Transition from the Pseudomorphic State to the Nonregistered State in Epitaxial Growth of Au on Pd(111)

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The epitaxial growth of Au on Pd(111) was studied by ion scattering/channeling, low-energy electron diffraction, and Auger analysis. A sharp transition from the pseudomorphic state to the state with misfit dislocations and strain was found. The critical thickness is 2.0 ± 0.2 Å in this layer-by-layer growth system. The Au coverage dependence of the lattice constants for substrate and overlayer were measured in detail.

Metallic, epitaxial thin-film structures are receiving considerable attention in the search for new materials with unusual solid-state properties. For example, Brodsky and Freeman have reported a strongly enhanced magnetic susceptibility in palladium in Au-Pd-Au thin-film, epitaxial structures.[1] The susceptibility increase is attributed to the expansion of the Pd lattice constant (normally 3.89 Å) resulting from the strain imposed by the epitaxial Au of larger lattice constant (normally 4.08 Å).

The fact that large changes in materials properties are induced by relatively subtle changes in lattice strain stimulates the need to characterize the lattice structure in such films and to test theoretical descriptions of epitaxial bicrystal formation. In this Letter we describe the first quantitative measurements of the strain in the overlayer and substrate in the epitaxial system Au on Pd(111). The observed strain and the critical thickness associated with the onset of misfit dislocations are compared with existing theories of epitaxial bicrystal growth.

The epitaxial system was characterized primarily by high-energy ion scattering, low-energy electron diffraction (LEED), and Auger analysis. The advantages of ion scattering in such studies were previously illustrated in the Au/Ag(111) system (lattice-constant mismatch of 0.2%).[2] In that case an almost ideal, pseudomorphic Au layer is grown to thicknesses exceeding 50 Å, i.e., Au atoms occupy the ideal fcc sites of the substrate. The present study of Au on Pd (lattice mismatch of 4.8%) extends this work to a considerably more complicated system. The experimental results show that in the initial growth the Au atoms occupy the ideal fcc sites of Pd and above a critical thickness of ~ 2.0 Å both Au and Pd move out of registry. A main point of this paper is the demonstration that a larger misfit

results in large changes in the overlayer and substrate strain and the critical thickness. A sharp transition from a pseudomorphic state to a state with misfit dislocations and strain was directly observed. The measured strain and critical thickness are in qualitative agreement with theoretical predictions.

The major theoretical developments in epitaxy have been made from the viewpoints of elastic misfit energy,[3] interfacial energy with model potentials, nucleation, and defects.[3] Pseudomorphic growth of the first monolayer was predicted by Frank and van der Merwe for the case of less than 10% misfit.[4] Jesser and Kuhlman-Wilsdorf[5] and later Ball[6] developed the elastic theory for the finite-thickness film. In many systems, there is an initial pseudomorphic growth which undergoes a sharp transition from the pseudomorphic state to a state with misfit dislocations and strain at a critical thickness h_c. In other words, both the dislocation density and average strain are functions of overlayer thickness h and misfit. At the critical thickness, for example, the strain begins to change from the maximum due to the lattice mismatch, and dislocations are created spontaneously.

The total elastic energy of a thin-film system has been written as

$$\epsilon_T(e,h) = \epsilon_{ms}(e,h) + \epsilon_{md}(e,h) + \text{const},$$

where ϵ_T is total energy per unit area, ϵ_{ms} is the misfit strain energy, e is the strain, and ϵ_{md} is the misfit dislocation energy for the unstrained area. Qualitatively the misfit strain energy is proportional to e^2 and the dislocation energy varies inversely as the strain. In our calculations the formula due to Ball[6] was used for ϵ_{md} and the result of Cahn[7] was used for ϵ_{ms} along the [111] direction of an fcc crystal. The equilibrium strain can be obtained from the mini-

