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Experimental evidence for room-temperature intermetallic compound formation at the Pd/Al interface

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The growth of Pd films on Al and Pd/Al interface formation were studied with use of ultraviolet photoemission spectroscopy (UPS) and low-energy ion scattering. At room temperature, the deposited Pd intermixes with the Al substrate and forms a thin surface alloy about 5 monolayers (ML) thick. Bulklike Pd states start to build up at E_F when the Pd coverage exceeds 4 ML. More than 8 ML of Pd are needed to completely cover the Al substrate and to fully develop the Pd metallic valence band. A Pd $4d$-derived band centered at 4 eV below E_F was observed both for monolayer Pd coverage on Al and for thick Al on Pd. It is argued that this deep-lying d band is due to the interaction between Pd and Al through the hybridization of the Pd d and Al s states.

INTRODUCTION

The electronic and geometrical structure of thin metal overlayers grown on chemically dissimilar metal substrates are mostly determined by the interaction with the substrate. In order to distinguish the effects of this overlayer-substrate interaction from effects derived from the reduced dimensionality, careful characterization is essential. In a series of recent studies,[1-3] Frick and Jacobi have argued that a Pd monolayer on Al(111) resembles an ideal free unsupported Pd monolayer due to the absence of strong d-d bonding between the overlayer and the substrate. The low-lying Pd d states centered at 4 eV below E_F, found for monolayer Pd coverage on Al(111), were interpreted by assuming an atomiclike $4d^{10}5s^0$ configuration for Pd within the monolayer.

In this paper, we present photoemission spectra and work-function measurements for Pd films on polycrystalline Al and Al films on polycrystalline Pd. Low-energy ion-scattering (LEIS) results will also be presented for Pd on Al. LEIS is important in this work because it probes only the top layer of the surface[4] and is capable of determining the details of growth when combined with photoemission. We found evidence which suggests extensive intermixing between the deposited Pd and the Al substrate and the formation of Pd-Al intermetallic compounds at the surface. A deep-lying d band was observed for both monolayer Pd coverage on Al and thick Al on Pd and is shown to be due to the interaction between Pd and Al through the hybridization of the Pd d and Al s states.

EXPERIMENTS

The experiments were preformed in an UHV surface-analysis chamber with a base pressure of 8×10^{-11} Torr. Photoemission was done using an uv discharge lamp with He I (21.2 eV) radiation and a PHI 15-255 double-pass cylindrical mirror analyzer (CMA) with the energy resolution set at 120 meV. The LEIS setup was similar to those described by Niehus *et al.*[5] and Vurens.[6] We used a PHI 04-191 ion gun, and the same analyzer used for photoemission was biased to serve as an ion detector. To specify the scattering angle, $\frac{5}{6}$ of the CMA entrance was blocked and the center line of the 60° slit was in the plane of the CMA axis and the ion gun. During LEIS experiments, the vacuum chamber was backfilled with helium to a 4×10^{-5} Torr pressure. The incident ion energy was 500 eV and the He ion current was 1 μA. The scattering angle was about 150°. Under these conditions, consecutively scanned LEIS spectra show that there is negligible sputtering due to the incident He ions during data taking.

Al or Pd substrates were prepared as thin films on a Ta(110) foil. Pd or Al overlayers were deposited onto the substrate at room temperature from thoroughly degassed thermal evaporation sources. To minimize incident He ion induced mixing, a fresh Al or Pd substrate layer was deposited for each Pd or Al thickness. The Pd coverages were monitored with a water-cooled quartz-crystal oscillator and calibrated with ultraviolet-photoemission-spectroscopy (UPS) spectra of Pd on Ta(110).[7] Al coverages were only timed.

