Photoemission study of Ag monolayer systems: Effects of the substrate

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(Received 10 September 1986)

Angle-resolved photoemission was used to study Ag(111) monolayers on six different substrates: Cu(111), Cu(001), Ni(111), Ni(001), Au(111), and Si(111)-(7×7). Overlayers that are incommensurate with the substrate (Ag on Cu(111), Ni(111), and Ni(001)) or commensurate with the substrate only over a large unit cell (Ag on Cu(001)) show electronic structures essentially independent of the substrate orientation and material, except for an overall shift in binding energy. The overlay electronic structure is somewhat different for the Ag/Au(111) system, where there is a nearly perfect overlay-substrate lattice match as well as substantial overlap in energy bands of like characters. In the Ag/Si system, partially disordered overlay growth and strongly corrugated substrate surface structure cause the overlay features in the spectra to broaden substantially.

The extent to which substrates affect the electronic properties of thin overlayer films is still not well known. Recent theoretical calculations for some metal overlayers indicate that the two-dimensional band dispersions are, in general, modified substantially from those of correspondingly unoccupied monolayers by the substrate-overlayer interaction (although an earlier calculation indicated otherwise). The subject is of fundamental interest as well as of practical importance. For example, there exists the possibility of modifying the properties of catalytic materials by choosing different substrates. Here we report an investigation of the electronic properties of Ag monolayers on six different substrates: Cu(111), Cu(001), Ni(111), Ni(001), Au(111), and Si(111)-(7×7). In all of these systems, the overlayer structure is very close to the hexagonal close-packed Ag(111) structure despite the wide variety of substrate materials and faces represented. There are numerous differences among the six systems, for example, three epitaxial relationships are observed: incommensurate, commensurate, and lattice matched. Four different substrate materials are utilized, one of which is a semiconductor. Thus, the results can provide a useful data basis for identifying empirically the relevant factors that may affect the overlayer electronic structure in these and other systems.

The experiment was performed at the Synchrotron Radiation Center of the University of Wisconsin—Madison. Synchrotron radiation dispersed with a Seya-Namioka monochromator (for the Ni, Au, and Si substrate systems) or with a Mark V Grasshopper (for the Cu substrate systems), was used as the light source. Angle-resolved photoemission spectra were measured using a hemispherical analyzer with full angular acceptance of 3° in a normal-emission geometry; a cylindrical-mirror analyzer with a wide acceptance cone was used for the angle-integrated measurements. The Si(111)-(7×7) substrate preparation has been described elsewhere. The Ni and Cu substrates were prepared by sputtering and annealing. The Au(111) substrate was prepared in the following manner: first, a Ag(111) single-crystal substrate was prepared by sputtering and annealing; then a thick layer of Ag was epitaxially grown on the substrate to smooth out residual roughness; finally, a thick layer of Au was grown on top of the Ag. Ag overlayers were deposited at room temperature on each of the substrates by evaporation at typical rates of 0.05–0.10 Å/s as determined with a quartz thickness monitor. After evaporation, both Ag/Cu samples were briefly annealed at 200°C; the Ag/Ni(111) and Ag/Ni(001) samples were briefly annealed at 300°C and 450°C, respectively. No annealing of the Si and Au samples was performed after the Ag overlayers were deposited to avoid intermixing and/or changes in morphology. All the substrates and overlayer systems were characterized by Auger spectroscopy, photoemission, and high-energy electron diffraction (HEED) to ensure cleanliness and surface quality and to determine or verify the growth behavior.

