

Ag/Cu(001): Observation of the development of the electronic structure in metal overlayers from two to three dimensionality

J. G. Tobin, S. W. Robey, L. E. Klebanoff, and D. A. Shirley

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
and Departments of Chemistry and Physics, University of California, Berkeley, California 94720

(Received 29 August 1983)

Angle-resolved photoemission was used to investigate the valence-band structure of the metal overlayer system $c(10 \times 2)\text{Ag}/\text{Cu}(001)$. At 1–2-monolayer coverages, the Ag adlayer exhibited d -band spectral behavior characteristic of two-dimensional dispersion. Evaporation of progressively more Ag onto the substrate produced a series of surfaces which by 3–5-monolayer exposures were converging toward a three-dimensional valence electronic structure characteristic of a bulk, Ag(111)-like system.

Metallic overlayer and thin slab systems have been the subject of several recent theoretical^{1–4} and experimental^{5–7} investigations. In this Communication we report the first complete angle-resolved photoemission (ARP) study of a metal overlayer system, Ag/Cu(001). Using polarized radiation to excite the photoelectrons, more than two-hundred overlayer valence-band spectra were collected and successfully interpreted within the direct transition model. The Ag valence d -band electronic structure was found to exhibit two-dimensional (2D) dispersive behavior at low coverages, changing into three-dimensional (3D) bulk dispersion at higher exposures of 3–5 monolayers.

Silver d -band dispersion was studied in the overlayer system Ag/Cu(001), which was prepared by evaporation of the silver onto a copper single crystal under ultrahigh vacuum conditions. The silver deposition was monitored by a quartz microbalance together with an Auger electron spectroscopy (AES)–low-energy-electron diffraction (LEED) calibration. Earlier work on this system had demonstrated⁸ an ordered hexagonal single-layer structure at one-monolayer exposure. This was described as a $c(10 \times 2)\text{Ag}/\text{Cu}(001)$ structure, in which silver atoms are arranged in a slightly strained hexagonal array. Figure 1 shows a model of the real-space hexagonal structure and also the two-dimensional surface Brillouin zones. In our experiments, a discontinuity in the slope of the overlayer-substrate Auger derivative intensity ratio was observed at one-monolayer exposure, as expected for layer-by-layer growth.⁹ The ordered $c(10 \times 2)$ LEED spots appeared at slightly higher silver exposures, confirming the calibration for one monolayer. At higher silver exposures, the overlayer thickness was monitored by the quartz crystal microbalance, the AES ratios, and the photoemission Ag/Cu d -band ratios, all of which gave generally consistent results. The silver exposures will be quoted in units of monolayers (ML) of silver. They are typically accurate to within $\pm 20\%$ or less.

Angle-resolved photoemission can be used to determine the energy and crystal momentum of the valence electronic states. The energies are referenced to the Fermi edge. The crystal momentum parallel to the ordered surface, $\vec{k}_{\parallel}$, is conserved in the direct transition model both during photoexcitation and as the photoelectron traverses the surface. We can therefore write

$$\vec{k}'_{\parallel} = \vec{k}_{\parallel} = \vec{q}_{\parallel} = \vec{q} \sin \theta_e. \quad (1)$$

