not the ionizer and quadrupole rods are in operation. Moreover, the most probable kinetic energies of Rydberg atoms are higher than those of non-Rydberg neutrals and lower than those of ions. Therefore, unwished contributions of Rydberg atoms in TOF distributions of neutrals and ions can be observed.

Attributing the formation of the Si\textsuperscript{*} atoms on the basis of the present results to one mechanism or the other would at this stage only be speculative. Therefore, more experiments supplying complementary information are needed to elucidate the mechanisms of formation of Rydberg atoms during laser ablation.
6. A Appendix: Electric-field ionization and TOF measurements of Rydberg atoms

Rydberg atoms are characterized by a principal quantum number, \( n \), and an angular quantum number, \( l \). They can be ionized by a (quantum mechanically obtained) critical electric field strength, \( E_c (V \text{ cm}^{-1}) \), which is given by \([14]\):

\[
E_c = \frac{6.4 \times 10^8}{n_{c+1}^4},
\]  
(6.A1a)

where \( n_c \) is the critical, maximum \( n \) level that Rydberg species can populate without being ionized by an electric field with strength \( E_c \). (The constant numerator is independent of the type of Rydberg atoms considered, because all Rydberg atoms are essentially similar to a H\(^+\) Rydberg atom.) The relation implies that the present TOF distributions are constituted of Rydberg atoms in states associated with a value of \( n \) of up to the maximum value allowed by Eq. 6.A1a. Hence, under the conditions used in these experiments \( n_{c+1} \) was given by:

\[
n_{c+1} = \left( \frac{4.8 \times 10^8}{V_d} \right)^{1/4}.
\]  
(6.A1b)

Besides, the yield of Rydberg atoms in a state associated with a value of \( n \), \( Y_n \), satisfies \([9]\):

\[
Y_n \approx Y_0 \exp \left( -\frac{l}{\tau} \right)
\]  
(6.A2)

where \( Y_0 \) is a constant, \( t \) is time and \( \tau \) (ns) is a radiative lifetime given by:

\[
\tau \approx 1.4(n - 1.3)^3.
\]  
(6.A3)

Consequently, TOF distributions are effected by the \( n \) level of the Rydberg atoms constituting them. Hence, Eqs. 6.A1 and 6.A2 together imply that a TOF distribution, \( TOF \), as measured in the present experiments, were a summation of individual TOF distributions, \( TOF_n \), constituted of Rydberg atoms which were excited to the same state associated to \( n \):

\[
TOF = \sum_{n-1}^{n_c} TOF_n.
\]  
(6.A4a)

Additionally, the yield \( Y_0 \) of Rydberg atoms obtained from a TOF distribution was given by:
$Y_\theta = \sum_{n-1}^{n_{\text{max}}} Y_n$,

(6.44b)

where $Y_n$ is the yield associated with a distribution $\text{TOF}_n$.

References

Chapter 7

Formation of crystalline, supersaturated $\text{Ag}_x\text{Ni}_{1-x}$ solid solutions by laser ablation deposition

Laser ablation was used in a vapour quenching method to deposit thin Ag-Ni films at room temperature. The films contained substantial amounts of a polycrystalline non-equilibrium $\text{Ag}_x\text{Ni}_{1-x}$ solid solution, as evidenced by X-ray and electron diffraction. The unusually high degree of supersaturation attained (up to 44 at.% Ag) has not been observed before for a system exhibiting such a strong demixing behaviour. The X-ray diffraction $\sin^2\psi$ method was employed to determine the strain-free lattice parameter of the solid solution. The solid solution decomposed by heating the film.

7.1 Introduction

Laser ablation deposition (LAD) has been used to grow thin films of a variety of materials [1]. This physical vapour deposition technique owes its interest mainly to the following characteristics. Firstly, laser ablation is possible for many materials, because most materials turn optically opaque due to high-power laser-radiation-induced optical breakdown [2,3]. Secondly, laser ablation proceeds congruently [1,3], that is, none of the constituent elements of the target vaporizes preferentially. This can result in the deposition of a film with a composition equal to that of the target; however, this is not always the case [1,4,5] (see also Chapter 8). Finally, LAD is associated with a very high quenching rate and a very high instantaneous deposition rate. The quenching rate is of the same order of magnitude as in the case of sputter deposition ($\sim 10^6$ K s$^{-1}$ [6]), because the kinetic energies of laser ablated species [1,2,7] (see also Chapter 4) are of the same order of magnitude as those of ion-sputtered species [6]. The instantaneous growth rate during LAD ($\sim 10^{-2}$-1 nm per laser pulse, corresponding to $\sim 10^3$-$10^5$ nm s$^{-1}$ [1,5] (see also Chapter 8)), however, is substantially higher than the growth rate during sputter deposition ($\sim 10$ nm s$^{-1}$ [6]). These properties were used here to form polycrystalline $\text{Ag}_x\text{Ni}_{1-x}$ solid solutions of a very high degree of supersaturation, of which the formation has not been reported
before. Note that the equilibrium Ag-Ni phase diagram shows that distinct solid solubility of either Ag in Ni or Ni in Ag cannot occur [8].

Upon quenching atoms in a state of high mobility, they can be 'frozen' into unconventional positions and a thermodynamically metastable, or unstable, phase can develop [9]. Thus, the formation of non-equilibrium phases can be realized. In a mixture of atoms of more than one element, solid solubility limits may be surpassed and a supersaturated alloy may be formed [10,11]. Two well known rapid quenching methods are the liquid quenching method [10], including for example melt spinning [12] and pulsed laser surface alloying [3,13], and the vapour quenching method [6], including for example sputter deposition [14].

A liquid quenching method cannot be used to form a concentrated Ag$_{x}$Ni$_{1-x}$ solid solution, because Ag and Ni are mutually insoluble not only in the solid state, but also in the liquid state [8]. Then, a vapour quenching method may be utilized to form such alloys. Thus far, sputter deposition and coevaporation of Ag and Ni on liquid-nitrogen-cooled substrates have been used to form supersaturated, amorphous Ag$_{x}$Ni$_{1-x}$ alloys [14-16]. Now, this chapter reports the preparation of supersaturated, crystalline Ag$_{x}$Ni$_{1-x}$ solid solutions, with Ag contents of up to 44 at.%, by employing LAD; the composition and microstructure of LAD-grown Ag-Ni films will be discussed in detail in Chapter 8.

7.2 Experimental

The experimental set-up and procedures are described only briefly here; they are described in more detail in the Chapters 3 and 8. Target material was ablated and deposited onto substrates in a processing chamber with a base pressure of about 5×10$^{-7}$ Pa. Due to the non-miscibility of liquid Ag and Ni, the Ag-Ni targets could not be prepared by arc-melting. Instead, they were made by cold-pressing pure Ag and pure Ni powder mixtures into pellets. The composition of the targets was determined with X-ray fluorescence (XRF); the target compositions were 25Ag-75Ni, 50Ag-50Ni, 75Ag-25Ni and 90Ag-10Ni, where the numbers indicate the atomic percentages of the constituent elements. To limit target degradation, the targets were rotated during ablation. The targets were ablated by laser pulses with a wavelength of 193 nm and a duration of 15 ns, supplied by an Ar/F$_{2}$/He-filled excimer laser operating at 10 Hz. The fluence used was about 6.0 J cm$^{-2}$; fluences of about 3.0 and 7.5 J cm$^{-2}$ yielded similar results. The deposition rate for a fluence of 6.0 J cm$^{-2}$ was about 8 pm per laser pulse. The substrates were Si (100) slabs covered with a thermally grown 500-nm-thick silicon oxide film. During deposition the substrates were at room temperature. To obtain films with a homogeneous thickness, the substrates were moved in a scanning mode parallel to the targets through the laser-produced plasmas. The thicknesses of the films grown were 100 and 500 nm. The gross compositions of the films were also determined using XRF.
Identification of the phases in the thin films was achieved by X-ray diffraction (XRD) analysis. Diffraction patterns were recorded from $2\theta=10^\circ$ to $160^\circ$ on a diffractometer employing CuKα radiation. From the Bragg angles of the reflections of the phases the lattice parameters of the phases present can determined. However, if the thin film considered is stressed, the lattice spacings measured from the peak positions are affected by the (residual) stress present. To assess the magnitude of this effect and in order to perform an appropriate correction the so-called XRD $\sin^2\psi$ method [17] was used to determine the state of stress. This method allows determination of a strain-free lattice spacing as follows.

For the thin films considered a biaxial state of stress is expected with the principal stresses $\sigma_1$ and $\sigma_2$ equal to each other and parallel to the film surface. The lattice spacing $d_\psi$ in a direction defined by the Euler angle $\psi$ with respect to the sample reference frame, as shown in Fig. 7.1, obeys (with $\sigma_\parallel=\sigma_1=\sigma_2$):

$$d_\psi = d_0 + 2S_1 d_0 \sigma_\parallel + \frac{1}{2} S_2 d_0 \sigma_\parallel \sin^2 \psi,$$

(7.1)

where $\psi$ is the angle between the normal of the diffracting set of lattice planes $(hkl)$ and the normal of the specimen surface, $S_1$ and $\frac{1}{2} S_2$ are the so-called X-ray elastic constants and $d_0$ is the strain-free lattice spacing. Thus, a plot of $d_\psi$ vs. $\sin^2 \psi$ should provide a straight line. From the slope of this line a value of $\sigma_\parallel$ can be obtained, provided $\frac{1}{2} S_2$ and $d_0$ are known. An accurate value for $\sigma_\parallel$ can be obtained by replacing $d_0$ in the expression for the slope by the experimental $d_\psi=0$, as the latter does not deviate from $d_0$ by more than 1%. From Eq. 7.1 it follows that there exists a unique direction, $\psi_0$, for which $d_\psi=d_0$:

$$\sin^2 \psi_0 = \frac{-2S_1}{\frac{1}{2} S_2}.$$

(7.2)

![Fig. 7.1. Definition of the Euler angles $\phi$ and $\psi$ and of the principal stress components $\sigma_1$, $\sigma_2$, and $\sigma_3$ with respect to the film surface.](image)
Hence, interpolation in the plot of \( d_v \) vs. \( \sin^2\psi \) at \( \psi=\psi_0 \) provides a value for the strain-free lattice spacing \( d_0 \).

