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Surface resonances and reduced symmetry in the heteroepitaxial Ag/Cu(110) system

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Submonolayer coverages (~0.65 ML) of Ag vapor deposited on Cu(110) are studied using synchrotron-based photoelectron spectroscopy and scanning tunneling microscopy (STM). Induced surface resonances, or modified bulk states, have been observed that are derived from Cu bulk bands of Σ_3 and Σ_4 character. These resonances are observed in photoemission geometries that forbid their detection assuming they have the symmetry character of the states from which they are derived. Based on this and the surface morphology as determined by STM, the symmetry of the surface is found to be sufficiently reduced, allowing for hybridization between the Ag *sp* and Cu *d* bands. This hybridization is the origin for the modification of the Cu bands near the surface, and the reduction in symmetry allows for the observation of these resonances regardless of the photoemission geometry.

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The field of metal-on-metal ultrathin films has proven to be an interesting and fruitful endeavor for both basic and applied scientific studies, due to the interesting physical and chemical properties of epitaxial systems. Many of these unique properties arise due to the low-dimensional character of thin films, and the fact that, in many cases, no bulk analogs exist in nature.[1–6] Variations in growth modes often result in interesting geometric structures on and sometimes within the surface layer. For example, the process of surface alloying and dealloying often occurs even for heteroepitaxial metal-on-metal systems that are immiscible in the bulk.[7] The resultant electronic structure of these metal-on-metal thin film nanostructures determines, e.g., their catalytic or magnetic properties.

Motivated by this, we have studied the atomic and electronic heteroepitaxial structure of the Ag on Cu(110) system at submonolayer coverages. From photoemission data, it is determined that *surface resonances*, or modified bulk states, of Cu exist in this system due to the presence of Ag atoms within and on the surface. Moreover, due to the reduced symmetry of the Ag-Cu-grown nanostructure, as revealed by scanning tunneling microscopy (STM) results, these resonances have reduced symmetry from the bulk states from which they were derived. This heteroepitaxial Ag/Cu system provides us with a model system to further explore the fundamental properties of surface alloying and dealloying in bulk immiscible metal-on-metal systems through the correlation of surface morphology with resultant electronic structure.

In this Brief Report we focus primarily on the existence and character of the surface electronic resonances that result from deposition of submonolayer concentrations of Ag on Cu(110), as seen using photoelectron spectroscopy. In combination with STM data, we will show that the unique nanostructure of this surface has a sufficiently reduced symmetry, thereby allowing for the observation of Cu-derived resonances otherwise forbidden by dipole selection rules. The proposed origin of these surface resonance states stems from a surface-localized hybridization between the Cu *d* bands and the Ag *sp* state.

This combined atomic and electronic structural study employed both synchrotron-based angle-resolved photoelectron spectroscopy (ARPES) and STM. The ARPES data were collected using a home-built hemispherical electron energy analyzer[8] and the Plane Grating Monochromator beamline at the Center for Advanced Microstructures and Devices, a 1.3-GeV electron storage ring.[9] Facilitating linearly polarized light and applying nonrelativistic symmetry selection rules enabled a determination of initial-state symmetries that depend on the photoemission geometry. The following two photoemission geometries were used: one in which the vector potential **A** was perpendicular to the Cu(110) $[001]$ direction (allowing initial states of Σ_1 and Σ_4 character of the C_{2v} symmetry group), and another in which the vector potential was perpendicular to the $[1\bar{1}0]$ direction (allowing initial states of Σ_1 and Σ_3 character).[10] In both cases the incident light was *p* polarized with an angle of 45° to the surface normal, and data were collected in normal emission geometry. The Ag was vapor deposited from a resistively heated W crucible onto a Cu(110)-oriented crystal, prepared by standard cycles of sputtering (Ne^+, 1 keV, 5 μA) and annealing (825 K). The STM measurements were made at the University of Aarhus, using a home-built variable temperature STM. The STM is very compact, with high resonance frequencies, and atomic resolution can be obtained on a routine basis in the sample temperature range from 150 to 320 K. The details of this variable temperature STM were described elsewhere.[2,11]

In order to interpret the electronic data properly, STM studies were performed to determine the atomic-scale structure of the heteroepitaxial Ag-Cu nanostructure. Briefly, the STM results reveal that in the low coverage regime ($0 < \theta_{\mathrm{Ag}} < 0.4$ ML), the growth of Ag on Cu(110) results in the formation of a surface confined, substitutional alloy phase.

