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Study of defects and thermal stability of ultrathin Cu films on Ta(110) and Ta(100) by thermal helium desorption spectrometry

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ABSTRACT

Thermal helium desorption spectrometry has been used to study the interaction of helium with defects in Cu films (5–300 Å) deposited on Ta(110) and Ta(100) single crystals by ultrahigh vacuum electron beam evaporation. The thermal stability of the Cu films was also investigated. Cu films on Ta(110) and Ta(100) at room temperature are metastable and on heating, the films transform into islands. The temperature at which this takes place is strongly dependent on the Cu film thickness and for a given thickness (>40 Å) occurs at a lower temperature on Ta(100) than on Ta(110). The activation energy for island formation is 1.6 ± 0.4 eV for 50 Å Cu/Ta(110) and 0.8 ± 0.1 eV for 100 Å Cu/Ta(100) obtained by Kissinger analysis. The geometry of the Cu islands resulting from annealing 50 Å Cu films at 1000 K for 10 s depends strongly on the Ta substrate orientation. There is evidence for the stressed states of both the Cu films and the Ta substrates. Helium release from monovacancies and vacancy clusters in Cu films (>75 Å) on Ta(110) and Ta(100) was detected at ~750 K and ~800–1000 K respectively. The sublimation of the Cu films from the Ta substrates could be observed by the release of retained helium at ~1300 K.

1. Introduction

The study of the growth, structure and thermal stability of an face centered cubic (fcc) film like Cu on a body centered cubic (bcc) substrate like Ta is not only important for understanding heteroepitaxy [1] but also for many technological applications [2]. Such a system is vital to study the effect of lattice and thermal mismatch between the film and the substrate on defects and thermal stability of the films. Cu/Ta is one of the material combinations employed in the current IC-metallization, where Cu is the interconnect material and Ta is used as diffusion barrier, and hence been a subject of many recent investigations [3–6]. Ultrathin Cu films on bcc substrates have been studied as a model bimetallic catalyst [7].

Kuhn et al. [7] studied ultrathin Cu films on Ta(110) and found that a monolayer (ML) of Cu forms a psuedomorphic film on Ta(110). Chen et al. [8] studied ultrathin Cu films on polycrystalline Ta and reported the dewetting of 5 Å Cu in the range 600–1000 K, and diffusion of Cu into Ta at 1100 K after a 5 min induction period. The agglomeration of Cu seed layers on Ta barrier layers used in Cu interconnection has been studied by a few groups [9–11]. Uedono et al. [12] investigated the role of vacancy clusters in self annealed electroplated Cu films (0.5–4 μm) on $Ta/SiO_2/Si$ using the positron annihilation. Klaver and Thijsse [13] studied the growth of Cu films on Ta(110) and Ta(100) using molecular dynamics (MD) simulations and reported absence of point defects in 25 Å Cu films on Ta(110) and Ta(100). Thermodynamical and mechanical stabilities of Cu films on Ta(110) has been recently investigated by density functional theory [14] and MD simulations [15] where an incoherent ML of Cu on Ta (110) was found to be thermodynamically stable while thicker layers were unstable and agglomerated into droplets on top of the ML. Fillot et al. [16] investigated surface diffusion of Cu on β-Ta(002) and α-Ta with (110) texture thin films and reported an activation energy of 0.83 ± 0.1 eV for the former case.

In this paper, we report thermal helium desorption spectrometry (THDS) [17,18] analysis of defects and thermal stability of ultrathin Cu films (5–200 Å) deposited on Ta (110) and Ta(100) in ultrahigh vacuum (UHV) by electron beam evaporation. We will compare the helium release from Cu films to that from ion implanted Cu(100) [19]. Earlier we have studied defects and thermal stability of thin Cu films (5–200 Å) on Mo(110) [20], Mo(100) [21] and Mo(poly) [22] using THDS. Hence we will also compare Cu films on Ta with those on Mo.

Thermal helium desorption spectrometry [17,18] gives information about defects in the subsurface region of a film, down to 10–100 Å below the surface, depending on the incident helium energy. After collisional slowdown and thermalization, the implanted helium atoms in the sample diffuse interstitially until they leave the sample or encounter a defect where they are trapped. These defects may be native defects, already present in the sample, or may have been created during implantation. In a film/substrate system, helium trapping can occur in the defects in the film, at the interface, or in the substrate. This depends on the diffusion length of the thermalized helium projected along the surface normal, which is a function of helium energy and the concentration profile of the

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defects. On heating the sample, the helium is released from these defects at temperatures that are characteristic of the helium-defect dissociation energies. Additionally, helium may also be released from the sample if morphological or thermodynamic changes take place in the film. Analysis of the helium desorption signal as a function of sample temperature therefore yields information on defects, thermal stability, film coverage, and ion damage effects. Although THDS is a rich technique in terms of the information that can be obtained, we will see that different types of experiments and careful combination of the results are needed to come to an adequate interpretation of the data. For a detailed THDS study of the helium-defect interactions in Cu films grown on Ta, we have therefore varied deposition conditions such as film thickness, substrate orientation, post-deposition annealing temperature, post-implantation overlayer thickness, and two of the THDS conditions: helium implantation energy and heating rate during desorption.

