

Surface states in the epitaxial growth of titanium on copper (111)

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The growth of Ti on a Cu(111) surface appears from the Auger electron yield to be layer by layer, although there is no evidence of an ordered film until low-energy electron diffraction beams characteristic of the basal plane of Ti appear at about six monolayers. Appearance-potential-spectroscopy studies of the unfilled $3d$ band of Ti reveal the presence of a band of surface states at the Fermi level even for coverages less than one monolayer. Heating the Ti film to 400°C results in the formation of an alloy film with the probable composition TiCu. At 550°C the amount of Cu in the surface region increases, leading to an alloy film with probable composition near TiCu₃. In both alloys the Cu atoms donate electrons to the Ti, with the result that d -band holes appear on the Cu sites. The Ti surface states are extinguished in the alloys, indicating that the nature of the Ti—Cu bond for adsorbed Ti atoms is distinctly different from bonding in the alloys.

I. INTRODUCTION

In the epitaxial growth of metal films on a metal substrate, the initial layer is frequently pseudomorphic, with the normal crystallography of the overlayer film not being in evidence until five or six layers have been deposited. The transition from pseudomorphic to normal frequently involves several layers that are poorly ordered. The electronic nature of the overlayer film during this transition is a matter of considerable importance in understanding epitaxy. Titanium films grown epitaxially on a Cu(111) surface represent a particularly interesting example.

The (0001) surface of bulk titanium is known to be characterized by a strong band of surface states at the Fermi level and extending a few tenths of an eV on either side of it. This is particularly striking since the Fermi level nearly corresponds to a local minimum in the bulk density of states. The band of surface states is thus easily identified in probes of either the filled¹ or unfilled states.² In particular, Jonker *et al.*² demonstrated that for clean Ti, the surface states are a prominent feature in the Ti $2p_{3/2}$ appearance-potential spectrum which reflects the unfilled density of states. Layer-by-layer calculations of the electronic structure of a free-standing Ti(0001) film by Feibelman, Appelbaum, and Hamann³ indicate that the film quickly assumes its bulk electronic structure as one moves in from the surface; in fact, almost by the second layer. As we shall show, titanium grows layer by layer (Frank—van der Merwe growth) on the Cu(111) surface, with the Ti basal plane exposed at sufficient thickness.

The use of a core-level probe such as appearance-potential spectroscopy is particularly advantageous for the study of thin epitaxial films since it enables the electronic structure associated with the overlayer atoms to be examined separately, without the obscuring contribution of the substrate. We have therefore undertaken a systematic study of the growth of Ti films on the Cu(111) surface using low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and appearance-potential spectroscopy (APS). Particular attention was given to the

dependence of the Ti surface state on film thickness.

We have also followed the conversion of the epitaxial film to Cu-Ti alloys by heating. We will show that the alloys formed are essentially common band alloys, with the Cu sites exhibiting d -band holes.

II. EXPERIMENTAL

The experiments were conducted in an ultra-high vacuum system with a base pressure of $<2 \times 10^{-10}$ Torr. The single-crystal Cu sample was oriented to the (111) face and cleaned *in situ* by repeated cycles of Ar-ion sputtering and annealing at 500°C. Surface cleanliness was checked by a cylindrical mirror Auger electron spectrometer and the structure was verified by low-energy electron diffraction. After cleaning, the Auger peak-to-peak signal ratios of carbon (272 eV) and oxygen (512 eV) to copper (58–61 eV) were less than 1%. The Ti films were evaporated on to the Cu substrate from a thoroughly outgassed, directly heated Ti-Ta—alloy wire. Typical deposition rates were one monolayer in three minutes. No pressure increase was observed during deposition from a well-outgassed filament. The resulting Ti films showed no carbon Auger signal and oxygen signals corresponding to between 0% and 5% oxygen contamination. The appearance-potential spectra were taken by the disappearance technique, using the LEED optics to measure the nearly elastic scattering yield as the energy of the electrons incident on the sample from the LEED gun was swept through the Ti and Cu $2p_{3/2}$ excitation thresholds. Only those electrons that had an energy less than 10 eV below the primary were detected. The first derivative of the elastic yield was measured by applying a $0.6 V_{p.p.}$ modulation to the sample potential. The second-derivative spectra were obtained by numerical differentiation.