For Ag\(_{x}\)Ni\(_{1-x}\) solid solutions 2\( S_1 \) and \( \frac{1}{2} S_2 \) are unknown. Therefore, here the estimates \( S_1=2\nu/E \) and \( \frac{1}{2} S_2=(1+\nu)/E \) will be applied, where \( \nu \) and \( E \) are the Poisson’s ratio and the Young’s modulus of the film material, respectively [17]; the respective linear composition weighted values for 26Ag-74Ni (see below) are 0.35 and 170 GPa (using data for \( \nu \) and \( E \) from [18]).

This method was applied to Ag\(_{x}\)Ni\(_{1-x}\) \{222\} line profiles, measured on a diffractometer employing CuK\( \alpha \) radiation, from 2\( \theta \)=91.0\(^\circ\) to 94.0\(^\circ\) at \( \psi=0^\circ \) and 39.23\(^\circ\).

### 7.3 Results and discussion

XRD patterns taken from fresh target surfaces showed that the targets were polycrystalline and composed of pure Ag and pure Ni grains, as expected. Patterns of target surfaces that had been subjected to prolonged laser irradiation were identical to those of the fresh targets. No reflections of additional phases were discernable. Although the depth of a laser-produced melt in a metal target is limited to only several tens of nanometres [3], the surface sensitive XRD method employed would detect phases that might have been formed by laser-induced alloying. Hence, significant surface alloying did not take place. It is concluded that the irradiated material was not mixed (as in a solid solution) before it was ablated to form a plasma.

The gross composition of the films grown by ablation of the 25Ag-75Ni, 50Ag-50Ni, 75Ag-25Ni and 90Ag-10Ni targets were 14Ag-86Ni, 26Ag-74Ni, 44Ag-56Ni and 78Ag-22Ni, respectively (XRF analysis). The fact that the overall film compositions were not equal to the target compositions can be ascribed to preferential reflection of ablated Ag species at the growing film surfaces [5] (see Chapter 8).

An XRD pattern of a 26Ag-74Ni film produced by LAD is shown in Fig. 7.2a. The film was polycrystalline, but not composed of a single phase. In addition to reflections originating from pure Ag and pure Ni, the diffractogram shows a prominent reflection at a Bragg angle of approximately 42\(^\circ\) that can be interpreted as the \{111\} reflection of a face centred cubic (fcc) phase with a lattice parameter in between those of pure Ag and pure Ni. Other (weak) reflections of this phase could be observed too. These results were confirmed by electron diffraction analysis. The fcc phase was identified as a Ag\(_{x}\)Ni\(_{1-x}\) solid solution. To our knowledge, this is the first time that the formation of such a non-equilibrium phase (at room temperature) is reported.

The 26Ag-74Ni film was heated in vacuum, with a pressure of about 10\(^{-5}\) Pa, to a temperature of 673 K at a rate of 1 K min\(^{-1}\). The XRD pattern recorded thereafter is shown in Fig. 7.2b. Clearly, by heating the reflection of the solid solution
Fig. 7.2a. An XRD pattern of a 100-nm-thick 26Ag-74Ni film, showing a prominent \{111\} reflection of a $Ag_xNi_{1-x}$ solid solution.

Fig. 7.2b. An XRD pattern of a 100-nm-thick 26Ag-74Ni film that was heated to 673 K at a rate of 1 K min$^{-1}$. With respect to the diffractogram (Fig. 7.2a) recorded prior to the heat treatment the $Ag_xNi_{1-x}$ \{111\} reflection has disappeared in favour of the pure Ag and pure Ni reflections, indicating that the solid solution has decomposed by the heat treatment.
disappeared entirely and the reflections of pure Ag and pure Ni gained intensity. Hence, the heat treatment applied led to decomposition of the solid solution into pure Ag and pure Ni. In view of the equilibrium Ag-Ni phase diagram, this result is compatible with the earlier conclusion that a crystalline, supersaturated \( \text{Ag}_{x}\text{Ni}_{1-x} \) solid solution was formed by LAD.

During the above described vacuum heat treatment the resistance of the film was measured as a function of the film temperature by a four-point probe method. The result is shown in Fig. 7.3. Starting at a value of about 1.9 \( \Omega \) at room temperature the resistance increased to a maximum value of approximately 2.3 \( \Omega \) at 423 K. This resembles a normal resistance behaviour of crystalline metallic materials. On continued heating the resistance decreased to about 1.3 \( \Omega \) at 673 K. This is ascribed to decomposition of the solid solution: the resistance decreases as the amounts of pure Ag and pure Ni increases, because the resistivities of pure elements are substantially lower than that of a corresponding solid solution [19].

Application of the \( \sin^2 \psi \) analysis, as described above, yielded the following results for the stress parallel to the surface, \( \sigma_{\parallel} \), and the strain-free lattice parameter, \( a_0 \), of the \( \text{Ag}_{x}\text{Ni}_{1-x} \) solid solution of the 26Ag-74Ni film: \( \sigma_{\parallel}=0.21 \) GPa and \( a_0=3.6915 \) Å. Discussion of the value of the stress is beyond the scope of this chapter (see Chapter 8 and [5]). The value of the strain-free lattice parameter can be used to assess the composition of the solid solution. Literature values of the lattice parameters of pure Ag and pure Ni [20] are shown in a plot of the lattice parameter versus the Ag content in Fig. 7.4. The straight line connecting these data points represents the
lattice parameter values predicted for the (metastable) solid solutions if Vegard’s law prevails [21]. A lattice parameter for a metastable Ag$_x$Ni$_{1-x}$ solid solution has not been presented until now.

The strain-free lattice parameter of the Ag$_x$Ni$_{1-x}$ solid solution of the 26Ag-74Ni film, which has been presented above, as well as the strained lattice parameters of the Ag$_x$Ni$_{1-x}$ solid solutions of this film and of the other films produced in this work were plotted too in Fig. 7.4, at values of the Ag content equal to the gross Ag content of the film. Also considering the (modest) effect of the correction for the residual stress, it follows from these data that fair agreement occurs with the Vegard prediction. Hence, the average composition of the supersaturated solid solution phases in the films was approximately equal to the gross composition of the films.

The significant line broadening observed for the reflections from the solid solution, as compared with the reflections from the pure elemental components (cf. Fig. 7.2a), can be interpreted as caused by non-homogeneity of the solid solution, the occurrence of microstrain and a very small crystallite size [5] (see Chapter 8).
7.4 Conclusions

It is concluded that crystalline, supersaturated Ag$_{1-x}$Ni$_x$ solid solutions can be produced (at room temperature) by LAD containing up to at least 44 at.% Ag, whereas the equilibrium solid solubility is negligible.

References

Chapter 8

Laser ablation deposition of Cu-Ni and Ag-Ni films; non-conservation of alloy composition and film microstructure

Laser ablation deposition was used to grow polycrystalline Cu-Ni and Ag-Ni thin films on amorphous substrates at room temperature. Analysis of the overall film composition was achieved by electron probe microanalysis and X-ray fluorescence. The films contained substantially less Cu and Ag than the targets, which was probably caused by preferential scattering of ablated Cu and Ag species upon incidence at the growing films. X-ray diffraction was employed to determine the phases and the residual macrostress present and to analyze the structural imperfection in terms of crystalite size and microstrain. The Cu-Ni films were entirely composed of a Cu$_x$Ni$_{1-x}$ solid solution. The Ag-Ni films were composed of a non-equilibrium Ag$_x$Ni$_{1-x}$ solid solution, which could contain at least 44 at.% Ag, and of pure Ag and pure Ni. The residual macrostress in the Cu-Ni films was compressive, whereas it was tensile in the Ag-Ni films. The occurrence of these stresses could be due to the combined effects of atomic peening and cooling after deposition and, in the case of the Ag-Ni films, of stress relaxation by partial decomposition of the Ag$_x$Ni$_{1-x}$ solid solution starting during film growth. The microstrains in the Ag$_x$Ni$_{1-x}$ solid solutions were higher than in similarly prepared pure elemental Ag and Ni films. Compositional inhomogeneity of the Ag$_x$Ni$_{1-x}$ solid solution crystallites contributed in particular to this effect. The strain-free lattice parameters of the solid solutions were found to be in fair agreement with those predicted by Vegard’s law.

8.1 Introduction

Laser ablation deposition (LAD) involves the formation of a laser-induced plasma and the subsequent deposition of plasma species onto a substrate. Since its introduction in 1965 [1], it has been shown that LAD can be used to grow thin films of a wide variety of materials [2]. However, only after the recent recognition of LAD as a technique for the production for high-$T_c$ superconducting YBa$_2$Cu$_3$O$_{6+δ}$ thin films [3], a strong interest for general application of this technique was evoked.
The main motives to apply LAD for the production of thin films are the following. Firstly, laser ablation is possible for almost any material, irrespective of its optical properties, because under high-power laser radiation most materials turn optically opaque by an optical breakdown [4,5]. Secondly, laser ablation proceeds congruently [2,5], so that the overall composition of the ablation-induced plasma is equal to the overall composition of the target material. Hence, deposition of thin films with a composition equal to that of the target might be realized relatively simply, thereby avoiding the use of usually more laborious and costly conventional vapour deposition methods as evaporation and sputtering. Finally, LAD is associated with a very high quenching rate and a very high instantaneous deposition rate. The quenching rate is of the same order of magnitude as in the case of sputter deposition (~10⁶ K s⁻¹ [6]), because the kinetic energies of laser ablated particles [2,4,7,8] (see also Chapter 4) are of the same order of magnitude as those of ion-sputtered particles [6]. The instantaneous growth rate during LAD (~8×10⁻³ nm per pulse, corresponding to ~800 nm s⁻¹ (this chapter)), however, is substantially higher than the growth rate during sputter deposition (~10 nm s⁻¹ [6]). These properties enable, for example, to form solid solutions of a very high degree of supersaturation [9] (see also Chapter 7).

The predominant number of studies on LAD dealt with the production of films of pure elements, semiconducting compounds and oxides [1,10-13]. Only a few reports concerned the formation of thin films of metallic alloys [1,14-19]. In this chapter we present the results of a study on the composition and the non-equilibrium microstructure of thin metallic alloy films grown by LAD. The model systems chosen were the binary alloys Cu-Ni and Ag-Ni. As far as their optical and thermophysical properties are concerned, these systems are similar. However, both in the liquid and solid state they show contrasting mixing behaviour. Cu and Ni can form solid solutions over the entire composition range [20], whereas Ag and Ni are not soluble at all into each other [20].

8.2 Experimental

The experimental set-up and procedures used to grow thin films by LAD are outlined only briefly here; they have been discussed in detail in Chapter 3. In addition, supplementary information on the target preparation and film analysis is given.

