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Structural and electronic properties of a surface alloy of Pd and Cu on Cu{001}

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The $c(2\times2)$ surface phase obtained from deposition of submonolayer amounts of Pd onto a clean Cu{001} surface is proven to have a top layer consisting of an ordered 50%-50% mixture of Pd and Cu atoms, and no ordered content in deeper layers, analogous to the structure found for Cu{001}$c(2\times2)$-Au. The structure of the top layer is almost planar, with the Pd atoms located 0.02 ± 0.03 Å outwards from the Cu atoms, and an interlayer distance from the Cu atoms to second (100% Cu) layer equal to the Cu{001} bulk interlayer spacing (1.807 Å). Angle-resolved photoemission spectra show that the valence band of the surface alloy is characterized by a well-defined Cu $3d$-derived band and by the appearance of features due to Pd. The narrower width of the observed photoemission peaks compared with the valence band of Cu-rich Cu-Pd alloys studied by others confirms the ordered-alloy nature of the Cu{001}$c(2\times2)$-Pd surface phase.

We report here the identification of a surface phase obtained from room-temperature deposition of Pd on Cu{001}, denoted Cu{001}$c(2\times2)$-Pd, as a surface alloy. This is only the second such alloy identified with reasonable certainty on the basis of quantitative structure analysis.

We define an (ordered) surface alloy as the result of a reaction between chemisorbed metal atoms and substrate metal atoms that leads to an ordered *mixed* layer (as opposed to an *over*layer) with no deep penetration into the bulk. There is, to date, only one reported case of quantitatively proven surface-alloy formation—the case of Cu{001}$c(2\times2)$-Au.[1] This phase had originally been studied by Palmberg and Rhodin,[2] who reported its formation and suggested that it may consist of a mixed layer on the ground that it was "difficult to see how (overlayers of Au on Cu) could be stable." Although Fujinaga[3] and later Graham[4] found this suggestion consistent with their own studies of Cu{001}$c(2\times2)$-Au, no quantitative analysis of the atomic structure of this phase was done until the low-energy electron diffraction (LEED) work of Wang *et al.*[1] This work proved the mixed-layer character of the surface phase and established that the mixed layer is buckled, with the Au atoms located about 0.1 Å outwards from the Cu atoms. This result proved helpful to the work of Hansen *et al.*,[5] who could attribute the striking changes observed with increasing temperature in the valence band of Au/Cu{001} to the formation of the surface alloy. It also proved useful to the theoretical calculation of Foiles,[6] who used the embedded-atom method to predict that Au should form mixed layers rather than overlayers on Cu surfaces. In accordance with the LEED results of Wang *et al.*,[1] Foiles found that incorporation of Au adatoms into a Cu{001} surface is energetically favored; that the mixed layer should be rippled with the Au atoms residing above the Cu atoms; and that the compositionally *ordered* surface layer of Au and Cu should exist in thermal equilibrium with a compositionally *disordered* bulk Cu containing dilute amounts of Au.

It appears reasonable to ask whether or not the phenomenon of surface-alloy formation is unique to the case of Au on Cu, and occurs solely because of the large affinity of Au for Cu and the ability of Au atoms to contract laterally when positioned in a surface environment. (The Au atom radius in Cu{001}$c(2\times2)$-Au obtained from near-neighbor distance and the Cu bulk radius is 11.2% contracted from the bulk Au radius, but in Cu_3Au the Au radius is contracted 4.3%.) The study reported here of the Cu{001}$c(2\times2)$-Pd structure reveals that the case of Pd on Cu is similar (the Pd atom radius in Cu{001}$c(2\times2)$-Pd is contracted 7.1% from the bulk Pd radius) albeit with some interesting differences. We note that both Fujinaga[3] and Graham[7] had suggested the likelihood of a mixed layer similar to the Au-Cu counterpart, although Auger electron spectroscopy (AES) had indicated that the surface may consist of a complete Pd layer.[7] We give below a brief description of our experimental procedures and of the results of our LEED analysis and ultraviolet photoemission spectroscopy (UPS) observations.

