

## Angle-resolved photoemission studies of epitaxial Ag films on Si(111)-(7×7)

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A 16-Å Ag film (about 7 atomic layers) grown epitaxially on Si(111)-(7×7) at about 100°C was studied by angle-resolved photoemission over a wide photon-energy range. Spectra taken of the well-ordered, smooth film showed sharp *d*-band peaks characteristic of single-crystal Ag(111), and a sharp peak derived from a surface state of Ag(111) in the band gap at point *L*. The bulk valence-band dispersions of Ag were reevaluated.

There has been considerable interest in the studies of thin films prepared by molecular-beam epitaxy (MBE).<sup>1</sup> Two related questions which often arise are whether or not these films have good crystalline order and what their electronic properties are. Due to the overlayer-substrate interactions and the reduced physical dimension of the overlayers in one direction the structure and properties of thin overlayers may be quite different from those of the corresponding bulk materials. Furthermore, MBE is usually performed at much lower temperatures than other surface-preparation procedures, e.g., conventional sputtering and annealing. So there are sometimes questions about the surface properties of MBE-grown materials.

The crystalline structure and electronic properties of thin films can be investigated with diffraction and angle-resolved photoemission measurements. In this paper, we report angle-resolved photoemission results for Ag films grown on a Si(111)-(7×7) substrate at about 100°C. Although there is a large lattice mismatch between Ag and Si (the lattice constants of Ag and Si are 4.09 and 5.43 Å, respectively), Ag deposited on Si(111)-(7×7) exhibits the (111) face with the [1 $\bar{1}$ 0] direction parallel to the Si [1 $\bar{1}$ 0] direction (parallel epitaxy) for coverages greater than a monolayer.<sup>2</sup> The growth mode is smooth layer by layer (Frank-van der Merwe mechanism) according to Auger-electron and electron-diffraction studies.<sup>2</sup> We find that for Ag-film thicknesses greater than a few monolayers, angle-resolved photoemission spectra are already very similar to those of bulk Ag. The surface state in the band gap at point *L* for the Ag(111) surface is observed on these films. The evolution of the spectra as a function of the thickness appears to be smooth and continuous. Below, we will present spectra obtained with a wide photon-energy range, i.e., 14–70 eV, for a 16-Å Ag film (corresponding to about 7 monolayers) on Si(111)-(7×7). We show that the energies of the electronic states, bulk and surface, of this thin Ag film are the same as those of single-crystal Ag(111), within experimental accuracy. These results also demonstrate that the film was well ordered and smooth despite its preparation at a relatively low temperature. The experimental bulk energy-band dispersion relations in the [111] direction will also be presented.

The experiment was done at the University of Wisconsin Synchrotron Radiation Center at Stoughton, Wisconsin. Synchrotron radiation from the 240-MeV storage ring, Tan-talus, was monochromatized with a 3-m toroidal-grating monochromator. The photoemitted electrons in the

sample-normal direction were analyzed with a hemispherical analyzer having an acceptance full angle of 3°. The photoemission geometry is shown in Fig. 1. The polished *n*-type Si(111) substrate was chemically stripped<sup>3</sup> immediately prior to insertion into the photoemission chamber. It was resistively heated to ~1250°C to obtain a contamination-free (7×7) surface, as determined by *in situ* Auger-electron and high-energy-electron-diffraction (HEED) measurements. The Ag was deposited from a small Ta boat, and the thickness was determined using a quartz thickness monitor. The epitaxially grown Ag films showed very sharp HEED patterns. In addition to the diffraction streaks corresponding to parallel epitaxy relative to the substrate described above,<sup>2</sup> most of the prepared films showed extremely weak (barely detectable) extra diffraction streaks corresponding to domains rotated by 30° about the surface normal. The average domain size was estimated to be at least 100 Å from the width of the diffraction streaks.

Angle-resolved normal-emission spectra for a 16-Å Ag film taken with photon energies  $h\nu=14-70$  eV are shown in Fig. 2. The binding energy scale is referred to the Fermi edge  $E_F$ . The overall instrument resolution is about 0.1 eV

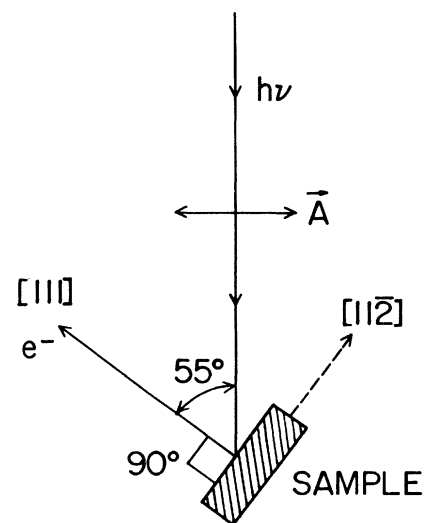


FIG. 1. Experimental geometry.  $h\nu$  denotes the incident photon beam; the polarization is indicated by  $\vec{A}$ . The photoelectrons leaving along the [111] surface normal were detected. The [112] direction of the Si substrate (and the Ag overlayer) is indicated.

