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X-ray studies of the growth of smooth Ag films on Ge(111)-$c(2\times8)$

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We have performed *in situ* reflectivity measurements using synchrotron radiation of Ag films deposited on Ge(111) over the thickness range of 3–12 atomic layers. The films deposited at a substrate temperature of 110 K are not well ordered, but become well ordered upon annealing, as evidenced by substantial changes in the x-ray reflectivity data. The thickness distribution for each annealed film, deduced from a fit to the reflectivity data, is remarkably narrow, with just two or three adjacent discrete thicknesses present, despite the large lattice mismatch between Ag and Ge. In some cases, the film thickness is nearly atomically uniform. The results are discussed in connection with recent models and theories of electronic effects on the growth of ultrathin metal films. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1763212]

Preparing smooth metal films on semiconductor substrates is a subject of considerable scientific and technological interest. Atomically uniform films are highly desirable, but are difficult to achieve in practice. Previous studies have suggested that growth at low temperatures followed by annealing at high temperatures is a promising way to create smooth films, as opposed to direct growth at high temperatures which tends to create highly three-dimensional structures. Yet this low-temperature-deposition-and-annealing procedure does not always yield smooth films, and a variety of interesting phenomena have been reported. For example, Ag films on Fe(100) can be prepared with atomic-scale uniformity up to 100 monolayers (ML).[1] Smooth Ag overlayers can be grown on GaAs(110) and Si(111) above a critical thickness of 6 atomic layers but below the critical thickness Ag forms islands with magic or preferred heights.[2,3] Studies of Pb grown on Si(111) by low temperature deposition also showed the formation of islands with preferred heights.[4] In addition, critical thicknesses, above which layer-by-layer growth sets in, have been reported.[5,6] These preferred, critical, and magic thicknesses have been attributed to quantum size effects.[1–9] Briefly, electrons in the metal film are confined by the vacuum and substrate barriers, and this confinement leads to modifications of the electronic structure and the electronic energy, which in turn affect the growth and morphology of the film.

In this letter, we report an *in situ* x-ray study of the growth and morphology of Ag films prepared by low temperature deposition onto Ge(111)-$c(2\times8)$ followed by annealing. This is a system previously predicted by model calculations to exhibit critical thickness behavior.[7] Under our growth conditions, we observe no evidence for such behavior. Rather, the deposited films become well-ordered after annealing, and the resulting films exhibit a very narrow thickness distribution of just two or three adjacent thicknesses. Some of them are quite close to being atomically uniform. One advantage of x-ray measurements is the deep penetration of the probe beam, permitting direct determination of the film thickness. By contrast, the widely used electron diffraction and scanned probe techniques sense the morphology of the top surface only, yielding little information about the actual thickness. While this study focuses on basic issues of film growth and electronic confinement, the results are potentially relevant to device concepts in the quantum regime.

The experiment was carried out at UNICAT (University, National Laboratory, and Industry Collaborative Access Team), Advanced Photon Source, Argonne National Laboratory. All x-ray measurements were performed with an incident beam energy of 19.9 keV. The sample was processed *in situ* in an ultrahigh vacuum growth chamber, which was coupled to a six-circle diffractometer via a double-differential-pumping rotary stage. The chamber was equipped with Knudsen cells and a reflection-high-energy-electron-diffraction (RHEED) system for surface characterization. Ge substrates were cut from commercial wafers into rectangular pieces of size $40\times5\ mm^2$ and mounted onto a liquid-nitrogen cooled sample stage within the chamber. The base temperature of the sample was 110 K. By passing a current through the sample, the sample temperature could be raised and controlled. Initial surface cleaning was achieved by repeated cycles of Ar^+ ion sputtering at a beam current of

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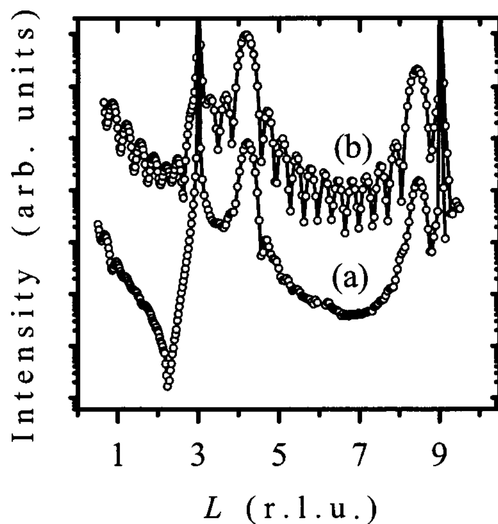

FIG. 1. Logarithmic reflectivity profiles for a Ag film with a nominal coverage of 12 ML plotted as a function of the perpendicular momentum transfer L in reciprocal lattice units (r.l.u.). (a) After deposition at 110 K, the result indicates a film that is not well ordered. (b) After annealing, multilayer interference fringes are observed, indicating a well-ordered film. The lines joining the data points serve as a guide to the eye. An offset is included for display clarity.