Appearance-potential spectroscopy measures the probability for the creation of excited core states of atoms by electron bombardment.⁴ Above a core excitation threshold, this probability depends on the states available to two electrons; the incident electron and the excited core elec-

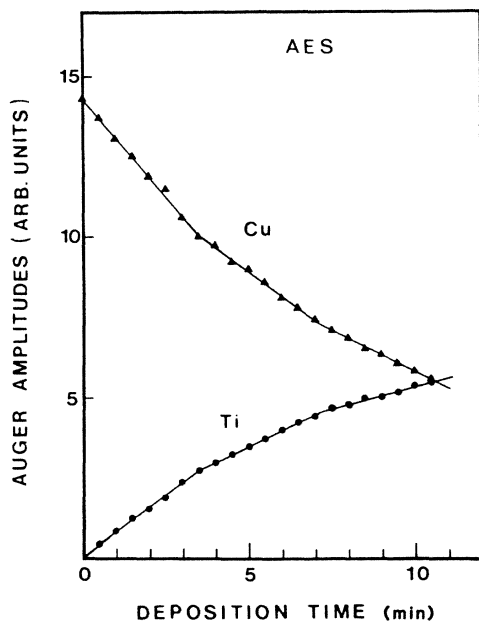


FIG. 1. The amplitudes of the first-derivative spectra for Ti $L_{3}M_{4,5}M_{4,5}$ and Cu $M_{2,3}M_{4,5}M_{4,5}$ Auger peaks as a function of deposition time. The breaks in the curves indicate the completion of the first and second monolayers.

tron. Assuming constant matrix elements, the electron-excitation probability $N_{\beta}(E)$ will vary as the self-convolution of the one-electron density of unfilled states broadened by the Auger lifetime of the core hole, i.e.,

$$N_{\beta}(E) = N(E) * N(E) * \rho(E + E_B), \quad (1)$$

where $N(E)$ is the density of unfilled states, E_B is the core binding energy, and $\rho(E)$ is a Lorentzian of the form

$$\rho(E) = \frac{1}{\pi} \frac{\Gamma}{E^2 + \Gamma^2}. \quad (2)$$

Γ is related to the core-hole lifetime τ by

$$\Gamma = \hbar / \tau. \quad (3)$$

The self-convolution in Eq. (1) obscures much of the detail in $N(E)$. This detail is recovered in part by plotting the derivative of $N_{\beta}(E)$,

$$\frac{dN_{\beta}(E)}{dE} = \frac{dN(E)}{dE} * N(E) * \rho(E + E_B). \quad (4)$$

To the extent that $dN(E)/dE$ is dominated by the Fermi discontinuity, it can be approximated by a delta function

$$\frac{dN(E)}{dE} \simeq N(E_F) \delta(E), \quad (5)$$

where $N(E_F)$ is a constant determined by the density of states at the Fermi level. With this substitution, Eq. (4) can be integrated to yield

$$\frac{dN_{\beta}(E)}{dE} \simeq N(E_F) [N(E) * \rho(E + E_B)]. \quad (6)$$

Thus the derivative of the electron-excitation function should resemble the one-electron density of unfilled states broadened by the core-hole lifetime. This approximation

is best for free-electron-like metals. For transition metals $N(E)$ exhibits a strong peak at E_F , resulting in a derivative spectrum that exhibits a pronounced undershoot following the threshold peak.

The Ti coverage was calibrated by identifying breaks in the slope of plots of the Ti Auger yield as a function of deposition time. These breaks have been shown to correspond to completion of the first and second monolayers (ML).⁵ Similar breaks could be detected in the decrease of the Cu Auger yield from the substrate (Fig. 1).

III. TITANIUM EPITAXY

Although the AES results indicate that the Ti film grows layer by layer, new LEED beams due to the Ti are not observed until the coverage reaches about 6 ML, at which time the pattern is characteristic of the Ti(0001) basal plane. The Ti LEED pattern has the same orientation as the Cu pattern, and the length of the Ti reciprocal-lattice vector is 0.9 times as large as for Cu. This is in good agreement with the relative near-neighbor distances in Cu (2.56 Å) and Ti (2.89 Å). The Ti LEED beams are diffuse when they first appear, but sharpen up rapidly with increasing thickness. At coverages below 6 ML the Cu(111) LEED pattern is gradually extinguished, and no distinct Ti diffraction features are observed, indicating that the Ti film is poorly ordered rather than pseudomorphic with the Cu(111) substrate. Presumably, the relatively large lattice mismatch of the Ti and Cu does not allow long-range order to form in the initial layers of Ti even though layer-by-layer growth occurs. This could re-

