PHYSICAL REVIEW B VOLUME 38, NUMBER 17 15 DECEMBER 1988-I

Reaction of thin Pd films with Al(111) and Al(110) surfaces

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(Received 14 July 1988)

High-resolution ion backscattering has been used to study the reaction of thin Pd layers with Al(111) and Al(110) surfaces. The measurements show that alloy formation occurs at the surface for a range of Pd coverages from 0 to 7×10^{15} atoms/cm^2. The results are discussed in terms of a reaction model in which each Pd atom effectively displaces one Al substrate atom, with an additional two monolayers of disordered Al at the interface. A Pd film ultimately grows on the reacted layer, expitaxially ordered in the case of the Al(111) surface.

Studies of the electronic and geometric structure of bimetallic interfaces are important for understanding the modified properties frequently observed for such systems.[1] Recently, the modified electronic and chemisorption properties of supported thin Pd films have been investigated as part of a continuing effort to determine the influence of the substrate electronic structure on the overlayer. In particular, thin Pd films on Al(110) (Ref. 2) and on Al(111) (Ref. 3) surfaces were reported to grow in layer-by-layer [Frank–van der Merwe (FW)] and in a Stranski-Krastinov (SK) mode, respectively. In both cases photoemission measurements for the first Pd monolayer were similar in exhibiting a narrow, atomiclike d level centered approximately 4–5 eV below the Fermi energy E_F. In addition, x-ray photoemission measurements of the valence-band density of states for several Al-Pd alloys have been reported showing, for example, a similarly narrow Pd-derived level 4.8 eV below E_F for the Al$_3$Pd alloy.[4]

The purpose of the present investigation was to use the high depth resolution and shadowing techniques of medium-energy ion scattering to determine the overlayer geometry for the above-mentioned Al-Pd systems. For both Al(110) and Al(111) surfaces we find that the Pd atoms do not form a simple overlayer on the substrate as previously reported, but react with and displace Al substrate atoms. This reaction is observed to continue for Pd coverages ranging from 0.4 to about 5 monolayers (ML) before the Pd begins to cover the Al atoms in the reacted layer to form Pd metal. Our low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) observations are consistent with those reported earlier for these systems. Furthermore, the reaction model which emerges from a consideration of our measurements can be used to understand the previous photoemission studies in terms of compound formation on the surface. In this Rapid Communication we give an overview of our results for the two Pd-Al systems studied. A more-detailed analysis will be presented elsewhere.[5]

The experiments were carried out in an UHV surface analysis chamber which includes facilities for LEED, AES, and high-resolution Rutherford backscattering spectroscopy (RBS).[6] The RBS measurements were made using a toroidal electrostatic analyzer with an energy resolution, $\Delta E/E$, of 4×10^{-3}. Also included in the chamber is a capability for Ar-ion sputtering, and controlled submonolayer metal deposition using a retractable, calibrated metal evaporation source. A collimated beam of 100.6-keV protons was incident on the Al surface along various low-index channeling directions, and the analyzer was positioned to collect scattered ions leaving the crystal along various major blocking directions. Since the technique of shadowing and blocking has been discussed in detail elsewhere,[6] we only mention here some important features of the measurements. When the incident ion beam enters the crystal along a major channeling direction, the first atom encountered along each string of atoms will cast a shadow along that row of atoms, resulting in a reduced hitting probability for subsequent atoms along the row. Since the deflection angle for the ion depends on the atomic number of the target atom, we expect considerable shadowing of the substrate Al atoms when Pd atoms form an ordered overlayer and sit near lattice sites of the substrate crystal structure. Second, the high-energy resolution of the electrostatic analyzer makes possible detailed line-shape analyses yielding information about thin-film morphology and composition. Finally, established calibration procedures and the known cross section for Rutherford scattering make possible the absolute measurement of atoms visible to the incident ion beam, including measurements of the amount of deposited adatoms.

