Defects and morphological changes in nanothin Cu films on polycrystalline Mo analyzed by thermal helium desorption spectrometry

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Thermal helium desorption spectrometry (THDS) has been used for the investigation of defects and thermal stability of thin Cu films (5-200 Å) deposited on a polycrystalline Mo substrate in ultrahigh vacuum. These films are metastable at room temperature. On heating, the films transform into islands, giving rise to a relatively broad peak in the helium desorption spectra. The temperature of this island formation is dependent on film thickness, being 417 K for 10 Å and 1100 K for a 200 Å film. The activation energy for island formation was found to be 0.3 ± 0.1 eV for 75 Å film. Grain boundaries have a strong effect on island formation. The defect concentration in the as-deposited films is $\sim 5 \times 10^{-4}$, for films thicker than 50 Å and more for thinner films. Helium release from monovacancies was identified in the case of a 200 Å film. Helium release was also seen during sublimation of the Cu film (\sim 1350 K). Overlayer experiments were used to identify helium trapped close to the film surface. An increase of the substrate temperature during deposition resulted in a film that had already formed islands. Argon-ion assistance (250 eV) during film deposition with an ion/atom ratio of ~ 0.1 resulted in a significant enhancement of helium trapping in the films. The argon concentration in the films was found to be 10^{-3} . The temperature of island formation was increased due to argon-ion assistance. The helium and argon desorption spectra are found to be similar, which is due to most of the helium becoming trapped in the defects created by the argon beam. The role of the Mo surface in affecting the defects at the film-substrate interface is investigated. The effect of variation of helium fluence and helium implantation energy is also considered. The present THDS results of Cu/poly-Mo are compared to those of Cu/Mo(100) and Cu/Mo(100) reported earlier. © 2005 American Institute of Physics. [DOI: 10.1063/1.1925765]

I. INTRODUCTION

Thermal helium desorption spectrometry^{1,2} (THDS) can provide much information about the defects in a deposited film, the structure of the film, and its thermal stability. The technique probes the 5-200 Å depth range under the film surface in the following way. Helium implanted into a thin film deposited on a substrate may become trapped in the defects present in the film. If the helium can travel far enough to reach the substrate, either during implantation or in the thermalized state (diffusion), helium trapping can also occur in the defects at the interface and in the substrate. If the helium energy exceeds the threshold energy for damage production, it creates defects additional to those present after the deposition of the film. This can sometimes be effectively exploited. On heating the sample, the helium is released from the defects at temperatures that are characteristic of the helium-defect dissociation energies. Helium may also be released from the sample if morphological or thermodynamic changes take place in the film when at least some of the helium is still trapped in defects. Examining the helium desorption signal as a function of temperature therefore yields information on defects, thermal stability, film coverage, and ion damage effects.

In earlier work we have studied Cu films (5-200 Å) deposited by electron-beam evaporation on Mo(110) (Ref. 3) and Mo(100) (Ref. 4) substrates using THDS. The motivation for selecting the Cu/Mo system was explained in these papers. The principal outcome of the experiments was that the Cu films were metastable at room temperature, transforming into islands at elevated temperatures. In this work we have applied THDS to Cu films on a polycrystalline Mo substrate. The main purpose was to find out whether the polycrystalline substrate would give rise to Cu films with different defect and stability properties. Moreover, in industrial applications the substrate is seldom single crystalline. In order to consider specific technological applications as well, we have also applied THDS to Cu films fabricated by 250 eV argon-ion-beam-assisted deposition (IBAD).^{5,6} In earlier work, defects in ion-implanted Cu single crystals have been explored by THDS.^{7,8} Some properties of Cu films deposited by IBAD have been reported,^{9–11} where the sub-strates were Si, Si/SiO₂, SiO₂,^{9,10} and SiN_x/SiO₂-coated Si.11

The experiments were carried out in an ultrahighvacuum (UHV) system capable of producing thermally

II. EXPERIMENTAL DETAILS

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evaporated thin films, with optional ion assistance, and their subsequent analysis by THDS.¹² The base pressure of the setup was 2.0×10^{-10} torr (2.7×10^{-8} Pa) after bakeout. Cu films (5–200 Å) were deposited on a 0.05 μ m polished, polycrystalline Mo substrate (\emptyset 10.0 × 2.0 mm², purity 99.95 wt %). X-ray-diffraction (XRD) diffractometer scans showed that the Mo substrate has a pronounced {110} out-ofplane orientation; the ratio of the net height intensities of the (110) and (200) Mo reflections is 11.4 times larger than the ratio for randomly oriented Mo. Optical microscopy indicated that the grain sizes are in the range of $50-500 \ \mu m$. Prior to the experiments the substrate was annealed several times to 2100 K in UHV for 1 min, to desorb the residual gases present on the surface. For film deposition, Cu lump (purity 99.999 wt %) was vaporized in a graphite crucible using a 3 kW electron-beam evaporator. The incident direction of the Cu vapor on the substrate was 15° off-normal. The deposition rate was 1 Å/s, which was monitored using a quartz-crystal oscillator. A 3 cm diameter Kaufman ion source is used for Ar⁺-ion assistance during deposition (normal incidence). The substrate temperature during film deposition was usually 300 K but higher in special cases. After deposition, the sample was implanted with 75 eV He⁺ or 1000 eV He⁺, usually with a fluence ϕ of 7.98×10^{13} or 9.24×10^{13} He⁺/cm², respectively, impinging at an angle of 20° off-normal. Finally, in the so-called desorption run the sample was heated using a 2.8 kV electron gun up to 2000 K at a rate β of 40 K/s, and the He desorption flux L (at./cm²/s) was monitored as a function of the sample temperature T using a quadrupole mass spectrometer. The spectrometer signal was calibrated repeatedly by admitting a known amount of helium in the system and registering the count rate; this procedure also yields a value for the mean residence time of helium in the desorption chamber under the existing pumping conditions (0.21 s). The temperature of the sample was measured using a W-Re thermocouple spot welded to the substrate.

