

Defects in Amorphous Silicon Films

**Thermal Desorption Spectrometry on
Amorphous Silicon Films Deposited with and
without Ion Beam Assistance**

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1. Introduction

Amorphous silicon films are used in a variety of devices, like flat panel displays,¹ electrographic drums for copiers,² and solar cells.³ When deposited at room temperature, these films contain many defects (point defects, small vacancy clusters, and voids), which influence the film properties to a large extent. For instance, they cause a deterioration of the photovoltaic properties because of the increased trapping chance and subsequent recombination of electrons and holes.⁴ In general, films with fewer defects can be produced by raising the substrate temperature, which results in a higher surface mobility of the deposited atoms. Although films can be grown to high perfection in this manner, it is desirable to reduce the deposition temperature in order to suppress segregation and diffusion of dopants in the growing film, and to avoid thermal stresses and interdiffusion in a multi-layer system.

A relatively new method (dating from the mid-1970's) to produce thin films with fewer defects without raising the temperature, is Ion Beam Assisted Deposition (IBAD), in which an ion beam is used to bombard the growing film during deposition. Ion-assisted deposition of metals has been found to change a variety of film properties, including adhesion, chemical inertness, diffusion properties, friction, surface roughness, resistivity, stress, micro-hardness, and magnetic properties.^{5,6,7} Many studies, on metals, have tried to establish what aspects play a dominant role in determining changes in film properties. From these studies it can be concluded that important features include porosity, crystallite size, preferred orientation, lattice strain, and impurities.^{5,7,8} Only little is known about the influence of ion assistance on atomic defects in the film and about the mechanisms that control atomic scale properties. Therefore, the physics that control the fundamental nanometer scale phenomena still needs to be explored.

This master's thesis presents a study of defects in amorphous silicon films deposited with and without ion beam assistance. The experimental technique employed to study the defects is Thermal Desorption Spectrometry (TDS).^{9,10,11} This technique uses ions of an inert gas as an atomic probe to detect the presence of defects in a solid. TDS studies on metals¹²⁻¹⁷ have shown that this method enables the study of small defects like impurities, vacancies, and small vacancy clusters in metals. Until now, most TDS studies described in literature have been performed on single-crystalline and poly-crystalline metals.

In our experiments, silicon films are deposited in an apparatus in which IBAD is combined in situ with TDS. All films are deposited at room temperature and their as-deposited structure is amorphous. Apart from using TDS to reveal as much as possible about the defect state of a thin film, it is an additional challenge to find out how far the TDS technique can be extended from crystalline materials to amorphous materials.

The purpose of this study is to find answers to the following questions. Is it possible to study defects in amorphous silicon films with the use of TDS? Is it possible to detect any difference between amorphous silicon films deposited with and without ion bombardment? What is the influence of an annealing treatment on the density and the sizes of defect in an amorphous silicon film?

This report is structured as follows. Chapter 2 gives a short review of the influence of an ion beam on film growth, the detection of defects with TDS, and the structure of amorphous silicon. Chapter 3 describes the experimental set-up, the experimental procedure, and the error estimation. After which chapter 4 presents and discusses the results of the experiments. Finally, chapter 5 presents the conclusions and recommendations for further work.

2. Theory

This chapter gives a short review of the three main subjects discussed in this thesis. Section 2.1 describes Ion Beam Assisted Deposition (IBAD) of thin films. Section 2.2 describes the detection of defects with Thermal Desorption Spectrometry (TDS) and presents the equations which are used to interpret the desorption spectra. Finally, section 2.3 describes the defect structure of amorphous silicon, in order to gain insight in the types and density of defects that are likely to be detected with TDS.

2.1. Ion beam Assisted Deposition (IBAD)

Ion beam assisted deposition is the process of simultaneous thin film deposition and directed ion bombardment. This technique is used to modify the growth process of the film, and has been well described in the literature.^{5-8,18,19} Here, we will only give a brief description.

2.1.1. General description of film growth

The processes which may occur during film growth from a vapor source are illustrated in figure 2.1. Single atoms arriving with an energy of tenths of eV's at the surface, diffuse over the surface until they are lost by some process such as re-evaporation, formation of a critical size nucleus, capture by an existing cluster, or trapping at a special site.

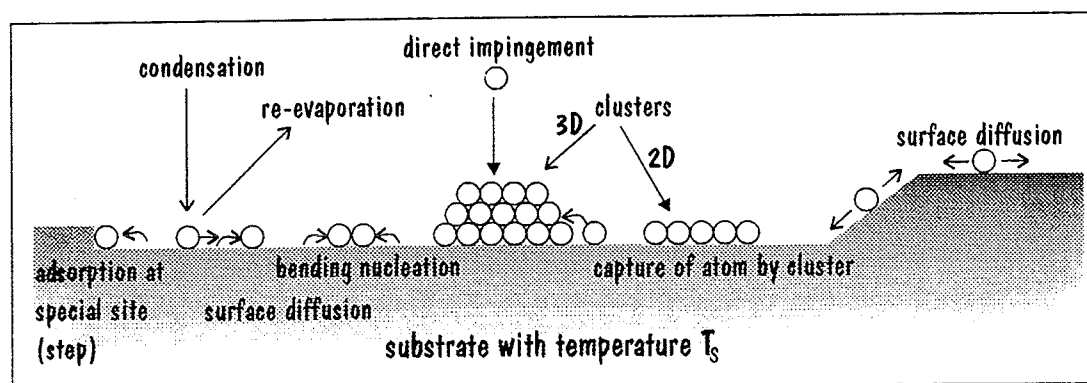


Figure 2.1: Atomic processes at a surface during nucleation and growth of a thin film.
From Venables (ref. 20)

In the early stages of film growth (first ~ 20 Å), three different modes are recognized; they are presented schematically in figure 2.2. Frank-van-der-Merwe or layer-by-layer growth involves the growth of the film layer by layer with complete coverage of the surface. Volmer-Weber or island-type growth results in the formation and growth of islands of several layers thick, before complete surface coverage occurs. Stranski-Krastanov or mixed growth is an intermediate case, in which the formation of a monolayer is followed by the growth of islands.

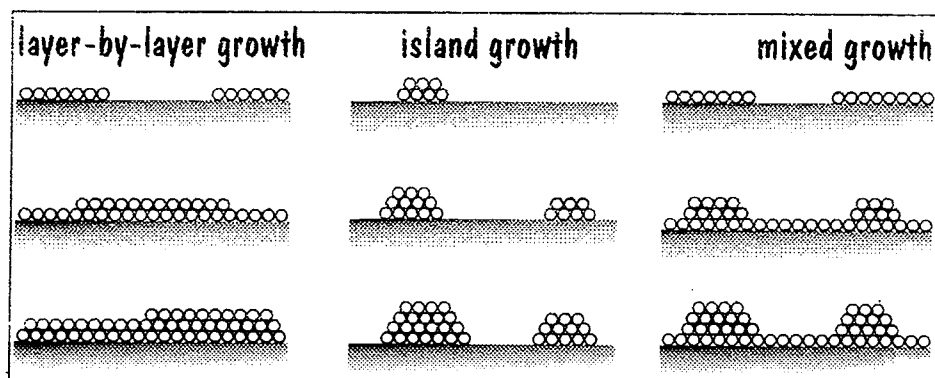


Figure 2.2: Three types of film growth

In general, the type of growth is controlled by 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 gradually decreases when (subsequent) layers are added. Mixed growth occurs when the gradual decrease in binding energy is disturbed by some factor such as lattice mismatch or orientation, and island formation becomes more favorable. The condition of the substrate surface also plays an important role. Pollution or initial roughness facilitate the process of nucleation of small clusters and hence promotes island growth. All three types of growth occur widely for crystalline films.

These types of growth only occur when there is sufficient adatom mobility to enable configurations to approach their equilibrium state. If the adatom diffusivity becomes sufficiently low, the mode of growth is controlled by kinetic rather than thermodynamic factors. Indeed, under slow adatom diffusion, clusters will form even when the adatoms are bound more strongly to the substrate than to each other. This result can be explained by the random probability statistics governing the point of attachment of an adatom to the substrate and is described in detail by Machlin.²¹ Consequently, amorphous silicon films which grow under low mobility conditions, can be expected to form islands.

The early stages of film nucleation and growth ultimately influence the microstructure of a deposited film. For example, the island type of growth is likely to induce inhomogeneous, columnar film growth, while layer-by-layer growth is more likely to result in homogeneous film growth. Movchan and Demchishin²² showed that the microstructure development is also strongly influenced by substrate temperature, expressed as a fraction of the melting temperature (T/T_m). Their findings are summarized in the Structure Zone Model (SZM) in which three zones (zone 1, 2, and 3) were identified. Thornton²³ extended this model to sputtered crystalline metal films by adding another parameter (sputtering gas pressure) to the model and established a fourth zone (zone T).

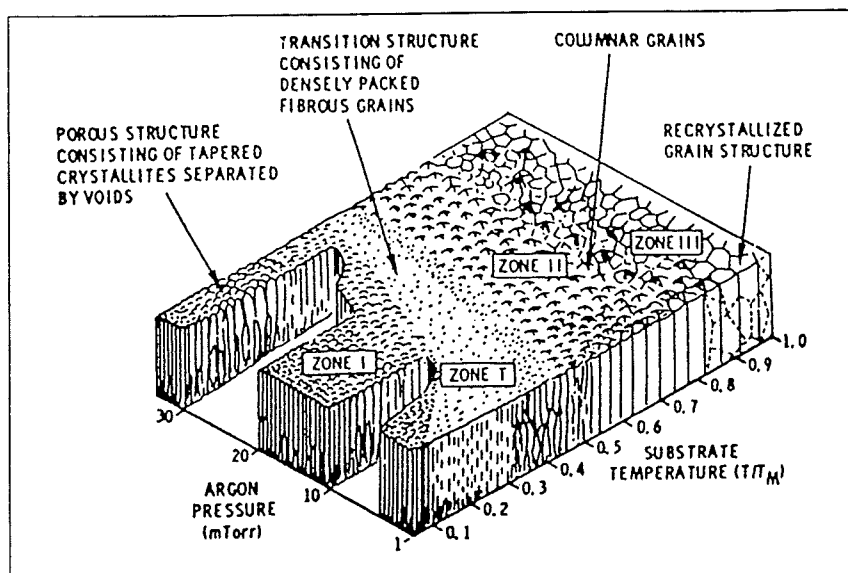


Figure 2.3 Schematic representation of the microstructure and surface topography as function of the substrate temperature according to the Structural Zone Model for Ar-sputtered films. From Thornton (ref. 24).

Figure 2.3 schematically shows the dependence of the microstructure and surface topography on the substrate temperature and argon sputtering gas pressure according to Thornton's model. Zone 1 microstructures form at $T/T_m < 0.3$ and are characterized by columns with pipes (or low density regions) along the grain boundaries. This structure results when the adatom diffusion is too limited to overcome the effects of shadowing.²⁵ Shadowing produces open boundaries, particularly under conditions of non-perpendicular flux, because the high points receive more flux than the low points (see figure 2.4). Zone T or transition microstructures form at $T/T_m \approx 0.3-0.5$ and are also dominated by shadowing effects but have finer structures which appear fibrous. Zone 2 microstructures form at $T/T_m \approx 0.5-0.8$ and are dominated by adatom surface diffusion processes. The structure has columnar grains that are well joint at the boundaries. Zone 3 structures, which form at $T/T_m \geq 0.8$ are dominated by bulk diffusion processes. Recovery and recrystallization processes typically occur in this temperature regime, driven by the minimization of strain energy and surface energy of the grains.

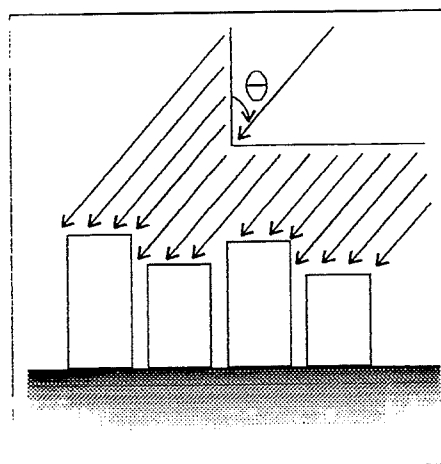


Figure 2.4 Schematic representation of shadowing of intercolumnar regions deposited under an angle with respect to normal incidence

It is important to stress that the SZM is based on experimental results for films of micrometer thickness. However, Hentzell et. al.²⁶ have proposed a zone model for thinner evaporated metal films, which is quite similar. Although the SZM was developed primarily to explain the relation between microstructure and preparation conditions in the case of crystalline metallic films, there have been several recent reports of its application to amorphous semiconductor films.^{23,27-29} According to these reports, the first two zones (zone 1 and zone T) apply to microstructure of amorphous films, while zones 2 and 3 apply only to the crystallized layers.

2.1.2. Influence of an ion beam on a growing film

The processes by which energy is transferred from an energetic ion to a solid are important fundamentals for a better understanding of how particle bombardment interacts with the growing film to modify the microstructure and the film properties. These processes are described next.

Some examples of the influence of an ion beam on the processes during film growth are illustrated schematically in figure 2.5. The incoming ion loses energy by inelastic collisions, which produce electronic excitations, and by elastic collisions, which replace atoms from their lattice positions. Inelastic collisions dominate in the MeV regime (which is much higher than the ion energies used in the experiments described in this report) and are neglected in this thesis. Elastic collisions dominate in the range of a few tenths of eV's to keV's. The displaced atoms produce additional collisions and each atom continues to undergo collisions until the energy drops below the level needed to displace an atom from its lattice position (~ 22 eV for silicon).³⁰ The remaining energy is dissipated as heat in lattice vibrations. Such a series of collisions is called a collision cascade.

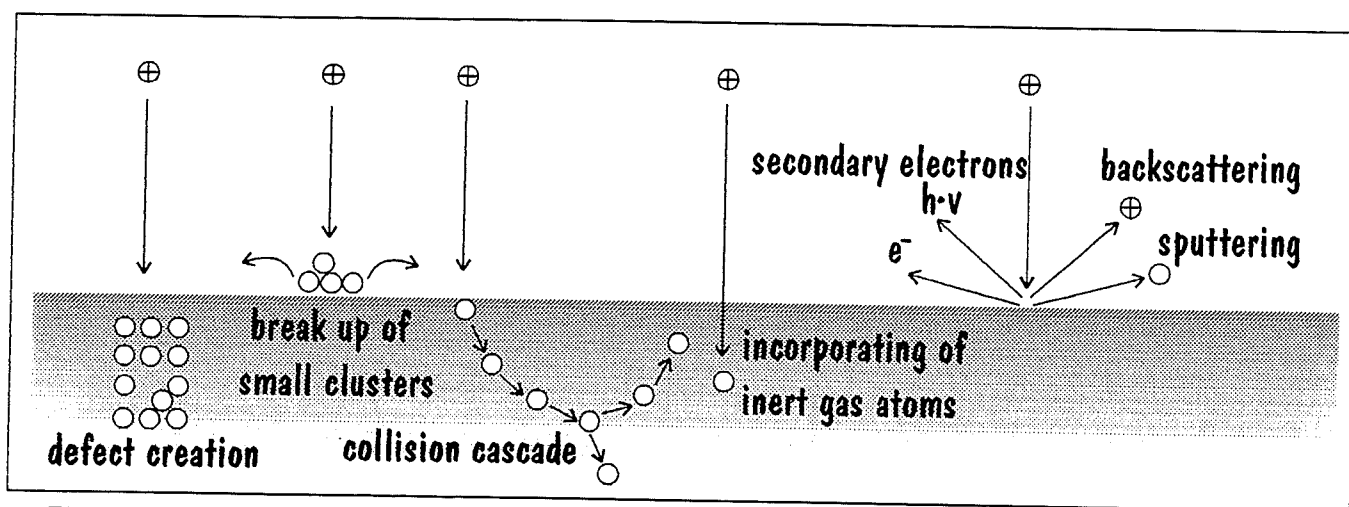


Figure 2.5 Atomic processes at and below the surface during ion bombardment of a growing film

Cascades near the surface can sputter atoms from the surface and cause desorption of adsorbed species.³¹ Just below the surface, collision cascades increase the kinetic energy of the film atoms. A part of this energy can be transferred to atoms at the surface, which results in an increase of the adatom mobility. Most important are head-on collisions between the energetic ions and adatoms. Through these collisions the mobility of the adatoms is increased, which enables them to find energetically more favorable positions.^{32,33} It is therefore often claimed³⁴⁻³⁸ that ion beam assistance results in more regularly stacked films containing fewer defects (like point defects, vacancy clusters, voids) than films prepared without ion bombardment.

Apart from the increase in energy of the surface layers, sputtering of adatoms, and increase in mobility of the adatoms, there are two additional effects of the ion beam assistance. (i) Bombardment of a small atomic cluster (formed during the early stage of the film growth) by an energetic ion can lead to dissociation of the cluster. Clusters reduced to sub-critical size are energetically unfavorable and will spontaneously dissociate to form adatoms, some of which desorb or diffuse towards larger clusters.³⁹ (ii) A collision sequence can lead to coalescence of voids near the surface and to the collapse of ledges overhanging initial voids.^{40,41} This process, known as forward sputtering, is illustrated in figure 2.6.

The ability to control the additional supply of energy is essential for growing IBAD films with varying degrees of imperfection. The influence of an ion beam on the growth of a film and on its resulting physical properties depends on the energy and mass of the bombarding ions, the substrate temperature, and the flux ratio of the ions and deposited atoms (normally defined as Ion-to-Atom arrival Ratio (*IAR*)). The role of ion bombardment on the fundamental processes during film growth is not generally understood, mainly because the influence of the separate parameters is hard to investigate on atomic scale. However, some general remarks about the influence of the different parameters can be made.

- The energy used in IBAD is on the order of a few tens to a few hundred eV. This energy should be high enough to increase the mobility of a large number of surface atoms, yet low enough to prevent a large fraction of the ion energy being lost deeper in the lattice and leaving vacancies that cannot be filled by arriving vapor species.
- In principle, an appropriate ion of any mass can be used. In practice heavier masses may be preferred for two reasons. First, since heavy ions have larger interaction radii than light ions, they are able to displace multiple adatoms in one collision. Secondly, the penetration depth of heavier ions is shallower, so that bulk defects, if created, are also shallower, and hence can more easily migrate to the surface where they annihilate.¹⁸
- In general, an increase in *IAR* causes a more regular arrangement of atoms resulting in a film containing fewer defects. This is easily understood because higher *IAR* results in more displaced atoms at the surface and hence in a higher surface mobility. Caution should be taken when bombarding with high energy ions. In this case an increasing *IAR* can lead to an increased incorporation of the bombarding ions, which can be unfavorable to the film properties (like conductivity).
- An increase in substrate temperature during deposition causes an increase in atom mobility. As is shown in the SZM a change in film structure from columnar films at low substrate temperatures to more homogeneous films at a higher substrate temperature is observed.

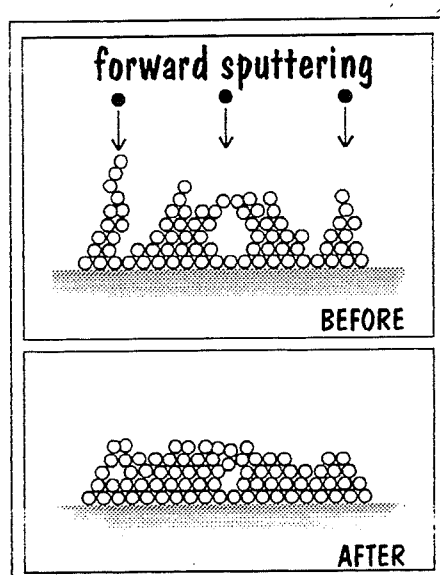


Figure 2.6 Forward sputtering: Coalescence of voids and collapse of an overhanging ledge

2.2. Thermal Desorption Spectrometry (TDS)

2.2.1. Description of a TDS experiment

Thermal desorption spectrometry is well described in the literature,⁴²⁻⁴⁵ and here only a brief description is given. In a TDS experiment ions are used as an atomic probe to detect the presence of defects in a solid. In the experiments described in this thesis, helium is used as probe atom because of its inertness and small atomic radius. The latter property enables helium to be bound to very small defects.

A TDS experiment exists of three successive steps, implantation, trapping, and desorption of helium. During the implantation step, helium is implanted into the film with low energy, creating

little or no extra damage. The threshold energy for damage production is given by

$$E_{th} = E_d \frac{(m + M)^2}{4mM} \quad (2.1)$$

where E_d is the displacement energy for silicon (= 22 eV), m is the mass of the implanted ion and M is the atomic mass of the solid. It can be calculated from eq. (2.1) that the E_{th} for the implantation of helium into silicon is about 50 eV.

Subsequent to the implantation, helium ions which now have become atoms, get trapped in the film. In contrast with the results for metals, the solution enthalpy of interstitial helium in silicon is low (0.5 eV), while the helium migration energy is large (1.2 eV). These values have been reported by Wieringen and Warmoltz⁴⁶ on the basis of permeation measurements in crystalline silicon. Because of this relatively high migration enthalpy, the implanted helium is expected to be immobile at the implantation temperature of about 300 K, and will become mobile during the heating step, at about 400 K.^{11,47} Consequently, following the implantation all helium atoms are expected to become trapped in defects or interstitial positions in the film.

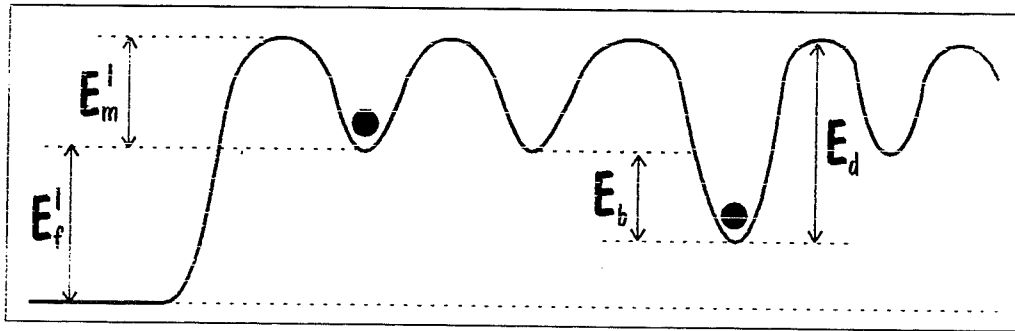


Figure 2.7 Energy diagram of helium atoms in a film with a defect that acts as a trap

The energetic picture of helium in a defect that can act as a trap is shown in figure 2.7. In order to bring helium from the vacuum into an interstitial position in a crystal, helium has to overcome an energy barrier, which is the sum of the interstitial formation enthalpy E_f^I , and the interstitial migration enthalpy E_m^I . If the enthalpy of helium in a solid is larger than E_m^I it can migrate over interstitial positions through the solid. A helium atom is dissociated from a trap if its enthalpy exceeds the dissociation enthalpy E_d , which is the sum of the binding enthalpy to the trap E_b , and the migration enthalpy.

During the desorption step, the film is heated with a constant heating rate. Helium dissociates from the defects, is released at the surface, and can be measured by a mass spectrometer.

Measurement of the helium release rate as a function of the temperature results in desorption peaks, which correspond to release of helium from the different defects present in the sample. An example of a desorption spectrum is given in figure 2.8. The area of the desorption peak yields information on defect concentrations. The position of the desorption peak on the temperature axis gives information on dissociation enthalpy and attempt frequency of helium in a defect. The shape of the peak gives information about the release mechanism involved.

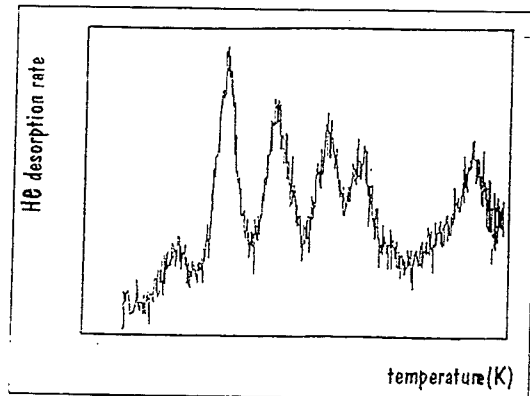


Figure 2.8 Example of a desorption spectrum

A TDS experiment gives unambiguous results when defect densities are low, thus when helium diffusion length to the surface is smaller than the average distance between the defects. At higher defect densities, retrapping of dissociated helium plays a role, which effects the shape of the desorption peak. Since in such cases the distribution of traps over the depth of the film is also important, the interpretation of the desorption spectra becomes more complicated.

2.2.2. Basis equations describing a TDS experiment

This section presents a brief theoretical description of a TDS experiment. A more general review is given by Hoondert.⁴⁸ The three processes of a TDS experiment, implantation, trapping, and desorption can be described by the following equation.

Let $c_i=c_i(x,t)$ denote the concentration of lattice sites of type i accessible for helium atoms, at depth x below the surface of the sample, at time t . In general there are many different types in a sample, for example interstitial positions and different kinds of defects in which the helium atoms can be trapped with different binding energies. Let N denote the number of site-types. Let furthermore $n_i=n_i(x,t)$ denote the concentration of helium atoms in the lattice sites of type i , and $v_{ij}=v_{ij}(x,t)$ denote the jump frequency of helium atoms out of a site of type i into a site of type j .

Then the helium concentration in the sample can be described by the N coupled partial differential equations

$$\frac{\partial n_i}{\partial t} = c_i \sum_j D_{ji} \frac{\partial^2 n_j}{\partial x^2} - n_i \sum_j D_{ij} \frac{\partial^2 c_j}{\partial x^2} + n_i \sum_j v_{ij} c_j + c_i \sum_j v_{ji} n_j + B_i \quad (2.2),$$

$(i=1,2,\dots,N)$

where

$$D_{ij} = \frac{1}{6} v_{ij} \lambda^2 \quad (2.3)$$

is the diffusion coefficient for $i \rightarrow j$ jumps (λ being the typical jump distance), and v_{ij} can be expressed as

$$v_{ij} = v_d \exp\left(\frac{\Delta S_{ij}}{k}\right) \exp\left(-\frac{E_{d,ij}}{kT}\right) \equiv v_{0,ij} \exp\left(-\frac{E_{d,ij}}{kT}\right) \quad (2.4)$$

in which v_d is the typical Debye frequency (10^{13} s^{-1}), k the Boltzmann constant, ΔS_{ij} the entropy difference associated with a helium atom jumping from an i -site to a j -site, and $E_{d,ij}$ the dissociation energy associated with such a jump. The Debye frequency and the entropy factor are often combined into a 'frequency factor' v_0 . Finally, $B_i=B_i(x,t)$ in eq. (2.2) is the helium implantation rate profile i.e., the concentration of helium atoms having slowed down to thermal energies into sites of type i per unit time. Clearly, when the helium ion beam is off, $B_i=0$. When the helium beam is on, we assume that $B_i(x)$ is proportional to the local concentration of i -sites, i.e., that

$$B_i(x) = \alpha c_i(x) \exp\left(\frac{x - R_p}{\Delta R_p}\right)^2 \quad (2.5),$$

where, R_p is the so-called projected range, of which the RMS width is ΔR_p , the straggle, and α is chosen in such a way that $\int_0^\infty B_i(x)dx$ corresponds to the total flux of implanted helium ions. The Gaussian shape is discussed in the next section.

In this theoretical description only one dimension is considered, because in the TDS experiments the ion-beam diameter (10^{-3} - 10^{-2} m) is much larger than the ion-implanted depth range (10^{-10} - 10^{-7} m), we assumed that the relevant film properties do not vary rapidly with the in-plane coordinates y and z .

In all cases presented here we assume that E_{dij} and ΔS_{ij} do not depend on the type of the receiving lattice site j , so that we can write E_{di} , ΔS_i , v_i , and hence also D_i , instead of E_{dij} , ΔS_{ij} , v_{ij} , and D_{ij} , respectively. Furthermore we assume in most cases that the trap concentrations c_i are functions of x only (not t).

In the following it is explained how these equations are used to describe the implantation and the desorption of helium in a TDS experiment.

2.2.3. Ion implantation

During the implantation step, helium atoms are ionized in an ion source, accelerated to the sample, and stopped at a certain depth in the film. The resulting implantation profile, $B(x)$ can be calculated using the Monte Carlo program TRIM (TRansport of Ions in Matter)⁴⁹. A few drawbacks of TRIM must be mentioned. TRIM assumes the target structure to be completely random and hence the sequence of collisions of the implanted projectiles and the recoil atoms is treated as a random process in which the distance between two successive collisions is constant. In practice the atoms in a crystalline solid are ordered in periodic structure and even atoms in amorphous silicon are not completely randomly ordered but are placed in a Continuous Random Network (which is described in more detail below). In both cases the distances between two successive collisions varies through the material and thus the constant value chosen by TRIM is only an approximation. Moreover, in a crystalline material the incoming ion can move great distances through channels formed in the crystallographic directions, which is not possible in the random model used by TRIM. Furthermore, TRIM evaluates the collisions one by one (the binary collision approximation). This approximation can only be applied at high ion energies when the stopping range is mainly due to electronic excitations, and the nuclear collisions are very far apart. At low ion energies the binary collision approximation breaks down, because the nuclear collisions occur at short distance from each other and are no longer independent. Therefore, with TRIM no calculations can be performed with implantation energies below 100 eV, and even the values near 100 eV are not very reliable.