The Al samples used in these measurements were cut and oriented to within 1° of the desired surface orientation. The Al(110) surfaces were first mechanically polished and then electropolished and chemically etched.[7] The Al(111) surfaces were mechanically polished with no additional chemical treatment. Both surfaces were then outgassed for several hours at 500 °C in UHV, followed by several hours of Ar$^+$-ion sputtering at 400 °C and annealing at 500 °C. These sputter-anneal cycles were continued until the ratio of the peak-to-peak amplitudes for the differentiated Auger signals of oxygen (*KLL*) and Al/(*LMM*) was reduced to less than 0.01, as measured with a single-pass cylindrical mirror analyzer operating with a coaxial 3-keV electron beam incident along the sample normal. The metal deposition source consisted of a twisted pair of 0.25-mm Marz-grade Pd wires, outgassed for several days in UHV. The source was initially calibrated *in situ* by measuring with RBS the amount of Pd atoms deposited under identical conditions to those used later in the experiment. The deposition rate with a total current of 4 A passing through the Pd wires was 0.6×10^{15} atoms/cm^{2}min, with the pressure at or below

4×10^{-10} Torr, and no significant rise in sample temperature above 25 °C during the deposition. Measurements made with a deposition rate of 0.2×10^{15} atoms/cm^{2}min did not give different results from those reported here. RBS measurements were collected for the initially clean surfaces in two separate scattering geometries for each surface. The typical procedure thereafter was to deposit Pd on the surface, collect Auger spectra, and check for a LEED pattern. RBS was then performed to determine the Pd coverage and to study the surface morphology. The pressure in the measuring chamber was at or below 2×10^{-10} Torr for the duration of the experiment, except during Pd deposition as noted above.

The general trend observed for the deposition of Pd on Al(111) and on Al(110) surfaces can be seen by examining the results for the (111) surface using the scattering geometry shown in Fig. 1. In this case, energy spectra were recorded for 100.6-keV protons incident along the [110] direction in the (110) scattering plane, with the center angle of the detector set at a scattering angle of 90°, to collect scattered ions leaving the sample along the [001] direction. The energy spectra of Fig. 2 show the surface peaks for Al and Pd with arrows indicating the energy for ions backscattered from an Al or Pd atom at the surface. The energy spectrum for the clean Al surface [curve (*a*) in Fig. 2] corresponds to 2.2 ML of Al atoms visible to the ion beam and detector. In this scattering geometry overlayer Pd atoms which sit on the Al surface in the threefold site above third-layer Al atoms (*C* site), and are near lattice positions, will strongly shadow the substrate Al atoms on the incoming path, resulting in a reduced ion yield from Al atoms as seen by the detector. If the Pd adatoms sit in so-called *B* sites above second-layer Al atoms, they will result in considerable Al blocking at an angle different from the bulk blocking direction, with little change in the yield along the [001] direction. However, it is seen in curve (*b*) of Fig. 2 that a coverage of 1.1 ML of Pd (1 ML equals 1.408×10^{15} atoms/cm^2) does not cause a decrease of the Al peak, but instead causes an additional 2.6 ML of Al atoms to be visible to the ion beam. In addition, the Al blocking profile for this coverage exhibits a surface blocking dip at 90°, nearly identical to that measured for the clean surface, except for the overall angle-independent increase of 2.6 ML just mentioned. It would appear then that neither *B* nor *C* sites are occupied by the Pd adatoms. In curve (*c*) of Fig. 2 (open circles) we show the spectrum for a coverage of 4 ML (5.7×10^{15} atoms/cm^2) of Pd. It will be noticed that the Al peak width has increased considerably, indicating that the additional displaced Al atoms are distributed in depth. Also, we note that there is still considerably Al yield at the surface energy. Finally, we show in curve (*d*) of Fig. 2 (filled circles) the energy spectrum for a coverage of 7.6 ML (10.7×10^{15} atoms/cm^2) of Pd. We note that the high-energy edge of the Al peak has broadened, and that the peak itself has shifted to lower energy, an indication that the surface Al atoms are now beginning to be covered by Pd atoms.