A clean Cu{001} surface was prepared *in situ* with a series of argon-ion bombardments (5×10^{-5} torr, 500 eV, 8 μA/cm^2) of 20-min duration, followed by annealing treatments at 600 °C for 10 min. Pd was deposited on the unheated CU{001} surface from a source consisting of a Pd ribbon wrapped in a Ta foil heated electrically to about 1000 °C. The deposition rate was calibrated in units of surface coverage by monitoring the linear increase of the (doubly differentiated) Pd AES line at 330 eV.

The LEED pattern was observed to change continuously from the 1×1 characteristic of the clean Cu{001} surface to a weak $c(2\times2)$ at a Pd coverage of about 0.5. The $c(2\times2)$ pattern remained then observable up to a coverage of about 2, but was best, in terms of sharpness and contrast, at a coverage of about 0.8, in excellent agreement with the observations of Graham.[7] The background in the LEED pattern increased monotonically with Pd deposition and was very high at a coverage of 2 or more.

LEED intensity data were collected with a television-camera-microcomputer system[8] at two angles of incidence, $\theta = 0°$ and $\theta = 10°$, $\phi = 0°$, including 9 (equivalent to four nondegenerate) integral-order and 4 (2 nondegenerate) fractional-order spectra. The calculations of expected LEED intensities were done with the CHANGE computer program,[9] with Moruzzi-Janak-Williams potentials[10] for both Cu and Pd, with 8 phase shifts and 45 beams. Two structural models were tested: (i) an overlayer of Pd atoms located on the fourfold hollows of the Cu{001} surface on a $c(2\times2)$ net, the Pd-Cu interlayer distance varying from 0.174 to 2.14 Å in steps of 0.05 Å (the calculated hard-sphere distance is 1.94 Å); (ii) a mixed top layer of alternating Pd and Cu atoms which was assumed to be either planar or buckled, the distance between this top layer and the second (100% Cu) layer varying from 1.607 to 2.007 Å in steps of 0.05 Å (bulk value 1.807 Å). The detailed analysis, involving both visual and r-factor[11] evaluation of the correspondence between calculated and observed intensity curves, will be reported elsewhere. We state here the results: the best-fit structure is an almost-planar mixed layer, the Pd atoms being located 0.02 ± 0.03 Å outwards from the Cu atoms, and the distance between the top mixed layer and the second (all Cu) layer being equal to the bulk interlayer distance of Cu along ⟨001⟩ (1.807 Å). Figure 1 exemplifies the fit of theory to experiment for three spectra at normal incidence. Thus, the LEED analysis proves quantitatively and for the first time that the Cu{001}$c(2\times2)$-Pd phase is a surface alloy and not an overlayer.

There are two immediately obvious differences between the Pd-Cu and the Au-Cu surface alloys investigated so far. One difference is structural (the Pd alloy is practically planar while the Au alloy is buckled) and the other is compositional (the Pd-Cu surface alloy requires an excess of Pd for its complete formation, so that some Pd atoms are expected to reside either above or below the alloy plane, as noted by Graham[7] as well, while the Au-Cu surface alloy has the expected stoichiometry).

Angle-resolved UPS studies provide qualitative confirmation of the LEED results. The UPS experiments were carried out on beamline U7 of the National Synchrotron Light Source with photon energies ranging from 12.5 to 130 eV. Two samples were used in the experiments: one of Cu{001} and one of Pd{001}, the former to demonstrate the changes that may occur in the valence band of Cu as a consequence of the formation of the surface alloy, the latter to provide comparison between clean Pd{001} and the surface alloy. We superimpose in Fig. 2 the electron distribution curves (EDC) after background subtraction as obtained for normal emission from clean Cu{001} (dashed curve), from clean Pd{001} (dash-dotted curve), and from Cu{001}$c(2\times2)$-Pd (solid curve) with photon energy 17 eV. The surface alloy EDC shows a central peak at −3 eV that corresponds to the main peak of clean Cu{001} shifted downward in energy by about 0.3 eV. This identification is supported by the observation that intensity and dispersion of this peak are similar to those in clean Cu{001} and by the resemblance of the spectrum to that of clean Cu{001} for 130-eV photons, for which the ionization cross section of Pd is a minimum.[12] The surface alloy EDC in Fig. 2 exhibits also peaks at −1.7 and −4.8 eV. The peak at −1.7 eV is clearly due to the presence of Pd, since it is absent in clean Cu{001}; the peak at −4.8 eV is also attributed to Pd by Rao *et al.*[13] However,