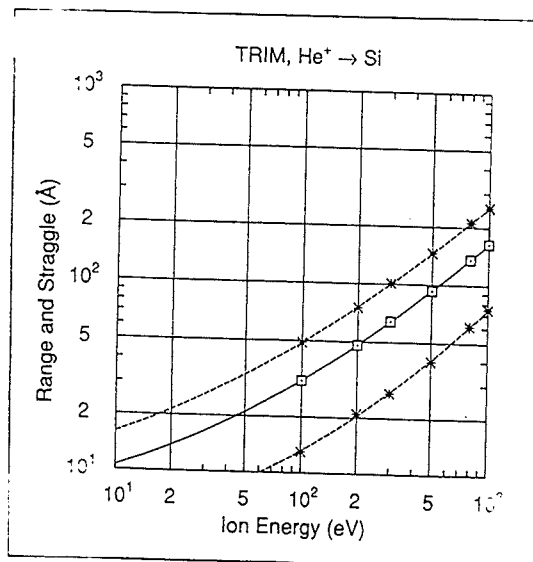


Figure 2.9 Average implantation depth as function of the implantation energy for the implantation of helium into silicon as calculated with TRIM. The symbols $\square$ denote the projected range R_p , the symbols $*$ indicate the range $R_p + \Delta R_p$ to $R_p - \Delta R_p$

It turns out that $B(x)$ as calculated with TRIM can be reasonably approximated by a Gaussian function of which the average implantation depth lies at $x=R_p$, R_p and ΔR_p for the implantation of helium into silicon, are calculated as function of the implantation energy and are shown in figure 2.9 and table 2.1.

Table 2.1: Average Implantation depth R_p , straggle ΔR_p and number of vacancies created per implanted ion, for the implantation of helium into silicon versus implantation energy, calculated with TRIM. The input values used are, helium mass: 4.0026 amu, density of silicon 2.321 gr/cm³, displacement energy 22 eV, lattice binding energy 1,2 eV, number of calculated ions 5000.

Implantation energy [eV]	R_p [Å]	ΔR_p [Å]	vacancies/ion
100	31	18	0.4
200	48	27	2
500	69	53	4
800	136	75	7
1000	164	89	8

TRIM can also be used to calculate the amount of vacancies created during implantation. The number of defects created by implantation of helium in silicon is calculated with TRIM for a range of implantation energies. The results of these calculations are shown in table 2.1. It should be noted that TRIM neglects the effect of the recombination of a Frenkel pair. Therefore, the values calculated by TRIM should be divided by 10 which in general gives a much better approximation. The values shown in table 2.1 are the uncorrected values.

Following the implantation and thermalization (slowing down to thermal energies), helium is trapped by an interstitial position or a defect. The resulting trapped particle profile can be calculated with eq. (2.2).

2.2.4. Desorption

2.2.4.1. first-order desorption kinetics

Subsequent to the helium implantation and trapping the sample is heated. During the heating cycle the following processes take place. First the helium atoms in the interstitial positions become mobile and start to diffuse till they become trapped in a defect or are released at the surface. At higher temperature helium atoms dissociate from the 'traps', start to diffuse and leave the sample. These processes, called desorption are described by eq. (2.2).

If, for the sake of simplicity, the system is assumed to consist of only two types of trapping sites, interstitial sites with a concentration of almost unity ($c_{int} \approx 1$) and 'traps' with a very low concentration ($c_t \ll 1$), and if the interstitial diffusion is so fast (D_{int} is large) that there is virtually no interstitial helium in the sample ($n_{int} = 0$), then eq. (2.2) can be rewritten into the simplified form

$$\frac{dN}{dt} = -Nv_0 \exp\left(-\frac{E_d}{kT(t)}\right) \quad (2.6),$$

where N denotes the total number of helium atoms trapped in the sample per unit area.

This equation can be solved for the known temperature program

$$T(t) = T_0 + \beta t \quad (2.7),$$

with T_0 the starting temperature (300 K) and β the heating rate (10 K/s or 40 K/s) after which the helium desorption flux L , i.e. the desorption spectrum, can be calculated as

$$L(T(t)) = \frac{-dN}{dt} \quad (2.8).$$

This process is called first order desorption and describes helium dissociation from a defect in a single activated jump.

A first order desorption peak can be recognized by its peak shape. When v_0/β is not too far from 10^{11} K^{-1} , the full width at half height, $\Delta T_{1/2}$ is to a good approximation equal to $0.078 T_{max}$. Where T_{max} is the temperature at which the maximum of the desorption flux occurs. Its value can be obtained from

$$\frac{\beta E_d}{kT_{max}^2} = v_0 \exp\left(-\frac{E_d}{kT_{max}}\right) \quad (2.9).$$

Helium interactions with defects in silicon differ considerably from those in metals (much lower solution enthalpy and much higher migration enthalpy), and it is reported by van Veen¹¹ that entropy effects play an important role. Van Veen argues that the dissociation energy of helium from any defect in silicon should not exceed 1.7 eV (being the sum of the solution enthalpy of interstitial helium in silicon (0.5 eV) and the helium migration enthalpy (1.2 eV)), assuming that the van der Waals binding of helium with silicon can be neglected. Applying the first order desorption equation (2.6) with v_0 of the order of the Debye frequency (10^{13} s^{-1}), desorption temperatures T_{max} no higher than 650 K would be expected. However, desorption spectra derived by van Veen show helium desorption at temperatures as high as 1200 K.¹¹ Van Veen explains the difference between expectation and result by the fact that entropy effects are so important that $v_0 = 10^{13} \text{ s}^{-1}$ is a much too high value. As can be seen from eq. (2.4), a negative entropy difference is needed to explain the discrepancy. It is reasoned that helium atoms in a defect have a relatively high entropy, upon leaving the defect helium arrives at an interstitial state where it can be considered as a harmonically vibrating particle in a deep potential well with a low entropy.

If one is sure that instrumental errors have been removed from the experimental desorption peak, and that the conditions for first-order desorption apply, E_d and v_0 can be determined by the time derivative of solution of $N(t)$ of eq. (2.6) to the experimental data. An alternative method, less prone to errors, is to measure a desorption peak with different heating rates β . The relation between T_{max} and β is given by eq. (2.9), which becomes after taking the logarithm,

$$\ln \frac{\beta}{T_{max}^2} = \ln\left(\frac{v_0 k}{E_d}\right) - \frac{E_d}{kT_{max}} \quad (2.10).$$

Thus, if a variation of heating rate is performed, E_d and v_0 can be determined from an Arrhenius plot in which $\ln(\beta/T_{max}^2)$ is plotted against $1/T_{max}$.

2.4.4.2. Numerical analyses using the computer program HOP

Analytical solutions for eq. (2.2) can only be derived for simple cases, like the one treated in the previous paragraph. Under practical conditions, which are often more complicated, one has to

rely on numerical methods to solve these equations. Hoondert⁴⁸ has described how eq. (2.2) is made suitable to implementation in the computer program HOP (Hopping Of Particles). One of the benefits of using computer algorithms to calculate the desorption spectra is that the diffusion process can be described more precisely. In analytical solutions it is assumed that atomic diffusion is a continuous process. This is an approximation since the distance between two interstitial positions (typically $\lambda=2 \text{ \AA}$) is not negligible small in comparison to the implantation depth of the ions (typically $R_p=50 \text{ \AA}$). The diffusion process is therefore better described by a series of jumps back and forth over discrete positions. Moreover, the equations can be solved for almost any conceivable experimental condition. For instance, high and non-uniform defect concentrations and an arbitrary number of different traps, with a variety of binding energies, concentrations, and distributions. Thus, by using HOP it is possible to calculate desorption spectra, given any trial combination of experimental conditions, and compare them with the experimental spectra.

2.3. Amorphous silicon

For a better understanding of the results to be presented in chapter 4, this section gives a brief review of some structural features of amorphous silicon films. Section 2.3.1 describes the arrangement of silicon atoms in the amorphous silicon network, and the kind of defects that might exist in this network. Section 2.3.2 describes structure development during the growth of thin amorphous silicon films.

2.3.1. Atomic structure and defects

The structure of amorphous materials exhibits only short-range order i.e the regions where a predictable arrangement of atoms occurs are very small. Within a very few atomic spacings, this order breaks down, and no long-range correlation in the geometric positioning of atoms is preserved. The physical state of amorphous silicon is believed to be best represented by a continuous random network (CRN).⁵⁰ The CRN of amorphous silicon as constructed by Polk⁵⁰ is shown in figure 2.10. In the ideal CRN model for amorphous silicon, each atom is fourfold coordinated and in this respect, the short-range order of the amorphous phase is equal to that of the crystalline phase. The lack in long-range order arises from the variation in bond angles in the amorphous structure, which deviate roughly 7° to 13° (i.e. 6-12% of the ideal value of the bond angle of 109.5°). According to most reports bond length distortions are insignificant ($\sim 1\%$).

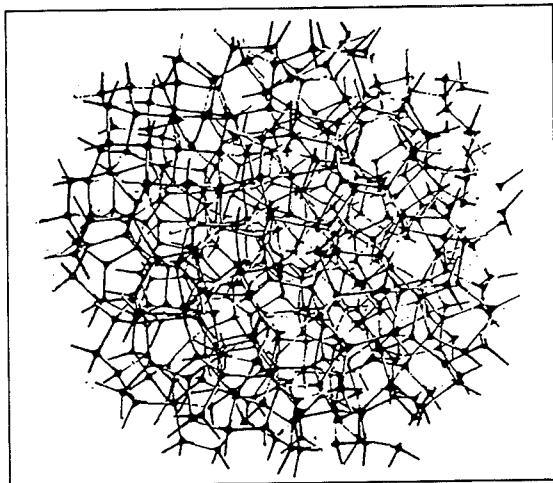


Figure 2.10 The Continuous Random Network (CRN) of amorphous silicon as build by Polk (1971). From Polk (ref. 50).

A CRN describes an 'ideal' random network, in which all bonds are connected. It has been shown that the structure of 'real' amorphous silicon is not ideal and consists many defects such as point defects, small vacancy clusters and voids. Examples of point defects are atoms that contain less than four bonds (undercoordinated atoms), self-interstitials, and impurities. There is

good evidence for the belief that the main defect in amorphous silicon is the dangling bond (a 3-coordinated group IV atom). The density of dangling bonds in device quality amorphous silicon films is about 10^{19} cm^{-3} . Examples of undercoordination of silicon atoms in the network are shown in figure 2.11. Also, 5-coordinated atoms have been suggested as a defect candidate,^{51,52} but the existence of this defect has not yet been proven experimentally.

Another characteristic of the amorphous silicon structure is the distribution of 5-, 6- and 7-membered rings of silicon atoms (see also fig. 2.11). Crystalline silicon is solely build up of 6-membered rings.

The amorphous films studied in this report are deposited at room temperature by electron beam evaporation. These films are known to contain interconnected voids.^{53,54,55}

These voids can be removed by annealing at about 480 K for a period up to one hour.⁵⁶ It is recently established that further anneals below the crystallization temperature ($\sim 1000 \text{ K}$) induce changes in the amorphous silicon network structure, which lead to a reduction in free energy of the amorphous structure.⁵⁶ This process is known as structural relaxation. The major contribution to this reduction in free energy is due to a decrease of the bond angle distortion.⁵⁵ During structural relaxation the number of dangling bonds is found to decrease roughly with a factor of three.⁵⁷ Roorda⁵⁶ has shown that this decrease in number of dangling bonds contributes only about $\sim 1\%$ to the total energy release.

It was initially believed that structural relaxation could solely be ascribed to a decrease of the bond angle distortion, leading to a decrease in structural disorder in the amorphous silicon network. More recently, it has been suggested that structural relaxation of amorphous silicon is entirely controlled by the disappearance of 'vacancy-like' defects in the amorphous silicon network⁵⁶. These 'vacancy-like' defects are expected to be accompanied by a strain field (disordered bonds), similar to that surrounding point defects in crystalline silicon. Consequently, the decrease in defect population induces a decrease in bond angle distortion, which explains the large energy release.

2.3.2. Growth of thin amorphous silicon films

In the initial stage (first $10 \text{ \AA}$) of the growth of amorphous silicon films, small two dimensional localized islands are formed on the substrate (see section 2.1.1). The subsequent development of the amorphous structure is dependent on the angle of incidence of the silicon vapor^{58,59} and the substrate temperature.

According to the literature, in almost all amorphous silicon films deposited at low temperatures (near room temperature) a large defect density is found.^{29,53,54,57,60-62} This result has been associated with the existence of a network of microvoids which develops during the growth of the material. The origin of these voids has been attributed to a lack of surface mobility of the deposited atoms. In later studies, the void structure in amorphous silicon films has been studied by electron microscopy,⁶³ low-angle x-ray scattering,⁶⁴ and porosity measurements.⁶⁵ From these studies it was concluded that the amorphous silicon films deposited at low temperatures consist of

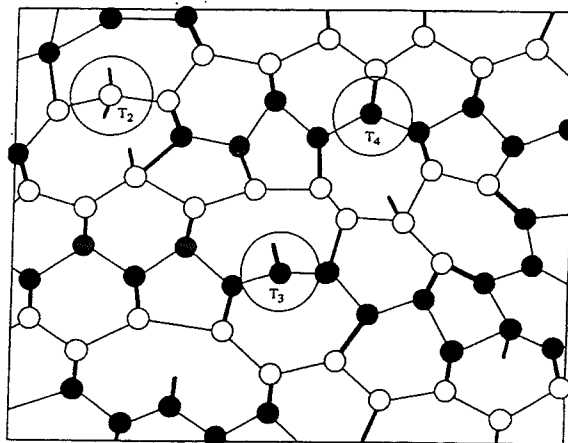


Figure 2.11 Schematic representation of the covalent bonds in amorphous silicon. T_2 , T_3 , and T_4 represent silicon atoms with 2, 3, and 4 bonds, respectively. The black circles have a bond pointing upwards. From Möller (ref. 3).

columns with low density regions between the columns. These results are in accordance with the Structure Zone Model (SZM) (described in section 2.3.1), which shows that a high substrate temperature result in uniform films, while columnar growth becomes more favorable at low temperatures. Columnar growth is also favored by increasing angle of incidence.⁵⁸

It is shown by Messier that the size of the columns and the voids between the columns in amorphous silicon films (prepared at $T/T_m \leq 0.5$) depends on the film thickness.^{53,57} This conclusion is based on extensive preparation and characterization studies of both thin and thick films (0.01 to 30 μm) of the tetrahedrally bonded amorphous semiconductors. An example of the findings described by Messier⁵⁷ is given in figure 2.12. This figure shows a schematic representation of interrelated structural units along with representative micrographs for amorphous germanium (a-Ge) films. From a series of a-Si:H films, prepared at $T/T_m=0.27$ under low bombardment conditions, Messier derived that as a function of film thickness five distinct levels of physical structure could be identified. The five characteristic column sizes are 1-3, 5-20, 20-40, 50-200 and 200-400 nm. The first appear in the first 100 Å of the film, the second in the range of 100 to 1000 Å, the third in films of 1000 to 10000 Å etc. It should be noted however, that according to Messier the appearance of distinct levels may be influenced by the finite number of observations.

The columnar structure appears to consists of nearly parallel, rod shaped regions of high density that are surrounded by voids (actually lower density regions). The smaller voids and columns are still present within the larger columns. This process continues to repeat itself with yet larger column and void sizes⁵⁷.

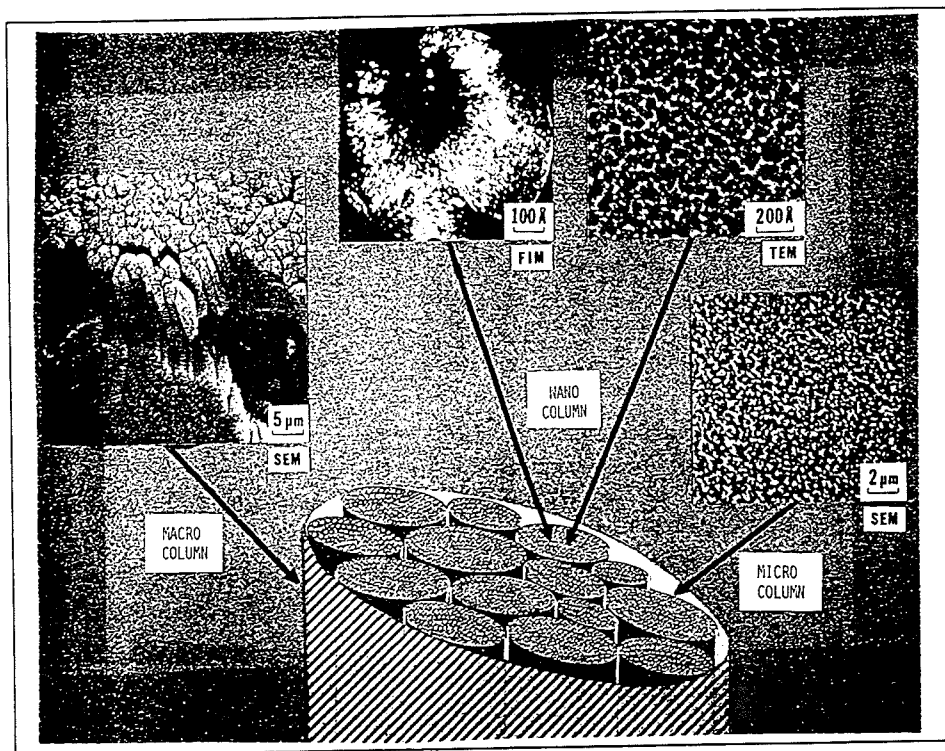


Figure 2.12: Schematic representation of the general physical structure of a thin film prepared under low mobility conditions. The scanning electron, transmission electron, and field ion micrographs are for sputtered amorphous germanium films. From Messier (ref. 57).

3. Experimental

This chapter provides information about the instrumentation used in the experiments, the experimental procedure, and the error estimation. The experimental procedure is a combination of two processes: deposition of films (with or without ion beam assistance) and investigation of the defect structure of the deposited films with Thermal Desorption Spectroscopy (TDS). Both facilities are combined in one apparatus, developed by T.P. Huijgen and J. van der Kuur. The experimental set-up and the experimental procedure of Ion Beam Assisted Deposition^{5,6} (IBAD), and of TDS^{43,44,66,67} are both well documented in literature. Here, we will give only a brief description. This chapter is structured as follows. Section 3.1 describes the experimental set-up. Section 3.2 describes the experimental procedure. Section 3.3 describes the error estimation. Finally, section 3.4 gives a short review about the additional techniques which are employed to estimate the impurity concentration, and to characterize the surface morphology, of both an amorphous and a crystallized layer.

3.1. Experimental set-up

The experimental set-up is shown schematically in figure 3.1. In addition figure 3.2 gives a schematic presentation of the complete IBAD system with all the interconnected devices. The TDS system is attached to the IBAD system and together they are placed in a vessel that is connected to a pump system. The base pressure of the system is 10^{-10} mbar after baking to about 520 K. These ultra high vacuum conditions are required because during desorption the partial pressure of the helium gas to be detected is low, and the signal-to-noise ratio should be as high as possible.

Silicon films are deposited (with a typical deposition rate of ~ 2 Å/s) on a substrate, positioned in a ceramic sample holder (shown in figure 3.3), which is placed at position 1 in fig. 3.1. The substrate consists of a polycrystalline molybdenum bottom part of 3 mm thickness and 10 mm diameter. The first amorphous silicon film is deposited on the clean molybdenum surface. After TDS i.e. heating to 1400 K a crystallized silicon film originates on top of the molybdenum substrate. All experiments described in this thesis are performed on the same substrate, and in this way a thick crystallized silicon layer (with a final thickness of 5 μm) is produced on top of the molybdenum substrate.

Silicon lumps are placed in a water-cooled copper holder and are evaporated with a 4 kW electron beam evaporation source. A carbon cup has been inserted as a diffusion barrier between the silicon pieces and the copper holder as shown in figure 3.4a. It turned out that in this way only very little silicon could be placed in the copper holder. Information obtained later⁶⁸ indicated that the diffusion barrier was not strictly necessary, because the copper holder is expected to be cooled well enough to prevent diffusion of copper into the silicon. We therefore placed later some silicon lumps on top of the lumps in the carbon cup as shown in figure 3.4b.

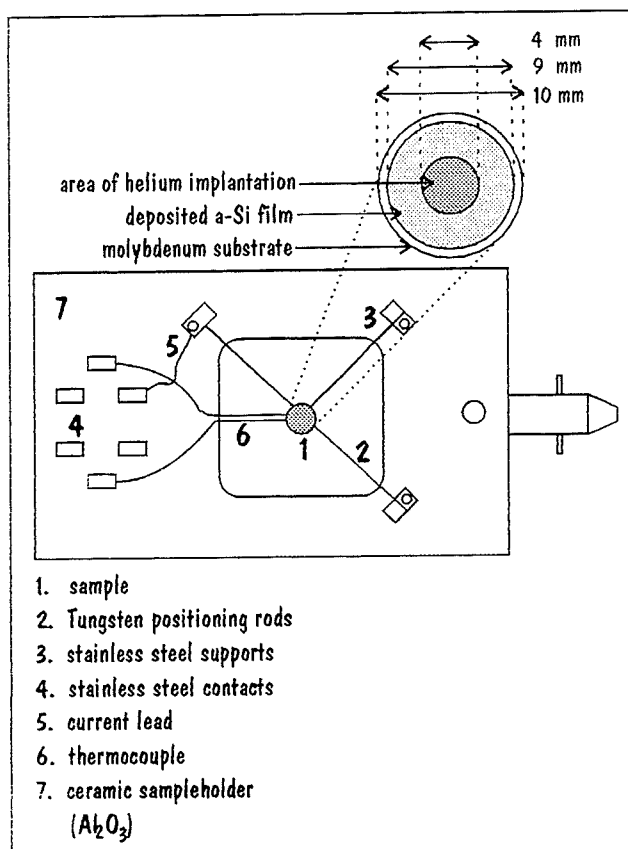


Figure 3.3 The ceramic sample holder and sample, with contacts for the current and temperature measurements.

grids. Upon leaving the ionization chamber the ions form an ion beam, which is aimed at the substrate. A filament producing electrons is placed just behind the grids to neutralize the ion beam. This is done to minimize the diversion of the beam caused by repulsive forces of ions in the beam. The Kaufman gun is operated at a gas pressure of 6×10^{-5} mbar (this pressure should be kept as low as possible to minimize charge exchange between the ions in the beam and neutrals in the background gas leaking out of the Kaufman source), producing a beam energy of a few eV to about 800 eV and a current of 1 - 10 μ A (depending on the energy). Only part of the beam reaches the sample. The ion current is monitored by measuring the electric current flow to the earth during bombardment.

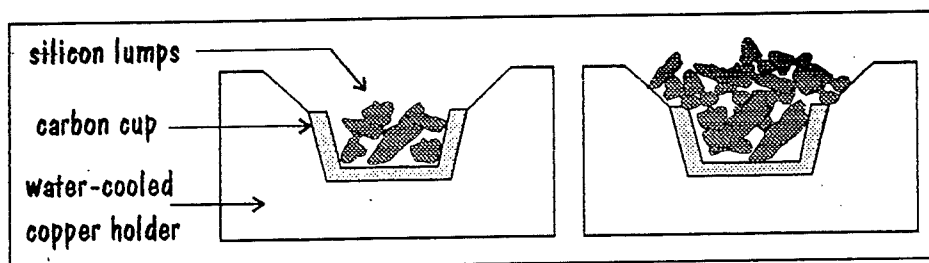


Figure 3.4 The water-cooled copper holder filled with silicon lumps and with a carbon cup inserted as diffusion barrier between copper and silicon (a) Only the carbon cup is filled (b) more silicon lumps are placed in the holder to increase the amount of deposition material.

Film thickness and deposition rate are controlled with a quartz crystal oscillator (QCO) masked from the ion beam. In this device, a quartz crystal oscillates in an electric field with a frequency dependent on the thickness of the film deposited on top of the crystal. Hence, the thickness increase can be monitored by measuring the frequency change of the crystal in the electric field. The position of the QCO is chosen in such way that the so called tooling factor is 1. In other words, the angle and the distance between the QCO and the evaporator source are equal to the angle and the distance between the substrate and the evaporator source.

An argon ion beam can be used to bombard the silicon film during deposition. This beam is produced with a Kaufman-type ion source, shown schematically in figure 3.5. Argon is let into the ionization chamber and is ionized by a filament (cathode). Ions diffusing out of the ionization chamber to the first grid (fig. 3.5) are extracted from the plasma and accelerated to the second grid by a potential difference between the two

During deposition, the output of the current meter and the quartz crystal are sent to a computer, which automatically adjusts the ion source power supply, and the evaporator power supply in order to produce stable ion and evaporated atom fluxes (see fig .3.2). This also leads to a stable Ion-to-atom Arrival Ratio *IAR*, represented as

$$IAR = 1.63 \times 10^{-3} \frac{\rho I_s}{MD} \quad (3.1),$$

where ρ is the density of the deposited material [g/cm^3], I_s is the ion current flow to the earth [μA], M is the molar mass of the evaporated species [g/mol], and D is the vapor deposition rate [$\text{\AA/s}$].

The implantation step is performed at position 2 (fig. 3.1). The ion source (Van Veen-type⁶⁶) producing helium ions is schematically shown in figure 3.6.

An inert gas (in our case helium) is let into the ionizing chamber where it is ionized. A magnetic field in the ionization chamber elongates the path of the electrons, to optimize the ionization efficiency. Ions are pulled out of the chamber by a negative Pierce extractor, are carried through an electrical field, and are accelerated to a Wien filter. In this Wien filter, an electrical and a magnetic field are perpendicular to each other, and the forces from both fields are equal for a specific relation between ion mass and ion charge. All ions that do not obey this relation are filtered out by deflection. When leaving the Wien filter section, the ions are either accelerated or decelerated to the chosen energy, which can be set to any value from a few eV to 3 keV. Subsequently, the beam is wobbled in two directions by two pairs of sweep plates to ensure an uniform implantation of the sample area behind the last aperture (0.125 cm²), see the insert of fig. 3.3. Finally, the beam is deflected 20° by two deflection plates, to remove the neutral particles from the ion beam. The ion source is operated with a gas pressure of about 2×10^{-8} mbar. The number of ions hitting the sample is recorded by measuring the current flow to the earth. A typical helium flux of 10^{13} He/cm² is implanted in the sample.

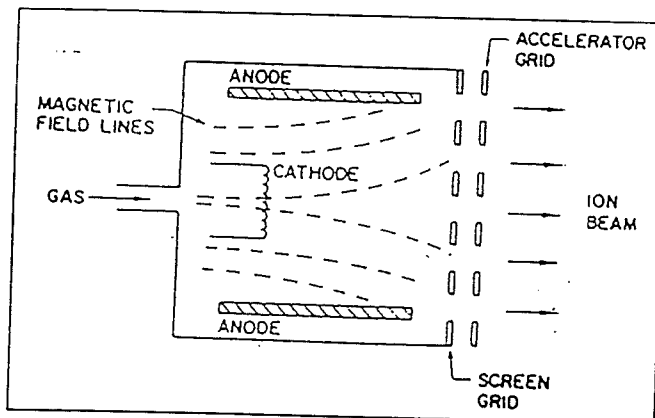


Figure 3.5: Schematic representation of a Kaufman gun. From Rossnagel (ref. 69).

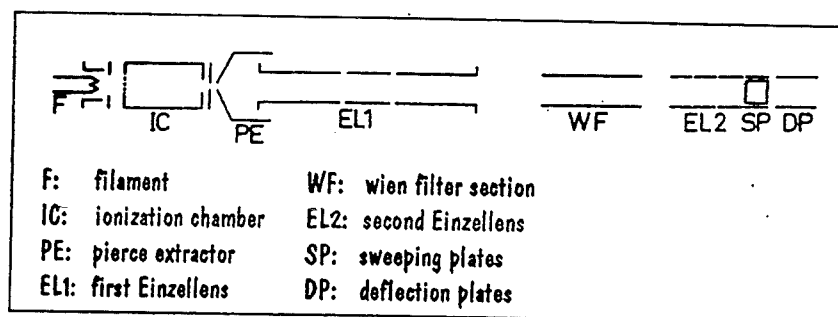


Figure 3.6 An overview of the optics in the ion source. From Buters (ref. 70).

The desorption step takes place at position 3 (fig. 3.1). The sample is heated at a constant heating rate by a grounded electron gun placed at the back of the substrate. The sample is held at

+1,5 keV to provide the acceleration field. The temperature of the sample is measured by a WRe26%-WRe5% thermocouple, and controlled by a feedback loop with a pre-calculated current-versus-temperature program and the temperature error as input signal (see, fig. 3.2). The helium release is detected by a quadrupole mass spectrometer. During the desorption, the vacuum vessel is pumped at such rate that the average residence time τ for helium in the vessel is 0.30 s.

3.2. Experimental procedure

Prior to the experiments the substrate is heated up to 1400 K to obtain a clean surface. Before a new film is deposited the substrate temperature has to be below 340 K. This temperature is found to be the optimum between a low (near room temperature) substrate temperature (in order to obtain reproducible deposition conditions) and a reasonable time between the desorption step and a new deposition step (~ 15 min.).