8.2.1 Film deposition

Targets of overall compositions 25Cu-75Ni, 50Cu-50Ni, 75Cu-25Ni and 90Cu-10Ni, the numbers indicating the atomic percentages of the constituting elements, were prepared by melting appropriate amounts of pure Cu (99.99%) and
pure Ni (99.95%) in an arc melter. The solidified raw pellets were mechanically shaped into discs of 18 mm in diameter and 4 mm of thickness. To obtain homogeneous compositions these targets were annealed at 1273 K for 100 hours. Electron probe microanalysis (EPMA) showed no significant near-surface compositional variations over lateral distances ranging between a few microns and 18 mm.

Targets of Ag-Ni alloys suited for laser ablation could not be prepared by arc melting, because Ag and Ni are insoluble in the solid as well as in the liquid state [20]; a solidified arc-melted pellet consisted of an almost pure Ag part and an almost pure Ni part. Therefore Ag-Ni targets of gross compositions 25Ag-75Ni, 50Ag-50Ni, 75Ag-25Ni and 90Ag-10Ni were prepared by cold pressing powder mixtures of pure Ag (99.99%) and Ni (99.99%) in discs of the fore-mentioned dimensions. The lateral compositional variations were minimized (with respect to the laser irradiated area) by selecting elemental powders that had a particulate size of only about a micron. Also, after cold pressing subsequent sintering or annealing was not performed to prevent coarsening of the Ag and Ni grains. In the targets the individual particulates were clustered to sizes of a few cubic microns, as established with EPMA.

In addition, solidified, arc-melted pure Cu, pure Ag and pure Ni targets were used to grow elemental thin films. Additional Cu-Ni targets were prepared according to the preparation method described for the Ag-Ni targets. Their use in the experiments is explicitly indicated in this paper.

Before deposition, effects of contamination possibly present on the targets were avoided by initial in-situ laser ablation at modest fluences in the absence of a substrate. After deposition the targets were mechanically polished.

The substrates were 10×10 mm²-large Si (100) slabs with a 500-nm-thick, thermally grown amorphous oxide layer on top. The oxide layers served as a buffer layer to avoid (1) reactions between the Si and the films and (2) a crystallographic orienting effect on the film by the monocrystalline Si substrate. Before inserting the substrates in the ultrahigh vacuum system for laser ablation and deposition, they were carefully cleaned with ethanol.

Material was laser ablated from targets and deposited onto substrates within an ultrahigh vacuum processing chamber. Its base pressure was about 5×10⁻⁷ Pa. During ablation the pressure rose to about 3×10⁻⁶ Pa.

The targets were mounted inside the processing chamber. During ablation the targets were rotated at 10 r.p.m. to limit ablation-induced target degradation. Substrates were introduced into the processing chamber via a load-lock chamber in order not to break the vacuum of the processing chamber. The substrates, carried by a molybdenum block that was at room temperature, were mounted on a manipulator that enabled a substrate holder to translate in three orthogonal directions and to rotate it around its surface normal. The target-substrate distance was 30 mm. Due to peaking of ablation-induced plasmas along the target-surface normal, the films grown on
stationary substrates had no uniform thickness. By translating the substrates in a scanning mode parallel to the target through the plasmas, material was deposited much more evenly: resulting films exhibited thickness variations of only about 5% over areas of 10×10 mm².

The target material was ablated by laser pulses of 193 nm wavelength and of 15 ns duration (full width at half maximum) supplied by an Ar/F₂/He-filled excimer laser operating at 10 Hz. The laser fluence, \( F \), at the target was determined from the ratio of (1) the laser beam power just in front of a viewport in the processing chamber, corrected for absorption by the viewport and (2) the spot size etched by 50 laser pulses in the surface of a 10-μm-thick PMMA coating on a Si sample; the viewport was kept clean by regularly removing contamination of ablated material. The uncertainty in the thus determined values of \( F \) was estimated to be about 20%. The elliptic spot area at the target surfaces was about 1.5×4.0 mm². Mainly, \( F \approx 6.0 \) J cm⁻² was applied; of values 3.0 and 7.5 J cm⁻² yielded similar results. The deposition rate for \( F = 6.0 \) J cm⁻² was of the order of 8×10⁻³ nm per laser pulse, which corresponds to about 800 nm s⁻¹ per pulse, because the difference between the times-of-flight for fast species and those for slow species to reach the substrate was about 10 μs [7] (cf. Chapter 4).

8.2.2 X-ray diffraction analysis

The thin films grown were analyzed by X-ray diffraction (XRD) for 1, identification of the phases present, 2, determination of the residual macrostresses present and 3, determination of the crystallite size and microstrains present.

1 Phase identification

XRD patterns used for phase identification (and for determination of crystallite sizes and microstrains) were recorded using a Philips PW 1800/00 Automatic Powder Diffractometer, equipped with a Cu X-ray tube, a graphite monochromator in the diffracted beam, set to select CuKα radiation, and a proportional Xe-gas counter. The patterns used for phase identification were recorded from \( 2\theta = 10^\circ \) to 160° employing a step size of 0.01° 2\( \theta \) and a scan speed of 0.02° 2\( \theta \) s⁻¹. The lattice spacings were calculated from the peak positions applying Bragg's law, and were used to identify the phases present.

2 Determination of residual macrostress

For the thin films considered a biaxial state of stress is expected with the principal stresses \( \sigma_1 \) and \( \sigma_2 \) parallel to the surface. The elastic lattice strain, \( \varepsilon_{\phi,\psi} \), in a direction defined by the Euler angles \( \phi \) and \( \psi \) with respect to the sample reference frame, shown in Fig. 8.1, depends on \( \sigma_1 \) and \( \sigma_2 \) as follows [21]:
Fig. 8.1. Definition of the Euler angles $\phi$ and $\psi$ and of the principal stress components $\sigma_1$, $\sigma_2$ and $\sigma_3$ with respect to the film surface.

\[
\varepsilon_{\phi,\psi} = -\frac{\nu}{E}(\sigma_1 + \sigma_2) + \frac{1 + \nu}{E} \sigma_\phi \sin^2 \psi,
\]  

(8.1)

where:

\[
\sigma_\phi = \sigma_1 \cos^2 \phi + \sigma_2 \sin^2 \phi,
\]

$\psi$ is the angle between the normal of the diffracting set of lattice planes $(hkl)$ and the normal of the sample surface, $\phi$ is the angle between $\sigma_\phi$ and $\sigma_1$, and $\nu$ and $E$ are the Poisson’s ratio and Young’s modulus of the film material, respectively. The strain $\varepsilon_{\phi,\psi}$ in the direction indicated by the angles $\psi$ and $\phi$ can be obtained from the lattice spacing, $d_{\phi,\psi}$, of the $(hkl)$ planes in the direction defined by $\psi$ and $\phi$ and the corresponding strain-free, reference lattice spacing $d_0$:

\[
\varepsilon_{\phi,\psi} = \frac{d_{\phi,\psi} - d_0}{d_0}.
\]

(8.2)

It should be realized that during a measurement of a single reflection only a fraction of the number of crystallites in a film is contributing to the recorded signal, and that other crystallites are selected when $\psi$ is changed. For a material consisting of elastically anisotropic crystals this implies that the elastic constants should be replaced by effective ones confined to the reflection considered, the so-called X-ray elastic constants: $-\nu/E \rightarrow S_1$, and $(1+\nu)/E \rightarrow \frac{1}{2} S_2$. Thus:

\[
d_{\phi,\psi} = d_0 + S_1 d_0 (\sigma_1 + \sigma_2) + \frac{1}{2} S_2 d_0 \sigma_\phi \sin^2 \psi.
\]

(8.3)

For constant $\phi$ a plot of $d_{\phi,\psi}$ vs. $\sin^2 \psi$ generally results in a straight line, from the slope of which a value of $\sigma_\phi$ can be obtained, provided $\frac{1}{2} S_2$ and $d_0$ are known. In
order to obtain a reliable value for \( \sigma_\phi \) from the slope, \( d_\phi \) need not be known precisely. In general, \( d_{\phi,0} \) will not deviate more than 1% from \( d_\phi \) and an accurate value for \( \sigma_\phi \) is obtained by replacing \( d_\phi \) by the experimental \( d_{\phi,0} \) in the expression for the slope.

From Eq. 8.1 it follows that there exists a unique direction, \( \psi_0 \), for which the strain equals zero, that is, for which \( d_{\phi,\psi}=d_\phi \). If \( \sigma_1=\sigma_2 \) this strain-free direction is given by:

\[
\sin^2 \psi_0 = \frac{-2S_1}{S_2}. \tag{8.4}
\]

Hence, interpolation in a curve of \( d_{\phi,\psi} \) vs. \( \sin^2 \psi \) provides a value for the strain-free lattice spacing.

The measurements were performed using a Philips PW 1050-\( \Omega \) diffractometer equipped with a Cu tube and a diffracted-beam graphite monochromator set to select CuK\( \alpha \) radiation. Reflections of both a W and a Si sample were used to calibrate the 2\( \theta \) Bragg angle scale of the diffractometer. For a 100-nm-thick 26Ag-74Ni film the residual macrostrains were determined from the Ag\textsubscript{x}Ni\textsubscript{1-x} \{222\} line profiles, measured from 2\( \theta \)=91.0\( \degree \) to 94.0\( \degree \) in steps of 0.1\( \degree \) 2\( \theta \). The tilt angle \( \psi \) was varied from 0\( \degree \) up to 39.23\( \degree \). For 100-nm-thick and 500-nm-thick 44Cu-56Ni films the residual macrostrains were determined from the Cu\textsubscript{x}Ni\textsubscript{1-x} \{222\} reflections measured from 2\( \theta \)=95.5\( \degree \) to 98.0\( \degree \) in steps of 0.1\( \degree \) 2\( \theta \). The tilt angle \( \psi \) was varied from 0\( \degree \) up to 45.00\( \degree \). Background intensity subtraction, K\( \alpha_2 \) profile component elimination [22] and peak position determination were performed using the Philips APD 1700 software package [23]. Fitting of a straight line to the data points of \( d_{\phi,\psi} \) plotted vs. \( \sin^2 \psi \) was performed according to the least-squares method.

3 Determination of crystallite size and microstrain

Crystallite-size and microstrain effects were studied by analyzing the broadening of measured XRD line profiles [24,25]. In general, a measured line profile, \( h \), is the convolution of the standard profile, \( g \), only broadened by instrumental effects and the X-ray wavelength distribution, with the structurally broadened profile, \( f \), which is desired to be known.