mum of $\epsilon_T(e,h)$ within the range $0 \leq e \leq e_{max}$, where e_{max} is the maximum strain associated with pseudomorphic growth. For each thickness an equilibrium strain is obtained (corresponding to $\partial\epsilon_T/\partial e = 0$) which can be thought of as the average strain (or atomic displacement) throughout the film. The critical thickness, h_c, corresponds to the film thickness at which $\partial\epsilon_T/\partial e = 0$ for $e = e_{max}$. Although the actual potentials are not realistic, and macroscopic elastic constants are used for the calculation, the critical thickness can be calculated within this model to an order of magnitude. In the present case, h_c is 5.0 Å along the [111] direction for the Au/Pd system and $\gtrsim 100$ Å for the Au/Ag system. Although these energy considerations yield a prediction for h_c they do not readily yield individual atomic positions throughout the layer. For $h < h_c$ the system is essentially pseudomorphic. Ion scattering calculations are then easily compared with experiment. For a thickness $h > h_c$, misfit dislocations and strain exist together. As the overlayer is thickened, the average strain decreases with most of the strain localized in a small region around a dislocation.

Experiments were performed in a UHV system equipped with LEED and Auger apparatus and a Au deposition source by which ~0.2 monolayer per minute Au can be deposited on a clean Pd(111) surface. The UHV system is directly connected to a van de Graaf accelerator for ion scattering/ channeling analysis. The principle of the ion scattering technique is explained elsewhere.[8] Briefly, the shadowing effect for the ion beam incident along a major crystallographic axis is used for the surface-structure determination. A pseudomorphic epitaxial overlayer reduces the scattering from the substrate. A strained system with relative atomic displacements of $\gtrsim 0.1$ Å destroys the shadowing effect.

The Pd(111) sample was cleaned *in situ* by sputtering and annealing. After cleaning, a sharp (1×1) LEED pattern was observed, and no impurities were detected by either Auger spectra or ion scattering. Au deposition was done at a slow rate in order to maintain equilibrium conditions and at room temperature where surface diffusion is fast enough to establish surface equilibrium and interdiffusion is negligibly slow. Note that the Au-Pd phase diagram describes a continuous solid solution with no ordered phases. Ion scattering, Auger, and LEED measurements were done at room temperature.

LEED patterns were (1×1) for all Au coverages.

The Au *surface* lattice-constant change as a function of thickness was extracted from these patterns. Using Auger analysis we ascertained that the Pd ($M_{4,5}N_{4,5}N_{4,5}$) peak shows an exponential decay, with Au overlayer thickness. This implies that the growth mode is layer-by-layer (Franck-van der Merwe) growth with little three-dimensional islanding. Ion scattering spectra were taken along the [00$\bar{1}$], [$\bar{1}\bar{1}\bar{1}$], and random directions to obtain the coverage of Au, the surface peak (SP) of Pd, and the χ_{min} of Au. The χ_{min} is the Au-Au shadowing effect, i.e., the yield of Au in the channeling direction to the yield of Au in a random direction. The ion scattering and LEED data were used to characterize the lattice spacings of the system.

Figure 1 shows the Au coverage dependence of the Pd(111) surface peak along the [00$\bar{1}$] direction. The experimental SP of clean Pd is almost the same as the calculated value based on a model of ideal termination of the surface. Angular scans confirmed (see Fig. 3) that the surface relaxation is less than 0.05 Å along the [111] direction. As Au was deposited, the surface peak of the Pd substrate was reduced as a result of the overlayer shadowing effect. The full line is the calculated Pd SP when the growth mode of Au is pseudomorphic. The suppression of the Pd SP by the Au layer indicates that interdiffusion at room temperature is negligible and sharp interface structures are possible. As the coverage of Au reaches about 1 monolayer, the Pd surface peak increases. At this critical thickness, the Au and Pd atoms move out of registry such that the elastic strain is lowered and misfit dislocations begin to be developed. Since Au atoms are out of registry, the shadowing effect decreases, such that the SP of Pd increases. In fact, the Pd surface
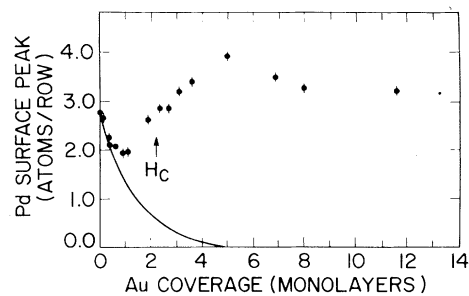