The effect of film thickness on the defect structure in the film is studied for films varying from 10 to 500 Å thickness. The deposition rate is varied from 0.5 Å/s for the thinnest films to 2 Å/s for the thickest films. It was never observed that this small variation in deposition rate does have a significant influence on the film structure. During ion beam assisted deposition, the sample is biased at -10 V to prevent the electrons in the ion beam and stray electrons to reach the sample. The effect of variations in the energy of the bombarding ions on the defect structure of the films is studied in the range of 25 eV to 2.5 keV. In addition the effect of a variation in *IAR* is studied by varying the implantation rate, between 0.5 and 2 A/s, and the current through the sample, between 1 and 4 µA, resulting in an *IAR* varying from 0.006 to 0.07. In some cases the film is annealed by an electron bombardment on the back of the sample (at position 3, fig. 3.1). This anneal step took place immediately following the deposition.

The film is implanted with helium ions with an implantation energy varying between 20 and 1000 eV, and fluences Φ between 5×10^{12} and 5×10^{14} He/cm². When the partial helium pressure has decreased to an acceptable low background level, the desorption step is performed. In all cases the sample is heated linearly in time up to 1400 K. In the initial experiments the heating rate β was 40 K/s and the counting time was 25 ms. Later on, it turned out that a β of 10 K/s and a counting time of 50 ms resulted in spectra with sharper peaks. We therefore decided to continue the measurements with a β of 10 K/s. During the heating step the QMS signal is measured alternately for two channels. On mass channel four the number of helium ions reaching the QMS is measured during 25 or 50 ms depending on the heating rate, and on mass channel eight a reference signal is measured over a same period of time. In this way the desorption spectra can be corrected for background effects by subtracting the reference signal from the helium signal. An example of a background effect is a pressure rise caused by the temperature increase of the sample.

As mentioned in section 3.1, the desorbed helium atoms spend an average (small) time τ in the desorption chamber before they are pumped away; τ is determined by the relation between the volume of the desorption chamber V and the pumping speed S ($\tau=V/S$). The helium residence time in our experiments is 0.30 s. In this situation the number of particles $N(t)$ in the desorption chamber changes as a function of time according to

$$\frac{dN(t)}{dt} = AL(t) - \frac{N(t)}{\tau} \quad (3.2),$$

with t the time, $L(t)$ the desorption flux from the sample and A the area of the implanted region (0.125 cm² in our experiments). Some of the particles will reach the QMS and are detected, the

others are pumped out of the desorption chamber without being detected. $N(t)$ is estimated by summation of the number of counts from the QMS with the detection efficiency measured during calibration. The detection efficiency of the quadrupole system is measured immediately after each desorption experiment. This is done by injecting a known amount of gas into the vacuum vessel and integrating the quadrupole response over time. The amount of helium is obtained by filling a ≈ 1 cc volume out of a 1 liter supply vessel filled up to a known pressure, measured by an absolute membrane manometer. A typical detection efficiency of 1 quadrupole pulse per 2×10^7 released helium atoms is obtained.

In order to derive $L(t)$ (the value we want to know) from $N(t)$ (the value we measure) the measured desorption spectra are corrected numerically for the finite residence time τ (deconvolution) according to

$$L(n\Delta t) = \frac{N(n\Delta t) - N((n-1)\Delta t) \exp(-\Delta t / \tau_{res})}{[1 - \exp(-\Delta t / \tau_{res})] A \tau_{res}} \quad (3.3),$$

where, Δt is the sample time, which is equal to the total of the counting time for the helium signal, the counting time for the reference signal, and two times a switching time (1.5 ms). After deconvolution the data are smoothed by averaging the over 11 data points to reduce unwanted noise. It is verified that the smoothing has no significant influence on the peak shape and on the information that we extract from the data.

3.3. Error estimation

3.3.1. Systematic errors

Errors in the film thickness and deposition rate are determined by the error in the film density, used as input for QCO. The value of the film density used is 2.32 g/cm^3 . From experiments on molybdenum films it is known that the density of the evaporated films is much lower than the density of defect-free molybdenum. Yet, no precise values for this deficiency are known. It is expected that the density of the amorphous silicon films is also lower than the literature value used. According to the literature this difference can be about 3-15 %.⁴

In the case of the IBAF films the thickness is also influenced by the sputtering yield of the argon atoms. Values of the sputtering yield for a variety of argon energies are given in table 3.1. As mentioned above the maximum IAR used during our measurement is 0.1 resulting in a maximum error in the film thickness of ~ 0.5 %.

Table 3.1 Sputtering yield for silicon bombarded with argon for a variety of argon energies. From Zalm (ref. 71).

Energy of bombarding argon ions [eV]	sputtering yield [atoms/ion]
100	0.0042
200	0.016
500	0.054

During the bombardment the ion fluence is determined by measuring the current flow to the earth. There are two factors that may cause errors in the fluence determination: (i) As ions hit the surface, electrons will be expelled, these so-called secondary electrons are also part of the current and obscure the measurement. (ii) Ions hitting the surface of the film can be back-scattered and might pick up an electron during the short interaction with the surface. The electrons that leave the sample in this way are also part of the current, and obscure the fluence measurements as well. The secondary electron coefficient (the number of electrons expelled per ion) is not known. The number of back-scattered ions for the implantation of argon into silicon calculated with TRIM turns out to be zero.

Another systematic error is caused by a decrease in ion current and thus a decrease in *IAR* during the deposition. This decrease is possibly caused by a temperature dependent current leakage in the Kaufman source parallel to the beam current. Consequently, the *IAR* of the first deposited atomic layers is higher than average and the *IAR* of the top part of the film is lower than average. The difference in ion current between the start and the end of the deposition is about 10%, which results in a maximum error of 5%.

During the implantation of helium, the fluence is determined by measuring the current flow to the earth as in the determination of the argon fluence. Thus, the fluence determination is also obscured by secondary electrons and back-scattered ions. To determine the secondary electron coefficient experiments were performed, in which the bias voltage on the sample is varied during the implantation while measuring the current through the sample. Unfortunately, it was not possible to determine the correction factor because of experimental problems with the electrical isolation. The number of back-scattered ions as calculated with the computer code TRIM are given in table 3.2 for the implantation of helium into silicon for a range of helium implantation energies.

Table 3.2 Back-scattered ions for helium implanted in to silicon versus implantation energy, as calculated with TRIM

Implantation energy [eV]	Back-scattered ions for helium implantation [%]
100	20
200	21
500	18
800	18
1000	17

As is described in section 2.2.3, with TRIM no calculations can be performed with implantation energies below 100 eV, and even the values near 100 eV are not very reliable.

3.3.2. Random errors

The temperature measurement is performed with a WRe26%-WRe5% thermocouple having an accuracy of better than 1 %. The random error in the heating rate β (and temperature) due to insufficient performance of the feedback loop are small ~1 %. Another error is caused by temperature of the cold junction, which is always taken to be 293 K but depends on room temperature.

The error in the helium detection efficiency appears to be about 10 %.

3.4. Detection of impurities and study of the surface morphology

At the end of all measurements an amorphous silicon film of 800 Å thickness is deposited on top of the crystallized layer and the impurity concentration of this film is studied with Secondary Ion Mass Spectrometry (SIMS) and Auger Electron Spectroscopy. The surface morphology of both the amorphous silicon film and the crystallized layer are studied with Secondary Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The sample that is used in all these studies is schematically presented in figure 3.7. It can be seen that only a part of the crystallized

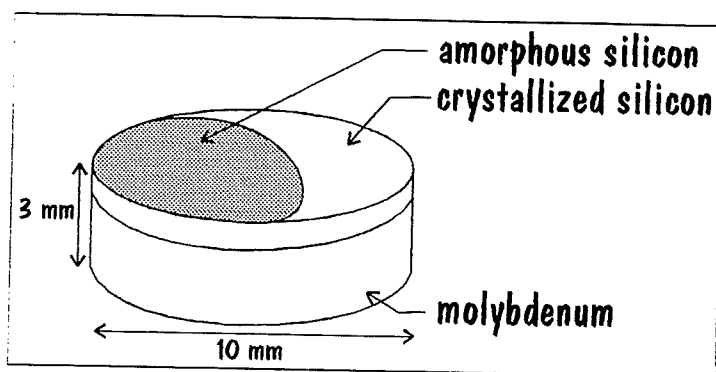


Figure 3.7: Schematic presentation of the sample used in the SIMS, AES, SEM and AFM measurements.

layer is covered by the amorphous silicon film. This was caused by problems with the aperture placed in front of the substrate. With this sample it is possible to perform not only measurements on the amorphous silicon film but also on the uncovered crystallized layer.

In SIMS an ion beam bombards the surface and sputters neutral atoms and ions both positive and negative, single and multiple charged and

clusters of particles, from the outermost film layers. The sputtered particles enter an energy filter and are collected in a mass spectrometer, where they are mass analyzed in order to identify the species present as well as to determine their abundance. The sputter ions employed are O_2^+ , and these are focused into a beam with an energy of 6 keV, which bombards the sample under an angle of 45° resulting in a sputtering rate of 2 nm/min.

In AES an electron gun aims a focused beam of ~ 2 keV electrons at the specimen surface, where it is scanned over the region of interest. Emitted Auger electrons are then energy analyzed. Depth profiling can be accomplished with incorporated ion guns that enable the specimen surface to be continuously sputtered away while Auger electrons are being detected. Multi-element composition depth profiles can thus be determined over total thickness of several thousand angstroms by sequentially sampling and analyzing arbitrary thin layers.

In SEM electrons are emitted from a cathode filament are drawn to an anode, focused by two successive condenser lenses into a beam with a very fine spot size (~ 50 Å). Pairs of scanning coils located at the objective lens deflect the beam over a rectangular area of the specimen surface. Electron beams having energies ranging from a few thousand to 50 keV, with 30 keV a common value are utilized. Upon impinging of the specimen, the primary electrons decelerate in the losing energy transfer in elastically to other atomic electrons and to the lattice. Through continuous random scattering events, the primary beam effectively spreads and fills a teardrop-shaped interaction volume with a multitude of electronic excitations. The result is a distribution of electrons that manage to leave the specimen.

In AFM the tip-sample force interaction is used to probe local properties of the sample surface. A topographic map of a sample surface is obtained, for instance, by keeping the force constant while scanning the sample relative to the tip.

4. Results & Discussion

This chapter presents and discusses the results of the experiments. The apparatus we used combines IBAD in situ with Thermal Desorption Spectrometry (TDS) which enables us to study:

- *amorphous silicon (a-Si) films deposited with and without ion bombardment*
- *bottom-up probing in which the probing atoms originate from below the deposited film*
- *structural relaxation and crystallization of the amorphous film*

The impurity concentration in both an amorphous and a crystallized silicon film is studied with Secondary Ion Mass Spectrometry (SIMS) and Auger Electron Spectroscopy (AES). The surface morphology of both films is studied with SEM and AFM. The results of these measurements are presented in section 4.1. Section 4.2 gives a review of some experimental details. Sections 4.3, 4.4, and 4.5 present and discuss the results of TDS experiments on amorphous silicon films. These results are subdivided in three subjects:

- *EVAP a-Si: amorphous silicon films deposited without ion bombardment (section 4.3)*
- *IBAD a-Si: amorphous silicon films deposited with ion bombardment (section 4.4)*
- *anneal series of EVAP a-Si (section 4.5)*

4.1. Incorporation of impurity elements

4.1.1. Detection of impurity elements with SIMS and AES

4.1.1.2. Secondary Ion Mass Spectrometry (SIMS)

In total five SIMS measurements have been performed, three on an amorphous film of 800 Å thickness, on top of the crystallized layer (of about 5 μm thickness) that had developed on the molybdenum substrate in the course of the measurements, and two on the crystallized layer without an amorphous film (see fig. 4.1 and fig. 3.7). The SIMS measurements were performed at the end of all TDS measurements. The elements examined are carbon, nitrogen, hydrogen, and oxygen, which are all present in the vacuum system; copper from the water-cooled copper evaporator holder; and molybdenum from the

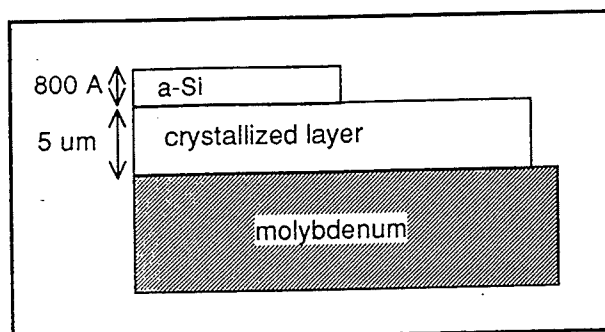


Figure 4.1: Side-view of the sample used in the SIMS, AES, SEM and AFM measurements. A polycrystalline molybdenum substrate is covered by a crystallized layer of ~ 5 μm thickness. A part of the crystallized layer is covered by a 800 Å amorphous silicon film.

substrate. In the SIMS measurements an oxygen ion beam was used for sputtering, therefore oxygen could not be detected. Normally, a cesium ion beam is used for the detection of oxygen, but the cesium source had broken down and could not be used.

Figure 4.2 shows the results of two SIMS measurements, one on the amorphous film (a) and one on the crystallized layer (b). The other three measurements gave similar results and are not presented here. It should be noted that during SIMS a crater was sputtered with a total depth of

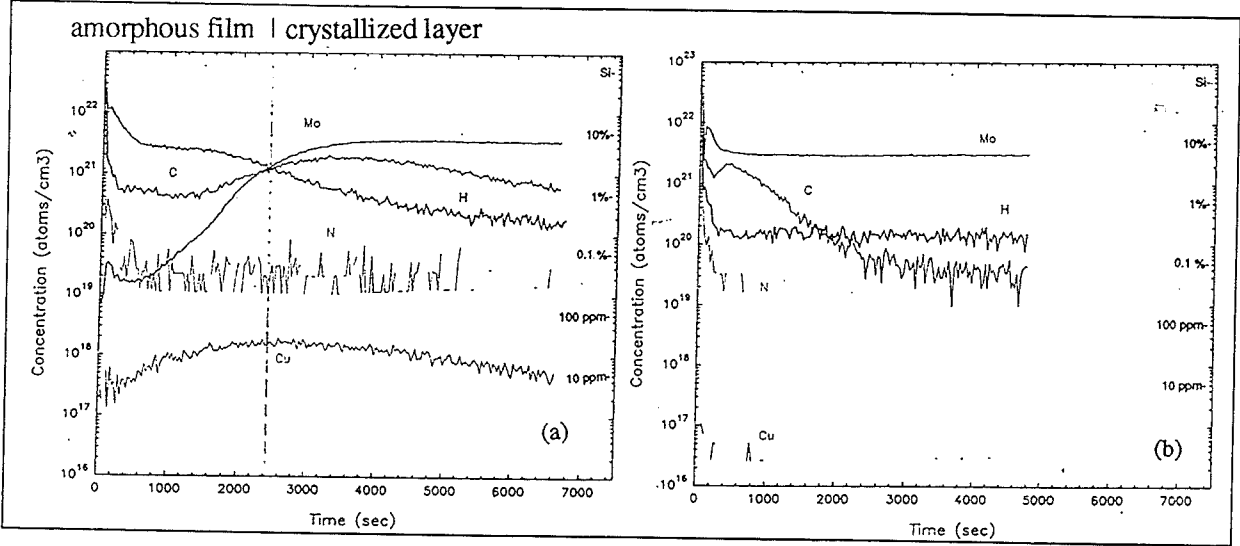


Figure 4.2 Concentration of molybdenum, carbon, hydrogen, nitrogen, and copper in an 800 Å amorphous silicon film (a) and in the crystallized layer (~ 5 µm) (b) as measured with SIMS. The sputtering rate is 0.33 Å/s and for sputtering a 6 keV O₂⁺ beam is used. For comparison of the amount of incorporated impurities, the number of silicon atoms per/cm³ is 5 x 10²² in pure crystalline silicon

about 2200 Å. Consequently, only the first 2400 seconds (800 Å) of the SIMS signal in figure 4.2a represent the impurity concentration in the amorphous film. The signal above 2400 seconds represents the impurity concentration in the crystallized layer below the amorphous film. The interface between the amorphous film and the crystallized layer is indicated in figure 4.2a. Table 4.1 shows the incorporation of molybdenum, copper, carbon, hydrogen, and, nitrogen in these films at 200 Å depth. The results for amorphous silicon are the averages of three measurements. The results for the crystallized layer are the averages of two measurements.

Table 4.1: Average values for the impurity incorporation in amorphous silicon and in the crystallized layer as measured with SIMS.

element	amorphous silicon [at. %]	crystallized layer [at. %]
Molybdenum	0.07	7
Copper	0.0005	0.00003
Carbon	0.9	4
Hydrogen	7	0.14
Nitrogen	0.04	-

These results show that molybdenum is incorporated in a relatively high amount in both the crystallized layer and the amorphous film. It should be noted that the molybdenum signal in the

crystallized layer is very high and might be saturated. At the interface between the amorphous film and the crystallized layer a wide concentration profile is shown. This profile might be a real effect, i.e. due to diffusion of molybdenum in the amorphous film during or after deposition, or a spurious effect due to the limited depth resolution of SIMS. This is examined with AES and the results of these measurements are discussed in more detail in the next section.

Only little copper is detected in both materials. The presence of copper in the film can be due to diffusion of copper from the water-cooled copper holder into the silicon melt. Copper diffuses very easily into the silicon even at rather low temperatures $D(600\text{ K}) = 1.2 \cdot 10^{-6} \text{ cm}^2/\text{s}$, ($E_d = 0.43 \text{ eV}$, $D_0 = 0.0047 \text{ cm}^2/\text{s}$, investigated in the range of 573-973 K)⁷². The lower incorporation of copper in the crystallized layer might be due to diffusion of copper to larger depths in the film during the anneal step. However, it is not clear why the copper signal in the crystallized layer with the amorphous film on top, is higher than in the uncovered crystallized layer (see, also figure 4.1).

Similarly, the incorporation of carbon in the film might also be caused by diffusion of carbon from the carbon cup inserted as thermal and diffusion barrier in the copper evaporator source. However, the diffusion of carbon in silicon is much slower $D(600\text{ K}) = 1.8 \cdot 10^{-26} \text{ cm}^2/\text{s}^{-1}$ ($E_d = 3.1 \text{ eV}$, $D_0 = 1.9 \text{ cm}^2 \text{ s}^{-1}$, investigated between 1343 and 1673 K)⁷² and can not explain the incorporation of carbon in the silicon film. The large carbon signal just below the surface of the crystallized layer is not understood.

Hydrogen is also present in relatively high amounts in both materials. Nitrogen does show up in the amorphous film, but is hardly detectable in the crystallized layer. As with copper it is not clear why the results of the crystallized layer with amorphous film on top differ from the results of the uncovered crystallized layer.

The results show a much higher presence of these impurities than is expected to be incorporated during deposition. Suppose that the background pressure P of H, N, C, and O-containing gases is 10^{-9} mbar during deposition. The number of particles L that hit the substrate surface per unit of time per unit of area can then be calculated with

$$L = \frac{P}{\sqrt{2\pi mkT}} \quad (4.1),$$

where m is the mass of the impinging particles, k the Boltzmann constant, and T the temperature. If m is taken as $1.8 \cdot 10^{-26} \text{ kg}$, the average mass of the impinging particles, it can be calculated that the impingement rate on our sample is about $5 \cdot 10^{-4} \text{ \AA/s}$. Then the upper limit (sticking factor 1) of incorporated impurity elements during deposition is approximately $5 \cdot 10^{-4}$ (500 ppm). Table 4.1 shows that the total incorporation of C, N and H in the amorphous film is about 100 times higher. The incorporation of these elements in the crystallized layer is about 10 times higher than the value calculated above.

The high incorporation of these gasses might be caused by adsorption of these elements during the transport of the sample outside the IBAD apparatus. This explanation can only elucidate our results if the surface of the films is rough, which enables impurity elements to be adsorbed in deep gaps and to be mixed in the film during SIMS. In order to examine this explanation we took a close look at the surface of both the crystallized layer and the amorphous with a light microscope, Secondary Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). The results of these measurements are presented in section 4.1.2.

4.1.1.2. Auger Electron Spectroscopy (AES)

Figure 4.3 shows the results of AES measurements on the crystallized layer and on the amorphous film. These measurements were performed on the same sample as that used for the SIMS measurements. The sputtering rate for both films is 25-30 $\text{\AA}/\text{min}$. Figure 4.3a clearly shows that the molybdenum signal measured with SIMS was indeed saturated. The molybdenum incorporation in the crystallized layer is as high as 34 % instead of 7%, which indicates that the

crystallized layer consists of MoSi_2 . From literature data it can be concluded that this film is initially formed by the diffusion of silicon into the molybdenum substrate, and has developed as result of diffusion of silicon in the MoSi_2 layer that is formed on top of the molybdenum substrate (see fig. 4.1). The diffusion of silicon in MoSi_2 starts at about 1100 K^{73,74}.

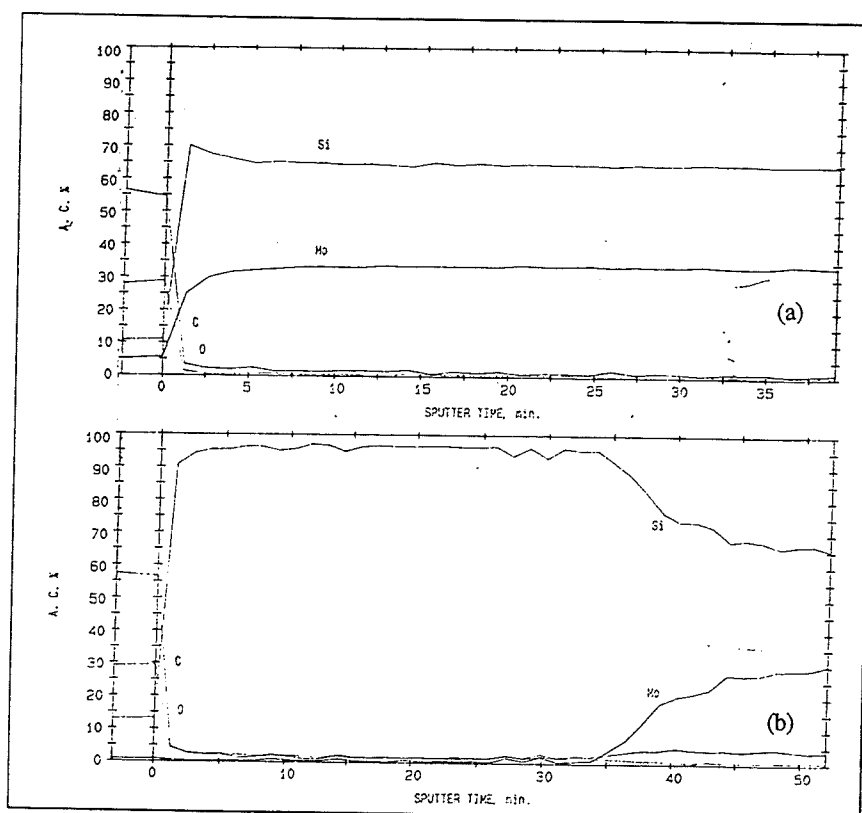


Figure 4.3 AES results on the crystallized layer (a) and the amorphous film (b). The sputtering rate is $27 \pm 3 \text{ \AA/min}$.

As can be seen from figure 4.3b, the AES results show a much smaller transition stage between the molybdenum concentration in the amorphous and the crystallized layer. It can be concluded that the wide molybdenum profile of figure 4.2 is not caused by diffusion, but is only a feature of the experimental technique (for example mixing of the film by the oxygen beam). These results are confirmed by diffusion experiments described in the literature, which show that at room temperature (and even up to 1100 K) no significant interdiffusion between Si and MoSi_2 takes place.^{73,74}

Since the small fraction of molybdenum incorporated in the amorphous silicon film (less than 0.1 %) cannot be explained by diffusion from the substrate, it must originate from another source. A possible source is the molybdenum film that had developed on the interior of the vessel during the deposition of molybdenum in earlier experiments. Small chips from this film may have fallen down into the silicon melt (especially from the mirror that is positioned above the silicon melt). We therefore examined the incorporation of molybdenum in the silicon melt with gas analyses. The results confirmed our explanation, about: 0,8 % Mo is incorporated in the silicon melt.

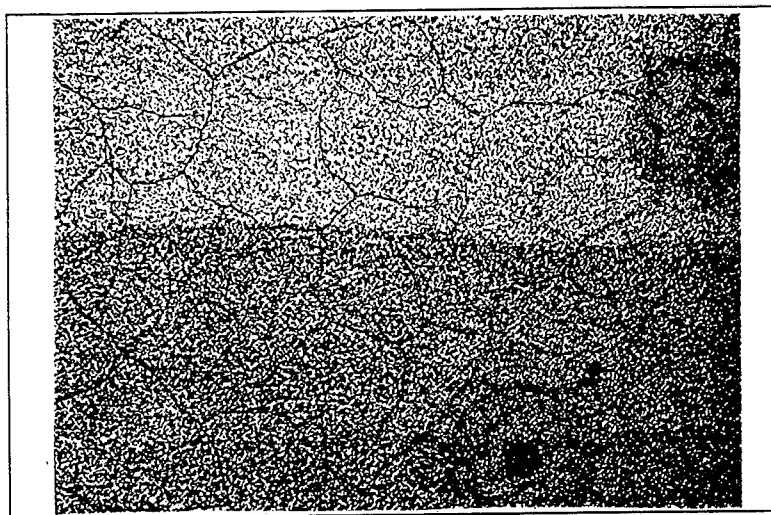


Figure 4.4 picture of the sample (magnification 140 x) showing the border between the amorphous film (dark gray) and the crystallized layer (light gray).



a)



b)

Figure 4.5 SEM pictures of the amorphous film (a) and the crystallized layer (b).

4.1.2. Surface topography

4.1.2.1. Light microscopy

Figure 4.4 shows a light-microscopic image of the sample (the same as is used in the SIMS and AES measurements) at the border between the amorphous film (dark gray) and the crystallized layer. This photograph clearly shows a network of cracks. The distance between these cracks is about 0.1 mm. These cracks are caused by shrinkage stress in the films as a consequence of the difference in expansion coefficient between molybdenum and MoSi_2 ($7.8 \times 10^{-6} \text{ K}^{-1}$ and $9.7 \times 10^{-6} \text{ K}^{-1}$, respectively).⁷⁴ Consequently, they are formed before the amorphous film is deposited. However, the cracks are still visible in the amorphous film because this film is not thick enough to cover them.

During transport of the sample impurities can be adsorbed in the cracks, which partly explain the high incorporation of impurity elements as detected with SIMS. However these results do not explain the difference in impurity concentration between the amorphous and the crystallized layers. This difference is discussed in more detail in the section 4.1.2.2.

Figure 4.4 also shows two circular objects in both the amorphous and the crystallized layer. The size of these objects is about 0.1 mm diameter and in total about 20 to 30 of these objects are found in the film. We do not know what they are.

4.1.2.2. Secondary Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)

Figure 4.5 shows SEM micrographs of the amorphous (a) and the crystallized layer (b). It can be seen that both the crystallized layer and the amorphous film show separate 'blocks' of about $0.8 \mu\text{m}$ diameter, with small particles (of about $0.07 \mu\text{m}$ diameter) on top. These images are studied in more detail with AFM and the results are shown in figure 4.6 and 4.7. These micrographs clearly show that the 'blocks' detected with SEM are formed by a rough 'mountain-like' surface structure. It can be seen in figure 4.7 that deep alleys (with a depth in the order of 100 nm and a length in the order of 600 nm) exist between the 'mountains', in which impurities can be adsorbed during transportation of the sample. Figure 4.6 shows that the small particles detected with SEM are irregularities in the surface structure.

The higher incorporation of impurities in the amorphous film in comparison with the crystallized layer (as derived from the SIMS results), is expected to be caused by roughness of the amorphous film, which enables the adsorption of impurities to a large depth in these films. From the AFM result no difference is detected between the crystalline and the amorphous film. According to the model of Messier (described in section 2.3.2) the amorphous film on top is expected to consist of small columns (20-50 nm diameter). The resolution of these micrographs is not high enough to study such small irregularities.

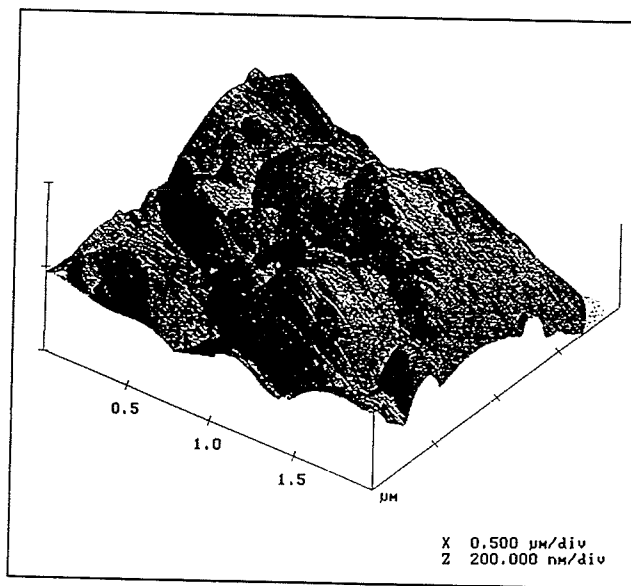


Figure 4.6: AFM picture of the crystallized layer.
The amorphous film showed similar results.

