ARGON IN THIN MOLYBDENUM FILMS

THE INFLUENCE OF ARGON ION BEAM ASSISTANCE ON THE GROWTH OF THIN MOLYBDENUM FILMS

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O HEER, onze HEER, hoe heerlijk heeft Gij Uw naam over deze wereld uit geschreeuwd.

Psalm 8:1

O LORD, our LORD, how wonderful have You cried out Your name over this world.



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Note to the reader

This thesis is a snapshot in time of work in progress. The time period allotted to graduation work is only limited. In some cases the analysis of the data could not be fully completed and is therefore given in preliminary form. Consequently, it cannot be ruled out that ongoing work will eventually lead to certain modifications of the interpretation of the data.



Summary

When an ion beam is directed onto a sample onto which a layer is being grown, the kinetic energy carried by the ions leads to a modification of the growth process. A disadvantage of this technique is that the ions can be build into the growing layer. Therefore it is important to understand how these ions behave in the layer after it is grown.

In our case argon is used as assisting ion. The technique that is used for investigating the layers is Thermal Helium Desorption Spectrometry (THDS). As a consequence of the heating of the sample up to 2000 K the argon in the layer is released also and both the helium and argon signal are recorded.

Molybdenum is an important material associated with nuclear material technology. It is used here because there is already a lot of information of THDS-experiments on molybdenum. The main difference with those experiments is that we grow a molybdenum film. In the other experiments, defects are created in the sample by deformation or bombardment with high energetic ions.

A molybdenum film can be produced by depositing molybdenum vapour on a molybdenum sample. At low temperatures, this will result in a molybdenum film with many defects, like vacancies, vacancy clusters, and holes. In order to get a film with fewer defects, the deposition temperature can be raised. In some cases it is impossible to raise the deposition temperature, as with the production of multilayers of materials which will interdiffuse at higher temperatures.

A method to produce thin films with (possibly) fewer defects without raising the temperature is Ion Beam Assisted Deposition (IBAD). IBAD generally refers to any thin film process in which a source of energetic ions is used to bombard the growing film. Not much is known about the influences of the ion bombardment on the processes during the growth of a molybdenum film. During this graduation project, we studied the influence of ion energy and ion doses on the number of defects that exist in the deposited film. A special look is given to the way argon interacts with the existing crystal structure.

THDS is used to investigate thin Mo layers (5-500 Å) deposited with or without ion beam assistance (0.2-22 eV per Mo atom). On first sight ion assistance enlarges the trap concentration in the film due to high energetic neutrals that are always present in the beam. The ion source produces 250 eV Ar⁺-ions. Due to interactions with the argon atoms in the vessel during IBAD, 250 eV neutral argon atoms are created.

The neutral argon atoms create defects in the layer and become trapped. From the argon desorption spectra it can be seen that there are (in general) four peaks, which means that there are four kinds of defects in the layer from which the argon is released. With respect to argon the bulk starts at a depth of four atomic layers. This is seen by three different surface related peaks, with activation energies for release that are influenced by the depth of the argon atom beneath the surface and the surface orientation. The fourth peak is a bulk peak, which moves to higher temperatures when the argon is buried deeper beneath the surface. The release mechanism for argon is called the "vacancy-mechanism" [1], by which the argon atoms make use of vacancies in the layer. It is similar to self-diffusion of molybdenum. This mechanism is different from that for helium, which is released from its trap and moves interstitially to the surface.

Symbols

Symbol	Quantity	Unit
D	magnetic field strength	т
D		I
C _{tr}		-
C _{vac}	vacancy concentration	-
D _{int}		m ⁻ /s
D _{Mo}	self diffusion coefficient for molybdenum	m ⁻ /s
D_0	prefactor	m ⁻ /s
d	film thickness	A
E _d	displacement energy	eV/atom
EIBAD	Kaufman ion energy on sample	eV/ion
$E_{\rm th}$	threshold energy for damage production	eV/atom
I _{FC}	measured Kaufman ion current on Faraday cup	nA
l _s	measured Kaufman ion current on sample	μΑ
k _B	Boltzmann constant	JK⁻¹
L	desorption flux	cm ⁻² s ⁻¹
М	mass	kg
т	mass	kg
N _{des}	number of steps before desorption	-
Ni	number of bound atoms	
N _{step}	number of steps	-
N _{surf}	number of steps from a surface	-
<i>n</i> _{Ar}	argon decorated defect concentration	cm ⁻²
n _{He}	helium decorated defect concentration	cm ⁻²
<i>n</i> int	interstitial particle concentration	cm⁻²
<i>n</i> tr	trapped particle concentration	cm ⁻²
р	total pressure	mbar
$ ho_{IBAD}$	pressure when Kaufman ion beam on	mbar
$Q_{ m dif}$	activation energy for diffusion	eV/atom
Q _{int}	activation energy for interstitial movement	eV/atom
Q _{tr}	activation energy for release from a trap	eV/atom
R _p	projected range	Å

Symbol	Quantity	Unit
S(x)	implantation rate function	s ⁻¹
T	temperature	K
To	starting temperature	K
T_{a}	anneal temperature	К
\mathcal{T}_{dep}	deposition temperature	К
T _m	melting temperature	К
Tp	temperature of peak maximum	K
t	time	S
<i>t</i> b	ion beam time	S
<i>t</i> s	sample time	S
Vs	sample bias voltage	V
X	depth below surface	Å
$Y_{ m sp}$	sputtering yield	atoms/ion
β	heating rate	Ks⁻¹
γ	ion-to-atom ratio	ions/atom
$\Delta R_{ m p}$	projected range straggle	Å
η	entrance probability	-
λ	mean free path	m
λ_{int}	interstitial jump length	Å
λ_{vac}	vacancy jump length	Å
ν	jump frequency	S ⁻¹
ν_0	frequency factor	s⁻¹
σ_{ce}	cross section for charge exchange	m ²
τ_{Ar}	average residence time of argon in desorption vo	lume s
τ_{He}	average residence time of helium in desorption volume s	
Φ	decoration fluence	cm⁻²
Φ_{Ar}	arrived argon fluence	cm ⁻²
Φ_{c}	implanted fluence (corrected)	cm⁻²
Φ_{des}	desorbed fluence	cm ⁻²
χ	normalised desorption flux (= $L/\Phi\beta$)	K ⁻¹

1. Introduction

The major application of thin films has been in microelectronics, but there are an increasing number of applications in communications, optical electronics, coatings, and in energy generation and conservation strategies. Molybdenum is an important material associated with nuclear material technology [2].

Molybdenum layers can be deposited by Physical Vapour Deposition (PVD) using an electron beam evaporator. However deposition of low-energy species from the vapour phase often yields films which are of poor quality, with low structural density and large microporosity. When the film forming elements are given a higher kinetic energy (by deposition at a raised sample temperature) or when other species with high energy level (with respect to the thermal energy) additionally impinge on the growing film, the properties of the films can be changed and can often be controlled to a wide extent [3, 4, 5]. An example of the last category is a relatively new technique which is called Ion Beam Assisted Deposition (IBAD).

Ion beam assistance during deposition of metals has been observed to produce beneficial modifications in a number of characteristics and properties of a thin film [e.g. 3]. These include adhesion, chemical inertness, diffusion properties, friction, surface roughness, resistivity, stress, microhardness, and magnetic properties. Important for the growth of films by ion beam assisted deposition at low sample temperatures are the densification, the texture, the grain size, the grain boundaries, and the morphology.

For this thesis it is also important that argon is incorporated in a molybdenum film when this film is deposited by argon ion beam assisted deposition with ion energies of 250 eV. An inert gas ion incident upon a solid surface with sufficient kinetic energy may enter the solid and come to rest there. To understand the kinetics within a molybdenum layer it is important to understand the interaction between argon and the molybdenum layer. Previous work on this subject has been done by Van Veen *et al.* [1] and Kornelsen and Sinha [6, 7, 8]. They directed energetic inert gas ions on molybdenum and tungsten in order to gain insight in the behaviour of inert gases in materials of nuclear fusion reactors.

To investigate the deposited layers a technique called Thermal Helium Desorption Spectrometry (THDS) is used. THDS is a defect probing technique based on the high mobility of helium in most materials and the strong binding of helium at defects. After low energy helium injection, a fraction of the helium is trapped by the defects. By subsequent thermal desorption measurement of the trapped helium, quantitative information is collected on the number and the type of defects. During the heating step the argon atoms in the layer are released also. This gives us information on the behaviour of argon atoms in the molybdenum layer and the release mechanisms.

Central theme of this research is understanding the influence of argon ion beam assistance on the growth of a thin molybdenum film. Within this research molybdenum is grown on a poly-crystalline substrate. Preliminary results of this research have been published earlier [9, 10]. From the literature only little is known about the influence of ion assistance on atomic defects in the growing film. Therefore it is important to understand the interaction between argon and molybdenum in the layer. Some important data on molybdenum can be found in table 1.

Questions that this graduation thesis intends to answer are the following. First we like to associate the peaks seen in the argon desorption spectra with defects present in the film and second we want to determine the release mechanisms of argon from the molybdenum lattice. In chapter 2 the theory behind the main experimental techniques and the growth of thin films will be described. In chapter 3 the experimental set-up is described. In chapter 4 the results will be presented and discussed. Finally, in chapter 5, the conclusions are given.

symbol	Мо
atomic number	42
atomic mass	95.94 u
atomic radius	2.01 Å
density	10.2·10 ³ kg/m ³
melting temperature	2898 K
crystal structure	B.c.c.
surface diffusion coefficient	~10 ⁻¹² m ² /s
self-diffusion coefficient	~10 ⁻²⁰ m ² /s

Table 1: Most important data on molybdenum for this thesis. The diffusion coefficients are given at a temperature of 1500 K.

2. Thin film deposition and Thermal Desorption Spectrometry

2.1. Physical Vapour Deposition using an electron beam evaporator

In this work, molybdenum films are deposited on an annealed poly-crystalline molybdenum substrate by Physical Vapour Deposition (PVD). The vaporised molybdenum comes from a pure molybdenum melt (impurity level of 50 a.p.p.m.). Because of the high melting temperature of pure molybdenum an electron beam evaporator is needed.

2.1.1. The electron beam evaporator

The underlying film growth method is physical vapour deposition. A material is vaporised by introducing thermal energy by electron impact on the material. The vapour condenses on the sample which is colder than the vapour source. When the mean free path is larger than the distance from vapour source to the sample, the molybdenum atoms reach the surface without collisions and have an energy of the order of 0.2 eV. A detailed description of the electron beam evaporator has been given by Ohring [11]. A short review is given in this section.

An electron-source, located out of sight with respect to the sample generates an intense beam of electrons (energy \approx 8 keV), see figure 1. A magnetic field deflects the electrons such that the centre of the molybdenum-charge is struck by the electrons. The target material sublimates, reaches a sufficiently high vapour pressure and evaporates at a certain rate. Since the outer portion of the charge is kept cool, only the centre of the target melts. The overall effect is that it appears as though the molybdenum is evaporated from a pure molybdenum-crucible. This results in the deposition of high purity films.



Figure 1: Electron beam evaporator, with B standing for the applied magnetic field.

Evaporation is a deposition technique operated in a low-pressure atmosphere. This implies that the mean free path of evaporated atoms is long compared to the typical source-sample distance. Particles originating at the evaporator traverse the space between source and sample without collisions with gas molecules, and hence their trajectories are straight lines. The particles which are reflected from the sample surface leave this surface unhindered and do not participate in the growth process any further. The growth rate depends linearly on the particle flux leaving the source, which in turn is proportional to the vapour pressure and therefore strongly dependent on the temperature.

In general, the mean free path for particles present in a gas is given by [49]

$$\lambda = \frac{k_B T}{\sqrt{2} \cdot p\pi d^2},\tag{1}$$

in which $k_{\rm B}$ is the Boltzmann constant, *p* the total pressure, *T* the temperature, and *d* the effective diameter of the gas particles. Taking $d = 3 \cdot 10^{-10}$ m and T = 300 K we find

$$\lambda = \frac{10^{-4} \quad mbar \cdot m}{p}.$$
 (2)

Consequently, at a pressure of 10⁻⁴ mbar, a mean free path of 1 m is realised. Background pressures in evaporation equipment are usually considerably lower than that pressure and hence atoms leaving the evaporator do not collide with background particles on their way to the sample.

2.1.2. General description of film growth

In the initial phase of atom condensation on a solid surface, two main processes take place, first arrival of atoms at the sample, second migration of atoms on the sample surface. This is schematically shown in figure 2. When the atoms arrive at a sample which is colder than the atom source the atoms may either re-evaporate or transfer their energy to the sample until they reach the sample temperature and stay at the sample. The sticking coefficient which describes the degree of re-evaporation is the ratio of the number of atoms sticking to the sample to the number of impinging atoms. In the case of metals at room temperature, the adsorption energy of the atoms on the sample is high ($\approx 5 \text{ eV}$) and so the sticking coefficient is also high, close to unity.



Figure 2: Atomic motion during nucleation and growth of a thin film. a: Atom deposition, b: reevaporation, c: adatom migration, d: nucleation, e: trapping at a special site [4] On its way to a fixed position (c), the atom loses its initial energy in just a few steps. After it has lost most of its energy, it migrates over the surface in diffusive random hops. The distance of hopping is a measure for the thermal surface mobility of the arriving atoms on the surface. Calculations, performed with data obtained on surface mobility of molybdenum on molybdenum [12-16], give a surface diffusion coefficient of the order of 10^{-12} m²/s at a temperature of 1500 K. Extrapolation of these results to room temperature give a maximum surface mobility for molybdenum of the order of one Ångström per hour. Such a surface mobility is so low that within our experiments this effect is negligible as we deposit at room temperature.

Making use of the energy the atom has on arrival, the adatom can be trapped at special sites (e) like ledges, kinks, etc., or when the adatom meets other atoms (d), it may form a small cluster, a nucleus. A nucleus may capture further atoms or decay again releasing migrating atoms. The nucleation rate describes how many nuclei are formed per unit time and area.

The stability of a cluster increases with increasing size; only those with a certain minimum size, the so-called critical size, are able to grow, others break up. Clusters may grow to larger sizes by incorporating impinging atoms, migrating atoms or subcritical clusters. When clusters meet, either by growth or by motion, they combine. This coalescence continues and forms a network of connected clusters. Next, the remaining voids are filled and eventually a film with full coverage is formed.

Several modes of thin film growth have been observed in practice as illustrated in figure 3. The layer-by-layer growth (Frank-van der Merwe) involves the growth of the film a layer at a time with complete coverage of the surface. The island type of growth (Volmer-Weber) results in the formation and growth of islands several layers thick before complete surface coverage occurs. The mixed layer-island growth (Stranski-Krastanov) is an intermediate case in which a monolayer first forms followed by the growth of islands.



Figure 3: The three basic film growth modes: island, layer-by-layer, and mixed layer/island growth.

Which growth mode prevails, depends mainly on the film-substrate interactions. Producing island growth when the condensing atoms are bound more strongly to each other than to the substrate and layer-by-layer growth when the interaction with the substrate is stronger and monotonically decreases as each layer is added. Mixed growth occurs when the monotonic decrease in binding energy is disrupted by some factor such as lattice mismatch or orientation and island formation becomes more favourable. All three types of growth are widely observed, but for metal-on-metal growth especially mixed growth is often observed [11].

In layer-by-layer growth of thin films, two kinetic processes play a role, one being nucleation during the early stages of monolayer growth, the other one being the migration of adatoms. For layer-by-layer growth, adatoms deposited on top of two-dimensional islands must be able to leave the island planes over the edges. If they cannot leave the island in time, further adatoms will be deposited and nucleation on top of the island with three-dimensional growth will take place before the flat islands grow together to a fully covering monolayer. The adatoms have enough time to reach the edges of the islands, however they have to overcome an activation barrier for descending.

2.1.3. Defects

There are materials - carefully grown silicon single crystals, for example - that have virtually perfect crystallographic structures extending over macroscopic dimensions. This is not generally true in the bulk of most materials. In thin crystalline films the presence of defects not only serves to disrupt the geometric regularity of the lattice on a microscopic level, it also significantly influences many film properties, such as chemical reactivity, electrical conduction, and mechanical behaviour. In thin metal layers the most common defects are grain boundaries, dislocations, and vacancies [11].

Grain boundaries [11] are surface defects that constitute the interface between two single-crystal grains of different crystallographic orientation. The atomic bonding, in particular grains, terminates at the grain boundary where more loosely bound atoms prevail. Like atoms on surfaces, there is less energy needed to move the atoms from their place than atoms within the grain interior. This causes the grain boundary to be a heterogeneous region where various atomic reactions and processes, such as solid-state diffusion and phase transformation, precipitation, corrosion, impurity segregation, and mechanical relaxation, are favoured or accelerated. Grain sizes in films are typically from 100 Å until 10000 Å [11] in dimension and are smaller, by a factor of more than 100, than common grain sizes in bulk materials as can be seen from figure 4. In molybdenum films, grown on a polycrystalline molybdenum substrate, the orientation between neighbouring grains is often just slightly different which leads to small angle grain boundaries. When the grain boundaries are covered with another layer of molybdenum, these regions will probably be the origin of all kinds of defects like vacancies, voids and dislocations.



Figure 4: Plot of maximum and minimum grain size variation with homologous sample temperature for 10 different evaporated metals. [17].

Dislocations are line defects that bear a definite crystallographic relationship to the lattice. The two fundamental types of dislocations are the edge- and the screw-dislocations. Film stress, thermally induced mechanical relaxation processes, and diffusion in films are all influenced by dislocations. Buters [2] showed that dislocations cannot be detected in molybdenum by thermal helium desorption spectrometry. This appears to be in contrast to the fact that Caspers and Van Veen had found a dissociation energy for dislocations of 1.5 eV [18].

Vacancies are point defects that simply arise when lattice sites are unoccupied by atoms. Vacancies are the most common kind of defects found in thin molybdenum films [1]. Normally they are separated in monovacancies and small vacancy-clusters. All defects seen with thermal helium desorption spectrometry were assigned to this kind of defects.

2.2. General influence of an ion beam on a growing film

Ion beam assisted deposition is the process of simultaneous thin film deposition and directed bombardment of energetic particles. This technique is used to modify the growth process of thin films, thereby changing the microstructure and properties of thin films.

