

Vacancy Annealing for Ag(001) Homoepitaxy at Low Temperature

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Introduction

Recent kinetic Monte Carlo (KMC) simulations have made excellent progress in predicting many of the surface morphological features observed in homoepitaxial growth experiments [1]. However, if theories of crystal growth are to accurately relate to real surfaces, then one must include all of the microscopic kinetic mechanisms that are relevant. Simulations have largely neglected the role of crystalline defects that *originate* at the growth front. The ability of x-ray scattering to probe the subsurface structure as well as the surface morphology enables the investigation of subsurface defects in epitaxial crystal growth.

Our recent x-ray scattering investigations have demonstrated that a substantial vacancy concentration is incorporated into noble metal films that are grown homoepitaxially at low temperature [2-4]. This is particularly interesting because the incorporation mechanism(s) must involve the atomic-scale kinetics that also determine the evolving surface morphology. Thus, when there is vacancy incorporation, it must be intimately tied to the considerations of surface morphology. Indeed, for the three cases that we have studied, substantial changes in surface morphology have been observed [2, 5-7], although the mechanisms for these changes is not understood. The purpose of the present study is to investigate the vacancy annealing behavior, which can provide insight into the mechanisms of vacancy incorporation.

Methods and Materials

Using an incident x-ray energy of 16.2 keV, the specular reflectivity was measured *in situ* in ultrahigh-vacuum (UHV) by using the newly constructed surface scattering spectrometer located at MU-CAT sector 6 at the APS. A Ag(001) crystal (10 mm in diameter by 3 mm thick) was mechanically polished to a miscut of $\sim 0.1^\circ$ and subsequently prepared in UHV by repeated sputtering and surface annealing cycles. Sputtering was performed by using an Ar pressure of 10^{-5} Torr, an acceleration voltage of 500 V, and a current of ~ 10 μ A. The sample was heated by electron bombardment, and the surface annealing was performed near 720°C. This procedure resulted in atomically smooth surfaces with a surface correlation length (facet size) of ~ 500 nm. Low temperatures were achieved through the use of a closed-cycle refrigerator. The surface temperature of the sample

was directly determined by measuring the thermal expansion. Ag was evaporated from a resistively heated crucible that had its deposition rate calibrated by measuring the x-ray intensity oscillations that occur at the anti-Bragg position during layer-by-layer growth at 350°C. The experiments reported here had a deposition rate of 1 monolayer per minute (ML/min). The specular reflectivity was obtained by performing a rocking scan at each desired wave vector perpendicular to the surface, which allowed proper identification of the specular component as well as subtraction of the diffuse background. The resulting specular reflectivity was fit to a model that included a strained film arising from the vacancies. This procedure, described elsewhere [3], permits an estimate of the vacancy concentration.

Results

The main result is shown in Fig. 1, where a 20-ML film was deposited on the substrate at a temperature between 100K and 150K. This film was subsequently annealed at successively higher temperatures over ~ 30 min for each point given in Fig. 1, where the reflectivity was measured and the vacancy concentration was estimated. It can be seen that there is very little change in vacancy concentration as the annealing temperature is increased until ~ 350 K, where the vacancy concentration precipitously vanishes. The solid curve corresponds to

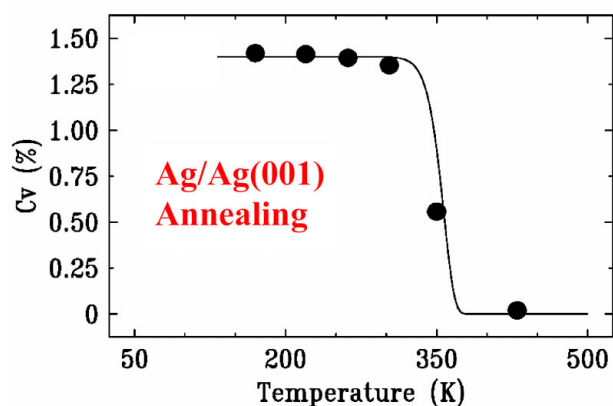


FIG. 1. Vacancy concentration, obtained from x-ray specular reflectivity according to the procedure outlined in Ref. 3, measured as a function of the annealing temperature.

1.1-eV activation energy and an attempt frequency of 6.8×10^{13} Hz.

Discussion

It is useful to discuss these results in the context of the dependence on growth temperature as well as to compare them with results for Cu(001) homoepitaxial growth. As can be seen from Fig. 2, the dependence of vacancy concentration on the growth temperature is similar for both Cu and Ag, indicating the kinetic similarity of these two metals. Indeed, reentrant smooth growth also occurs similarly for both of these (001) homoepitaxial metals [5, 6].

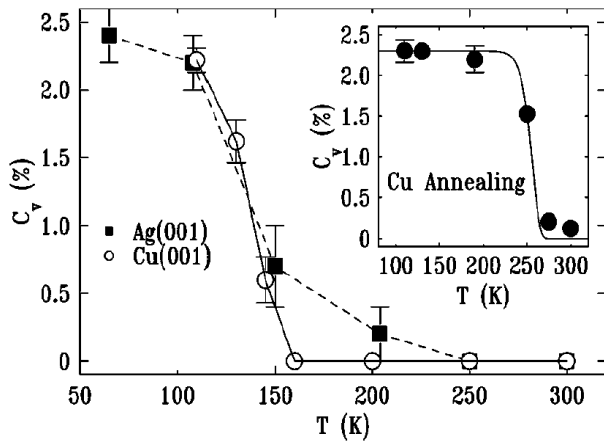


FIG. 2. Comparison of the dependence on the growth temperature of the vacancy concentration for the homoepitaxial growth of Cu and Ag (001), taken from Ref. 2. Inset shows dependence upon annealing for Cu.

However, it appears that vacancies in Ag and Cu anneal at substantially different temperatures. Although in both cases, the temperature at which vacancies anneal is substantially higher than the temperature at which vacancies are unable to incorporate (which is due to the additional kinetic barriers needed for vacancy mobility), the annealing temperature for Ag is much higher than that for Cu. This should be considered in relation to the respective vacancy annealing temperatures in the bulk metals, where electron irradiation studies show that vacancies anneal around ~ 250 K in both metals [8]. In the case of Cu, we observed an annealing temperature that is essentially identical to the bulk case. However, the vacancy mobility occurring at ~ 350 K in our Ag films is nearly 100 K higher than what is observed for similar studies on bulk Ag. For the bulk metals [8], monovacancy

mobility is responsible for the annealing in Cu, whereas as divacancy mobility is responsible for the annealing temperature in bulk Ag. Thus, one possible explanation for our results could be that the onset of monovacancy mobility is responsible for annealing in both metals (the monovacancy mobility temperature is higher than for divacancy mobility [8]). However, other, more complex kinetics barriers (e.g., clustering) could intervene, so that further experimental and simulation studies would be necessary in order to better understand the mechanisms of vacancy incorporation and mobility in homoepitaxial metals.

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