4.1.3. Influence of impurity incorporation on the TDS results

The results presented in the previous sections show that the amorphous film contains a little (~700 ppm) molybdenum. Both the amorphous and the crystallized layer contain a very small

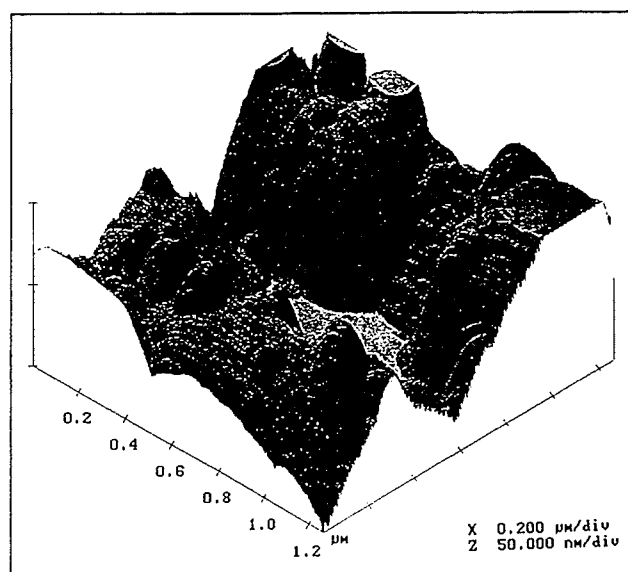


Figure 4.7 AFM picture of the crystallized layer. This picture clearly shows that deep (in the order of 100 nm) 'alleys' exist between the 'mountains' in which impurities can be adsorbed during transportation of the sample. The light gray horizontal planar boundaries are caused by the scanning limits of the AFM. The parallel lines are caused by the scanning method and are no features of the sample.

amount of copper (~5 ppm and ~3 ppm, respectively). The small incorporation of copper is not expected to have any significant influence on the TDS spectra. Both films also show incorporation of H, C, O, N. The presence of these elements is thought to be mainly due to adsorption in the cracks or small gaps of the films during transportation of the sample (thus after the sample has left the IBAD apparatus), although calculations (section 4.1.1.2.) indicate that small amounts ($\ll 500$ ppm) of these elements can also be incorporated during deposition.

In general, the presence of impurities in pure crystalline materials does have a large influence on the TDS spectra. Helium can be trapped in the deformed regions surrounding impurity atoms, resulting in accompanying desorption peaks in the TDS spectra. As is discussed in section 2.3.1, amorphous silicon differs from crystalline materials in the sense that it has no long range periodicity in its structure. As-deposited

amorphous silicon is expected to contain many defects. Therefore, 'deformed' regions are inherent to the amorphous structure, and it is improbable that small amounts of impurities influence the desorption spectra significantly.

4.2. Experimental details

Before the results of the TDS experiments are presented some experimental details are summarized.

- In the initial experiments the heating rate β was 40 K/s and the counting time 25 ms. Later we decided that $\beta = 10$ K/s and a counting time of 50 ms resulted in spectra with sharper peaks. For all results presented the heating rate is indicated.
- Most series are corrected for background by subtracting the reference signal from the helium signal. If series are not corrected then this is specifically noted in the figure caption.
- In the following 'energy dependence' and 'fluence dependence' refer to the helium ions used for defect probing, not to argon ions used for IBAD.
- Fluence values are shown without corrections for back-scattered ions and secondary electrons, unless otherwise noted (because the correction factors are not very well known).

- All results presented in the section below are deconvoluted for residence time delay and subsequently smoothed by averaging over 11 data points to reduce unwanted noise.
- During ion beam assisted deposition, the sample is biased at -10 V to prevent the electrons in the ion beam and stray electrons to reach the sample. Argon ions initially accelerated with an energy of E , will therefore have an energy of $E + 10$ eV when they reach the sample. This extra energy gain is nowhere included in the data presented.
- The standard values used in the experimental series are film thickness $d = 200$ Å, helium implantation energy $E_{ion} = 200$ eV, and implanted helium fluence $\Phi = 10^{13}$ He⁺/cm².

4.3. Evaporated (EVAP) amorphous silicon

This section presents the results of TDS measurements on thin evaporated (EVAP) amorphous silicon films. The questions discussed are:

- Is it possible to study defects in amorphous silicon films with TDS?
- and if this turns out to be possible,
- Which types of defects can be detected?

In order to find an answer to these questions we have performed four series of measurements, in which we varied the helium implantation energy, the implanted helium fluence, and the film thickness. The film thickness variation is studied by two methods: ordinary helium implantation, in which helium is implanted in the top layer, and bottom-up probing, in which helium originates from below the film. This section presents and discusses the results of these experiments.

4.3.1. Variation in helium decoration energy

By increasing the implantation energy, the implantation depth and the possibility of damage creation are both increased. Hence, a variation in implantation energy can be performed in order to gain insight in the depth distribution of defects, and in the lowest implantation energy that causes significant damage production for the implanted fluence employed. As is calculated in section 2.1, the threshold energy for damage production E_{th} for helium implanted into silicon is about 50 eV. If a desorption peak is due to defects created by the helium beam, it will appear only above the threshold energy for defect creation and increase with increasing implantation energy.

4.3.1.1. Results

Figure 4.8a shows helium desorption spectra for 200 Å thick amorphous silicon films, implanted with a fluence Φ of 10^{13} He/cm², and with implantation energies E_{ion} ranging from 20 to 1000 eV. We chose a thickness of 200 Å to assure that all helium atoms thermalize in the amorphous film and not in the crystallized layer (see figure 2.9). Much thicker film are not desirable because the amount of silicon deposition material is limited. The implanted fluence of 10^{13} He/cm² is thought to be the optimum between a good signal to noise ratio, and a minimum disturbance of the solid.

All desorption spectra are plotted in normalized form, i.e. as $L(T)/\Phi\beta$, where $L(T)$ is the helium desorption flux [He/cm²/s], T is the temperature of the sample [K], and β is the heating rate [K/s]. This means that a straightforward integration of a spectrum yields the desorbed helium fraction, i.e. the number of helium atoms desorbed relative to the number of helium atoms implanted. If all helium atoms have left the specimen at the highest temperature, the total desorbed fraction is equivalent to the total trapping probability.

For the separate peaks in the spectra, integrated intensities I (He/cm^2) are calculated according to

$$I = \int_{T_1}^{T_2} L(T) \frac{dT}{\beta} \quad (4.2),$$

Figure 4.8b presents the desorbed fractions I/Φ associated with the peaks in figure 4.8a versus E_{ion} . The following points can be mentioned:

- The energy dependence of I/Φ shows a relatively large increase for low implantation energies varying from $\sim 10\%$ at 20 eV to $\sim 40\%$ at 100 eV. Above 100 eV the trapping is only slightly increased from $\sim 40\%$ for 100 eV implantation to $\sim 50\%$ for 1000 eV. The low value at 500 eV is probably due to an error in the current measurement.
- At low implantation energies (≤ 200 eV) a broad peak is present between about 400 to 700 K. We designate this peak as the α peak.
- The α peak first increases with E_{ion} . Above 200 eV its area decreases.
- The shape of the α peak changes with helium energy. One feature is that the position of the peak maximum T_{max} shifts to higher temperatures with increasing implantation energy.
- Above an implantation energy of about 50 eV, a second broad peak, called the γ peak, appears between about 700 K and 900 K, and increases with increasing implantation energy.

Below these five points are discussed in more detail

4.3.1.2. Trapping probability

If helium is immobile in amorphous silicon at room temperature we should expect a trapping probability of 100 %. At first sight the trapping results of figure 4.8b seem to indicate a much lower trapping in our films. However, as mentioned in section 4.2, these data are not corrected for secondary electrons and back-scattered

ions. Both these effects lead to an overestimation of the implanted fluence, hence our trapping probabilities are too low. The percentages of back-scattered ions as calculated by TRIM are given in table 3.2. As was noted in section 3.3, the values calculated with TRIM are not very

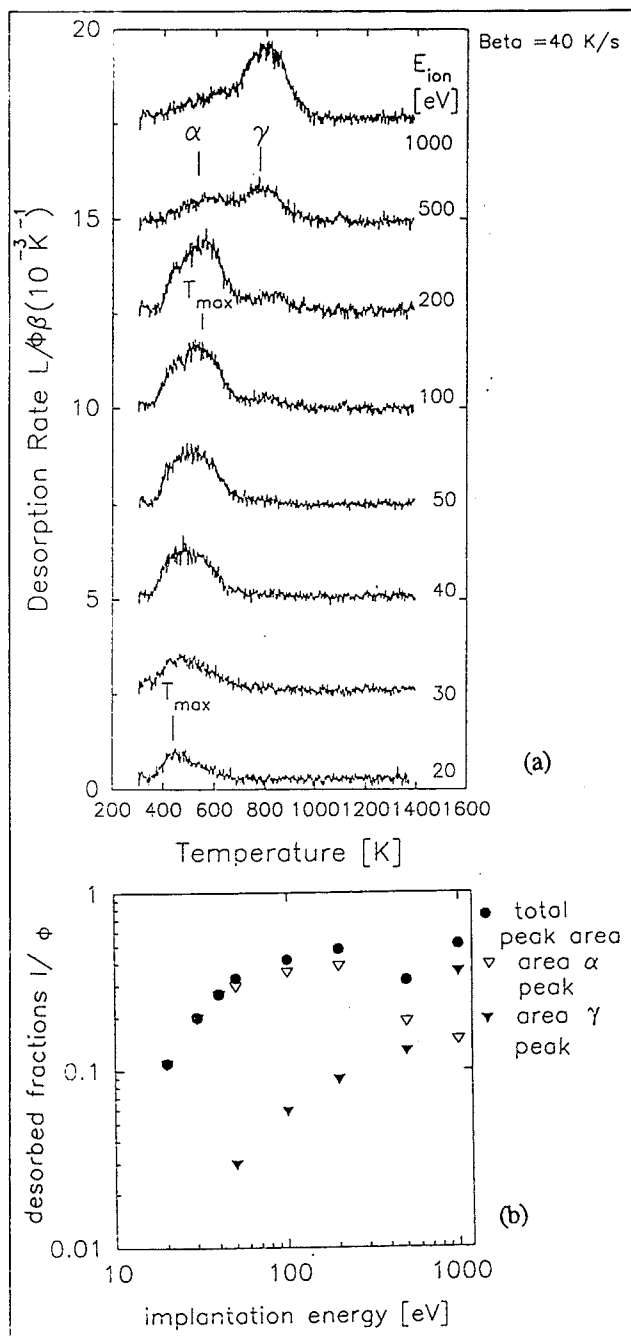


Figure 4.8: Variation in implanted helium energy in an amorphous silicon film of 200 Å thickness. Implanted fluence $10^{13} \text{ He}/\text{cm}^2$. (a) Helium desorption spectra. (b) Desorbed fraction as a function of the implanted helium energy.

reliable for low implantation energies (below a few hundred eV). Moreover, with TRIM no calculations below 100 eV can be performed. Although the exact values might therefore not be very reliable, table 3.2 clearly shows that the percentage of back-scattered ions decreases with increasing implantation energy. This points out that the increase in trapping with increasing implantation energy can be ascribed to a decrease of back-scattering.

We expect the influence of secondary electrons for the used energy range to be constant, as is the case for other materials like molybdenum and tungsten. Unfortunately, no values of the secondary electron coefficient for silicon are known to us. From work on molybdenum and tungsten it is known that this value is about 25-30 %. When the trapping results are corrected with these values, the total trapping turns out to be close to 100 %. This result is consistent with the assumption of the immobility of helium in silicon at room temperature.

It should be noted, however, that these results can not rule out the alternative possibility that helium is mobile in silicon at room temperature. As can be derived from figure 4.9, a trapping concentration of almost 100 % is also found if helium is assumed to be mobile at room temperature, as long as the defect concentration is higher than about 10^{-3} ($R_p \sim 50$ Å). If we assume that helium is mobile at room temperature, the sharp increase in trapping at the low energy side of fig. 4.8b can also be due to the increased depth range, and thus the decreasing probability that helium reaches the surface without being trapped.

Summarizing, we cannot decide on the (im)mobility of helium on the basis of the present results, since for high trapping probabilities TDS is insensitive to the value of the trap concentration.

4.3.1.3. The α peak

The α peak is very broad, about 4 to 5 times wider than a first order desorption peak if the values of the width at half height $\Delta T_{1/2}$ in relation to T_{max} are compared. The broad shape of the α peak indicates a distribution of helium/defect dissociation energies. In

general, the helium/defect dissociation energy increases with increasing trap size. Hence, the α peak indicates the existence of a range of small traps of varying sizes. This result is in agreement with what is expected for an amorphous material, in which the sizes of the interstitial positions and atom-size defects vary from place to place as result of the varying arrangement of the surrounding atoms.

Interstitial sites in amorphous silicon are not as clearly defined as in crystalline silicon, but can be defined as the open spaces between the silicon atoms in an ideal CRN. Examples of atom-sized defects in amorphous silicon can then be defined as one or a few missing atom(s) in the CRN. These atom-sized defects can be surrounded by one or more dangling bonds (see section 3.2.1). As mentioned in section 4.1 other possible traps are deformed regions surrounding incorporated impurities.

Yet, it is not clear whether the broad α peak should be assigned to helium desorption from interstitial sites, atom-size defects, traps caused by the incorporation of impurity atoms, or a combination these three. In order to get a better insight in this problem the following values should be derived:

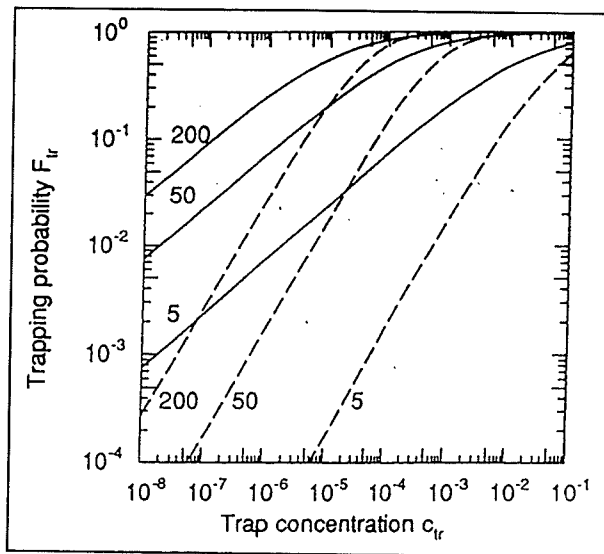


Figure 4.9: Trapping probability F_{tr} for a truncated Gaussian as implantation profile for various values for R_p (in Å) as function of the trap concentration c_{tr} . The solid lines are results for a constant trap concentration extending to infinite depth, the dashed lines are for a constant trap concentration extending to R_p .⁴⁷

- the range of helium desorption energies from the α traps, and
- the concentration of α traps.

An estimate of these values can be obtained from the position and the shape of the α peak by calculations with HOP. A few preliminary calculations were performed.

Before starting with the HOP calculations a reasonable value for ν_0 must be chosen. Desorption spectra of the crystallized layer, which are presented in appendix C, showed a series of first order desorption peaks. Upon fitting these peaks to the first order desorption theory it turned out that the resulting ν_0 was not equal to the Debye frequency (10^{13} s^{-1}) but varied between about 10^6 and 10^{11} s^{-1} (see appendix C, tables C1 and C2). In these HOP calculations we chose a frequency of 10^9 s^{-1} , which is about the average. It should be noted that in first instance it was thought that the spectra in appendix C represent the spectra of crystalline silicon. From the AES results we learned later that these spectra are more likely to be due to MoSi_2 , or at least from crystalline silicon with a high concentration of molybdenum.

Therefore, the value for ν_0 chosen here for amorphous silicon is not much more than a reasonable guess. However, an error in the absolute value of ν_0 would not seriously invalidate the analysis to be presented. Higher values for ν_0 would still yield very similar results, if only higher energies would be used (these energies are about 0.2 eV higher if $\nu_0 = 10^{13} \text{ s}^{-1}$ is chosen instead of $\nu_0 = 10^9 \text{ s}^{-1}$). The opposite is true for lower values of ν_0 .

In the previous section it has been derived that the total trapping is close to 100%. Fig. 4.9 shows that a total trap concentration of 80 to 100 % represents a defect concentration of $\geq 10^{-3}$ if helium is mobile at room temperature. Therefore, HOP calculations are performed for three different trap concentrations 1 (all interstitial positions act as traps), $\sim 1.5 \cdot 10^{-2}$, and $\sim 1.5 \cdot 10^{-3}$, respectively. In the first trial helium is immobile at room temperature in the other two trials helium is mobile at room temperature. In the latter trials, the binding energy of helium to an interstitial position is chosen to be 0.2 eV.

It can be reasoned that in order to simulate the broad α peak in the experimental results, the concentrations of the traps should decrease with increasing binding energy. Otherwise the stronger binding traps will dominate in the spectra, which results in a spectrum that increases in intensity with increasing helium desorption temperature. Therefore, we have tried a series of concentration spectra with a maximum of six traps, in which the defect concentration decreases with increasing defect number n , such that $c_{\text{trap}} = a (p)^n$. For p we have chosen the values $1/2$, $1/3$, $1/5$, and $5/12$. Moreover, E_d of all six traps is varied in order to obtain the same peak width as in the experimental spectra, with the restriction that the E_d always decrease with the same amount with increasing trap number. We also tried to fit the α peak with less than six

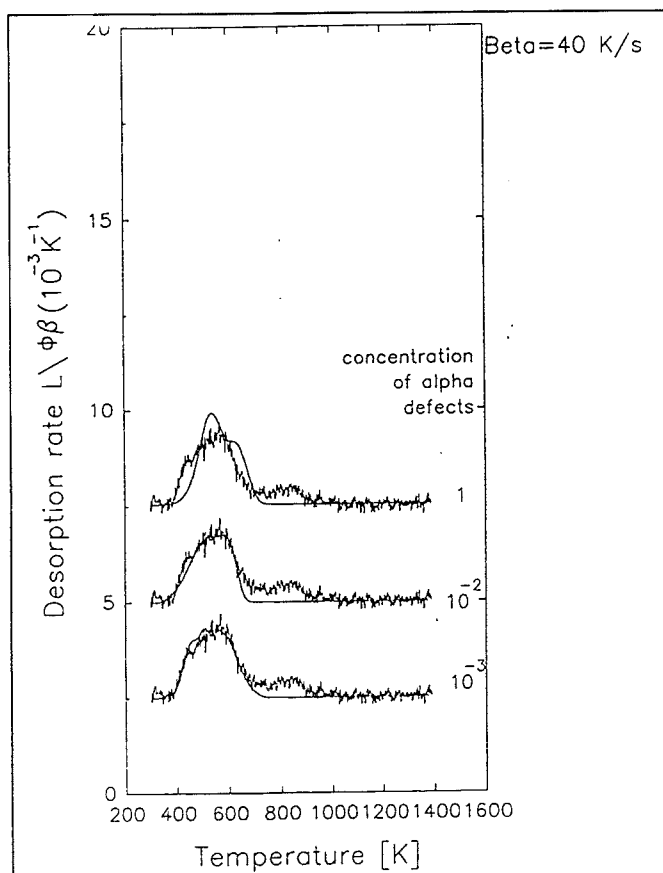


Figure 4.10: Results of HOP fits to the α peak for three different concentrations of α traps. The fit parameters are presented in table 4.2.

traps. Finally, a fit with six traps and $p=1/3$ was found to result in the best fits. For the simulation of the α peak, the desorption spectra for a 200 Å film are chosen. The trap concentration is assumed to be uniform throughout the film. The best fits were obtained for the parameters shown in table 4.2.

Table 4.2: Parameters used in HOP calculations. Film thickness 200 Å, $\beta=40$ K/s, $R_p=48$ Å, $\Delta R_p=27$ Å, E_d for interstitial helium = 0.2 eV, $\lambda=2$ Å, and n (silicon density) = 0.050 Å^3 . Energies are expressed in eV.

Total α defect concentration						
defect nr.	$\Sigma c_{\text{trap}} = 1$		$\Sigma c_{\text{trap}} \approx 1.5 \cdot 10^{-2}$		$\Sigma c_{\text{trap}} \approx 1.5 \cdot 10^{-3}$	
	E_d^*	c_{trap}^*	E_d	c_{trap}	E_d	c_{trap}
1	0.5	0.9	0.70	1×10^{-2}	0.75	1×10^{-3}
2	0.7	0.1	0.75	3.3×10^{-3}	0.835	3.3×10^{-4}
3	-	-	0.80	1×10^{-3}	0.92	1×10^{-4}
4	-	-	0.85	3.3×10^{-4}	1.005	3.3×10^{-5}
5	-	-	0.90	1×10^{-4}	1.09	1×10^{-5}
6	-	-	0.95	3.3×10^{-5}	1.175	3.3×10^{-6}
interstitial sites	-	-	0.2	$1 - \Sigma c_{\text{trap}}$	0.2	$1 - \Sigma c_{\text{trap}}$

* We also tried to fit the α peak with 6 defects with $\Sigma c_{\text{trap}} = 1$, and various energy ranges and concentrations but it didn't result in better fits.

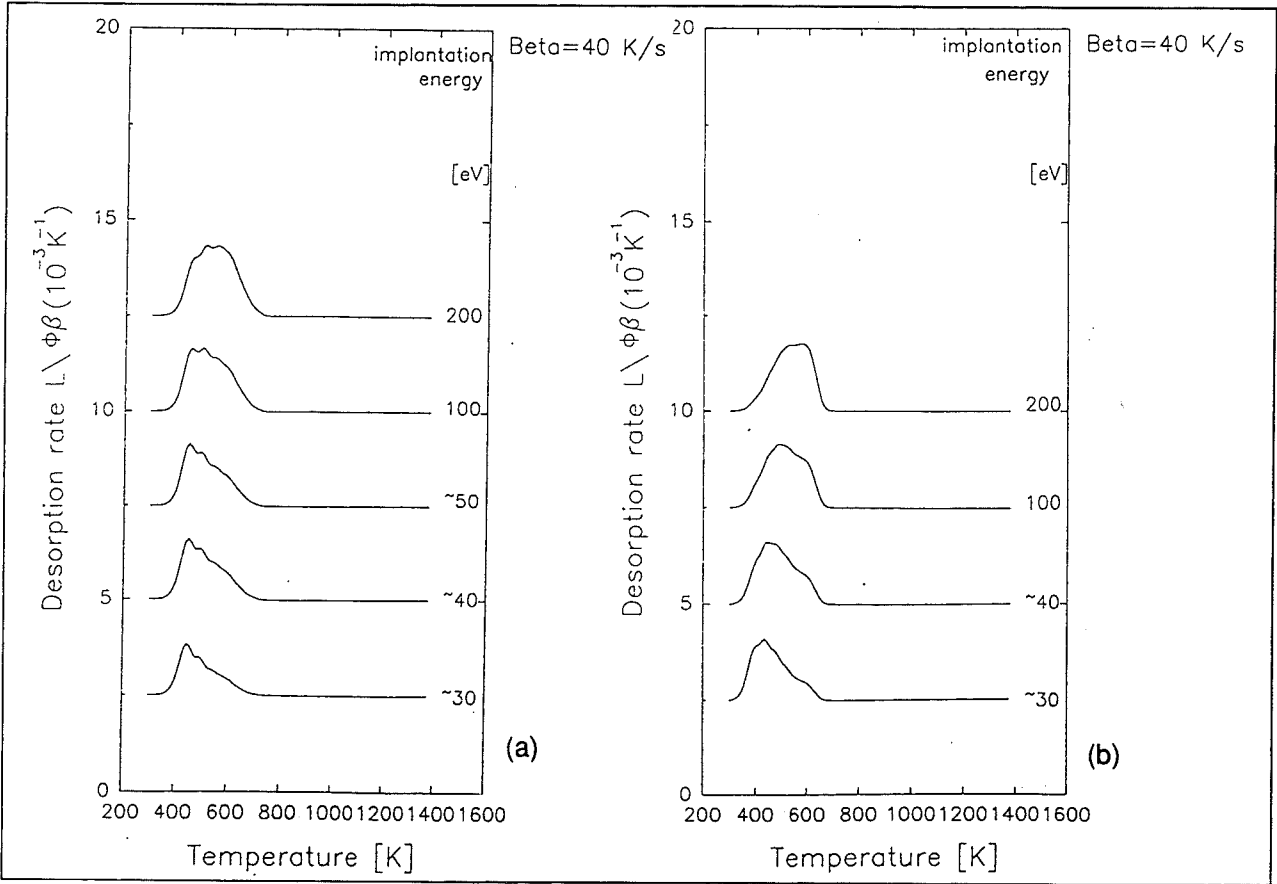


Figure 4.11: HOP simulations of the variation in implantation energy. The accompanying fit parameters are given in table 4.2 for $\Sigma c_{tr} \approx 1.5 \times 10^{-3}$ (a), and $\Sigma c_{tr} \approx 1.5 \times 10^{-2}$ (b).

The resulting fits are presented in figure 4.10. It can be seen that HOP calculations performed with $\Sigma c_{\text{trap}} \approx 1.5 \cdot 10^{-3}$ and $\Sigma c_{\text{trap}} \approx 1.5 \cdot 10^{-2}$ both show good fits. For $\Sigma c_{\text{trap}} = 1$ no good fit could be derived. Calculations with this high defect concentration yield an incorrect peak shape, caused by a second peak on the right side of the 'primary' α peak. This second peak is always lower than the 'primary' α peak. Detailed studies of the origin of this peak showed that it is caused by retrapping of helium at large depths in the amorphous film. This peak appears in all calculated spectra with a defect concentration ≥ 0.1 .

Table 4.2 shows that the range of helium desorption energies from the α traps is dependent on the chosen trap concentration and varies between about 0.75 - 1.175 eV for a total defect concentration of $\approx 1.5 \cdot 10^{-3}$, and 0.7 - 0.95 eV for a total defect concentration of $\approx 1.5 \cdot 10^{-2}$. This is about as far as we can get in this work.

In order to be able to directly relate the desorption peaks to certain types of defects additional information is required about

- The helium dissociation energy from both interstitial positions and atom-sized defect in the silicon CRN.
- General values of the concentration of different interstitial sites in the CRN.

This information should be considered in further research.

4.3.1.4. Change of α peak with increasing implantation energy

The observed shift of T_{max} of the α peak to higher temperatures with increasing implantation energy can be ascribed to retrapping. The implantation depth increases with implantation energy, and the deeper the helium is implanted, the stronger is the effect of retrapping. Helium atoms trapped in shallow α traps desorb at relatively low temperatures and can be retrapped in similar or deeper α traps, on their way to the surface. Because of the stronger binding of the deeper α traps, or the delay in movement to the surface caused by retrapping in traps of similar depth, helium that first desorbs at low temperatures and is retrapped, appears at higher temperature in the spectra.

This explanation is examined by computer calculations with HOP for total defect concentrations of $\Sigma c_{\text{trap}} \approx 1.5 \cdot 10^{-3}$ and $\Sigma c_{\text{trap}} \approx 1.5 \cdot 10^{-2}$. In these calculations we used the parameters from table 4.2. The results are shown in figure 4.11a and 4.11b, respectively. Both figures show that the shift of T_{max} of the α peak can indeed be ascribed to the increased depth range of the implanted helium (see fig. 2.9) and thus to retrapping.

4.3.1.5. Appearance and increase of the γ peak

The γ peak (fig. 4.8) appears at higher desorption temperature than the α peak, which indicates that the γ traps are deeper than the α traps, pointing to vacancy clusters or voids. Yet, the possible size of these defects is not known. A method that can give additional information about the size and the number of voids in the film is Transmission Electron Microscopy (TEM).

The growth of the γ peak with increasing implantation energy can be explained by two effects:

- The increase of the implantation depth with increasing helium implantation energy (see fig. 2.9), which increases the probability for probe atoms to get trapped in traps that exist at a larger depth in the film, or in traps with a low concentration. (This second explanation arises from the increase in retrapping with increased implantation depth.)
- The increasing production of γ traps with increasing helium implantation energy.

The production of defects by probe atoms can be studied by two methods: (i) fluence variation, which usually shows a more than linear increase of the desorption peak with increasing fluence when the defects are produced during helium implantation; and (ii) bottom-up probing, in which helium originates from below the film, and has not enough energy to create defects. If a peak shows up in a bottom-up experiment, it cannot be due to a defect produced by the helium ions. Both experiments have been performed and the results are described in section 4.3.2 and 4.3.4, respectively.

4.3.1.6. Decrease of α with increasing γ

The decrease of the α peak with increase of the γ peak (fig. 4.8) can be explained by retrapping. Helium initially bound to α traps, is released at relatively low temperature and can be retrapped in γ traps on its way to the surface. At higher temperatures the retrapped helium is released again, together with the helium originally trapped in the γ traps. Consequently, the resulting spectra show an α peak that contains less helium, and a γ peak that contains more helium than the original proportion of helium in the α and γ defects immediately after implantation. This explanation should be examined with HOP in further research.

