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Pd on Cu(111) studied by photoelectron diffraction

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Abstract

The PdCu alloy system, which has important catalytic properties, has been the subject of many experimental and theoretical studies using a large number of different techniques. Theoretical and experimental structural studies converge in predicting ordered alloys for the Pd/Cu(110) and Pd/Cu(100) surfaces. No such agreement exists for the Pd/Cu(111) surface, however; indeed, few structural studies have been performed for this surface. Here, we report the first application of X-ray photoelectron diffraction (XPD) (using synchrotron radiation) in combination with LEED to determine the structure of ultra-thin epitaxial Pd films (\sim 1 ML) evaporated on Cu(111) single crystal surfaces. The analysis of the data was performed with the multiple scattering diffraction program of Chen and Van Hove. For the preparation condition used, a random surface alloy seems to form in the first three layers. The first interlayer distance expands whereas the second seems to contract. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last decade surface alloys systems have attracted a great deal of attention. We can distinguish two classes of bimetallic surface alloys formed by depositing B atoms onto a surface of metal A. The first class corresponds to combinations of metals that are immiscible in the bulk [1]. In this case, the alloy is restricted to the outermost layers of the A solid and this type of surface alloy represents a true equilibrium configuration [2]. The formation of this type of surface alloy depends on a series of factors such as: type and concentration of elements, temperature, and geometry of the surface. The second class of surface alloy comprises those metals that exhibit bulk solubility, often forming a series of solid solutions over a wide compositional range. Single and multilayer surface alloys have been observed for both of these classes [3].

Surface alloys are important in applications such as that of heterogeneous catalysis, where the electronic structure and geometric arrangement of the surface atoms strongly influence the reaction. A deeper understanding of the physical and chemical phenomena associated with the creation of surface alloys appears to be essential in order to

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further progress in catalysis [4]. To date, the crystallographic structures of relatively few surface alloys have been determined [3].

Studies of the properties of the PdCu system have been motivated by its important commercial applications as a catalyst in such reactions as the oxidation of CO and alkenes [5], and the hydrogenation of such organic substances as benzene and toluene [6]. It also shows promise as a catalyst for the reduction of NO and oxidation of CO by the reaction $2CO + 2NO \rightarrow 2CO_2 + N_2$ [7], which is of great interest to the automotive industry. PdCu surface alloys exemplify the second class of surface alloy described above. Recently, various studies of PdCu surface alloys have aimed to elucidate the growth and formation mechanisms [2,8–15]. These studies usually involve a Cu crystal substrate cut along one of the low index planes upon whose surface Pd is evaporated in small quantities. The different planes present distinct properties and the growth of the Pd films differs for each direction.

For example for Pd/Cu(100) and Pd/Cu(110), experimental studies [2,8–13] demonstrate the formation of an ordered surface alloy, in agreement with theoretical predictions [14–18]. The situation for Pd on Cu(111) is somewhat different, however. Available experimental evidence from scanning tunneling microscopy (STM) [19,20] indicates substitutionally disordered superficial alloying, in contrast with theoretical predictions of ordered phases from total energy calculations [21]. Since structural studies of Pd on Au(111) have elucidated some of its catalytic properties [22], it appears, therefore, that a careful structural study of the Pd/Cu(111) is indicated.

In this paper, we report atomic structure determination from X-ray photoelectron diffraction (XPD) using synchrotron radiation and LEED for 1 ML of Pd evaporated on Cu(111). These results, which are part of a larger study, indicate that, even at temperatures under 600 K, Pd incorporates itself into the first three surface layers of the Cu crystal and forms a substitutional random alloy. The interlayer distances as well as the concentrations exhibit an oscillatory behavior. These findings are consistent with the results of STM studies [20] and indicate the utility of XPD even in studies of random alloys.

