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CONCENTRATION-DEPENDENT SURFACE-STATE SHIFTS: Au on Cu(001)

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ABSTRACT

High-resolution angle-resolved photoemission has been used to investigate the behavior of the Cu(001) $\bar{M}_2$ surface state as a function of Au coverage and substrate temperature. Binding-energy shifts of this state are dependent on the concentration of Au atoms substituted into the top surface layer of the Cu(001) substrate. The results demonstrate the use of surface-localized Tamm states as a specific probe of the chemical environment in the surface plane.

DISCUSSION

Experimental probes sensitive to the substrate surface electronic structure of metal/metal overlayer systems are often hampered by an inherent inability to distinguish surface from bulk effects. Although core-level photoemission is an excellent probe of adsorbate geometrical [1] and electronic structures, [2,3] extensive deconvolution procedures are often required to extract information from partially-resolved surface, bulk and adsorbate-shifted components of the metal substrate [4]. To enhance surface sensitivity and specificity, it has been suggested [5] that surface-localized [6] states, in analogy to core levels, could be used as a probe of the local potential in the substrate surface layer. Experimentally, one has only a single, well-resolved spectral feature to measure, eliminating difficulties implicit in the interpretation of core-level spectra. Using the system Au/Cu(001), we have demonstrated the feasibility of this approach. Previous photoemission studies reporting perturbations of this state have been limited to the bulk single crystal alloys of Cu₉₀Au₁₀(001)[7] and Cu₈₇Au₁₃(001)[7] and the c(2x2) surface of 1/2 monolayer (ML) of Au/Cu(001) [8,9]. However, our results represent the first systematic study correlating binding energies with the surface concentration of adsorbates.

In this report, we present a high-resolution angle-resolved photoemission study of the Cu(001) $\bar{M}_2$ surface state as a function of Au depositions on room-

temperature and low-temperature (-100°C) substrates. Au/Cu(001) is a system with a well-studied case of surface alloy formation [3,8-14] which can be used to demonstrate the sensitivity of surface states to the chemistry of the surface plane. For depositions of $1/2$ ML or less at room temperature, Au is incorporated into the surface layer forming an ordered surface alloy. Correspondingly, we have observed a shift to lower binding energy of the $\bar{M}_2$ surface state, which depends linearly on the concentration of Au in the Cu(001) surface layer. At low temperatures this alloy phase does not form: Au atoms adsorb upon an apparently intact Cu(001) substrate [9,10]. Under these conditions, our results show that the surface state is attenuated by the Au coverage, but not shifted in energy. These observations demonstrate the sensitivity of the surface state's binding energy to in-plane interactions. For Au depositions between $1/2$ and 1 ML at room temperature, we observe the alloy surface state shift to higher binding energy, back towards the original $\bar{M}_2$ surface state energy. Guided by the results for lower Au coverages and our core-level photoemission results, both high-resolution core shifts [3,9] and photoelectron diffraction [11,12], we interpret this shift in terms of a decreasing Au concentration in the top layer, in support of an intriguing de-alloying model [3]. We suggest that in judiciously chosen overlayer systems [15] the Cu(001) surface state may provide an excellent probe of the substrate surface environment.

These experiments were performed in an ultra-high vacuum spectrometer (base pressure $\approx 2 \times 10^{-10}$ torr) equipped to perform LEED, Auger electron spectroscopy (ARPES). Sample preparation and the evaporation of Au are described elsewhere [14]. Au depositions were monitored using a quartz crystal microbalance. Absolute calibration of the microbalance was determined by an AES-LEED experiment, in which specific LEED patterns and breaks-in-slope in Auger intensities were used as measures of absolute coverage. From these calibrations our estimates of thickness should be accurate to within 5 and 10%. Photoemission measurements were performed with an angularly-resolved hemispherical analyzer [14], utilizing unpolarized He I ($h\nu = 21.22\text{ eV}$) resonance lamp emission. The He I radiation was incident normal to the surface to maximize the s polarization of the light. Photoelectrons from the valence band were collected at 63° from the surface normal, in the $\bar{\Gamma}\bar{\Sigma}\bar{M}$ plane, near $\bar{M}$ in the surface Brillouin zone (SBZ). The overall experimental resolution was better than 40 meV full-width at half-maximum (FWHM).

ARPES energy distribution curves, near $\bar{M}$, for a series of Au depositions onto a room temperature Cu(001) substrate are shown in Fig. 1. The clean Cu(001) $\bar{M}_2$ surface state, in the bottom-most spectrum of Fig. 1, at a B^F (binding energy with respect to the Fermi energy) = 1.78 eV and an experimental $\Delta E_{FWHM} \approx 56$ meV is in excellent agreement with previous results [16,17]. The Cu(001) surface state is a Tamm state composed of d_{xy} derived orbitals which are localized to planes parallel to the surface. This surface state is highly sensitive to the potential describing the local surface environment. Euceda *et al.* [18] have calculated that the Cu(001) $\bar{M}_2$ state experiences a repulsive potential attributed to the surface narrowed d density of states and a 12% excess sp surface charge. This repulsive potential pushes the surface d_{xy} states out of the bulk continuum and into the bulk gap near $\bar{M}$. Thus, the $\bar{M}_2$ surface state should be extremely sensitive to modified, surface-localized potentials induced by alloy formation.