RESULTS

Figure 1 shows the photoelectron energy distribution curves (EDC's) for a series of increasing Pd coverages on Al. These spectra were angle integrated and were taken using the He I emission line with a photon energy of 21.2 eV. They are individually scaled to the maximum within the binding energy range shown. The Al substrate spectrum is shown by the lowest curve and characterized by a small peak marked (f) extending from E_F to 4 eV below E_F due to the Al sp band. The lack of states, 5–8 eV below E_F which are due to common impurities, shows that our substrate is clean. Depositing 1 monolayer (ML) of Pd reduces the intensity of peak (f) and induces a pronounced feature extending from 2.0 to 5.5 eV binding energy with centroid at 4.0 eV binding energy. Careful inspection of this feature suggests that it consists of at least two peaks, one at 4.8 eV marked (a) and the other at 3.6

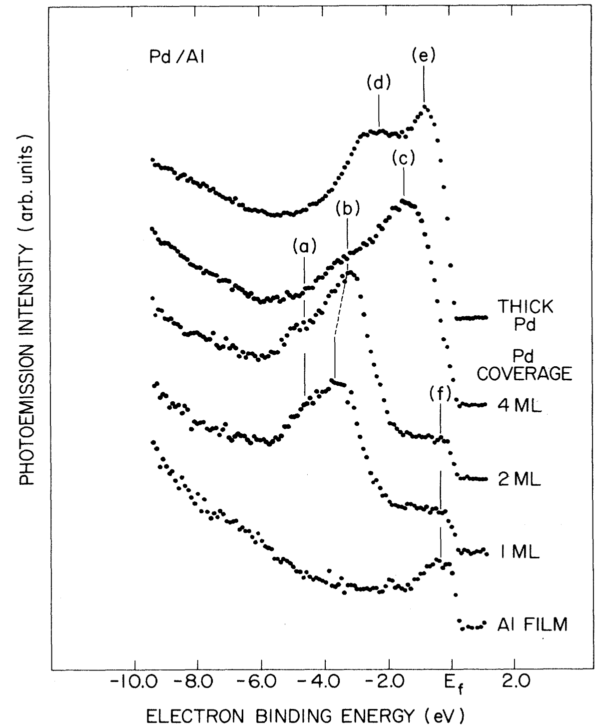

FIG. 1. Angle-integrated photoemission spectra obtained with photon energy 21.2 eV for various coverages of Pd on Al.

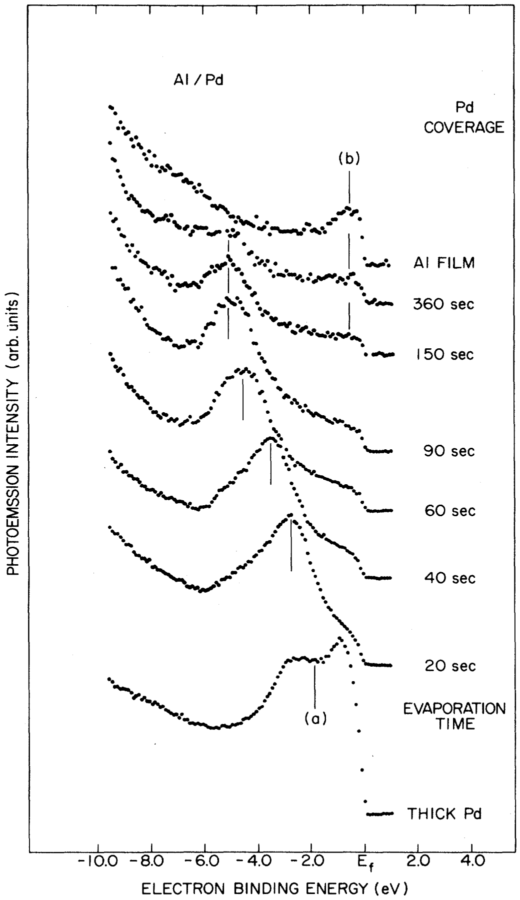

FIG. 2. Angle-integrated photoemission spectra obtained with photon energy 21.2 eV for various coverages of Al on Pd.

eV marked (b). Doubling the Pd coverage increases the intensities of both peaks, and peak (b) grows faster than peak (a). At 4 ML coverage, a new Pd 4d induced peak centered at 1.3 eV binding energy marked (c) appeared across E_F and dominated the spectrum, while states from peak (a) and (b) were still seen as shoulders on the high-binding-energy side of peak (c). Between 2 and 4 ML coverage, the overall d band broadens and its centroid moves from 4.0 to 2.0 eV binding energy. For higher Pd coverages, peak (c) evolves into peak (e) and peak (d) seen for a thick-Pd film shown in the top curve.