A typical He desorption spectrum (L vs T) consists of a number of peaks, each peak signifying the dissociation of He from a particular trapping site. In each desorption run the Cu film evaporates from the substrate at ~1350 K (note that Cu does not dissolve in Mo), but the sample heating was continued to 2000 K in order to detect helium that may have been trapped in the Mo substrate. This continued heating also served the purpose of annealing the substrate before deposition of the next Cu film. At regular intervals the substrate was given additional annealing treatments to 2000 K to maintain the surface cleanliness.

The desorption spectra have been corrected for the mean residence time of helium by deconvolution. The helium fluence was measured by the current on the sample and was corrected for ion backscattering by using the values of 0.43 and 0.34 for the backscattered fractions of 75 and 1000 eV helium ions, respectively, obtained from simulations performed with stopping and range of ions in matter (SRIM-2003.20).¹³ The helium fluence was also corrected for secondary electron generation using a yield value of 0.30.



FIG. 1. Normalized helium desorption spectra of a 100 Å Cu film deposited on polycrystalline Mo at room temperature and annealed to the indicated temperatures in Kelvins for 10 s, cooled to room temperature, and implanted with 1000 eV helium of fluence of 9.24×10^{13} He/cm². The top spectrum was obtained by depositing 10 Å Cu film at room temperature and implanted with 1000 eV helium. The bottom spectrum was obtained for bare Mo substrate, which is also reproduced just below the 982 K spectrum. The peak labels are explained in the text.

III. RESULTS AND DISCUSSION

In all the desorption spectra shown here the *normalized* helium desorption flux χ is plotted as a function of *T*, where $\chi(T) = L(T)/\phi\beta$, expressed in K⁻¹. This means that the integral area under a spectrum is equal to the trapped helium fraction (because no helium remains in the sample above 2000 K). The reason for choosing the helium ion energy as 75 eV in most cases is that this energy is below 85 eV, the threshold energy for Frenkel pair creation in bulk Cu [calculated using the minimum displacement energy of 19 eV for Cu (Ref. 14)]. In this case the helium beam does not produce defects but only acts as a source of probe atoms that decorate the existing defects. In cases where it was desirable to produce additional defects, for instance, in the defect-free poly-Mo substrate, a helium energy of 1000 eV was used.

A. Effect of annealing

We begin by presenting a special series of measurements in order to demonstrate the principal phenomena occurring in the Cu/Mo system and the kind of information that can be extracted from THDS data. The helium desorption spectra are shown in Fig. 1. Spectrum Mo was obtained after the bare Mo substrate was implanted with 1000 eV helium. The spectra 300–982 K were obtained when 100 Å Cu was deposited on Mo at 300 K, after which the sample was annealed to the indicated temperatures in Kelvins for 10 s, allowed to cool to 300 K, and implanted with 1000 eV helium. Shown just below the spectrum 982 K is a copy of the bottom spectrum Mo. Spectrum 10 Å Cu was obtained when 1000 eV helium was implanted into 10 Å Cu deposited at 300 K on Mo. Spectrum Mo reveals the defects created by 1000 eV He in Mo. The desorption peaks E, F, G, and H have been identified earlier^{15,16} and were also observed in our previous work.^{3,4} They are caused by the following helium-defect reactions (V denotes a vacancy, and He^{*} a mobile helium atom):

E peak (820 K): $\text{He}_n V \to \text{He}^* + \text{He}_{n-1}V$ (n = 5 - 8), F peak (950 K): $\text{He}_n V \to \text{He}^* + \text{He}_{n-1}V$ (n = 3 - 4), G peak (1010 K): $\text{He}_2 V \to \text{He}^* + \text{He}V$, H peak (1200 K): $\text{He}V \to \text{He}^* + V$.

Because of overlap the F and G peaks are difficult to distinguish. Desorption at temperatures higher than 1200 K is due to helium being released from vacancy clusters $\text{He}_n V_m(n,m \ge 2)$ and is indicated by peaks I (1333 K), J (1538 K), and K (1704 K).

In spectrum 300 K, obtained for 100 Å Cu on Mo, a very sharp peak marked M is seen at 1333 K. The sharpness of the peak [full width at half maximum (FWHM)=1.9% of the peak temperature and its shape points to zeroth-order desorption kinetics, and the peak temperature is close to the melting temperature of Cu (1358 K). From this it can be concluded that the peak represents helium release during sublimation of the Cu film. Helium retained in the Cu film up to such a high temperature is undoubtedly present in the form of helium-vacancy clusters.¹⁷ It is also clear that no He release takes place above 1333 K. This implies that no He was trapped in vacancy clusters in the Mo substrate which would have given rise to I, J, and K peaks; the complete absence of the H peak (1200 K) in spectrum 300 K shows that no He was trapped in single vacancies in Mo either. The conclusion is that the He beam produces damage only in the 100 Å Cu film. This is consistent with the longitudinal range of 1000 eV He in Cu, which is 72 Å (straggle 41 Å) according to SRIM-2003.20 simulations.¹³ Later in this section we will go back to the broad desorption peak between 700 and 1000 K (marked L), which we just showed to originate from copper-trapped helium only.

In the spectra 639-982 K, which represent Cu films annealed to increasingly higher temperatures before helium implantation, an increasing amount of helium release above 1333 K is observed. This gives important information. Helium release at these temperatures, i.e., helium release from the Mo substrate, is possible only if the thickness of the Cu film continuously decreases in certain regions upon annealing, making way for more and more helium to generate defects in Mo and to become trapped. Because Cu itself does not desorb at the indicated annealing temperatures,^{18,19} it is definitely a structural rearrangement in the Cu film that is responsible for the helium beam creating damage in Mo. In fact, the figure shows that spectrum 982 K coincides almost perfectly with the spectrum for bare Mo, except for the M peak in 982 K. In other words, a 100 Å Cu film annealed to 982 K no longer poses a significant energy barrier to the He beam; therefore the conclusion must be that at this temperature the Cu film has thinned down to at most a few ang-



FIG. 2. Backscattered electron image of a 100 Å Cu film deposited at room temperature and annealed to 857 K for 10 s and cooled to room temperature. The grain boundaries are those of the Mo substrate. The island formation of the Cu film is clearly seen. Without annealing the Cu film would be observed as totally structureless.

