Epitaxial growth and electronic structure of Au films on fcc (111) metals studied by electron reflection spectroscopy

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The reflection coefficient for low-energy electrons on clean fcc (111) metal surfaces shows details determined by the electronic potential in the first few surface layers. This is used to monitor the epitaxial growth of Au overlay films on Pd, Ag, and Ni substrates. On Pd, the lattice constant of the initial Au layers contracts to conform to the Pd but after about three layers assumes the value for bulk Au. Observed shifts of the Au peaks are consistent with predictions of band theory. For Ag and Ni substrates the first few Au layers grow with the bulk lattice constant. The decrease of substrate peak intensity with thickness is consistent with layer-by-layer growth for all three substrate metals. On Pd, thicker Au films show quantum size-effect oscillations at low energies, implying film-thickness uniformity on an atomic scale. These results are compared with those of other techniques. We conclude that electron reflection is a sensitive and relatively simple way of monitoring the growth stages of epitaxial layers.

INTRODUCTION

The task of monitoring the early growth stages of an epitaxial film requires a technique which is surface sensitive and can yield information about important parameters such as lattice constants, symmetry, and growth morphology of the overlayer.[1] Low-energy electron diffraction (LEED) can provide information about symmetry and certain types of ordered surface structures.[2] Careful analysis of LEED beam profiles can yield information about the surface lattice structure, defect densities, and steps. Transmission electron microscopy (TEM) in ultrahigh vacuum can monitor first-layer development, lattice mismatch, and surface reconstruction.[3] Auger spectroscopy can detect layer-by-layer growth and, to some degree, can see different growth patterns.[4] Ion backscattering is effective in providing details of first-layer development and can determine registry of the overlayer with respect to the substrate with great sensitivity.[5] Angle-resolved photoemission spectroscopy (ARPS) has been employed to study the valence band structure of metal overlay films.[6] Low-energy electron reflection spectroscopy has been used to observe directly quantized size effect (QSE) energy levels in overlay metals and thus gives good evidence of layer-by-layer growth for these films.[7]

The majority of past experiences with nonmetallic substrates, or experiments with metal substrates in which the vacuum conditions are not adequate, leave the impression that film growth proceeds by forming many isolated islands at localized nucleation sites, followed by three-dimensional growth of the islands to form a continuous film when the islands coalesce. However, extensive studies with LEED provide numerous examples where submonolayer films are found to be ordered and where further growth proceeds layer by layer. Recent experiments with TEM, Auger spectroscopy, and ion-backscattering techniques are able to show convincingly that metal-on-metal epitaxy can proceed by a layer-by-layer growth mechanism.[1-7]

The present work arises from experiments where it was found that the elastic reflectance spectra of very low energy electrons (0—30 eV) from the (111) surfaces of bulk fcc metals show prominent sharp peaks at the energy of the Γ_2' point in the band structure.[8] Theoretical analysis of the reflection experiment showed that the peaks are brought about by a narrow band gap in which electrons cannot propagate into the metal. The peaks can be as narrow as 0.25 eV and are unique in energy and intensity for each metal. Comparison with calculated band structures and ARPS data showed that the peaks closely coincide with bulk band structure. Since in this energy range (about 20 eV) the electrons penetrate only a few atomic layers, these features should be especially sensitive to surface composition and structure. Therefore, the details of elastic reflectance spectra taken during epitaxy should reflect electronic energy states of the developing metal film. On (111) surfaces the Γ_2' peak occurs below the energy of the first external Bragg peak so threshold effects due to the emergence of external reflected beams do not complicate the data. Preliminary experiments showed that films as thin as two or three atomic layers produce structure due to both substrate and overlay film.[8,9] This paper reports the results of a study of the growth of Au overlayers on single-crystal Pd, Ag, and Ni substrates. The ways in which the spectra change with Au film thickness contribute to understanding the growth process. Differences between the growth on the three substrates are determined primarily by the degree of lattice mismatch among the different combinations. The results generally agree with previous results of TEM, LEED, Auger spectroscopy, and ion-backscattering experiments.