2. Experimental methods and data analysis

The experiments used a bending magnet beam line and the Spherical Grating Monochromator (SGM) [23] at the Brazilian Synchrotron Radiation Laboratory (LNLS). The measurements were performed with a surface analysis system which is equipped with LEED optics, a fixed geometry high resolution hemispherical electron analyzer (Omicron HA125HR with multi-detection) mounted in the plane of the storage ring, a differentially pumped argon ion sputter gun for in situ sample cleaning and a two axis (θ, ϕ) sample manipulator equipped for heating the sample to 1300 K by electron bombardment. A base pressure of $1 \times$ 10⁻¹⁰ Torr was maintained. The sample was rotated through polar and azimuthal angles during the angular scans reported.

The electro-polished 10 mm diameter Cu(1 1 1) crystal was mounted on a thick Ta foil support that could be aligned by three set screws. The backside of the crystal could be bombarded directly by an electron beam (20 mA, 1.5 kV) for heating. With the manipulator mounted in the system the sample was aligned precisely with a He–Ne laser so that its surface plane was normal to the axis of the electron analyzer (the alignment was also verified after the system was baked and always varied less than 2°).

Sample cleaning was done by argon ion bombardment (1 kV) and annealing until no impurities could be observed with XPS using AlK α radiation. After cleaning, the sample was annealed to get a sharp LEED pattern. The LEED pattern, apart from allowing us to check crystallinity, also permitted us to determine precisely the initial azimuthal angle so that the XPD azimuthal angular scans always started from exactly the same orientation relative to the analyzer.

The Pd film was deposited on the room temperature substrate at a rate of approximately 0.25 $ML \min^{-1}$ from the tip of a Pd wire heated by electron bombardment. We estimated the final thickness to be one monolayer by using the areas of the Pd 3d and Cu 3p photoelectron peaks, by supposing the growth to occur layer by layer, and by applying a well-known approximation [12] relating the intensities and the evaporated thickness.

The validity of this approximate thickness depends on the validity of our suppositions. Since the Cu—Pd bond has a lower energy than Pd—Pd and Cu—Cu the supposition of layer by layer growth is probably valid and we feel that our other approximations are reasonable.

The XPD data was measured in the angular mode, by varying the azimuthal angle (ϕ), in steps of 3° over a range of almost 150°. Since Cu(111) has threefold symmetry, this procedure assured us that we measured all the structures. The polar angle (θ) , defined by the analyzer axis and the normal to the surface, was varied in 5° steps from 15° to 55° (we made no measurements for $\theta \approx 50^{\circ}$). The analyzer's axis subtended an angle of 60° relative to the propagation direction of the photon beam, so that the electric polarization vector of the radiation was at 30° to the analyzer axis. The exciting photon's energy was 700 eV, which was high enough to ensure a good degree of forward focusing. The intensity of the radiation was monitored by a high transmission Au grid positioned in front of the analysis chamber and the data was normalized appropriately. The evaporated films were annealed at 600 K for 1 min. After a full angular scan, we verified the absence of such contaminants as C, O and N.

In order to analyze our data we tested various model clusters with the MSCD [24] computer code, comparing the experimental and theoretical values of the conventional quantity χ , which is defined as:

$$\chi(K,\theta,\phi) = \frac{I(K,\theta,\phi) - I_0(K,\theta,\phi)}{I_0(K,\theta,\phi)}$$
(1)

where $I(K, \theta, \phi)$ represents the area of the Pd 3d photoelectron peak as a function of the angles θ and ϕ and the kinetic energy K and $I_0(K, \theta, \phi)$ denotes a background equal to the free atomic photoemission cross-section. Because I_0 varies slowly at the energies for which we make the measurements, we make little error if we approximate I_0 as the smooth part of I in the energy scans. For the azimuthal angle scans, I_0 is constant and we replace it by the average of the intensities [24]. The degree of agreement between experiment and theory was quantified by considering the reliability factor R_a , defined as:

$$R_{a} = \sum_{i} \frac{(\chi_{c}^{i} - \chi_{e}^{i})^{2}}{(\chi_{c}^{i})^{2} + (\chi_{e}^{i})^{2}}$$
(2)

where χ_c^i and χ_c^i are, respectively, the calculated and experimental values of χ . From its definition, it is clear that the smaller the R_a factor, the better the agreement with experiment.