stroms over much of its area. In earlier work^{18,19} it is shown that only the first two monolayers (MLs) of Cu on Mo(110) and Mo(100) are thermodynamically stable; the rest of the Cu film agglomerates into three-dimensional (3D) crystallites on annealing. Figure 2 confirms that, also in the present case of a polycrystalline Mo substrate, the 3D crystallites take the shape of islands. The figure shows a backscattered electron image (BEI) of 100 Å Cu/Mo annealed to 857 K for 10 s. The XRD diffractometer scans indicated that, averaged over the entire sample, the Cu islands do not have a pronounced out-of-plane orientation; the ratio of the net height intensities of the (111) and (200) Cu reflections is only 1.4 times larger than the ratio for randomly oriented Cu. The height of these islands was found to be ~ 650 Å using energy dispersive spectroscopy (EDS). Auger electron spectroscopy (AES) measurements confirmed the existence of approximately two MLs of Cu between the islands. Therefore the observed morphological transition is a Cu-on-Cu dewetting effect. In spectrum 982 K of Fig. 1 the H peak of Mo is shifted to 1150 K compared with the H peak for a bare Mo substrate (1200 K). Since such a shift is also seen for spectrum 10 Å Cu it must be caused by the presence of a Cu film on the Mo. A possible reason for this shift could be that a negative lattice misfit causes the near-surface region of the substrate to be stretched in tension.²⁰ The difference in coefficient of thermal expansion of Cu and Mo may also play a role (see Sec. III F).

Now that we have demonstrated that the annealing temperatures of 639 and 982 K roughly define the temperature range over which the island formation in the Cu film takes place, we turn again to spectrum 300 K and note that this temperature range is almost exactly the range over which the broad peak L extends. One can therefore associate this peak to helium release as a result of the island formation in the Cu film. This means that the L peak is, in fact, an *in situ* recording of the island formation kinetics. Kissinger analysis²¹ for a 75 Å Cu film studied with different heating rates yields an activation energy of 0.3 ± 0.1 eV for the L peak. This is less



FIG. 3. Normalized helium desorption spectra of Cu films (5-200 Å) deposited at room temperature and implanted with 75 eV helium of fluence of 7.98×10^{13} He/cm². The film thickness in angstroms is indicated. The bottom spectrum was obtained for the bare Mo substrate. The dashed lines indicate the peak A (see text).

than the activation energy of 1.2 ± 0.1 eV obtained for island formation in the case of 100 Å Cu on Mo(100).⁴

Finally, additional information about the origin of the M peak can be obtained from spectrum 10 Å Cu, which was obtained after implanting 1000 eV helium into a 10 Å Cu film deposited on Mo (no annealing). The fact that the M peak is seen in 300–982 K but not in 10 Å Cu strongly suggests that the helium released in the M peak comes from the island regions of the Cu film and not from the thin regions. The reason is that in the 10 Å Cu film at most the top \sim 5 Å undergo island formation on annealing, which amounts to much less Cu in the island regions than in the case of the annealed 100 Å film.

All the above arguments show that a 100 Å Cu film grown on polycrystalline Mo at 300 K is metastable. On annealing the stable island structure is formed. The forces controlling the shape and dimensions of the islands are those which drive the surface free-energy minimization of the Cu film; the stresses in the film that result from the deposition on the mismatching Mo substrate are an important factor. The kinetics is controlled by mobility of Cu atoms.

B. Effect of film thickness

Low-energy helium implantation (75 eV) was used to investigate the trapping and release of helium in films of various thicknesses without producing extra defects. Figure 3 shows the normalized helium desorption spectra for different Cu film thicknesses deposited on Mo at 300 K. Before discussing the results, we should emphasize that, although the mean projected range of 75 eV helium in Cu is only 13 Å, the interstitial diffusion after thermalization causes the helium implantation profile to broaden significantly. This allows helium to probe defects in a much deeper subsurface range than 13 Å. A good estimate of the diffusion length is 2 Å/ $c_{\rm tr}^{1/2}$, where $c_{\rm tr}$ is the average trap concentration. As we will show later, $c_{\rm tr} \sim 5 \times 10^{-4}$ in the present Cu films (above



FIG. 4. Measured total trapped fraction of 75 eV helium as a function of Cu film thickness (data points) compared with calculated values (dashed line), see text.

a thickness of about 50 Å), which means that the diffusion length is approximately 100 Å. This implies that helium can reach the Cu/Mo interface in almost all films studied here although increasingly less helium is able to do so as the film thickness increases.

Integration of the spectra of the 0–200 Å films yields the trapped helium fraction $f_{\rm tr}$ for each thickness. The results are plotted in Fig. 4 as data points. One observes that the trapping reaches a maximum value of 31.8% for a 40 Å film; at increasing thickness the trapping decreases. Before discussing the individual spectra in Fig. 3, we will first analyze the trapping curve in Fig. 4.

Using the numerical method outlined in the Appendix, we have calculated the trapped helium fractions in the films under the assumption of a zero defect density in the substrate (as follows from the bottom spectrum in Fig. 3) and a trap concentration profile consisting of an exponentially decreasing term away from the Cu/Mo interface plus a uniform background. To allow for enhanced trapping at the interface we have added a third component to the defect profile, one that is limited to the first 5 Å of the film. The best simultaneous fit to the films of 50 Å thickness and more *and* to the 5 Å film is given by

$$c_{\rm tr}(z) = 5.1 \times 10^{-3} \exp[-(d-z)/23 \text{ Å}] + 0.3 \times 10^{-3} + \begin{cases} 5.0 \times 10^{-3} & (d-z < 5 \text{ Å}) \\ 0 & (d-z > 5 \text{ Å}) \end{cases},$$
(1)

where *d* is the film thickness and *z* the depth below the surface, so that *d-z* is the height above the interface. The resulting trapping curve is the dashed line in Fig. 4. No satisfactory agreement is found for the 10-30 Å films. The conclusion must be that no reasonable trap profile can be found that describes the films of all thickness simultaneously. This is confirmed by a second fitting method in which piecewise uniform trap concentrations in the film were adapted in an incremental way. The following procedure was applied. First a 5 Å thick film was modeled. It was found that a uniform trap concentration of 8.8×10^{-3} in such a film gives rise to a trapped helium fraction of 16.5%, which is the experimental value for the 5 Å film in Fig. 4. Next, a 10 Å thick film was modeled and the trap concentration in the first



FIG. 5. The trap concentration as a function of film thickness calculated on the basis of a piecewise uniform model (see text).