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Driven by the compressive strain in this phase (13% lattice mismatch), further Ag deposition leads to the formation of dealloyed zigzag chains of Ag dimers and trimers ($0.4 < \theta_{\mathrm{Ag}} < 0.6$ ML), where the Ag-Cu surface alloy remains between the chains [Fig. 1(a)].[7] A schematic of the dimer-trimer model is depicted in Fig. 1. As the Ag coverage is increased further ($0.6 < \theta_{\mathrm{Ag}} < 0.9$ ML), the dimer-trimer chains coalesce to form the broader striped structure seen in Fig. 1(b). It is in this coverage regime that the ARPES discussion is concerned. The coalescence of the one-dimensional Ag chain structure with increasing coverage eventually results in a hexagonal Ag overlayer, which has a two-dimensional structure nearly equivalent to a hexagonal close-packed Ag(111) surface. The structural details of this striped Ag dimer-trimer phase[7] closely parallel those observed in the Au/Ni(110) system.[12] In both cases, this latter growth phase is a vacancy-stabilized chain structure, wherein the adatom metal chains (dimer-trimers) are positioned in slightly incommensurate positions (rather than in the twofold hollow sites), and are stabilized energetically by the formation of monovacancies and divacancies beneath dimers and trimers, respectively. The facts that the adatoms are not in the anticipated twofold hollow sites, and that vacancies are present beneath the Ag chains, suggest that the potential ''felt'' by the Cu atoms at the interface is drastically different from that of the native surface. Although structurally similar, STM results do reveal differences between the Au/Ni(110) and Ag/Cu(110) heteroepitaxial systems. One key difference is the lack of long-range order evident in the Ag/Cu(110) system. This lack of long-range order combined with the structural details described above results in a surface morphology with a significantly reduced symmetry compared to that of the Cu(110) substrate. As will be evident from the photoemission results presented below, this reduction in symmetry also becomes apparent in the electronic structure.

Starting from the clean Cu(110) crystal and using various photon energies in the normal-emission geometry, the bulk band structure along the Σ high-symmetry line was determined. Our results agree well with previous experimental[13] and theoretical studies.[14] It is necessary to emphasize that on the clean Cu(110) surface the nonrelativistic selection rules pertaining to the allowed transitions are strongly obeyed, that is, upon rotating the crystal about the surface normal, the appropriate states of a given symmetry representation are observed. Energy distribution curves (EDC's) for the clean Cu(110) for various photon energies and photoemission geometries are shown in Fig. 2, depicted as solid lines. The Cu *d* bands are seen to range from ~2 to 4.5 eV, and the Cu *sp* band (Σ_1) is visible in Fig. 2(b) at ~1 eV. Figures 2(a) and 2(b) correspond to the photoemission geometries with $\mathbf{A} \perp [001]$ and $\mathbf{A} \perp [1\bar{1}0]$, respectively. Figure 3 also shows data for the clean Cu(110) surface, depicted as solid squares mapped onto the theoretical band structure of Burdick,[14] using the free-electron final-state approximation.