In our analysis, we used clusters of approximately 216 atoms with radius of 10 Å and depth of 12 Å (five layers) [24]. We permitted up to 10 multiple scatterings and fourth order in the Rehr-Alber expansion [24]. Since there was no reason to suppose an ordered alloy a priori, the MSDC package was modified [25] to be able to treat random alloys. Two different methods were applied for the random alloy case. In the first method, we tested many different, randomly selected ensembles of Pd and Cu atoms, and constrained each ensemble to have the required concentration. The second method we implemented was based on the Average T-Matrix Approximation (ATA) where each lattice site is occupied by an atom whose atomic scattering amplitude is equal a weighted combination of those of Pd and Cu. We have shown elsewhere that both methods produce very similar results [25]. Since the first method is very computationally time consuming, the results we present here were calculated using the ATA.

3. Results and discussion

In Fig. 1, we exhibit a typical LEED pattern from a 1 ML Pd film deposited on the Cu substrate. The LEED pattern is very similar to that of pure Cu, and displays no sign of any kind of superstructure, which would seem to indicate three possibilities: either we have a first layer of Pd with the same structure as that of the Cu(111) substrate, or the Pd has diffused into the substrate, leaving an outer layer of pure Cu(111), or the Pd has formed a random substitutional alloy. In the last case, the only effect on the LEED pattern would be an increase in the diffuse background.

To determine which of these three possibilities describes the Pd/Cu(111) system, we measured XPD intensities from Pd 3d emission over a wide range of polar and azimuthal angles. In Fig. 2(c),



Fig. 1. LEED patterns for normally incident primary electrons of 90 eV energy. (a) Clean Cu(111) and (b) approximately 1 ML of Pd on Cu(111) annealed at 600 K for 1 min.

we present a planar projection of the data taken with photons of energy 700 eV. The variables used in the projection are defined by $x = \theta \cos(\phi)$, $y = \theta \sin(\phi)$ and $z = \chi(\theta, \phi, K)$ converted into a gray scale (since we did not measure data for $\theta \approx 50^\circ$, the intensity which appears in Fig. 2(c) for this angle is an artifact of the smoothing procedure of our plotting program). In Fig. 2(a) and (b), respectively, we present simulated patterns for 700 eV photons corresponding to the first two possibilities mentioned above. Fig. 2(a) represents a pure Pd first layer, and Fig. 2(b) corresponds to a Cu(1 1 1) capping layer on top of the Pd layer (i.e.,



Fig. 2. Planar projections of photoelectron diffraction (as described in the text) from Pd 3d emission excited with 700 eV photons. (a) Theoretical simulation of a 1 ML Pd(111) surface layer in perfect registry with the Cu(111) substrate, (b) theoretical simulation of Cu(111) capping layer (Cu(111)/Pd(111)/Cu(111)) and (c) raw experimental data.

a Cu/Pd/Cu(111) sandwich); in both cases, the Pd layer has the structure of the surface of a truncated Cu(111) crystal. It is clear that Fig. 2(a), a pure Pd top layer, is completely incompatible with the experimental data (application of the analysis described below yielded $R_a = 1.01$). In the case of Fig. 2(b), corresponding to a Cu capping layer, the main features at $\theta = 34.8^{\circ}$, which correspond to scattering of photoelectrons emitted by Pd atoms in the second layer by the nearest three atoms in the first layer, are quite similar to experimental features in Fig. 2(c). On closer examination, however, many secondary structures (such as those for $\theta \approx$ 20° and 45°) are missing. We applied the analysis described below to the Cu capping layer model and the agreement with experiment achieved was very poor ($R_a = 0.53$): in Table 1, we summarize the parameters from the analysis using the Pd overlayer and Cu capping layer models. These results encourage us to discard the first two possibilities and lead us to consider further the third possibility, that Pd forms a random surface alloy on Cu(111). We should note that discrepancies for $\theta \approx 50^{\circ}$ between the pattern in Fig. 2(c) and that in Fig. 2(b) are not significant because we did not measure intensities for this angle.