Figure 2 shows EDC's for Al films on Pd substrate. Since this experiment is meant to demonstrate the movement of the Pd d band as Al is deposited on the Pd substrate, only relative Al coverages are given by Al evaporation times. At a relatively small Al coverage (20 sec), the modified Pd states resemble those seen for 2-ML Pd on Al in Fig. 1 and those for a 7-min Pd evaporation time on Al(111).[2] At 90-sec Al coverage, this band is centered at 5.0 eV below E_F with a half width of 1.6 eV. For higher Al coverages, the Al sp band marked (b) starts to build up at E_F, and the d band stays at 5.0 eV binding energy with its intensity reduced.

Figures 3(a) and 3(b) show plots of work function versus coverage for Pd on Al and Al on Pd, respectively. For Pd on Al, the work function is initially at 4.27 eV which agrees with the literature value for polycrystalline Al.[8] It then increases slowly to 4.38 eV at 1-ML Pd coverage followed by a faster linear rise from 1- to 4-ML Pd coverage. For Al on Pd, the work function is initially at 5.1 eV which is the value expected for polycrystalline Pd,[8] then decreases rapidly with evaporation time and converges to 4.1 eV as the evaporation time exceeds 90 sec. The variation of work function and the modification of the valence band occur over the same range of Al coverages.

Figure 4 shows LEIS data for a series of Pd coverages on Al. The low- and high-energy peaks are due to the scattering from Al and Pd respectively. The Al peak shape is simply Gaussian-like and the approximately 30-eV linewidth is mainly due to the energy spread of the incident ion beam. The Pd peak consists of three components that may be related to the details of the scattering process. The important feature is the observation of a measurable Al signal even at 8-ML Pd coverage. In Fig. 5 normalized Pd and Al intensities[9] are plotted as a function of Pd coverage. Several growth regimes can be defined by this plot. From 0- to 1-ML Pd coverage, the Al and Pd signals change rapidly. From 1 to 3 ML, the Al and Pd signals change slowly. From 3 to 4 ML, the Al and Pd signals change rapidly again. Beyond 4 ML, both the Al and Pd signals coverage slowly to their end-point values.

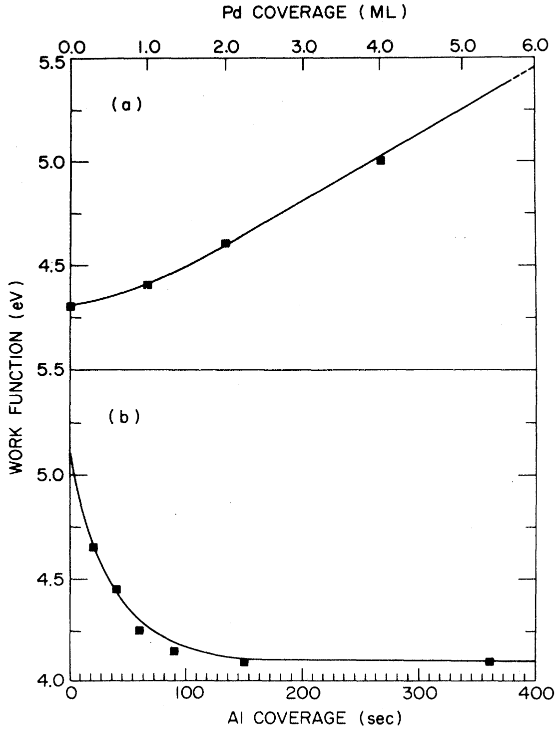

FIG. 3. (a) The work function of Pd deposited on Al as a function of Pd coverage. (b) The work function of Al deposited on Pd as a function of Al coverage.