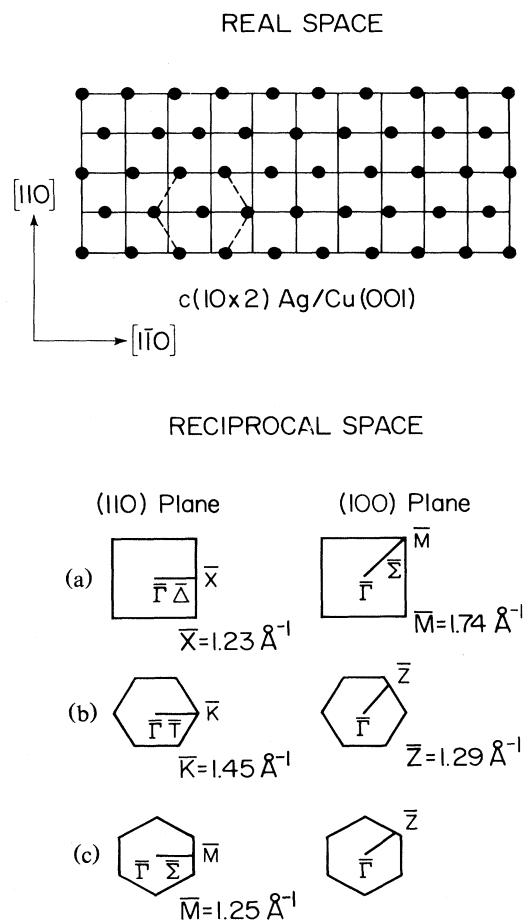


FIG. 1. Depiction of one of the two orthogonal domains of $c(10 \times 2)\text{Ag}/\text{Cu}(001)$ in real space. The Ag atoms are shown as filled circles and the Cu(001) surface lattice as squares. The actual registry with the substrate is unknown. The surface Brillouin zones of Cu(001) and both undistorted hexagonal Ag domains as well as the paths across each zone taken when rotating off normal in the Cu(001) planes (110) and (100) are shown. Only the domain associated with (c) was observed with LEED. This is tentatively explained as being due to crystal face tilt. Regardless, it will not affect the photoemission results.

This relation is valid in the absence of parallel umklapp processes, which should not be present for near-normal, low-energy photoemission. Here $\vec{k}_{\parallel}$ is the crystal momentum and $\vec{q}_{\parallel}$ is the external momentum of the photoelectron, parallel to the surface. The external polar angle of emission relative to the surface normal is denoted by θ_e .

An off-normal ARP study of the silver overlayer system at low coverages was performed with the use of polarized radiation from laboratory HeI (21.2 eV) and NeI (16.8 eV) sources. The two-dimensional valence-band structure of the silver overlayer, derived from the off-normal study, is shown in Fig. 2. The polarization dependence and the $\vec{k}_{\parallel}$ dispersion of the states were found to agree for the two photon energies (different sets of $\vec{k}_{\perp}$). The findings that B^F is independent of $\vec{k}_{\perp}$ and that the bands disperse with $\vec{k}_{\parallel}$ provide conclusive evidence for a two-dimensional electronic band structure in the silver overlayers near one-monolayer coverage on Cu(001).

To provide an independent confirmation of the assignment of the features to the silver valence states, a polarization dependence-group theoretical analysis was performed. The observed behavior follows C_{6v} single-group selection rules, as would be expected for a hexagonal overlayer. Figure 2 shows the assignment of the states at $\bar{\Gamma}$, the surface Brillouin zone center, where atomic effects should dominate. Future publications will include a detailed explanation of the analysis.

A normal-emission study was performed at the Stanford Synchrotron Radiation Laboratory. Since $\vec{k} = \vec{k}_{\perp}$ at normal emission, this was a direct probe of any energy dependence of the overlayer valence bands upon $\vec{k}_{\perp}$. In particular, the effect of increasing the silver exposure was explored. Valence-band spectra were collected over the photon energy range 6–32 eV on samples of $\frac{1}{2}$, 1, 2, 3, 4 and 5 monolayers of Ag/Cu(001), as well as on clean Cu(001).

The determination of $\vec{k}_{\perp}$ from $\vec{q}_{\perp}$ is usually rather involved. Even if the overlayer has sufficient periodicity in the perpendicular direction to ensure crystal momentum conservation in the photoexcitation process, some knowledge of the inner potential and the final-state band

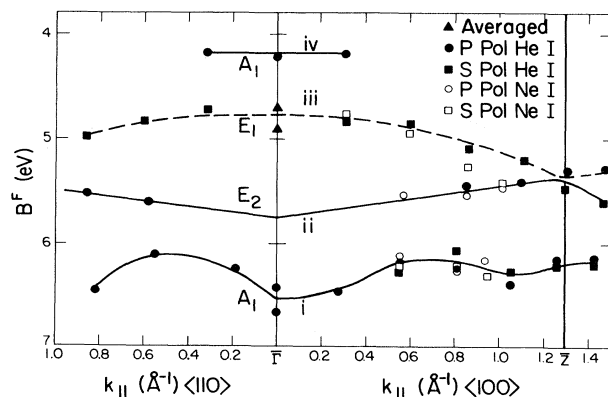


FIG. 2. Map of the binding energy (B^F) with respect to the Fermi level (E_F) vs the parallel component of the momentum ($k_{\parallel}$), for the silver states observed at near-monolayer coverages. The triangles at B^F near 4.8 eV at $\bar{\Gamma}$ are the averaged values of the spin-orbit split peaks observed with s - and p -polarized He I and Ne I radiation.