Here, the \( h, g \) and \( f \) profiles are assumed to be Voigt functions (see Fig. 8.2). A Voigt function is a convolution of a Cauchy and a Gauss function. As a Voigt function is the convolution of symmetrical functions, the profiles \( h, g \) and \( f \) should be symmetrical. Therefore, the \( \alpha_2 \) component of a profile should be eliminated by computation before the analysis can be applied [22].

The constituent Cauchy and Gaussian integral-breadth components of the experimental \( h \) and \( g \) profiles, taken as Voigt functions, can be obtained from the experimental ratios \( 2w/\beta \), where \( \beta \) denotes the integral breadth, that is, the ratio of the peak area and the peak height, and \( 2w \) is the full width at half peak height. Then,
Fig. 8.2. The experimental Cu$_x$Ni$_{1-x}$ (111) line profile recorded from a 100-nm-thick 44Cu-56Ni film. It was fitted with a Voigtian comprising an $\alpha_1$ and an $\alpha_2$ component. As the difference between the Voigtian and the experimental line profile was negligible, the fit is only shown in the magnifications of the peak and the trailing edge of the experimental line profile.

because of the convolution theorem, the integral breadths of the Cauchy and Gaussian components of the $f$ profile, $\beta_c^f$ and $\beta_g^f$, can be calculated according to:

$$\beta_c^f = \beta_c^h - \beta_c^g$$  \hspace{1cm} (8.5a)

and:

$$\beta_g^f = \sqrt{(\beta_g^h)^2 - (\beta_g^g)^2}.$$  \hspace{1cm} (8.5b)

Finally, according to the single-line method [24,25] the crystallite size $D$ and the microstrain $\varepsilon$ are obtained from:

$$D = \frac{\lambda}{\beta_c^f \cos \theta}$$  \hspace{1cm} (8.6)

and:
\[
\bar{\varepsilon} = \frac{\beta_g'}{4 \tan \theta},
\]

where \( \beta \) is taken on a 2\( \theta \) scale in radians, and \( \lambda \) and 2\( \theta \) are the X-ray wavelength and Bragg angle of the \( \alpha_1 \) component of the \( f \) profile, respectively. The crystallite size \( D \) represents a volume weighted size. It can be smaller than the grain size, because a grain can be composed of a number of coherently diffracting crystallites. The microstrain measure \( \bar{\varepsilon} \) represents an average of the strain variation. Both \( D \) and \( \bar{\varepsilon} \) pertain to the direction perpendicular to the diffracting lattice planes.

The standard profile \( g \) was measured from Si powder that was annealed for 3 hours at 1073 K to become strain-free. Because the angular positions of the reflections of the Si powder do not coincide with the angular positions of the line profiles to be analyzed, the required values of \( \beta_{c}^e \) and \( \beta_{g}^e \) were obtained by interpolation between values taken from measured reflections of the Si powder.

The \{111\}, \{200\}, \{311\} and \{222\} line profiles present in the XRD patterns recorded from Cu-Ni and the \{111\}, \{200\} and \{311\} ones (if detectable; cf. Table 8.2) in the XRD patterns recorded from Ag-Ni films were analyzed in the above manner using the Philips APD 1700 software package for profile-parameter determination [23].

### 8.2.3 Electron probe microanalysis

The local composition and thickness of the films was measured by electron probe microanalysis (EPMA), using a Cameca SX50 Microprobe, equipped with three crystal spectrometers. Employing an incident electron energy of 20 keV the depth range of the emitted X-rays ranged from 0.5 to 1.2 \( \mu \)m for the \( K\alpha \) lines of Cu and Ni and the \( L\alpha \) line of Ag. The composition was calibrated with respect to pure elemental standards. The data evaluation was performed by using the Cameca P&P thin film code [26].

### 8.2.4 X-ray fluorescence analysis

X-ray fluorescence (XRF) was employed to determine the overall composition of the targets and the films over lateral surface areas of about 5 mm in diameter. For the XRF analyses a Philips 1404/00 sequential spectrometer was used. It primarily consisted of a Cr X-ray tube, a monochromator equipped with several Bragg diffractors for the different wavelength intervals, a mass-flow detector and a scintillation detector. Quantification of the data was accomplished with a fundamental parameter approach [27,28].
8.2.5 Transmission electron microscopy

Transmission electron microscopy (TEM) and electron diffraction was performed using a Philips EM400 microscope. The microscope was equipped with an energy-dispersive X-ray analyzer (Be window) for qualitative compositional analysis. Specimens for TEM and electron diffraction analysis of planar sections were prepared simply by depositing films on so-called TEM windows. These windows were specially constructed silicon substrates that contained a high number of silicon nitride membranes, which were 13 nm thick and had an area of 200×200 μm² [29]. The films examined had a thickness of about 100 nm. By simply cleaving the substrate along prepared grooves in the substrate, individual plan-view TEM specimens supported by a membrane were directly obtained.

8.3 Results and discussion

8.3.1 Thickness profiles

A film grown by physical vapour deposition of material onto a stationary substrate, having a lateral surface area larger than the source from which the material was vaporized, has a thickness profile that depends on the spatial angular distribution of the flux of desorbed material. Here, a Ag-Ni film was grown by LAD onto a substrate that remained stationary during deposition. The resulting film thickness was measured, using EPMA, as a function of the lateral distance to the centre of the film. The thickness profiles thus determined along the film axes that during deposition were parallel and perpendicular to the long axis of the laser spot on the target surface are shown in Fig. 8.3. Clearly, the profile perpendicular to the long axis of the laser spot was broader than the one parallel to it. The data points for the thickness profiles parallel and perpendicular to the long axis could be fitted well with functions proportional to $\cos^{5.4}\theta$ and $\cos^{9.6}\theta$, respectively, where during deposition $\theta$ was the angle between the target normal and the vector from the centre of the target area being ablated to the location of the considered film area. Thickness profiles of this type have also been obtained in the case of LAD of various other materials [30-32]. The $\theta$ dependencies of the shown thickness profiles can be imagined (in first order approximation) as the projection of the spatial angular flux distribution of ablated species on the substrate. In turn, this spatial angular flux distribution is due to the expansion mechanism of laser-produced plasmas. A discussion of the expansion of laser-ablation-produced plasmas and the associated consequences for the thickness profiles of LAD-grown thin films is beyond the scope of this chapter (see for further discussion of expansion: Chapters 2 and 4 and [7,33-36], and for further discussion of thickness profiles: Chapters 2 and 4).
Fig. 8.4. The thickness of a 100-nm-thick 264g-4ATi film grown on a substrate that was moved in a scanning mode, as a function of the distance from the centre of the film; in this experiment the target-substrate distance was 15 mm.

Fig. 8.3. The thickness of a 264g-4ATi film grown on a substrate that remained stationary during deposition, as a function of the distance from the centre of the film along the film axis that was perpendicular (●) and parallel (○) to the long axis of the elliptical laser spot; in this experiment the target-substrate distance was 15 mm. The abrupt increase in thickness at 7 mm for the profile parallel to the long axis of the laser spot was due to a droplet.

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To obtain films of more uniform thickness than in the above discussed case, in all other experiments of this work the substrates were moved in a scanning mode parallel to the target surface through the depositing flux of ablated material. The thickness profile of a film thus produced is shown in Fig. 8.4. Clearly, over the entire substrate area of 10×10 mm² the thickness variations were limited to within about 5% of the average film thickness.

8.3.2 Droplets

Scanning electron micrographs (Figs. 8.5a and b) show that the films contained many solidified, ablated droplets. The emission of macroscopic molten particulates, droplets, is inherent to laser ablation of solids (see also Chapter 2). Ablation can proceed through two modes of evaporation, viz., surface evaporation and volume evaporation [5] (see also Chapter 2). The latter mode occurs for weakly photon-absorbing materials, such as ceramics [5,37,38]. For such materials high-power laser irradiation can lead to a subsurface temperature substantially higher than the surface temperature and the evaporation temperature. As a result nucleation and growth of gas bubbles beneath the surface can take place. When the local pressure in these bubbles becomes sufficiently high, material is removed explosively. This mechanism can lead to deposition of relatively large droplets on a film surface. For a material with a short photon absorption length, such a as metal, surface evaporation is the dominant process. In the case of a metal target, a droplet may arise by recoil of ablated species into the laser-induced melt and by local exfoliation of material due to melting-induced specific volume-induced irregularities at the target surface [5,39].

The number of droplets embedded in both the Cu-Ni and the Ag-Ni films increased with the laser fluence, because more energy had become available for the said recoil and exfoliation effects; analogous data were obtained for other LAD-grown metallic alloy films [16,19]. Moreover, the number of droplets incorporated in the 500-nm-thick films was substantially higher than the number of droplets incorporated in the 100-nm-thick films. This was due to the fact that during ablation in the course of time the said melting-induced irregularities at the target surface, shown in Fig. 8.6, and thence the exfoliation effects became more pronounced.

The number of droplets incorporated in the Cu-Ni films was substantially lower than in the Ag-Ni films (cf. Fig. 8.5). The droplets in the Cu-Ni films had a composition equal to the overall composition of the films, as shown by EPMA analysis. The composition of the droplets in the Ag-Ni films, however, ranged from highly Ag-rich to highly Ni-rich. The droplet composition was independent of the droplet size. Recognizing that the relevant optical and thermophysical properties of Cu-Ni and Ag-Ni are similar, these observations can to a large extent be ascribed to differences between the mass densities of the Cu-Ni targets and the Ag-Ni targets, as follows.
Fig. 8.5a. A scanning electron micrograph of a 100-nm-thick 44Cu-56Ni film. Note the relatively low number density of droplets in the Cu-Ni film as compared with the Ag-Ni film shown in Fig. 8.5b.

Fig. 8.5b. A scanning electron micrograph of a 100-nm-thick 26Ag-74Ni film. Note the relatively high number density of droplets in the Ag-Ni film as compared with the Cu-Ni film shown in Fig. 8.5a.
Due to the preparation by arc melting, a Cu-Ni target was massive and the droplets in a Cu-Ni film are thought to have arisen both by the recoil of ablated species in the laser-induced melt and by the local break-off due to specific volume irregularities as described above. A Ag-Ni target, however, was composed of relatively loosely bound Ag and Ni powder particulates, thereby having a non-compact structure. An individual particulate in a non-compact target has inferior thermal contact with its surroundings as compared with a comparable amount of mass in a massive target. Therefore, upon laser irradiation a particulate in a non-compact target can heat up relatively pronouncedly, melt at an earlier stage and thus can be more easily removed in an explosive way than the said comparable amount of mass from a compact target. The observed variable composition of the solidified droplets in the Ag-Ni films thus reflected the locally varying composition of the corresponding target during laser ablation.