There are differences in the growth of Ag on the six different substrates. Unstrained Ag(111) grows on Ni(111) in parallel epitaxy, that is, Ag[110]||Ni[110], etc., while Ag(111) grows on Ni(001) in large domains in two orthogonal orientations: Ag[110]||Ni[110] or Ag[110]||Ni[100] with about equal populations due to the fourfold symmetry of the substrate. The growth of Ag(111) on Cu(111), in parallel epitaxy, is very similar to that observed for Ag/Ni(111). In these three systems, large flat monolayer-thick Ag(111) islands are formed at coverages below a monolayer. Consequently, the photoemission intensities of Ag-derived features are proportional to coverage without changes in spectral shapes. Close to and beyond one-monolayer coverages, extra features associated with Ag atoms in the second layer appear in our photoemission spectra. To avoid this undesirable situation, the Ag/Ni(111), Ag/Ni(001), and Ag/Cu(111) data reported here for 1.2 Å (1/2-monolayer) equivalent Ag coverage. The structure of Ag on Cu(001) at one monolayer coverage is c(10×2) in two orthogonal domain orientations; this structure can be described as a Ag(111) monolayer slightly strained to conform to the substrate lattice without a significant change in the areal atomic density. The Ag/Cu(001) data presented here are for a Ag cover-
age of 2.4 Å (one monolayer). The growth of Ag on Au(111) represents a different situation: Ag and Au are lattice matched. Since the overlayer grows in a smooth layer-by-layer fashion in parallel epitaxy, we are able to show data from a complete monolayer (2.4 Å) of Ag(111)/Au(111).\textsuperscript{6,7} Also presented are data for 1.8 Å (about \frac{1}{2}-monolayer) equivalent Ag coverage on a Si(111)-(7×7) substrate. At this Ag coverage, HEED studies show a Ag(111) pattern superimposed upon a Si(111)-(1×1) pattern in a parallel-epitaxy configuration. It has been determined from previous studies that Ag grows on Si(111) in a nearly layer-by-layer fashion, but the overlayer is not as well ordered and smooth as compared with the other systems described above.\textsuperscript{3,9}

Figure 1 shows normal-emission spectra taken from the six overlayer systems described above using p-polarized light with a fixed photon energy of h\nu=22 eV. Similar spectra were also taken from the six substrates without the Ag overlayers present to aid in identifying the Ag-derived features, which are marked with vertical bars in Fig. 1. The remaining features are identified as being substrate related or as surface states, which are observed near the Fermi edge in the Ag/Cu(111) and Ag/Au(111) spectra.\textsuperscript{5–7} We have many more spectra taken off normal and with other photon energies; these will be published in a more complete forthcoming paper.

Six difference spectra, generated by subtracting the spectra from each bare substrate from that of the same substrate covered with Ag, are displayed in Fig. 2 to aid identification of the overlayer-related features. Due to inelastic scattering and diffraction processes, the substrate signal is attenuated by the overlayer. Because the degree of attenuation depends on the photoelectron kinetic energy and is not known precisely, the two spectra used to generate each of these “difference spectra” were normalized (independent of energy) by inspection before subtraction. As a result, some of the substrate signal still appears in these difference spectra at some energies, although at a greatly reduced intensity; in a few locations there are “dips” from excessive substrate signal subtraction. Some unusual features just below the Fermi edge in the Ag/Au(111) and Ag/Cu(111) difference spectra are the result of a known shift in the position of the surface state binding energy as the Ag coverage changes.\textsuperscript{5–7}

Except for the case of Ag on Si(111), all spectra in Figs. 1 and 2 show certain similarities, as suggested by the dashed curves. The two-dimensional band dispersions of Ag(111) monolayers on Ni(111) and Ni(001) are actually identical within experimental uncertainties.\textsuperscript{4} In the normal-emission spectra shown in Figs. 1 and 2, four Ag peaks are observed in the case of Ag/Ni(111) and three for Ag/Ni(001): in off-normal spectra (not shown), six distinct bands can be identified, corresponding to five d bands and one sp band of Ag. Some of the indicated Ag peak positions shown in Figs. 1 and 2 are confirmed by extrapolating the off-normal data. The peak positions can be uncertain by about ±0.1 to 0.2 eV for peaks not well resolved. Two close “split” peaks at 4.37 and 4.60 eV in the Ag/Ni(111) spectra are not separately resolved in the case of Ag/Ni(001), where only the intensity-weighted

**FIG. 1.** Normal-emission spectra from six Ag overlayer systems taken with a photon energy h\nu=22 eV. The substrate face and overlayer coverage are indicated. Features which are due to the presence of the Ag overlayers are marked with vertical bars. The binding energies are referred to the Fermi level E_F.