FIG. 1. Pd surface peak as a function of Au coverage along the [00$\bar{1}$] direction for 1.8-MeV He$^+$ incident at room temperature. The full line corresponds to the scattering with the assumption of pseudomorphic growth. h_c is the calculated critical thickness.
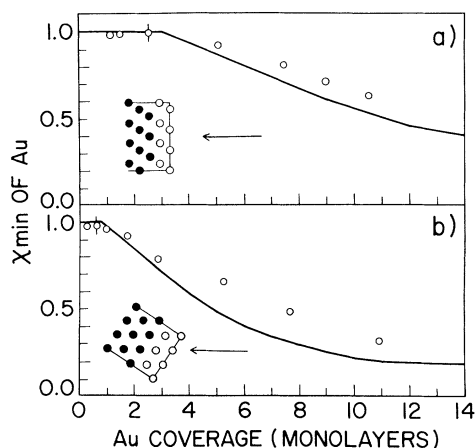
FIG. 2. Minimum yield of Au as a function of Au coverage (monolayers) for 1.8-MeV He$^+$ (a) along the [$\overline{1}\overline{1}\overline{1}$] direction and (b) along the [00$\overline{1}$] direction. The full lines are the predicted yields with the assumption of pesudomorphic growth.

FIG. 3. Angular scans of the Pd SP and χ_{min} of Au along the [00$\overline{1}$] direction in the (011) plane for 1.8-MeV He$^+$. Filled circles are clean Pd SP, filled triangles are the Pd SP at 0.9 monolayer (ML) of Au, open squares are the Pd SP at 2.9 ML of Au, and open circles are the Pd SP at 7.7 ML of Au. Filled squares are χ_{min} of Au at 7.7 ML of Au. The arrows indicate the minima of the scans.

peak increases well above the zero-coverage value, indicating a substantial substrate distortion due to the Au overlayer. The experimental critical thickness is ~1 monolayer, 2.0 ± 0.2 Å, while the elastic theory calculation is 5.0 Å. After about 5 monolayers, the number of dislocations is saturated by their repulsive interaction.[9] The Pd SP gradually decreases as a result of channeling effects in the defected Au layers.

Figure 2(a) shows the χ_{min} of Au along the [111] direction. For the first 3 layers, χ_{min} remains about 100%, since ABC stacking sites can be distinguished along the [111] direction and the first 3 Au layers will not be shadowed. In the [00$\overline{1}$] case [Fig. 2(b)] the χ_{min} decreases at ~1 monolayer consistent with the crystal symmetry. This is a good indication that there are no major stacking faults in the Au growth. The measured χ_{min} is slightly higher than the calculated one (solid line) for pseudomorphic growth, presumably because of the strain and defects.

The yield of the surface peak as a function of small tilt-angle variations about a crystal axis (angular scans) can be used to determined surface atom displacements.[8] The angular scans of the Pd SP and the Au χ_{min} along the [00$\overline{1}$] axis in the (011) plane are shown in Fig. 3. The zeros of the angular scans were determined by the minimum in the Pd bulk minimum yield. As mentioned, there is almost no relaxation or reconstruction for the clean (111) surface. Relaxation would be indicated by asymmetry in the angular scan. As Au covers the surface, the Pd lat-
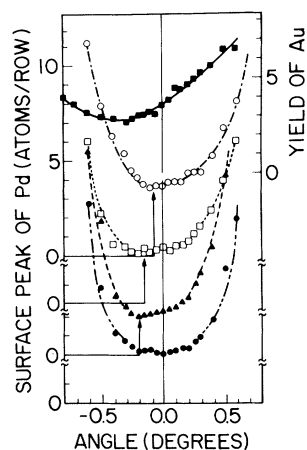
tice spacing is elongated along the [111] direction such that the minimum of the Pd SP is shifted in angle. The angular scan of the Au χ_{min} is also shown (filled squares) for a coverage 7.7 monolayers. It is clear that the unit cell of Au is also elongated along the [111] direction. The asymmetry is used as a measure of the average lattice-constant deviation from a cubic structure and yields the "perpendicular lattice constant" averaged over the first few layers of Au. At the same
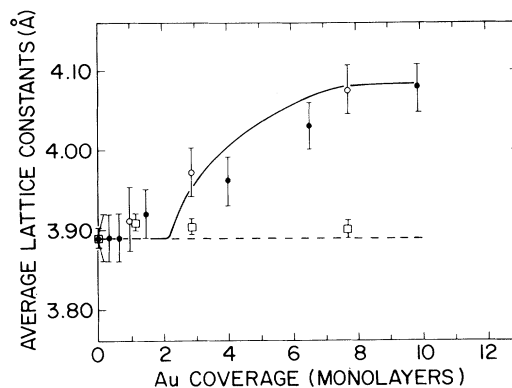