A short general description of ion beam assisted deposition is given by Ensinger [4]. More complete descriptions are given by Smidt [3], Atwater [19], and Hirvonen [5]. This chapter is a review of the most important aspects relevant for this work.

2.2.1. Ion Beam Assisted Deposition (IBAD)

Physical vapour deposition of thin molybdenum films is apparently accompanied by the incorporation of large non-equilibrium concentrations of vacancies and micropores [11]. One way to improve the microstructure of a film is to deposit at raised sample temperature. When the temperature is high enough, this will result in defect free layers. A negative effect of deposition with raised sample temperature is that diffusion between successive layers may occur. The idea of deposition on a heated sample is to give the arriving atoms at the surface a higher mobility so that the vacancies created near the surface can be filled. Using ion beam assisted deposition it is possible to raise the temperature in the direct surroundings of the argon impact. In this way the temperature in the direct surroundings can become high enough for greater mobility of the molybdenum atoms (sort of a recrystallization effect). The possibility of growing defect free layers using ion beam assisted deposition has, for example, been shown by earlier work on silicon [19, 20, 21] and 2D-simulations on nickel by Müller [22] (figure 5).



Figure 5: Typical microstructure obtained for condensing Ni vapour atoms of 0.1 eV kinetic energy, arriving at normal incidence; a. without ion beam assistance, b. with 10 eV Ar⁺ bombardment and an ion-to-atom arrival ratio of 0.16, c. with 75 eV Ar⁺ bombardment and an ion-to-atom arrival ratio of 0.16.

2.2.2. Process parameters

Ion beam assisted deposition is a process with many different influences on film growth due to the many parameters that can be changed. The main parameters of IBAD are the arrival rates of the different species, the energy of the assisting ions, the incidence angles, and the sample temperature.

There are three arrival rates: the number of arriving film-forming atoms per unit time and area, the impingement rate of ions, and the arrival rate of residual gas atoms. From the first two the important IBAD process parameter "ion-to-atom arrival ratio" γ can be derived which is the ratio of the number of impinging ions to the number of condensing atoms. The last arrival rate may in our experiments be neglected due to UHV conditions of 10⁻¹¹ mbar.

The energy of the bombarding particles is an important parameter, particularly in the range up to a few hundreds of eV, because some processes such as e.g. defect production and sputtering have a threshold below which the process does not occur. The energy of the atoms is of secondary importance unless it is very high. In case of thermal evaporation it is in the range of several 0.1 eV, depending on the temperature of the vapour source. Due to limitations of our ion source we have mainly used 250 eV Ar⁺ ions (also in combination with lower energy ions), which is too high for the growth of defect free layers using IBAD.

From the foregoing parameters another important process parameter can be derived, the average energy transferred from the assisting ions to a film forming atom, the energy-to-atom arrival ratio. Among other things this is a measure for the number of ion induced generations of phonons in the direct surroundings of the striking ion, and thus an important parameter for IBAD.

The main parameter related to the sample is its thermal energy level, namely the temperature. When an atom arrives at a sample it can gain energy by the thermal vibrations of the surface atoms. At room temperature this energy is insignificant, but at raised sample temperature this energy can be high enough to increase the surface mobility to such a level that a defect free layer is grown (layerby-layer growth at 1500 K for molybdenum [12-16]). Another effect of a higher sample temperature is that vacancies become mobile within the lattice. For this effect two values can be found. Van Veen et al. [1, 29] found 500 K and 900 K is found and presented in section 4.2.1. This value has been obtained for the bulk of molybdenum and might be less for the vacancies near the surface due to relaxation [23]. Raising the sample temperature during deposition is not always desirable. Therefore with IBAD it is necessary to try to imitate the influence of a raised sample temperature. This means that one has to try to raise the temperature in the growing layer and not in the other layers. In theory this can be done by energetic particles which lose their energy in the direct surroundings of the impact, which gives rise to a local temperature increase. Critical combinations for IBAD are described by Brighton and Hubler (figure 6) [24]. More on the energy of the arriving assisting ions will be said in the next section.



Figure 6: Critical ion-to-atom arrival rate ratio as a function of the ion energy [24].

One more parameter that influences the resulting film properties is the angle of ion incidence (normally defined as the angle relative to normal of the surface plane). The angle of ion incidence is important with respect to the orientation of the surface. When impinging in the channel direction of the layer, the ions can penetrate much deeper into the layer than in any other direction [25].

2.2.3. Energy regimes when performing IBAD

The processes by which energy is transferred from an energetic ion to a solid are important fundamentals for understanding how particle bombardment interacts with the growing film to modify the microstructure and properties of the film. The impact of an energetic ion with a solid produces a variety of effects. The incoming ions lose their energy by two main processes, elastic 'nuclear' collisions and inelastic 'electronic' energy loss processes. Inelastic collisions result from Coulomb interactions with the electrons in inner and outer shells of the atoms in the target which produce ionisation or excitation of the electrons. Such collisions play a very insignificant role below a few keV. Elastic collisions can displace atoms from their lattice positions. The displaced atoms, the so-called 'recoils', produce additional collisions in a short period of time. The series of events is called a collision cascade (figure 8). Cascades which occur near the surface can sputter atoms from the surface and cause desorption of adsorbed species. During the cascades, vacancies and other defects can be produced in the bulk. Furthermore the cascades can increase the diffusion rate and the interaction between interstitials and vacancies. The composition of the surface layers can be changed by implanted atoms, preferential sputtering, ion mixing, and segregation. Secondary electrons and photons may be emitted from excited atoms in the surface and these particles may in turn interact with atoms or molecules adsorbed on the surface.



Figure 7: Packing density vs. Ar ion kinetic energy for a fixed ion-to-atom arrival ratio [22].

As mentioned earlier, low energy ion bombardment during growth of thin films from the vapour phase exerts a strong influence on the properties of the films, particularly their microstructure as shown in figure 5 and 7. The basic mechanisms of film growth under ion irradiation can be divided in two regimes, the low ion energy range below 1 keV and the high ion energy range above 1 keV. For IBAD the low energy range is the most important one.

The lower limit of this scale is given by the activation of surface processes. The energy for physisorption is typically 0.1 eV, which is about the energy of the arriving molybdenum atoms. These are thermal species which do not influence a growing film.

In the regime up to several tens of eV, the ions are largely ineffective in influencing the physical properties of the film. In this low-energy regime, a considerable number of ions do not enter the solid, but are reflected. Most of them leave the surface as neutrals in the ground state. At this level, ions are only able to influence the atoms in the near-vicinity of their impingement position. They will not cause residual damage, but rather support the annealing of defects frozen in as a result of the limited adatom mobility when a film is grown from the vapour phase at low sample temperature. The ions are not able to penetrate into the material and will therefore not generate secondary collisions. Hence, virtually no sputtering will occur.

In contrast to the thermal species which are deposited at the surface, ions with energies in the range of hundreds of eV in ion beam assisted deposition are energetic enough to break through the surface barrier. In addition to surface effects, they create a number of subsurface effects. They penetrate into the material and create point defects and cause sputtering. Depending on ion/target combination, at perpendicular incidence a large part of the ions in this energy regime will stay in the solid and become implanted. More on this energy regime will be said in the next section, because this regime is the regime important for our experiments.

When highly energetic ions (energies up to several MeV) enter the lattice of the growing film along lattice planes or channels, they are able to penetrate deeply into the lattice with a greatly reduced rate of damage creation by atomic collisions. Electronic energy losses dominate at MeV energies so the ions lose their energy by electronic excitation. Ballistic radiation damage is strongly reduced. After loosing most of their energy, nuclear processes become dominant and the ions create lots of damage deep under the surface; this is called "end of range damage".

2.2.4. The influence of energies in the range of hundreds of eV

In the energy range of hundreds of eV the energy loss is mostly due to nuclear elastic collisions. Elastic collisions result in a sharing of the energy and momentum between beam and struck atoms. The incoming ion possesses enough kinetic energy to knock atoms out of their lattice positions. Some of the knocked-on atoms (recoils) possess energies high enough to create secondary collisions, etc. In this way, collision cascades develop as can be seen in figure 8. By contrast to higher energies, at low ion energies the cascade is not isotropic. The primary knock-on atoms absorb most of the energy. The resulting strong atomic motion along the trajectory of the ions leads to a rearrangement of the lattice. A material transport both in direction of the incident ion beam and in any other direction takes place. Radiation damage such as point defects, interstitials, vacancies, and defect agglomerates are created. The damage is partially annealed during the process and partially it remains, which depends on the nature of the target material and the temperature. When a high number of defects are created, they can agglomerate to two- and three-dimensional defects such as dislocation loops and vacancy-clusters. Collision cascades may be directed away from the direction of ion incidence. If nearsurface collisions are energetic enough to overcome the surface binding energies, they may lead to removal of atoms from the outer atomic layers. This sputtering leads to a reduction in growth velocity and, as a result, in final film thickness. It may also lead to changes in composition when different constituents of the film have different sputtering yields.



Figure 8: Impression of a collision cascade developing in time, obtained from Molecular Dynamics calculations [26]. The dark sphere in the upper left picture is a 250 eV argon ion just before impact on a Mo (100)-oriented growing film. The other large spheres are the molybdenum atoms that are influenced by the impact. Small spheres are the molybdenum atoms without special significance. Several phenomena can be seen in this picture sequence: The argon atom (arrow) creates a cluster of 4 vacancies, each expelled Mo atom giving rise to a replacement collision, i.e. a chain of jumping atoms. Three adatoms are created and one self-interstitial (the dumbbell in the bottom chain). The argon atom remains trapped in the self-created vacancy cluster.

Surface or near-surface atoms which are involved in collision cascades, but are not able to leave the solid, may nevertheless leave their lattice sites and remain on top of the surface as adatoms. The collision energy for adatom creation is lower than for sputtering. These adatoms can nucleate to adatom islands. Additionally, surface vacancies are created. Adatoms can influence the nucleation kinetics on the surface. The interaction between the surface and subsurface zone and the incoming ions influences nucleation kinetics and growth of thin films, and, as a result, film features such as grain size and crystallographic orientation. Ion bombardment influences the nucleation density. It is determined by the balance of formation rate and annihilation rate of the nucleation sites and the nuclei. The production rate depends on the ion/sample combination, the ion energy and the ion irradiation intensity.

A particular important effect of ion bombardment is the enhanced adatom mobility. These are ion induced generation of phonons which couple to an adatom and shallow collision cascades which affect the adatom. Both are limited to short ranges. Mobile adatoms are not only generated by transferring energy from ions to single adatoms, but also by additional formation of adatoms from already existing clusters.

Ion bombardment can induce dissociation of small clusters, both by direct impact and by impact in the near vicinity of a cluster if it is situated in the range of the collision cascade. Upon ion impact, clusters can be depleted at their edges or completely broken up when they are small and non-stable, as shown in figure 9. The created adatoms move across the surface, are re-evaporated or captured by larger clusters. As a result of this ion induced effect, the island size is enhanced.



Figure 9: Creation of mobile adatoms from the edge of a cluster by ion irradiation of by ion induced dissociation of small clusters. [4]

When films are deposited from the vapour phase at low sample temperature, they develop structures with open grain boundaries, often columnar. The columns can be large elongated single grains or consist of smaller grains which are more equiaxed. Ion bombardment can disturb the columnar growth and lead to closer growth of the grains. The films exhibit higher density. Bombardment of the grain surfaces can lead to renucleation. The grains become smaller and columnar growth can be interrupted [4].

On the other hand, bombardment under appropriate conditions can suppress secondary nucleation on top of islands, by removing adatoms prior to nucleation, leading to changes in the growth mode from island growth to layer growth.

2.3. Thermal Desorption Spectrometry (TDS)

Kornelsen [25] for the first time systematically measured the thermal desorption of inert gases implanted into a polycrystalline tungsten wire. Once the measured desorption peaks could be associated with the proper point defects, Thermal Desorption Spectrometry (TDS) has become a very useful technique to study point defect interactions in solids.

2.3.1. Description of a TDS experiment

Thermal helium desorption spectrometry is a technique using helium as an atomic probe to detect the presence of defects in a solid. Helium is used because of its chemical neutrality, the small atomic radius, and the low activation energy for interstitial diffusion. The helium can be implanted with low energy into the solid creating little or no extra damage. Because the helium atoms are very small they can penetrate relatively deep into the material in which they are implanted (tens of Ångströms). Together with the low activation energy for interstitial diffusion this gives the helium the possibility to reach defects at a relatively great depth (up to hundreds of Ångströms).

Part of the helium will be reflected as neutral helium atoms. The sub-surface injected helium ions neutralise very quickly by tunneling of an electron from the surface, when they come very close to the surface, consequently forming atomic helium. Due to the overwhelming amount of conduction band electrons, an additional consequence of this process is the creation of secondary electrons.

After implantation the neutral helium starts to diffuse through the lattice. Most helium diffuses out through the crystal surface (or through grain boundaries); the remaining part of the helium will be trapped in defects. After a known amount of helium is implanted ('decoration'), the sample temperature is raised linearly with respect to time. At certain characteristic temperatures the trapped helium atoms will dissociate from the defects. They will diffuse through the material and will be released through the surface, where it can be measured as a pressure rise. This release process may be interrupted by retrapping. Measurement of the helium desorption rate as a function of the temperature results in well-defined desorption peaks at different temperatures which correspond to release from the different defects present in the sample [2]. This is illustrated in figure 10. Different trap types can be assigned to potential energy wells with different depths. The deeper the well, the stronger the helium is bound to that trap. An example of a desorption spectrum is given in figure 11. The shape of a desorption peak, characterised by its width and symmetry, gives information about the release mechanism of the helium and - under certain conditions - about the depth distributions of defects and trapped helium atoms. The area of the desorption peak gives information about the concentration of a particular trap associated with the desorption peak.





Figure 10: Potential energy diagram of one helium atom trapped in a film at a vacancy V and at an interstitial position I. Within this picture E^{υ} stands for the dissociation energy, E^{\flat} the binding energy, E^{\uparrow} the formation energy, and E^{M} for the migration energy. [27]

Figure 11: Example of a helium desorption spectrum. The heating rate is 40 K/s.

The principles of THDS have been described by Van Gorkum and Kornelsen [28] and by Van Veen *et al.* [29].

2.3.2. Defect production with energetic ions

Before the technique of helium desorption spectrometry can be applied its use has to be justified. This means that the helium has to be implanted below the threshold energy E_{th} for damage production.

In an ion source, gas atoms are ionised and accelerated in the direction of the sample. When the energetic ions (in the range of a few hundreds of eV) penetrate through the surface layer, they are stopped by collisions with sample atoms (nuclear stopping) and eventually their energies will be thermal. The time involved in this process is in the range of picoseconds. A sample atom will be detached from its lattice position when the energy transferred during the collision is larger than the threshold energy E_{th} . In that case a Frenkel-pair is formed. The threshold implantation energy E_{th} follows from the classical head-on-head two-particle collision description where the energy needed for damage production is given by

$$E_{th} = E_d \frac{\left(m+M\right)^2}{4mM},\tag{3}$$

in which *m* denotes the ion mass, *M* the target mass, and E_d the displacement energy of the molybdenum atoms in the sample. For molybdenum the average displacement energy in the bulk is 30.5 eV [30] (in [30] it is argued that at 300 K this value is to be preferred over the usually cited value 35 eV) and the average displacement energy at the surface is about half of the bulk value [19]. When put into formula 3 this gives for helium colliding with molybdenum a threshold energy for the bulk of 200 eV and a threshold energy for the surface of 100 eV.

Implantation of helium in molybdenum is in this work normally carried out at an energy of 100 eV. With such energies it is confirmed in [21, 31] that the probe atoms do not create vacancies in the bulk but in head-on collisions may create vacancies at the surface.

2.3.3. Basis equations describing a THDS experiment

This section presents a brief theoretical description of a TDS experiment. A more general review is given by Hoondert [32].

The basic equations for diffusion, trapping, and release of inert gas atoms from a metal lattice were first formulated by McNabb and Foster [33]. TDS experiments are performed with an ion-beam diameter $(10^{-3}-10^{-2} \text{ m})$ which is much larger than the ion implantation depth range $(10^{-10}-10^{-8} \text{ m})$. For film thicknesses up to 50 Å this means that just one dimension has to be considered. A second dimension has to be considered for thicker layers because in these layers the grain boundaries become important. This second dimension will be neglected any further. Assuming that the ion-implanted particles diffuse interstitially through the target sample, the key equations for the case of one type of non-saturable traps are, expressed in a continuum form [32],

$$\frac{\partial n_{\text{int}}(x,t)}{\partial t} = D_{\text{int}}(t)\frac{\partial^2 n_{\text{int}}(x,t)}{\partial x^2} - v_{\text{int}}(t)c_{tr}(x,t)n_{\text{int}}(x,t) + v_{tr}(x,t)n_{tr}(x,t) + S(x,t)$$
(4)

$$\frac{\partial n_{tr}(x,t)}{\partial t} = v_{\text{int}}(t)c_{tr}(x,t)n_{\text{int}}(x,t) - v_{tr}(x,t)n_{tr}(x,t), \qquad (5)$$

with *x* the depth perpendicular to the surface, *t* the time, n_{int} the interstitial particle concentration, n_{tr} the trapped particle concentration, c_{tr} the trap concentration, S(x,t) the implantation profile after thermalization, i.e. the concentration of thermalized particles arriving at depth *x* per unit time, and D_{int} the interstitial diffusion coefficient given by

$$D_{\rm int} = \frac{\lambda_{\rm int}^2 v_{\rm int}}{6} \,, \tag{6}$$

where λ_{int} is the interstitial jump length, and

$$v_{\rm int} = v_0 \exp\left(-\frac{Q_{\rm int}}{k_B T(t)}\right),\tag{7}$$

$$v_{tr} = v_0 \exp\left(-\frac{Q_{tr}}{k_B T(t)}\right) \tag{8}$$

are the frequency factors for interstitial jumps and jumps out of a trap, respectively. Q is the activation energy for these jumps, v_0 a frequency factor (which may be different for the two cases indicated), k_B the Boltzmann constant, and T the temperature.