structure is required. While no detailed information exists for $c(10 \times 2)\text{Ag}/\text{Cu}(001)$, normal photoemission in Ag(111) proceeds via a single, particularly simple and well-understood free-electron-like final state in this energy range.^{10,11} Thus it is meaningful to compare the photon energy dependences of the binding energies (B^F) of the Ag $4d$ -derived peaks in the silver overlayer systems with those of Ag(111), if both are studied at normal emission. In one limit, the peaks in Ag(111) will disperse with photon energy, while in the other limit a true two-dimensional system should produce only flat bands, since $\vec{k}_{\parallel}$ is invariantly zero.

As predicted above, at 1 and 2 monolayer exposures the

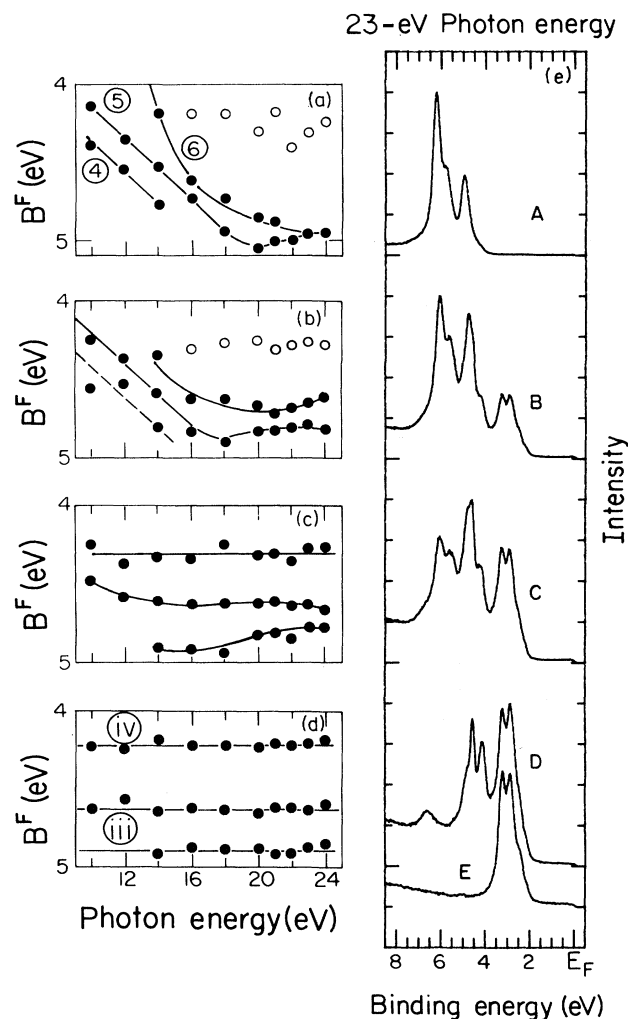


FIG. 3. Mapping of the binding energies (B^F) of the silver features vs photon energy for (a) Ag(111), (b) 5 ML, (c) 4 ML, and (d) 2 ML of $c(10 \times 2)\text{Ag}/\text{Cu}(001)$. The band iii states ($B^F > 4.5$ eV) at 2 ML become bands 4, 5, and 6 in Ag(111). The weak leading shoulder in Ag(111) at B^F near 4.2 eV is shown with open circles and is due to band iv. (e) Normal-emission spectra collected with $h\nu = 23$ eV and 100 meV total resolution full width at half maximum, for curve A Ag(111), curve B 5 ML of $c(10 \times 2)\text{Ag}/\text{Cu}(001)$, curve C 4 ML, curve D 2 ML, and curve E clean Cu(001). All observable peaks are due to the silver valence bands except the doublet of peaks at $B^F < 4$ eV, which originates from copper.