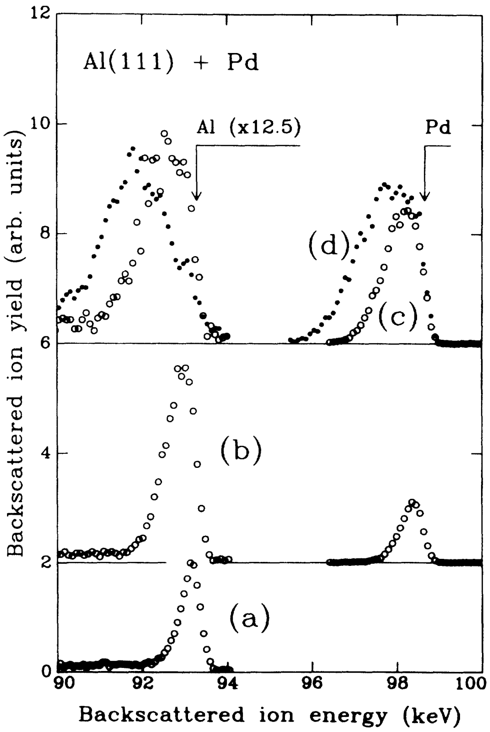

FIG. 2. Backscattering energy spectra for 100.6-keV protons on Al(111)+Pd, using the scattering geometry of Fig. 1, for several Pd coverages (atoms/cm^2): (*a*) clean surface, (*b*) 1.6×10^{15}, (*c*) 5.7×10^{15} (open circles), and (*d*) 10.7×10^{15} (filled circles). The energies for backscattering from Al and Pd surface atoms are indicated. The spectra have been offset as indicated by the horizontal lines, and the Al spectra have been multiplied by a factor of 12.5.

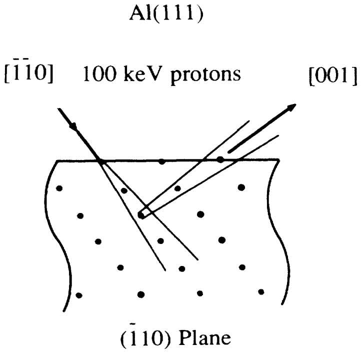

FIG. 1. Side view of the (110) scattering plane perpendicular to the Al(111) surface showing the scattering geometry used for the energy spectra of Fig. 2.

In Fig. 3 we plot the area of the measured Al surface peak as a function of Pd coverage, determined from the Pd surface peak area. Such curves have been especially useful in developing models for thin-film reaction and morphology in studies of metal silicides.[8] There are three main points to note in the results of Fig. 3. First, there is a slope somewhat larger than unity between 0 (clean surface) and about 1-ML Pd coverage. Second, there is an increase from approximately 1 ML to about 5 ML with a slope of one displaced Al atom for each deposited Pd atom. Finally, there is an apparent saturation of the curve about 5-ML coverage. Together, the results of Figs. 2 and

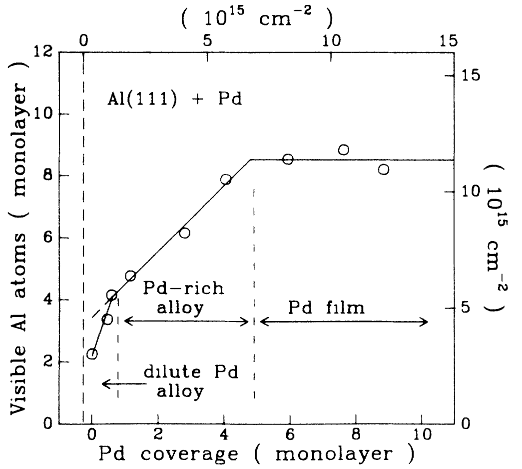

FIG. 3. Number of Al atoms visible to the beam and detector as a function of the Pd coverage. The solid lines are intended to guide the eye. Three stages of growth are indicated.

3 are sufficient to demonstrate that Pd atoms are reacting with the Al(111) surface to form a surface alloy rather than a simple overlayer with the SK morphology. First, we note that the reaction continues for up to nearly 5 ML of Pd coverage, displacing Al substrate atoms so that they become visible to the ion beam. The unity slope suggests that we are forming a PdAl compound.[9,10] If, on the other hand, we were growing Pd in an SK morphology we might expect some displacement of Al atoms for the first ML of Pd coverage, as observed, followed by a line with zero slope in Fig. 3, corresponding to the island growth stage as seen, for example, with Ag on Si.[8] We expect a line with zero slope because the formation of Pd islands should not continue to displace Al substrate atoms at such a high rate when the islands are separated from the substrate by the intervening first Pd monolayer. Second, the persistence of Al yield at the Al surface energy means that there are uncovered substrate atoms between the islands of reacted material and/or that there are Al atoms visible to the ion beam near the surface of the reacted material. The peak analysis described below supports the latter picture. Third, in the case of SK growth we would expect broadening of the high-energy edge of the Al peak beginning at 1 ML of Pd coverage as the Pd islands begin to gradually cover the substrate. We observe, however, that the slope of this leading edge remains at the instrumental resolution up to 4 ML as seen in curve (*c*) of Fig. 2, and only then broadens as the reacted material is covered by Pd atoms. Finally, we note that no reduction of the Pd yield from that expected for a random geometry was seen for coverages of less than 8 ML of Pd. This absence of Pd blocking by Pd atoms tends to rule out Pd island formation. As a result of the above arguments, we conclude that there is no evidence for SK growth in these experiments.