The terms on the right hand side of equation 4 have the following meaning. The first one is the diffusion term, containing the spatial curvature of the concentration profile of particles moving on the interstitial sites of the lattice; the second, a sink term, represents the trapping of these interstitial particles in the defects; the third, a source term, denotes the particles being released from a trap back into an interstitial position; and the last term describes the ion-beam implantation of particles. Equation 5 contains the same trapping and release terms as equation 4, but with opposite sign. Since equations 4 and 5 can only be solved analytically in a very limited number of cases, a numerical solution method is almost always applied.

Information on implantation profiles in a great number of materials can be calculated with the Monte Carlo program TRIM (TRansport of Ions in Matter) [34], although especially for low energies the results should be treated with caution. It is found that S(x,t) can be reasonably approximated by a truncated gaussian function,

$$S(x,t) = \frac{A(t)}{\Delta R_{\rho} \sqrt{2\pi}} \exp\left(-\frac{1}{2} \left(\frac{x - R_{\rho}}{\Delta R_{\rho}}\right)^{2}\right), \qquad (x>0)$$

$$S(x,t) = 0$$
, (x<0) (10)

with A(t), ΔR_p and R_p parameters that depend on the ion-target combination, the ion energy, and the ion flux Φ . The normalisation constant A(t) is given by
$$A(t) = \frac{2\eta\Phi(t)}{\rho_0 \left(1 + \operatorname{erf}\left(\frac{R_p}{\sqrt{2}\Delta R_p}\right)\right)},$$
(11)

where η is the entrance probability and ρ_0 the atomic number density in the target sample. R_p is called the projected range and ΔR_p the range straggling.

2.3.4. Helium implantation

It is very important to know exactly the number of helium atoms that are implanted into the layer. This number is important with respect to the defect concentration in the layer.

When helium ions approach the layer they lose their charge when they come close to the layer. The arriving helium ions are single charged and thus the necessary electrons can be counted as the number of arriving ions. However, the number of electrons is not equal to the number of helium atoms that penetrate into the layer. It has to be corrected for two phenomena. The first one is the creation of secondary electrons. This has been well described for helium on molybdenum by Hagstrum [35]. He finds that 27.4% of the arriving helium ions (100 eV) create a secondary electron. This number is almost constant with energy in the low energy regime of ion impact, as Hagstrum finds for 1000 eV a percentage of 26.4%. Thus, secondary electrons generate in about 27.4% of the cases a double count of the arriving helium ion. The second phenomenon that has to be accounted for is backscattering. Not all the arriving helium ions will enter the layer, but some will be scattered back into the vacuum. The backscattered helium atoms are nevertheless counted by picking up an electron, although they do not take part in the further process. The percentage of backscattered helium atoms can be estimated using the Monte Carlo computer program TRIM [34]. For 100 eV helium ions on a molybdenum sample TRIM finds a percentage of 45.9% for backscattering.

2.3.5. Desorption peaks

After implantation and trapping of the particles the sample can be heated, with a constant heating rate. At a certain temperature the kinetic energy of the particle is high enough to overcome the particle-trap dissociation energy Q_{tr} . At this point the particle becomes interstitial and starts its travel to the surface. An atom will be able to migrate when its energy is larger than the migration energy (see figure 10). Interstitial atoms often need less energy to migrate than atoms trapped in a defect. After the binding energy to the trap is overcome, the helium atom will diffuse through the material. It will either diffuse to the surface, or become trapped in another defect. This latter effect is called "retrapping". In situations where the distance between defects is comparable to or smaller than their distances to the surface, the retrapping effect must be accounted for. This is the case for high trap concentrations, or when a relatively thick layer is deposited on top of a base layer containing the helium. A model to solve this problem with use of diffusion-equation 4 is given by Buters [2] and Hoondert [32].

From TDS experiments usually three types of peaks are observed in desorption spectra for metals and metal-like systems:

- 1. First order desorption peaks
- 2. Diffusional desorption peaks
- Sequential dissociation processes such as vacancy release from a defect cluster resulting in a lower binding energy of the remaining trapped probe atom and subsequent very rapid release.

The first order desorption peak will occur at low defect concentrations because then the retrapping probability of the released helium can be neglected, and also when the interstitial diffusion is fast. For metals, the diffusion time for helium to the surface can be neglected because the energy of migration of the helium is small ($\approx 0.2 \text{ eV}$) [1]. For this case the desorption rate of the helium atoms dissociating from a trapped state *i* is given by a first order desorption equation [32],

$$\frac{dN_i}{dt} = -v_0 N_i \exp\left(-\frac{Q_{tr}}{k_B T(t)}\right),\tag{12}$$

where N_i denotes the concentration of atoms still trapped in the material. If the film is raised in temperature with a linear heating rate β then

$$T(t) = T_0 + \beta t , \qquad (13)$$

here T_0 is the starting temperature, which should be much lower than the dissociation temperature. For the temperature T_p at which the desorption peak has its maximum value one then obtains the equation

$$\ln\left(\frac{\beta}{k_B T_p^2}\right) = \ln\left(\frac{v_0}{Q_{tr}}\right) - Q_{tr} \frac{1}{k_B T_p}.$$
(14)

This equation should be solved numerically. However, by measuring T_p for different heating rates β and plotting $\ln\left(\frac{\beta}{k_B T_p^2}\right)$ versus $\frac{1}{k_B T_p}$ one can obtain values for Q_{tr}

and v_0 . In most cases equation 12 is directly fitted to peaks in the spectrum.

At higher defect concentrations a helium atom can be retrapped after release from its first defect. There are two kinds of retrapping. The first is the retrapping in a defect with a higher dissociation energy. This will result in another peak at a higher temperature. The second kind of retrapping can occur when the concentration of the kind of defect from which the helium atom dissociates is very high (order 10⁻³) in the direct surrounding of that defect. When this is the case the helium atom can retrap in a same kind of defect. In this case it will take longer before the helium reaches the surface. This results in a broader desorption peak at a slightly higher temperature. This self-retrapping effect is called "diffusional release".

Helium release from different traps occurs at different energies. Van Gorkum and Kornelsen [28] and Van Veen *et al.* [29] found that for all metals the release sequence is essentially the same.

Starting at very low energies helium will first become interstitially mobile within the metal lattice. For molybdenum the energy needed for this process is 0.2 eV, which means that helium is mobile in molybdenum at room temperature.

The next helium release is from defects close to the surface, where the binding energies are usually lower than in the bulk on account of lattice relaxations in the proximity of the surface. After that, the helium atoms are released from substitutional impurities. Subsequently helium is released from monovacancies, and at the highest temperatures helium is released from vacancy-clusters, which may be partly filled with impurity atoms.

The reactions that go with these release mechanisms are usually indicated as (V denotes a vacancy)

- Monovacancies: $HeV \rightarrow He + V$
- Vacancy clusters: $HeV_n \rightarrow He + V_n$
- Impurities: $HeArV \rightarrow He + ArV$

Due to UHV conditions of 10⁻¹¹ mbar in our experiments argon is the only impurity in the layer, and is incorporated during IBAD. All these reactions can be extended to more and more complex reactions when taking in consideration that traps can be multiple filled with helium atoms, which will be released one by one or all at once. The consequences of this on the spectra and the various peaks are described by the 'filling theory' which is described by Buters [2] and Van Veen *et al.* [29].

From the trapping probability of a helium atom, which is an experimentally accessible quantity, the concentration of defects in the layer can be calculated, assuming one knows the depth distribution of the defects. For a rough estimate of that concentration figure 12 can be used. Figure 12 shows the trapping probability as a function of the trap concentration for films with several thicknesses. The lines are calculated on the basis of equations 4 and 5 with the computer code HOP (Hopping Of Particles) [32]. Within HOP one defines an implantation profile of the helium atoms, one or more trap concentration profiles, and a layer thickness. Figure 12 is calculated for a uniform trap concentration through the specified layer, and a zero concentration in the substrate. To compute desorption peaks, different kinds of traps are given different dissociation energies and the temperature is made to increase with time; in this way also retrapping can be simulated.



Figure 12: The helium (100 eV) trapping probability as a function of the concentration of defects in a molybdenum film. The lines are calculated lines by HOP for various layer thicknesses.

Figure 12 can in principle be used for the total trap concentration in the layer. For a single defect it gives just a rough estimation for the concentration because of retrapping. Figure 12 can also only be used for defects that are present in the layer before helium decoration. Defects that are created by the incoming helium ions must be excluded.

2.4. Thermal desorption of inert gases from a metal

Argon and other rare gases are believed to be released from the bulk of a metal by what Van Veen *et al.* [1] calls the "vacancy mechanism". In this light it is important to note that for all metals vacancy-assisted self-diffusion becomes an important transport mechanism at a relative temperature of $T/T_m = 0.5$ (for molybdenum this means a temperature of 1450 K). When diffusion in solids by a vacancy mechanism is discussed, one talk about jump rates of the vacancy and the activation energy for vacancy migration.





Interstitial diffusion $D_{int} = \frac{1}{6} v_{int} \lambda_{int}^2$



$$D_{vac} = \frac{1}{6} v_{vac} \lambda_{vac}^2$$





Self-diffusion $D_{Mo} = \frac{\gamma_6}{f} c_{vac} v_{vac} \lambda_{vac}^2$

Argon-diffusion $D_{Ar} = \frac{1}{6} f c_{vac} v_{Ar} \lambda_{vac}^{2}$

Figure 13: Different important diffusion mechanisms.

Within figure 13 *D* is the diffusion coefficient, v is the jump frequency, λ is the jump length which will be almost the same in every equation, c_{vac} is the vacancy concentration as molybdenum needs a vacancy the diffuse, and *f* is a geometrical constant with a value of about 0.75. When argon-diffusion is the same as Mo-self-diffusion the argon jump frequency has to be equal to the vacancy jump frequency ($v_{Ar} = v_{vac}$).

An important effect of release of a rare gas due to this vacancy-mechanism is a bigger displacement of the desorption peak temperature when the rare gas is trapped deeper under the surface. This is because the diffusion coefficient is low. Contrary to helium, argon is not released from its trap. The helium is released from the trap and will diffuse through the layer interstitially. When the helium is not retrapped, this is a fast process and will give first-order desorption peaks. Argon is not released from its trap, but will jump to another vacancy. This is a slow mechanism, because the jumps have to be made until the surface is reached and a vacancy is needed for every jump. When the argon is trapped deeper in the layer, more steps are needed and the peak will shift towards higher temperatures.

Although HOP can solve this problem numerically, an estimate of the variation of peak temperature with penetration depth can be obtained from a modification of the first-order desorption equation 14

$$\frac{dn_{tr}(t)}{dt} = -n_{tr}(t)v_0 \exp\left(-\frac{Q_{tr}}{k_B T(t)}\right).$$
(15)

For an atom executing a random-walk, as in isotropic diffusion, equation 15 describes the atomic "stepping" rate dN_{step}/dt rather than the desorption rate. If the atoms make on the average N_{des} steps before desorption, then the desorption rate would be

$$\frac{dn_{tr}(t)}{dt} = \left(\frac{1}{N_{des}}\right) \left(\frac{dN_{step}(t)}{dt}\right) = -\left(\frac{n_{tr}(t)v_0}{N_{des}}\right) \exp\left[-\frac{Q_{dif}}{k_B T(t)}\right],$$
(16)

where Q_{dif} is now the activation energy of diffusion given by

$$Q_{dif} = Q_{vac.migration} + Q_{vac.formation}.$$
 (17)

Random-walk theory suggests that $N_{des} \approx N_{surf}^2$ for an atom at a linear distance of N_{surf} steps from a surface. Thus the solutions [32] to the desorption equation 16 are applicable with v_0/β replaced by $v_0/\beta N_{surf}^2$. An identical conclusion has been drawn by Erendts and Carter [36] on the basis of the diffusion equations.

An example of a shifting peak can be seen in figure 14. This figure shows peaks calculated with HOP. In these calculations a vast amount of argon is put at a depth indicated at the right-hand side of the figure. The argon is released by what Van Veen *et al.* [1] calls the "vacancy-mechanism". As can be clearly seen, the peak appears at higher temperatures when the argon is placed deeper in the layer. More on this will be said in chapter 4.



Figure 14: HOP calculations showing a peak shifting to higher temperature when the argon is placed deeper in the layer.

A last thing that should be kept in mind is that the argon release may pertain to a quite different trapping configuration than that in which the ion came to rest at the bombardment temperature, since intermediate stages of annealing may occur as the solid is heated. This can be illustrated in the following way. When the argon is shot into the layer, it may come to rest in a large cluster of vacancies. During heating of the sample the cluster may be reduced in size dramatically, such that it looks as if the argon is released from a monovacancy.

3.1. Experimental overview



Figure 15: Schematic picture of the experimental set-up showing the sample positions during (1) layer deposition, (2) defect decoration with helium, and (3) thermal desorption spectrometry. See text for further information.

The experimental set-up is shown schematically in figure 15. It consists of a vacuum vessel with a base pressure of 10^{-10} mbar. The total experiment consists of three stages each performed with the sample at a different location in the apparatus: (1) the position where the molybdenum film is deposited, (2) the position where the helium is implanted into the film, and (3) the position where the helium desorbs from the heated sample. During the first stage of the experiment a Mo film is deposited on a polished, annealed Mo substrate, using a 3.2 kW electron beam evaporator (15° off-normal incidence), with the possibility of using a 3 cm Kaufman (Ar⁺) ion

source, equipped with a 1 cm exit grid, for ion beam assistance. An electron gun (e) can be used to deposit layers at elevated sample temperature. A quartz crystal oscillator (Q) is used for monitoring the deposition rate. A Faraday-cup (F) is used for current calibration. In the second stage a mass-filtered He⁺ ion beam (20° off-normal incidence) is used to decorate the defects. The ion energy is usually chosen as 100 eV, which leads to a mean thermal implantation depth of about 20 Å below the surface. Helium fluences (Φ) have been varied between 10¹³ and 10¹⁶ cm⁻². During the third stage the sample temperature (T) is increased linearly with time at a rate of 40 K/s up to 2000 K by heating the sample from the back side using a 2.5 kV electron beam (250 W). The sample temperature is measured with a WRe26%-WRe5% thermocouple. During the temperature ramp the He and Ar desorption rates are monitored as a function of the sample temperature, using a quadrupole mass spectrometer (QMS). The data obtained from the QMS form the essential result of an experimental run. Such a 'thermal desorption spectrum' is a collection of peaks, each signifying the dissociation of He or Ar at a particular energy, i.e. the dissociation of He or Ar from a particular type of defect in the material.

Having discussed the principles of the electron beam evaporator in section 2.1, we will next discuss the Kaufman ion gun used for IBAD and the ion gun used for TDS. The principle of a Kaufman source is shown in figure 16. This figure shows a gas inlet where the inert gas is led into the ionisation chamber. The incoming argon is ionised by a filament (cathode) following the reaction $Ar + e^- \rightarrow Ar^+ + 2e^-$. The ions that diffuse to the first grid are extracted from the plasma and accelerated to the second grid by a potential difference between the two grids. Outside the ionisation chamber an ion beam is formed (figure 17). The inert gas ions in the beam have a positive charge and will repel each other, and consequently the ion beam will diverge. The divergence of the beam is about 8 degrees. This value will be somewhat higher for higher beam currents and for less energetic ions. The Kaufman gun needs a relative high gas pressure to operate, which results in a pressure of at least $3 \cdot 10^{-5}$ mbar in the vacuum chamber. The Kaufman gun can produce an ion energy of 25 eV to 1.5 keV and a beam current of 0.6 mA to 2 mA [37]. With the Kaufman gun a variety of gases can be used like argon, helium, krypton, neon, etc.

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Figure 16: Kaufman ion source. Argon ions are created in the ionisation chamber and given the wanted energy with the two grids.

Figure 17: Kaufman ion beam with a divergence of 8 degrees. In this figure also the sample and Faraday cup for current measurement can be seen. The sample diameter is 9 mm.

The most important parts of the TDS equipment are: the ion source, an electron gun directed at the back of the sample, and a quadrupole mass spectrometer. Here only a short description of the ion source is given, while the other are more self-evident.



Figure 18: Helium ion source with: 1. cathode, 2. ionisation chamber, 3. Pierce extractor, 4. first Einzel lens, 5. Wien filter, 6. second Einzel lens, 7. deflection plates.

The ion source is schematically shown in figure 18. The inert gas (helium) in the ionisation chamber is bombarded by electrons from the cathode and a plasma is formed. A magnetic field is present in the ionisation chamber in order to elongate the paths of the electrons. The ions are pulled out of the chamber by a negative Pierce extractor, after which the ions are carried through an electric field and accelerated to a Wien filter. In this Wien filter an electric and a magnetic field are applied in such way that the forces on the ions from both fields cancel each other for a specific relation between ion mass and ion charge. All ions that do not satisfy this relation are deflected out of the beam. Finally the beam is deflected twenty degrees by two sets of deflection plates to remove the neutral particles from the ion beam. The ion source works with a gas pressure of $3 \cdot 10^{-8}$ mbar. The ion energy can be chosen between a few eV up to 3 keV.

3.2. Experimental details

As is shown in figure 15 the TDS parts and the IBAD parts of the apparatus are placed in the vacuum chamber which is connected to a pump system in order tot pump the whole apparatus down to UHV conditions. The preparation of well-defined surfaces with negligible contamination requires ambient pressures below 10^{-10} mbar. These low pressures are also needed for TDS. A combination of different pumps is necessary in order to obtain background pressures in the order of 10^{-10} mbar, since each pump can only operate over a limited pressure range. To achieve this kind of pressure, use is made of two turbo pumps, one oil diffusion pump especially for high helium pumping speeds, and two rotary pumps as backing up pumps for the turbo pumps. With this combination of pumps the desorption chamber is pumped at such a rate that the average residence time τ_{He} for helium in the chamber is 0.28 s and the average residence time τ_{Ar} for argon 0.71 s.

An important step in achieving UHV conditions in the main vacuum chamber is the bake-out process. After baking, a base pressure of less than 10^{-10} mbar $(10^{-8}$ Pa) is reached. At this base pressure it takes at least 1 hour [23] for a monolayer of gas atoms to cover the specimen surface. Thus it is ensured that during a desorption experiment and during film growth the surface is nearly free of any undesired and unknown contamination. In the current apparatus, the pressure decreases after performing experiments for some days to $\approx 10^{-11}$ mbar. This effect appears to be related to the continuous sequence of evaporation and noble gas flushing.