Oscillations due to the presence of QSE states in the Au overlay films are found in these experiments for thicker Au films deposited on Pd substrates. These oscillations

are in the energy range where the Pd substrate has a broad forbidden energy gap in the bulk bands. Measurement of the energy spacing of the oscillations gives an independent determination of the Au overlay thickness. The observation of whole level spacings, as contrasted with that observed for tunneling experiments, provides direct evidence that the Au overlayer is nearly atomically uniform in thickness over regions comparable in size to the electron beam. For these lower energies, a few eV above the vacuum level, the mean free path for electrons in Au is considerably longer and QSE states can be observed for films from 20 to 120 Å thickness.

EXPERIMENTAL

The experimental apparatus has been described in detail before.[8] Briefly, it consists of an ultrahigh vacuum (UHV) chamber with ion, Ti sublimation, and cryogenic pumping. The substrate crystal, about 1 cm in diameter, is mounted on a manipulator which allows for adjustment of position and angle. The substrate is first cleaned by argon ion sputtering while heating, and is then annealed by further heating in the vacuum. LEED optics are used to check for alignment and surface structure and a cylindrical mirror analyzer (CMA) Auger system is used to check for surface cleanliness. In the experiment it is found that good quality reproducible reflectance spectra characteristic of the individual metals under study can be produced only with clean well-annealed surfaces. The total pressure in the system is held to less than 10^{-9} Torr and clean surfaces can be maintained for many hours.

Au is deposited from a W spiral filament source mounted in a stainless-steel enclosure equipped with a shutter. The Au flux is measured with a quartz-crystal microbalance positioned nearby. The source is first calibrated for a short heating and evaporation cycle which deposits about 0.5 Å of Au per cycle. The amount is repeatable for many cycles and is estimated to be in error by not more than a few percent for each cycle. A second, and probably more accurate means of thickness calibration is provided by the QSE oscillations for thicknesses above 40 Å and is found to agree quite well with the microbalance results. All quoted thicknesses assume uniform coverage, i.e., layer-by-layer growth. Furthermore, for all stages of growth of the Au overlayer films the LEED shows the equilibrium fcc (111) threefold diffraction pattern, with no evidence for other ordered phases or effects due to disordered polycrystalline growth.

The reflection experiment consists of directing a beam of electrons at the substrate from a focused electron gun 3 cm distant and varying the energy continuously by sweeping the voltage applied to the electron cathode source. Since the strength of the peaks decreases with angle, the beam is aligned at normal incidence to better than a few tenths of a degree. The collected current I_c is measured while maintaining the sample at ground potential and sweeping the energy of the incident electrons linearly over the required range. A total current of 1 μA is typically collected. The second derivative of the current I_c'' with respect to the beam voltage is obtained by applying 1-kHz modulation voltage of about 0.3 V amplitude to the

cathode and detecting the second harmonic signal at 2 kHz with a commercial lock-in amplifier. The modulation amplitude is about equal to the thermal energy spread of the electron gun and is sufficient to resolve the sharpest peaks. For clean metals in this energy range, most of the electron reflection is elastic and specular, and a reflectance peak appears as a *dip* in I_c or a *peak* in I_c''. All of the spectra studied are reproducible, stable with time, and show no sign of alloying. The energy scale is referred to the Fermi level of the target metal using a cathode work function of 2.8 eV.