**FIG. 2.** Six difference spectra for the system displayed in Fig. 1. These spectra were generated by subtracting the normal-emission spectra of each bare substrate from that of the same substrate covered with Ag. Features which are due to the presence of the Ag overlayers are marked with vertical bars.
average peak position is determined. The Ag peak with a binding energy of 5.97 eV observed for the Ag/Ni(111) system does not appear in normal-emission spectra from Ag/Ni(001), but a band near this energy is seen in spectra taken slightly off normal. One feature, with a binding energy of 2.97 eV, is only clearly observed in the Ag/Ni(001) spectra; the band associated with this peak is known to have mainly d character in normal emission and sp character off normal. This peak is probably also present in the Ag/Ni(111) case, but the intensity is too weak for a positive assignment.

When we compare just the two copper substrate systems in Fig. 2, most of the Ag features are again situated at approximately the same binding energies. One feature located at about 4.20 eV and observed in our data as well as data taken by Tobin, Robey, and Shirley is only present for the c(10×2)Ag/Cu(001) system; we believe that that feature is derived from an indirect transition associated with a band seen in off-normal spectra. There is excellent agreement of both the positions and relative intensities of the remaining Ag features in these two systems. Once again we see two “split” peaks, but here the splitting is slightly larger: about 0.30 eV, whereas a 0.23-eV splitting is observed for Ag/Ni(111). Tobin et al. suggest that these features are related to a band that has basis functions composed of Y(l = 2, m = ±1) spherical harmonics which are spin-orbit split in normal-emission spectra; the assignments of the states are based upon polarization dependence of the Ag bands as observed in photoemission spectra.

A comparison of both normal-emission and off-normal spectra taken from Ag overlayers on the two different substrate materials, Ni and Cu, shows that the locations of the features agree quite well if all of the features from the two Ag/Ni systems are displaced by 0.32 eV away from the Fermi edge. Apparently the energy shift is much more dependent on the substrate material than on the substrate surface configuration (or face). This shift can be related to the difference in binding energies of Ag on the Ni and Cu substrates. The relative intensities of the peaks in these two systems are also roughly the same, except for the indirect-transition feature observed in Ag/Cu(001).

Normal-emission spectra taken from the lattice-matched overlayer system Ag/Au(111) are also displayed in Figs. 1 and 2. Two of the features, with binding energies of 5.09 and 4.52 eV, are clearly due to the presence of the Ag overlayer since there are no prominent features observed at these energies in spectra taken from the uncovered Au sample. The source of the feature with a binding energy of 6.09 eV is not as easily determined; thus, it is marked with a question mark. Both Ag and Au have bands located close to the position of the observed feature and the source of this peak cannot be easily determined by a simple subtraction of our spectra. To aid identification of this “unknown” feature, angle-resolved spectra (not shown) were also taken at a photon energy of 32 eV at Ag coverages of 0, 1/4, and 2 monolayers both in a normal-emission geometry and off normal in two different mirror planes. As the thickness of the Ag overlayer on the Au substrate is increased, the feature remains quite intense and shifts slightly in energy when observed in normal emission. In off-normal scans, the shift between the Au feature and the “unknown” feature (observed at 4/Ag monolayer Ag coverage) becomes as large as 0.2 eV. As a result, it appears that this feature is at least partially derived from the Ag overlayer. The remaining peaks are rapidly attenuated with increasing Ag overlayer thickness and, therefore, are definitely substrate related.

Based on the overall similarities of these systems, it seems likely that the two Ag/Au(111) features, at 4.52 and 5.09 eV, correspond to the two “split” Ag overlayer bands located nearby in the Ag/Cu systems. This would imply a substantially larger splitting for Ag/Au(111) of about 0.57 eV in contrast to the splittings of 0.30 and 0.23 eV for the Ag/Cu and Ag/Ni systems. The feature at 6.09 eV for the Ag/Au system, as explained above, has partial contribution from the Ag overlayer. Since the Ag contribution is essentially at the same energy as the substrate contribution, it is plausible that the Ag contribution corresponds to a surface resonance rather than a twodimensional state localized within the overlayer. This interpretation is supported by a recent calculation of the electronic properties of lattice-matched Ag/Rh systems.