4.3.2. Variation in implanted fluence

Figure 4.12a and 4.13a show the normalized desorption spectra for a series of fluences varying from 5×10^{12} to 2×10^{14} He/cm² for two implantation energies 40 eV and 200 eV, respectively. The film thickness is 200 Å. An implantation energy of 40 eV is below the threshold for defect creation, therefore we can be certain that none of the features of this TDS series is due to defect creation by the helium probe atoms. The 200 eV spectrum shows both the α and the γ peak which enables us to study the influence of fluence increase on both peaks. Figure 4.12b and 4.13b show the resulting desorbed fractions I/Φ as function of Φ .

The results show that the normalized areas of both the α and the γ peak are independent of the implanted fluence. In general the independence of the area of a desorption peak on the implanted fluence indicates that no significant damage is created under the applied conditions. To be more precise, however, fluence-independence of a normalized peak area merely means that the trapping probability of an incoming helium ion in that particular defect is independent of the time of implantation. Hence, the fluence-independence is also found when damage is produced and each helium atom that creates a defect is trapped in the defect it has just created. Therefore, this result does not prove that the probe atoms do not create significant defects. Bottom-up experiments can distinguish between these two possibilities and are performed to obtain more insight in the nature of the γ traps. The results of these experiments are described in section 4.3.4.

An additional fluence variation for 500 eV implantation energy is shown in appendix A. This series shows results completely similar to the 40 and 200 eV series.

4.3.3. Variation of film thickness

A variation in film thickness is performed in order to gain insight in the possible change of defect types with increasing film thickness, and in the existence of defects at the interface between the crystallized layer and the amorphous film. Two series of thickness variations are performed, one with an implantation energy of 40 eV (below the threshold energy for damage creation) and one with an implantation energy of 200 eV. The latter is chosen because it enables us to study changes in both the α and the γ peaks.

4.3.3.1. Results

Figure 4.14a shows helium desorption spectra of amorphous silicon films with thickness d varying from 0 Å to 500 Å. Helium is implanted with an energy of 200 eV and a fluence of 10^{13} He/cm². Figure 4.14b shows the desorbed fractions I/Φ versus d .

The following points should be mentioned.

- The 10 Å film shows a clusters of peaks B, which are quite similar to the peaks which appear in the crystalline spectra (0 Å film). The 20 Å film yields a spectrum that is already very much like the amorphous-film spectrum of fig. 4.8.

- A 'new' peak β at 630 K appears in the spectra for $d = 50 \text{ \AA}$ and $d = 100 \text{ \AA}$. At $200 \text{ \AA}$ the α peak restores to its original form and the γ peak appears.
 - At $500 \text{ \AA}$ the α peak increases and the γ peak shifts to a position γ' at about 900 K.
 - I/Φ shows an increase in the total trapping for $d = 50 \text{ \AA}$ and $d = 100 \text{ \AA}$.
- In the following sections these four points are discussed in more detail

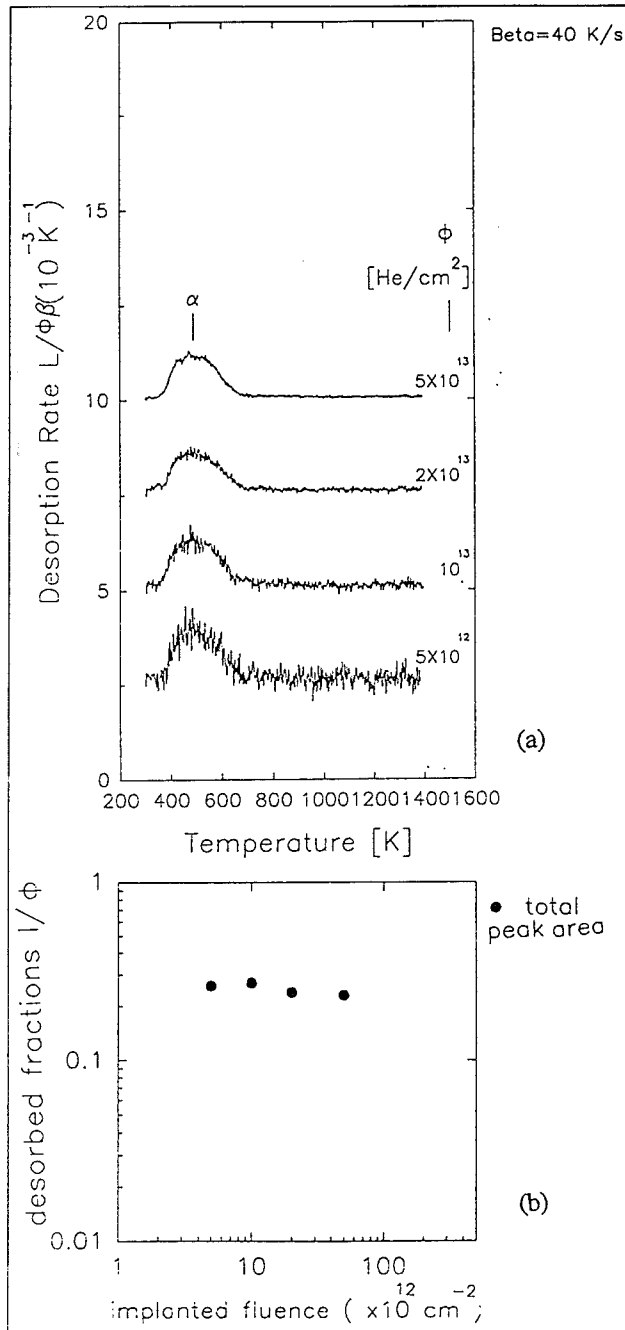


Figure 4.12: Variation of implanted fluence in an amorphous silicon film of $200 \text{ \AA}$ thickness. The energy of the implanted helium ions is 40 eV. (a) Helium desorption spectra. (b) Desorbed fraction as a function of the implanted fluence.

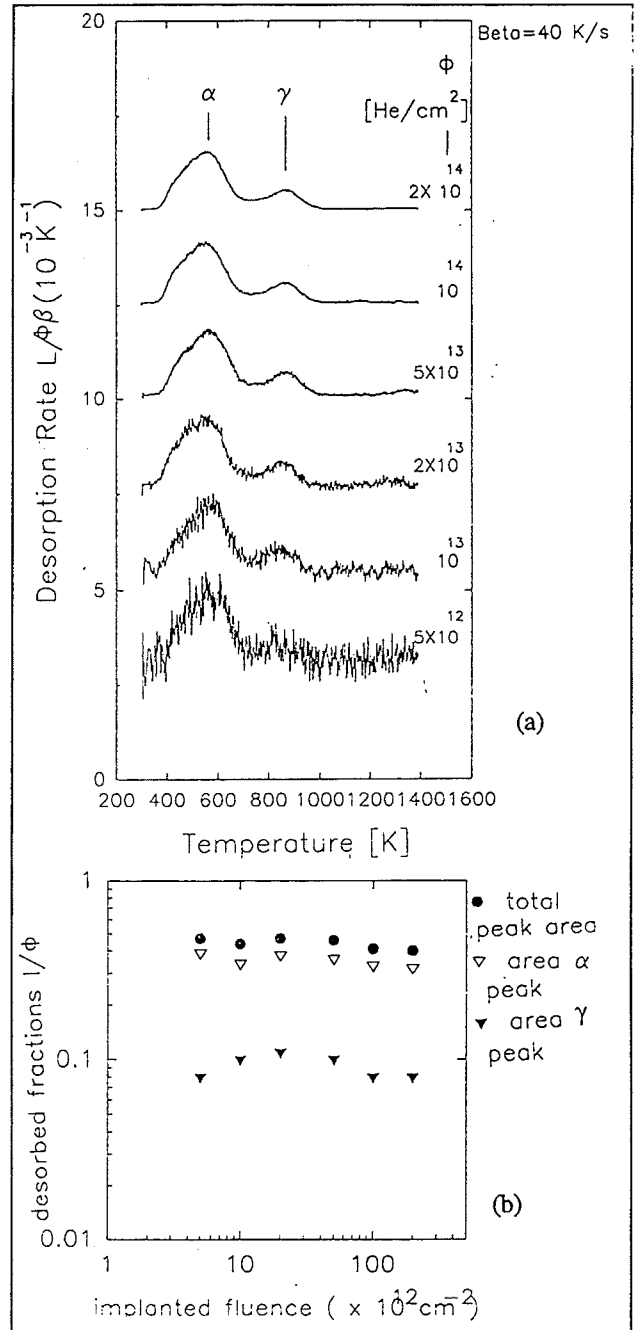


Figure 4.13: Variation of implanted fluence in an amorphous silicon film of $200 \text{ \AA}$ thickness. The energy of the implanted helium ions is 200 eV. (a) Helium desorption spectra. (b) Desorbed fraction as a function of the implanted fluence.

The results of the 40 eV series merely show small changes in the shape of the α peak and do not add much information. Therefore this series is not discussed here. These results are presented in appendix A.

4.3.3.2. Cluster of peaks B

During the implantation step, helium travels through the 10 Å amorphous film and thermalizes in the crystallized layer below the amorphous film. In the early stages of film growth, thin amorphous films consist of many small islands that do not cover the crystallized layer completely (see section 2.2.1). Consequently, most of the helium atoms that are released from traps in the crystallized layer are not retrapped in the amorphous silicon film, and show up as a cluster of peaks B in spectrum.

When the thickness is increased to 20 Å the amorphous film covers a larger area of the crystallized layer and now a significant part of the implanted helium is trapped in the amorphous film. Also helium trapped in shallow defects in the crystallized layer can be retrapped in the amorphous film on top and shows up in the α peak. The helium trapped in the “700 K traps” in the crystallized layer desorbs at higher temperatures and is not retrapped in the amorphous film. Consequently, the peak at 700 K still appears in the spectrum.

4.3.3.3. β peak

The spectrum for $d = 50$ Å shows a ‘new’ and rather sharp peak β at 630 K. In this experiment helium is implanted near the interface between the amorphous film and the crystallized layer ($R_p = 48$ Å). Therefore, the appearance of this β peak points to the existence of defects at this interface. This hypothesis will next be tested.

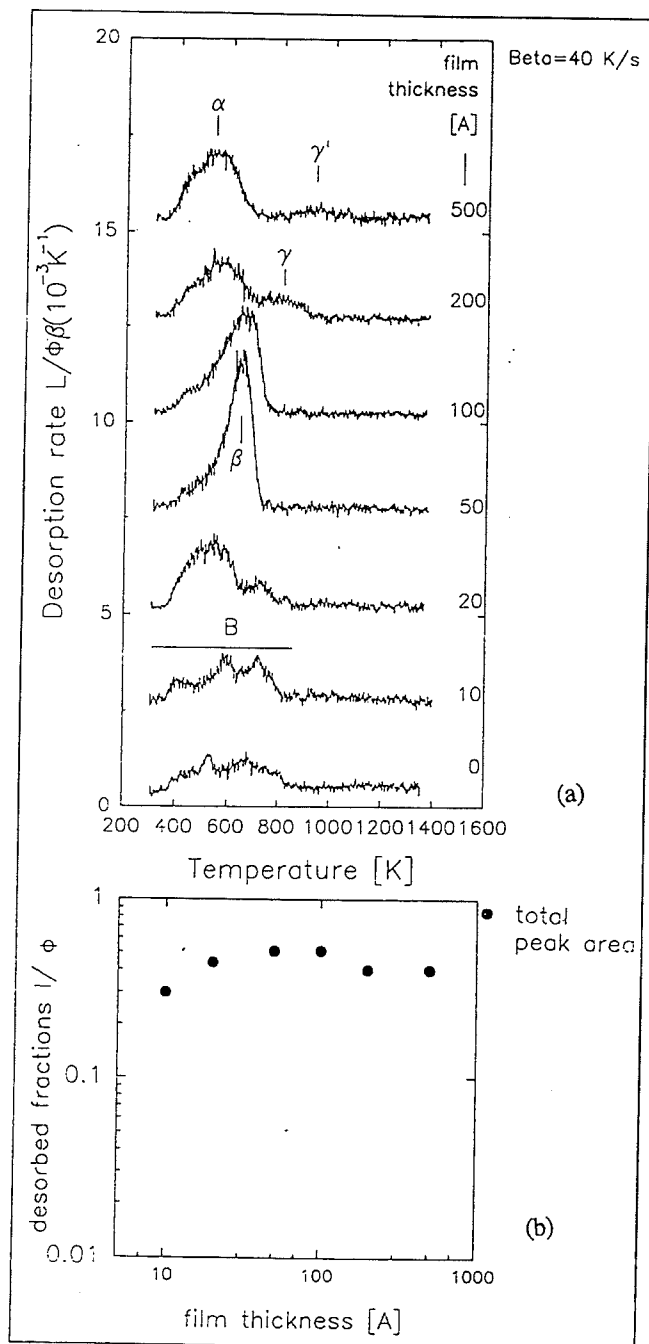


Figure 4.14: Variation in film thickness of an amorphous silicon film implanted with 200 eV helium. The implanted fluence is 10^{13} He/cm². (a) Helium desorption spectra. (b) Desorbed fraction as a function of the film thickness.

The absence of the β peak in the 10 Å and 20 Å spectra points out that in these thin films no significant number of interface defects exists. These results can be explained by the schematic presentation of the early stages of film growth, as is shown in figure 4.15. This figure shows that a 10 Å film is build up of many small islands, which increase in size when the film thickness increases. When the film thickness has increased to 50 Å the islands have become so large that some of them collapse and grow together to form amorphous columns (as is discussed in section 2.3.2). The empty spaces between the former islands are left behind as interface defects.

The absence of the β peak in the 200 Å and 500 Å spectra indicate that 200 eV helium is not implanted deep enough to become significantly trapped at the interface. This behavior is simulated with HOP, with C_{trap} and E_d of the α - defects taken from table 4.2, for a total defect concentration in the order of 10^{-2} . The β peak is fitted with one type of defect in a interface layer of 5 Å width. These interface defects are given an energy of 1.1 eV and a concentration of 10^{-2} . The results, presented in figure 4.16, support our hypothesis. They clearly show that the β peak decreases with increasing film thickness. It should be noted that in this model the γ defects are not taken into account. If these defects are added to the simulation we expect an even faster decrease of the β peak, and a quick disappearance of the β peak, as is shown in the experimental TDS results.

In order to study the β peak in more detail, we performed an energy variation for an amorphous silicon film of 50 Å thickness. The implanted fluence is 10^{13} He/cm². The results shown in 4.17, clearly show that the β peak becomes more pronounced with increasing implantation energy and thus with increasing trapping probability at the interface.

Because of the narrow shape of the β peak T_{max} can be easily estimated. Therefore we performed a heating rate variation series in order to derive values for E_d and v_0 from an Arrhenius plot (as described in section 2.3). The results are shown in figure 4.18.

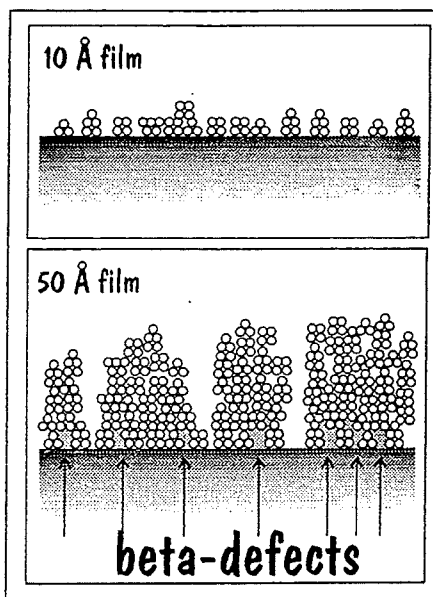


Figure 4.15: Schematic presentation of the formation of β defects at the interface between the crystallized layer and the amorphous film

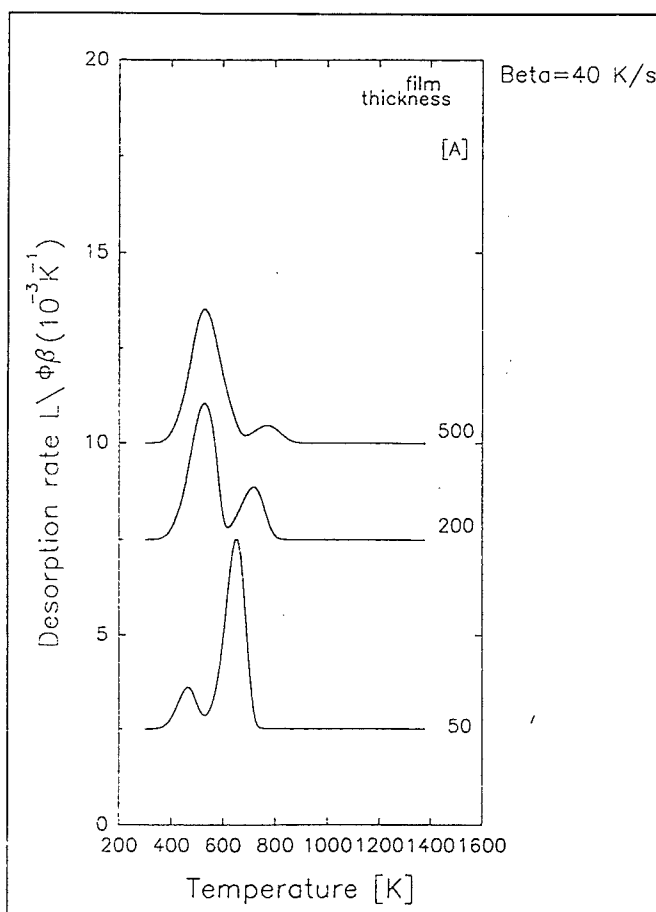


Figure 4.16: HOP simulations of the disappearance of the β peak with increasing film thickness.

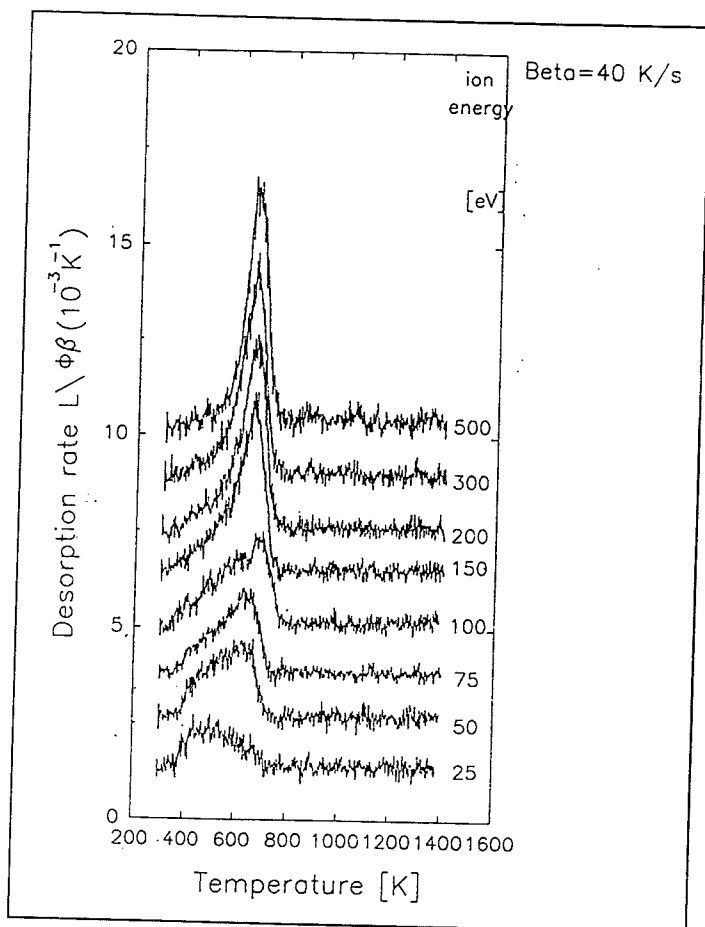


Figure 4.17: Helium desorption spectra for a variation of helium implantation energy in an amorphous silicon film of 50 Å thickness. Implanted fluence 10^{13} He/cm².

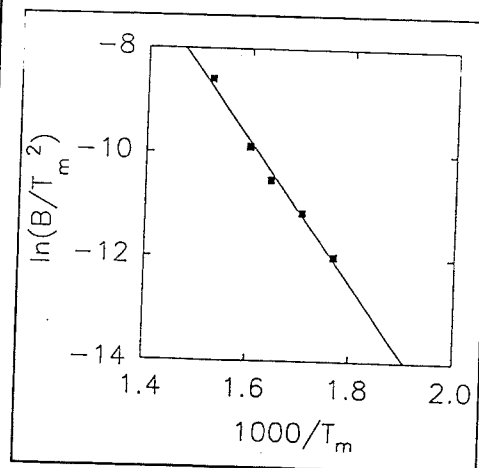


Figure 4.18: Arrhenius plot for the β peak, as derived from a heat-up variation.

The resulting values for E_d and v_0 are 1.2 eV and 2.7×10^9 s⁻¹, respectively. It should be noted that although the β peak can not be precisely fitted to a first order peak shape, the values for E_d can still be estimated in this way. The values for v_0 should be considered with more caution.⁴⁸

4.3.3.3. γ' peak

When d is increased to 500 Å the γ peak disappears and the γ' peak appears at about 900 K (see fig. 4.14). The high temperature of the γ' peak indicates that the γ' traps are even deeper than the γ traps. We have earlier ascribed the γ peak to voids. In this light the γ' traps are thought to be caused by even larger voids. The nature of the γ and γ' peak is studied in more detail with bottom-up experiments which are discussed later.

4.3.3.4. Trapping

As can be seen from figure 4.14b, the total trapping is higher for a film thickness of 50 Å and 100 Å than for the other films in this series. This increase indicates that helium is mobile at room temperature (because if helium is immobile at room temperature the total trapping is always 100 %). The increased trapping can then be explained by the increased trapping probability caused by the interface defects. In further research this explanation for increased trapping should be examined with HOP.

4.3.4. Bottom-up experiments

Figure 4.19 shows a schematic presentation of a different kind of thickness variation experiment. An amorphous film with a thickness of 50 Å is implanted with 200 eV helium with a fluence of 10^{13} He/cm². This thickness and implantation energy are chosen because of the relatively narrow shape of the desorption peak (as can be seen in fig. 4.14a) i.e. almost all helium is released from the base layer at the same time. On top of this film a new amorphous film of thickness D is deposited and subsequently the desorption step is performed. In this type of experiment, helium desorbing from the base layer travels through the entire overlayer. We call this type of experiments bottom-up probing.

4.3.4.1. Results

The desorption spectra of the bottom-up probing experiments are shown in figure 4.20a for various thicknesses D of the film on top. Figure 4.20b shows the desorbed fractions I/Φ as function of D . The following points can be mentioned:

- The β peak appears in all spectra and decreases for $D > 100$ Å. This peak shows a slight shift to higher desorption temperatures for increasing D .
- The spectrum for $D = 150$ Å shows large peak at 750 K, which we designate as the γ' peak. The spectrum for $D = 200$ Å shows a large peak γ (at 800 K), and the spectrum for $D = 500$ Å shows at large peak γ'' (at 900 K). Note that the γ and γ' peaks have been observed before (figs. 4.8 and 4.14)
- For small D 's, a small 'peak' is seen on the left side of the β peak. In the 100 Å film a small 'peak' appears on the right side of the β peak.
- The total desorbed fraction shows no significant changes with increasing D .

4.3.4.2. The γ peak

If we compare the results of these experiments with the results of the energy variation (fig. 4.8a), it can be seen that both figures show the γ peak at about 800 K. In the bottom-up probing experiments, the helium atoms originate from below the film and consequently probe the film without causing damage. *Consequently, the observation of the γ peak can not be ascribed to defects induced by the helium atoms.* Therefore, the appearance of this peak in figure 4.8 can only be ascribed to the increased depth range of high-energy helium.

4.3.4.3. The γ , γ' , and γ'' peaks

If we compare the results of the ordinary thickness variation (fig. 4.14) with the results of the bottom-up experiments (fig. 4.20), it can be seen that both figures show the γ peak at 800 K and the γ' peak at 900 K in the 200 Å and 500 Å spectra. However, the heights of the γ peaks and the γ' peaks are much smaller in the ordinary film thickness variation than in the bottom-up

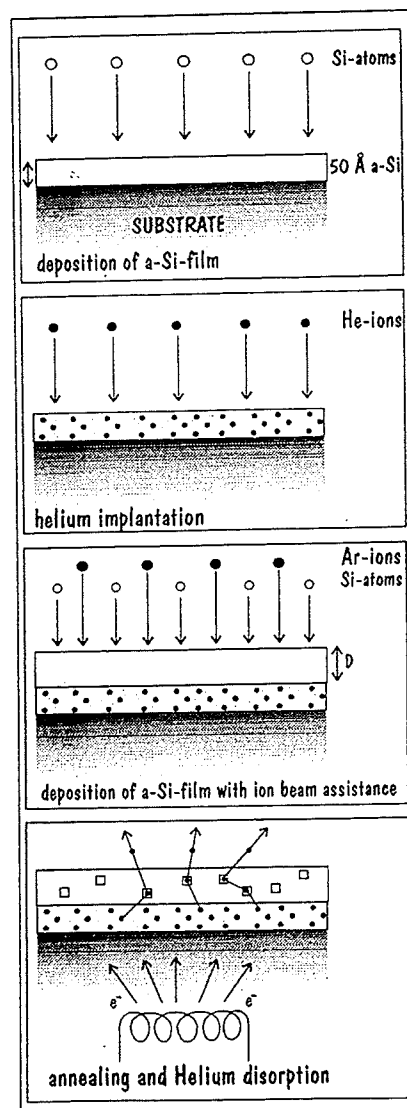


Figure 4.19: Schematic presentation of an bottom-up probing experiment. In this illustration the overlayer is deposited with AR-ion assistance.

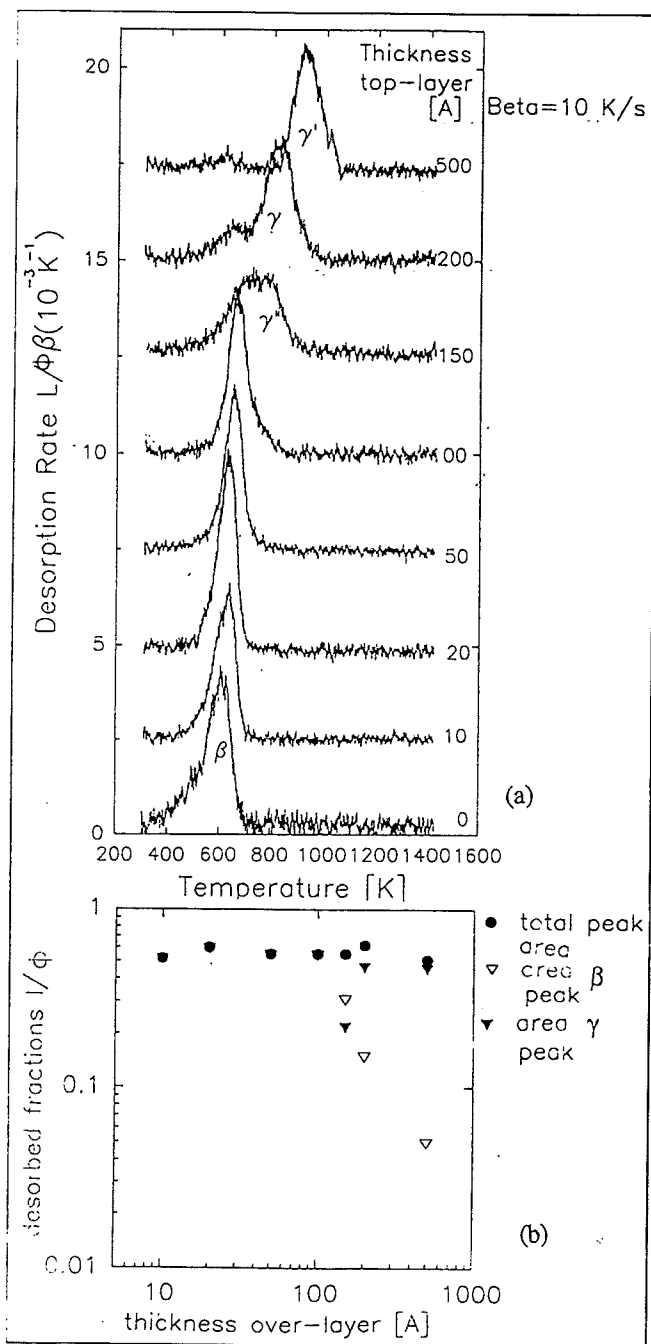


Figure 4.20: Variation in thickness of the over-layer in a bottom-up probing experiment on amorphous silicon. Thickness base layer 50 Å, implanted fluence 10^{13} He/cm^2 , energy of implanted helium ions 200 eV. (a) Helium desorption spectra. (b) Desorbed fraction as a function of the overlayer thickness.