The molybdenum films are deposited on a molybdenum sample with a diameter of 9 mm. The ion source power supply and the evaporator power supply are automatically adjusted in order to maintain a stable Ion-to-atom Arrival Ratio (IAR). For details of the two feedback mechanisms, see Van der Kuur [21]. The deposition rate of the molybdenum layers can be controlled from 0.5 Å/s to 4 Å/s and the IAR from 0.04 to 0.6.

For a nice and steady beam from the Kaufman ion source, the assisting argon ions are given an energy of 250 eV. This energy is too high for IBAD to produce defect free layers, as we have seen in section 2.2. To decrease the energy of the arriving argon ions a positive bias voltage is applied to the sample to decelerate the ions to the desired energy.

This technique has one big disadvantage. The Kaufman ion source needs a high argon pressure in the source to operate. For the vacuum chamber this comes down to a pressure of $3 \cdot 10^{-5}$ mbar. On their way to the sample the energetic argon ions 'collide' with the argon atoms present in the vacuum chamber. During the 'collisions' an electron can be transferred from the argon ion to the thermal argon atom according to the reaction: $Ar^+ + Ar \rightarrow Ar + Ar^+$. During this the energy of the particles is not changed. Many such 'collisions' occur at relative high pressure and thus many energetic neutral argon atoms are produced. The result is that these collide with the growing molybdenum layer as they are not decelerated by the applied electric field. This means that part of the arriving argon particles still has the energy with which they left the Kaufman ion source. For understanding the influence of the less energetic arriving argon ions it is important to know the amount of neutrals that are created.

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The amount of energetic neutrals in the beam can be found by plotting the measured ion current against the pressure. Graphs of such measurements are shown in figure 19 and 20. In figure 19 the current is measured with the Faraday cup and in figure 20 the current is measured on the sample. The current measured on the Faraday Cup is less because the area for measurements of the Faraday cup is less than the area of the sample. Also is the Faraday cup positioned out of the main beam as can be seen in figure 17. From a certain pressure the Kaufman source will start to operate. At first when the pressure increases more particles become charged and the current will rise until some saturation value. The fact that the current reaches its maximum at different pressures is again due to different places in the beam. The pressure is corrected for argon as the pressure gauge is calibrated for nitrogen and is measured in the vacuum chamber (and not in the Kaufman source). Higher pressure means a greater number of collisions and charge exchange reactions and therefore more neutrals and fewer ions, so the current will decrease. The probability of reaching the target at a distance ℓ without undergoing charge exchange is $\exp(-\ell/\lambda)$ with λ the mean free path. Hence,

$$I(p) = I(0) \exp\left(-\frac{\ell}{\lambda(p)}\right).$$
(18)

Using equation 1,

$$\lambda(p) = \frac{k_B T}{\sqrt{2}p\sigma_{ce}},\tag{19}$$

where σ_{ce} is the cross section for charge exchange collisions equal to πd^2 , one obtains

$$I(p) = I(0) \exp\left(-\frac{p}{p_{ce}}\right)$$
(20)

with

$$p_{ce} = \frac{k_B T}{\sqrt{2}\ell\sigma_{ce}}.$$
(21)

Table 2: The values for l(0) and p_{ce} obtained from the fits of figure 19 and 20 for the Faraday cup and the sample. From this the fraction of neutrals are calculated at a working pressure of $4 \cdot 10^{-5}$ mbar and also the value for the distance and for the cross section for charge exchange is calculated using equation 21. The values for the cross section for charge exchange are in both cases a factor two higher than values obtained by Kaufman and Robinson [37, 38], who found a value of 25.5 Å² for 250 eV argon ions. This factor is not yet understood.

	Faraday cup	sample
/(0)	136 nA	14.3 μA
p _{ce}	2.72 10 ⁻⁴ mbar	1.97·10 ⁻⁴ mbar
fraction neutrals	14%	18%
l	0.21 cm	0.23 cm
σ _{ce}	50.3 Å ²	64.6 Å ²

The results of a fit of an exponential function through the drawn points in figure 19 and 20 are given in table 2. From this the fraction neutrals in the beam is $\frac{I(0) - I(p)}{I(0)}$

for a given working pressure. This equation might be used because one does not expect any neutrals at very low pressure. The difference in the results for the number of neutrals found with the Faraday cup and the sample is due to measuring at two different places in the beam. Firstly the Faraday cup is situated out of the centre of the beam. Secondly the Faraday cup is closer to the ion source resulting in less collisions and less neutrals created. These two reasons make the number of neutrals in the beam calculated from the sample more reliable. This gives a number of 18% of neutrals in the beam at a pressure of $4 \cdot 10^{-5}$ mbar. More on the number of arriving argon ions will be said in the next section.



Figure 19: Measured current I_{FC} in the Faraday cup against the argon pressure *p*.



Figure 20: Measured current l_s on the sample against the argon pressure *p*.

From our experiments it can be seen that the trapped argon atoms originate from fast argon atoms and not from the less energetic argon ions, this is shown in figure 21. Although spectra will be discussed in more detail in chapter 4, at this point a series of spectra should be used to illustrate the effects of neutrals. The spectrum at the bottom of figure 21 shows a helium spectrum for a 200 Å deposited layer without ion beam assistance. Just above that spectrum a spectrum is shown of a 200 Å layer with ion beam assistance with the sample on a positive bias voltage of 260 V. In this way ions cannot reach the sample. This shows the effect of the energetic neutrals. From the bottom to the top the ions are slowed down increasingly less and thus arrive at the sample with higher energy. The first significant difference can be seen at an ion energy of 100 eV. Therefore at lower energies the ions do not influence the number of defects and the defects are therefore created by the energetic neutrals.



Figure 21: Helium desorption flux for various argon ion energies E_{IBAD} on the sample. This is the energy the ions have after deceleration. The energy, in eV, is indicated at the right-hand side. Within the beam a vast amount of neutrals is present with an energy of 250 eV.

Just as in the case of argon, when decorating the sample with helium, it is very important to know the number of ions that have been implanted in the sample. The number of arriving helium ions is recorded by measuring the current on the sample. Charge exchange transitions take place between the incident ion and surface atoms at ion-atom separations of several Ångströms by electron tunnelling. This will happen to 99.8% [39] of the arriving helium ions. A side effect of this tunneling is the creation of secondary electrons. The secondary electrons are counted in the measured current and thus we have to correct for this effect. In our case 100 eV helium ions that are counted but do not enter the layer are backscattered helium ions. The Monte Carlo computer code TRIM [34] gives an estimate for the number of backscattered helium atoms. The result is that 46% of the arriving helium ions of 100 eV are backscattered.

For knowing the right amount of implanted helium atoms, we have to correct for the secondary electrons and for backscattering helium atoms. Mostly our layers are decorated with 100 eV helium at an amount of $2 \cdot 10^{14}$ helium atoms per cm². After correction for secondary electrons this leaves $1.6 \cdot 10^{14}$ helium atoms per cm². And finally correcting for backscattering gives a decoration dose of $8.5 \cdot 10^{13}$ helium atoms per cm², giving a correction factor of 0.43. The amount of implanted helium atoms is important for calculating the defect concentration in the layer.

In previous work [9] it was found that the mean penetration depth of 100 eV helium in molybdenum is 19 Å. After losing all of its energy the helium atom will start to move through the molybdenum interstitially. Doing so the 100 eV helium atoms give information about the top 50 Å of a molybdenum layer, depending on the trap concentration, which can be found by HOP.

When the desired helium dose is implanted and the helium pressure is decreased to the standard background level, the sample is heated with a constant heating rate by an electron gun facing the back of the sample. The temperature of the sample is measured by a WRe26%-WRe5% thermocouple, and controlled by a feedback loop with a pre-calculated filament current table and the temperature error as input signals. During heating the sample is biased at +2500 V.

Immediately after each desorption experiment, the detection efficiency of the quadrupole system is measured. This is done by injecting a known amount of gas into the desorption chamber and comparing this value with the total counts given by the quadrupole mass spectrometer. A typical detection efficiency of 1 pulse per $6 \cdot 10^6$ released helium atoms and 1 pulse per $4 \cdot 10^6$ argon atoms is obtained. The TDS signal intensities are corrected for the different *m*/*e* detection efficiencies and the residence times for each desorbing species.

After the heating scan, up to $T = 2000 \text{ K} (\approx 0.7 T_m)$, the sample undergoes free cooling to room temperature. During heating the film undergoes considerable grain growth. It was periodically confirmed that the deposited layer becomes free of point defects after the heating run, and thus that the accumulating stack of layers kept functioning as a reproducible sample.

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3.3. Error estimation

3.3.1. Systematic errors

During ion beam assisted deposition the energetic argon species will sputter the growing molybdenum film. Removal of deposited film atoms by sputtering reduces the growth rate of the film and so the film thickness will be less then the measured thickness. The sputtering rate of the arriving argon can be estimated with TRIM [34] and the results are shown in table 3. The layer thicknesses presented in this thesis are not corrected for this factor.

Table 3: The sputtering yield Y_{sp} as calculated by TRIM and reported by Ohring [11] and Smith [40] as a function of the energy of the arriving argon ions E_{IBAD} for a sample temperature of 300 K.

E _{IBAD} (eV)	Y _{sp} (atoms/ion)		
	TRIM	Ohring	Smith
100	0.28		
200	0.50		
250	0.58		
500	0.94	0.80	0.55
1000	1.40	1.13	0.95

The layer thickness we found has been checked a few times by Transmission Electron Spectroscopy (TEM). This was done for relative thick layers (>1000 Å) compared with layers we normally use in our experiment. The layer thickness found with TEM turned out to be 30% thicker than the layer thickness we measured with our quartz crystal oscillator. This is for 5% due to distance differences to the source. The rest can possibly come from screening in the melt as during deposition a groove is made in the molybdenum chunk in the evaporator. Another mismatch that can occur is due to possible differences between the deposited layer on the substrate and on the crystal. The layer thicknesses presented in this thesis are not corrected for this factor because the error may be dependent on film thickness. Recent calculations [41] have shown that no significant temperature gradients exist in the sample area where the helium is implanted. The helium is implanted in the centre of the molybdenum surface with a diameter of 4 mm. However, between the centre and the point on the sample where the temperature is measured there is a maximum temperature difference of 10 K depending on the sample temperature. This will give a small peak shift to lower temperatures. A larger peak shift is generated by the high bias voltage on the thermocouple together with the sample. This causes the thermocouple to attract electrons. The electrons give rise to an extra voltage on top of the thermo voltage, which causes to a peak shift of maximum 45 K to higher temperatures, also depending on the sample temperature. The temperatures presented in this thesis are not corrected for these two factors.

The systematic error in the thermocouple response is estimated to be less than 1% according to the manufacturer's specifications.

The Ar⁺ current we measure during ion beam assisted deposition is measured with a Faraday cup placed out of the centre of the beam (see figure 17). In order to calculate the ion-to-atom arrival ratio, the measured current on the Faraday cup has to be converted to the number of arriving argon ions on the sample. This is not a straightforward process. Since direct current measurements on the sample are affected by secondary electrons. A second, movable, Faraday cup was mounted at the place of the sample to perform measurements on current differences. The results of these measurements are shown in figure 22 as a function of a voltage applied on the movable Faraday cup in order to simulate the effect of a sample put on a voltage. As can be seen the current measured in the movable Faraday cup is highly influenced by the voltage applied to it, as the current measured in the fixed Faraday cup is not. The variation of the measured current in the movable Faraday cup is not yet completely understood. When the voltage on the Faraday cup is raised the effective diameter of the hole in the Faraday cup will be reduced. From measurements it was also found that electrons emitted by the pressure gauge had some effect on the beam. From the data of figure 22 a so-called tooling factor in order to convert the current measured on the fixed Faraday cup to the current measured on the movable Faraday cup can be calculated. The results for three different ion beam currents I_p and no voltage applied on the Faraday cup are shown in table 4. As can be seen, the factor with which the current on the fixed Faraday cup must be multiplied is about 1.6. Calculations on electric field lines [41] showed that the applied voltage has only effect near the edge of the sample, and so it is justified

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to use a tooling factor of 1.6 over the whole range up to a voltage of 250 V. At 250 V no ion can reach the sample and the current has to be zero. That the measured current on the movable Faraday cup is not zero at 250 V is due to the hole in the Faraday cup. All results are corrected by this tooling factor.



Figure 22: Measured currents in the fixed and movable Faraday cup as a function of the voltage applied on the movable Faraday cup for three different ion beam currents I_p . The fixed Faraday cup is the one used during IBAD; the movable Faraday cup is used here to simulate the sample. The beam voltage is 250 V.

Table 4: Tooling factor for different ion beam currents l_p for IBAD. The values are obtained from figure 22 when no voltage is applied to the Faraday cup ($V_s = 0$ V). The tooling factor is the ratio of the current density measured on the movable Faraday cup and the current density measured on the fixed Faraday cup.

<i>I</i> _p (mA)	I _{FC,fixed} (nA)	I _{FC, movable} (nA)	Tooling factor
0.6	62	122	1.6
1.0	67	132	1.6
2.0	74	139	1.5



Figure 23: Schematically presentation of the molybdenum beam and the argon beam with respect to the position of the aperture and the sample.

Another problem with IBAD is a phenomenon we call "parallax" (figure 24b). In front of the sample an aperture is located. Because the beams are coming from two different directions the grown layer and the ion beam do not overlap completely (figures 23 and 15). The parallax has the effect that 20% (figure 24) of the argon does not incident on our growing layer, but aside of it. Hence, in each IBAD experiment 20% of the argon dose is implanted in the sample where no film growth takes place. This argon fraction does not give any information on the film in the desorption spectrum.



Figure 24a: Position of the argon flux with respect to the position of the evaporated molybdenum due to the aperture. Figure 24b: Real situation of an EVAP layer deposited on top of a sample on which argon is colliding.

The effect of parallax has a great influence on the argon spectra of layers with a thickness up to 10 Å. For thicker layers this effect becomes less important as will be shown in the next chapter. For helium the effect does not arise, because the helium is implanted in the centre of the sample, with a diameter of 4 mm, which is small enough as is shown in figure 24b.

3.3.2. Random errors

The sensitivity of the mass spectrometer for helium and argon is measured by letting a known amount of each gas into the vacuum chamber and comparing the number of atoms with the number of counts from the mass spectrometer. The relative accuracy of the measurement is within 20% as estimated from repeated experiments.

In addition to the systematic errors in the temperature measurements there is also a random error. The thermocouple voltage is not measured with respect to a fixed temperature but is measured with respect to the room temperature. This causes temperature shifts of up to 10 K between measurements done in summer and those done in winter.

Beside the parallax that is created by the position of the evaporator with respect to the ion source, there is also some parallax as a result of small random variations in the position of the sample during film growth. The reproducibility of the position is not better than 1 mm. This causes some variations in the percentage of argon that is not buried by the growing layer.



4. Results & Discussion

4.1. Experimental details

In this section a short review is given of the various process parameters used in the experiments (table 5). Some of them are kept constant while others are changed over a certain range. Differences with the values given in this section are noted at the place where the experiment is discussed.

Experimental parameter	Fixed	Variable
Substrate type	poly crystalline molybdenum	
Deposition material	Мо	
Evaporation rate	1 Å/s	
Film thickness		0 - 500 Å
Deposition temperature	300 K	
Type of assisting ions	Ar ⁺	
Ar ⁺ energy		5 - 250 eV
Argon pressure during IBAD		3·10 ⁻⁵ - 6·10 ⁻⁵ mbar
Ar ⁺ /Mo ratio	0.16	0.006 - 1.0
annealing time	30 s	
Type of decoration atom	Не	
He decoration fluence		4.10 ¹³ - 2.10 ¹⁴ cm ⁻²
He⁺ energy	100 eV	
Heating rate	40 K/s	
Final temperature	2000 K	

Table 5: Experimental parameters.

In this chapter many results will be presented as desorption spectra plotted above each other.

- Each spectrum consists of a plot of the desorption flux on a linear scale against the crystal temperature in degrees Kelvin.
- All helium spectra are corrected for background by subtracting the reference signal from the helium signal.

- All spectra have been smoothed and deconvoluted for residence time delay by 4th order Savitzky-Golay smoothing and differentiation over a number of data points which follows from $\frac{1}{2}\frac{3.5\tau}{t_s}$, in which τ is the residence time and t_s is the sample time (25 ms).
- The number density for molybdenum is $6.4 \cdot 10^{14}$ molybdenum atoms per Å per cm². From this the argon fluence Φ_{Ar} per cm² built into the layer can be calculated as follows:

$$\Phi_{Ar} = 6.4 \cdot 10^{14} \gamma \, d \,, \tag{22}$$

with *d* the layer thickness in Å and γ the ion-to-atom arrival ratio.

- The IAR and the argon fluence Φ_{Ar} are not corrected for secondary electrons and backscattering.
- The normalised desorption flux χ is defined as the desorption flux L divided by the heating rate β and the corrected decoration fluence Φ_c;

$$\chi = \frac{L}{\beta \Phi_c} \,. \tag{23}$$

The area under the helium desorption spectra is in this way a direct measure for the trapped helium fraction.

4.2. Molybdenum films deposited with ion beam assistance as seen from the helium view point

In section 4.2.1 helium desorption spectra will be presented from which the differences between EVAP films and IBAD films can be seen. Helium desorption spectra give information about the defects and the defect concentration in a deposited layer. In section 4.2.2 the influence of the different IBAD parameters will be discussed. These sections are just a summary of the most important results. A more detailed description of the influence of argon ion assistance is presented by Pols [31] and Van der Kuur [21]. An overview of the different peaks that can be seen in the helium desorption spectra is given in table 6.

