Photoemission Observation of an Intrinsic Surface-State Band in a Disordered $Cu_{0.9}Al_{0.1}(111)$ Alloy

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An intrinsic Shockley-type surface-state band has been found in a random substitutional CuAl(111) single-crystal alloy containing 10 at.% Al. The surface state is located at the center of the (111) two-dimensional Brillouin zone. Its energy is considerably lower than in pure Cu and depends on surface conditions. The study of the surface state shows that alloying effects are strong near the Fermi level. The Tamm-type surface state present in pure Cu(111) is absent in the alloy.

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A number of surface-induced electronic states have been found in the noble metals since the first discovery of a Shockley-type surface state in a pure Cu(111) crystal.[1] It is conceivable that in addition to the ordered solids, disordered systems which have a random crystal potential may also exhibit intrinsic surface states. Namely, coherent-potential–approximation (CPA) calculations[2] predict that although the wave vector $\vec{k}$ is not a good quantum number in disordered alloys, the Bloch spectral function, which for an ordered crystal consists of a continuous array of δ-function peaks along a fixed $\vec{k}$ direction, has peaks and ridges well defined on the scale of their separation. This prediction of the CPA is supported experimentally by recent photoemission measurements on CuNi (Ref. 3) and AgPd (Ref. 4) alloys. If the projected CPA "band" structure shows gaps which extend below the Fermi level for the crystal face under study a basic criterion for the existence of a surface-state band in the alloy should be fulfilled.

We report here on the observation of a Shockley-type surface state in a random substitutional $Cu_{0.9}Al_{0.1}(111)$ single-crystal alloy.[5] This state is located at the center of the (111) two-dimensional Brillouin zone, around the $\bar{\Gamma}$ symmetry point. The energy of the state depends on surface conditions. For a (1×1)-$(\sqrt{3}\times\sqrt{3})R\,30°$Al structure[6] which originates from a one-third monolayer coverage of Al on the disordered 1×1 bulk structure, the surface state appears at the energy of -1.2 eV below the Fermi level E_F at the $\bar{\Gamma}$ point. For the disordered 1×1 configuration obtained by removing the Al overlayer the state is located at -0.8 eV. This observation indicates that the surface state is not only associated with the Al-rich surface, but is also inherent to the disordered alloy with the normal 1×1 structure.

In the present experiment we have used the combined techniques of angle-resolved ultraviolet photoemission spectroscopy (UPS), Auger-electron spectroscopy (AES), and low-energy electron diffraction (LEED). Photoemission was measured from clean $Cu_{0.9}Al_{0.1}(111)$ and Cu(111) single crystals as a function of the polar angle of emission, Θ, and the energy of incident photons, $\hbar\omega$, at the energy resolution of the analyzer of 40 meV and the angular resolution of 3°– 4° full opening of the electron beam cone. The Al-rich $\sqrt{3}\times\sqrt{3}$ surface was obtained by annealing the clean sample at 770 K for 30 min. This surface contained 33 at.% Al, as deduced from the AES spectra, which was consistent with the surface geometry according to the LEED patterns. To convert the surface to the normal 1×1 configuration the sample was bombarded by 600-eV Ar^+ ions for 2.5 min. The bombarding reduced the Al content in the surface region to a level approximately equal to that in the bulk (10 at.% Al).

The main results of the present experiment are compiled in Fig. 1 where normal emission measured at the photon energy of 16.85 eV is shown for Cu(111), $Cu_{0.9}Al_{0.1}(111)$ with the $(\sqrt{3}\times\sqrt{3})R\,30°$Al overlayer, and $Cu_{0.9}Al_{0.1}(111)$ with the (1×1) configuration. The peak labeled S is interpreted as the intrinsic surface state. We can find all characteristic features of the Shockley-type surface state of pure Cu for peak S in the alloy. (i) In normal emission the peak remains stationary in energy, as $\hbar\omega$ is varied, indicating that the energy of this peak depends only on $k_{\parallel}$. (ii) An exposure of the surface to oxygen reduces the intensity of peak S somewhat more rapidly than it does for peak intensities of the bulklike transitions. (iii) Peak S shows a dispersion relation $E(k_{\parallel})$ which is similar to the dispersion of the surface state of pure Cu(111) (Fig. 2). (iv) Polarization effects on the intensity of peak S are strong (Fig. 3).