RESULTS

Figure 1 shows spectra representative of clean Pd and for a Au epitaxial film on Pd. Curve A is the collected current for a clean Pd surface over an energy range extending from the turn-on energy of the electron gun (equal to the work function of Pd) to over 20 eV. The spectrum shows the Γ_2' dip near 18 eV caused by the narrow forbidden gap in Pd. At low voltages there is another dip for energies less than about 7.1 eV. The L_1 edge of Pd, indicated by the dashed line which is the theoretical value,[10] lies at about 7.1 eV. This dip in current is associated with
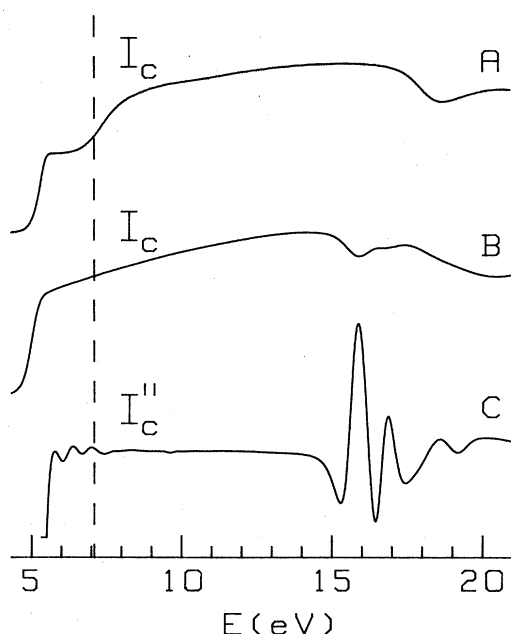

FIG. 1. Curve A is the collected current I_c vs the energy of the incident electrons for clean Pd. Dips in I_c are due to an increase in elastic electron reflectivity. The dip near 18 eV is the Γ_2' band gap and the dashed line at 7.1 eV indicates the L_1 band edge. The dip below the L_1 edge is caused by the increased reflectivity within the forbidden band. Curve B shows the same metal with a 70-Å Au overlay film. Curve C is the second derivative of curve B, where upward peaks are interpreted as peaks in reflectivity. The double peaks just above 15 eV are essentially the same as for bulk Au, and occur at the Γ_2' point of Au(111). The doublet character is believed to be due to surface reconstruction. The oscillations below 7.5 eV are due to QSE energy levels in the Au film. The spacing of the states is 0.6 eV, yielding a thickness of 74 Å from the dispersion curves of Au.

the wide forbidden band of bulk energies below L_1. Curve B is the same surface with a 70-Å Au film deposited at room temperature. Curve C is the second derivative of curve B and is identical to spectra obtained from bulk Au(111), with the exception of the oscillatory structure just below the L_1 edge. The double peaks near 16 eV are separated by about 0.8 eV with the lower-energy component typically double the intensity of the upper one. Only a single peak is predicted for bulk fcc metals and only one is observed for most.[8] The doublet for Au has been attributed to the previously reported reconstruction of the Au(111) surface.[11]

The small oscillations below the L_1 edge are due to QSE states in the Au film. They are apparently most easily observed in this energy range because the reflection coefficient for electrons inside the Au at the Au-Pd interface is enhanced by the forbidden energy gap in Pd. Assuming that one period of oscillation is associated with an individual QSE level, the observed spacing can be used to compute the film thickness. The energy level spacing ΔE is given by $\hbar v_g(\pi/w)$ where w is the film thickness and v_g is the electron group velocity in Au.[12] Using the known bulk dispersion curve (energy versus momentum) for Au in this energy range and crystal direction,[13] and assuming that whole energy level spacings are observed, a thickness of 74 Å is obtained. This agrees well with the value of 70 Å measured by the microbalance. The QSE effects are observable from about 20 Å and higher, and useful period values have been obtained over the range 35—120 Å. The limited range of energy over which the oscillations are seen is sufficient to determine the period itself but not its variation with energy. A plot of the periods against reciprocal thickness over the range 40—120 Å produces a straight line whose slope yields a value for v_g of $(2.0 \pm .3) \times 10^6$ m/s compared with the value of 2.1×10^6 m/s obtained from the theoretical bands at 6.5 eV.[13] The amplitude of the oscillations can be increased by as much as a factor of 4 by heating to about 150 °C for a few minutes. This is probably the result of an improved perfection of the film resulting in an increased lifetime and suggests that better QSE data may be produced with higher than room-temperature substrates. The QSE oscillations do not shift appreciably on this energy scale as the angle of incidence is increased to 7°, as is expected for a QSE mechanism. However, moving the electron beam around on the surface produces large changes in both the amplitude and phase of the oscillations. Such behavior is attributed to unavoidable variations of the average Au thickness across the crystal face due to the relatively close proximity of the Au source (about 3 cm).