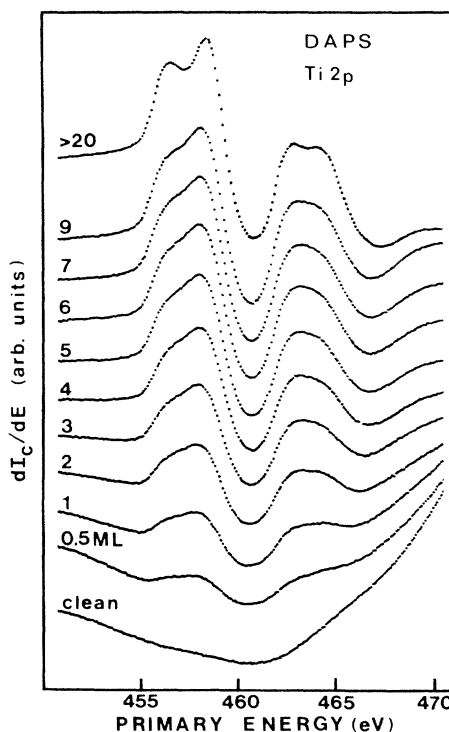


FIG. 2. Series of first-derivative disappearance-potential spectra of Ti 2p levels showing the development of Ti(0001) surface states with overlayer thickness.

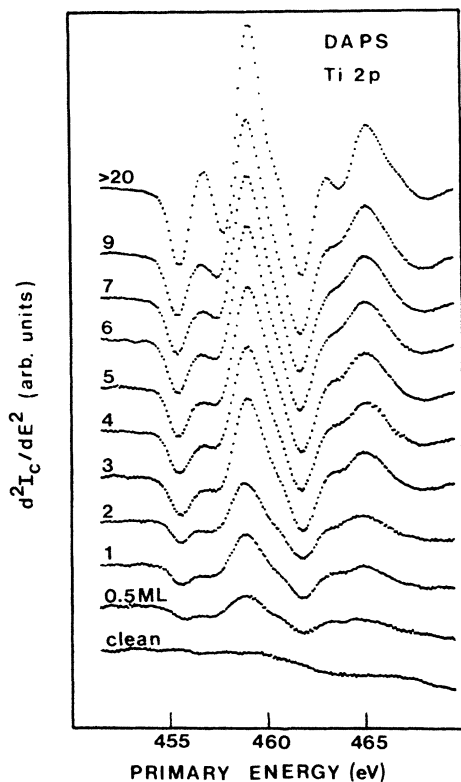


FIG. 3. The second-derivative spectra for the same overlayer thicknesses as shown in Fig. 2.

sult in a large number of vacancies in the first layers of Ti.

From plots such as those shown in Fig. 1, one can calculate the mean escape depth of electrons in Ti films. From separate determinations with deposition rates varying from 1 ML in 9 min to 1 ML in 2.5 min the mean escape depth of 58–61 eV electrons was calculated to be 1.95 ± 0.7 ML. The relatively large variation is believed to be due to deposition rate dependent perfection of the film. Similarly, from the overlayer Auger signal, a value of 1.9 ML was determined for the mean escape depth of 418 eV electrons in Ti. In this case the saturation value of the Ti signal strength must be measured and the result is based on one such measurement.

The Ti $2p_{3/2}$ appearance-potential spectrum was scanned repeatedly as Ti was deposited, as shown in Fig. 2. The region of the spectrum scanned shows both the $2p_{3/2}$ and the $2p_{1/2}$ excitation edges. Features in the $2p_{3/2}$ spectrum are somewhat better resolved than in the $2p_{1/2}$ because of the greater lifetime of the $2p_{3/2}$ hole. For films more than 20 ML thick, the spectrum exhibits double peaks. As Jonker *et al.* have demonstrated,² the first (lower-energy) peak corresponds to the unfilled surface states and the second peak to the unfilled $3d$ states of bulk Ti. Although the surface states apparent in Fig. 2 are not fully resolved for thinner films, they are clearly evident as shoulders down to the smallest coverages of only a fraction of a monolayer of Ti. This is even more evident in the second-derivative appearance-potential spectrum, as shown in Fig. 3. It is seen from this figure that the relative contribution of the surface states to the spectrum changes very little with coverage.