To verify the above explanation, some Cu-Ni films were made from the additional, non-massive Cu-Ni targets, which were prepared in the same way as the Ag-Ni targets (see Section 8.2.1). Indeed, not only the number of droplets incorporated in these films was comparable to the number incorporated in the Ag-Ni films, but also the droplet composition ranged between highly Cu-rich and highly Ni-rich, analogous to the variation in Ag content for the droplets in the Ag-Ni films.
8.3.3 Film composition

The composition of the films was measured, using EPMA, as a function of the lateral distance of the measuring spot to the centre of the film. The results for the 26Ag-74Ni film are shown in Fig. 8.7. Similar results were obtained for the other Ag-Ni films and for the Cu-Ni films, irrespective of the preparation of the targets.

Clearly, the film composition was independent of the location of the measuring spot, implying that the composition of the ablation-produced vapour was independent of the direction in which ablated material was emitted. Apparently, a relation between the mass of the ablated species and the direction of emission does not occur, in agreement with results obtained from angle-resolved time-of-flight spectrometry of laser ablated neutrals (see also [7] and Chapter 4). The abrupt increase in the Ag content at 7 mm from the centre in Fig. 8.7 was due to a Ag-Ni droplet of which the composition was not equal to the overall film composition (see Section 8.3.2).

A striking observation was that the Cu and Ag contents of the films were significantly lower than those of the targets from which the films were made. In general, laser ablation is expected to proceed congruently [1,5], that is, the composition of a laser-induced plasma is equal to the composition of the irradiated target material. This can be explained as follows.

![Graph showing Ag content as a function of distance](image)

Fig. 8.7. The Ag content of the 100-nm-thick 26Ag-74Ni film grown on a substrate that remained stationary during deposition, as a function of the distance from the centre of the film along the film axis that was parallel to the long axis of the elliptical laser spot, corresponding to the thickness profiles shown in Fig. 8.3; in this experiment the target-substrate distance was 15 mm. The abrupt increase in Ag content, corresponding to the abrupt increase in thickness at 7 mm (cf. Fig. 8.3), was due to a droplet.
Due to the high amount of energy supplied to the target surface during laser ablation and the associated very short heating and cooling times, the composition of the melt of the laser-irradiated target material may be equal to the composition of the solid. Under powerful laser irradiation the atoms in a laser-produced melt can acquire thermal energies far in excess of their binding energies. Consequently, the binding energies are of minor importance for the evaporation rates and the laser-irradiated target-surface material can evaporate congruently, that is, evaporate without a change of composition. As the lateral distances over which the composition of the targets varied were short (only the powder-pressed targets exhibited significant compositional variations; see Section 8.2.1) compared with the size of the laser-irradiated area, the average composition of the surface-adjacent material in the irradiated area equalled the average target composition. Hence, the plasma compositions were expected to have been equal to the target compositions. This discussion suggests that the film compositions should have been equal to the target compositions. However, this was found not to be the case.

As the film composition did not vary with the distance to the centre of the film surface, XRF was used to measure the composition averaged over a relatively large lateral film area of 5 mm in diameter. The Cu and Ag contents in the Cu-Ni and Ag-Ni films deposited employing $F \approx 6.0 \text{ J cm}^{-2}$ are plotted as a function of the Cu and Ag contents of the corresponding targets in Figs. 8.8a and b, respectively. Analogous data for films made with $F \approx 3.0$ and $7.5 \text{ J cm}^{-2}$ showed equal results. It follows that the Cu and Ag contents of the films were substantially lower than those of the targets they were made from. Further, the relative Ag deficiency in Ag-Ni films was higher than the relative Cu deficiency in Cu-Ni films.

Effects that might have been responsible for the Cu and Ag deficiencies in the films are (1) preferential evaporation of Cu and Ag species from the growing films, (2) preferential sputtering of Cu and Ag atoms from the growing Cu-Ni and Ag-Ni films by the impact of high-energetic ablated species and (3) preferential scattering of Cu or Ag species upon incidence at the growing films. To investigate if one or more of these effects contributed to the composition anomaly observed, material reemitted from the growing films was collected on additional substrates mounted next to the targets.

Because the so-called collisional region of a laser-induced plasma is confined within a few microns above the target surface [5,35] (see also Chapters 2 and 4), recondensation of material from this region on the additional substrates was impossible. The targets used were a 50Cu-50Ni and a 50Ag-50Ni target. The films deposited on the additional substrates were found to have the compositions 62Cu-38Ni and 75Ag-25Ni, respectively. The average thicknesses of these films were about 5% and 20%, respectively, of the average thicknesses of the corresponding films deposited on the normal substrates. Clearly, the amounts of Cu and Ag reemitted from the growing films on the normal substrates were significantly larger than the amounts of reemitted Ni. Moreover, the Ag/Ni ratio of reemitted material
Fig. 8.8a. The overall Cu content of the 100-nm-thick Cu-Ni films as a function of the Cu content in the Cu-Ni targets.

Fig. 8.8b. The overall Ag content of the 100-nm-thick Ag-Ni films as a function of the Ag content in the Ag-Ni targets.

was substantially higher than the corresponding Cu/Ni ratio, whereas the Ag/Ni ratio for the Ag-Ni films on the normal substrates was substantially lower than the corresponding Cu/Ni ratio. So, at least qualitatively the Cu and Ag deficiencies in the
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films on the normal substrates can be well explained by relatively high Cu/Ni and Ag/Ni ratios of reemitted species from the growing films.

During deposition the substrates were mounted on a molybdenum block at room temperature (cf. Section 8.2.1). Although moderate heating of the films may have occurred during film growth (see Section 8.3.5), at temperatures less than, say, 400 K the partial vapour pressures of Cu, Ag and Ni are less than $10^{-9}$ Pa [40]. Although the Cu/Ni and Ag/Ni partial vapour-pressure ratios are in qualitative agreement with the Cu and Ag deficiencies of the films deposited on the normal substrates, the said partial vapour pressures are orders of magnitudes to low to allow significant (preferential) evaporation.

The energy thresholds for sputtering of solid materials by impact of energetic ions, atoms and molecules are about 40 eV [41]. Under the ablation conditions applied neutrals constitute the overwhelming majority of ablated particles [2,4,5]. The kinetic energies of these neutrals have been reported to be in the range from only a few eV [7,8,42] (see also Chapter 4) up to 50 eV [43,44] or more [45]. Moreover, it can be calculated that in (dilute) Cu-Ni and Ag-Ni alloys Cu and Ag, respectively, segregate to the surface of the alloy [46]; in the case of Cu-Ni it has been shown experimentally that the outermost atomic surface layer indeed contains only Cu atoms [47]. Hence, preferential sputtering of Cu and Ag by impact of ablated particles could have been responsible for the observed composition anomaly. However, because the kinetic energy of ablated neutrals is dependent on the laser fluence [7] (cf. Chapter 4) and the sputtering yield of particles from film surfaces is strongly dependent on the kinetic energy of these particles [41], one would expect that possible preferential sputtering would depend on the laser fluence. This is incompatible with the present data, because the film composition was independent of the laser fluence, (see above).

Hence, we are left with the remaining possibility that the Cu and Ag deficiencies of the films were caused by preferential scattering of Cu and Ag particles upon incidence at the growing films. The existing data do not allow a quantitative assessment of this mechanism for the present systems.

8.3.4 Phases

XRD diffractograms of LAD-grown Cu-Ni and Ag-Ni films are shown in Figs. 8.9a and b. The indicated overall composition of the films was determined with XRF. The Cu-Ni films were polycrystalline and single-phase. All reflections, except those from the Si substrate, originated from a face centred cubic (fcc) structure with a lattice parameter in between those of pure Cu and pure Ni. Therefore, the film was identified as being a solid solution of Cu and Ni.

The Ag-Ni films were polycrystalline as well, but not single-phase. In addition to reflections originating from pure Ag and from pure Ni phases, the diffractograms show reflections characteristic of an fcc phase with a lattice parameter in between
Fig. 8.9a. An XRD pattern of a 100-nm-thick 44Cu-56Ni film made from an arc-melted target.

Fig. 8.9b. An XRD pattern of a 100-nm-thick 26Ag-74Ni film made from a powder-pressed target.

those of pure Ag and pure Ni. This phase was identified as a solid solution of Ag and Ni. The value of the lattice parameter suggests that this phase could contain at least up to about 44 at.% Ag [9] (see also Chapter 7). To our knowledge, this is the first
time that the formation of a crystalline \( \text{Ag}_{x}\text{Ni}_{1-x} \) solid solution with such a high Ag content is reported.

(In separate experiments, XRD and low-angle XRD analysis of \( (\text{Ag/ Ni})_{50} \) multilayers showed that in these stacks also substantial amounts of the said polycrystalline, supersaturated \( \text{Ag}_{x}\text{Ni}_{1-x} \) solid solutions were formed if the thickness of the separate bilayers were less than approximately 0.1 nm; for bilayers thicker than about 1 nm only pure Ag and pure Ni phases could be observed.)

As discussed in Section 8.3.2, the films incorporated many droplets. Diffraction patterns of the films made separately from the additionally prepared powder-pressed Cu-Ni targets (see Section 8.2.2) exhibit distinct reflections from pure Cu and from pure Ni (cf. Fig. 8.9c). It has been shown that the overall composition of the Cu-Ni films was independent of the type of preparation adopted for the targets (cf. Section 8.3.3). However, the droplets had a composition equal to the film composition for targets prepared from the melt, as usual, whereas this composition varied between very Cu-rich and very Ni-rich for the targets prepared from powders. The Cu and Ni reflections in the diffraction patterns from the films prepared from the powder-pressed targets were thus ascribed to diffraction by the Cu- and Ni-rich droplets. Then, by analogy, because the composition of the droplets in the Ag-Ni films ranged between highly Ag-rich and highly Ni-rich, it is suggested that the Ag and Ni reflections in the diffraction patterns of the Ag-Ni films were caused (primarily) by the droplets.
From a 50Ag-50Ni target a 50-nm-thick Ag-Ni film was deposited onto a TEM window. Because even weak mechanical forces can fracture such a window, this film was not analyzed by XRF or XRD. However, considering the results discussed in Section 8.3.3, the film composition must have been approximately 26Ag-74Ni.

Plan-view TEM photos showed that the film was polycrystalline. In addition, electron diffraction patterns of the film were recorded, thereby excluding diffraction from the droplets. A series of high-intensity diffraction rings present in the patterns could be ascribed to an fcc phase with a lattice parameter equal to that of the Ag$_x$Ni$_{1-x}$ solid solution, thereby confirming the fore-mentioned XRD results.