From our discussion of the LEED patterns in Fig. 1, we conclude that the Pd atoms occupy the Cu matrix randomly. We used the ATA method to calculate the Pd 3d XPD intensities as functions of azimuthal angle and determined the layer concentrations and the interatomic distances in two steps: first, we fixed the interatomic distances at those of bulk Cu and minimized the R factor for all the experimental polar angles as a function of the concentrations in all the layers we use to model

the Pd diffusion; then, we fixed the concentrations at those values found in the first step and again minimized the R factor as a function of the interatomic distances.

Here, we discuss two models with optimized concentrations and interatomic distances. The first, or model one, corresponds to Pd occupation of the first two layers and the second, or model two, treats Pd occupation of the first three layers.

For model one, the minimum in the R factor corresponds to Pd concentrations of 20% in the first layer and 70% in the second; the optimized planar lattice constants are those of Cu(111). In Table 1, we present the parameters used with model one.

In Fig. 3, we present comparisons between the experimental and theoretical azimuthal scans for model one (light line) for six polar angles. For each polar angle, we display the corresponding individual *R* factor (R_{a1}). Despite the relatively low mean *R* factor (0.23 ± 0.09) the theoretical intensities for model one described the experimental data poorly for some angles, especially for $\theta = 20^{\circ}$, 40° and 45° .

Because of the poor agreement of the model intensities with experiment exhibited in Fig. 3, we allowed for the possibility of diffusion of Pd into the third layer (i.e., model two). Here, the *R* factor was minimized for Pd concentrations of 20%, 70% and 20% in the first, second and third layers, respectively. Once we determined the concentrations in the three layers, we made the final determination of the structural parameters for model two. In Fig. 4, we present a contour map of the *R* factors as functions of the interlayer distances: d_{12} , first to second layer and d_{23} second to third. From the contour

 Table 1

 Comparison of the final parameters for five models

Structure	R_a	d_{12} (Å)	Δd_{12} (%)	d_{23} (Å)	Δd_{23} (%)	$\theta_{\rm D}$ (K)	V_0 (eV)
Cu(111)	0.17	2.09	0	2.09	0	240	9.0
Pd overlayer	1.01	2.09	0	2.09	0	175	9.3
PdCu: capping layer	0.53	2.19	+5	2.07	-1	175	9.3
PdCu: model 1	0.23	2.20	+5	2.05	$^{-2}$	175	9.3
PdCu: model 2	0.16	2.20	+5	2.05	-2	175	9.3

The quantity R_a is the respective R factor. The symbols d_{12} and d_{23} denote, respectively, the spacings between the surface and second layers and between the second and third layers; the quantities Δd_{12} and Δd_{23} represent the respective percentage changes relative to the bulk Cu(111) layer spacing. The Debye temperature and inner potential are represented by θ_D and V_0 , respectively.



Fig. 3. Comparison of MSCD-ATA [25] simulations with experimental photoelectron diffraction azimuthal scans for Pd 3d photoemission excited with hv = 700 eV from Pd/Cu(111). Solid circles represent raw experimental data; light lines correspond to theoretical simulations for model one (see text), which involves Pd in the first two layers. Heavy lines are theoretical simulations for model two, which has Pd in three layers (see text). The parameters used for these two models are described in the text and in Table 1.

map, one obtains $d_{12} = 2.20 \pm 0.1$ Å and $d_{23} = 2.05 \pm 0.3$ Å, an 5% expansion of the first interlayer distance and an apparent 2% contraction of the second (although the large uncertainty should be noted). Bulk Cu values for the in plane interatomic distances produced a minimum in the *R* factor. We present the structural parameters for model two in Table 1. From comparison of models one and two, it is interesting to note that both models yield the same values for the interlayer spacings. It would appear, therefore, that extraction of interlayer distances from the XPD data is only weakly linked to the values of the layer Pd concentrations which optimize the fit to experiment.