5 Å was held fixed at the value of 8.8×10^{-3} just found. It was then found that a uniform trap concentration of -1.9 $\times 10^{-3}$ in the second 5 Å of the film was needed to arrive at a trapped helium fraction of 21.0%, which is the experimental value for the 10 Å film in Fig. 4 (we will go back to this negative trap concentration shortly). By repeating this procedure until the largest thickness value was reached (200 Å) we obtained a piecewise approximation of the trap concentration profile that exactly reproduces all observed trapped helium fractions. The result is shown in Fig. 5. As a global trend we observe a high trap concentration immediately near the interface (as expected), decreasing to small values towards the surface. In the top 180 Å of the film the concentration gradually decreases from $c_{\rm tr} \approx 2 \times 10^{-3}$ to $c_{\rm tr} \approx 0.3$ $\times 10^{-3}$. While these values are quite reasonable, the negative trap concentration of -1.9×10^{-3} between 5 and 10 Å forms a problem. Even allowing for experimental errors in the trapped fractions, which would lead to errors in the trap concentrations produced by the data analysis, such a large negative value is unphysical. The explanation must be that the assumption that the trap concentration in the earlier parts of the film is unchanged by the deposition of subsequent parts is not valid. The conclusion is that the deposition of 5 Å Cu over the first 5 Å Cu film leads to a decrease in the trap concentration in the first 5 Å part. In other words, the interface region of the Cu film still changes when the deposition is already in the 5-10 Å range. Additional evidence for this is found in results from molecular-dynamics simulation of Cu growth on Mo(110).^{22,23}

Now we return to discussing the individual spectra in Fig. 3. The spectrum 0 Å is obtained after decorating the bare Mo substrate with 75 eV He⁺. The fact that almost no helium release is seen at any temperature except for a very small broad peak around 450 K indicates that the Mo substrate is defect-free. The peak at 450 K can be attributed to surface-related binding sites in the Mo substrate.¹⁵ The peak was higher in the earliest measurements and it kept on decreasing over the course of the experiments. One can conclude that depositing a film, desorbing it, and bombarding the specimen with Ar ions during film growth (as was some-



FIG. 6. Normalized helium desorption spectra of a 10 Å Cu film deposited at room temperature and implanted with 75 eV helium of fluence of 7.98 $\times 10^{13}$ He/cm², over which Cu films of various thicknesses are deposited. The overlayer thickness in angstroms is indicated.

times done) alter these near-surface trapping sites in the Mo substrate. In Sec. III E it will be shown that this has an effect on the growth of a 10 Å Cu film.

For Cu films, He release in the lower-temperature range is seen to first increase until 30 Å and then decrease for thicker films. On closer inspection, the desorption signal appears to consist of two contributions: A, a broad, asymmetrical release peak that has its maximum at 450 K and extends up to 900 K (dashed lines in Fig. 3), and B, a more narrow and symmetrical peak that is first visible at 410 K for the 10 Å film and subsequently moves to higher temperatures as the film thickness increases. The origins of these two contributions can be explained with the help of Fig. 6, in which the results of overlayer experiments are shown. In these experiments first a 10 Å Cu film was deposited, subsequently 75 eV He was introduced, and finally a Cu overlayer was grown (thickness indicated in the figure). The main difference with the films of Fig. 3 is that in the overlayer case the He is trapped in the bottom of the Cu films rather than throughout the whole film. It can be seen that the overlayer spectra do not show A component, at least not in the lowtemperature part before island formation. Since in these films the helium is not trapped close to the surface, it is safe to conclude that the A component is due to helium trapped close to the surface. However, after island formation part of the A component is still observed in Fig. 6. This confirms that island formation has exposed the helium close to the surface. The B component of the spectra in Fig. 3 can be interpreted by noting that in the case of the 100 Å Cu film it is similar to the L peak seen in spectrum 300 K of Fig. 1. As explained in Sec. III A, this helium release is due to island formation in the Cu film. Based on what we know about this process in Cu films in single-crystalline Mo, it is very likely that all B components in Fig. 3 can be identified with island formation and are therefore, in fact, L peaks. Also here we find a thickness dependence of the temperature of island formation in the Cu film, although the temperatures are lower

0.0025 X 10³He/cm 0.0020 79.8 He desorption flux χ (K⁻¹) 0.0015 20 0.0010 0.0005 0 0 500 1000 2000 2500 1500 Temperature (K)

FIG. 7. Normalized helium desorption spectra of a 75 Å Cu film deposited at room temperature and implanted with 75 eV helium of different fluences as expressed in 10^{13} He/cm².

than those in single-crystalline substrates. We will discuss this below. A sharp peak just above 1300 K, similar to the M peak of Fig. 1 and to analogous peaks for single-crystalline substrates, is seen for film thickness from 40 to 200 Å, and it shifts slightly to higher temperature with thickness. This M peak indicates that some helium-defect complexes are stable until the Cu film sublimes. Helium release from monovacancies (H^{Cu} peak) is seen at 775 K for the 200 Å Cu film in Fig. 3, which agrees with the peak observed by Buters *et al.*⁷ for Cu(100) single crystal at 780 K. For thinner films, the H^{Cu} peak is absent due to the low temperatures of the L peak, showing that island formation drives out helium trapped in monovacancies. The small helium release between 900 and 1000 K in the spectra in Fig. 3 might be related to defects at the interface (see Sec. III F).