### 8.3.5 Macrostress

The lattice spacing of the Ag$_x$Ni$_{1-x}$ solid solutions in Ag-Ni films measured for variable angle $\phi$ (see Fig. 8.1) did not show any dependence on $\phi$. This means that the principal stresses in the plane of the surface, $\sigma_1$ and $\sigma_2$, were equal. For this reason, in the stress measurements conducted thereafter the specimens were rotated around their surface normals. Hence, in the sequel the symbol $\sigma_{\|}$ ($\sigma_{\|}=\sigma_1=\sigma_2$) is used for the stress parallel to the surface and the subscript $\phi$ (see for example Eq. 8.1) is dropped.

The lattice spacing $d_{\phi}$ for data obtained from the {222} reflection of the Ag$_x$Ni$_{1-x}$ solid solution in a 100-nm-thick 26Ag-74Ni film is plotted as a function of $\sin^2\psi$ in Fig. 8.10a. Using Eq. 8.1 and the composition weighted values for the Poisson’s ratio and Young’s modulus for 26Ag-74Ni, 0.35 and 170 GPa respectively (obtained from data for pure Ag and pure Ni [48]), from the slope of the straight line fitted through the data is obtained: $\sigma_{\|}=210$ MPa (see also Table 8.1).

The lattice spacing for data obtained from the {222} reflections of the Cu$_x$Ni$_{1-x}$ solid solution in both a 100-nm-thick 44Cu-56Ni film and a 500-nm-thick 44Cu-56Ni film is plotted as a function of $\sin^2\psi$ in Fig. 8.10b. Using Eq. 8.1 and the composition weighted values of the Poisson’s ratio and Young’s modulus for 44Cu-56Ni, 0.33 and 170 GPa respectively (obtained from data for pure Cu and pure Ni [48]), it is obtained from the slopes of the straight lines fitted through the data: $\sigma_{\|}=-355$ MPa and $\sigma_{\|}=-460$ MPa for the 100-nm- and 500-nm-thick films, respectively (see also Table 8.1).

It is concluded that the stress in the Cu-Ni films was compressive, whereas it was tensile in the Ag-Ni film. Further, the absolute value of the stress in the Cu-Ni films was larger than that in the Ag-Ni film.

Residual stresses in a thin film on a substrate can be viewed as arising from elastic accommodation of a misfit of the equilibrium lateral interface dimensions of film and substrate, while the film is cohesively bonded to the substrate. Sources of misfit can be of thermal nature or of growth-induced nature.

Growth-induced coherence stress can arise from a mismatch between a lattice spacing of the film and one of the substrate if epitaxial growth occurs. Because in the
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**Fig. 8.10a.** The lattice spacing $d_\psi$ as a function of $\sin^2 \psi$ obtained from the Ag$_x$Ni$_{1-x}$ (222) reflection recorded from a 100-nm-thick 26Ag-74Ni film. The solid line is obtained by least-squares fitting of a straight line to the data.

**Fig. 8.10b.** The lattice spacing $d_\psi$ as a function of $\sin^2 \psi$ obtained from the Cu$_x$Ni$_{1-x}$ (222) reflection recorded from a 100-nm-thick (●) and a 500-nm-thick (○) 44Cu-56Ni film. The solid lines were obtained by least-squares fitting of straight lines to the data.

In the present experiments the films were grown on amorphous oxide layers, such coherence stresses were absent.
Table 8.1. Residual stress analysis (XRD) of one Ag-Ni and two Cu-Ni films. The results presented were obtained by fitting straight lines to the experimental data in plots of $d_\psi$ vs. $\sin^2 \psi$ (see Eq. 8.3) employing the [222] reflections of the Ag$_x$Ni$_{1-x}$ and Cu$_x$Ni$_{1-x}$ solid solutions: $d_{\psi=0}$ and $\%S_\psi d_{\psi}$ (part cut from the ordinate and slope of the straight line), as well as the stress value calculated from the slope, $\sigma_{||}$, the strain-free lattice spacing, $d_0$ obtained according to Eq. 8.4, and the corresponding lattice parameter $a_0$.

| film         | $d_{\psi=0}$ (10$^{-1}$ nm) | slope (10$^{-3}$ nm) | $\sigma_{||}$ (MPa) | $d_0$ (10$^{-1}$ nm) | $a_0$ (10$^{-1}$ nm) |
|--------------|-----------------------------|----------------------|---------------------|----------------------|----------------------|
| 100-nm 26Ag-74Ni | 1.0665                      | 1.501                | 210                 | 1.0669               | 3.6916               |
| 100-nm 44Cu-56Ni | 1.0305                      | -2.986               | -355                | 1.0290               | 3.5645               |
| 500-nm 44Cu-56Ni | 1.0304                      | -3.717               | -460                | 1.0288               | 3.5631               |

A difference between the thermal expansion coefficients of a film and its substrate results in thermal stress development upon a temperature change of the film-substrate assembly. If the difference between thermal shrinkages of film and substrate, occurring upon cooling, is entirely accommodated by the film it follows for the stress $\sigma_{||}$ [49]:

$$\sigma_{||} = \frac{E}{1 - \nu} (\alpha_s - \alpha_f)(T - T_0), \tag{8.8}$$

where $\alpha_s$ and $\alpha_f$ are the linear thermal expansion coefficients of substrate and film, respectively, and $T_0$ and $T$ are the start and the end temperatures, respectively. If the observed stress would be entirely of thermal origin, $T_0$ would denote the temperature at which the film and its substrate were in a stress-free state. The composition weighted values of $\alpha_f$ for 26Ag-74Ni and 44Cu-56Ni (obtained from data of pure Ag, Cu and Ni [48]) are $1.48\times10^{-6}$ K$^{-1}$ and $15.0\times10^{-6}$ K$^{-1}$, respectively; the $\alpha_s$ value for the substrate material is $7.6\times10^{-1}$ K$^{-1}$ [48].

It follows from Eq. 8.8 that since $T_0$ must be greater than or equal to $T$, stresses of thermal origin in both the Ag-Ni and the Cu-Ni films were tensile. Hence, at least for the Cu-Ni films, another source of stress was operative.

Apparently, in view of the above discussion, the stresses in the films were in particular due to growth-induced misfit, in addition to a possible minor thermal misfit. Then, the following qualitative explanation is proposed for the difference between the stress in the Cu-Ni and in the Ag-Ni films.

Due to the impact of the laser ablated species, which have high kinetic energies [2,4,7,8] (see also Chapter 4), growing films are subjected to so-called atomic peening. This causes compressive internal stresses in the films [50,51].
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addition, by the energy transfer upon impact of species with substantial kinetic energies, some heating of the films occurs too. Moreover, the films are also heated by substantial, instantaneous release of the heat of condensation associated with the high instantaneous deposition rates of incident species. The net result is a compressive residual stress in the films, as observed for the Cu-Ni films.

LAD of Ag-Ni resulted in the formation of a Ag\textsubscript{x}Ni\textsubscript{1-x} solid solution in the films. Such a solid solution is highly unstable [20] and, possibly induced by the fore-mentioned moderate heating of the films, this solid solution partially demixes into pure Ag and pure Ni phases. This decomposition is associated with heat release that contributes to heating of the film. The high atomic mobility during the phase transformation will bring about relaxation of the stress present [52]. If the growth stresses initially induced by atomic peening are completely relaxed by the subsequent partial decomposition of the solid solution, the stress measured at room temperature for the Ag-Ni film can be fully of thermal origin. Application of Eq. 8.8. using the fore-mentioned value of $\sigma_0$ for the Ag\textsubscript{x}Ni\textsubscript{1-x} solid solution, then yields $T_0 = 387$ K. A demixing process with associated stress relaxation cannot take place in the Cu-Ni films, because the Cu\textsubscript{x}Ni\textsubscript{1-x} solid solution is a stable phase [20].

8.3.6 Lattice parameter and composition of the solid solution

The lattice parameters of the Cu\textsubscript{x}Ni\textsubscript{1-x} and Ag\textsubscript{x}Ni\textsubscript{1-x} solid solutions, as calculated from the corresponding peak positions in the XRD patterns, are shown as a function of the respective overall film compositions in Figs. 8.11a and b, respectively. The straight lines in the figures represent Vegard's law, that is, the hypothetical linear dependence of the lattice parameter of the solid solution on the atomic fraction of one of the components in a binary alloy. Vegard's law has been shown to hold for Cu\textsubscript{x}Ni\textsubscript{1-x} solid solutions [53]; for Ag\textsubscript{x}Ni\textsubscript{1-x} solid solutions lattice-parameter data have not been reported before. Apparently, the Figs. 8.11a and b show that the experimental dependence of the lattice parameter on composition of the solid solution in the LAD films diverges from Vegard's law for both the Cu\textsubscript{x}Ni\textsubscript{1-x} and the Ag\textsubscript{x}Ni\textsubscript{1-x} solid solutions. This deviation could have been due to the presence of residual internal stresses in the films, which were discussed in the preceding section. Hence, the measured lattice spacings and the correspondingly calculated lattice parameters had to be corrected for the stresses in the films in order to obtain the strain-free values, which are to be used in a comparison with predictions based on Vegard's law. The correction was performed on the basis of the sin$^2\psi$-method, as outlined in Section 8.2.2, employed for the lattice parameters of the Cu\textsubscript{x}Ni\textsubscript{1-x} solid solution in a 100-nm- and a 500-nm-thick 44Cu-56Ni film and the Ag\textsubscript{x}Ni\textsubscript{1-x} solid solution in a 100-nm-thick 26Ag-74Ni film (see also Table 8.1). These results are also shown in Figs. 8.11a and b, respectively.

As deduced from the XRD phase analysis, the composition of the solid solution must have been approximately equal to the gross composition of the
Fig. 8.11a. The lattice parameter, \( a \), of the Cu\(_{x}\)Ni\(_{1-x}\) solid solution as a function of the overall Cu content of the film. The, as-measured, strained values shown are for the 100-nm-thick Cu-Ni films (●). The value after correction for the presence of residual stress (see text) is shown for the 100-nm-thick 44Cu-56Ni film (○). The straight line represents the lattice parameters that can be expected according to Vegard's law.