Т (К)	Description	Reaction
RT.	Helium is interstitially mobile within the molybdenum	He*
	lattice	
450	Helium is released from surface defects	$HeV \rightarrow He^* + V (S)$
630	Helium is released from argon-vacancies	$HeArV \rightarrow ArV + He^*$ (A1)
770	Two (or more) heliums are released from argon-	$He_2ArV \rightarrow ArV + 2 He^* (A2)$
	vacancies	
850 -	Helium is released from multiple filled vacancies	$He_nV \rightarrow He_{n-1}V + He^* (E, F, G)$
1000		
980	Helium is released from multiple filled argon-divacancies	$He_2ArV_2 \rightarrow HeArV_2 + He^* (G')$
1180	Helium is released from argon-divacancies	
		$HeArV_2 \rightarrow ArV_2 + He^* (H')$
1200	Helium is released from monovacancies	$\text{HeV} \rightarrow \text{He}^* + \text{V}^*$ (H)
>1300	Helium is released from more complex vacancy clusters	

Table 6: Temperature of defect reactions involving helium observed in Mo [1]. The * stands for mobile. Peak notations are given in parenthesis.



4.2.1. Differences between IBAD and evaporated (EVAP) molybdenum layers



Conditions: EVAP, Decoration, $\Phi_c = 8.5 \cdot 10^{13} \text{ He}^+/\text{cm}^2$.

0.006 TTT d (Å) 300 0.005 200 100 0.004 He desorption flux χ (K⁻¹) 50 0.003 30 20 0.002 10 0.001 5 n 0 2000 2500 0 500 1000 1500 Temperature (K)

Figure 26: Helium desorption spectra for various layer thicknesses d, in Å, indicated at the righthand side. The meaning of S and H is explained in the text.

Conditions: IBAD, $E_{IBAD} = 250 \text{ eV}, \gamma = 0.045$, Decoration, $\Phi_c = 8.5 \cdot 10^{13} \text{ He}^+/\text{cm}^2$.

Layer thickness, creation of defects

Figures 25 and 26 show spectra of layers of various thicknesses, figure 25 for EVAP layers and figure 26 for IBAD layers. These measurements are done to gain insight on the evolution of the layer during the first few hundred Ångströms of the growth. For a more detailed explanation of the different peaks see Van der Kuur [21], Pols [31], and Korevaar *et al.* [10].

When one looks at figure 25 there are two peaks that have to be mentioned, they are labeled in the figures with S and H. The H peak is associated with helium that is released from a monovacancy, in the bulk, with only one helium atom in it. These monovacancies are created during film growth. The S peak comes from many defects with one thing in common; they are all present in the top of the layer. These defects are believed to be created by the 100 eV He^+ ion beam.

Comparison of figure 25 and 26 show no significant difference in the number of helium atoms associated with the S peak. After noticing that the S peak does not change in height when the two series are compared, it is immediately clear that the total number of other defects in the IBAD layers is much higher than the number of defects in the EVAP layers. Calculations of the defect concentration for the layers up to 50 Å (assuming unsaturable traps), using figure 12, give a total defect concentration of $2 \cdot 10^{-4}$ for EVAP layers and a defect concentration of $1 \cdot 10^{-3}$ for IBAD layers. Another difference that can be seen immediately is the arising of two sharp peaks in the IBAD layers, one at 630 K and one 770 K. Since the peaks cannot be seen in the EVAP layers the peaks have to be associated with defects that are caused by argon. The peak at 630 K will be called the A1 peak and the peak at 770 K the A2 peak. Van Veen *et al.* [29] and Buters [2] associated the peaks with a single (A1) and a multiple (A2) filled monovacancy in which also an argon atom is present.

Penetration depth, Different growth

Now that we have seen certain aspects of the influence of argon on a growing layer it is important to know in more detail the consequences of an argon impact. This can be obtained by bombarding the bare molybdenum substrate with argon particles of 250 eV. The spectrum from this experiment is presented in figure 27 (bottom spectrum). The grey spectra in figure 27 are the same spectra as can be seen in figure 25. When looking at the bottom spectra of figure 27 it becomes immediately clear that argon particles of 250 eV created a lot of damage in the molybdenum sample. Also from this spectrum it can be seen that the argon particles create damage in the top layers only. This can be seen by the fact that no H peak is visible, whereas the H peak represent vacancies in the bulk. Now it is possible to use the damaged molybdenum sample as base for growth of a molybdenum film. The layer thickness deposited (EVAP) on top of it is shown at the right-hand side of the spectra. First of all can be seen that after depositing two monolayers molybdenum (4 Å) the vacancies created by the argon impact become vacancies in the bulk (the H peak and the A1 and A2 peaks start to show). Another important thing that can be seen from the spectra becomes clear when looking at the spectra at the top, the 20 Å. When growing 20 Å on an annealed substrate only monovacancies (H) arise in the layer (grey curve). On the contrary when the base

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layer exists of molybdenum with damage created by energetic argon particles, also larger defects arise after depositing 20 Å on top of it. Thus a layer with more defects gives rise to a deposited layer with more defects. Some more on these spectra will be said in section 4.3.5.



Figure 27: Helium desorption spectra for various overlayer thicknesses *d*, in Å, indicated at the righthand side. The grey spectra are the same spectra as in figure 25. Conditions: Sputtering, $E_{\text{IBAD}} = 250 \text{ eV}$, $\Phi_{c,\text{Ar}} = 3.2 \cdot 10^{14} \text{ Ar}^{+}/\text{cm}^{2}$, EVAP, Decoration, $\Phi_c = 8.5 \cdot 10^{13} \text{ He}^{+}/\text{cm}^{2}$.

Annealing, migration temperatures for vacancies and vacancy clusters

More information on the defects present in the layer and the mechanisms belonging to the removal of the defects from the layer can be obtained by annealing the layers after deposition. Figure 28 shows the helium desorption spectra of 50 Å EVAP layers that are heated to the specified anneal temperature T_a after deposition. After the heating step, the sample cools down and helium is implanted. The same is done in the experiment shown in figure 29, but in this case 50 Å IBAD layers are used.





Conditions: EVAP, d = 50 Å, Anneal, Decoration, $\Phi_c = 8.5 \cdot 10^{13} \text{ He}^+/\text{cm}^2$.



Figure 29: Helium desorption spectra for various anneal temperatures T_a , in K, indicated at the right-hand side. Conditions: IBAD, d = 50 Å, $\gamma = 0.04$ (250 eV) +

0.16 (25 eV), Anneal, Decoration, $\Phi_c = 8.5 \cdot 10^{13} \text{ He}^+/\text{cm}^2$.

Figure 28 shows that an EVAP layer is free of defects after annealing the layer to 1300 K. For this temperature and higher temperatures, only defects near the surface, which are created by the incoming helium atoms, are visible. After annealing to 900 K the EVAP layer is free of monovacancies and the vacancy clusters are annealed out above 1200 K. When the different defects are decorated with argon, as can be seen in figure 29, a far higher anneal temperature is needed in order to make the layer free of defects. The vacancies are pinned by the argon in it, and all helium that is visible after annealing to 1300 K has to do something with argon decorated defects.

The fact that the A2 peak at first increases with increasing anneal temperature might be due to defect modifications at certain temperatures.

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Saturation, defects in the first few layers

The last effect of the argon beam that can be shown from the helium point of view, can be seen in figure 30. Here the ion beam is directed to the substrate without depositing a layer. The substrate is put on a bias voltage of 250 V. In this way only the neutrals can reach the substrate. The time the substrate is exposed to the beam is varied and is denoted by the beam time $t_{\rm b}$.





Figure 30: Helium desorption spectra for various argon ion beam times t_b , in seconds, indicated at the right-hand side.

Conditions: Sputtering, $E_{\text{IBAD}} = 250 \text{ eV}$, Decoration, $\Phi_c = 8.5 \cdot 10^{13} \text{ He}^+/\text{cm}^2$. Figure 31: Desorbed helium fluence as a function of the implanted argon fluence as follows from figure 30. The curve is a fitted exponential function to the data.

The bottom spectrum shows no exposure to the ion beam, with only helium decoration of the bare substrate. The peak that can be seen is the damage created by the 100 eV helium atoms and has to be subtracted from the other spectra. After doing this, it can be seen that the energetic neutral argon atoms create a lot of damage near the surface of the substrate (no H peak). A curious thing about this is that it seems that after a period of time the argon atoms do not create any more damage. This can be seen by comparing the spectrum of 30 seconds with that one of 300 seconds. In figure 31 the amount of desorbed helium is plotted as a function of the argon decoration fluence. This helium saturation value does not have to be

equal to the total number of created defects as some defects can be multiple filled with helium atoms. Using figure 12 one finds a saturation trap-concentration of $8 \cdot 10^{-3}$ assuming unsaturable traps and a thickness of 4 Å. Why a thickness of 4 Å has to be used will be explained in section 4.3.2.

4.2.2. The influence of the different parameters for IBAD



Figure 32: Helium desorption spectra for various ion beam energies E_{IBAD} , in eV, indicated at the righthand side. The IAR changes with ion energy.

Conditions: IBAD, d = 50 Å, Decoration, $\Phi_c = 2 \cdot 10^{14}$ He⁺/cm².

$E_{\rm IBAD}$

The influence of the argon ion energy is shown in figure 32. In this experiment a layer of 50 Å is deposited with various argon ion energies. As can be clearly seen, an A1 and A2 peak become visible after use of an energy of 100 eV. This means that argon is built into the layer using ion energies of 100 eV or higher. Also large vacancy clusters are formed using energies higher than 100 eV. When the ion

energy is increased the total fraction of trapped helium increases. This means that more defects are created when the ion energy is increased.

IAR

The other important parameter for IBAD is the ion-to-atom arrival ratio (IAR). The influence of this parameter is shown in figure 33 and 34. In figure 33 the influence of the IAR, in the low regime of this parameter, is shown on a 50 Å IBAD layer. The bottom spectrum shows the 50 Å EVAP layer. At very low IAR the influences of the ion beam are not significant. From an IAR of 0.01 the A1 and the A2 peak start to show. Figure 34 shows the results for much higher IAR on a 200 Å IBAD layer. Here it can be seen that there are not many changes up to an IAR of 0.2. Above this value a big ridge starts to develop between 500 K and 1100 K. This indicates that many point defects are present, as the ridge is formed by many overlapping peaks. Differences between the spectra of the two figures are mainly due to various layer thickness, various helium decoration fluences, and various argon ion energies.





Figure 33: Helium desorption spectra for various ion-to-atom arrival ratios γ , indicated at the right-hand side.

Conditions: IBAD, d = 50 Å, $E_{IBAD} = 100$ eV, Decoration, $\Phi_c = 2 \cdot 10^{14}$ He⁺/cm². Figure 34: Helium desorption spectra for various ion-to-atom arrival ratios γ , indicated at the right-hand side.

Conditions: IBAD, d = 200 Å, $E_{\text{IBAD}} = 250 \text{ eV} (18\%) + 25 \text{ eV} (82\%),$ Decoration, $\Phi_c = 4 \cdot 10^{13} \text{ He}^+/\text{cm}^2$.

4.2.3. Summary

- From the layer thickness variation it can be found that the net effect of energetic argon atoms is a production of defects instead of annihilation of defects. The defect concentration in a grown IBAD layer is about 1.10⁻³, which is about five times as high as in an EVAP layer. The A1 and A2 peak are only visible in IBAD layers and thus have to do something with argon associated defects.
- 2. From the use of different base layers for layer growth it can be found that the defect concentration in the film increases with increasing defect concentration in the base layer.
- 3. From the anneal experiment it can be seen that when argon atoms are present in the layer, the defects are present in the layer up to higher anneal temperatures.
- 4. Argon atoms create damage near the surface, but the amount of damage created is limited, as can be seen from the experiment with varying ion beam time.


4.3. Molybdenum films deposited with ion beam assistance as seen from the argon view point

4.3.1. Previous work done by other groups

Some work has been done on the explanation of argon desorption from a molybdenum sample in which argon was implanted. A possible explanation for the different peaks is given by Van Veen et al. [1]. Some other results of argon desorption spectra from molybdenum are shown by Naik et al. [44], but in that case the experiments and results were not very good and Naik et al. gave just a qualitative interpretation of the results. Kornelsen and Sinha published many results on several rare gases in different metals. they showed [6, 7, 8] that all rare gases (except helium) acted similar in the same kind of metal, so their results can also be used for comparison. Within all those experiments the rare gases are implanted into the bare substrate by high energetic bombardment of the bare substrate. Changing the energy of the ions will cause different implantation depths. When the energy is increased the penetration depth of the argon atoms will increase and it will take longer for the argon atom to reach the surface. The difference with the experiments discussed in this thesis is that in our experiments the argon is implanted while growing a molybdenum film. In this way the mean depth of the argon within the molybdenum film can be changed by varying the film thickness.

In the next parts of this section a review will be given of the results obtained by the mentioned groups.

Kornelsen and Sinha [6, 7, 8] reported on thermal release of inert gases from a <100> tungsten surface. For argon bombardment of tungsten they found five argon peaks below 1650 K and one above 1700 K. The first five argon peaks are associated with desorption via a single activated step from sites within, at most, 10 Å of the crystal surface. The single peak above 1700 K is thought to be the result of diffusion at constant activation energy of deeper penetrated ions.

For the five argon peaks (Kornelsen and Sinha call them α -peaks) under the 1650 K the following properties are found:

1. The peak positions are independent of the ion energy and of the direction of ion incidence.

- 2. The peak shapes are reasonably consistent with first-order desorption from sites of a single activation energy.
- 3. All the peaks can be observed at ion energies only twice the threshold value for entrapment.

It is concluded that most of the α -entrapment occurs in only four or five different kinds of sites. The differences might involve:

- interstitial and substitutional positions in the lattice,
- different distances from the site to the surface,
- different locations of a nearby lattice defect (e.g., a vacancy) relative to the site and the surface.

The resulting variations in lattice relaxation near the surface could give rise to the series of characteristic binding energies observed. If a lattice defect is involved it must interact with the particular trapped atom that produces it, since the peaks exhibit first-order behaviour. The appearance of all the α -peaks at ion energies so close to the threshold, and the independence of peak position on ion energy supports the conclusion that the sites must be very close to the crystal surface and must involve desorption via a single activation step. The fact that the different gasses give roughly similar peak patterns suggests that they occupy the same kinds of sites. The minor changes in the number of peaks and their positions would imply that there are some configurations which are stable for some ions but not for others, and that for a given site the lattice relaxation and therefore the binding energy varies somewhat with the particular ion trapped.

Kornelsen found several reasons to believe that the α -peaks have to originate from the first 10 Å:

- 1. After removing 10±2 Å of the tungsten substrate 99% of the argon had disappeared.
- 2. The first-order shape of the peaks.
- The appearance of all the α-peaks at ion energies so close to the threshold value for peak production.
- 4. The independence of peak position on ion energy.

The peak above 1700 K is called the β desorption peak. It has the following properties:

1. It is present only for ion energies \geq 400 eV. This means that the ions have enough energy to penetrate through the surface layers. (TRIM [34] predicts a R_p and a ΔR_p of 10 Å and 6 Å respectively for argon with an energy of 400 eV on tungsten.)

- 2. The lowest temperature at which it appears (i.e. at the lowest ion energy) is between 1700 and 1800 K.
- 3. Its position shifts monotonically to higher temperature with increasing ion energy.
- It has a width at half amplitude of ~500 K and, unlike the low temperature peaks, is approximately symmetrical.
- For high ion energies (>1 keV) its position is sensitive to the direction of ion incidence.

This last property is attributed to channeling which is especially effective when the ions are directed very close to the <100> axis in the crystal.

Kornelsen and Sinha [8] also reported on the influence of the different crystal orientations. The peaks associated with release from near surface defects are clearly influenced by the crystal orientation. Except helium, all rare gases act in the same way after they are implanted into a tungsten substrate. The estimated median penetrations [25] are 70, 20, and 20 for the [100], [211], and [110] faces respectively, for 4 keV Kr⁺ on tungsten. This also shows the channelling along the <100> and thus the great influence the crystal orientation has on the results of desorption spectra. Kornelsen and Sinha suggest two points of interpretation based on this results:

- 1. The low-temperature peaks involve the release of gas trapped within, at most, three lattice constants of the crystal surface. The characteristic energies are associated with a combination of the distance of the trapped atom from the surface (for example, one, two, or three atom layers) and associated distinctive arrangements of the lattice atoms around the trapping sites. The fact that the number and the position of the low-temperature peaks vary both for different ions on the same crystal face and for the same ions on different crystal faces means that neither the properties inherent to the crystal lattice as a whole, nor those inherent to its surface configurations, can by themselves describe the low-temperature gas release the nature of the trapped atom must be included.
- 2. The high-temperature peak involves the release of gas atoms by their diffusion as single impurities from depths greater than three lattice constants, where the influence of the surface on their migration energy is negligible. As a corollary, it must be concluded that the activation energy of diffusion (4.50 eV) is the same for the four inert gases (Ne, Ar, Kr, Xe) to within 5%. Shifts of the peak to higher temperature are associated with increasing average depth of the entrapped atoms. All variations with ion type, ion energy, and crystal directions are consistent with the expected variations in median penetration depth.

In the experiments of Van Veen *et al.* [1] highly energetic argon atoms were mainly used to create defects within a (110) molybdenum crystal. The substrate was then decorated with helium to look at the kind of defects present in the sample. During TDS the argon signal was also measured, which gives some extra information on the kind of defects.



Figure 35: Argon desorption spectra obtained after Ar ion irradiation of a (110) Mo crystal to a dose of $1.2 \cdot 10^{13}$ Ar/cm² at the energies shown on the figure. [1]

One of the experiments showed the results of bombarding the substrate with argon at different energies (figure 35). The results are one peak at 500 K, one peak at 1000 K, one at 1300 K that are all independent of the implantation energy, and one peak around 1500 K that shifted to higher temperatures when the energy of the argon atoms is increased. This last peak is associated with argon coming from the bulk of the molybdenum substrate, as it does not occur at energies lower than 500 eV and shifts to higher temperatures when the energy is increased. As the first three peaks do not shift to higher temperatures with higher energies they have to be

related to defects near the surface. They are named Ar^S, Ar^I, and Ar^{II} meaning the surface layer (S), the first few atomic layers (I), and the second few atomic layers (II), respectively. The shifting peak was called Ar^B standing for defects in the bulk. The reactions attributed to the different release mechanisms are shown in table 7.

Table 7: Temperature of defect reactions involving argon observed in Mo [1]. The * stands for mobile. Peak notations are given in parenthesis.