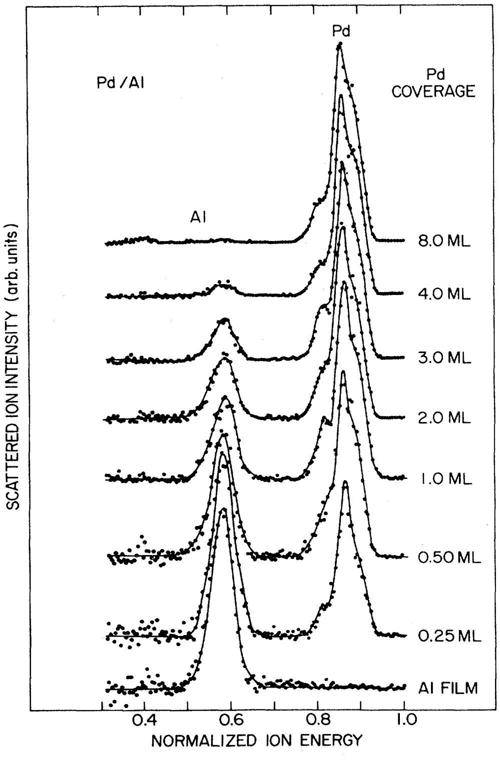

FIG. 4. LEIS spectra for various coverages of Pd on Al.

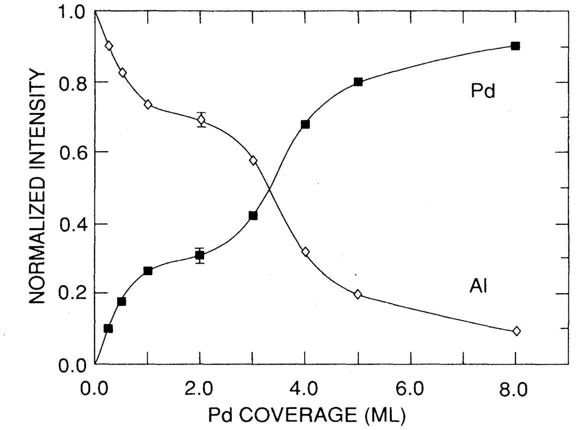

FIG. 5. Normalized LEIS intensity for Al and Pd as a function of Pd coverage on Al.

DISCUSSION

The spectra of Pd on polycrystalline Al are similar to those found for Pd on Al(111)[2]. The key feature of a Pd monolayer on Al is the deep-lying Pd 4*d* emission centered at 4.0 eV below E_F. The work function of this surface is 4.4 eV, so this *d* state is 8.4 eV below the vacuum level, very close to the 8.33 eV ionization potential of a Pd atom.[10] The deep-lying Pd *d* state could be explained by assuming atomiclike Pd within the monolayer. On the other hand, as shown in Fig. 2, a similar deep-lying Pd 4*d* state was also observed for thick Al on Pd. It is difficult to understand this latter result on the basis of an atomic level model. In the studies of Pd monolayers on Nb(110) (Ref. 11) and Ta(110),[7] the centroid of Pd 4*d* states is shifted about 2 eV deeper relative to E_F for submonolayer coverages and Pd 4*d* states start building up at E_F after the first layer is deposited. The metallic Pd valence band is fully developed by 4-ML Pd coverage. These milestones occur at greater Pd coverages on polycrystalline Al and on Al(111).[2] This suggests that the Pd-Al interaction prevents the rapid convergence to the metallic Pd valence band when Pd is deposited on Al and also causes the deep-lying *d* states found for both monolayer Pd coverage on Al and thick Al on Pd.