Fig. 8.11b. The lattice parameter, \( a \), of the Ag\(_{x}\)Ni\(_{1-x}\) solid solution as a function of the overall Ag content of the film. The, as-measured, strained values shown are for the 100-nm-thick Ag-Ni films (●). The value after correction for the presence of residual stress (see text) is shown for the 100-nm-thick 26Ag-74Ni film (○). The straight line represents the lattice parameters that can be expected according to Vegard's law.
film (see Section 8.3.4). Then, in view of sign and magnitude of the stress correction, it follows from the data in Fig. 8.11a that the lattice parameter of the Cu$_x$Ni$_{1-x}$ solid solution was in fair agreement with the prediction from Vegard’s law. Similarly, it can be argued on the basis of Fig. 8.11b that the lattice parameter of the Ag$_x$Ni$_{1-x}$ solid solution was in fair agreement with the prediction from Vegard’s law. The XRD and TEM phase analysis showed that pure Ag and pure Ni were also present in the Ag-Ni film. Hence, the composition of the solid solution needs not be exactly equal to the overall composition of the film and this can explain the remaining apparent deviation from Vegard’s law.

8.3.7 Crystallite size and microstrain

The integral breadth of the only structurally broadened profile $\beta'$, the crystallite size $D$ and the microstrain $\varepsilon$ as obtained by analysis, according to the method outlined in Section 8.2.2, from various line profiles in the XRD patterns of the Cu-Ni and the Ag-Ni LAD-grown films are presented in the Tables 8.2a and b. Similar data for pure Cu, pure Ag and pure Ni LAD-grown films are also given in the Tables 8.2a and b. From these tables the following conclusions can be drawn.

The Cu$_x$Ni$_{1-x}$ line profiles of the Cu-Ni films exhibited line broadening in between those of the corresponding line profiles of the pure Cu and pure Ni films (cf. $\beta'$ data in Table 8.2a). The Ag$_x$Ni$_{1-x}$ line profiles of the Ag-Ni films exhibited much more broadening than the corresponding line profiles of the pure Ag and pure Ni films (cf. $\beta'$ data in Table 8.2b); the size and strain data in Table 8.2b indicate that this was due in particular to a much larger microstrain for the Ag$_x$Ni$_{1-x}$ solid solution phase.

The broadening denoted as strain broadening here refers to the occurrence of lattice-spacing variations within the crystallites. This can be caused by two effects: 1, the presence of stresses varying on a microscale (for example resulting from the effect of atomic peening during film growth (see Section 8.3.5) and by 2, compositional inhomogeneity within the crystallites. Both effects are thought to have been operative here. Thus, effect 1 may explain the observation that the strain in <100> oriented crystallites was generally higher that the strain in <111> oriented crystallites (<311> oriented crystallites take an intermediate position); this can reflect that fcc metallic crystals in general more easily deform in the <100> direction than in the <111> direction. Effect 2 may explain the observation that the microstrain for the Ag$_x$Ni$_{1-x}$ crystallites was much larger than that for the Cu$_x$Ni$_{1-x}$ crystallites: the occurrence of pronounced compositional variations within the Ag$_x$Ni$_{1-x}$ crystallites is not unlikely in view of the equilibrium Ag-Ni phase diagram [20]; the Ag$_x$Ni$_{1-x}$ solid solution has a great tendency to decompose, in contrast with the Cu$_x$Ni$_{1-x}$ solid solution. (This discussion is also consistent with the interpretation given for the observed macrostresses; see Section 8.3.5)
Table 8.2a. The integral breadth of the structurally broadened profile, \( \beta' \), the crystallite size, \( D \), and the microstrain, \( \varepsilon \), corresponding to various line profiles recorded from Cu-Ni, pure Cu and pure Ni films.

<table>
<thead>
<tr>
<th>film</th>
<th>phase</th>
<th>( {hkl} )</th>
<th>( \beta' )</th>
<th>( D ) (nm)</th>
<th>( \varepsilon ) (10(^{-5}))</th>
</tr>
</thead>
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<td>100-nm 21Cu-79Ni</td>
<td>( \text{Cu}<em>x\text{Ni}</em>{1-x} )</td>
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<td></td>
<td></td>
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<td>9</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>{311}</td>
<td>2.004</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>{222}</td>
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<td>11</td>
<td>2</td>
</tr>
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<td>4</td>
</tr>
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<td></td>
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<td>12</td>
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An "*" added to \( \{hkl\} \) implies that line-profile analysis according to the procedure given in Section 8.2.2 was not performed as the shape of the profile concerned did not comply with a Voigt function.

Further support for the strain broadening of the \( \text{Ag}_x\text{Ni}_{1-x} \) solid solution as significantly due to compositional variations (corresponding to lattice-spacing variations) within the \( \text{Ag}_x\text{Ni}_{1-x} \) crystallites is obtained from the observation that this broadening very strongly increases with the Ag content (cf. Table 8.2b), whereas no
Table 8.2b. The integral breadth of the structurally broadened profile, $\beta^*$, the crystallite size, $D$, and the microstrain, $\varepsilon$, corresponding to various line profiles recorded from Ag-Ni, pure Ag and pure Ni films.

<table>
<thead>
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<th>film</th>
<th>phase</th>
<th>{hkl}</th>
<th>$\beta^*$</th>
<th>$D$ (nm)</th>
<th>$\varepsilon$ ($10^3$)</th>
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An "*" added to \{hkl\} implies that line-profile analysis according to the procedure given in Section 8.2.2 was not performed as the shape of the profile concerned did not comply with a Voigt function.

such dependence on composition occurred for the Cu$_x$Ni$_{1-x}$ solid solution (cf. Table 8.2a).

In view of the crystallite-size and microstrain data, the microstructure of the Ag-rich and Ni-rich phases differed strongly from that of the Ag$_x$Ni$_{1-x}$ solid solutions.
and also from that of the pure Ag and pure Ni films: much less structural line-profile broadening was observed for the Ag-rich and Ni-rich phases. This can be understood as follows. Firstly, the droplets in the Ag-Ni films were identified with Ag-rich and Ni-rich phases (see Section 8.3.2). The cooling and solidification mechanisms for large particulates, as droplets, differs significantly from those for the majority of the laser ablated species that are of atomic size and produced the Ag$_{x}$Ni$_{1-x}$ solid solutions. Relatively slow cooling and solidification, as held for the droplets, brings about a more perfect microstructure. Secondly, the partial decomposition of the Ag$_{x}$Ni$_{1-x}$ solid solution starting during film growth will lead to the development of Ag-rich and Ni-rich phases with a more perfect microstructure than that of the parent phase.

8.4 Summary and conclusions

Cu-Ni and Ag-Ni thin films were grown on amorphous substrates at room temperature using LAD.

The films contained a large number of solidified droplets; the droplet number density on the films made from non-compact, powder-pressed targets was substantially higher than that on the films made from compact targets. Using compact targets the droplet composition equalled the gross film composition, whereas using targets made by pressing of elemental powders the droplet composition ranged from Ag-rich (or Cu-rich) to Ni-rich.

The overall composition of the films did not equal the overall composition of the targets they were made from. The Cu-Ni films were Cu deficient and the Ag-Ni films were Ag deficient, as compared with the targets. This can be ascribed to preferential scattering of ablated Cu and Ag species upon incidence at the growing film surfaces.

The Cu-Ni films were single phase: a polycrystalline Cu$_x$Ni$_{1-x}$ solid solution. The Ag-Ni films were composed of a polycrystalline Ag$_x$Ni$_{1-x}$ solid solution and of polycrystalline, pure Ag and pure Ni phases. The Ag$_x$Ni$_{1-x}$ solid solution could contain up to at least 44 at.% Ag, reaching an extremely high supersaturation; its lattice parameter approximately obeyed Vegard's law.

The residual macrostress in the Cu-Ni film was compressive, whereas it was tensile in the Ag-Ni film. In the case of the Cu-Ni film the effect of atomic peening (introduction of compressive stress) dominated the effect of a possible minor cooling (introduction of tensile stress). In the case of the Ag-Ni film an additional effect was due to partial decomposition of the metastable Ag$_x$Ni$_{1-x}$ solid solution starting during film growth, which contributed to heating of the film and relaxation of the peening-induced stress, and as net result a tensile stress was observed after cooling.

Pronounced structural imperfection occurred for the Cu$_x$Ni$_{1-x}$ and Ag$_x$Ni$_{1-x}$ solid solutions: the crystallite sizes were smaller than 30 nm and the microstrains were up to $5\times10^{-3}$ for Cu$_x$Ni$_{1-x}$ and $25\times10^{-3}$ for Ag$_x$Ni$_{1-x}$ solid solutions. Compositional
variation in the Ag\textsubscript{5}Ni\textsubscript{1-x} solid solution led to the extremely large apparent microstrain data. Depending on their origin the Ag-rich and Ni-rich phases could have a more perfect microstructure than the associated Ag\textsubscript{5}Ni\textsubscript{1-x} solid solutions: Ag-rich and Ni-rich droplets experienced relatively slow cooling and solidification and Ag-rich and Ni-rich phases developed by partial decomposition of the Ag\textsubscript{5}Ni\textsubscript{1-x} solid solution starting during film growth.

References

[8] R.P. van Ingen, unpublished (concerned angle-resolved time-of-flight spectrometry of Nb atoms and Nb\textsuperscript{+} atoms).
Summary

This thesis reports an experimental study of laser ablation and deposition of alloys. Laser ablation is explosive formation of a plasma from target material utilizing laser pulses with a sufficiently high energy flux and of a sufficiently short duration. If the plasma particles are deposited onto a substrate one designates the technique laser ablation deposition (LAD).

After the general introductory Chapter 1, in Chapter 2 the known basic physics of laser ablation is reviewed. The experimental set-ups built and used for the present research and the associated experimental procedures are described in Chapter 3.

To study the basic mechanisms of laser ablation, in particular those involved in the expansion of laser-ablation-produced plasmas, angle-resolved time-of-flight (ARTOF) spectrometry was employed. This technique provided time-of-flight (TOF) distributions and associated yields of neutrals, positive ions and highly excited neutrals originating from laser ablated alloys, as a function of the detection angle. The results have been discussed in the Chapters 4, 5 and 6.

In Chapter 4 the expansion of laser-ablation-produced plasmas has been discussed on the basis of ARTOF and angle-resolved yield (ARY) distributions of O, Cu and Nd atoms and of NdO molecules laser ablated from a Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ alloy. The TOF distributions indicated that the kinetic-energy (KE) distributions of laser ablated neutrals were equal, regardless of the neutrals' mass and regardless of the detection angle. The experimental TOF distributions were fitted with normalized Maxwell-Boltzmann distributions superimposed onto angle-dependent flow-velocity contributions. The associated temperatures and kinetic flow energies for the four types of particles considered were similar. The ARY distributions were strongly peaked along the normal of the target surface. These results indicated that the expansion of the ablation-induced plasmas was jet-like. This can be caused by two mechanisms: (1) ablation of neutrals from the target surface followed by collisions amongst those neutrals in the plasmas just above the target surface and expansion of those plasmas, and (2) ablation of neutrals from microscopic small gas bubbles just below the target surface.