Following deposition of ~0.65 ML of Ag, the EDC's in Fig. 2, depicted with symbols, were obtained. The Ag *d* states can be seen with energies between 4.5 and 7 eV. Of particular interest is the emergence of states denoted as *A* and *B* in Figs. 2(a) and 2(b), respectively. Although these states

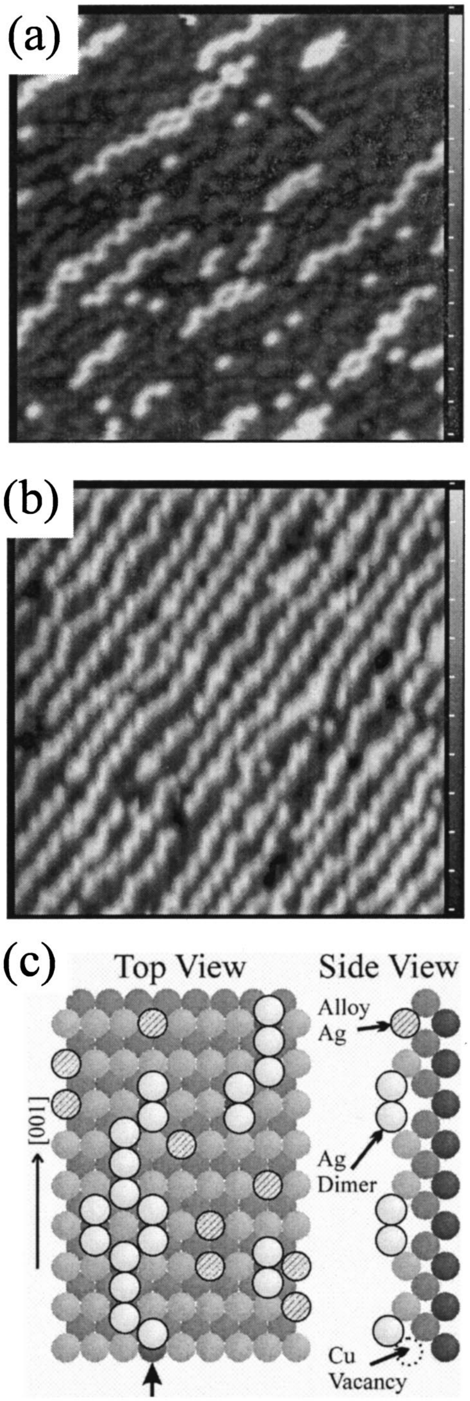

FIG. 1. STM images, acquired at 150 K, of Ag on Cu(110) after deposition of (a) ~0.4 ML (200×200 Å) and (b) ~0.65 ML (300×300 Å) at 450 K. (a) Dealloyed zigzag chains of Ag dimers and trimers are imaged bright, and the residual surface alloy can be seen in the areas between the chains. (b) As the coverage increases, the Ag chains coalesce. The [001] direction is along the chains from bottom left to top right. It is this coverage regime where the ARPES discussion is concerned. (c) Schematic illustration of the dimer-trimer model showing top and side views. The side view, corresponding to the $(\bar{1}10)$ plane of atoms denoted by the arrow, depicts the resultant configuration for the vacancy-stabilized Ag dimers with the remaining surface alloy between the chains.