FIG. 4. Au coverage dependence of the lattice constants: filled circles are the Au lattice constant in the (111) plane (from LEED), open circles are the average Au lattice constant along the [111] direction, and open squares are the Pd lattice constant along the [111] direction. Solid line is the calculated, average Au lattice constant.

time, the change of the Au lattice parameter for the topmost monolayers in the surface plane can be measured by LEED to yield the "parallel lattice constant." The change of the lattice parameters in the plane and perpendicular to the surface plane for Au and the perpendicular surface lattice parameter for Pd are shown in Fig. 4. The lattice parameter of Au corresponds to the Pd value during the initial pseudomorphic growth. After the critical thickness of about 1 monolayer, it gradually increases to the normal Au value. The full line is the calculated change in the average overlayer lattice parameter based on total elastic energy theory and known elastic constants.[10] The results agree qualitatively with prediction. The change of the Pd substrate lattice parameter should be noted here; this has not been detected by other experiments.

Consider the implications of these measurements with respect to Brodsky's work on magnetic susceptibility in Au-Pd-Au sandwiches. The highest susceptibility is observed in few-monolayer epitaxially grown films, consistent with our observation of significant strain. The maximum strain would correspond to the perfect pseudomorphic state. In studies of multilayer films of Pd-Au-Pd we have found poor Pd epitaxy for Au thicknesses beyond 2 layers. Perhaps this explains the lack of large effects in the multi-sandwich structures reported by Brodsky. In addition, we note the recent work of Narusawa and Gibson[11] concerning an ion scattering study of Ge epitaxial growth on Si(111) (mismatch of 4%). There is a similarity in their measured substrate SP as a function of Ge layer thickness to the Pd/Au data shown in Fig. 1. These data could be explained by two-dimensional growth with the critical thickness of 5 monolayers as calculated

by the present elastic energy calculation.

In conclusion, we present direct observation of the transition from a pseudomorphic state to the state with misfit dislocations and strain. The change of lattice parameters and strains are found in detail. In the Pd substrate the lattice is slightly elongated to resemble the Au lattice along the [111] direction, while the overlayer Au, initially pseudomorphic, assumes its normal lattice parameter in a layer-by-layer growing mode. The structure of the overlayer is in reasonable agreement with the predictions of the elastic theory.

[1]M. B. Brodsky and A. J. Freeman, Phys. Rev. Lett. 45, 133 (1980).

[2]R. J. Culbertson, L. C. Feldman, and P. J. Silverman, Phys. Rev. Lett. 47, 657 (1981).

[3]Epitaxial Growth, edited by J. W. Matthews (Academic, New York, 1975), Parts A and B.

[4]F. C. Frank and J. H. van der Merwe, Proc. Roy. Soc. London, Ser. A 198, 205, 216 (1949).

[5]W. A. Jesser and D. Kuhlmann-Wilsdorf, Phys. Status Solidi 19, 95 (1967).

[6]C. A. B. Ball, Phys. Status Solidi 42, 357 (1970).

[7]J. W. Cahn, Acta Metall. 10, 179 (1962).

[8]L. C. Feldman, J. W. Mayer, and S. T. Picraux, Materials Analysis by Ion Channeling (Academic, New York, 1982).

[9]For example, see F. R. N. Nabarro, Dislocation in Solids (North-Holland, New York, 1979).

[10]G. Simmons and H. Wang, Single-Crystal Elastic Constants and Calculated Aggregate Properties: Handbook (MIT Press, Cambridge, Mass., 1971).

[11]T. Narusawa and W. M. Gibson, Phys. Rev. Lett. 47, 1459 (1981).