Photoemission results show the existence of a strong interaction between Pd and Al but cannot establish the details of overlayer growth. Both Auger and photoemission spectroscopy probe a surface region several layers thick and have difficulty in determining whether a deposited layer is actually the top layer or intermixes with the substrate to form a surface alloy over a more extended region. LEIS can resolve this problem in a direct way when combined with the information from photoemission. The LEIS spectra in Fig. 4 show that significant amounts of Al persist at the top layer even after several Pd monolayers have been deposited on Al.[12] The plots in Fig. 5 show that there is a big drop in the Al signal from 3- to 4-ML Pd coverage on Al. This is consistent with the corresponding photoemission result which indicates that bulklike Pd 4d states start to build up at E_F. These observations suggest that Pd either starts clustering before covering the the substrate or intermixes with it forming a surface alloy about 5-ML thick. The photoemission result, however, rules out the possibility of simple Pd clustering because Pd bulk features should build up at E_F well before 4-ML Pd coverage is achieved. It has already been shown that Pd bulk features with states near E_F can be seen when the cluster size approaches about 15 atoms,[13] and much larger clusters would be expected at 4-ML Pd coverage.

The alloying hypothesis is further supported by the XPS studies on bulk alloys.[14] $PdAl_3$ has a filled d band centered at 4.8 eV below E_F. The d band for PdAl consists of two peaks at 4.6 and 3.6 eV below E_F and the centroid of the overall band is at 4.1 eV below E_F. Peak (a) and peak (b) seen for monolayer Pd coverage on Al and also on Al(111) (Ref. 2) are separated by about 1 eV. This separation, which is too large to be explained by the spin-orbit splitting of 0.4 eV for d state in the Pd atomic $4d^{10}5s^0$ configuration,[15] is now easily attributed to the alloys $PdAl_3$ and PdAl formed when a monolayer of Pd is deposited on Al. As more Pd is deposited, more Pd-rich compounds, like PdAl, are formed relative to $PdAl_3$ and thus peak (b) grows faster than peak (a). The features seen in the photoemission spectra of Al on Pd can be explained similarly by the formation of surface alloys.

Although our experiments are on a polycrystalline substrate, the similarity of our photoemission results of Pd on Al to those found for Pd on Al(111),[2] and the fact that the complete development of metallic Pd valence band on Al(111) (Ref. 2) and the complete covering of the Al substrate by Pd in our LEIS study occur at the same high-Pd coverage (more than 8 ML), suggest that alloying or a strong interaction also occurs between Pd and the Al(111) substrate. This is also supported by the fact that the deep-lying d states found for monolayer Pd coverage on Al(111) (Ref. 2) cannot simply be assigned to the atomic $4d^{10}5s^0$ configuration for Pd within the monolayer because of the following arguments. Self-consistent band-structure calculations on a free-Pd(100) monolayer[16] show that the d band is no longer filled as in atomic configuration $4d^{10}5s^0$. This means that the Pd-Pd interaction is already strong enough to start mixing 4d and 5s states which leads to 4d to 5s charge redistribution. The in-plane densities of atoms for Al(111) and Pd(111) are 0.138 and 0.154 (atoms/Å^2), respectively, both larger than that for Pd(100) which is 0.131 (atoms/Å^2).[17] We therefore expect stronger Pd-Pd interaction in an either commensurate or incommensurate Pd monolayer on Al(111) than a free standing Pd(100) monolayer. This should result in more overlap between 4d and 5s states and lead to more 4d to 5s charge redistribution. Hence the d band of a Pd monolayer on Al(111) should not be filled, and thus a deep-lying d state is impossible without taking the interaction with the Al substrate into account.