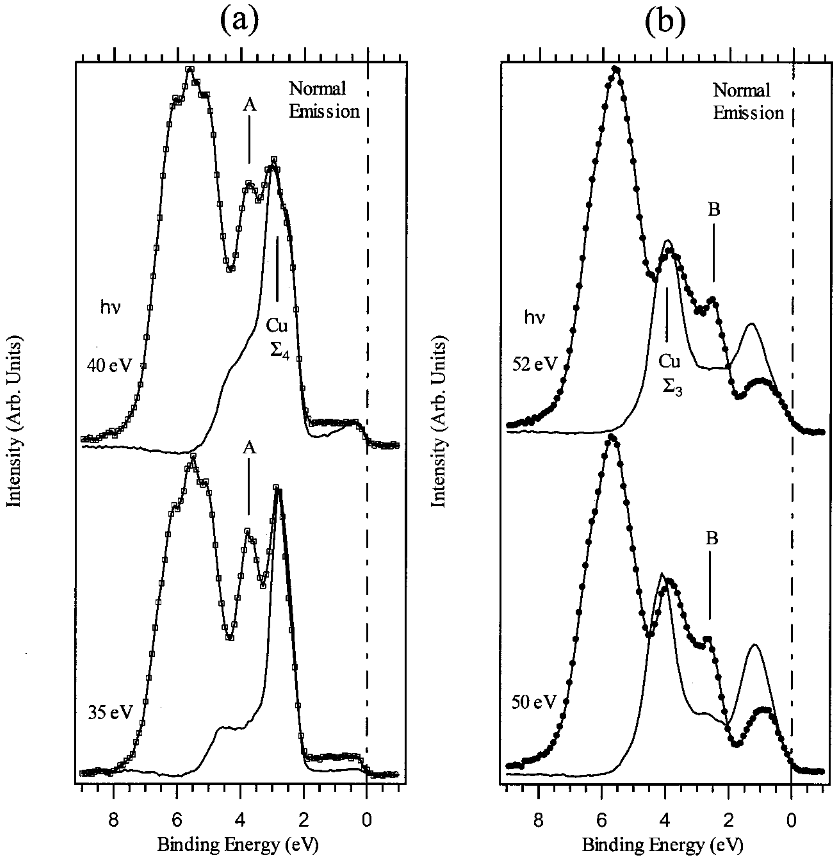

FIG. 2. EDC's of clean Cu(110) (curves without symbols) and Ag/Cu(110) with a coverage of $\theta_{\mathrm{Ag}}\sim 0.65$ ML (curves with symbols). (a) $\mathbf{A}\perp[001]$. (b) $\mathbf{A}\perp[1\bar{1}0]$. Different photon energy spectra are shown that exhibit clearer resolution of resonances, labeled *A* and *B*. State *A* (B) is derived from the Cu $\Sigma_{3(4)}$ band. It is, however, observed in a "forbidden" photoemission geometry because of the reduced symmetry of the surface.

appear after deposition of Ag and thus may be attributed to those of Ag, an examination of the band structure of Ag reveals no bands remotely close to these energies. Even though Ag and Cu are noble metals, both with their filled *d* bands substantially removed from the Fermi edge, the amount of energetic overlap between the *d* bands is negligible.

Assuming that these newly appearing states are derived from Cu bands, we compared the spectra of the clean Cu(110) surface and that of the Ag/Cu(110) nanostructure, and found that each state, *A* and *B*, is nearly energetically equivalent to the bulk Cu states of Σ_3 and Σ_4 character, respectively. Because of this, we assert that states *A* and *B* are surface resonances, or modified bulk states, of the Cu atoms in the interfacial region between the Ag dimer-timer chains and the Cu bulk. Some notable aspects of these observed states will be addressed in what follows. These include (i) energy shifts from the bulk states from which they are derived, (ii) the dispersion of these states through the Brillouin zone along the Σ line, and (iii) the symmetry of these states.

In Fig. 3 we map these experimentally determined bands onto the theoretical band structure of Burdick,[14] using the free-electron final-state approximation. In addition, data for the clean Cu(110) surface are shown, depicted as solid squares. As mentioned above, states labeled with *A* and *B* in Fig. 2 are nearly energetically equivalent to two Cu bulk states. As seen in Fig. 3, these states, depicted by open symbols and connected with dotted lines, map very closely with the bands of clean Cu when the wave vector is closer to the Brillouin-zone edge near the *K* point. As the dispersion of the states along the Σ line approach the zone center, these resonances begin to disperse quite differently from the measured bulk dispersion of the substrate. For qualitative purposes we have displayed the Ag *sp* band (dotted line) as calculated by Christensen,[15] although it is acknowledged that the precise alignment is not absolute because the real crystal potential is not known in this case. As the measured dispersion of the Cu resonances approaches the crossing of the apparent Ag *sp* band with the Cu *d* bands, the energy splitting from the bulk states from which they were derived increases, dispersing to lower binding energy. This suggests that a possible mechanism for the modification of the Cu bands near the surface is induced through a localized hybridization between the Ag *sp* band and Cu *d* bands.