C. Variation of helium decoration fluence

Figure 7 shows the normalized helium desorption spectra of 75 Å Cu films deposited on polycrystalline Mo and decorated with 75 eV helium of varying fluences as indicated in the figure. The shape of the spectra changes very little with the increase of helium fluence. No well-defined new peaks appear when the number of helium atoms trapped in the film increases. This indicates that, as traps become more and more multiple filled, trap mutation does not give rise to new modes of helium release before island formation (and its resulting helium desorption) intervenes. Also, the total trapped fraction of helium is found to be almost constant $(21.5\% \pm 1.5\%)$, even though the helium fluence is varied by a factor of 20. This shows that the trapping probability is virtually the same for each incoming helium atom, and therefore that on implantation no new traps are formed or trap saturation occurs.

D. Variation of helium implantation energy

Figure 8 shows the normalized desorption spectra of helium implanted with various energies (50-1500 eV) in 100 Å Cu films deposited on poly-Mo. It can be seen that for



FIG. 8. Normalized helium desorption spectra of a 100 Å Cu film deposited at room temperature and implanted with different helium energies with a fluence of 2×10^{14} He/cm². The helium energy in eV is indicated.

energies above 100 eV increasingly more damage is created in the Cu film by the helium beam. The intensity of the sharp peak at \sim 1350 K (M peak) increases. It is not only the increase of the helium energy that accounts for the M peak increase. It is in addition due to the increase of the helium range in Cu. The evidence for this argument comes from the overlayer experiments explained in Sec. III B. From the top spectrum in Fig. 8 it can be concluded that 1500 eV helium still has left enough energy to create damage in the Mo substrate after traversing the Cu film. This is deduced from the appearance of the Mo-related peaks at 1000 K (peak G), 1200 K (peak H), and the helium desorption above 1350 K.

E. Role of the substrate surface

Figure 9 shows desorption spectra of 10 Å Cu films deposited at different moments (the times increasing from bot-



FIG. 9. Normalized helium desorption spectra of a 10 Å Cu film deposited at room temperature and implanted with 75 eV helium of fluence of 7.98 $\times 10^{13}$ He/cm². The labels a–g refer to spectra measured after increasing time periods since a system bakeout. See text for explanation.

tom to top) after a bakeout of the UHV system, and implanted with 75 eV helium of fluence of 7.98 $\times 10^{13}$ He⁺/cm². In the spectra a and b, peaks are seen at \sim 400 and \sim 900 K. The spectrum b was obtained to check the reproducibility of spectrum a. Between b and c, over 40 desorption experiments were performed (Cu film deposition with and without Ar-ion assistance followed by desorption during which the substrate was heated to 2000 K). In spectrum c the peak at 400 K has changed shape; the peak at 900 K has almost disappeared and vanishes completely in spectrum d. As mentioned in Sec. III B, the 75 eV spectrum of bare Mo also kept changing with time, i.e., the area of the surface peak decreased with the number of desorption measurements. Hence the peak at 900 K (in a and b) can be attributed to helium release from Cu/Mo interface defects. These defects therefore seem to be very sensitive to the Mo substrate surface state or surface cleanliness. The peak at 900 K reappeared after a new bakeout (not shown) but not after the sample was just exposed to the atmosphere at room temperature for 1 day (spectrum g). This suggests that the substrate surface is altered due to trace contamination originating from other parts of the apparatus during bakeout. Apparently this contamination is not removed by the initial cleaning annealing treatment alone.

The spectrum e is special in that it was measured for a 10 Å Cu film deposited on the Mo substrate held at 465 K, after which it was allowed to undergo free cooling to room temperature and was implanted with 75 eV He. This measurement was done immediately after d, which was obtained for a film deposited at room temperature. The peak at 420 K is seen to decrease as well as to broaden, indicating that the film deposited at a higher temperature has already assumed a partially islanded structure. Also, the peak at 900 K reappears. The explanation is that thermal mismatch between the film and the substrate has given rise to structural defects at the Cu/Mo interface before helium implantation. Spectrum f shows a 10 Å Cu film deposited again at room temperature after spectrum e.

F. Effect of substrate temperature during deposition

Figure 10 shows the normalized helium desorption spectra of a 100 Å Cu film deposited at different temperatures, allowed to undergo free cooling to room temperature, and implanted with 1000 eV helium. With the increase of substrate temperature the following changes are observed. Helium release above 1325 K seen as a weak tail absent in the 300 K spectrum starts to appear in the 466 K spectrum and increases further in the 690 K spectrum. This helium release must be due to helium trapped in Mo, since no Cu is left above 1325 K. The intensity of the L peak decreases and its peak temperature shifts to higher values reaching 980 K for the 690 K spectrum. The H peak of Mo, which is completely absent in the 300 K spectrum, reappears in the two spectra of deposition at higher temperatures. Using the arguments of Sec. III A, one can conclude from all these that the films deposited at 466 and 690 K have already (partly) gone through the island formation process. This is consistent with the results of Mundschau and Bauer²⁴ [Cu on Mo(110)], So-



FIG. 10. Normalized helium desorption spectra of 100 Å Cu films deposited at different substrate temperatures as indicated in Kelvins and implanted with 1000 eV helium of fluence of 9.24×10^{13} He/cm². The spectrum just below 690 K spectrum was obtained for bare Mo substrate.

ria and Poppa¹⁸ [Cu on Mo(100)], and our work⁴ [Cu on Mo(100)], where it was found that at elevated substrate temperatures, growth of Cu beyond two MLs takes place in the form of 3D islands. To illustrate one further point, in Fig. 10 the spectrum of the bare Mo substrate is shown just below the spectrum of the Cu film deposited at 690 K. Here it is seen that the temperature of the H peak of Mo is not lowered due to the presence of the Cu film unlike in Sec. III A. This leads us to conclude that the different coefficients of thermal expansion of the film and the substrate, which have a different effect than in the case of room-temperature deposition (Sec. III A), play a role for the exact temperature of H peak.