For Au depositions of 1/2 ML or less, the effect on the $\bar{M}_2$ surface state can be seen in Fig. 1. The surface state shifts to lower binding energy with increasing coverage, simultaneous with the development of a sharp c(2x2) LEED pattern by 1/2 ML. Note that only one peak is observed, never two. Also, this shift is specific to the surface state: The bulk Cu(001) d states at and above 2 eV are only weakly attenuated by the deposited Au, but never shifted. Palmberg and Rhodin [10] proposed that the c(2x2) structure was associated with the ordered substitution of Au atoms into the Cu(001) surface in a checkerboard array similar to the surface of Cu₃Au(001). A number of geometrical [11-13] and electronic [3,8-9] studies have confirmed that hypothesis. We show in Fig. 2 a compilation of our surface state binding energy results, including a linear least-squares fit to the experimental results with a slope of -0.65 ± 0.04 eV/ML. (Note that the sample work function, based on normal-emission ARPES results, also shifts linearly with increasing Au coverages of 1/2 ML or less, 0.93 ± 0.05 eV/ML.) These coverage-dependent surface state shifts agree remarkably well with previously reported results. Asonen *et al.* [7] reported a modified $\bar{M}$ surface state at $B^F = 1.65$ eV (open square, Fig. 2) on the bulk alloy Cu⁹⁰Au¹⁰(001). Graham [8] has reported similarities in the electronic structures near $\bar{M}$ of c(2x2) Au/Cu(001) and its bulk alloy analog Cu₃Au(001). Surface state binding energies of 1.5 eV [19] and 1.6 eV for the c(2x2) AuCu(001) and Cu₃Au(001) alloy (open circle and triangle) respectively are shown in Fig. 2. Note that even though the Au surface concentrations for these two surfaces are identical, their binding energies differ slightly. This may indicate a sensitivity to minor geometrical differences in

Figure 1. ARPES spectra collected at 63° from the surface normal, near $\bar{M}$ in the Cu(001) SBZ, utilizing normal incidence He I radiation. Au depositions, performed on a room temperature substrate, are shown with increasing coverages (ML) from bottom to top. Selected LEED patterns are also indicated.

Figure 2. A plot of surface state binding energies (eV) versus Au coverage (ML) from this study are shown as solid circles. Included are results from: a c(2x2) Au/Cu(001) (open circle) and Cu₃Au(001) (open triangle) from Refs. 8, 19; and the bulk alloy Cu₉₀Au₁₀(001), with an Au surface enrichment of 20 at. %, (open square) from Ref. 11. The line drawn is a linear least-squares fit to our data, with a slope of -0.65 ± 0.04 .

Figure 3. Same as figure 1, except the sample temperature was below -100° C. A sharp c(14x2) LEED pattern is observed near 1 ML.

surface structure. The Au atoms in the c(2x2) surface are known to be slightly buckled by 0.1 Å, whereas in Cu₃Au(001) the lattice is approximately 4% larger than Cu(001) and no Au buckling is observed [13]. These structural differences might alter the local-surface-charge density that ultimately effects the $\bar{M}_2$ surface state.

This surface state shift, observed between 0-1/2 ML, is accompanied by a change in the state's width from ~56 meV to ~260 meV FWHM. Energy conservation and the small sp density of states (i.e. band gap) at $\bar{M}$ contribute to clean Cu(001)'s extremely narrow surface state [17]. When Au is added, we would expect the sp density of states to become much larger, as suggested by the increase in the measured sp plateau height in Fig. 1. This has the effect of shortening the hole lifetime and increasing the state's FWHM. Also, the alloy surface state may be subjected to momentum broadening mechanisms. Au atoms may act as defect sites, blurring the $\bar{M}$ region of the SBZ.

At coverages above 1/2 ML, the alloying process is reversed. Figure 1 shows the alloy surface state losing intensity and rapidly shifting to higher binding energy as the coverage is increased, simultaneous with the loss of the c(2x2) LEED pattern and the development of a hexagonal LEED pattern. At coverages slightly above 3/4 ML the alloy surface state is all but eliminated, with the development of a weak feature on the low binding-energy side of the bulk Cu d bands. By a coverage of 1.1 ML this feature is a peak at a binding energy, $E_F \approx 1.8$ eV, nearly identical to the original $\bar{M}_2$ surface state. The conclusion that, with the addition of 1/2 ML of Au, the c(2x2) Au/Cu(001) surface alloy has transformed into a metal overlayer is supported by our core-level photoemission results [3,11].

To confirm that the $\bar{M}_2$ surface state is sensitive to only in plane interactions and not just the quantity of deposited Au, evaporations were performed on a Cu(001) substrate held at temperatures below -100°C. At this temperature, it has been shown [9,10] that the Au forms an overlayer structure without intermixing. The contrast between room temperature and cold substrates can be observed in Fig. 3. The $\bar{M}_2$ surface state is slowly attenuated, but never shifted in energy as a function of increasing coverage. Note that an extremely weak shoulder is observed, indicating that this interface is not completely abrupt: some Au atoms appear to have intermixed with the substrate or possibly an alloy-like structure is forming at a step. Additional temperature effects will be discussed more fully in a future publication.

In this report, binding-energy shifts of the Cu(001) $\bar{M}_2$ Tamm surface state have been attributed to the concentration of Au atoms substituting into the Cu

surface matrix. Sensitivity to geometrical position, as well as Au concentrations of less than 0.1 ML, suggests that this state might be employed as a probe of similar metal overlayer systems. Furthermore, this chemical perturbation of a surface state should prove to be a challenging test of state-of-the-art computational capabilities [16,18].

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