bands are indeed flat and consistent with C_{6v}/C_{3v} selection rules, showing no three-dimensional behavior. At three monolayers, two new bands appear: This is attributed to the presence of the octahedral center layer in a three-monolayer slab. At four monolayers and above, dispersion is evident in the B^F values of the silver features and the bands appear rather similar to those of Ag(111). This is illustrated in Fig. 3, which shows a partial comparison of the band structure at 2, 4, and 5 ML of $c(10 \times 2)$ Ag/Cu(001) with Ag(111).¹² More generally, the spectra of the silver overlayers at higher exposures are becoming visually very similar to those of Ag(111), as is evident in Fig. 3. Note especially the change in the feature at $B^F = 4.2$ eV: At 2 ML it is a well-defined peak while at higher exposures it becomes the weak shoulder observed in Ag(111). Moreover, several features characteristic of Ag(111) (Refs. 10 and 11) were found in the silver overlayer spectra, particularly at exposures of 4 and 5 ML:

(1) A "22-eV" resonance in d -band intensity in Ag(111) has been interpreted as originating near Γ , the center of the three-dimensional Brillouin zone. In this resonance, a sharp increase in valence-band intensity is observed in the $h\nu = 21$ –23-eV range, where the photon energy matches successively the energy separation between each initial state d band and band 7. It is evident in the 5-ML spectrum of Fig. 3 as an enhancement in the intensity of the highest- B^F peak, near 6 eV. In more detailed studies, the profiles of the resonance in the 4- and 5-ML $c(10 \times 2)$ Ag samples were mapped and found similar to that of Ag(111).

(2) The constant kinetic energy feature at 17 eV above the Fermi level also arises from the flat region of band 7 near Γ . Higher-energy electrons scatter into band 7, producing a constant kinetic energy peak that appears to move

across the spectra collected at photon energies of 26–32 eV.

(3) The normal-emission surface state is observed in Ag(111) at $h\nu = 6$ –12 eV and in the $c(10 \times 2)$ Ag/Cu(001) over the same energy range and at the same binding energy. However, the overlayer state is much broader and asymmetric. The presence of the state indicates Ag(111)-like electronic structure. Its width and asymmetry may indicate sp electronic interaction with the substrate Cu(001).^{3,4}

In summary, within the framework of an evaporated metal overlayer system, we have documented the effect upon the overlayer electronic structure of varying the thickness of the overlayer. It has been shown that at coverages of 1–2 monolayers the ordered Ag overlayer d bands show two-dimensional dispersion in the surface plane and no dispersion in the perpendicular direction. As the exposure is increased, the spectral behavior of the overlayer becomes very similar to that of Ag(111). Thus the development of the valence-band structure of a metal overlayer system from two to three dimensionality has been demonstrated for the first time.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. It was performed in part at the Stanford Synchrotron Radiation Laboratory, which is supported by the NSF through the Division of Materials Research. One of us (J.G.T.) acknowledges support by the NSF. Discussions with M. G. Mason were enlightening and greatly appreciated.

¹P. D. Loly and J. B. Pendry, J. Phys. C **16**, 423 (1983).

²J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. B **25**, 643 (1982).

³D.-S. Wang, A. J. Freeman, and H. Krakauer, Phys. Rev. B **26**, 1340 (1982).

⁴J. Tersoff and L. M. Falicov, Phys. Rev. B **25**, 2959 (1982).

⁵R. Miranda, F. Yndurain, D. Chandesris, J. Lecante, and Y. Petroff, Phys. Rev. B **25**, 527 (1982); Surf. Sci. **117**, 319 (1982).

⁶G. C. Smith, C. Norris, C. Binns, and H. A. Padmore, J. Phys. C **15**, 6481 (1982).

⁷M. El-Batanouny, D. R. Hamann, S. R. Chubb, and J. W. Davenport, Phys. Rev. B **27**, 2575 (1983); M. El-Batanouny, M. Stron-

gin, and G. P. Williams, *ibid.* **27**, 4580 (1983).

⁸P. W. Palmberg and T. N. Rhodin, J. Chem. Phys. **49**, 134, 147 (1968); J. Appl. Phys. **39**, 2425 (1968).

⁹D. C. Jackson, T. E. Gallon, and A. Chambers, Surf. Sci. **36**, 381 (1973).

¹⁰P. S. Wehner, R. S. Williams, S. D. Kevan, D. Denley, and D. A. Shirley, Phys. Rev. B **19**, 6164 (1979).

¹¹N. E. Christensen, Phys. Status Solidi (b) **54**, 551 (1972).

¹²J. G. Tobin, S. W. Robey, D. A. Shirley, W. J. Gignac, J. G. Nelson, and R. S. Williams, Lawrence Berkeley Laboratory Report No. LBL-15135 (unpublished).