Т (К)	Description	Reaction
RT.	Argon is interstitially mobile within the molybdenum	Ar*
	lattice	
500	Argon is released from surface sites	$Ar \rightarrow Ar^* (Ar^S)$
1000	Argon is released from vacancies near the surface	$ArV \rightarrow Ar^* + V^* (Ar^I)$
1100	A vacancy is released from an argon-vacancy cluster	$ArV_2 \rightarrow ArV + V^*$
1180	Argon is released from vacancies double filled with	$Ar_2V \rightarrow 2 Ar^* + V^*$
	argon	
1400	Argon is released from close near the surface	$V + ArV \rightarrow ArV_2^* (Ar'')$
1600	Argon is released from the bulk	$V + ArV \rightarrow ArV_2^* (Ar^B)$

Proposal of Van Veen et al. for the argon peaks:

Ar^s: Argon in interstitial positions located between the first (surface) and second atomic layer, and also argon in near surface irregularities.

Ar^I: Argon in substitutional positions in the 2nd layer. The release is a first order dissociation process as can be derived from the peak shape. This suggests release preceded by a jump of an adjacent surface atom to a position on top of the surface. With this jump, room is made for the argon atom to leave.

Ar^{II}: Argon in substitutional positions in a zone stretching from the 3rd to ~5th layer. Near the surface the formation energy of the vacancy required to allow the substitutional atom to be released is lower than expected for release from the bulk. Calculations show that a decrease of 0.2 eV in the vacancy formation energy produces a higher jumping probability towards the surface than for the bulk Ar atoms. This may explain the lower release temperature.

Ar^B: Substitutional argon atoms in deeper layers. The release temperature is dependent on the average depth of the Ar atoms.

From the experiments also threshold energy values have been found for defect production in successive layers. These values are presented in table 8. For comparison our values found are included. The spectra and the differences are discussed in section 4.3.5.

Table 8: Threshold energy E_{th} for the different peaks found in the argon desorption spectra. The second column presents the values found by Van Veen *et al.* for a <110> substrate, the third column presents the values that are found by our group for a <100> substrate.

peak	E _{th} (eV)	<i>E</i> _{th} (eV)
Ar ^s	< 100	< 100
Ar'	>100	>100
Ar"	>300	>150
Ar ^e	> 300	> 150

Table 9: Temperature and description which is associated with the different states mentioned by Naik *et al.* [44].

T (K)	Description
550	State A: The peaks observed in this state are particularly prominent for krypton at all
	incident ion energies utilised while they can be seen clearly in case of argon and neon at
	lower incident energies only. The peaks are characteristic of the possible entrapment at
	sites immediately below the surface. It is possible that the release in this state is effected
	by the diffusion of the impurities at the surface and at grain boundaries.
850	State B: The values of the binding energy observed for this state are close to the value of
	2.2 eV for energy of vacancy migration in molybdenum reported by Flynn [45].
1150	State C: This state is attributed to the release of trapped atoms effected by the self-
	diffusion of the host atoms at the surface.
1350	State D: Values of binding energy in this state are believed to be associated with the self-
	diffusion of the host atoms in the region of entrapment, effecting the release of the
	trapped atoms.

The only argon desorption spectra found for a polycrystalline molybdenum substrate are presented by Naik *et al.* [44]. They also used other inert gas atoms. At least four different states of binding of the trapped atoms were observed in the spectra. The results are difficult to interpret due to the relatively poor quality of their spectra. In addition, during TDS their samples could only be raised in temperature to 1573 K. At this temperature we found still defects present in the layer, and it is also suspected that the substrate is not completely recrystallized at that temperature. This implies that the measurements should be treated with caution.

With that in mind we mention that Naik *et al.* find four argon peaks at temperatures of 550, 850, 1150, and 1350 K. All peaks grow when the argon fluence is increased. A saturation of the number of ions trapped with increasing ion dosage has not been observed since the maximum ion irradiation dosage utilised in their work is limited to 3.88e14 ions/cm².

As mentioned above, Naik *et al.* have used a poly-crystalline molybdenum substrate. This is different from Kornelsen and Sinha and Van Veen *et al.* who performed their measurements at mono-crystalline substrates. They find that the desorption peaks lower than 1500 K are first order peaks. Naik *et al.* do not find any first order desorption peaks in their spectra. Their peaks are considerably broader than those due to first-order desorption from sites of a single discrete activation energy.

The 1350 K peak of Naik *et al.* also shifts to the right when the ion energy is increased. From low to higher temperature they associate the peaks with state A, B, C, and D, respectively. A description of these states is given in table 9.

From Kornelsen and Sinha and Van Veen et al. four things can be learned:

- In molybdenum there should be three peaks associated with defects near the surface. When in our experiments argon is irradiated in the molybdenum, after which an argon free layer is deposited on top of it, the peaks should not be visible in the spectra anymore. This unfortunately will not be seen, because of the "parallax", which is discussed in section 3.3.1.
- 2. The peaks associated with defects near the surface are first-order desorption peaks with an activation energy dependent on the surface orientation. In the experiments presented in this thesis a poly-crystalline surface is investigated. This should give rise to many first-order desorption peaks, which will not form a firstorder desorption peak when they have been added.

- 3. The argon that resides in the bulk should be seen by a shifting peak to higher temperatures when the argon is buried deeper in the layer. With the growth of a layer we can position the argon atoms at any specified depth we like, and thus this effect should be clearly seen in our experiments.
- 4. The mechanism for release of argon from a molybdenum lattice should be the same as for self-diffusion of molybdenum (the vacancy-mechanism). This can also be investigated by putting the argon at specified depths beneath the surface.

4.3.2. The influence of the IBAD parameters on the built in argon amount

Before discussing any of the results it is necessary for understanding of the various figures where the different peaks in the argon desorption spectra come from (table 10). The proof for the assigning of the different peaks to the different places within the molybdenum layer will be given in the next sections and stated in section 4.3.5. As can be immediately seen the assigning of peaks to different defects is comparable to the things stated above in section 4.3.1.

Table 10: Various peak temperatures T_p present in the argon desorption spectra and the places where the argon comes from within the molybdenum layer.

<i>T</i> _p (K)	Description
450	Ar from the first layer
950	Ar from the second layer
1350	Ar from the third layer
> 1400	A shifting peak to higher temperatures when the argon has to come from deeper places.

With the ion source it is not possible to generate beams that have a high enough fluence to be significant in the IBAD process, yet a low enough energy to prevent incorporation of part of the argon ions in the growing film. As explained earlier, the reason for this is that the method of decelerating a high-energy beam is not perfect and leaves a certain fraction of high-energy neutrals in the beam. Therefore the first thing to study is the amount of argon being built into the layers, and to investigate how this amount is influenced by the different parameters that can be varied during IBAD.

A very important parameter in IBAD is the energy of the arriving argon ions. Directly related to this energy is the penetration depth of the ions, which in turn affects the probability of argon entrapment.





Figure 36: Argon desorption spectra for various ion beam energies E_{IBAD} , in eV, indicated at the right-hand side.

Conditions: IBAD, d = 30 Å.

Figure 37: Argon desorption fluence as a function of the argon ion energy obtained from the data in figure 36.

Figure 36 shows a 30 Å IBAD layer deposited with various ion beam energies. The bottom spectrum with an ion energy of 100 eV is almost flat, which means that almost no argon is built into the layer. The argon is built into the layer for energies of 150 eV and higher. Figure 37 shows the argon desorption fluence as a function of the argon ion energy. When the argon ion energy is increased the amount of argon built into the layer increases. Fits to the data gave a third degree polynomial.

IAR, saturation

Another very important parameter in IBAD is the ion-to-atom arrival ratio. The argon desorption spectra for a 50 Å IBAD layer with various IARs are shown in figure 38 and table 11. When looking at figure 38 the total amount of argon built into the layer increases with increasing IAR while the IAR is below 0.1. This increase of total built in argon is totally contained in the argon desorption peak around 1500 K, which means that the other defects are saturated. As will be shown later this peak around 1500 K is associated with argon from the bulk while the other peaks have something to do with the surface. This means that the surface defects are more or less saturated with argon, while the bulk defects are not. This can be partly understood when assuming parallax.

When the IAR is increased above 0.1 the total amount of built in argon does not change very much. This can also be seen in table 11 (column 3 and 4). This is a saturation effect similar to the one we have already encountered in figure 31.

Table 11: Results belonging to the spectra shown in figures 38 and 39. The corrected implanted argon fluence $\Phi_{c,Ar}$, the desorbed argon fluence $\Phi_{des,Ar}$ (those two columns are plotted in figure 43). The forth column presents the argon concentration in the molybdenum film c_{Ar} . Also presented are the percentage of the implanted helium that is trapped in the A1 and A2 peaks, and the calculated concentration c_{r} of defects associated with the A1 and A2 peak using figure 39, for various ion-to-atom arrival ratios γ .

γ	$\Phi_{c,Ar} (10^{15})$	$\Phi_{des,Ar}$ (10 ¹³)	C _{Ar} (10 ⁻⁴)	$\Phi_{des,He,(A1+A2)}$ (10 ⁻²)	C _{tr,(A1+A2)} (10 ⁻⁵)
	(cm ⁻²)	(cm ⁻²)		$\Phi_{c,He}$	
0.030	0.17	0.96	3	1.9	2
0.061	0.35	1.36	4	2.5	2
0.098	0.56	1.52	5	4.1	3
0.13	0.73	1.60	5	4.5	4
0.15	0.87	2.45	8	5.7	5
0.16	0.90	2.47	8	5.6	5
0.19	1.10	2.17	7	6.7	6
0.21	1.19	2.27	7	5.2	5

The same can be found from the helium desorption spectra (figure 39). The total amount of A1 and A2 defects increases up to an IAR of 0.15. Above this value the amount of A1 and A2 defects become more or less constant at a defect concentration of $5 \cdot 10^{-5}$ which can be found using figure 12 and a thickness of 50 Å.





Figure 38: Argon desorption spectra for various ion-to-atom arrival ratios γ , indicated at the right-hand side.

Conditions: IBAD, d = 50 Å, $E_{\text{IBAD}} = 250 \text{ eV} (18\%) + 25 \text{ eV} (82\%).$ Figure 39: Helium desorption spectra for various ion-to-atom arrival ratios γ , indicated at the righthand side. (Same experiment as figure 38.) Conditions: IBAD, d = 50 Å, $E_{\text{IBAD}} = 250$ eV (18%) + 25 eV (82%), Decoration, $\Phi_c = 8.5 \cdot 10^{13}$ He⁺/cm².

total amount of implanted argon atoms

To change the number of bombarding argon ions the substrate can be exposed to the beam for various times. The argon desorption spectra of this experiment are shown in figure 40. In this experiment the bare substrate is exposed only to the neutrals in the beam by putting the sample to a bias voltage of 250 V (the helium signal has already been presented in figure 30). As can be clearly seen from figures 40 and 41, the amount of argon that can be built into the bare substrate is limited. Thus the molybdenum layers can become saturated by argon atoms. This might be the explanation why the percentage of built in argon reduces with increasing IAR. The spectra in figure 40 show just surface related defects as 250 eV argon ions do not penetrate very deep into the molybdenum lattice.





Figure 40: Argon desorption spectra for various ion beam time t_b , in seconds, indicated at the right-hand side. (Same experiment as figure 30.) Conditions: Sputtering. $E_{\text{IBAD}} = 250 \text{ eV}$.

Figure 41: Desorbed argon fluence as a function of the implanted argon fluence as follows from figure 40. The curve is a fitted exponential function:

$$\Phi_{des.Ar} = 2.1 \cdot 10^{13} \left[1 - \exp\left(-\frac{\Phi_{c,Ar}}{2.4 \cdot 10^{14}}\right) \right]$$

Figure 41 shows the dose dependence of the number of trapped argon atoms in the layer, with saturation at a higher dose. The solid curve of figure 41 is a fit to the experimental data. The saturation is due to the fact that when the number of trapped argon atoms increases two things might happen. First, the incoming argon atom experiences the present argon and leaves, and second, the incoming argon atom sputters the present argon atom out of its position and takes its place [46]. The consequence of both mechanisms is the same, *viz.* that the total number of argon atoms in the layer becomes constant. This might be presented with the following formula:

$$\frac{d \Phi_{des,Ar}}{d \Phi_{c,Ar}} = \frac{1}{\Phi_{\gamma_e}} \left(\Phi_{des,sat} - \Phi_{des,Ar} \right).$$
(24)

The argon fluence Φ multiplied by the surface area gives the total number of argon atoms:

$$\frac{d N_{trapped}}{d N_{implanted}} = -p N_{trapped} + q , \qquad (25)$$

with

.....

$$\rho = \frac{1}{\sigma \Phi_{\gamma_e}} \tag{26}$$

and

$$q = \frac{\Phi_{des,sat}}{\Phi_{y_e}} \,. \tag{27}$$

In these equations *p* denotes the probability for an argon atom in the layer to be sputtered away by an incoming argon ion, σ denotes the effective area under which 1 argon atom is present, and *q* is the probability for an incoming argon ion to become trapped. From the fit to the data one obtains: $\Phi_{1/e} = 2.4 \cdot 10^{14}$ cm⁻² and $\Phi_{des,sat} = 2.1 \cdot 10^{13}$ cm⁻². Using equation 27 one finds for the trapping probability of an incoming argon ion 9%. In the case of saturation the probability for being sputtered away by an incoming argon ion becomes 1. From equation 26 one finds that σ has to be equal to 42 Å². This means that when effectively one argon atom is present in the molybdenum layers every 42 Å² the layers are saturated with respect to argon ion bombardment. In a first approximation this seams a reasonable value.

From the saturation value of $2 \cdot 10^{13}$ argon atoms per cm² one can also calculate the maximum argon concentration. From figure 40 one finds a penetration depth of 4 Å for 250 eV argon atoms (This penetration depth will become clear after the next section). Then the maximum concentration of argon atoms built into the layer is $8 \cdot 10^{-3}$. Verifying this amount with all the argon spectra showed that this amount is never exceeded in the experiments. A maximum fraction of Ar retained in surface-related trapping sites of 0.005 is before mentioned by Van Veen *et al.* [43]. The argon concentration is also equal to the total trap-concentration as obtained

from figure 31 in section 4.2.1. This means that at such high argon concentration all defects shown in the helium spectra up to a temperature of 1000 K are generated by incorporated argon atoms.

The concentration of 8.10⁻³ comes down to one argon atom every four molybdenum atoms if we walk through the lattice in a straight line. This might be the maximum amount of argon possible in a molybdenum lattice as Van Veen et al. [1] mentioned that the stress created by a substitutional argon atom would be felt within a radius of 3 to 5 lattice parameters around the atom. The stresses might prevent other argon atoms to reside in the neighbourhood of an argon atom. Filius [42] found that this saturation is a quasi-saturation (figure 42). Increasing the argon fluence first showed an increase in the number of built in argon atoms and then became saturated, but for far higher argon fluences it was found that the amount of built in argon started to rise again. This was explained by argon clustering together and in this way become attractive places for new incoming argon. Filius found quasisaturation values of 2.10¹² argon atoms per cm² for an argon energy of 100 eV, and two to three times higher for an energy of 150 eV. From figure 41 it can be seen that a value of 2.10¹³ argon atoms per cm² is found for an argon energy of 250 eV, which is a value in the line of expectation. The quasi-saturation value is energy dependent, because the higher the energy, the greater the penetration depth, and thus more places for the argon atoms to reside. A higher energetic particle contains also more power to overcome existing stresses within the lattice.



Figure 42: Total amount of retained argon as a function of argon irradiation dose. The dashed line shows quasi-saturation due to gas-sputtering [42].

Saturation in growing layers

Now that we know about argon saturation in a molybdenum substrate it is important to compare this with growing layers. In figure 43 the data from table 11 are plotted with respect to the saturation curve as shown in figure 41. The data points are layers of 50 Å deposited with various ion-to-atom arrival ratios. Figure 43 indicates that the data points are in reasonable agreement with the curve. However, this is not what one expects. The curve represents argon trapping in a bare substrate (i.e. in a 4 Å layer down from the surface), while the data points represent argon trapping in a 50 Å IBAD-film (ten times thicker). One would expect a ten times higher saturated argon incorporation. Apparently the trapping probability during IBAD is ten times lower. The argon concentration obtained for this layers has a maximum of only $8 \cdot 10^{-4}$ (table 11) argon atoms per molybdenum. This matter is not understood. More information can be obtained by studying argon trapping as a function of IBAD-film thickness.



Figure 43: Desorbed argon fluence as a function of the implanted argon fluence. The curve is the same curve as found in figure 41. The points are the data obtained from figure 38 and listed in table 11.



Figure 44: Desorbed argon fluence as a function of the implanted argon fluence. The data presented are deposited molybdenum layers of various thicknesses. The four data sets belong to various ion-to-atom arrival ratios during deposition. Also the saturation curve is plotted and the curve for 10% argon trapping probability.

Figure 44 presents IBAD layers of various thicknesses. The four data sets belong to four series of experiments. The ion-to-atom arrival ratio is indicated in the figure. The drawn lines are a guide to the eye. For comparison also the trapping curve for the

substrate is plotted and a straight line representing a trapping probability of 10%. For all four data series it can be seen that first the amount of trapped argon atoms increases with increasing argon fluence according to the 10% line. Above a certain value the trapping probability for incoming argon ions decreases, seen by a change in slope of the lines. For all data curves this is around a layer thickness of 30 Å. This is the same thickness for which Van der Kuur [21] and Pols [31] see the start of grain boundaries. Grain boundaries act as fast diffusion paths for argon and helium, and this might be the reason for the reduced argon trapping probability.

Comparing the 50 Å data of figure 43 with the four 50 Å points in figure 44 (not especially indicated), one must conclude that the data of figure 43 very likely contain systematic errors.

From this section it could be learned that the amount of argon that can be built into the layer is limited. With respect to growing layers this means that with high enough ion-to-atom arrival ratios argon saturated layers can be grown. In figure 41 this can be predicted by extrapolating the straight slope to a higher total desorbed Ar fluence (figure 44) which is equal to the maximum argon concentration of $8 \cdot 10^{-3}$ in the specified layer thickness. This will only be true when no grain boundaries are present.