In the case where the symmetry of the surface is strictly maintained, hybridization between states of different symmetries may not be allowed. Specifically, if the Cu *d* bands under consideration are of symmetry characters Σ_3 and Σ_4 and the Ag *sp* band has character Σ_1, then hybridization may be symmetry forbidden. However, it is important to distinguish that this hybridization concerns a mixing of states between different atoms, not a hybridization between states of a given atom. The hybridization referred to here is much less restrictive, because, as a new material is formed through epitaxy, a renormalization occurs, thereby allowing states of originally different symmetry character to have a nonzero overlap integral. Moreover, the symmetry in this surface is not maintained, as can be seen from the photoemission and

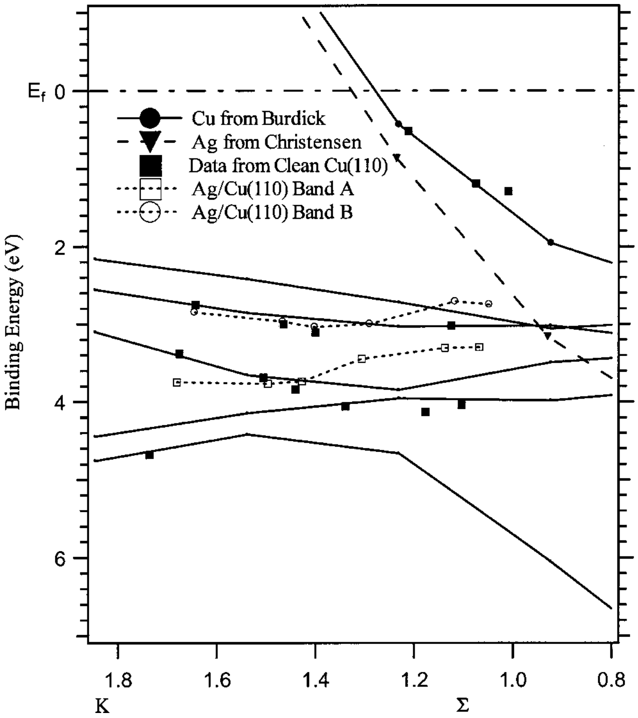

FIG. 3. Experimental bands mapped onto the theoretical band structure of Burdick (Ref. 14). Open symbols connected with dotted lines show dispersion of resonances labeled *A* and *B* from Fig. 2. Solid squares are data from clean Cu(110). The Ag *sp*-band from Christensen (Ref. 15) is for qualitative purposes. Bands *A* and *B* disperse away from the states from which they were derived as they approach the apparent crossing of the Ag *sp* band and Cu *d* bands.

STM data. We have shown that state *A* is derived from the Cu bulk band of Σ_3 symmetry. In the photoemission geometry corresponding to Fig. 2(a), only states of Σ_1 and Σ_4 are allowed transitions, assuming that the C_{2v} symmetry group is maintained in the Ag/Cu(110) system. Similarly, state *B* is derived from the Cu bulk band of Σ_4 character, and should not be observed with the photoemission geometry of Fig. 2(b). This, together with the known modifications of the atomic geometric structure, suggests that the symmetry of the surface has been reduced. This breaking of symmetry enhances hybridization between the Ag *sp* band and Cu *d* bands, and provides a reasonable mechanism for the modification of the Cu bands near the surface. Due to the localized nature of the Ag-Cu nanostructure (see Fig. 1), it may be more fitting to discuss this hybridization in terms of Ag atomic orbitals rather than "bands" perturbing the Cu *d* bands. In either case, the consequent structure of this submonolayer phase provides the necessary reduction in symmetry in the Cu bands to allow for this sp-d hybridization to occur.

In summary, for the heteroepitaxial Ag on Cu(110) system at submonolayer coverages, we investigated the electronic structure using ARPES and the morphology of the grown nanostructure using STM. The existence of surface resonances whose symmetry character is reduced from the bulk Cu bands from which they were derived has been shown, and Ag $sp-$Cu d hybridization has been proposed as the origin of their modification. These resonances have been shown to disperse differently from the bulk bands, and have been observed in photoemission geometries in which they would otherwise be forbidden if not for the reduction in the surface symmetry.

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