The top spectrum in Fig. 1, from Ag/Si(111), has a very different appearance. The broad peaks are clearly due to the Ag overlayer since Si(111) has no similar features with this intensity near these energies. The HEED patterns of this system are not as sharp as those for the other systems, and it is known that the growth is not exactly layer by layer. If the overlayer grows in small islands, the crystal momentum can be smeared out, leading to a broadening of overlayer features. A similar broadening should be observed in angle-integrated photoemission spectra, where electrons are simultaneously collected from initial states with many different crystal momenta. If the above explanation is correct, the Ag/Si normal-emission spectra should show some resemblance to angle-integrated photoemission spectra taken from Ag monolayers. To test this idea, we show angle-integrated and normal-emission spectra from Ag/Ni(111) together with the Ag/Si(111) normal-emission spectra in Fig. 3. As expected, the Ag features in the angle-integrated spectrum for Ag/Ni(111) are somewhat broader than the corresponding normal-emission features and they appear closer in energy to the Ag/Si(111) normal-emission features; however, the effect of angle averaging is still not sufficient to explain the severe broadening seen in the case of Ag/Si(111). Perhaps the complicated Si(111)-(7×7) surface has a greater diversity of Ag bonding sites when compared to the other systems. It is known from scanning tunneling microscopy work that the Si(111)-(7×7) surface has protrusions and deep holes in the unit cell. This could lead to more extreme broadening as a result of a larger variation in the crystal potential, as seen by the Ag overlayer.

To conclude, we have studied the growth and electronic properties of Ag monolayers on six different substrates: Ni(111), Ni(001), Cu(111), Cu(001), Au(111), and Si(111)-(7×7). On the Cu(111), Ni(001), and Ni(111) substrates, where Ag does not grow in a commensurate fashion, the overlayer electronic properties are very similar despite the large differences in the electronic and atomic structures of the substrates. Apparently, the differences in
crystalline and amorphous materials, for which the density of states are similar despite the large differences in symmetry. The \( (10 \times 2) \mathrm{Ag/Cu(001)} \) system, although commensurate, has a large surface unit cell. The limit of the very large unit cell is equivalent to incommensuration. Thus, it is perhaps not surprising that the \( \mathrm{Ag/Cu(001)} \) system behaves similarly, except for the indirect-transition feature which may be related to the ordered structure. An overall shift of 0.32 eV in binding energy is observed between the \( \mathrm{Ag/Ni} \) and \( \mathrm{Ag/Cu} \), regardless of which of the two substrate faces is used. In the case of \( \mathrm{Ag(111)/Au(111)} \), the overlayer grows in a lattice-matched fashion and has electronic features with a somewhat different appearance. The causes of the difference are likely the commensuration of the crystal potential as well as the near-exact overlap of energy bands of like characters leading to the formation of surface resonances. The growth of \( \mathrm{Ag on Si(111)-(7 \times 7)} \) is not as well ordered as in the other systems. A severe broadening of the overlayer features is observed. Momentum broadening within the surface plane appears to be insufficient to explain the observed features. Large variations in the potential due to the intrinsic corrugation of the substrate surface is likely the source of the severe broadening.

This material is based upon work supported by the National Science Foundation under Contract No. DMR-831121. Some of the equipment used for this research was obtained with grants from the National Science Foundation (Grant No. DMR-8352083), the IBM Research Center (Yorktown Heights), and the Central Research Department of the E.I. du Pont de Nemours and Company. The Synchrotron Radiation Center of the University of Wisconsin—Madison is supported by the National Science Foundation under Contract No. DMR-8020164. We acknowledge the use of central facilities of the Materials Research Laboratory of the University of Illinois, which is supported by the Department of Energy, Division of Materials Sciences, under Contract No. DE-AC02-76ER01198, and the National Science Foundation under Contract No. DMR-8020250.

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