G. Effect of ion bombardment during deposition

IBAD, a technique in which the growing film is bombarded with energetic particles, is a method applied in thinfilm fabrication to modify the microstructure and properties of thin films. For reviews, see Smidt²⁵ and Hirvonen.²⁶ In this section we consider THDS analysis of Cu thin films (200 Å) deposited with 250 eV Ar⁺ assistance on poly-Mo at room temperature. Figure 11(a) shows the normalized helium desorption spectra for Ar⁺/Cu (ion/atom) deposition ratios as shown for a 100 eV helium implantation fluence of 8.26 $\times 10^{13}$ He⁺/cm². Note that even though 100 eV helium exceeds the threshold for damage production in bulk Cu (85 eV), the damage production is not very significant, as was confirmed by THDS measurements (Sec. III D). The longitudinal range and straggle of 100 eV helium are 17 and 10 Å, respectively.¹³ For comparison, helium desorption spectra of films deposited without ion assistance are reproduced from Fig. 3 and are shown as thin curves in Fig. 11(a). The corresponding argon desorption spectra for the IBAD films are shown in Fig. 11(b).

The 0 Å spectra are not really IBAD spectra (because no film was deposited) but were obtained after the Mo substrate



FIG. 11. (a) Normalized helium desorption spectra of 5-200 Å Cu films deposited with 250 eV Ar-ion bombardment with an ion to atom ratio as indicated and implanted with 100 eV helium of fluence of 8.26 $\times 10^{13}$ He⁺/cm². For comparison non-IBAD films are reproduced from Fig. 3 as thin lines. The film thickness in angstroms is indicated. The bottom spectrum was obtained by bombarding Mo with 250 eV Ar of fluence of 4.23 $\times 10^{15}$ Ar/cm². (b) The corresponding argon desorption spectra normalized by the total amount of argon in the film.

was bombarded by 250 eV Ar⁺ with a fluence of 4.23 $\times 10^{15}$ Ar⁺/cm² and implanted with 100 eV helium. Ar ions of 250 eV have a longitudinal range and straggle of 8 and 5 Å, respectively in Mo.¹³ The threshold energy for Frenkel pair creation by Ar in bulk Mo is 40 eV calculated adopting a minimum displacement energy value of 33 eV for Mo.²⁷ In this context it will be useful to recall the work of van Veen et al.²⁸ and van der Kuur et al.²⁹ on Ar behavior in Mo. The helium trapped in Mo must be due to defects created by Ar beam since 100 eV He is below the threshold for Frenkel pair creation in bulk Mo (215 eV). There are no distinct peaks (E, F, G, H, I, J, and K) due to helium release from monovacancies and polyvacancies in Mo or distinct peaks due to helium associated with substitutional argon and argonvacancy complexes. It has been shown²⁹ that this absence is due to the close proximity of the defects created by Ar beam to the surface of Mo substrate. In the 0 Å argon desorption spectrum of Fig. 11(b) the argon release has been explained²⁸ by the following defect reactions, where ^{*} denotes a mobile species:

 Release of Ar located in between the surface (first layer) and second layer of the Mo substrate in interstitial positions and also near-surface irregularities.

Ar^S peak Ar \rightarrow Ar^{*} (\sim 500 K).

(2) Release of Ar present in substitutional positions in the second layer.

Ar^I peak Ar $V \rightarrow$ Ar^{*} (1000 K).

(3) Vacancy-assisted release of Ar present in substitutional positions in a region covering the third to approximately fifth layers.

 $\label{eq:ArII} \mbox{Ar}^{\rm II} \mbox{ peak } V + \mbox{Ar} V \rightarrow \mbox{Ar} V_2^* \quad (1400 \mbox{ K}).$

In our case the peaks Ar^S, Ar^I, and Ar^{II} are at temperatures of 604, 1017, and 1388 K, respectively.

Now we return to the helium desorption spectra of Fig. 11(a) for the 5–200 Å Cu films deposited with 250 eV Arion assistance. It is clear that the defects created by the argon beam result in a considerable enhancement of helium trapping in the Cu films especially in the A component (the broad release between 300 and 900 K, see Fig. 3) of the helium spectra. The island formation peak (L) has about the same intensity as for the non-IBAD films. It is difficult to account for this behavior since one would expect more helium to desorb during island formation for IBAD films. There are no sharp argon-related peaks in the helium desorption spectra, such as the two peaks due to helium trapping at substitutional argon found for IBAD Mo films.²⁹ This could be due to the intervention of island formation. The concentration of argon atoms in all the films is $\sim 10^{-3}$, which is derived by integrating the non-normalized argon spectra of Fig. 11(b). In the 20-50 Å helium spectra, island formation occurs at a higher temperature when compared with the non-IBAD films. This enhanced stability against agglomeration is apparently due to the modification brought about by the ion bombardment during film deposition, which is often reported to include improved adhesion and orientation, higher atomic density of the film, and stress relaxation. In order to precisely find out which of these modifications contribute to the observed enhancement of thermal stability of IBAD films more experiments need to be done. For 20-50 Å IBAD films the argon spectra [Fig. 11(b)] are very similar to the corresponding helium spectra. This is a significant observation. It means that helium and argon release are not driven by the atoms' own defect dissociation energies but by the processes happening in the film as it is heated. The principal characteristic temperature ranges of these are those of surface defect relaxation (A component), island formation (L peak), interface defects (P peak), and film sublimation (M peak). Above 75 Å the argon spectra start to differ from the helium spectra. This is because of the different distributions of trapped Ar and He in the Cu film. While the Ar is distributed almost uniformly throughout the film because of its use during deposition, the

helium distribution, because of its implantation after deposition, is limited by its range in the film. A closer look at the data indicates that even for 75-200 Å films, for every peak in the argon spectrum there is a corresponding peak in the helium spectrum, although with a different intensity. To summarize, IBAD films contain more defects due to the employed argon energy, and island formation takes place at a higher temperature.