Figure 2 shows a series of reflectance spectra for Au deposited on Pd at room temperature for successive depositions of about 0.5 Å each. For these curves the second derivative I_c'' is plotted. As the Au overlayer builds up, there is a gradual decrease in intensity of the Pd Γ_2' peak and a growth of the Au spectrum, evolving into one very similar to bulk Au for a thickness above about ten layers, 23 Å. First, it is noticed that the Pd peak is extinguished after three or four layers of Au. There is some ambiguity in this observation because after about three layers the Pd peak appears to be replaced by a secondary peak, which is
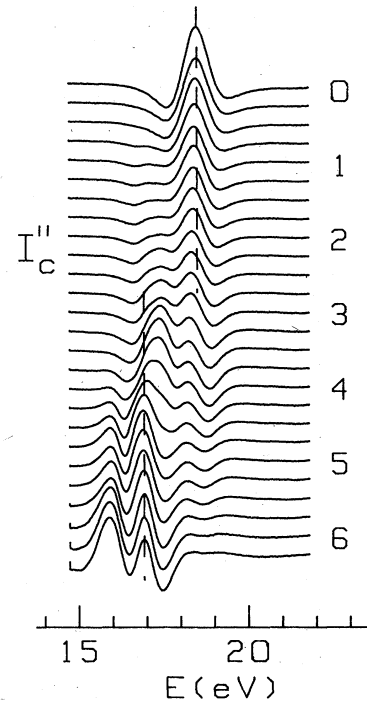

FIG. 2. Reflectance spectra for an initially clean Pd(111) surface at room temperature as Au is deposited. Thicknesses are indicated in layers with one layer equal to 2.35 Å. The second derivative of the collected current I_c'' is plotted versus the energy of the incident electrons. The single peak for clean Pd, located by the dashed line above 18 eV, is the Γ_2' point, while the double peaks at 16 and 16.9 eV are the characteristic doublet for Au. Due to the lattice mismatch of these two metals, the initial appearance of the higher-energy Au peak is shifted upward from its bulk value (dashed line) indicating a contraction of the Au lattice, while the small downward shift of the Pd peak is caused by a slight expansion of the Pd lattice. The lower component of the Au doublet appears after about four layers and is believed to be caused by reconstruction of the Au surface.

actually due to Au. Nevertheless, most or all of the Pd surface is covered at five layers. Second, the characteristic double peak of Au does not form at first, but starts as a broad single peak shifted towards the Pd peak. This upward shift of $+0.3$ eV is believed to result from a contraction of the first Au layers as they conform to the smaller Pd lattice constant. The lattice mismatch for this combination is $+4.6\%$. There is a small downward shift of the Pd peak, indicating a slight expansion of the Pd lattice at the surface. The direction of the observed peak shifts indicates that the initial stage of film growth is pseudomorphic, i.e., the Au lattice is contracted to match the Pd lattice and after a buildup of four or five layers goes through a transformation to the bulk lattice. This is necessarily accompanied by defect formation, possibly an array of misfit dislocations.[14] Third, the lower energy component of the Au doublet does not appear until about 10 Å thickness and after the Au film has evolved from its pseudomorphic phase.

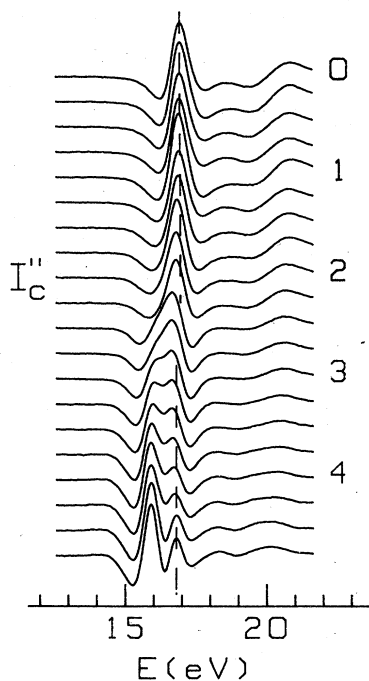Figure 3 shows electron reflectance data for Au on