The second explanation is in accordance with all previous results and indicates that the size of the voids in the film increases with increasing film thickness. As is described in section 3.2.2. Messier found a similar effect, which he incorporated in his growth model of the structure of tetrahedrally bonded amorphous films deposited under low mobility conditions. According to this model the films consist of rod shaped amorphous columns surrounded by small low density regions consisting of voids. If we employ this model to explain our results it can be seen that the γ -type peaks can be assigned to helium desorbing from voids between the columns. The size of

experiments. The bottom-up spectra also show a new peak for a film thickness of 150 Å. This peak γ'' appears at 750 K and is assigned to traps that are smaller than the γ and γ' traps. There are two possible explanations for the appearance of the γ'' , γ and γ' at successively higher temperatures for larger film thickness:

- There is only one type of defect, let us say γ'' defects. Helium is originally trapped in the γ'' traps but on its way to the surface it is retrapped (in γ' defects), which results in a delay in the traveling time to the surface and causes the γ'' peak to shift to higher temperatures. This shift results in the γ peak for the 200 Å films and the γ' peak for the 500 Å film.
- In thicker films, defects with increasingly larger helium/defect dissociation energies exist.

If we take a better look to the results of the energy variation (fig 4.8) and the 'ordinary' thickness variation (fig. 4.14) it can be concluded that the first explanation does not match with the results. The γ' peak does also appear in the thickness variation of fig 4.14. In this experiment the helium is implanted at the same depth in the 200 Å film and the 500 Å film. Consequently, retrapping can not explain the appearance of the γ' peak. This explanation also disagrees with the result of the energy variation of figure 4.8. This figure shows that although the increase in implantation energy increases the implantation depth, the increased chance to get retrapped only results in an increase of the γ peak and not in a shift of the γ peak to the position of the γ' peak.

helium desorbing from voids between the columns. The size of the voids between the columns increases with increasing film thickness which is also in accordance with the results of Messier. According to the model five characteristic column sizes can be identified: 10-30 Å, 50-200 Å, 200-400 Å, 500-2000 Å, and 2000-4000 Å. The first appear in the first 100 Å of the film, the second in the range of 100 to 1000 Å, the third in films of 1000 to 10000 Å etc. The low density regions surrounding these columns consist of voids, which also increase with increasing film thickness.

In this model no distinction is made between films in the range of 100 to 1000 Å thickness, which indicates that that our films of 150 Å, 200 Å and 500 Å are expected to have similar column and void sizes. In the above it is shown, however, that our results indicate that even in this range the size of the voids depends on the film thickness. The possibility of this result was already noted by Messier. He reported that the distinct levels could be caused by the limited number of results.

The existence of columns in amorphous silicon films it clearly shown in a few reports.^{27,28,53,57} Especially etched amorphous silicon films turned out to show a clear columnar structure when studied with SEM. An example of a micrograph of etched amorphous silicon film as derived with SEM is given in figure 4.21.

One question which arises from the above results is still unanswered. Why do the bottom-up experiments show much larger γ -type peaks than the ordinary TDS experiments? In section 4.2.1 we proposed that this could be explained by the fact that these larger voids only appear at larger depths in the film and not very close to the surface. The bottom-up spectra support this explanation, because all helium atoms must pass through the region where these traps are located, whatever its depth. However, this explanation is not in accordance with the assumption that these voids exist between the columns. Another explanation was based on the increasing trap chance with increasing implantation depth. It can be estimated that, when a closest packing of cylindrical columns is assumed, the area of the low density regions in a horizontal plane parallel to the surface is much smaller than the area of the columns (10% versus 90 %). It can thus be understood that only a small fraction of the helium ions that are implanted at the top is trapped in the voids (see fig. 4.22). In this case it is also clear that the possibility that helium is trapped in a void increases with increasing diffusion path and thus with increasing implantation depth.

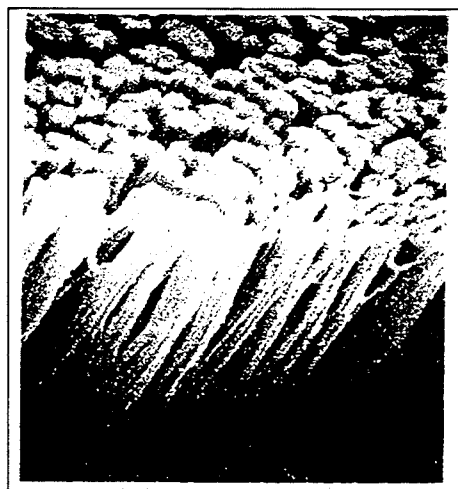


Figure 4.21: SEM micrographs of etched amorphous silicon films. This picture clearly shows the separate columns in an amorphous silicon film.

From Ross (ref. 28).

4.3.5.3. Change in shape of β peak & shift to the right

For a small thickness of the overlayer a small 'peak' is seen on the left side of the β peak (most clearly seen for 0 Å thickness, fig. 4.20). This 'peak' is caused by helium desorbing from α defects in the base layer. When the thickness of the overlayer increases, helium desorbing from the α defects is retrapped in the overlayer and the 'peak' shifts to the right towards the position of the β peak. In the 100 Å film a small 'peak' appears on the right side of the β peak. This peak is ascribed to ' γ -like' defects in the 100 Å films.

As can be seen from figure 4.20 the β peak shifts a little to the right with increasing film thickness. This shift can be explained by the increasing number of traps with increasing film

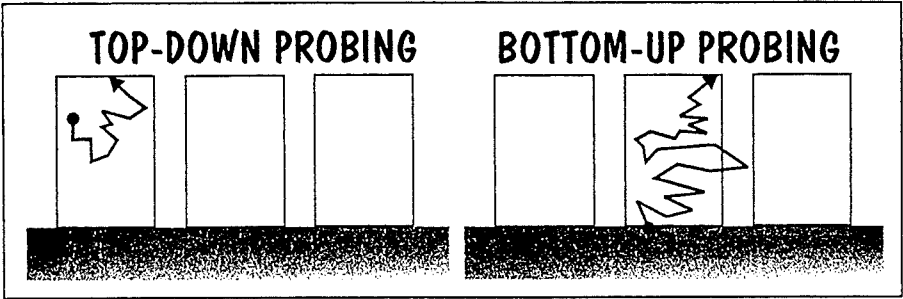


Figure 4.22: Length of the diffusion path of a helium atom in a top-down TDS experiment compared with the diffusion path of a helium atom in a bottom-up experiment.

thickness and thus by an increase in retrapping of helium on its way to the surface. The size of the shift to the right depends on the concentration of defects in the film. Therefore, it seems

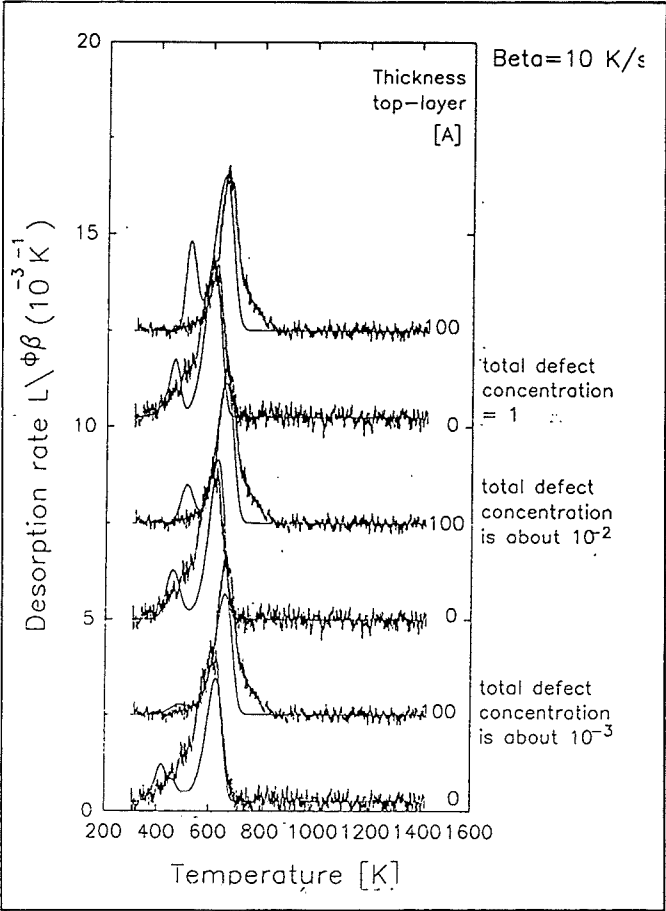


Figure 4.23: HOP simulations of the shift of the β peak to higher temperatures with increasing thickness of the overlayer in a bottom-up experiment. The accompanying fit parameters are given in table 4.2.

possible to estimate the defect concentration in the film from a simulation of these experiments with different series of defects concentrations. The results of three series of HOP calculations with different concentrations of α defects, similar to those in table 4.2, are presented in figure 4.23. The β peak is fitted with one type of defect in a interface layer of 5 Å width. These interface defects are given an energy of 1.1 eV and a concentration of 10^{-2} . This is only an approximation since the small peak at the left side of the β peak is neglected and therefore a part of the α peak is still visible in all spectra.

To our surprise these results give in all three cases almost similar shifts of the β peak. Yet, this can be understood if it is realized that although the concentration of traps is different in these three cases, the energy of the traps is changed as well. As can be seen in fig. 4.10 these two factors together result in very similar α peaks, and it is therefore not very surprising that these factors have an effect on the delay of the movement of helium to the surface. Unfortunately

this result also shows that the shift of the β peak can not be used to determine the defect concentration if the precise range of desorption energies is not known. At the other hand, it is reassuring to find that the results of the bottom-up simulations and the simulations of the traditional TDS experiments are consistent.

4.3.6. Conclusions

In the helium desorption spectra three different peaks are identified, which are called the α , β , and γ peaks.

The α peak is very broad, about 4 to 5 times wider than a first order desorption peak. It can be concluded that this peak indicates the existence of a broad range of shallow traps of slightly varying sizes. The corresponding range of helium/defect dissociation energies is about 0.7-1.0 eV.

The β peak is ascribed to defects at the interface between the amorphous film and the crystallized layer.

The γ peak is assigned to voids that exist in the low density regions between the columns in a thin amorphous film. Evidence has been found that the size of the γ traps increases with increasing film thickness. These results can be explained by the model of Messier which shows that columns and voids between the columns grow with increasing film thickness.

The trapping of helium in amorphous silicon is very pronounced, and when corrected for back-scattered ions and secondary electrons about $\sim 100\%$. This result would suggest that helium is not mobile in amorphous silicon at the room temperature. However, already a defect concentration of 10^{-3} results in a large trapping probability ($> 80\%$). There are two indications that helium is indeed mobile at room temperature in amorphous silicon.

- The trapping increases when helium is implanted near the interface (see fig. 4.14b). This result can only be explained by the increase of the trapping probability near the interface.
- It proved to be impossible to simulate an α peak if the concentration of α defects is ≥ 0.1 .

4.4. Amorphous silicon deposited with argon IBAD

This section presents the results of TDS experiments on thin amorphous silicon films deposited with argon ion beam assistance. The questions discussed in this section are:

- are we able to detect any difference between the defect structure of IBAD amorphous silicon and EVAP amorphous silicon? and if this turns out to be possible,
- what are the differences and how can they be explained?

In order to find answers to these questions we performed three series of measurements in which we varied the ion-to-atom arrival ratio IAR , the energy of the bombarding ions, and the film thickness. The results are compared with the measurements on amorphous silicon films deposited without ion beam assistance (EVAP amorphous silicon), which we discussed in the previous section.

4.4.1. Variation in argon energy and *IAR*

A variation in energy of the bombarding argon ions is performed in order to estimate the energy at which significant changes emerge between the TDS spectra of EVAP and those of the IBAD films. In addition to these experiments, we performed an *IAR* variation, in order to examine the influence of this parameter on the defect structure of the IBAD films. As is shown in the section 4.3, the thickness variation measured using the bottom-up method gives the best insight in the characteristics of the γ defects in the EVAP film. Therefore, similar experiments are performed with IBAD films to study the changes in the appearance of the γ peak.

The experiments discussed next show a very sharp peak around 1000 K, which was also detected in the reference signal. In order to study this peak in more detail the results presented next are not corrected for background.

4.4.1.1. Results

Figures 4.24 and 4.25 show the results of TDS experiments on amorphous silicon films deposited under argon bombardment. Figure 4.24a shows spectra for selected energies of the bombarding argon ions (E_{Ar}), varied between 20 and 500 eV. The *IAR* is 0.05 for all energies in the range of 20 to 200 eV, and 0.1 for the spectrum of 500 eV. Figure 4.25a shows spectra for selected *IAR* ranging from 0.006 to 0.07, E_{Ar} is 200 eV. In both series the implanted fluence is 10^{13} He/cm² and the film thickness is 200 Å. These values are chosen to enable easy comparison with the EVAP spectra. For the same reason the EVAP spectrum is added to both figures. In figure 4.24b and 4.25b, the desorbed fractions are plotted versus E_{Ar} and versus the *IAR*, respectively.

The following points can be mentioned:

- Both series show a large α peak. The shape of this peak clearly differs from the shape of the α peak in the EVAP spectra.
- The γ peak is not detected in the IBAD films
- Both series show an ϵ peak, which increases with increasing energy of the bombarding argon ions and with increasing argon implantation energy. The ϵ peak appears when the energy of the bombarding ions is increased to 100 eV, and the peak height increases with increasing beam energy. The same peak is found in the *IAR* series where it appears at an *IAR* of 0.03 and increases with increasing *IAR*.
- The desorbed fractions show no significant change in trapping with increasing implantation energy or *IAR*.

4.4.1.2. α peak

As is described in section 2.3.2, one of the technological objectives of ion beam assistance is to manufacture a more regular film with fewer defects. If we take a brief look at the results of figure 4.24 and figure 4.25 it seems as if in this case the opposite is true. The α peak in the IBAD spectra is a little larger than in the EVAP spectra, which at first sight seems to indicate that the argon ions create defects instead of reducing them. However, at the same time the γ peak has disappeared and the total trapping did not show significant changes.

The α peak seems to exist of at least two distinguishable sub-peaks, α_1 and α_2 . In order to get a better insight in which defects are caused by IBAD, we have subtracted an "EVAP spectrum" from all "IBAD α -spectra". The results are presented in appendix B. We had hoped to find a small peak that could be ascribed to one type of defect. Because of retrapping these results do not show unambiguous results and do not add any significant information.

The increase of the α peak by the ion assistance can be explained by two possible causes: (i) a decrease of the number of γ defects, which results in an increased trapping in the α defects. (ii) production of α -type defects by the argon beam, for example incorporation of argon in the film,

or enhancement of existing defects. In further work HOP simulations should be performed to distinguish between these to explanations.

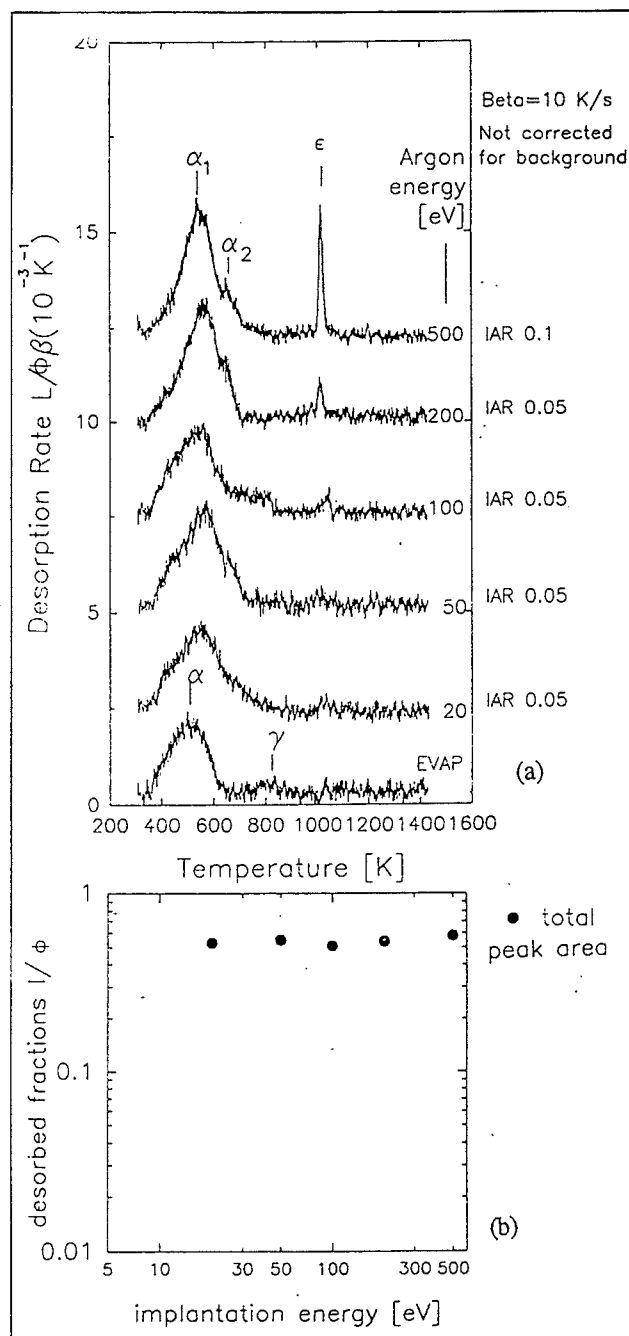


Figure 4.24: Variation in energy of the bombarding argon ions during the deposition of an amorphous silicon film of 200 Å thickness. Implanted fluence 10^{13} He/cm², energy of implanted helium ions 200 eV. (a) Helium desorption spectra. (b) Desorbed fraction versus argon energy.

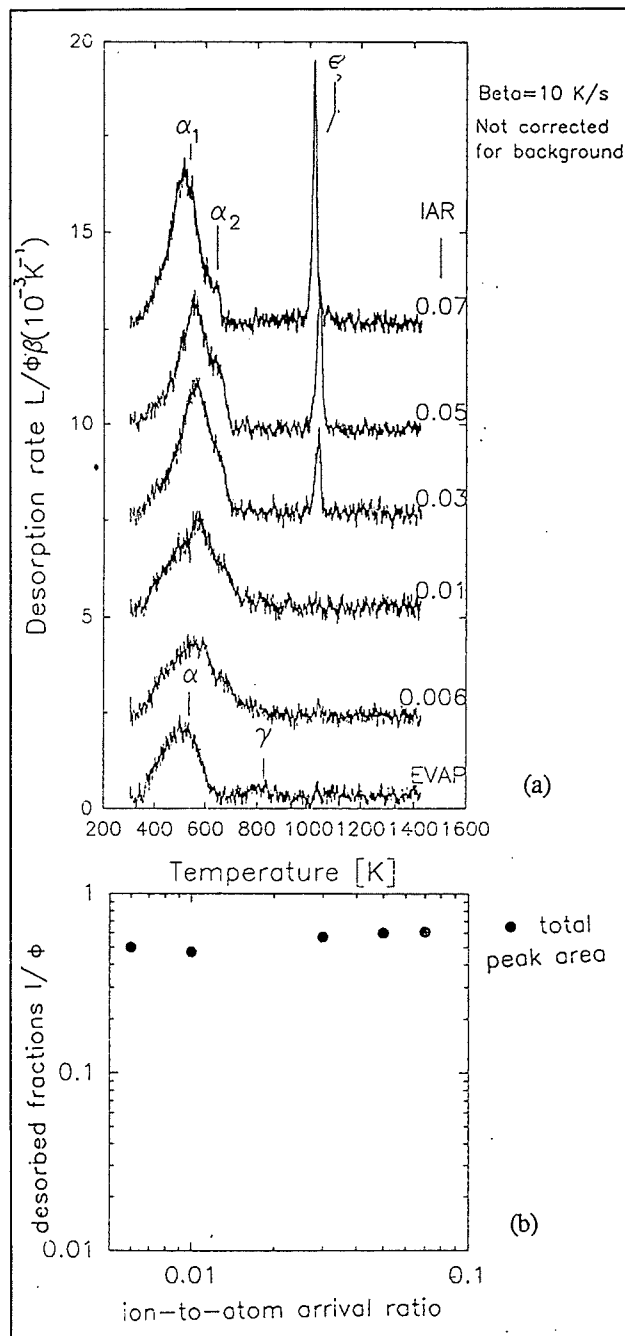


Figure 4.25: Variation in ion-to atom arrival ratio (IAR) during the deposition of an amorphous silicon film of 200 Å thickness. Implanted fluence 10^{13} He/cm², energy of implanted helium ions 200 eV. (a) Helium desorption spectra. (b) Desorbed fraction versus IAR

4.4.1.3. γ peak

As is discussed above it can be seen that the γ peak, which is detectable in the EVAP spectra does not appear in the IAD spectra of figure 4.24 and 4.25. From these results it can be concluded

that the γ defects disappear as a consequence of the ion bombardment during deposition. In order to study the disappearance of the γ defects in more detail we performed bottom-up probing experiments. The results of these experiments are presented in section 4.4.2.

4.4.1.4. ϵ peak

The very sharp ϵ peak at about 1000 K is found in both figure 4.24 and 4.25. This peak is also observed in the reference spectra, which indicates that it is not caused by the release of helium from the film. It is clear that with increasing *IAR* and argon energy, the number of argon atoms in the film increases. Hence, the increase of the ϵ peak with these parameters points to the release of argon. In order to examine this explanation and to get an indication of the amount of argon that is incorporated in the films, we performed a series of argon desorption experiments. The results of these experiments are described next.

It is surprising that although the mass spectrometer is tuned to helium, we still measure the release of argon. This can be explained by the fact that the release of argon produces a rather large pressure rise. The mass filter in the mass spectrometer is very sensitive for pressure rises and becomes less selective at higher pressures.

4.4.2. Bottom-up experiments

4.4.2.1. Results

A series of bottom-up experiments is performed to study the γ peak in more detail. The results are shown in figure 4.26a. In this series the thickness of the top layer is varied between 10 Å and 500 Å. An amorphous silicon film of 50 Å thickness is implanted with 200 eV helium, and subsequently covered by IBAF films of increasing thickness. The *IAR* is 0.06 and the energy of the bombarding argon ion is 200 eV. Figure 4.26a also shows a spectrum for the bare 50 Å amorphous film (EVAP). In figure 4.26b, the desorbed fractions are plotted versus the thickness of the top-layer.

The following features are shown:

- The γ -type peaks are absent in all spectra apart from the 500 Å film where a small γ peak appears at about 800 K.
- The β peak is shown in all spectra and shifts slightly to the higher temperatures with increasing overlayer thickness
- The ϵ peak appears in films of about 20 Å and increases with increasing thickness of the amorphous film on top

4.4.2.2. γ peak

Figure 4.26 shows (more clearly than figures 4.24 and 4.25) that the γ traps are almost completely absent in the IBAF films. Only when the film thickness is increased to 500 Å a small peak appears at 800 K. This result shows a spectacular difference between the EVAP (fig 4.20) and the IBAF films. In order to give a clear overview of the differences between these series, figure 4.27 shows the results of both bottom-up probing experiments in one graph. The disappearance of the γ peaks indicates that ion beam assistance during the film growth results in a film containing (almost) no large traps.

Since the γ peaks are assigned to voids existing between amorphous columns, it can be concluded that the disappearance of these peaks is related to a change in film growth from a columnar growth to a layered growth. This change is ascribed to the enhanced mobility of silicon atoms that arrive at the surface, as result of the ion beam assistance. The increased mobility enables the silicon atoms that arrive at the surface, to overcome the effect of shadowing, resulting in a homogenous film without columns.

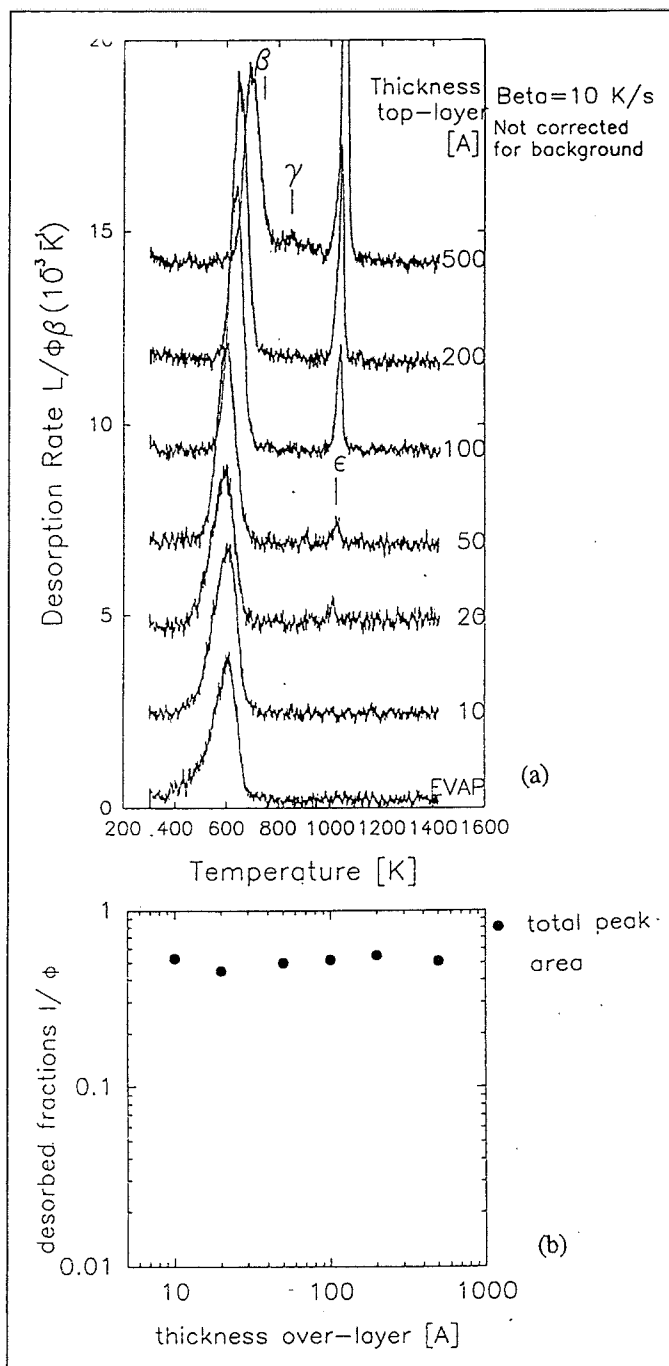


Figure 4.26: Variation in thickness of the overlayer in a bottom-up probing experiment of amorphous silicon deposited under argon bombardment. Thickness base layer 50 Å, implanted fluence 10^{13} He/cm^2 , energy of implanted helium ions 200 eV. (a) Helium desorption spectra. (b) Desorbed fraction versus thickness overlayer.

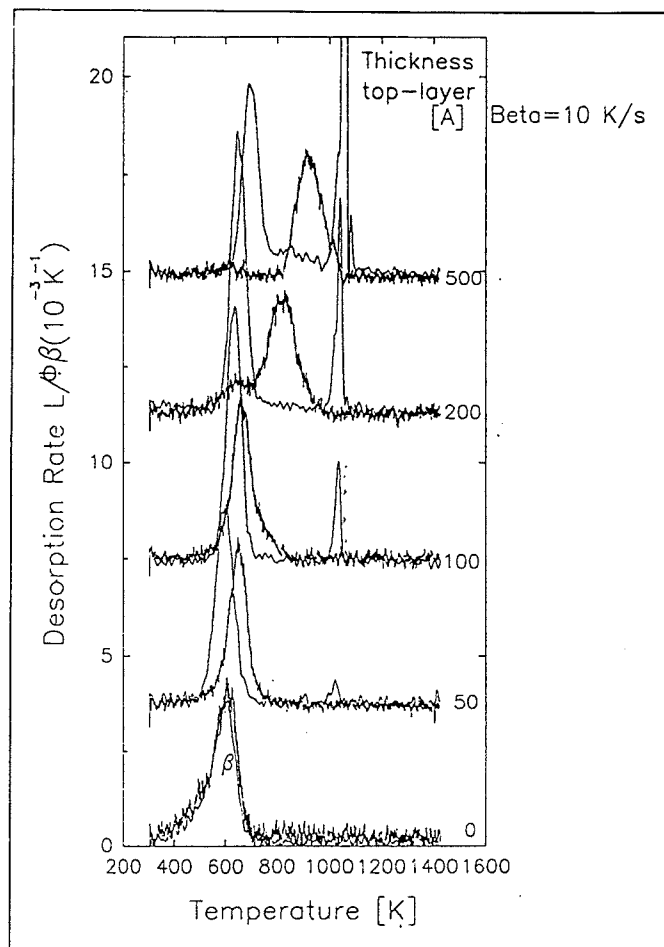


Figure 4.27: Bottom-up probing experiments with and without ion bombardment of the overlayer plotted together in one figure.

These series of IBA experiments should be compared with experiments in which the substrate temperature is varied. Both methods increase the mobility of surface atoms during deposition. It is therefore interesting to determine whether ion beam assistance and increased substrate temperature result in a similar film structure. Due to problems with the electron gun in the deposition position (see figure 3.1), we were not yet able to perform these measurements.

4.4.2.3. β peak

One of the most important features of this series (fig. 4.27) is that the β peak does not disappear when the film thickness increases. This result is in contrast with the results of the bottom-up series with EVAP films on top and is a result of the disappearance of the γ defects.