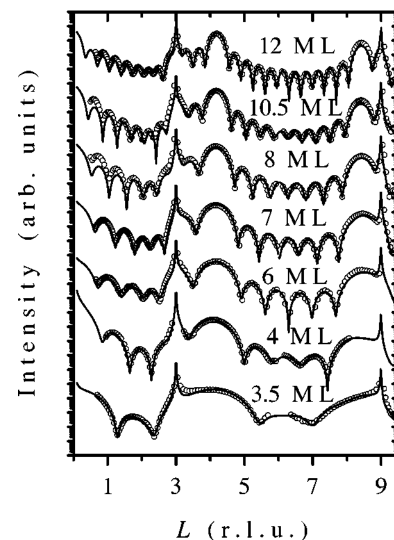

FIG. 2. Logarithmic reflectivity profiles for annealed Ag films with the nominal thicknesses indicated. The results are offset vertically for display clarity. Curves are best fits.

1 μA for 10 min at 700 K and annealing to 900 K for 10 min. After many cycles, a sharp $c(2\times8)$ pattern was observed by both RHEED and x-ray diffraction. The rate of Ag deposition was monitored by a quartz thickness monitor, and was set to 0.0015 ML/s. Here, 1 ML is defined as the surface density of Ag(111), 1.5×10^{15} atoms/cm^2. In each run, a nominal amount of Ag was deposited with the sample at the base temperature. The sample was then annealed to room temperature (except where noted). Reflectivity scans were taken after the sample cooled back to the base temperature. A new thickness was prepared either by incremental deposition or on a regenerated clean substrate.

The reflectivity rod was measured by either of two methods. One method was to take ridge scans (line scans) with the incident and detector angles kept at the specular condition while varying L,[10] the perpendicular momentum transfer measured in Ge(111) reciprocal lattice units (1 r.l.u. $=0.641$ Å^{-1}). Line scans were also taken at nearby off-specular conditions for background subtraction. The other method was to take ω scans,[11] obtained by rocking the sample's incident angle while keeping the detector at a fixed exit angle. The rocking curves were analyzed to yield a scattering intensity. It was verified that the two methods, with appropriate geometric corrections, were equivalent.

After deposition at the base temperature, the films were not well ordered. An example is shown in Fig. 1(a). In this case, 12 ML of Ag were deposited. The logarithmic reflectivity curve shows sharp peaks at $L=3$ and 9, which are Bragg peaks from the Ge(111) substrate. The peaks at $L\sim4.15$ and 8.3 are the (111) and (222) Ag Bragg peaks, verifying the (111) orientation of the film. There are some minor modulations in between the Ag Bragg peaks, indicating that the film is not well ordered. After annealing to room temperature, the modulations become very pronounced, as seen in Fig. 1(b). The modulation peaks arise from constructive interference among the atomic layers within the film and are characteristic of well-ordered films. From one Ag Bragg peak to the next, themselves included, there are 12 peaks, indicating a dominant film thickness of 12 ML. A significant roughness would give rise to a superposition of interference fringes with different periods, smearing out the modulation. Similar results were observed for other thicknesses.

Figure 2 shows reflectivity curves for annealed films with their nominal thicknesses indicated. Each curve has been fitted using a standard kinematical model,[11–13] and the fits are shown as solid curves. The model allows multiple thicknesses within each film. Also allowed in the fitting are layer relaxations corresponding to slight deviations from the ideal bulk layer positions.[11–13] The relaxation parameters deduced from the fit are very small (no larger than 3% compression for the top surface layer, and smaller for the rest).

The fits also yield the layer occupancy, defined as the fractional surface area of the film covered by a particular layer thickness. These are shown in Fig. 3. From the sum of the fractional occupancies one can deduce the actual Ag coverage for each film. These actual coverage values, indicated in the figure, are very close to the nominal values. The dif-

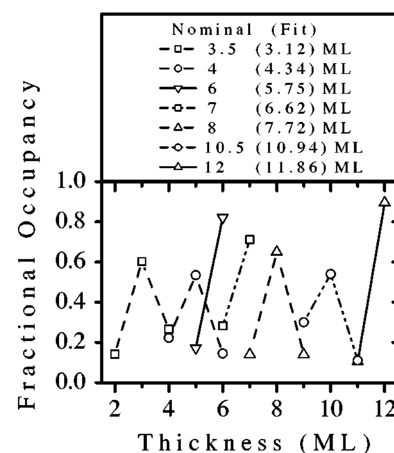

FIG. 3. Fractional layer thickness occupancies extracted from fits to the reflectivity data. The nominal coverages and the coverages deduced from the fit are indicated. The results associated with each film are connected by line segments for clarity.