As noted above, it has been reported that on the Al(111) surface the Pd atoms form islands (SK growth) which coalesce at a coverage of 8 to 10 ML, and at which point a hexagonal LEED pattern is observed.[3] We also observe a hexagonal LEED pattern for the Pd-covered Al(111) surface, beginning with a coverage of 7.6 ML, although the individual spots are much broader than the original substrate spots. Furthermore, blocking of the Pd-ion yield in the geometry of Fig. 1 is observed for these higher coverages, meaning that islands of bulk Pd are forming with a major axis oriented along the [110] substrate string. It is obvious then that some memory of the substrate orientation has been retained through the reacted layer, resulting in an epitaxial Pd overlayer. To understand this behavior we have performed a detailed analysis of the Pd and Al surface peak shapes. Curve-fitting procedures similar to those used for the silicides[8] have been used to deconvolute the measured Al peaks into three separate components: (1) a component for the uncovered Al surface, represented by a fraction of the original clean surface peak; (2) a component for islands of reacted Pd-Al material, with a line shape given by the shape of the Pd peak; and (3) a component due to the Al surface which is covered by islands of reacted material. From such an analysis we conclude that the data are consistent with the following reaction model. For Pd coverages from 0 to about 1 ML, we find that each Pd atom effectively displaces three Al atoms in the substrate. This is suggestive of forming an Al_3Pd compound, which in turn enables us to understand the photoemission results[3] as being due to a dilute Pd compound.[4] However, it is difficult to confirm with ion scattering alone the actual stoichiometry of a compound when the layer is this thin, since there may also be considerable displacement of Al atoms at the metal-compound interface. Thus we could not distinguish, using the data of Fig. 3 alone, between the formation of an Al_3Pd compound on Al(111) as opposed to the formation of a Pd adlayer with 3 ML of displaced Al atoms at the interface between the substrate and adlayer. We note that it is necessary for the Pd atoms to remain at or near the surface layer to attenuate the Al Auger signal as observed.[3,4]

After formation of the initial reacted layer, a PdAl compound forms, leading to the unity slope seen in Fig. 3. Again, this is consistent with the photoemission experiments since the AlPd valence band measured in x-ray photoemission[4] tends to replicate the broadened *d* bands seen in ultraviolet photoemission spectroscopy.[3] For Pd coverages in excess of 5 ML, the reaction at the interface appears to stop and a bulk Pd overlayer begins to form. We believe that it is possible to maintain some memory of the substrate orientation using the (111) plane of the cubic AlPd structure,[10] so that the Pd film which eventually grows on the reacted layer is ordered and oriented with respect to the substrate surface.

Finally, we mention briefly our observations for Pd on the Al(110) surface. The same type of reaction model appears to explain the results with a few notable exceptions. For Pd coverages from 0 to about 1 ML [1 ML on Al(110) equals 0.862×10^{15} atoms/cm^2] each Pd atom effectively displaces three Al atoms. At a coverage of 4 ML of Pd, a more Pd-rich phase is forming with an apparent slope of about 1.8 Al atoms displaced for each deposited Pd atom, and Al atoms are still present at the surface. At 8-ML coverage, there is an indication based on the Al peak shape, and on the reduction of Al yield at the

Al surface energy, that the reaction has stopped and that Pd atoms are beginning to cover the reacted layer. No LEED pattern is observed yet at this coverage. Details of these measurements will be given elsewhere.[5]

In summary, we have performed an ion-scattering investigation, combined with LEED and Auger analysis, of Pd deposited on Al(111) and Al(110) surfaces. The results are not consistent with FM or SK growth as reported in earlier studies. Instead we observe the continued displacement of substrate atoms for coverages up to 5 ML of Pd. We propose a reaction model consisting of the initial growth of a thin reacted layer of dilute Pd alloy, followed by the overgrowth of a more Pd-rich phase, until the reaction stops at a coverage of about 7×10^{15} atoms/cm^2.

We gratefully acknowledge the contributions of J. H. M. Kuyper (FOM) and A. J. Riemersma (University of Amsterdam) in preparing the Al crystals for these experiments. We have also benefitted from discussions with Walter Slijkerman, Bart Pluis, and Tom Taylor. One of us (R.J.S.) wishes to thank his hosts at the FOM-Institute for Atomic and Molecular Physics for the hospitality and support during his stay there, and to acknowledge partial support by the National Science Foundation under Grant No. DMR 8401196. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

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