2. Experimental details

The experiments were performed in an UHV system [23] capable of preparing vapor deposited thin films with optional ion assistance and their subsequent analysis by THDS. The base pressure of the system after bakeout was 8×10^{-9} Pa. The Ta(110) and Ta(100) substrates, each 10.0 mm in diameter, 2.0 mm in thickness and having 99.999 weight % purity, were obtained from the Surface Preparation Laboratory (Zaandam, Netherlands). The final polishing step was done with 0.05 μm diamond paste. The surface misorientation after the final polishing was confirmed to be smaller than 0.5° as measured by Laue diffraction. Prior to the experiments the substrate surface was cleaned by successive annealing cycles to 2200 K in the UHV system. The recommended [24] annealing temperature range (2700–3000 K) in UHV for cleaning Ta (110) and Ta(100) could not be achieved by our heating system. The cleanliness and long-range order of the surface could not be monitored due to the absence of in-situ Auger Electron Spectroscopy and Low Energy Electron Diffraction in the UHV chamber. Nevertheless, low-energy helium implantation has never indicated the presence of any observable defects in the Ta substrates after annealing or between the implantation/desorption cycles (see Section 3.3).

For film deposition, Cu lump (purity 99.999 weight %) 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, monitored using a quartz crystal oscillator. The pressure during deposition did not exceed 1.5×10^{-7} Pa. The substrate temperature during film deposition was usually ~300 K. After deposition, the sample was implanted with 1000 eV or 75 eV mass-filtered helium ions, depending on the desired type of experiment, usually with a fluence ϕ of 2.0×10^{14} He^+/cm^2, impingent 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 feedback-controlled linear rate β of 40 K/s, and the helium desorption flux L (helium atoms/cm^2/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 the 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 helium desorption spectrum (L versus T) consists of a number of peaks, each peak signifying the desorption of helium from a particular trapping site in the sample. The Cu–Ta system is immiscible [25] and has a positive heat of mixing of + 12 kJ/mol [26]. Therefore, Cu is not expected to diffuse from the film into the substrate on heating. On the contrary, in each desorption run the Cu films were observed indirectly to desorb from the substrate in the temperature range 1300–1350 K, but we continued the sample heating to 2000 K in order to detect helium that may still be trapped in the Ta substrate at higher temperatures.

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 has not been corrected for ion backscattering and secondary electron generation. In all 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}. Hence the integral area under a spectrum is equal to the originally trapped helium fraction, since no helium was found to be retained in the sample above 2000 K.

The principal helium implantation energies were 75 eV and 1000 eV. A helium energy of 75 eV is below the threshold energy (E_{th}) for Frenkel pair creation in bulk Cu, $E_{th} = 85$ eV, calculated assuming binary elastic

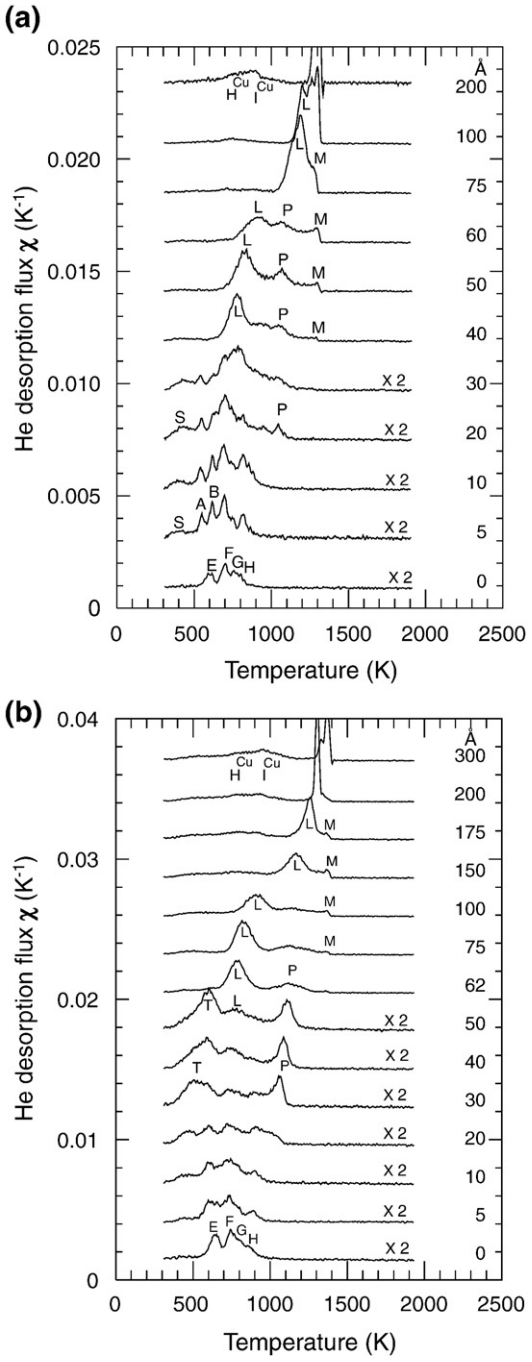

Fig. 1. Normalized helium desorption spectra of Cu films of different thicknesses as indicated deposited on (a) Ta(110) and (b) Ta(100) at room temperature and implanted with helium of 1000 eV energy and fluence 2×10^{14} He/cm^2. For Ta(110), the 0–30 Å spectra are multiplied by a factor of 2. For Ta(100), the 0–50 Å spectra are multiplied by a factor of 2.