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ferences mainly reflect the flux variations of the evaporator and errors associated with the thickness monitor reading. Figure 3 shows that the most uniform film is the one with a nominal coverage of 12 ML. Its structure is dominated by the intended thickness of 12 ML, with just 10% of the surface area covered by 11 ML. The film with a nominal coverage of 6 ML is also quite close to being single thickness.

Conceivably, there are many ways to prepare a film. In our experiment, the films with nominal coverages of 3.5, 4, 6, and 12 ML were prepared identically, namely, depositing onto a clean Ge surface and annealing to room temperature. This method, low temperature deposition on a clean substrate and anneal to room temperature, produced the best films. The 7 ML film was obtained by incremental deposition on the 6 ML film. It still consists of just two discrete thicknesses. However, on further deposition and annealing, the film roughness increased rapidly (results not shown). The 8 ML film was prepared by starting from a fresh Ge surface, but annealing to only 200 K. Subsequent deposition on this film and annealing to room temperature produced the 10.5 ML film. In both cases, the films consist of three discrete thicknesses. Annealing to higher temperatures has also been attempted, and the films invariably become rougher.

The present results show that nearly atomically uniform Ag films can be prepared on Ge(111). Based on the available data set, we can conclude that the best films are obtained by starting from a fresh substrate surface, depositing at low temperatures, and annealing to room temperature. Under our growth conditions, we observe no clear evidence for preferred or magic island heights or critical thicknesses. On substrates with large lattice mismatches, Ag films tend to grow along the (111) direction to minimize the surface energy, as in the present case. This suggests that epitaxial strain is a relatively minor issue. For Ag(111), the Fermi level is located within a relative gap, and thus its electronic character is somewhat like a semiconductor. This minimizes the effects of electronic Friedel oscillations, and thereby reduces the tendencies to form preferred, magic, and critical thicknesses.[5,8,9] In a sense, the Ag/Ge system represents a different paradigm. Both strain effects (generally important for semiconductor epitaxial systems) and electronic effects (generally important for metal-on-semiconductor systems) are relatively weak. This allows fairly smooth films to be prepared over a wide thickness range.

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[1] J.J. Paggel, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **81**, 5632 (1998); D.-A. Luh, T. Miller, J.J. Paggel, M.Y. Chou, and T.-C. Chiang, Science **292**, 1131 (2001).
[2] A.R. Smith, K.-J. Chao, Q. Niu, and C.K. Shih, Science **273**, 226 (1996); L. Huang, S. Jay Chey, and J.H. Weaver, Surf. Sci. **416**, L1101 (1998).
[3] L. Gavioli, K.R. Kimberlin, M.C. Tringides, J.F. Wendelken, and Z. Zhang, Phys. Rev. Lett. **82**, 129 (1999).
[4] K. Budde, E. Abram, V. Yeh, and M.C. Tringides, Phys. Rev. B **61**, R10602 (2000); V. Yeh, L. Berbil-Bautista, C.Z. Wang, K.M. Ho, and M.C. Tringides, Phys. Rev. Lett. **85**, 5158 (2000); M. Hupalo, S. Kremmer, V. Yeh, L. Berbil-Bautista, E. Abram, and M.C. Tringides, Surf. Sci. **493**, 526 (2001); M. Hupalo, V. Yeh, L. Berbil-Bautista, S. Kremmer, E. Abram, and M.C. Tringides, Phys. Rev. B **64**, 155307 (2001).
[5] H. Hong, C.-M. Wei, M.Y. Chou, Z. Wu, L. Basile, H. Chen, M. Holt, and T.-C. Chiang, Phys. Rev. Lett. **90**, 076104 (2003).
[6] A. Crotini, D. Cvetko, L. FLoreano, R. Gotter, A. Morgante, and F. Tomasini, Phys. Rev. Lett. **79**, 1527 (1997); L. Floreano, D. Cvetko, F. Bruno, G. Bavdek, A. Cossaro, R. Gotter, A. Verdini, and A. Morgante, Prog. Surf. Sci. **72**, 135 (2003).
[7] Z. Zhang, Q. Niu, and C.-K. Shih, Phys. Rev. Lett. **80**, 5381 (1998); Z. Suo and Z. Zhang, Phys. Rev. B **58**, 5116 (1998).
[8] C.M. Wei and M.Y. Chou, Phys. Rev. B **66**, 233408 (2002); **68**, 125406 (2003).
[9] P. Czoschke, H. Hong, L. Basile, and T.-C. Chiang, Phys. Rev. Lett. **91**, 226801 (2003).
[10] R. G. van Silfhout, J.F. van der Veen, C. Norris, and J.E. Macdonald, Faraday Discuss. Chem. Soc. **89**, 169 (1990).
[11] I.K. Robinson and D.J. Tweet, Rep. Prog. Phys. **55**, 599 (1992).
[12] R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989).
[13] J. Als-Nielsen and D. McMorrow, *Elements of Modern X-Ray Physics* (Wiley, New York, 2001).

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