FIG. 3. Reflectance spectra for Au deposited on the Ag(111) surface at room temperature. Thicknesses are indicated by the number of layers. The lattice mismatch is small and the Γ_2' peaks for the Ag and Au surfaces are unshifted from their bulk values (dashed lines) to within the accuracy of the measurement. The growth mechanism is believed to be layer by layer and the Au doublet appears after about four layers of Au are deposited.
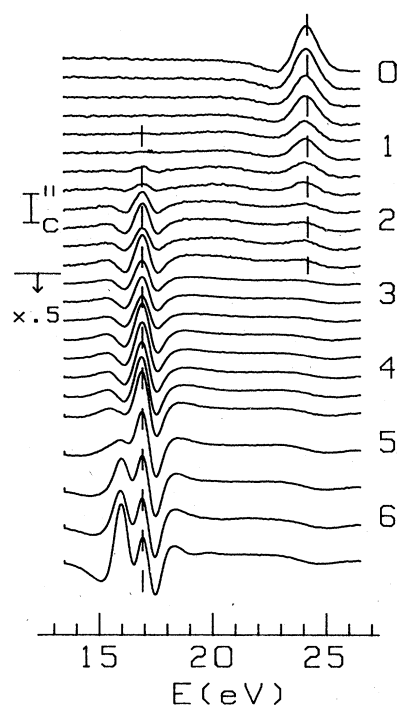

FIG. 4. Reflectance spectra for Au deposited on the Ni(111) surface at room temperature. Thicknesses are indicated by the number of layers. The lattice mismatch is large for this combination but the Γ_2' peaks of Au and Ni (dashed lines) are unshifted indicating no change in lattice constant of either metal. The Au film grows with its bulk lattice constant and the second Au peak appears after about four layers of Au are deposited.

Ag(111). For this case the lattice mismatch is small, -0.2%. First, the positions of the Γ_2' peaks are essentially the same as their bulk values. Although the overlap of the two peaks is enough to cause some apparent shifts, there is no indication of a large strain in either metal. Since the mismatch is small between Au and Ag, no shift of the Au peak from its bulk value is expected during epitaxy. Due to uncertainties in the calibration of the energy scale, mostly because of cathode work-function uncertainties (± 0.2 eV), it is not possible at present to make precise comparisons with other spectra taken for bulk Au in order to measure a small strain which might be predicted for these two metals. Second, as with the Pd substrate, there is a gradual decrease in intensity of the Ag substrate peak over the first three or four layers. Third, the lower-energy component for the Au appears after about four layers and then evolves into the bulk Au double peaks after about ten layers.

Figure 4 shows the data for Au deposited on Ni. The peak of Ni is well separated from the Au peaks so there is no interference between them. The lattice mismatch of $+13.6\%$ is considerably larger than for Au on Pd. First, there is no sign of a shift of either the Au or the Ni Γ_2' peaks. This implies that there is no tendency of the Au overlay film to conform to the lattice spacing of Ni. Second, the Ni substrate signal is obscured after three or four layers of Au are deposited. The initial growth stage must therefore involve a layer-by-layer formation of Au.

The lattice constant is equal to bulk Au and the overall symmetry and growth habit are determined by the Ni(111) surface. Third, the formation of the Au doublet begins after about three layers.

DISCUSSION

Some details about the epitaxial growth of Au on these substrates may be inferred from these results. For Au on Pd, the lattice constant of the initial two or three monolayers of Au is contracted to match the Pd while the latter is slightly expanded. This can be checked by obtaining the expected shift of the Γ_2' peak of Au from bulk band-structure calculations which have been done to obtain the dependence of the band energies upon lattice expansion.[13] The value obtained is $+0.28$ eV compared to the observed $+0.3$ eV. The agreement is quite close and suggests that the interpretation is the correct one. The small downward shift of the Pd Γ_2' peak with Au coverage can be estimated from a simple model based on the change in the reduced zone empty band energies due to the change in zone dimension.[10] The observed shift of -0.15 eV results from an expansion of the Pd lattice by about $+0.01$ Å. Finally, the complete extinction of the Pd peak intensity after about four layers of Au suggests that the growth is layer by layer, or nearly so, since this thickness is com-

parable to the mean free path of electrons at this energy. The shift of the Au peak to its bulk value after four or five layers implies that there must be a number of misfit dislocations created to allow for this shift, but details of defect structure are not directly observed.