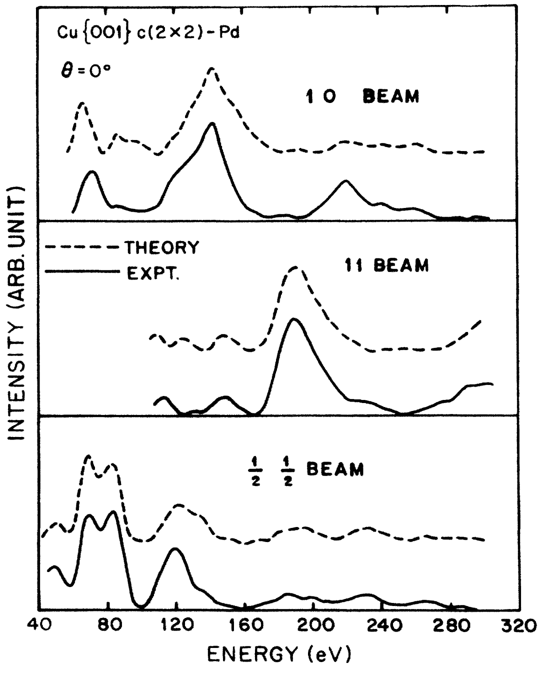

FIG. 1. Normal-incidence experimental and theoretical LEED spectra from the surface alloy Cu{001}$c(2\times2)$-Pd.

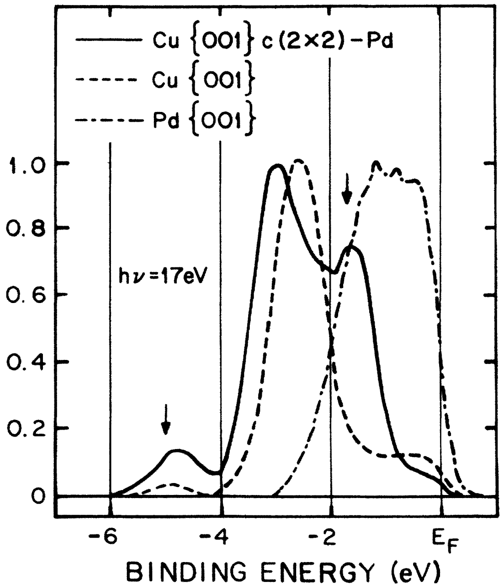

FIG. 2. Angle-resolved electron-distribution curves (background subtracted) for normal emission from Cu{001} (dashed), Pd{001} (dash-dotted), and Cu{001}$c(2\times2)$-Pd (solid) obtained with 17-eV photons. The arrows point to the positions of the Pd-derived bands as calculated by Rao *et al.* (Ref. 13).

we note that our clean Cu{001} spectrum also has a peak at the same energy, which is missing in the data of Ref. 13. A peak around 5 eV in Cu{001} is present in the data of Ilver and Nilsson,[14] and has been shown to have the angular variation and dispersion with photon energy predicted by band theory,[15,16] but Ilver and Nilsson's data were not taken at normal emission. The data of Stöhr *et al.*,[17] which *were* taken at normal emission, exhibit no peak around -5 eV for energies between 32 and 60 eV. In some of our data the peak at -4.8 eV is slightly enhanced by the presence of Pd so that we cannot rule out a possible contribution from Pd to the emission at -4.8 eV, as suggested by Rao, Bansil, Asonen, and Pessa.[13]

Finally, we note that the Cu and Pd peaks in the surface alloy of Fig. 2 (for 17-eV photons) are narrower than those found for the disordered bulk alloy in Fig. 6 of Ref. 13 (for Ne I 16.85-eV photons), suggesting consistency with the ordered structure for the surface alloy as determined by LEED in the present work.

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