Observation of a True Interface State in Strained-Layer Cu Adsorption on Ru (0001)

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For coverages up to one monolayer, Cu adsorbs in a pseudomorphic structure on the Ru(0001) surface with a 5% tensile strain. Angle-resolved photoemission near the K point in the surface Brillouin zone reveals a state -1.5 eV below the Fermi level which appears localized in the Cu and outermost Ru layers. This state is confirmed by surface linearized, augmented plane-wave calculations to be the antibonding partner of a pair of Cu($3d$)-Ru($4d$)–derived interface states.

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The observation and interpretation of surface-state dispersion has played an important role in the characterization of surface geometric structure and bonding.[1] Similarly, one would expect states localized at an interface between two materials to provide important clues as to the nature of the interface. Although interface states have been both theoretically predicted by realistic calculations[2] and observed experimentally in the realm of semiconductor-semiconductor interfaces,[3] for metal-metal interfaces the only known examples of interface states have wave functions that are localized on atoms on only one side of the interface.[4] These states are essentially the same as surface states which remain if the metals are separated such that one has metal No. 1–vacuum and vacuum–metal No. 2 surfaces. Accordingly, they give little insight regarding the bonding of the two metallic components of the interface.

We report in this Letter the first observation and theoretical calculation of a "true" interface state in a metal-metal system, i.e., a state which only exists as a result of the formation of the interface and for which the wave function is large near the metal atoms on both sides of the interface. These conclusions are drawn from the results of an angle-resolved ultraviolet photoemission (ARUPS) study of Cu films grown on the Ru(0001) surface for various Cu coverages from submonolayer to monolayer (ML) through multilayer. For coverages of up to 1 ML, such films have been shown to grow pseudomorphically (1×1) on the Ru(0001) surface,[5] which results in a tensile strain in the Cu overlayer of about 5% with respect to the Cu(111) bulk lattice.

The Ru sample used in these studies was cleaned by exposure of the surface to approximately a 1000-langmuir (1 langmuir $=10^{-6}$ Torr-sec) O_2 dose through a microchannel-plate doser at a temperature of 1450 K followed by a vacuum bake at 1550 K for 300 sec. The cleanliness was verified by Auger spectroscopy. For C, whose Auger structure is obscured by that of Ru, we used the accepted scheme of measuring the negative-to-positive peak ratios in $dN(E)/dE$ Auger data for the Ru structure near 270 eV.[6,7] Cu was evaporated onto the Ru(0001) surface at room temperature from a resistively heated W filament wrapped with high-purity Cu wire. The Cu source was thoroughly outgassed prior to Cu evaporation and no contamination could be detected as a result of the deposition. The Cu coverages were accurately established by thermal programed desorption measurements.[8]

ARUPS energy distribution curves (EDC's) were measured using a Vacuum Generators ADES 400 system with a He-discharge lamp. The energy resolution was approximately 0.1 eV and the angular window was $\pm1°$. He I photons ($h\nu=21.2$ eV) impinged on the surface along the surface normal and photoelectrons were detected at various positions along the Γ-K line in the surface Brillouin zone (SBZ). The azimuthal orientation was established by LEED.

EDC's corresponding to a polar electron-emission angle of 52° are shown in Fig. 1 as a function of Cu coverage, Θ. These results show a structure located about 1.5 eV below the Fermi level which grows in intensity with Θ for $\Theta<1$ ML. For $\Theta>1$ ML, the intensity of this feature remains fixed relative to that of the Ru structure near the Fermi energy. To make this clear, we have normalized the curves of Fig. 1 at the Fermi energy. The pure Cu states therefore grow with Θ, while the Cu-Ru state at -1.5 eV saturates at $\Theta=1$ ML. That the -1.5-eV feature can be clearly seen even for rather thick Cu overlayers results from the fact that photoemission from pure Cu is weak for binding energies less than about 2 eV—the 3d-band onset.

The structure at -1.5 eV in the EDC's only stands

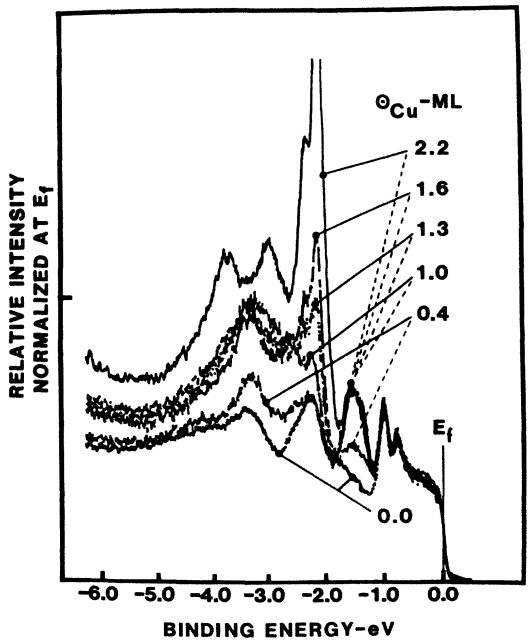

FIG. 1. ARUPS EDC's taken with He I radiation at normal incidence and an electron emission angle of 52° are shown as functions of Cu coverage. The intensity of the various curves has been normalized at the Fermi level, E_F. The individual curves are matched to their corresponding Cu coverages in monolayers by the solid lines while the saturating behavior of the interface state at approximately -1.4 eV is identified by the dashed lines.