Figure 4.27 clearly shows that below an overlayer thickness of 100 Å, the IBAD films show a considerably smaller shift of the β peak than the EVAP films. This result is not in accordance with the expectations. In the previously discussed results the shift of the β peak is ascribed to a diffusive delay in the movement of helium atoms to the surface, due to the increased retrapping probability of helium atoms in α defects with increased film thickness. The smaller shift of the β peak observed for IBAD films would then indicate a decrease in concentration of α traps or a decrease in size (which is related to the helium desorption energy) of the α defects. Figure 4.24 and 4.25, however, show none of these effects. It is also possible that in the IBAD films the defect density on larger depths in the film is considerably smaller than near the surface. This should result in less delay in the movement of helium to the surface, and thus a smaller shift of the β peak. It can be concluded that the shift of the β is still not fully understood and should be studied in more detail in further work.

4.4.3. Argon desorption measurements

The amount of argon incorporated in the film and the argon release process are studied with argon desorption measurements. Before the results are discussed, first some literature results of argon desorption from silicon are summarized.

In literature it is seen that argon desorption spectra for amorphous silicon show a very sharp desorption peak.^{17,75,76} In these studies single crystalline silicon is made amorphous by argon bombardment. It is concluded that on annealing the silicon crystallizes and the implanted argon is swept out by the recrystallization front. If the implanted argon fluence is increased to above 10^{18} Ar/cm² the crystallization peak starts to shrink while desorption peaks at higher temperatures start to grow, indicating that another release mechanism takes over. It should be noted that these peaks represent defects that survive crystallization. It is thought that they represent argon release from large bubbles. An example of these argon desorption spectra is presented in figure 4.28. Argon desorption studies on sputtered amorphous silicon films presented in literature (in which argon was solely build in during the sputtering process), showed similar release as for surface layers made amorphous by implantation.⁷⁵ On the basis of these literature results we expect a single argon peak at the crystallization temperature.

Unfortunately, we had some problems with the rate meter and the calibration valve during these experiments, and only two measurements turned out to give reliable results. Figure 4.29 shows the argon desorption spectra for two argon desorption experiments for an *IAR* of 0.02 and 0.08. The thickness of the deposited film is 200 Å, and the energy of the bombarding argon atoms is 200 eV. The helium desorption spectra of similar films fall in the series shown in figure 4.25 (although these particular *IAR* values were not measured).

The following features are shown:

- The spectrum for *IAR* = 0.02 shows a sharp (much sharper than a first-order peak) asymmetric argon desorption peak ϵ at 1007 K. It should be noted that this temperature is much higher than the argon release temperature shown in the literature results (fig. 4.28)
- The ϵ -peak in the spectrum for *IAR* = 0.08 is build up of about six separate peaks indicated with ϵ_1 to ϵ_6 . The peak temperature of the three sharp peaks ϵ_3 , ϵ_4 , and ϵ_5 are located at respectively 976, 995 and 1005 K. The peak temperature of the broader peaks ϵ_1 , ϵ_2 , and ϵ_6 appear at about 860, 940 and 1024 K, respectively

- Almost no argon desorption is detected below the temperature at which the ϵ -peaks appear. This result is in contrast to the results derived for helium desorption experiments, which show that (most) helium is released from the film before crystallization.
- The incorporation of argon in the spectrum for $IAR=0.02$ is about 2% and the incorporation of argon in the spectrum with an IAR for 0.08 is about 14 %. This has been derived from the peak areas.

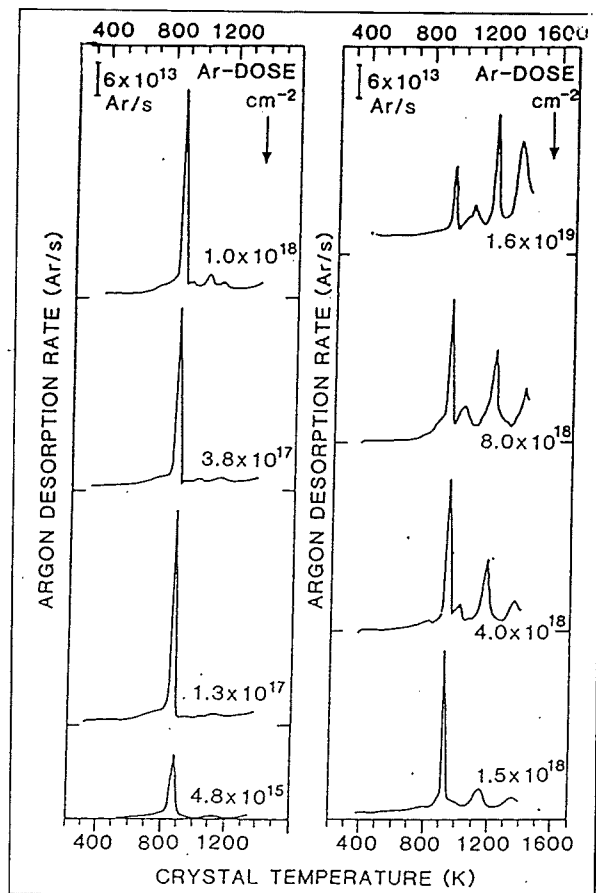


Figure 4.28: Argon desorption spectra from *a*-Si (110) single crystal which has been irradiated with 1 keV Ar^+ . The argon irradiation fluences are as indicated. From Filius (ref. 17).

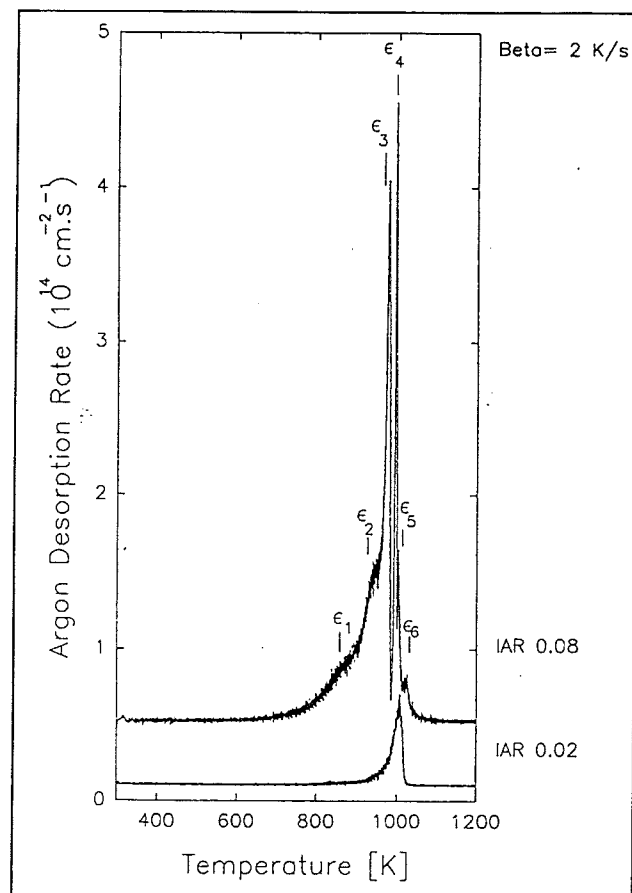


Figure 4.29: Argon desorption spectra for an amorphous silicon film of 200 Å thickness. The energy of the bombarding ions is 200 eV.

The temperature of the maximum argon release rate corresponds to the temperature of the ϵ -peaks in the IBA series of figure 4.24, 4.25, 4.26. Thus, the results confirm the assumption that the ϵ peak is due to argon released from the sample.

Because of problems with the calibration the calculated fractions of argon incorporation are not very accurate, the error can be as large as a factor of two. The IAR in these measurements differs by a factor of two, hence we expected a factor of two in argon release from the films. The much larger difference is therefore thought to be due to inaccuracy of the calibration.

In the spectrum for $IAR=0.02$, the release of argon is dominated by a very sharp peak at 1007 K. The peak shape is in accordance to the literature results. As described above, in the literature the release mechanism is ascribed to the movement of the crystallization front, which sweeps the argon to the surface during the crystallization of the amorphous film. If this model is applied, the expected argon release temperature can be calculated from the thickness of the film. In the epitaxial regrowth model proposed by Williams,⁷ the recrystallization front moves towards the surface with a velocity $v=v_0 \exp(-Q/kT)$ where v_0 is a pre-exponential factor [m/s] and Q the activation energy of motion [eV].

The relation between the thickness d [m] of the amorphous film and the observed recrystallization temperature T_c [K] is then given by

$$d = \frac{v_0}{\beta} \int_{300}^{T_c} \exp\left(-\frac{Q}{kT}\right) dT \quad (4.3),$$

where β is the heating rate (dT/dt) [K/s].

It is shown by van Veen⁷⁵ that the best fit is found for $v_0=2.1 \times 10^6$ m/s and $Q=2.8$ eV (these values are derived from heating rate variations, and variation of the film thickness of films made amorphous under argon bombardment). Applying these values to calculate the crystallization temperature of our 200 Å thick film, we find $T_c = 932$ K (for $\beta=2$ K/s). This value is not in agreement with the experimental value of the T_{max} in the argon desorption experiments ($T_{max} = 1007$ K/s). The accuracy of the literature values is not known to us. However, the difference between our results and the literature results can arise from the incorporation of impurities (molybdenum) in our films and the different substrate, which can alter the crystallization process.

If we take a close look at the spectrum for $IAR=0.08$, it appears that about six separate peaks can be detected. These peaks are indicated with ϵ_1 to ϵ_6 . We suggest that the appearance of these six separate peaks indicate that the crystallization does not start simultaneously and at a constant distance from the surface, but at slightly different times at various places in the film. This behavior is in contrast with the model proposed above and is expected to be due to the incorporation of impurity atoms. However, it must be noted that this suggestion is based on only one experiment, and additional experiments (for example with a pure silicon substrate) are necessary to derive valuable conclusions. Moreover these six peaks do only appear in the $IAR=0.08$ spectrum and not in the $IAR=0.02$ spectrum. We do not yet have an explanation for this difference.

4.4.4. Conclusions

From the results presented above it can be concluded that significant differences are observed between IBAD amorphous silicon and EVAP amorphous silicon. The most important difference is the almost complete disappearance of the γ peak. The disappearance of this γ peak indicates that ion beam assistance during the film growth results in film containing fewer voids. This result is in accordance with the literature where it is stated that ion beam assistance during the film growth results in an increased mobility of the silicon atoms at the surface, which enables them to overcome the effect of shadowing, resulting in a homogenous films without columns.

An additional result is a small increase and a change in shape of the α peak. This change is thought to be due to the disappearance of the γ defects, but might also be due to an increase in α defects produced by the argon beam (like incorporated argon atoms).

The amount of argon that is incorporated in the film is on the order of a few percent. The shape (six separate peaks instead of one) and the positions of the peaks are not in exact agreement with the literature. It might be interesting to perform additional argon desorption experiments to take a closer look at these results.

4.5. Anneal experiments

This section presents the results of a series of anneal experiments on thin EVAP amorphous silicon films. After deposition (but before He^+ ions are implanted), the as-deposited amorphous silicon films are heated to a certain anneal temperature T_a at 40 K/s, held there for a few seconds, and are then allowed to cool down to (almost) room temperature. In this way the structural relaxation processes that take place below T_a can be studied. With these experiments we want to answer the following questions:

- How do the α and γ defects respond to annealing?
- What happens upon crystallization?

4.5.1. Results

Figure 4.30a shows the results of a series of anneal experiments on amorphous silicon films of 200 Å thickness. T_a is varied between 400 K and 1400 K. After the film has cooled down to $T < 340$ K it is implanted with helium with a fluence of 10^{13} He/cm^2 and with an implantation energy of 200 eV. Figure 4.30b presents the desorbed fractions I/Φ associated with the various peaks versus the anneal temperature.

The following points can be mentioned:

- The α peak becomes sharper when the anneal temperature increases.
- Both the α and γ peaks shift to the higher temperatures with increasing anneal temperature below crystallization.
- The spectra of the films annealed to 700 and 800 K show an increased intensity of the γ peak in comparison to the films annealed below 700 K. The intensity of the γ peak decreases again upon annealing to 900 K.
- A clear difference is shown between the films annealed below and above 1000 K.
- The trapped fraction of implanted helium decreases just before crystallization

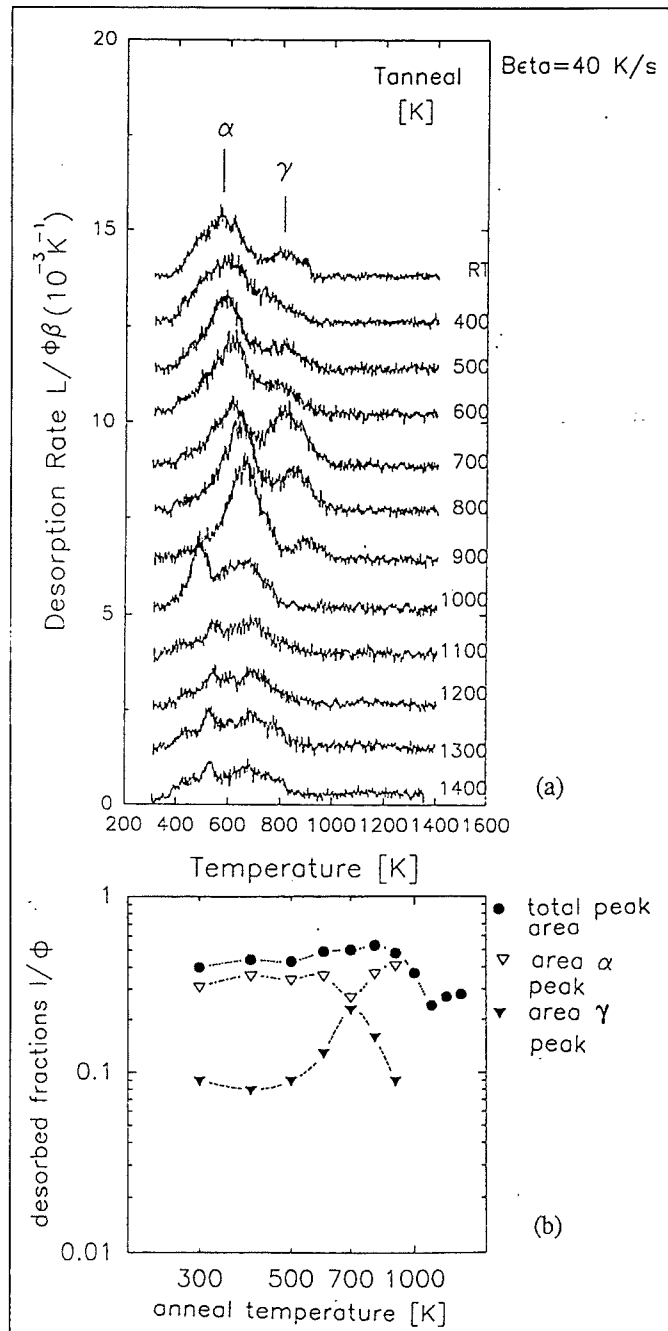


Figure 4.30: Variation in anneal temperature of an amorphous silicon film of 200 Å thickness. Implanted fluence 10^{13} He/cm^2 , energy of implanted helium ions 200 eV. (a) Helium desorption spectra. (b) Desorbed fractions versus anneal temperature.

Appendix A, presents an additional anneal series performed with an implantation energy of 40 eV. The results of this series do not add much information to the result presented above and are therefore not discussed here.

Also an additional anneal series in which the samples were held 120 sec at T_a are performed and showed no significant differences with the series of figure 4.30.

4.5.2. Discussion

The changes in the shape of the α peak point to a rearrangement in the atomic structure, while the shift to higher temperatures shows that stronger trapping α -type defects become relatively more numerous. It would be interesting to perform HOP calculations to simulate the change of the α peak with increasing temperature. In these calculations the α peak should be fitted with six defects with E_d as the initial c_v as in table 4.2. We expect that the change in the shape of this peak can then be simulated by decreasing the concentration of shallow α defects and simultaneously increasing the deep α defects. These calculations are not yet performed, but are recommended for further work.

The shift of the γ peak may be explained by mobile defects attaching themselves to the existing voids, whereby the voids grow in size. The increase in intensity of the γ peak points out that apart from growth of the γ traps also additional γ traps are created upon annealing at 700 or 800 K. The decrease of this peak upon anneal to 900 K indicates that γ trap (voids) become unstable at this temperature and collapse.

At 1100 K and upwards the spectrum of the crystallized layer is obtained. The structure of the crystallized layer does not show detectable changes upon annealing above this temperature. The 1000 K spectrum is hard to interpret because it has similarities with both the amorphous and the crystalline spectra. As is seen in the argon desorption measurements the crystallization takes place at about 1000 K when the film is heated with a heating rate of 2 K/s. From eq. (4.3) it can be calculated that this is in accordance to a temperature of about 1100 K when heated with a heating rate of 40 K/s. This indicates that the film annealed to 1000 K is still amorphous. This result is in accordance to additional TDS experiments performed with 40 eV (shown in appendix A).

The 1000 K spectrum shows that the γ traps have completely disappeared, the number of α traps has decreased and a new peak appears at about 500 K. These results indicate that a more regular atomic arrangement has evolved in which the number of trapping sites for helium has decreased. We do not have an explanation for the appearance of the peak at 500 K.

As is discussed in the previous sections, the γ defects are assigned to voids probably located in the low density regions between the rod shaped columns in the amorphous film. In view of this model the results of the anneal experiments can be interpreted as a rearrangement of small and larger defects in the low density regions in which some voids grow by attachment of small defects and new voids appear by the clustering of small defects. It will be interesting to confirm these suggestions by performing additional experiments with TEM.

Somewhat to our surprise, figure 4.30b shows a decrease of the trapped fraction just before crystallization takes place (the 40 eV series shows similar results), while the trapped fraction after crystallization is more or less constant and much lower than the trapped fraction in amorphous silicon. This result indicates that helium is mobile in crystalline silicon at room temperature, which is in contrast to the results of permeation measurements reported in the literature.^{11,46} Moreover, the decrease of the trapped fraction *before* crystallization is an indication of the structural relaxation processes that take place in the amorphous structure.

In the anneal experiments the films have been heated at 40 K/s. We have just shown that this treatment leads to significant changes in the desorption spectra. It should therefore be noted that

the film structure does also change during the desorption step, implying that the experimental method influences the objects of the measurement. In general it is assumed that helium stabilizes the defects in which they are trapped. Thus, if helium is not retrapped in the film, one may expect that the change in film structure during desorption does not influence the measurement itself. However, in our experiments retrapping plays an important role. Therefore, this problem should be studied in more detail in further work.

Although our experiments are focused on amorphous silicon we have also performed a few additional measurements on the crystallized layer. These experiments were primarily performed in order to find out whether the amorphous film after the anneal to 1400 K had turned into a defect-free crystallized layer. In the initial experiments the spectra showed sharp peaks which are ascribed to the incorporation of impurities. Later the spectra totally changed. This sudden change in the appearance of the spectra is still unexplained. Since our main focus is amorphous silicon we will not discuss these spectra here. However, these spectra can be used as comparison in further research and are therefore presented in appendix C.

4.5.3. Conclusions

The results clearly show that the defect structure of the amorphous film changes upon annealing below crystallization temperature.

Changes below $T_a = 800$ K are explained by a rearrangement of the atoms in the amorphous structure in which the deeper α traps become relatively more numerous and voids increase in size and initially also in number. It is suggested that during the anneal, mobile defects attach themselves to the existing voids, whereby the voids grow in size.

At temperatures between 900 and 1100 K, the voids collapse and the number of α traps increases, indicating that a more regular arrangement of atoms has originated.

Crystallization takes place at $T_a \approx 1100$ K. The structure of the crystallized layer does not show detectable changes upon anneal above this temperature up to 1400 K. The trapped helium fraction decreases upon crystallization, indicating that helium is mobile at room temperature in the crystallized layer.

5. Conclusions & Recommendations

5.1. Conclusions

- The results of our experiments show that we have successfully studied defects in amorphous silicon using TDS. In view of the noncrystallinity, some types of defects do not show up separately, as in studies of crystalline metals, but rather as traps having a continuous range of helium binding energies. Three distinct types of traps are detected: (i) small traps that might be assigned to interstitial positions, atom-size defects, deformed regions surrounding incorporated impurity atoms, or a combination of these three; (ii) small defects at the interface between the amorphous film and the crystallized layer; (iii) and stronger binding traps which are assumed to be voids.
- The voids increase in size with increasing film thickness. This result is in accordance with literature results and is ascribed to an increase in column size, and a simultaneous increase in the size of the voids between the columns, with increasing film thickness.
- Significant differences are detected between the amorphous silicon films deposited with and without ion beam assistance. The most important difference is the almost complete absence of voids in the films deposited under ion bombardment. This is ascribed to the enhanced mobility of silicon atoms that arrive at the surface, as result of the ion beam assistance. The increased mobility enables the silicon atoms that arrive at the surface to overcome the effect of shadowing, resulting in a homogeneous film without columns. (shadowing produces open boundaries, particularly under conditions of non-perpendicular flux, because the high points receive more flux than the low points).
- With TDS we can detect changes in the defect structure of the amorphous film upon annealing below the crystallization temperature. The changes are explained by a rearrangement of the atoms in the amorphous structure, and changes in the void structure in the low density regions.
- Our amorphous silicon films are contaminated with molybdenum (~700 ppm), and possibly with a small amount (<500 ppm) of carbon, hydrogen and nitrogen. Although the incorporation of these elements may influence the spectra of amorphous silicon somewhat, it is not yet clear which features of the spectra, if any, should be ascribed to the presence of these elements.
- Computer calculations with HOP (Hopping Of Particles) can help to distinguish between possible explanations for the changes in experimental derived desorption spectra and facilitate a more detailed interpretation of these spectra.

5.2 Recommendations

- Additional experiments with STM, TEM, and small angle X-ray diffraction should be performed to confirm our expectations that our films are built up of columns that become wider with increasing film thickness, and to gain more insight in the (columnar) structure and the development of this structure during film growth.
- It is interesting to compare the interface defects of films deposited without ion bombardment with those of films deposited with ion bombardment. The object is to get more insight in the development of the first atomic layers during the film growth.
- Experiments with a lower energy (for instance 20 eV instead of 200 eV) of the bombarding ions (to decrease the incorporation of argon), can yield additional information on the development of defects in the amorphous film.
- Experiments with increased substrate temperature should be performed to examine whether the resulting increase in mobility of the silicon atoms leads to similar results as ion beam assistance
- In this work a few preliminary HOP calculations have been performed. Still many extra simulations with HOP are needed to gain a better insight in some of the results that are yet not fully understood.
- Apart from the implantation of helium into the free surface on top (as in traditional TDS experiments) and into a base layer (as in bottom-up experiments), a third method in which helium is co-implanted in the film during deposition should be employed in further work. With the method of co-implantation large implantation depths can be obtained without increasing the implantation energy (which can result in the unwanted production of additional defects) and without being restricted by the temperature at which helium is first released from the base layer.
- The use of neon instead of helium as probe atoms might yield more information about the nature of the α defects, because of the expected difference in binding energy of neon to α defects. Moreover it will be interesting to examine whether neon is released from the film between the release temperature for argon and helium.
- The experiments performed on the crystallized layer should be duplicated on a pure silicon substrate (instead of MoSi_2).

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Appendix A

Result of additional TDS series

The results of three additional TDS series are shown in figure A.1, A.2, and A.3.

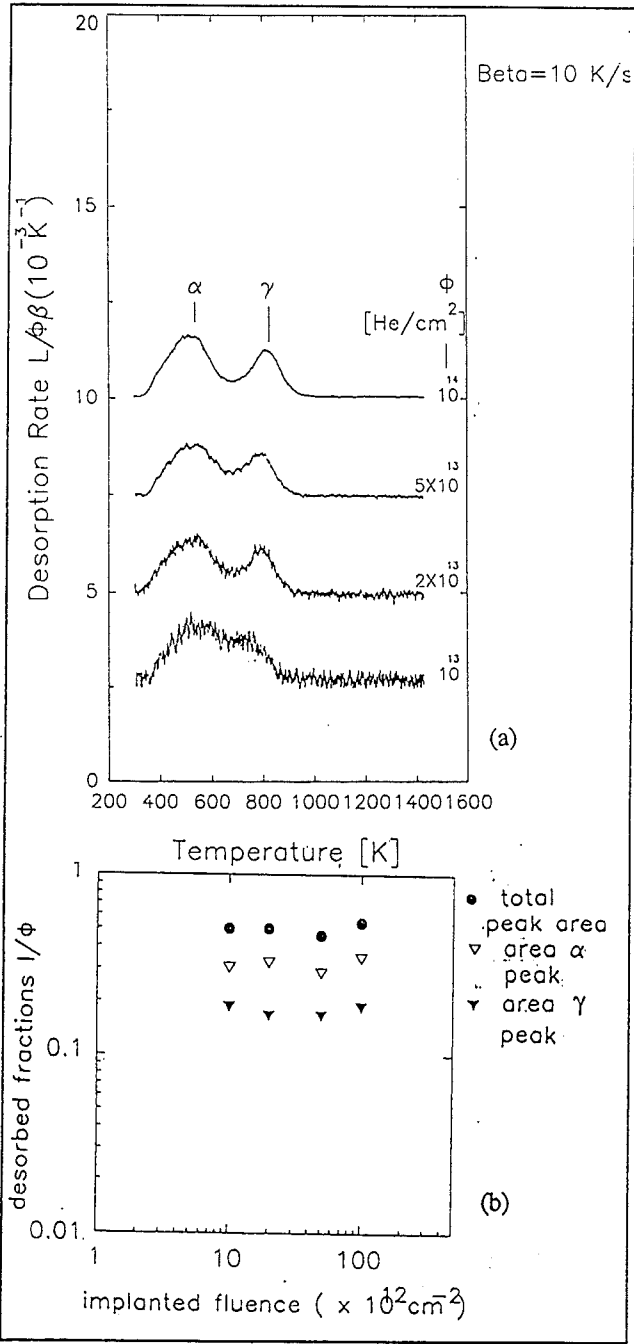


Figure A.1: Variation in implanted fluence in an amorphous silicon film of 200 Å thickness. The energy of the implanted helium ions is 500 eV. (a) Helium desorption spectra. (b) Desorbed fraction as a function of the implanted fluence

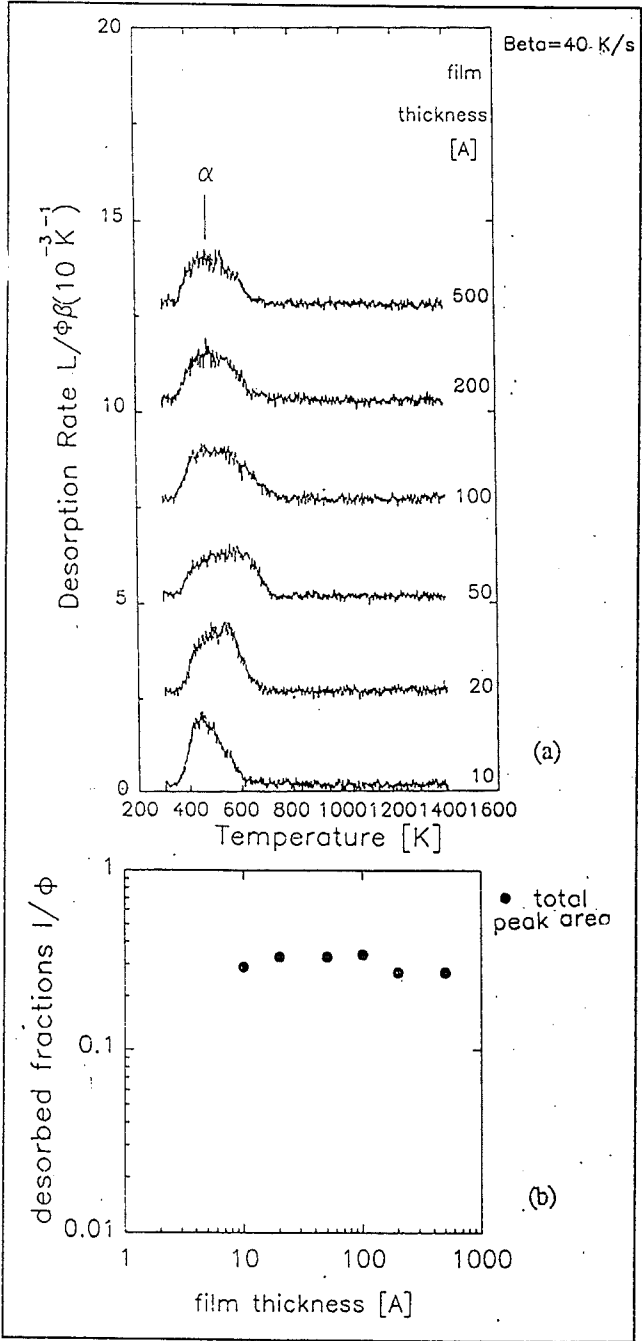


Figure A.2: Variation in film thickness of an amorphous silicon film implanted with 40 eV helium. The implanted fluence is 10^{13} He/cm². (a) Helium desorption spectra. (b) Desorbed fraction as a function of the film thickness

Figure A.1a shows the normalized desorption spectra for a series of fluences varying from 5×10^{12} to 2×10^{14} He/cm². The film thickness is 200 Å and the implantation energy is 500 eV. Figure A.1b shows the resulting desorbed fractions I/Φ as function of Φ .