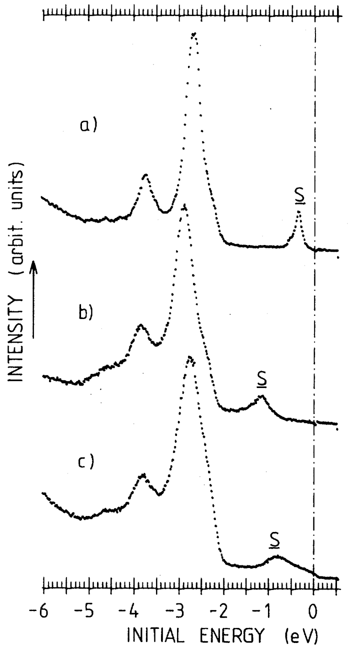

FIG. 1. The angle-resolved photoelectron spectra showing the presence of a Shockley-type surface state S in (a) pure Cu(111); (b) $Cu_{0.9}Al_{0.1}(111)$ with the $(\sqrt{3}\times\sqrt{3})R30°$Al overlayer; (c) $Cu_{0.9}Al_{0.1}(111)$ with the normal 1×1 surface. The polar angle of emission was $\Theta = 0°$ and the angle of incidence $\Psi = 55°$. $\hbar\omega = 16.85$ eV.

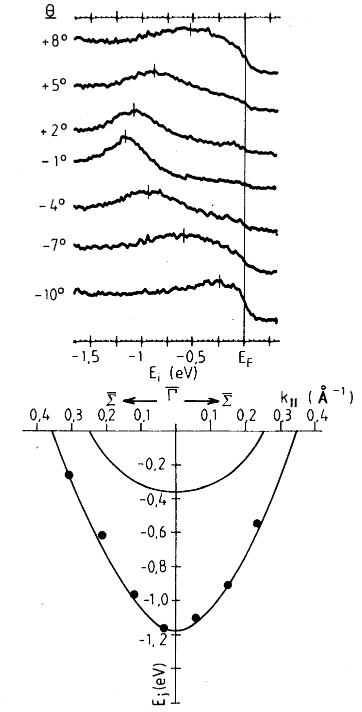

FIG. 2. The energy dispersion of the surface state as a function of polar angle and $k_{\parallel}$. The upper and lower $E(k_{\parallel})$ curves are for pure Cu (Ref. 9) and $Cu_{0.9}Al_{0.1}(111)$ with the $(\sqrt{3}\times\sqrt{3})R30°$Al overlayer, respectively.

According to Fig. 1, peak S in $\sqrt{3}\times\sqrt{3}$ $Cu_{0.9}Al_{0.1}$ is 0.8 eV lower than the surface state in pure Cu. This large difference in the peak positions is partly due to the fact that a Shockley-type surface state is sensitive to the location of the surface potential step. In the alloy, the Al overlayer changes the position and the shape of the surface barrier relative to pure Cu. We examined the surface-barrier effect theoretically by carrying out a one-step model calculation of photoemission for pure Cu(111) using the time-reversed LEED formalism.[7] The calculation showed that moving the surface barrier outwards from the crystal caused a lowering of peak S in energy by the amount of 0.08 eV/(0.1 a.u.) but left the bulk features substantially unchanged. This observation is in reasonable agreement with that of Gurman[8] who found a change of 0.1 eV in the surface energy due to the displacement of the surface barrier by 0.1 a.u. Consequently, the measured difference of 0.4 eV in the peak positions for the two alloy surfaces corresponds to an effective displacement of the surface potential step of about 0.5 a.u.[9]

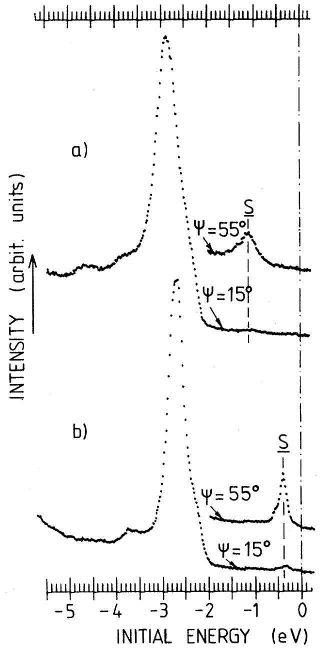

FIG. 3. Polarization effects on the surface states S in (a) $Cu_{0.9}Al_{0.1}(111)$ with the $(\sqrt{3}\times\sqrt{3})R30°$Al overlayer; (b) pure Cu. $\hbar\omega = 16.85$ eV; $\Theta = 0°$.