4.3.3. Built in argon as a function of layer thickness

film thickness, shifting Ar peak, grain boundaries

Variation in layer thickness should show the same as the energy variations performed by Van Veen and Kornelsen. When in those experiment the ion energy is increased, the penetration depth of the argon atoms increase and a "shifting" peak above 1400 K will be expected beside the peaks arising from defects close to the surface. When growing an IBAD layer the first arriving argon is buried by the growing layer. These argon atoms will become argon which is not situated near the surface. The deeper the argon is built into the layer the more the shifting peak will move to higher temperatures because the time it takes for the argon to reach the surface is longer. The peaks obtained in this way should though be broader than the peaks obtained by Van Veen and Kornelsen, because the argon is distributed over a greater depth range (depending on layer thickness). In all experiments described in this section an ion beam is used with ion energies of 250 eV. Without deposition there is no peak visible around 1500 K, as can be seen from figure 40. This means that a 250 eV argon atom does not penetrate very deep into the layer, which is also found by TRIM [34]. In the figures 45 and 46 and also in table 12 the results are presented for various IBAD layer thicknesses *d*.

30



25 Ar desorption flux L (cm⁻²s⁻¹) $/10^{12}$ 500 20 200 100 75. 15 60 50 10 30 20 5 10 5 0 500 1000 1500 2000 0 2500 Temperature (K)

d (Å)

Figure 45: Argon desorption spectra for various layer thicknesses *d*, in Å, indicated at the righthand side. The spectra are normalised with respect to the IAR and the layer thickness. The grey spectra are calculated spectra using HOP. Conditions: IBAD. $E_{IBAD} = 250 \text{ eV}, \gamma = 0.045$.

Figure 46: Argon desorption spectra for various layer thicknesses d, in Å, indicated at the right-hand side.

Conditions: IBAD, γ=0.03 (250 eV) + 0.13 (25 eV).

From figure 45 and table 12 it can be clearly seen that the percentage of built in argon increases with decreasing layer thickness. The change of percentage built in argon can be understood when we look at the growth of an IBAD molybdenum layer [21]. After good surface coverage for the first few layers, islands are formed. The islands become columns and grain boundaries are formed between the different columns after a layer thickness of about 30 Å. Grain boundaries act as fast diffusion paths for helium and for argon. So when the layer becomes thicker the chance for an argon atom to get in a grain boundary becomes greater. This reduces the amount of argon that can be built into the layer. Another indication that grain boundaries start to grow at a thickness of 30 Å can be seen when looking at the increase in area presented by the surface related argon defects shown in figures 45 and 46. An increase of argon coming from surface related sites means that there is effectively more surface available for the argon atoms to leave. This is true because grain boundaries act as surface.

Also it can be seen from table 12 that the argon concentration in this experiment does not exceed the $8 \cdot 10^{-3}$ as given in the previous section. The percentage argon seen by the helium atoms in the A1 and A2 peak is also greater for thinner layers. The amount the helium "sees", can only be used up to a layer thickness of 50 Å as this 50 Å is about the information depth of the helium atoms. The percentage of helium that is trapped in the A1 and A2 peak stands for a concentration of defects in the layer, which can be found using figure 12. For layers thicker than 50 Å again the 50 Å line in figure 12 has to be used because the helium gives only information about the top 50 Å of the layer.

Table 12: Results belonging to the spectra shown in figure 45. The corrected implanted argon fluence $\Phi_{c,Ar}$, the desorbed argon fluence $\Phi_{des,Ar}$ (those two columns are plotted in figure 44 (diamonds)). The forth column presents the argon concentration in the molybdenum film c_{Ar} . Also presented are the percentage of the implanted helium that is trapped in the A1 and A2 peaks (figure 26), and the calculated concentration c_{tr} of defects associated with the A1 and A2 peak using figure 12, for layer thicknesses *d*.

d (Å)	$\Phi_{c,Ar} (10^{15})$	$\Phi_{des,Ar}$ (10 ¹⁴)	CAr	$\Phi_{des,He,(A1+A2)}$ (10 ⁻²)	Ctr,(A1+A2)
	(cm ⁻²)	(cm ⁻²)		$\Phi_{c,He}$	
5	0.14	0.12	4·10 ⁻³	7.6	2·10 ⁻³
10	0.29	0.27	4·10 ⁻³	10.4	1.10 ⁻³
20	0.56	0.40	3·10 ⁻³	6.4	2·10 ⁻⁴
30	0.87	0.76	4·10 ⁻³	5.7	1.10-4
40	1.16	0.80	3·10 ⁻³	4.5	6·10 ⁻⁵
50	1.14	0.71	2·10 ⁻³	3.9	3·10 ⁻⁵
60	1.73	0.87	-	5.9	4·10 ⁻⁵
100	-	-	2·10 ⁻³	5.5	4·10 ⁻⁵
200	5.78	1.15	9·10 ⁻⁴	5.4	4·10 ⁻⁵
300	8.67	1.28	7·10 ⁻⁴	6.2	4·10 ⁻⁵

The argon desorption spectra for a layer thickness up to 10 Å show two peaks; one at 1000 K and one at 1400 K. If the layer becomes thicker the second peak is divided into two peaks. One that stays at a temperature of 1350 K and one that shifts to higher temperatures with increasing layer thickness. The shifting has to be due to the argon that originates from deeper within the layer. Deeper in the layer means that the way to the surface is longer and it will take longer for an argon atom to reach the surface. This phenomenon can be associated with diffusional lag as can be simply simulated with HOP [32].

Figure 46 shows a peak at 1200 K for a layer thickness of 500 Å. This peak has been observed in other spectra, but always in relatively thick layers (>200 Å). First results obtained on an (100) molybdenum crystal (not published) shows that this peak is always present in (100) grown layers, independent of layer thickness. This can be understood as follows. The (100) is the fastest growing direction for molybdenum. Layers deposited on a polycrystalline molybdenum substrate will therefore eventually show a spectrum dominated by the (100) peaks. From figure 46 it is also seen that this peak is an additional peak, which means that it originates from another combination between argon and a defect as discussed so far. Van Veen et al. [1] mention a peak at 1180 K which can be described by the following reaction: $Ar_2V \rightarrow 2Ar^* + V^*$. From the previous results, which showed that if the layer is saturated with argon the trap concentration is equal to the argon concentration, one finds that the argon ions create their own defect. This, however, does not necessarily have to be the case if the surface orientation is (100). Kornelsen [25] has found that in tungsten, which is also a bcc material, the (100) orientation is a channel direction for krypton, the same may apply for argon in molybdenum. In the (100) direction it then might be possible for the argon atoms to lose their energy in the channels without creating any defects. Eventually the argon atoms would then become interstitial, and as they are interstitially mobile they can act as a probe atom and trap at a defect already filled with argon.

Another thing that occurs for thicker layers (and also for high energies) is the dividing of the peak at 1000 K. This splitting must also be due to changes in orientation of the surface.

overlayers, how deep do the argon atoms reside

It is possible to look at argon with an overlayer deposited on top of the argon. In this way we look totally to the diffusion of argon through the molybdenum lattice, except for the low peaks at 1000 K and 1350 K that come forward due to the systematic

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error described as parallax (section 3.3.1). To do this we have deposited an IBAD film and deposited an EVAP layer on top of it. In figure 47 the argon desorption spectra are shown for argon present in a 10 Å IBAD layer under the EVAP overlayer. In figure 48 the argon has been implanted into the bare substrate by exposing the sample for 30 seconds to a 250 eV argon ion beam, followed by the deposition of an EVAP layer.



Figure 47: Argon desorption spectra for various overlayer thicknesses d_2 , in Å, indicated at the right-hand side.

Conditions: IBAD, $d_1 = 10$ Å, $\gamma = 0.04$ (250 eV) + 0.15 (25 eV)., EVAP.



Figure 48: Argon desorption spectra for various overlayer thicknesses *d*, in Å, indicated at the right-hand side. The grey spectra are calculated spectra using HOP.

Conditions: Sputtering, E_{IBAD} =250 eV, $\Phi_{c,Ar}$ = 3.2·10¹⁴ Ar⁺/cm², EVAP.

The diffusional lag mechanism shows immediately when looking at figure 47. The shifting of the peak to higher temperatures with increasing layer thickness is just the same as for normal layer thickness variations (figure 45), except for a greater peak shift in the case of overlayers. This is due to the higher mean trapping distance of the argon in the overlayer experiment with respect to the normal layer thickness variation.

With the measurements shown in figure 48 it is tried to give an exact development of the different peaks visible in the argon desorption spectra with respect to the distance the argon resides underneath the surface. In figure 47 a peak

all the peaks are already visible. This means that the argon resides already too deep beneath the surface in a 10 Å IBAD layer for investigation. To overcome this problem the argon has been implanted into the bare substrate (figure 48). As can be seen from the bottom spectrum in figure 48 a ridge is visible around 500 K, two peaks around 950 K and a little peak around 1350 K, and no peak around 1500 K which should be associated with argon from deeper layers as shown previously. This spectrum is taken as the starting-point for all other argon spectra shown in figure 48. By depositing increasingly thicker layers on top of the substrate containing the argon atoms, the argon atoms are made to reside increasingly deeper into the sample. After depositing one monolayer of molybdenum (2 Å) the peak at 450 K is totally gone as all the other peaks seem to shift to the peak aside of them. Depositing two monolayers of molybdenum on top of it (4 Å) makes the peak at 900 K disappear and the peak around 1500 K is now quite clear. In this spectrum this peak is still a superposition of the peak associated with defects near the surface at 1350 K and the peak associated with the argon from the bulk. Deposition of more and more molybdenum on top of the layers makes all the peaks at lower temperatures than 1500 K disappear (except for the reminants of the peaks due to parallax) and the shifting peak can be seen quite clearly. An interpretation of these observations will be given in section 4.3.5.

4.3.4. The release mechanism of argon from a molybdenum lattice

If we look at diffusion there are three mechanisms that are important with respect to molybdenum layers, *viz.* interstitial diffusion, vacancy diffusion and self-diffusion of molybdenum (figure 13).

Before proceeding something has to be said about the activation energy necessary for the movement of argon through the molybdenum layer. As described in section 2.3.3 the activation energy can be obtained by repeating desorption experiments with use of different heating rates. The argon desorption peaks of such a series are shown in figure 49. The experiment consisted of first depositing a 10 Å IBAD layer after which a 5 Å EVAP layer is deposited on top of it. The spectra shown are normalised with respect to the heating rate β . This experiment is chosen because the peak visible is the shifting argon peak. The peak temperatures T_p for the various heating rates β are given in table 13.





Figure 49: Argon desorption spectra for various heating rates β , in K/s, indicated at the right-hand side.

Figure 50: Kissinger plot using equation 14 and values from table 13.

Conditions: IBAD, $d_1 = 10$ Å, EVAP, $d_2 = 5$ Å.

Table 13: The peak temperatures T_p for the shifting argon desorption peak as a function of the heating rate β .

β (K/s)	<i>Т</i> _р (К)
5	1377
10	1417
20	1439
40	1454
80	1500

With use of the values given in table 13, equation 14 can be solved numerically with a so called Kissinger plot (figure 50). The values obtained in this way for the activation energy and the jump frequency are: $Q_{tr} = 4.16$ eV and $v_0 = 4.9 \cdot 10^{13}$ s⁻¹ respectively. Of these the activation energy is correct and the jump frequency is dependent of the mechanism. The jump frequency found from the Kissinger plot belongs to a first-order desorption mechanism and must be changed. For determining the correct jump frequency, from twelve different desorption spectra the peak temperature is determined. The experiments belonging to the spectra have been simulated with HOP and the peak temperatures obtained in this way are compared with the experiments. In this way the jump frequency can be optimised with respect to the obtained activation energy of 4.16 V. The jump frequency obtained in this way is $1.75 \cdot 10^{16} \text{ s}^{-1}$. Kornelsen finds for argon in tungsten an activation energy for the shifting peak of 4.50 eV per atom with a jump frequency within one order of magnitude of 10^{13} s^{-1} [6].

Using equations 6 and 7 and an activation energy Q_{tr} of 4.16 eV, a jump frequency v_0 of $1.75 \cdot 10^{16} \text{ s}^{-1}$, a temperature of 1500 K and a jump length of 2 Å, results in a diffusion-coefficient of $1.3 \cdot 10^{-18} \text{ m}^2/\text{s}$. This value for the diffusion coefficient is a factor 100 larger than found for the self-diffusion in the literature. Brown and Ashby [47] obtained a value for self-diffusion of molybdenum of $1.6 \cdot 10^{-20} \text{ m}^2/\text{s}$ at a temperature of 1500 K. To obtain this they used a pre-factor D_0 of $1.8 \cdot 10^{-4} \text{ m}^2/\text{s}$, and an activation energy Q_{tr} of 460.6 kJ/mol = 4.8 eV per atom. Maier *et al.* [48] obtained a value of the order of $1 \cdot 10^{-20} \text{ m}^2/\text{s}$ over a temperature range of 1360 K to 2773 K. They used a pre-factor of $8 \cdot 10^{-4} \text{ m}^2/\text{s}$ and an activation energy of 488.2 kJ/mol = 5.1 eV per atom. A factor hundred in the diffusion coefficient comes down to an activation energy shift of 0.6 eV to lower energy. The lower activation energy for argon with respect to molybdenum hopping from one vacancy to another might be expected. The reason for this is that an argon atom is smaller in radius than a molybdenum atom and has a weaker bond with the surrounding molybdenum atoms.

Results obtained with HOP using an activation energy of 4.16 eV, a jump frequency of $1.75 \cdot 10^{16}$ s⁻¹ and assuming a vacancy mechanism are shown in figure 45 and 48 with grey lines. The shape of the peaks and the position of the peaks obtained with HOP are in good agreement with the shape and position obtained with the experiments. From this it might be concluded that argon is released from the molybdenum by the same mechanism as self-diffusion (the vacancy mechanism).

4.3.5. Discussion of the argon peaks and their release mechanisms

Ar^s, Ar^J, Ar^J, Ar^B

In the previous sections already something has been said about the argon peaks and the release mechanism behind the shifting argon peak. In order to easily distinguish the argon peaks, we will follow the peak naming convention as proposed by Van Veen *et al.* [1]. The peak as 450 K is called the Ar^S, the peak at 950 K is called the Ar^I, and the peak at 1350 K is called the Ar^{II}. The peak at about 1500 K, which shifts to higher temperatures with increasing implantation depth is called the Ar^B peak.

In figure 48, and as discussed in section 4.3.3, it is seen that after deposition of one atomic layer, the Ar^S peak disappears. The Ar^S peak therefore has to be associated with argon that resides in the first atomic layer. This peak can be seen when the argon is implanted into the bare substrate. The reason that it is not visible in the deposited layers is that the total amount of argon in the layer is far greater than the amount near the surface.

In figure 48 it is seen that after deposition of two atomic layers, the Arⁱ peak disappears. The Arⁱ peak therefore has to be associated with argon that resides in the second atomic layer. The peak temperature depends on the surface orientation. When the surface becomes very rough the peak will split into two (or more) peaks around the temperature of 950 K. This can be seen when looking at relatively thick layers (>200 Å) and relatively high argon ion energies (>200 eV).

The Ar^{II} peak is associated with argon that resides in the third atomic layer. This follows from figure 48 also. After depositing a layer of 4 Å, the argon in the first layer has become argon in the third layer. After depositing layers of 4 Å and 5 Å, the peak at 1350 K is the "only" visible peak.

The Ar^B peak is associated with argon that resides in the bulk of the molybdenum. When the argon is buried deep into the layer by depositing layers with a thickness of more than 4 Å, this peak is very clearly visible. It shifts to higher temperature when the argon is buried deeper, which is due to diffusional lag. From this shifting to higher temperatures it appears that the argon is released via a mechanism similar to the self-diffusion mechanism of molybdenum as was shown in section 4.3.4.

$(A1+A2) \mapsto Ar^{B}$

In the helium desorption spectra are two peaks associated with argon. As was found by Van Veen et al. [29], Van der Kuur [21], and Pols [31], a peak called the A1 peak is associated with one helium in a monovacancy filled with one argon atom, and the A2 peak is associated with two heliums in a monovacancy filled with one argon atom. Now that the temperatures for argon release from the molybdenum lattice are known, we can associate the defect belonging to the A1 and A2 peak by variations of temperature during the experiment. There are two different temperatures which can be varied. From the anneal experiment discussed in section 4.2.1 it can be seen that the A1 and A2 peak disappear after an annealing temperature of 1600 K. This temperature is, as we already know, associated with the shifting Ar^B peak. Another temperature that can be varied is the deposition temperature. Figures 51 and 52 show the helium and argon desorption spectra, respectively, of an IBAD layer of 50 Å deposited at various substrate temperatures. From table 14 it can be seen that at deposition temperatures of 1180 K and 1360 K the amount of argon released from the layer as seen from the argon desorption spectra is equal to the amount of argon that is associated with the A1 and A2 peak. Thus the defect belonging to the A1 and A2 peaks in the helium desorption spectra is the same as the Ar^B peak in the argon desorption spectra.





Figure 51a: Helium desorption spectra for various deposition temperatures T_{dep} , in K, indicated at the right-hand side.

Conditions: IBAD, d = 50 Å, $\gamma = 0.03$ (250 eV) + 0.13 (25 eV), Decoration, $\Phi_c = 8.5 \cdot 10^{13} \text{ He}^+/\text{cm}^2$.

Figure 51b: The same as figure 51a, but just the two top-most spectra shown.

Table 14: Results belonging to the experiment shown in figures 51 and 52. The percentage argon that is built into the layer according to the argon spectra and to the amount that is seen by the helium in the A1 and A2 peak for various deposition temperatures T_{dep} .

T _{dep} (К)	$\frac{\Phi_{des,Ar}}{\Phi_{Ar}} (10^{-2})$	$\frac{\Phi_{Ar(A1+A2)}}{\Phi_{Ar}} (10^{-2})$
300	0.7	0.09
390	2.0	0.11
500	1.3	0.15
630	-	0.11
700	2.0	0.15
890	0.7	0.18
960	0.5	0.17
1180	0.14	0.14
1360	0.07	0.07





Figure 52a: Argon desorption spectra for various deposition temperatures T_{dep} , in K, indicated at the right-hand side. Conditions: IBAD, d=50 Å,

 $\gamma = 0.03 (250 \text{ eV}) + 0.13 (25 \text{ eV}).$

Figure 52b: The same as figure 52a, but just the two top-most spectra shown.