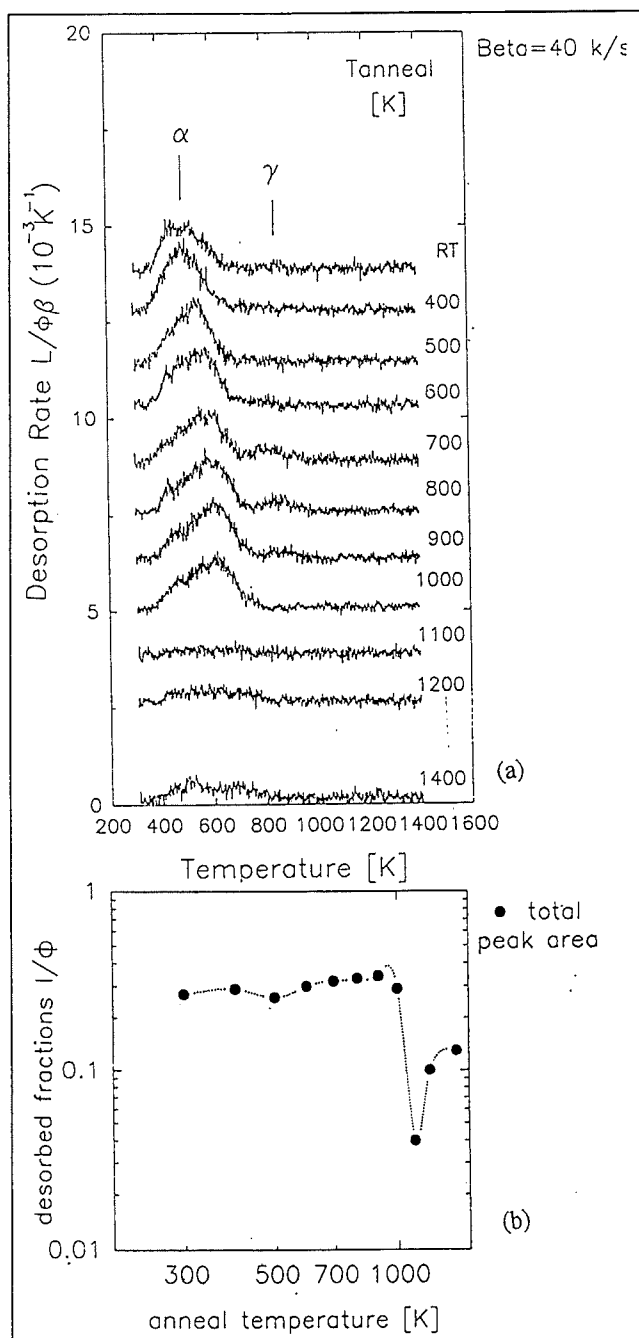


Figure A.3: Variation of anneal temperature of an amorphous silicon film. Film thickness 200 Å, helium implantation energy 40 eV. Implanted fluence 10^{13} He/cm². (a) Helium desorption spectra. (b) Desorbed fraction as a function of the anneal temperature.

Figure A.2a shows helium desorption spectra of amorphous silicon films with thickness varying from 10 Å to 500 Å. The helium is implanted with an energy of 40 eV and an implanted fluence of 10^{13} He/cm². Figure A.2b shows the desorbed fractions I/Φ as function of the film thickness.

Figure A.3a shows the results of a series of anneal experiments. T_a is varied between 400 K and 1400 K. After the film has cooled down to $T < 340$ K it is implanted with helium with a fluence of 10^{13} He/cm² and with an implantation energy 40 eV. Figure A.3a presents the desorbed fractions I/Φ associated with the various peaks versus the anneal temperatures.

Appendix B

Study of the α peak in the IBAD spectra

Figure B.1 and B.2 show the results of subtraction of EVAP-spectra from IBAD spectra in figure 4.24 an 4.25 respectively.

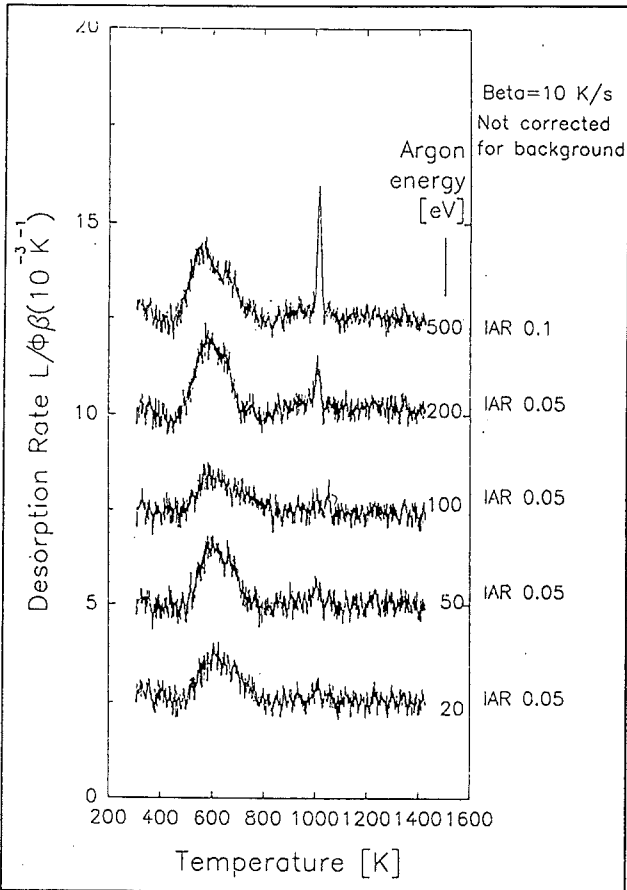


Figure B.1: Results of subtraction of EVAP-spectra from IBAD spectra in figure 4.24

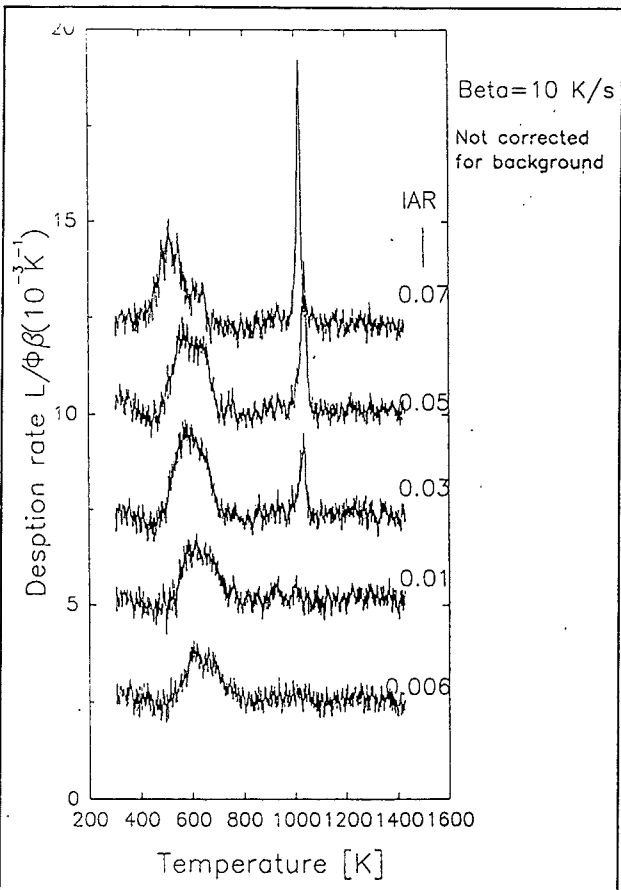


Figure B.2: Results of subtraction of EVAP-spectra from IBAD spectra in figure 4.25

Appendix C

TDS on the crystallized layer

Although our experiments are focused on amorphous silicon we have also performed some experiments on the crystallized layer. These experiments were primarily performed in order to find out whether the amorphous film after an anneal to 1400 K had turned into a defect-free crystalline layer. The first measurements showed a spectrum with various narrow peaks. We therefore decided to perform a helium fluence variation and a variation in helium implantation energy in order to gain more insight in the origin of the different peaks. We also performed a heating rate variation. It turned out that these spectra are complex and hard to interpret without data from additional experimental techniques. The results in this section are therefore only presented as comparison for additional research and are not discussed in detail.

C.1. Fluence and energy variation

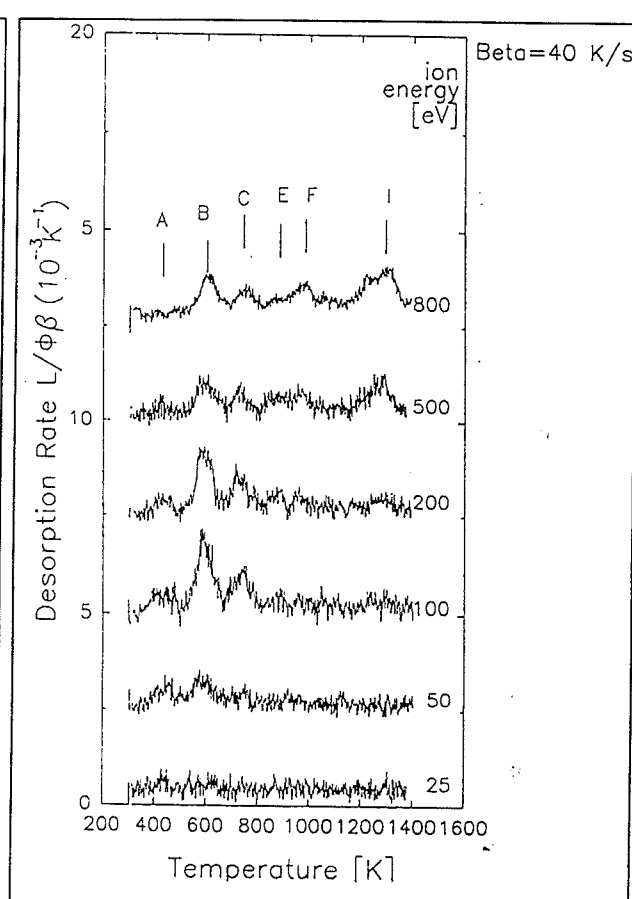
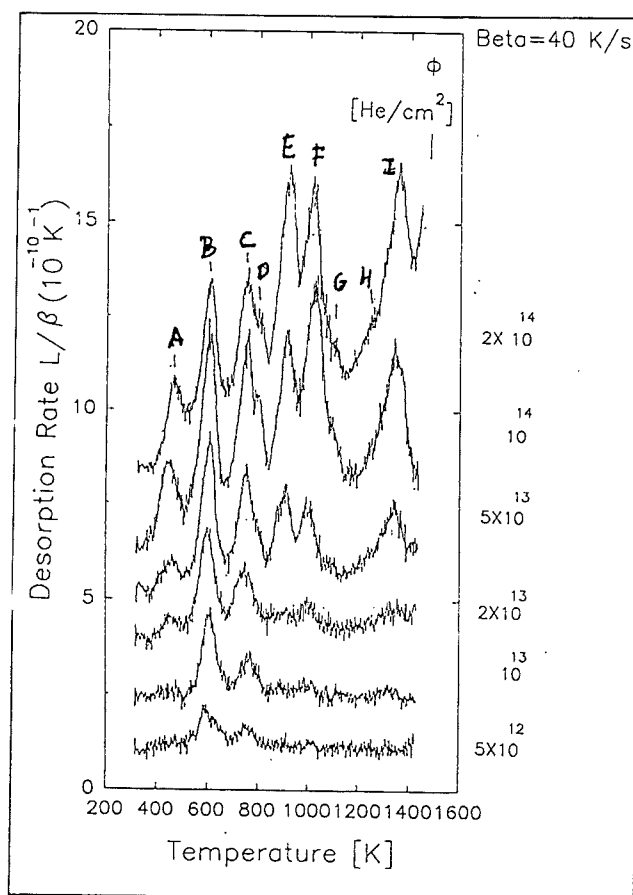


Figure C.1: Helium desorption spectra for a variation of implanted fluence in the crystallized layer. The energy of the implanted helium ions is 200 eV. Note that the spectra are not shown in normalized form.

Figure C.2: Helium desorption spectra for a variation of the helium implantation energy. Implanted fluence 10^{13} He/cm^2 .

Figure C.1 presents the results of a fluence variation on the crystallized layer. The implanted fluence is varied from 5×10^{12} to 2×10^{14} He/cm² and the helium implantation energy is 200 eV. Note that the spectra are not show in normalized form. Figure C.2 presents the results of an energy variation on the crystallized layer. The implantation energy is varied from 25 eV to 800 eV and the implanted fluence is 10^{13} He/cm². The following points should be mentioned:

- Both figures show seven separate peaks, indicated as A, B, C, D, E, F and I. The fluence variation also shows two additional small peaks G and H, both peaks are almost completely overlapped by the F and I peak, respectively.
- The peaks that appear at relatively high temperatures (E, F, G, H, and I) can only be detected in the spectra for high fluence and/or high energy.

The spectra for the fluence variation are fitted to the first order desorption equation (eq. 2.6). From these fits we derived values for the helium desorption energy (E_d) and the attempt frequency (ν_0). As an illustration, figure C.3 shows the result of a fit to a spectrum of the crystallized film implanted with 200 eV helium and a fluence of 5×10^{13} He/cm². The straight line in this figure represents the background. The separate spectra of the fluence variation are all fitted in this way and the resulting values for E_d and ν_0 are presented in table C.1.

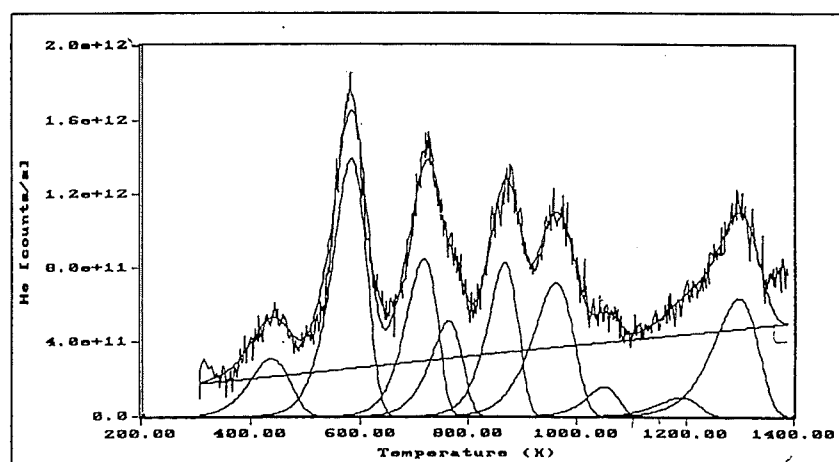


Figure C.3: Fits of the first-order desorption process to a desorption spectrum of an amorphous silicon film of 200 Å thickness, implanted with 200 eV helium. Implanted fluence 5×10^{13} He/cm².

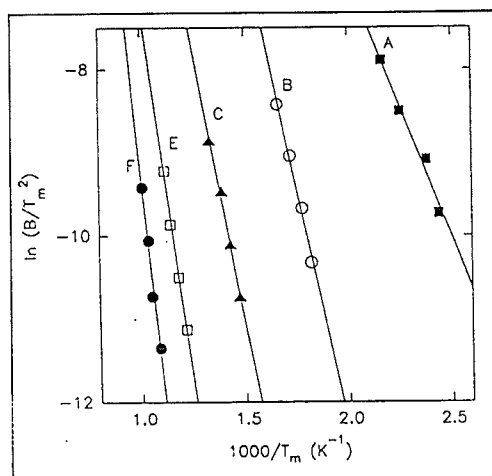


Figure C.4: Arrhenius plot resulting from a beta variation of the crystalline spectra

Table C.1: Fit parameters E_d and ν_0 , derived from first-order desorption fits to the fluence variation of figure C.1.

	peak A		peak B		peak C		peak D		peak E	
implanted fluence [He/cm ²]	E_d [eV]	ν_0 [s ⁻¹]	E_d [eV]	ν_0 [s ⁻¹]	E_d [eV]	ν_0 [s ⁻¹]	E_d [eV]	ν_0 [s ⁻¹]	E_d [eV]	ν_0 [s ⁻¹]
5×10^{12}	-	-	0.74	$2.0 \cdot 10^6$	0.9	$1.0 \cdot 10^6$	-	-	-	-
1×10^{13}	0.57	$5.4 \cdot 10^6$	0.97	$2.1 \cdot 10^8$	1.1	$1.6 \cdot 10^7$	-	-	1.5	$3.1 \cdot 10^8$
2×10^{13}	0.58	$5.4 \cdot 10^6$	0.95	$2.1 \cdot 10^8$	1.0	$1.6 \cdot 10^7$	-	-	1.5	$3.1 \cdot 10^8$
5×10^{13}	0.43	$9.1 \cdot 10^4$	0.90	$7.7 \cdot 10^7$	1.5	$5.4 \cdot 10^{10}$	1.7	$1.5 \cdot 10^{11}$	2.3	$3.1 \cdot 10^{13}$
1×10^{14}	0.44	$1.5 \cdot 10^5$	0.93	$1.8 \cdot 10^8$	1.4	$7.0 \cdot 10^9$	2.0	$1.7 \cdot 10^{13}$	2.2	$6.8 \cdot 10^{12}$
2×10^{14}	0.58	$3.9 \cdot 10^6$	0.89	$8.5 \cdot 10^7$	1.4	$7.0 \cdot 10^9$	2.0	$1.7 \cdot 10^{13}$	2.2	$6.0 \cdot 10^{10}$

	peak F		peak G		peak H		Peak I	
implanted fluence [He/cm ²]	E_d [eV]	ν_0 [s ⁻¹]	E_d [eV]	ν_0 [s ⁻¹]	E_d [eV]	ν_0 [s ⁻¹]	E_d [eV]	ν_0 [s ⁻¹]
5×10^{12}	-	-	-	-	-	-	-	-
1×10^{13}	2.2	$2.5 \cdot 10^{11}$	4.1	$1.6 \cdot 10^{16}$	-	-	4.1	$1.6 \cdot 10^{16}$
2×10^{13}	2.1	$2.5 \cdot 10^{11}$	2.1	$6.6 \cdot 10^7$	-	-	2.1	$6.6 \cdot 10^7$
5×10^{13}	2.1	$1.5 \cdot 10^{11}$	3.3	$9.2 \cdot 10^{15}$	3.3	$6.7 \cdot 10^{13}$	3.5	$3.5 \cdot 10^{13}$
1×10^{14}	2.1	$6 \cdot 10^{10}$	3.3	$9.0 \cdot 10^{15}$	3.0	$1.0 \cdot 10^{13}$	3.5	$3.5 \cdot 10^{13}$
2×10^{14}	2.1	$6 \cdot 10^{10}$	3.3	$9.0 \cdot 10^{15}$	3.0	$1.0 \cdot 10^{13}$	3.5	$3.5 \cdot 10^{13}$

C.2. Heating rate variation

We also performed a variation in heating rate and the resulting peak temperatures are plotted in an Arrhenius plot shown in figure C.4. From this plot and with eq. (2.10), E_d and ν_0 are derived. These values are presented in table C.2.

Table C.2: Helium desorption energy E_d and attempt frequency ν_0 for a series of peaks in the crystalline spectra as derived from a variation in heat-up rate.

Peak #	E_d [eV]	ν_0 [s ⁻¹]
Peak A	0.5	$1.9 \cdot 10^6$
Peak B	1.0	$7.5 \cdot 10^8$
Peak C	1.2	$1.2 \cdot 10^8$
Peak E	1.6	$1.4 \cdot 10^9$
Peak F	2.2	$1.9 \cdot 10^{11}$

C.3 Reproducibility

As part of our routine procedures we have checked not only on the reproducibility of the experiments on the amorphous film regularly, but also on those of the crystallized layer. At first the reproducibility turned out to be very good. The spectra presented in the previous sections

were obtained in this period. However, suddenly after more than 100 measurements a completely different crystalline spectrum was found. These 'new' crystalline spectra again could be well reproduced. From this time onwards, the 'old' crystalline spectra were never detected again. Even after deposition of many new amorphous silicon films the 'old' spectra could not be obtained. At the same time the amorphous spectra had not changed at all.

A few additional series of measurements are performed in order to gain more insight in the 'new' crystalline spectra. Figure C.5 presents the results of a fluence variation of the 'new' crystalline spectra. This figure shows that these spectra do change slightly with increasing fluence. However still no clear conclusions can be drawn from these results. It is also examined whether this spectrum is sensitive to annealing at high temperature. Results of this anneal series are given in figure C.6. Both series do not present much significant information about the nature of the change of the spectra. We still have no explanation for the sudden change in the spectra, this problem needs to be investigated in detail.

The anneal series of the amorphous film presented in section 4.5 (fig. 4.30) and the bottom-up probing series with a EVAP film on top presented in section 4.3 (figure 4.14) are both performed in the period after the sudden change of the helium desorption spectra from the crystallized layer.

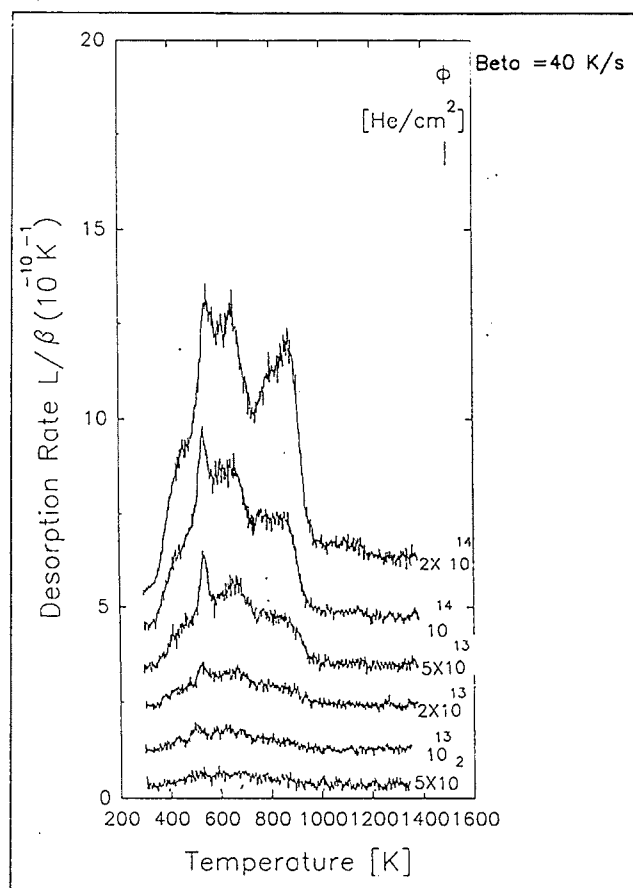


Figure C.5: Helium desorption spectra for a variation in implanted fluence in the 'new' crystallized layer. Energy of implanted helium ions 200 eV. Note that the spectra are not shown in normalized form.

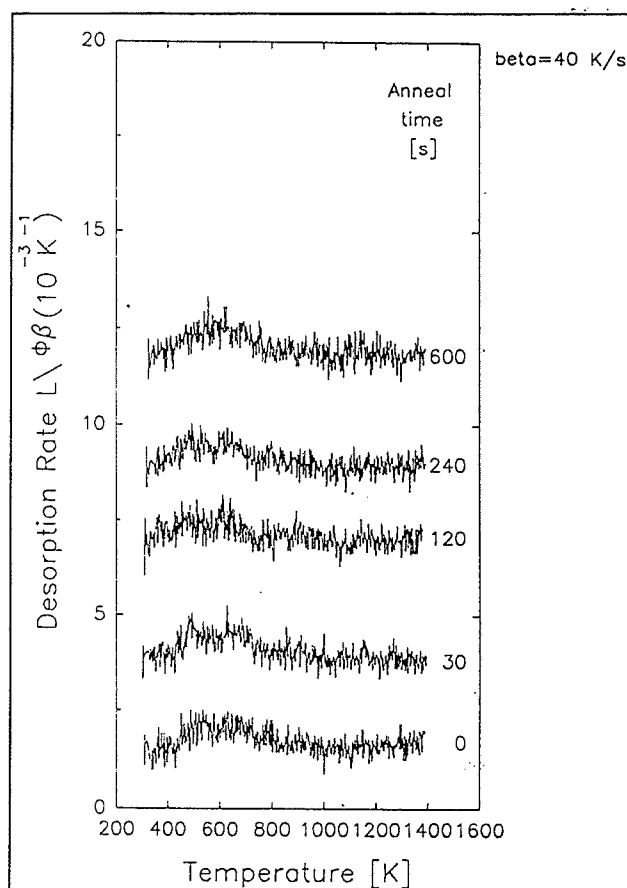


Figure C.6: Helium desorption spectra for a variation in anneal time at 1400 K for the 'new' crystalline spectra. Implanted fluence 10^{13} He/cm². Implantation energy 200 eV.

Summary

The requirements on deposited thin films are becoming increasingly demanding. In many cases, the defect density has to be as low as possible, and impurity diffusion and thermal stresses in the films have to be avoided. A relative new method to grow thin films that can satisfy all these requirements is Ion Beam Assisted Deposition (IBAD). In this technique an ion beam is used to bombard the growing film. The ion beam is believed to increase the mobility of the surface atoms, which results in a more regular atomic arrangement. Ion-assisted deposition of metals has been found to improve a variety of film properties. However, there is still little insight into the atomic processes which cause these improvements.

This master's thesis describes the first steps of a study of the influence of ion bombardment on the defect structure of thin amorphous silicon films. The experimental technique employed is Thermal Desorption Spectrometry (TDS). Literature offers hardly any data about the use this technique in studies on amorphous films.

The results of our experiments show that we can successfully study defects in amorphous silicon with TDS. In view of the noncrystallinity, some types of defects do not show up separately, as in studies of crystalline metals, but rather as traps having a continuous range of helium-binding energies. Three distinct types of traps are detected: (i) small traps that might be assigned to interstitial positions, atom-size defects, deformed regions surrounding incorporated impurity atoms, or a combination of these three; (ii) small defects at the interface between the amorphous film and the crystallized layer; and (iii) stronger binding traps which are assumed to be large voids. These voids increase in size with increasing film thickness. This result is in accordance with literature and can ascribed to an increase in column size and a simultaneous increase in the size of the voids between the columns with increasing film thickness.

Significant differences are detected between amorphous silicon films deposited with and without ion beam assistance. The most important difference is the almost complete absence of voids in films deposited under ion bombardment. This is ascribed to the enhanced mobility of silicon atoms that arrive at the surface, as a result of ion beam assistance. The increased mobility enables silicon atoms that arrive at the surface to overcome the effect of shadowing (i.e. the formation of columns), resulting in a homogeneous film without columns.

Additional computer simulations with HOP (Hopping Of Particles) have been shown to facilitate the interpretation of our results.

Samenvatting (Dutch summary)

Aan dunne opgedampte lagen worden steeds hogere eisen gesteld. Zo moet in veel gevallen de defectdichtheid laag zijn en moet de diffusie van onzuiverheden en spanningen in de laag worden voorkomen. Een relatief nieuwe methode voor dunne laag depositie, waarbij aan al deze eisen wordt voldaan is Ion Beam Assisted Deposition (IBAD). Met deze techniek wordt de laag tijdens het opdampen gebombardeerd met een ionenbundel. Het is bekend dat deze methode voor verbetering van verschillende eigenschappen kan zorgen, maar er is nog geen goed inzicht in hoe de atomaire processen deze verbeteringen mogelijk maken.

Dit afstudeerverslag beschrijft de eerste stappen van een onderzoek naar de invloed van ionenbombardeement op de defectstructuur in dunne lagen van amorf silicium. De experimentele techniek die is gebruikt is Thermal Desorption Spectrometry (TDS). Uit de literatuur zijn weinig gegevens bekend over het gebruik van deze methode voor onderzoek aan amorfe lagen.

Tot nu toe kan het volgende worden geconcludeerd. Uit de resultaten van onze experimenten blijkt dat het goed mogelijk is om laagjes amorf silicium te onderzoeken met TDS. In tegenstelling tot kristallijne materialen kunnen sommige typen defecten in de amorfe lagen niet afzonderlijk worden gedetecteerd, maar in groepen van defecten met een continu verloop van helium dissociatie energieën. In de laagjes opgedampt zonder ionen bombardement zijn drie defectsoorten aangetoond, (i) defecten aan het grensvlak tussen de kristallijne en de amorfe laag; (ii) kleine vacature-achtige defecten in de bulk en (iii) grote holtes in de gebieden tussen de amorfe kolommen. De breedte van deze holtes neemt toe met toenemende laagdikte. Dit resultaat is in overeenstemming met de literatuur en wordt toegeschreven aan de toenemende grootte van de kolommen met toenemende laagdikte.

In de lagen die met ionenbundelassistentie zijn opgebracht blijken de grote holtes bijna compleet afwezig te zijn. Dit resultaat wordt toegeschreven aan de verhoogde mobiliteit van de siliciumatomen die het oppervlak bereiken, welke het gevolg is van de ionenbundel assistentie. De verhoogde mobiliteit zorgt ervoor dat siliciumatomen aan het oppervlak zich kunnen verplaatsen naar energetisch gunstige posities waardoor het effect van schaduwvorming (d.w.z. kolomvorming) wordt tegengegaan.

Tot slot is aangetoond dat computersimulaties met HOP (Hopping Of Particles) aanvullende informatie opleveren voor de interpretatie van de experimentele TDS spectra.