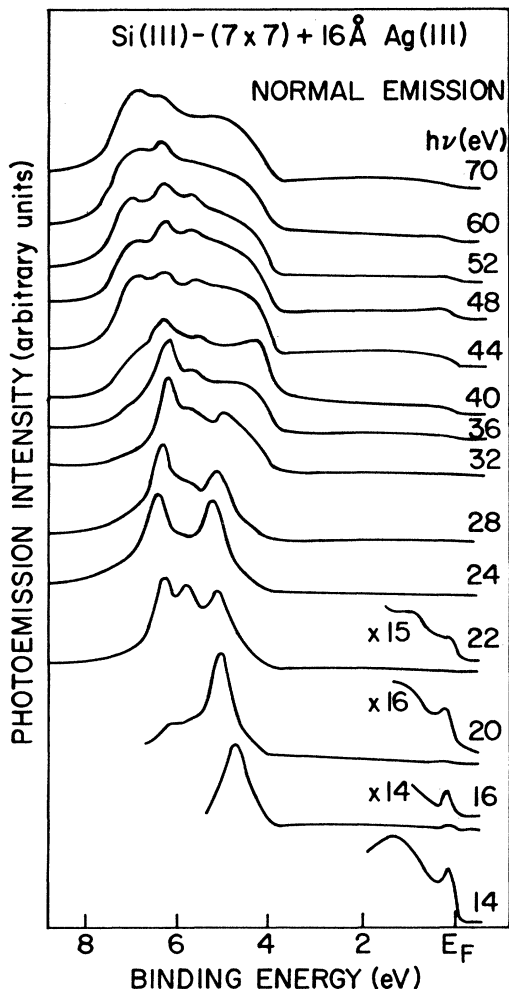


FIG. 2. Photoemission spectra for Si(111) + 16 Å Ag in the photon energy range  $h\nu=14-70$  eV obtained with a normal-emission geometry. The binding energy scale is referred to the Fermi edge  $E_F$ .

for  $h\nu=14$  eV, 0.2 eV for  $h\nu=44$  eV, and 0.3 eV for  $h\nu=70$  eV. The major spectral peaks in Fig. 2 are located at 4–8 eV below  $E_F$ ; they are derived from the Ag 4d bands. There is a very sharp peak located just below  $E_F$  for  $h\nu=14-22$  eV. It is derived from a surface state of Ag(111) in the band gap at point  $L$ , as reported previously by Roloff and Neddermyer<sup>4</sup> and Heimann, Neddermyer and Roloff<sup>4</sup> in their work on single-crystal Ag. There are a number of previous angle-resolved photoemission measurements of single-crystal Ag(111),<sup>5-8</sup> in particular, the work of Wehner *et al.* (Ref. 5) includes a set of normal-emission spectra for  $h\nu=6-32$  eV, which can be used for direct comparison with our spectra. In the region of overlapping photon energies, our spectra (Fig. 2) are quite similar to those reported in Ref. 5 in terms of the number of observed peaks, the peak positions, and even the relative peak intensities. For example, the three spectra with  $h\nu=20, 22,$  and  $24$  eV in Fig. 2 show one, three, and two outstanding peaks in the  $d$ -band region; this behavior is also noted in Ref. 5.

Upon careful examination, however, there are small discrepancies between our spectra and those in Ref. 5, giving rise to the question of whether the discrepancies are due

to the differences in samples (i.e., a thin film vs a single crystal) or due to experimental uncertainties. Although some of our peaks have the same binding energies as those in Ref. 5, the majority have greater binding energies, with the maximum disagreement being 0.25 eV at  $h\nu$  near 22 eV. However, the very high-resolution spectra of Roloff *et al.*<sup>4</sup> and Heimann *et al.*<sup>4</sup> for  $h\nu=16.85,$  and  $21.22$  eV are in agreement (within experimental accuracies) with ours when properly interpolated. A 0.25-eV discrepancy in binding energies between Refs. 4 and 5 at  $h\nu \approx 16$  and 22 eV was noted in Ref. 5, although no satisfactory explanation was given. We too have no satisfactory explanation for the disagreement in binding energies with Ref. 5, but since our results are in agreement with the very high resolution results in Ref. 4, we argue that our thin-film sample is indeed very much like a single-crystal sample, and the discrepancy is most likely not sample related. For  $h\nu=14-22$  eV, the surface state of Ag(111) near  $E_F$  can be seen in Fig. 2 with a measured width of 0.15 eV in agreement with Ref. 4.<sup>9</sup> The surface-state peaks in the spectra of Ref. 5 are not as pronounced, probably due to a somewhat larger instrument-resolution width. The small differences in