For temperatures lower than 1180 K the amount of argon from the argon desorption spectra is greater than the amount of argon that is associated with the A1 and A2 peaks in the helium desorption spectra. This means that initially the argon released from the molybdenum through the Ar^B peak is associated with different defects in the layer. As is shown by Van Veen *et al.* [1] ArV₂ becomes ArV at a temperature of 1250 K. This contribution to the Ar^B peak cannot be found from the helium desorption spectra when just looking at the A1 and A2 peaks, but comes forth in other peaks that are not as clearly visible as the A1 and A2 peaks. When the deposition temperature is raised to temperatures higher than about 1000 K, the chance for ArV₂ to be created might become negligible and only ArV defects exist in the layer, which can then be seen by the A1 and A2 peaks.

The association between the A1 and A2 peaks and the Ar^B peak can also be seen from a measurement discussed in the previous section. The experiment consisted of bombarding the bare substrate for 30 seconds with argon ions and deposition of molybdenum monolayer by monolayer. After this was done, helium is implanted and also the helium desorption spectra are measured, which are shown in figure 27. Comparison between the helium spectra shown in figure 27 and the argon spectra shown in figure 48 immediately show the association between the Ar^B peak and the A1 and A2 peaks. After depositing a layer of 4 Å the Ar^B peak becomes visible in the argon spectra, at the same time the A1 and A2 peaks arise in the helium spectra. Therefore the defect shown by the A1 and A2 peaks in the helium desorption spectra are associated with argon in a monovacancy not to close to the surface and therefore the A1 and A2 peaks in the helium spectra are associated with defects in the bulk of the molybdenum layer.

Other peaks

Under special conditions several other peaks arise in the argon desorption spectra. A few of them are already mentioned in the previous sections, as there are a splitting Ar^I peak and a peak at 1200 K. These additional peaks are found only after deposition of relatively thick layers and/or using high argon ion energies. Due to preferential growth and higher surface roughness this might have something to do with the surface orientation. As is shown by Kornelsen and Sinha [8] the surface orientation has a large influence on the peak temperature.

A last ridge of argon desorption peaks can be seen in layers and overlayers with thicknesses \geq 100 Å. This ridge is visible at temperatures higher than the peak temperature belonging to the Ar^B peak, as can be seen in figures 45 and 46. From the helium desorption spectra it is known [10, 21, 31] that peaks at the same temperature are visible in the helium spectra for relatively thick IBAD overlayers as the peaks that are visible in the argon spectra. The temperatures in the helium spectra are associated with vacancy clusters which are created during the closing of grain boundaries due to the temperature increase during desorption [21]. The (filled) vacancy clusters are stable up to temperatures higher than for ArV-defects. Therefore, once the argon atoms start to move through the lattice they can be trapped by the large vacancy clusters. The argon and helium atoms residing in the clusters are liberated at higher temperatures, depending on the size of the vacancy cluster.

On their way to the surface the ArV pairs can also meet other ArV pairs with which they can combine and form possibly more stable Ar_2V_2 pairs. This might also give rise to argon desorption peaks near the 1800 K.

Threshold energy

Now that the different argon desorption peaks are associated with argon residing from different depths, threshold energies for defect creation can be obtained by varying the argon ion energy. This experiment is performed on a (100) surface, for which the argon spectra are shown in figure 53.

The threshold energies obtained from figure 53 are presented in table 8. For comparison the values obtained by Van Veen *et al.* [1] are also given. The differences in the threshold energies we have found as compared to the values of Van Veen *et al.* are probably due to the different surface orientation of the substrates that are used. In our case a (100) Mo crystal is used, while Van Veen used a (110) Mo crystal. The threshold energies found for a (100) Mo crystal is apparently lower than for a (110) Mo crystal. This might be due to channeling. For molybdenum the <100> direction is the most favourable for channelling as can be concluded by the experiments of Kornelsen and Sinha [8]. This means that argon atoms can penetrate deeper into the (100) substrate than in the (110) substrate, giving rise to lower threshold energies.



Figure 53: Argon desorption spectra for various ion beam energies E_{IBAD} , in eV, indicated at the righthand side. The left figure shows the low energy range and the right figure shows the spectra up to 1 keV. The sample used for this measurement is a (100) molybdenum substrate. This measurement is performed for comparison with measurements of Van Veen *et al.* [1]. Conditions: Sputtering, t_b =30 s.

Peak shape

A last subject that has to be discussed is the peak shape. As already discussed in chapter 2, there are three different kinds of peaks. A first-order peak, associated with a fast release mechanism like the helium desorption peaks in the helium spectra, a broad diffusion peak, associated with release via a diffusional mechanism like the Ar^B peak, and a combination of the two mechanisms. Van Veen *et al.* [1] and Kornelsen and Sinha [6, 7, 8] mentioned that the peaks with a fixed position from the surface layers are all first-order desorption peaks and that the Ar^B peak is a diffusion peak. The diffusional release of the Ar^B peak has already be shown.

Fits to equation 12 performed on the argon desorption spectra show that the Ar^s peak cannot be reproduced with a first order desorption peak. The same is true for the Ar^I peak. This latter probably is due to our poly-crystalline molybdenum substrate. The surface contains many grains with different orientation as is shown with XRD (X-Ray Diffraction). Many different surface orientations give rise to many peaks originating from the same defect but with slightly different peak temperatures. Fitting the Ar^{II} peak in the argon desorption spectra, as shown in figure 40, has the result that the Ar^{II} peak can be described with a first-order desorption peak. From fits on other measurements, where the Ar^{II} peak is visible on its own, the same result is found. The activation energy associated with this defect is found to be 3.3 eV. The fact that this peak can be described by a first-order desorption peak means that argon release from this defect is independent of the surface orientation. This might be understood by considering that due to relaxation the argon in the third atomic layer rather makes a step to the second atomic layer than to the fourth. The activation energy for release from the second atomic layer has already passed and thus this process is a one-step process.

Naik *et al.* [44] found for all inert gases (except helium) a peak near 1350 K in their spectra after release from a molybdenum substrate. However Naik *et al.* do not find it to be a first-order desorption peak, because they cannot see the peak independent of the other peaks. Naik *et al.* also did not find first-order desorption peaks for the other argon peaks. This is quite satisfying to our case, because he also used a poly-crystalline molybdenum surface. Van Veen *et al.* and Kornelsen and Sinha on the contrary used a mono-crystalline molybdenum surface.

In order to be able to correctly interpret both argon and helium desorption spectra, the interactions between argon and helium have to be understood.

The helium atoms do not influence the argon desorption spectra. This can be shown by varying the helium decoration fluence and looking at the argon spectra. Figure 54 shows 50 Å IBAD layers decorated with various helium fluences. The shape of the argon spectra does not change with varying helium decoration fluences, and so the helium has no influence on the argon desorption peaks. This was also not to be expected because the helium is released from the argon related defects at temperatures where the argon is still immobile [21, 29, 31].



Figure 54: Argon desorption spectra for various helium decoration fluences Φ , in cm⁻², indicated at the right-hand side.

Conditions: IBAD, d=50 Å,

 $\gamma = 0.02 (250 \text{ eV}) + 0.11 (5 \text{ eV})$, Decoration.



Figure 55: Both helium and argon desorption spectra for various IBAD overlayer thicknesses d_2 , in Å, indicated at the right-hand side. The grey lines are the argon desorption spectra and the black lines the helium desorption spectra. Conditions: IBAD, $d_1 = 10$ Å, $\gamma = 0.03$ (250 eV) + 0.15 (5 eV), Decoration, $\Phi_c = 8.5 \cdot 10^{13}$ He⁺/cm², IBAD.

The influence of the argon atoms on the helium spectra is two folded. The first influence is that the helium is bonded to argon incorporated defects and therefore introduces additional peaks in the helium desorption spectra. This is where the helium is used for, as they are good probe atoms. The second influence can be seen by the appearance of the same peaks in the argon and helium desorption spectra. Figure 55 shows an example of this. In this figure argon and helium desorption spectra are plotted together. In this experiment a 10 Å IBAD base layer is grown on the molybdenum substrate. This layer is decorated with a corrected helium fluence of 8.5.10¹³ helium atoms per cm². After that another IBAD overlayer is deposited on top of it. The conformity between the helium and argon desorption spectra can be seen by the 50 Å and the 100 Å overlayer. This conformity is just seen by overlayers or when high helium fluences are used (>1.10¹⁵ He⁺/cm² (not shown)). What causes this conformity is not quiet understood yet. When looking at the peak temperatures it has to be noted that the helium is released just 20 K earlier on the temperature scale than the argon. HOP results show that the difference on the temperature scale for helium and argon released from the same defect deep under the surface is far greater than 20 K, more in the order of 200 K for a defect residing at a depth of 50 Å. Three possibilities might explain the conformity. First, it is purely coincidental, vacancy clusters give rise to helium desorption peaks in the area above 1500 K as has been seen from EVAP layers and the Ar^B also resides in this area. Second, the vacancy clusters belonging to the peaks are not situated very deep under the surface. For these defects both the helium as the argon atoms act as probe atoms and thus the similarity is a consequence of the defect. Third, the helium atoms move to the surface together with the argon via the vacancy mechanism, but from a certain moment near the surface the helium atoms are released from the defect. This release then can give rise to a 20 K lower peak temperature.

The effect that the argon atoms are released in the same temperature interval as the helium temperature interval has also been reported by Filius [42]. He found that the helium atoms desorb just 50 K below the release temperature of the argon atoms. He concluded that this indicated that helium is released by desorption and not by bubble diffusion together with the argon atoms, since in the case of bubble diffusion both argon and helium are released simultaneously.

4.3.7. Summary

- 1. The percentage of argon built into the layer decreases with increasing IAR.
- The argon associated with the A1 and A2 peaks in the helium desorption spectra is not equal to the amount that can be found from the argon desorption spectra (for deposition temperatures lower than 1180 K).
- 3. The maximum concentration of argon that can be found in the molybdenum layers is 8e-3.
- 4. With increasing argon ion energy, the argon penetrates deeper into the molybdenum layer, and the higher the total amount of built in argon. The threshold energy for implantation of argon into a poly-crystalline molybdenum substrate is 100 eV.
- 5. With increasing depth of the argon atoms beneath the surface of the molybdenum, the time required for the argon atoms to reach the surface also increases.
- 6. The Ar^s peak near 450 K is associated with argon in the first atomic layer.
- 7. The Ar¹ peak near 950 K is associated with argon in second atomic layer.
- 8. The Ar^{II} peak near 1350 K is associated with argon in the third atomic layer. This is the only first-order desorption peak. It has an activation energy of 3.3 eV.
- 9. The Ar^B peak around 1500 K is associated with argon in the bulk. This peak shifts to higher release temperature when the argon is built deeper into the layer. The mechanism for release is similar to self-diffusion of molybdenum, as evidenced by the shift in the peak temperatures with increasing argon depth.
- 10.In thick layers a peak near 1200 K becomes visible and the Ar^I peak splits into two peaks. This is due to changes in surface orientation.
- 11. The defect associated with A1 and A2 peaks in the helium desorption spectra are similar to the Ar^B peak, while the Ar^B peak is also associated with other kind of defects as for example ArV₂ becomes ArV around 1250 K.
- 12. The ridge that becomes visible around 1800 K might be associated with vacancy clusters residing not too far under the surface.
- 13.Helium does not have a measurable influence on the argon desorption spectra. The argon on the contrary seems to influence the helium desorption spectra for overlayers of 50 Å and 100 Å and for helium decoration doses higher than 1.10¹⁵ He⁺ per cm².

5. Conclusions & Recommendations

5.1. Conclusions

The energy of the argon ions used in our IBAD experiments have the effect of net defect creation instead of annihilation. The defect concentration of layers deposited without ion beam assistance is about $2 \cdot 10^{-4}$. With IBAD, the defect concentration is about a factor 5 higher. The defects created with argon are all made in the first few Ångströms of the layer. Another consequence of the relative high energy of the argon ions is that argon atoms are incorporated in the layer. The higher defect concentration of argon atoms are a consequence of the 250 eV argon ions used in the experiments. The total argon concentration in the molybdenum layer is limited due to self-sputtering and is approximately $8 \cdot 10^{-3}$. In the argon desorption spectra four peaks can be distinguished:

- An Ar^s peak, which appears at 450 K, associated with argon that resides in the first atomic layer. Deposition of one atomic layer on top of it makes that this peak disappears completely.
- An Ar^I peak, which appears at 950 K, associated with argon that resides in the second atomic layer. There are two atomic layers, deposited on top of it, needed to make this peak disappear. The peak temperature of this peak is dependent on the surface orientation. When the surface becomes very rough the peak will split into two or more peaks around the temperature of 950 K. This combination of peaks could not be described with first-order desorption peaks, though the high temperature flank of the peak came very close to the flank of a first-order desorption peak.
- An Ar^{II} peak, which appears at 1350 K, associated with argon that resides in the third atomic layer. It is the only peak that can be described with a first-order desorption peak and has an activation energy of 3.3 eV. This means that the argon associated with this peak is released in one step from the molybdenum lattice.

An Ar^B peak associated with argon that resides in the bulk of the molybdenum.
When the argon is buried deep in the layer this peak is very clearly visible. It shifts to higher temperature when the argon is buried deeper, which is due to diffusional lag. From the shifting to higher temperatures it appears that the argon is released via a mechanism similar to the self-diffusion mechanism of the molybdenum. The activation energy of the argon release is 4.16 eV.

Because of the high energy needed for argon release nothing can be said off the additional defect the argon atom resided in.

5.2. Recommendations

From the experiments performed thus far, on a poly-crystalline molybdenum sample, no clear evidence could be found for the release mechanisms belonging to the argon associated with the Ar^{s} , the Ar^{l} , and the Ar^{ll} peaks. Van Veen *et al.* [1] and Kornelsen and Sinha [7] mentioned first-order desorption peaks for all three of the peaks, but this is not found in our experiments. Experiments on a mono-crystalline molybdenum sample could be useful to clear this point up. However a first view on results obtained from a (100) molybdenum crystal showed no significant first-order desorption peaks.

To obtain defect free layers with IBAD a beam with less energetic neutrals is needed. This means another ion source or a modification of the existing ion source. For good knowledge on the number of arriving argon ions during IBAD another way for measuring the current is needed, because to many unknown factors prevail in the way it is done at this moment.
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Samenvatting (Dutch summary)

Als een ionenbundel op een preparaat wordt gericht, waarop een laag gegroeid wordt, zal de kinetische energie die de ionen met zich meedragen leiden tot een modificatie van de groei. Een nadeel van deze techniek is dat onder bepaalde condities de ionen ingebouwd worden in de groeiende laag. Het is daarom belangrijk om te begrijpen hoe deze ionen zich gedragen in the laag nadat ze zijn ingebouwd.

In ons geval is argon gebruikt als assisterend ion. De techniek die gebruikt wordt voor het onderzoeken van de lagen is "Thermal Helium Desorption Spectrometry" (THDS). Tijdens het opwarmen van het preparaat tot 2000 K komt zowel het argon als het helium vrij uit de laag. Beide signalen worden gemeten.

Molybdeen is een belangrijk materiaal in verband met kernreactor technology waar het gebruikt wordt in de reactor wanden. In dit onderzoek is molybdeen gebruikt omdat er al een hoop information is over THDS-experimenten aan molybdeen. Het belangrijkste verschil met die experimenten is dat wij een molybdeen film groeien, terwijl in die andere experimenten defecten worden gecreëerd in the preparaat door deformatie en bombardementen met hoog energetische ionen.

Een molybdeen film kan gemaakt worden door depositie van molybdeen damp op een molybdeen substraat. Bij kamer-temperatuur ontstaan dan relatief veel defecten in de molybdeen laag, zoals vacatures en vacature-clusters. Om een laag met minder defecten te krijgen, kan de depositie-temperatuur verhoogd worden. In sommige gevallen is een verhoging van de depositie-temperatuur echter niet wenselijk (b.v. als er interdiffusie op kan treden tussen de verschillende lagen).

Een methode om dunne lagen te maken met (mogelijk) minder defecten zonder the temperatuur te verhogen is "Ion Beam Assisted Deposition" (IBAD). Met IBAD duidt men normaal gesproken ieder dunne lagen groeiproces aan waarbij een bron met energetische ionen wordt gebruikt tijdens het opdampen van een laag. Niet veel is bekend over de invloeden van het ionen-bombardement op de processen tijdens de groei van een molybdeen laag. Tijdens dit onderzoek is de invloed van de ionen-energie en de ionen-dosis op het aantal defecten bekeken. In dit werk is in het bijzonder gekeken naar de interacties tussen argon en molybdeen. THDS wordt gebruikt om dunne Mo Iagen (5 - 500 Å), opgedampt met en zonder ionen bundel assistentie (0.2 - 22 eV per Mo atom), te onderzoeken op defecten. Op het eerste gezicht vergroot ionen-assistentie de defect-concentratie in de film door de hoog energetische neutralen die altijd aanwezig zijn in de bundel. De ionenbron produceert 250 eV Ar⁺-ionen. Door interactie met de argon atomen aanwezig in de vacuumketel, tijdens IBAD, worden 250 eV argon atomen gecreëerd.

De neutrale argon atomen creëren defecten in de laag en worden daarin gevangen. In de argon-desorptie-spectra zijn vier pieken zichtbaar. Dit betekent dat er vier verschillende plaatsen in de laag voorkomen waaruit het argon vrij kan komen. Drie van deze pieken zijn gerelateerd aan het oppervlak en behoren tot plaatsen in de eerste vier atoomlagen. De exacte positie van de desorptie-pieken wordt bepaald door de oppervlakte orientatie. De vierde piek is een bulk piek. Deze piek verschuift naar hogere temperaturen als het argon dieper onder het oppervlak begraven wordt. Het ontsnappingsmechanisme voor argon wordt het "vacaturemechanisme" genoemd [1], waarbij argon gebruik maakt van vacatures aanwezig in de laag. Het komt overeen met het mechanisme achter "self-diffusion" van molybdeen. Dit mechanisme is anders dan voor helium, wat bevrijdt wordt uit zijn defect en interstitieel naar het oppervlak beweegt.

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