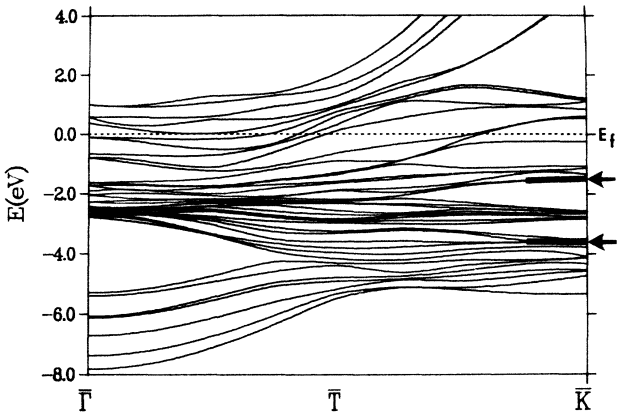

FIG. 2. Energy-level dispersions along the Γ-K symmetry line for a five-layer Ru(0001) film covered on both faces by a 1-ML 1×1 Cu overlayer. States indicated by heavy lines and arrows are strongly weighted on the outer Cu overlayers and first underlying Ru layers of the film.

out clearly for a region of polar angles from approximately 45° to 58°. Outside this region, it begins to blend with the clean Ru features. From the 1-ML data of Fig. 1, it appears that this feature resides at the upper edge of a gap bounded on the high side by the peak at approximately -1.0 eV and at the lower energies by a strong peak at about -3.4 eV. The peak at approximately -2.3 eV in the clean spectrum becomes less distinct at the 1-ML Cu level and is reminiscent of the surface state found in the clean Ru band-structure calculations done earlier by Feibelman.[9] The polar angle of 52° used in obtaining the data of Fig. 1 corresponds to a k value representative of the K point in the SBZ for the structure having a binding energy of -1.5 eV.[10]

The feature at a binding energy of -1.5 eV is not seen for either clean Ru or the surface of bulk Cu. This, along with its behavior as a function of Cu coverage, strongly suggests that this structure is the result of photoemission from an interface state in the Cu/Ru bimetallic surface, i.e., a state which exists because of the junction between Cu and Ru. To test this suggestion, we have carried out a state-of-the-art surface electronic structure calculation using the surface linearized, augmented plane-wave (SLAPW) method,[11] modeling the 1-ML-Cu/Ru adsorption system by a five-layer Ru(0001) slab with a pseudomorphic (i.e., 1×1) Cu adlayer on either side. In the calculation, the Ru atoms of the slab were placed at bulk Ru relative positions. In the absence of structural measurements for Cu(1×1)/Ru(0001), the Cu atoms were placed in plausible adsorption sites, namely threefold hollows (both hcp and fcc sites were investigated[12]) with the Cu-Ru bond length chosen to equal the average of the Ru-Ru and Cu-Cu nearest-neighbor distances in the respective bulk metals. The calculations were semirelativistic,[11] and represented the effects of exchange and correlation with the local density-functional exchange-correlation potential[13] based on the Wigner interpolation formula.[14] Further details of the calculational method can be found in Ref. 11 and in Mattheiss and Hamann.[15]

Results of the SLAPW calculation for the Cu atoms in hcp sites[12] are shown in Fig. 2, which is a plot of the calculated electron energy levels as a function of k along Γ-K in the SBZ. The heavy lines in the figure correspond to states whose wave functions have at least 35% of their electron density in Cu muffin tins and 35% in outer-layer-Ru muffin tins and which have less than 7% in any of the three central Ru-layer muffin tins. These criteria are satisfied by a group of states near K at a binding energy of about -1.4 eV and another, also near K, lying in the vicinity of -3.6 eV. Angular momentum decomposition of the wave functions corresponding to these states indicates that they are a bonding-antibonding pair of states largely formed from Cu($3d$) and Ru($4d$) orbitals.

Without any adjustment of the separation of the Cu and outermost Ru layers, the calculated energy of the antibonding state is -1.4 eV, which is in excellent

agreement with the energy of the observed Cu-Ru feature. The bonding interface state is predicted to lie at -3.6 eV. However, in this energy range there are also pure Cu d states and, in addition, the lifetime of holes in these deeper levels should be shorter, giving rise to a broader peak.

Moving the Cu's to fcc threefold hollows,[12] we again find Cu-Ru interface states near K. In this case, they lie at -1.3 and -3.5 eV. The fact that their energy splitting is the same as in the hcp geometry is a consequence of their strong localization in the Cu and outer Ru layers. Their common 0.1-eV upward shift results from the fact that the one-electron potential in the neighborhood of the fcc site is slightly less attractive than near the hcp site.

As a sensitivity test, we have recalculated the Cu/Ru spectrum moving the Cu layer 0.1 bohr closer to the outer Ru's. This yields binding energies of the antibonding and bonding Cu-Ru states at K of -1.4 and -3.7 eV. The increased splitting of the interface states results from increased Cu($3d$)-Ru($4d$) overlap at the reduced Cu-Ru separation. The effect on the antibonding state, which is the one observed experimentally, is too small, however, to attempt to refine the geometry on the basis of its energy.

Thus, the calculations verify the existence of a true interface state, as strongly suggested by the experimental results, in the system involving Cu pseudomorphically grown on the Ru(0001) surface. In closing we would like to point out that the sharp d-band features normally associated[16] with Cu do not begin to appear in the EDC's of Fig. 1 until Cu coverages of greater than 1 ML are achieved. For coverages of 1 ML or less, it is clear that the Cu $3d$ levels mix strongly with the Ru $4d$ states. This conclusion is in direct contradiction to an earlier ARUPS study on the Cu/Ru system.[17] However, the fact that during the first monolayer Cu grows pseudomorphically on Ru(0001) with a 5% tensile strain, coupled with TPD results which indicate that the Cu/Ru binding energy for the first monolayer[8,17] is significantly higher than for subsequent layers, would be difficult to understand without a strong Cu/Ru interfacial interaction.

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