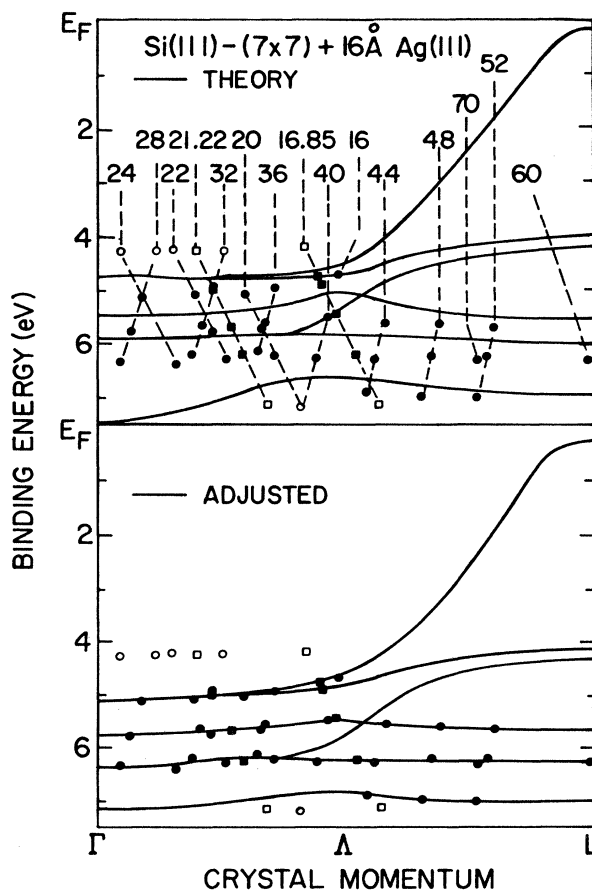


FIG. 3. Valence-band-dispersion relations of Ag along the [111] ( $\Gamma-A-L$ ) direction. Circles and squares are data points obtained from Si(111) + 16 Å Ag (present work) and single-crystal Ag(111) (Ref. 4), respectively. Solid and open symbols correspond, respectively, to strong peaks and weak shoulders in Fig. 2. The photon energies (in eV) are indicated using dashed lines. The solid curves in the upper panel are the theoretical curves of Christensen; they are adjusted to fit the experimental data shown in the lower panel.

the relative peak intensities between our spectra and those in Ref. 5 are probably related to differences in experimental geometry which are not fully specified in Ref. 5.

The bulk-transition peaks in Fig. 2 have been analyzed to provide the experimental bulk band dispersions along the [111] direction shown in Fig. 3, according to the three-step direct-transition model<sup>10</sup> and the procedure described in Ref. 5. For the final state, we extrapolated Christensen's calculated seventh band<sup>11</sup> to the Brillouin-zone boundary and extended it to higher energies with a free-electron-like dispersion relation having an inner potential of 6.34 eV.<sup>10</sup> The results for the Ag 4*d* bulk band dispersions are shown in the upper panel of Fig. 3 (circles) together with the data points obtained from Ref. 4 (squares); solid and open symbols represent strong peaks and weak shoulders, respectively. The photon energies (in eV) corresponding to the data points are indicated using dashed lines. The data points from weak shoulders (open symbols in Fig. 3) correspond to nondirect transitions, and their positions probably reflect points of high state densities (critical points),<sup>5</sup> since their positions do not fit into the known band structure. The solid curves in the upper panel of Fig. 3 are the theoretical results of Christensen.<sup>11</sup> To bring theory and experiment into agreement, we adjusted Christensen's curves. The results are shown in the lower panel of Fig. 3. The adjustment mainly involved shifting Christensen's curves to higher binding energies, typically by about 0.3 eV. The indirect-transition peaks at 4.25- and 7.25-eV binding energies were assumed to correspond to critical points at *L* and  $\Gamma$ , respectively. The band gap at point *L* between the up-

permost *sp* band and  $E_F$  was set to be 0.3 eV.<sup>12</sup> The curves in the lower panel of Fig. 3 can be considered as experimental band-dispersion relations. Note that the very high-resolution data from Ref. 4 (squares in Fig. 3) are in good agreement with ours, as mentioned above.

In summary, we have provided clear evidence that a 16-Å Ag film grown on Si(111)-(7×7) shows electronic states, bulk and surface, similar to those of single-crystal Ag(111). The electron escape depth under our experimental conditions is less than the film thickness; therefore the photoemission spectra are nearly the same as those of single-crystal Ag(111). Ag films of high quality can be grown on Si(111) at fairly moderate temperatures (about 100 °C in the present case), and the surfaces are smooth enough to support a very sharp surface state.<sup>13</sup> We have also reevaluated the bulk band-dispersion relations for Ag.

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<sup>1</sup>See, for example, L. L. Chang and R. Ludeke, in *Epitaxial Growth*, edited by J. W. Mathews (Academic, New York, 1975), Chap. 2, Sec. 2, pp. 37-72.

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