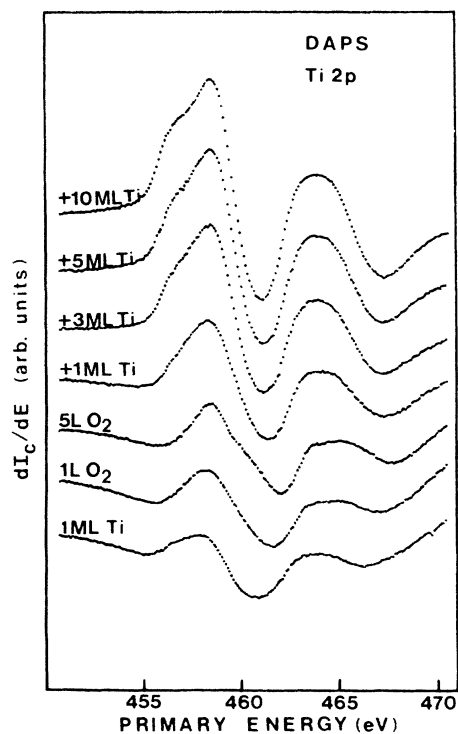


FIG. 4. Effect of oxygen on the Ti(0001) surface state. Beginning with the bottom spectrum, 1 ML of Ti is deposited on the clean Cu(111) surface. Exposure to only 1 L of O_2 destroys the surface state shoulder of the first-derivative disappearance-potential spectra spectrum and a spectrum typical of surface containing oxide is seen at 5 L of O_2 . When more Ti is deposited on this oxygen-exposed surface, the spectrum soon returns to that of a clean overlayer with corresponding thickness.

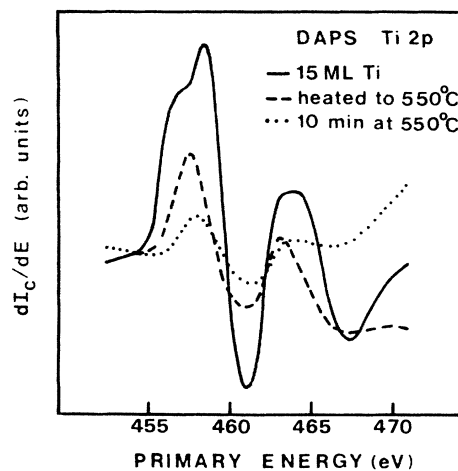


FIG. 5. Effects of heating on the disappearance-potential spectrum of Ti $2p$ levels for a 15-ML Ti layer on the Cu(111) surface. Alloying achieved by heating to 550°C destroys the surface state and shifts the curve maximum to lower energies. Further heating decreases the signal and shifts the threshold to higher energies.

The existence of a band of surface states for submonolayer quantities of Ti is an unexpected result. Even more unexpected is that for films of a monolayer or less, the spectrum should exhibit both peaks: that associated with surface states and the second peak which is normally associated with the bulk.

It was also observed by Jonker *et al.* that exposure of the Ti to small amounts of oxygen suppressed the surface states while leaving the bulk peak essentially unaffected.² The present study found essentially the identical result for thick Ti films (>20 ML). It was not, however, clear what to expect in the case of Ti films only one monolayer thick. The result is shown in Fig. 4. Exposure to 1 L ($L = \text{langmuir} = 10^{-6}$ Torr sec) of oxygen effectively eliminates the shoulder associated with the surface states, while having little effect on the "bulk" peak. By 5 L exposure, a new feature is beginning to develop on the high-energy side of the main peak, indicative of the formation of TiO_2 . If additional Ti is now deposited over the oxidized film, the surface states are quickly reestablished.