In an attempt to better understand the relative strength of the Pd-Pd interaction and the origin of deep-lying Pd 4d states, we calculate the interatomic matrix elements between a Pd atom and its nearest-neighbor Pd atoms. Since we are mainly concerned with the Pd 4d to 5s redistribution, we will only calculate V_{ss}, V_{sd}, and V_{dd} matrix elements. They are given by[18,19]

$$V_{ss}=C_{ss}N/d^2 \,, \tag{1}$$

$$V_{sd}=C_{sd}N/d^{3.5} \,, \tag{2}$$

$$V_{dd}=C_{dd}N/d^5 \,, \tag{3}$$

where n is the number of Pd nearest neighbors and d is the nearest-neighbor distance. C_{ss}, C_{sd}, and C_{dd} are constants. Using (1), (2), and (3), these matrix elements are calculated for various Pd arrangements and normalized to those for a Pd(100) monolayer. The results are summarized in Table I. It is clear from this table that both for the Pd(111) monolayer and for a commensurate Pd monolayer on Al(111), the ss, sd, and dd interatomic matrix elements are all larger than those for a Pd(100) monolayer, and the Pd-Pd interaction is indeed stronger in an either commensurate or incommensurate Pd monolayer on Al(111) than in a Pd(100) monolayer. From Table I we also see that the Pd-Pd interaction in PdAl is about the same as in a Pd(100) monolayer. This means that the d band should not be filled if we only consider the Pd-Pd interaction in PdAl. The fact that the d band

TABLE I. Pd-Pd interatomic matrix elements for various Pd arrangements normalized to those for a Pd(100) monolayer.

Pd arrangement	N	d (Å)	V_{ss}	V_{sd}	V_{dd}	Ref. for d and N
Pd(100) monolayer	4	2.75	1.00	1.00	1.00	10
Pd(111) monolayer	6	2.75	1.50	1.50	1.50	10
Al(111)[a] monolayer	6	2.86	1.39	1.31	1.23	10
PdAl compound	6	3.00	1.26	1.11	0.97	20

[a] Commensurate Pd monolayer on Al(111).

is filled in PdAl suggests that the origin of the deep-lying Pd 4*d* states is the Pd-Al interaction. This is confirmed by the band-structure calculations[14] which show that the Pd 4*d* states are filled in $PdAl_3$ and PdAl by the *s* electrons from the electropositive Al. This band filling is mainly due to the hybridization of the Pd *d* and Al *s* states as the calculations indicate that there is always Pd *d* character in the bands above E_F. This differs from the situation for Pd metal where all the unoccupied *d* states are near E_F; the unoccupied *d* states in $PdAl_3$ and PdAl alloys are more spread out which makes it difficult to detect them using inverse photoemission spectroscopy (IPS). This explains the flat IPS spectrum seen at monolayer Pd coverage on Al(111) (Ref. 3) which the authors claimed as a proof for atomiclike Pd.

Finally we comment on the plausibility that the deposited Pd alloys with the Al substrate. We mention that we have also observed evidence of alloying in the studies of Ni on Al. Alloying is not observed for Pd on Nb (Ref. 11) or Ta (Ref. 7), where there is growth of a stable monolayer. We think that the surface and interface energy terms which stabilize the monolayer may be too small compared to the large heat of formation of Pd-Al or Ni-Al compounds. To further understand this behavior, total-energy calculations are needed for Pd-Al bilayer and intermixed Pd and Al layers. The lower energy is expected for the intermixed layers based on the results of present experiments.

CONCLUSION

At room temperature, deposited Pd intermixes with the Al substrate forming a thin surface alloy about 5-ML thick which consists of $PdAl_3$ and PdAl intermetallic compounds. Bulklike Pd states start to build up at E_F only as the coverage exceeds 4 ML. More than 8 ML of Pd are needed to completely cover the Al surface and to fully develop the Pd metallic valence band. The *d* states centered at 4 eV below E_F were found for both monolayer Pd coverage on Al and thick Al on Pd. This deep-lying *d* band is due to the interaction between the deposited Pd (Al) and Al (Pd) substrate through the hybridization of the Pd *d* and Al *s* states.

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