H. Effect of substrate orientation

We have earlier reported on the THDS analysis of Cu films grown on single-crystalline Mo(110) (Ref. 3) and Mo(100).⁴ It was observed⁴ that the Cu films for the same thickness responded differently to the process of island formation and to sublimation. In this section we compare the 75 eV helium-implanted film thickness variation series of the Cu films on poly-Mo with those on Mo(110) and Mo(100). It would seem logical to observe a weighted sum of the (110), (100), and possibly other orientation spectra. Since the poly-Mo substrate has a strong (110) texture its comparison with Mo(110) will be considered first. Figure 12(a) shows the spectra for poly-Mo (reproduced from Fig. 3) and Mo(110) (thin curves). The most striking difference is that in the 20–200 Å spectra the peak for island formation (L peak) in poly-Mo is much lower than in Mo(110). Hence one observes not a weighted sum but a single spectrum with its own individual character. It is very surprising as to how it is possible that the grain boundaries, which form only a minute volume fraction of the substrate, can have such an effect. A possible explanation for this is that the differently oriented crystals of Cu on poly-Mo have grain boundaries, which on heating generate stress and enhance the rate of island formation. While on Mo(110) it is a single-crystal Cu(111).³⁰ There are other differences, too. For the poly-Mo the M peak is seen for the 30-200 Å spectra, while for Mo(110) it is only found for the 20-50 Å spectra; for the same thickness the temperature of the former is slightly higher than the latter. The total trapped fraction of helium as a function of film thickness for Cu/poly-Mo is less than for Cu/Mo(110) for film thicknesses up to 40 Å, above which they are similar.

Figure 12(b) is the same as Fig. 12(a) with the exception that thin curves now represent Cu films on Mo(100). In the 10-200 Å spectra, the L peak for polycrystalline Mo is at a lower temperature when compared to Mo(100). There is no transition from L to L* peak after 70 Å in the case of poly-Mo unlike in Mo(100). The M peak is seen for 30-200 Å spectra in poly-Mo while it completely absent for Mo(100). But in experiments involving 1000 eV helium implantation, for 75-200 Å spectra the M peak for poly-Mo is at a slightly lower temperature when compared to Mo(100). The total trapped fraction of helium as a function of film thickness for Cu/Mo-poly is similar to Cu/Mo(100). In summary Cu/poly-Mo has a character of its own as revealed by the island formation and sublimation peaks in its spectra, which is different when compared to Cu/Mo(110) and Cu/Mo(100).



FIG. 12. Normalized helium desorption spectra of 5-200 Å Cu films implanted with 75 eV helium of fluence of 7.98×10^{13} He⁺/cm² (a) Cu/poly-Mo (thick lines) compared to Cu/Mo(110) (thin lines) (b) Cu/poly-Mo (thick lines) compared to Cu/Mo(100) (thin lines).

IV. CONCLUSIONS

Cu films (10-200 Å) deposited on polycrystalline Mo substrate at room temperature are metastable. On annealing they undergo a structural transformation and assume the shape of islands. The kinetics of this process is seen in the helium desorption spectra as a broad peak. The peak temperature of island formation is thickness dependent varying from 417 K for 10 Å film to 1100 K for 200 Å film. The activation energy for the island formation in the case of 75 Å Cu film was found to be 0.3 eV. The average defect concentration in the Cu films is $\sim 5 \times 10^{-4}$. Defects close to the surface of the Cu film were identified by overlayer experiments. Monovacancies are present in the as-deposited Cu films. The total trapped fraction of helium in the Cu film was constant when the helium fluence was increased. The substrate surface state is responsible for defects at the filmsubstrate interface. Increase of substrate temperature during deposition leads to film whose structure is in the form of islands. Argon-ion bombardment during deposition leads to the increase of helium trapping in the films. The temperature of island formation peak for IBAD films is higher than non-IBAD films. For an ion/atom ratio of ~0.1 the argon concentration in the films is 10^{-3} . Helium and argon release from Cu films to most part are similar; most of the helium atoms are bound to defects created by argon. Argon release from near-surface region of the Cu film, interface, and during the film desorption is observed. For the same film thickness, the peak temperature of island formation for Cu/poly-Mo was found to be much lower than Cu/Mo(110) and Cu/Mo(100).

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APPENDIX

A numerical model of a THDS experiment (implantation, trapping, heating, diffusion, and desorption) can be formulated in one set of master equations. A brief summary is given here. Let $c_i = c_i(z, t)$ denote the concentration of "lattice sites" of type *i* accessible to helium atoms, at depth *z* below the surface of the sample, at time t. Lattice site is used here loosely, to indicate any of the different types of locations where a helium atom may be found, such as interstitial positions or different kinds of defects in which the helium atoms can be trapped, with different dissociation energies. Let N_s denote the number of such lattice site types, $n_i = n_i (z, t)$ the concentration of helium atoms in the lattice sites of type *i*, v_{ii} the frequency of thermally activated helium jumps from an *i* site to a *j* site, λ the relevant jump distance, and B_i $=B_i(z,t)$ the helium implantation profile—or more precisely, the concentration of helium atoms having slowed down to thermal energies and arriving on *i*-type lattice sites per unit time. Then the helium concentration in the sample can be described by the N_s coupled differential equations

$$\begin{aligned} \frac{\partial n_i}{\partial t} &= B_i + c_i \sum_{j=1}^{N_s} \nu_{ji} \left\{ \frac{1}{6} n_j (z - \lambda) + \frac{4}{6} n_j (z) + \frac{1}{6} n_j (z + \lambda) \right\} \\ &- n_i \sum_{j=1}^{N_s} \nu_{ij} \left\{ \frac{1}{6} c_j (z - \lambda) + \frac{4}{6} c_j (z) + \frac{1}{6} c_j (z + \lambda) \right\} \\ &(i = 1, 2, \dots, N_s), \end{aligned}$$
(A1)

with

$$\nu_{ij} = \nu_{0,ij} \exp(-E_{d,ij}/kT),$$
 (A2)

$$B_i(z,t) = \alpha c_i(z,t) \exp\left[-\frac{1}{2}(z-R_p)^2/\Delta R_p^2\right].$$
 (A3)