IV. ALLOY FILMS

Ti and Cu alloy readily, with at least three intermediate phases at Ti_2Cu , TiCu , and TiCu_3 .⁶ The composition of the last phase is also referred to as Ti_2Cu_7 .⁷ It might be expected that the initial layer of Ti would react with the Cu substrate to form a surface alloy. There is, however, no indication of this in the Ti $2p_{3/2}$ appearance-potential spectrum following deposition at room temperature which exhibits only very gradual changes as the thickness of the Ti film is increased. If, however, the Ti covered sample is heated, alloying readily takes place, as evidenced by the reappearance of Cu in the Auger spectrum. Two cases were observed depending on the heating temperature. At 400–450°C the final intensity ratio of Cu (58–61 eV) to Ti (418 eV) Auger signal was ≈ 2.2 , while heating to 550°C produced a phase for which the same ratio was ≈ 5 . Extended heating (≤ 20 min) further increased the ratio to ≈ 8 at 550°C, but at 400°C the Auger signals were nearly stabilized. The same trend can also be seen in the

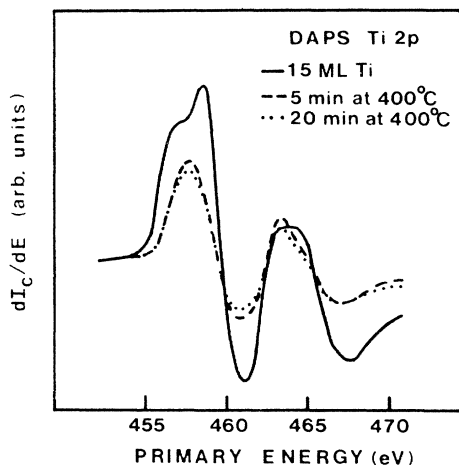


FIG. 6. Effects of heating at 400°C on the disappearance-potential spectrum of Ti $2p$ levels for a 15-ML Ti layer on a Cu(111) surface.

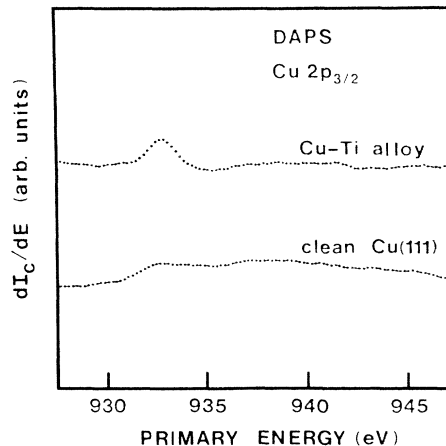


FIG. 7. Comparison of Cu $2p_{3/2}$ disappearance-potential spectrum for a clean Cu(111) surface and for a Ti-Cu surface alloy prepared by heating at 550°C. The clean surface spectrum shows only a weak steplike edge. The shape of the alloy spectrum indicates the existence of d -band holes at the Cu sites.

corresponding appearance-potential spectra (Figs. 5 and 6). Gershinskii *et al.*⁸ have investigated reactive diffusion in Cu-Ti thin-film systems and concluded that with an excess of Cu only TiCu and Ti_2Cu_7 compounds are formed. Liotard *et al.*⁹ have studied thin-film bilayers of Ti and Cu and found sequential formation of TiCu and TiCu_3 . Based on these results we believe that the intermediate phases produced were TiCu at lower temperatures [400°C and TiCu_3 (or Ti_2Cu_7) at higher temperatures ($\geq 550^\circ\text{C}$)]. The increase of Cu with annealing time at 550°C can be explained by the solubility of Cu in TiCu_3 .⁹ As shown in Figs. 5 and 6, the Ti $2p$ appearance-potential spectra are markedly different for the alloyed films. The low-energy peak, corresponding to the unfilled surface states, disappears entirely in the alloyed films. There is also some difference between the two phases: the Ti $2p$ spectrum

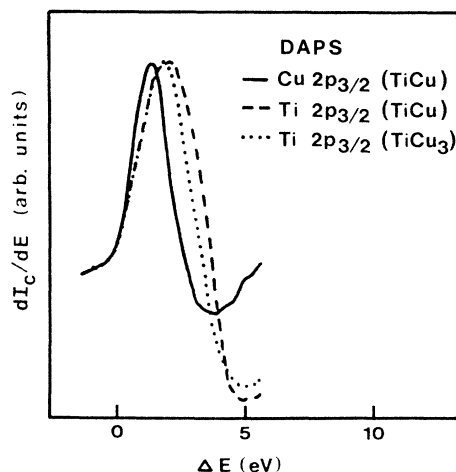


FIG. 8. Comparison of Ti $2p_{3/2}$ and Cu $2p_{3/2}$ disappearance-potential spectra for Ti-Cu surface alloys. The spectra have been shifted in energy so that thresholds are aligned, thus ΔE is the energy above threshold. The peak heights after the threshold are normalized to the same height. The Ti spectra are broader than the Cu spectrum and the negative dip in the Ti spectra is deeper than in the Cu spectrum.