The emission of positive ions from laser-produced plasmas has been discussed in Chapter 5 on the basis of ARTOF and ARY distributions of Si$^+$ and of O$^+$, Cu$^+$ and Nd$^+$ ions emitted upon ablation of Si and Nd$_{1.85}$Ce$_{0.15}$CuO$_4$. The TOF distributions indicated that the KE distributions of the O$^+$, Cu$^+$ and Nd$^+$ ions were similar regardless of the ions' mass and regardless of the detection angle. This was similar to the fore-mentioned case of the laser ablated neutrals. However, the TOF distributions and the associated yields of the ions did not change with the detection
angle. Moreover, the most probable kinetic energies of the ions were substantially higher than those of the neutrals. These results have been explained on the basis of ambipolar diffusion of ions and electrons from laser-induced plasmas.

In the ARTOF distributions of neutrals and ions that were measured with a quadrupole mass spectrometer 'obscure' contributions were observed. In Chapter 6 it has been shown from the results obtained from laser ablation of Si that those contributions can be ascribed to highly excited neutrals, the so-called Rydberg atoms. These atoms could be detected due to electric-field ionization at the channeltron of the mass spectrometer. The ARTOF and ARY distributions of the Rydberg atoms showed a striking resemblance with the fore-mentioned TOF and ARY distributions of the laser-ablated neutrals. Nevertheless, conclusions about the formation and emission mechanisms of these atoms cannot be drawn.

To investigate the application of LAD for the production of metal alloy films, the composition and microstructure of Cu-Ni and Ag-Ni thin films, grown on amorphous substrates at room temperature, were studied. The results are discussed in the Chapters 7 and 8. The model systems Cu-Ni and Ag-Ni were chosen, because Cu and Ni are soluble into each other, whereas Ag and Ni are not soluble into each other at all.

However, apart from the expected Ag and Ni crystallites in the Ag-Ni films also polycrystalline, highly supersaturated Ag$_x$Ni$_{1-x}$ solid solutions were formed. The formation of such metastable alloys at room temperature was not attained with evaporation and sputtering and hence has not been reported before. Therefore, a brief discussion of the compositions and the (strain-free) lattice parameters of these solid solutions has been presented separately in Chapter 7.

The Cu-Ni and Ag-Ni films were significantly deficient of Cu and Ag, respectively, as compared with the targets. This can be ascribed to preferential scattering of ablated Cu and Ag particles upon incidence at the growing films. Hence, the composition of films produced with LAD need not always be equal to those of the targets.

The microstructure of the films was studied particularly with X-ray diffraction. The Cu-Ni films consisted entirely of polycrystalline Cu$_x$Ni$_{1-x}$ solid solutions and the Ag-Ni films consisted of pure, polycrystalline Ag and Ni, and of the said Ag$_x$Ni$_{1-x}$ solid solutions. The residual stresses in the Cu-Ni films were compressive as a result of the dominating effect of atomic peening by ablated, incident species. On the other hand, the stresses in the Ag-Ni films were tensile, due to partial decomposition of the solid solution during film growth, which contributed to heating of the films and relaxation of the peening-induced stress. Finally, the structural broadening of the diffraction line profiles have been discussed in terms of crystallite sizes, microstrains and composition gradients.
Samenvatting

Dit proefschrift rapporteert een experimentele studie van laser-ablatie en depositie van legeringen. Laser-ablatie is de explosieve vorming van een plasma uit target-materiaal m.b.v. laserpulsen met een voldoende hoge energieflux en met een voldoende korte tijdsduur. Indien de plasmadeeltjes op een substraat gedeponeerd worden noemt men de techniek laserablatiedepositie (LAD).

Na het algemeen inleidende Hoofdstuk 1 wordt in Hoofdstuk 2 de bekende basisfysica van laserablatie besproken. De experimentele opstellingen die voor dit onderzoek gebouwd en gebruikt zijn en de bijbehorende experimentele procedures zijn in Hoofdstuk 3 beschreven.

Om de basismechanismen van laserablatie te bestuderen, met name die betrekking hebben op de expansie van laserablatiegeproduceerde plasma’s, is hoekopgeloste vluchtijd- (HOVT) spectrometrie gebruikt. Deze techniek leverde vluchtijd-(VT) verdelingen en de bijbehorende opbrengsten van neutralen, positieve ionen en hoog aangeslagen neutralen als een functie van de detectiehoek. De resultaten zijn besproken in de Hoofdstukken 4, 5 en 6.

In Hoofdstuk 4 is de expansie van laserablatiegeproduceerde plasma’s besproken op basis van HOVT- en hoekopgeloste opbrengst-(HOO) verdelingen van O, Cu en Nd atomen en van NdO moleculen die van een Nd_{1.85}Ce_{0.15}CuO_{4} legering geableerd waren. De VT-verdelingen duidden erop dat de kinetische-energie (KE) verdelingen van laser-geableerde neutralen gelijk waren, ongeacht de massa van de neutralen en ongeacht de detectiehoek. De experimentele VT-verdelingen werden gefit met genormaliseerde Maxwell-Boltzmann-verdelingen die op hoekafhankelijke stroomsnelheidsbijdragen gesuperponeerd waren. De bijbehorende temperaturen en kinetische stroomsnelheidsenergieën voor de vier typen deeltjes waren nagenoeg gelijk. De HOO-verdelingen waren sterk langs de normaal van de targets gepikte, deze resultaten duidden erop dat de expansie van laserablatiegeproduceerde plasma’s jetachtig is. Dit kan door twee mechanismen veroorzaakt worden: (1) ablatie van neutralen van het target-opervlak gevolgd door botsingen tussen die neutralen in de plasma’s vlak boven het target-opervlak en expansie van die plasma’s en (2) jetachtige ablatie van neutralen vanuit microscopisch kleine gasbellen van onder het target-opervlak.

De emissie van positieve ionen uit lasegeproduceerde plasma’s is besproken in Hoofdstuk 5 op basis van HOVT- en HOO-verdelingen van Si^{+} en van O^{+}, Cu^{+} en Nd^{+} ionen die geëmitteerd waren bij ablatie van Si en Nd_{1.85}Ce_{0.15}CuO_{4}. De VT-verdelingen duidden erop dat de KE-verdelingen van de O^{+}, Cu^{+} en Nd^{+} ionen gelijk waren, ongeacht de massa van de ionen en ongeacht de detectiehoek. Dit was eender
als in het voorgenoemde geval van de lasergeableerde neutralen. Echter, de VT-
verdelingen en bijbehorende opbrengsten van de ionen veranderden niet met de
detectiehoek. Bovendien waren de kinetische energieën van de ionen aanzienlijk hoger
dan die van de neutralen.

In de HOVT-verdelingen van neutralen en ionen die met een quadrupool-
massaspectrometer gemeten waren werden 'vreemde' bijdragen waargenomen. M.b.v.
de resultaten die verkregen zijn bij laserablatie van Si is in Hoofdstuk 6 aangetoond
dat deze bijdragen toegeschreven kunnen worden aan hoog aangeslagen neutralen, de
zgn. Rydberg-atomen. Deze atomen konden detecteerd worden t.g.v. electrische
veldionisatie bij het channeltron van de massaspectrometer. De HOVT- en HOO-
verdelingen van de Rydberg-atomen vertoonden een opvallende gelijkenis met de
voorgenoemde VT- en HOO-verdelingen van de laser-geableerde neutralen. Niettemin
kunnen er geen conclusies getrokken worden over de vormings-
emissiemechanismen van deze atomen.

Om de toepassing van LAD voor de produktie van films van metaallegeringen
te onderzoeken zijn de samenstelling en microstructuur van dunne Cu-Ni- en Ag-Ni-
films, die op amorfie substraten gegroeid waren, bestudeerd. De resultaten zijn in de
Hoofdstukken 7 en 8 besproken. De modelsystemen Cu-Ni en Ag-Ni zijn gekozen
omdat Cu en Ni in elkaar oplosbaar zijn, terwijl Ag en Ni totaal niet in elkaar
oplosbaar zijn.

Echter, behalve de verwachte Ag- en Ni-kristalliten werden in de Ag-Ni-
films ook polykristallijne, supervierzadigde Ag$_x$Ni$_{1-x}$ vaste-oplossingen gevormd. De
vorming van zulke legeringen is niet mogelijk gebleken m.b.v. opdampen en sputteren
en daarom nog niet eerder gerapporteerd. Daarom is een korte bespreking van de
samenstellingen en de (spanningsvrije) roosterparameters van deze vaste oplossingen
apart in Hoofdstuk 7 gepresenteerd.

De Cu-Ni- en Ag-Ni-films hadden een significant tekort aan respectievelijk Cu
en Ag vergeleken met de targets. Dit kan toegeschreven worden aan preferentiële
verstrooiing van Cu- en Ag-deeltjes aan de groeiende films. De samenstellingen van
dunne films die met LAD gemaakt zijn behoeven dus niet altijd gelijk te zijn aan die
van de targets.

De microstructuur van de films was met name bestudeerd m.b.v.
röntgendiffractie. De Cu-Ni-films bestonden volledig uit polykristallijne Cu$_x$Ni$_{1-x}$
vaste-oplossingen en de Ag-Ni-films bestonden uit polykristallijn Ag en Ni, en uit de
genoemde Ag$_x$Ni$_{1-x}$ vaste oplossingen. De restspanningen in de Cu-Ni-films waren
duikspanningen t.g.v. het dominerende effect van 'atomic peening' van geableerde,
invallende deeltjes. Anderzijds waren de restspanningen in de Ag-Ni-films
trekspanningen t.g.v. partiële ontmenging van de vaste oplossingen tijdens de
filmgroei, wat bijdroeg bij de verwarming van de films en relaxatie van de peening-
geïnduceerde spanningen. Tenslotte is de structurele verbreding van de
Samenvatting
diffractielijnprofielen besproken in termen van kristallietgrootte, microspanningen en samenstellingsgradiënten.
Nawoord

Bij deze wil ik een ieder die op enigerlei wijze positief heeft bijgedragen aan de totstandkoming van dit proefschrift vriendelijk voor zijn/haar bijdrage bedanken.

R.P.v.I.