The corresponding theoretical intensities for model two with optimized concentrations and dis-



Fig. 4. Contour map of R_a as a function of the first (d_{12}) and second (d_{23}) interlayer distances using model two (described in the text and Table 1), which involves Pd diffusion to the third layer. The region labeled "A" corresponds to the minimum in the *R* factor ($R_a = 0.1600$); regions "B" represent $R_a = 0.1615$. The increment from one contour to the next is 0.0015.

tances are also presented in Fig. 3, along with the corresponding individual *R* factor (R_{a2}). It is clear that inclusion of diffusion into the third layer greatly improves the overall agreement with experiment, especially for $\theta = 20^{\circ}$ and 40° . The mean *R* factor also decreases, to a value of 0.16 ± 0.01 . It was not possible to determine, from our data, whether there was any significant Pd concentration in the fourth layer.

In order to illustrate the significance of the agreement presented in Fig. 3, we display, in Fig. 5(a), comparison between theory and experiment for Cu 3p emission from a pure Cu(111) surface taken at two different polar angles (the theoretical interatomic distances were those of pure Cu(111)). The degree of agreement between theory and experiment for model two of Pd/Cu(111) in Fig. 3 is comparable with that achieved for pure Cu in Fig. 5.

We should note that the Cu 3p emission was not useful in determining the concentrations and the structural parameters for the alloy [25]. Fig. 5(b) shows that three very different structural models (i.e., model two above and two models involving only pure Cu, described in the caption of Fig. 5)



Fig. 5. Comparison of MSCD-ATA [25] simulations and experimental photoelectron diffraction azimuthal scans for Cu 3p emission. (a) Clean Cu(111): solid circles are raw experimental data (hv = 800 eV); the lines represent simulations using Cu(111) parameters described in the text. (b) 1 ML Pd on Cu(111): solid circles are raw experimental data (hv = 700 eV); heavy lines represent simulations for model two defined in the text ($R_{a2} = 0.229$); light lines are simulations for pure Cu(111) but using the structural parameters derived for the alloy ($R_a = 0.221$); dotted lines are simulations for Cu(111) with parameters of pure Cu(111) ($R_a = 0.24$).

exhibit the same degree of agreement with Cu 3p XPD for three different polar angles: the simulations are almost indistinguishable and the model R factors (in the figure caption) are almost identical. It is because of this insensitivity of the agreement between experimental and theory to the structural model used that we report XPD analyses only for Pd 3d emission.

In Fig. 6, we present theoretical and raw experimental planar projections. The theory corresponds to the parameters of model two. Comparison of the projections reveals that experimental features (such as those at $\theta = 20^{\circ}$ and 45°) which are absent in other models, such as that represented in Fig. 2(b), are present in Fig. 6(a), indicating the good agreement of model two with experiment.



Fig. 6. Planar projection of photoelectron diffraction in (as described in the text) of Pd 3d emission excited with photons of 700 eV. (a) Theoretical simulation of the random alloy cluster model two with three layers of diffused Pd (20/70/20%Pd) and (b) raw experimental data.

4. Conclusions

Using LEED in conjunction with XPD we have shown that the deposition of ~ 1 ML of Pd on the (1 1) face of Cu leads to the formation of random alloy at least three atomic layers thick. This result is very different from what happens on the (1 0 0) and (1 1 0) faces of Cu where the alloys formed are usually ordered, but it corroborates results from STM studies [20] where no long range order could be observed, despite a certain short range order. The Pd concentration appears to be oscillatory, the second layer having a higher Pd concentration than either the surface or third layers. The first interlayer distance appears to expand and the second seems to contract. The extracted values of the interlayer distances depend little on the values of the Pd concentrations in the layers for the models studied.

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