In the terms between curly braces in (A1) the z dependence is explicitly indicated to show the jump directions of the helium atoms. The three terms on the right-hand side of (A1) denote, respectively, the increase of helium atoms in i sites by implantation, the increase of helium atoms in *i* sites by jumps from neighboring j sites, and the loss of helium atoms from i sites by jumps to j sites (the hypothetical 3D cubic lattice used in the description involves no loss of generality with respect to the real crystal structure). In (A2), $\nu_{0,ii}$ is the attempt frequency of $i \rightarrow j$ jumps, which includes an entropy factor $\exp(\Delta S_{ij}/k)$, $E_{d,ij}$ the corresponding dissociation (activation) energy, and k the Boltzmann constant. In (A3), $B_i(z)$ is assumed to be proportional to the local concentration of isites and to have a Gaussian shape with projected range R_n and straggle ΔR_p . The constant α is chosen in such a way that, after multiplication by the atomic number density in the sample, the integral of $B_i(z)$ over z and summed over i is equal to the total helium implantation flux. When the helium beam is off, $B_i(z)=0$. In this description only one dimension is considered, which relies on the fact that the grain size is much larger than the helium depth range. Also, higherdimensional effects such as island formation cannot be described by the current equations. Note that formally c should be interpreted as an *effective* concentration, since many defects in solids appear to a diffusing helium atom larger than they are, because of the attractive forces arising from the stress field around the defect; in this context the so-called trap radius is supposed to be included in c. In a continuum representation, which is an approximation only, Eq. (A1) takes the more familiar form

$$\frac{\partial n_i}{\partial t} = B_i + c_i \sum_{j=1}^{N_s} \left\{ D_{ji} \frac{\partial^2 n_j}{\partial z^2} + \nu_{ji} n_j \right\}$$
$$- n_i \sum_{j=1}^{N_s} \left\{ D_{ij} \frac{\partial^2 c_j}{\partial z^2} + \nu_{ij} c_j \right\} \quad (i = 1, 2, \dots, N_s), \quad (A4)$$

where

$$D_{ij} = \frac{1}{6} \nu_{ij} \lambda^2 \tag{A5}$$

is the diffusion coefficient associated with $i \rightarrow j$ jumps.

In order to calculate trapped helium fractions, Eq. (A1) is numerically solved for a semi-infinite medium (z>0), with the film surface at z=0 and the film/substrate interface at z=d, and assigning the following lattice site types and concentration profiles:

$$i, j = 1$$
 vacuum "sites" $c_1 = 1$ for $z < 0$ and
 $c_1 = 0$ for $z > 0$,

$$i, j = 2$$
 interstitial sites $c_2 = 0$ for $z < 0$ and
 $c_2 = 1 - c_3(z) - c_4(z)$ for $z > 0$,

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 $c_4 = 0$ elsewhere.

Note that this scheme is the simplest possible. It involves only one trap type in the film and one in the substrate, the traps are assumed to have a stationary depth profile, and the traps are assumed unsaturable (i.e., can trap any number of helium atoms). In many THDS situations this is too simple. However, in order to calculate the trapping behavior (no heating) of 75 eV He ions at 300 K the scheme suffices, and very few parameters have to be chosen, because once a helium atom is trapped it will no longer move out of its site. The values used for the relevant parameters are $v_{0,ii}$ =10¹³ s⁻¹, $E_{d,2j}$ =0.2 eV, λ =2.56 Å, R_p =6.6 Å, and ΔR_p = 3.9 Å. The last two numbers were obtained from MARLOWE simulations.³¹ Other values used are $E_{d,1i}$ =40 eV (to make sure that helium atoms escaped to the vacuum cannot move back into the sample) and $E_{d,3j}=E_{d,4j}=2$ eV (as an arbitrary helium-trap dissociation energy, large enough to retain helium at 300 K). All that is left then is to assume a trap profile $c_3(z)$, and possibly also $c_4(z)$, and solve the equations (A2) over a certain implantation period t_{imp} . The trapped helium fraction $f_{\rm tr}$ at the end is calculated from the results according to

$$f_{\rm tr} = \frac{\int_0^\infty dz \sum_{i=3}^4 n_i(z, t_{\rm imp})}{t_{\rm imp} \int_0^\infty dz \sum_{i=2}^4 B_i(z)}.$$
 (A6)

If the calculated f_{tr} does not agree with the experimental value, the assumed trap profile is adjusted and the calculation is repeated.

Note that much more information can be obtained from such calculations than discussed here. For example, $n_3(z)$ and $n_4(z)$ show where in the sample the helium is trapped, and $n_3(z)/c_3(z)$ and $n_4(z)/c_4(z)$ represent the mean trap occupancies at depth z.

1. Special case: First-order desorption kinetics

To derive first-order desorption kinetics from Eq. (A1), we only consider interstitial (i, j=1) and trapped (i, j=2) helium and disregard z dependence (which will be motivated below). The equations then become

$$\frac{\partial n_1}{\partial t} = c_1 \nu_{21} n_2 - n_1 \nu_{12} c_2, \tag{A7}$$

$$\frac{\partial n_2}{\partial t} = c_2 \nu_{12} n_1 - n_2 \nu_{21} c_1 = -\frac{\partial n_1}{\partial t}.$$
 (A8)

This is true locally, as if no surface was present. However, in reality the surface is a sink for the interstitial particles, and interstitial diffusion to the surface is so fast that all z dependence may be disregarded and that n_1 is very small. This

implies that the first term in Eq. (A8) may be neglected. Since $c_1 \approx 1$, one arrives at

$$\frac{\partial n_2}{\partial t} = -n_2 \nu_{21} = -n_2 \nu_{0,21} e^{-E_{d,21}/kT},\tag{A9}$$

which is identical to the first-order desorption equation. Dropping the index 21 and writing $T = \beta t$ to describe a linear heating desorption experiment, one obtains

$$\frac{\partial n_2}{\partial T} = -n_2 \frac{\nu_0}{\beta} e^{-E_d/kT}.$$
(A10)

Since $-\partial n_2/\partial T$ is proportional to the helium desorption flux, the peak temperature T_{max} can be calculated by differentiating Eq. (A10) with respect to T and setting the result equal to 0. One thus arrives at

$$\ln \frac{\beta}{T_{\max}^2} = \ln \frac{\nu_0 k}{E_d} - \frac{E_d}{k T_{\max}},\tag{A11}$$

which forms the basis of the Kissinger analysis.

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