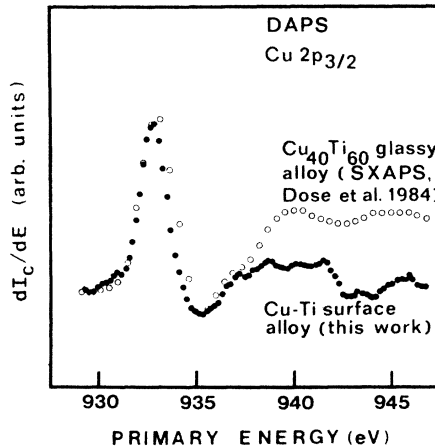


FIG. 9. Comparison of Cu $2p_{3/2}$ appearance-potential spectra for a Cu-Ti surface alloy prepared by heating at 550°C and for a Cu-Ti metallic glass (Ref. 12). The surface alloy showed an ordered LEED pattern with the same symmetry and orientation as Cu(111) and lattice constant near that of Cu.

from TiCu_3 is sharper and somewhat narrower than for TiCu (Fig. 8). As the surface gets more Cu rich, a decrease in the appearance-potential signal of Ti is seen, together with a slight shift of the spectrum to higher energy (Fig. 5).

The change in the Cu $2p_{3/2}$ appearance-potential spectrum as compared with that of the clean Cu(111) surface is even more dramatic, as shown in Fig. 7. Pure Cu, for which the d band is filled, exhibits only a step at the $2p_{3/2}$ threshold, corresponding to the s - p states. For the alloy film, however, the Cu spectrum exhibits a distinct threshold peak characteristic of the $3d$ transition elements, indicating that in the alloy there are d -band holes on the Cu sites. A comparison of the Cu $2p_{3/2}$ spectrum with that of the Ti $2p_{3/2}$ spectrum in the alloys, as shown in Fig. 8, shows that the Cu d -band peak is somewhat narrower than the d -band peak for Ti in the alloys, in contrast to the earlier work of Houston and Park on Ti-Ni alloy films, in which case the d -band peaks were nearly identical.⁴

The Cu spectrum obtained in the present study for a Ti-Cu alloy is very similar to the soft x-ray appearance-potential spectrum obtained by Dose *et al.*¹⁰ for a $\text{Cu}_{0.40}\text{Ti}_{0.60}$ glassy alloy (Fig. 9). Although no attempts were made here to derive the local density of states

(LDOS) from the disappearance-potential spectra, the results support the hybridization model of transition-metal-alloy states¹⁰⁻¹² and also the idea that the LDOS are similar in glassy and ordered alloys.¹²

Very pronounced changes in the Ti $2p$ spectrum as a result of alloying would seem to be strong evidence that the Cu-Ti bond in the case of monolayer films of Ti is very different from the bond in the alloy.

V. CONCLUSIONS

Although, based on the AES results, the growth of Ti on a Cu(111) surface appears to be layer by layer for the initial layers, there is no evidence of an ordered film until LEED beams characteristic of the basal plane of Ti appear at approximately 6 ML. As growth is continued beyond 6 ML, the ordering of the film improves, as evidenced by sharpened diffraction beams.

The $2p_{3/2}$ appearance-potential spectrum of the thick, ordered film exhibits two distinct peaks as previously reported for bulk Ti samples.² The low-energy peak corresponds to that portion of the band of surface states that extends above the Fermi level, and the second peak is associated with the unfilled d -band states of the bulk. Remarkably, however, although not fully resolved, both features are in evidence down to coverages of less than 1 ML. Exposure of the Ti film to oxygen shows that the surface peak is readily extinguished as previously reported.

Heating the Ti film to 400 – 550°C results in alloying with the Cu substrate leading to surface layers with probable compositions TiCu and TiCu_3 . The Cu atoms apparently donate electrons in the alloys, with the result that d -band holes appear on the Cu sites, as evidenced by the development of a distinct d -band peak in the Cu $2p_{3/2}$ appearance-potential spectrum of the alloys. The Ti $2p_{3/2}$ spectrum of the alloys exhibits only a single peak in contrast to the Ti spectrum for monolayer and submonolayer films, indicating that the nature of the Cu-Ti bond for adsorbed Ti atoms is distinctly different from bonding in the alloys.

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