Peak S for 1×1 $Cu_{0.9}Al_{0.1}$ is placed 0.4 eV lower than the surface state in pure Cu (Fig. 1). We attribute this difference to alloying effects on the bulk electronic structure. In particular, the uppermost bulk band with the Λ_1 symmetry appears to be strongly influenced by alloying. Since the bulk bands are not much perturbed by a removal of the Al overlayer [cf. Figs. 1(b) and 1(c)], the L_2' symmetry point which for pure Cu is located at -0.9 eV must be placed below -1.2 eV in $Cu_{0.9}Al_{0.1}$ to allow for peak S to lie entirely inside the sp hybridization gap. In other words, a shift of the L_2' point is an order of magnitude larger than the overall shift observed for the d bands of the alloy (Fig. 1).

Figure 2 shows the dispersion $E(k_{\parallel})$ of peak S for $\sqrt{3}\times\sqrt{3}$ $Cu_{0.9}Al_{0.1}$ and for pure Cu. It can be seen that the surface state in the alloy tends to cross E_F at $k_{\parallel}\cong0.35$ Å^{-1} and in Cu (Ref. 10) at $k_{\parallel}\cong0.25$ Å^{-1} quite symmetrically with respect to the $\Gamma-L$ direction in both cases. Accordingly, the radius of the L neck must be considerably greater (at least 40%) in $Cu_{0.9}Al_{0.1}$ than in pure Cu, provided the surface-state band of the alloy lies above the sp gap for all $k_{\parallel}\leq0.35$ Å^{-1}. It can be estimated from the band structure of Cu that a 40% increase in the L neck radius corresponds to an increase of the electron concentration by 0.2 electron/atom which is equal to the difference between the electron concentrations in $Cu_{0.9}Al_{0.1}$ and Cu.[11]

Polarization effects on peak intensities are illustrated in Fig. 3. We measured normal emission using unpolarized (Ne I) light incident at two different angles, $\Psi=55°$ and 15°, relative to the surface normal. By comparing the spectra in Figs. 1 and 3 one may see that the selection rules are equally strong for Cu and $Cu_{0.9}Al_{0.1}$; with $A_z\cong0$, only the states of Λ_3 symmetry have been excited.[12] This validity of the symmetry selection rules is a further evidence for the existence of rather well-defined energy bands in $Cu_{0.9}Al_{0.1}$.

The Tamm-type surface state originating from a perturbation in the potential of the outermost layer is centered at the $\overline{M}$ symmetry point of the (111) two-dimensional Brillouin zone of Cu.[13] We cannot find this state in $Cu_{0.9}Al_{0.1}(111)$ for either the $\sqrt{3}\times\sqrt{3}$ or 1×1 configurations. Therefore, an expected weakening of the surface perturbation in the first $Cu_{0.9}Al_{0.1}$ layer, due to the presence of the $\sqrt{3}\times\sqrt{3}$ Al overlayer, cannot be responsible for the absence of the Tamm state in the alloy. On the other hand, a band smearing due to disorder is so small (as can be concluded from the observed linewidths for the d states) that the Tamm state, if existed, should be clearly resolvable from its parent d band. The remaining explanations we may find for the disappearance of the Tamm state are the possibilities that the nonhybridization gap at the $\overline{M}$ point of pure Cu has been removed in $Cu_{0.9}Al_{0.1}$ or the surface perturbation has been weakened upon alloying.

In summary, we have presented the first angle-resolved photoemission observation of an existence of the Shockley-type surface state and effects of the surface conditions on this state in an alloy system. We have also shown that the deeper potential, necessary at the higher valence polyvalent Al sites to accommodate the extra valence electrons, perturbs strongly the alloy s-p conduction band.

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by photoemission, will be given in another paper where the experimental data are also compared with predictions of the Korringa-Kohn-Rostoker CPA band calculations by R. S. Rao, P. Prasad, and A. Bansil (to be published).

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