For thicker films the Au develops relatively free of imperfections since QSE states can be observed up to 120 Å thickness, so the mean free path for electrons at these energies must be comparable. The period of the observed QSE oscillations is found to be equal to the actual energy-level spacing based on measured thickness and known band structure. For Au in this energy range, the dispersion varies smoothly and is free electronlike, so the use of the simple formula, previously quoted, to relate thickness to energy level spacing is justified. Previously, QSE states were also observed in tunneling experiments in polycrystalline-oriented Au films.[12] The effects of roughness were especially evident in this case where the films were composed of an ensemble of grains each with differing thicknesses characterized by a distribution about 10% wide. Observed tunneling spectra are an average over this distribution. In tunneling experiments, QSE oscillations appear with an apparent period equal to a fraction of the actual level spacings. Periods equal to $\frac{1}{2}$ or $\frac{1}{3}$ of the energy-level spacing, the commensurate spacings, are observed if the films possess even a few percent roughness.[12] However, for the present case, fractional spacings are not observed. This is analyzed in some detail in Ref. 12, and formula (14) of that reference was applied to these results in order to estimate the maximum degree of thickness nonuniformity allowed for these experiments. It was found that the films do not vary in thickness more than about one or two atom layers over the surface, in this case a macroscopic area equal to the size of the beam, about 4 mm^2. QSE oscillations were not observed for Au on the Ag or Ni substrates. Thickness uniformity or surface smoothness may not be sufficient, or there may be more fundamental reasons related to bulk imperfections or reflection effects at the interface between the Au and metal substrates which may limit the electron lifetime.[12]

For Au on Ag, the data show no sign of lattice distortion of either substrate or overlay Au films, and the Ag peak is extinguished after three or four layers of Au, indicating layer-by-layer growth. The Au Γ_2' peak emerges after coverage of about three layers and is not shifted appreciably from its bulk value. Therefore, it is concluded that the Au is in registry with the Ag lattice and layer-by-layer growth continues even to thicker growth stages. For Au on Ni, the Ni Γ_2' peak is also extinguished with only three or four layers of Au, indicating layer-by-layer growth in this case even though the lattice mismatch is large. There is no tendency for the Au lattice constant to conform to the Ni. It is possible some strain, misfit dislocations and grain boundaries are present in the initial stages of growth.

Comparison of these conclusions with previous results of other techniques indicates good overall agreement. For the case of Au on Pd, Yagi and co-workers concluded on the basis of their TEM measurements that epitaxy proceeds in a layer-by-layer fashion even for the initial layers.[14] These same workers also directly observed misfit

dislocations during the transition stage. Similar conclusions were reached by Kuk and co-workers from their recent ion-backscattering experiments.[15] They found that the first few layers grew layer by layer with the Au in registry with the Pd substrate, and after a thickness of about two or three layers the lattice constant shifts to the bulk Au value. This was true of both the lattice constant in the plane of the substrate, obtained from their LEED measurements, as well as that for the perpendicular direction, obtained from the ion-scattering data. The present electron reflection experiments tend to measure the perpendicular component but some influence of the other directions should also be felt because these directions must be included to obtain a realistic picture of the electronic structure seen by reflectance.[8] In addition, on the basis of LEED and Auger spectroscopy experiments Kuk et al. noticed a slight expansion of the substrate Pd lattice by about + .01 Å in agreement with the change estimated from the observed shift of the Pd Γ_2' peak.

For Au on Ag the results agree with the conclusions reached using LEED and Auger spectroscopy and most recently the ion-backscattering experiments of Culbertson and co-workers.[16] The latter workers found a clear layer-by-layer growth pattern from the very first layers and a Au lattice constant equal to that of the underlying Ag substrate.

All of the electron reflection results show only a single Au peak during the initial phase of growth which then transforms into the double peak after a few layers. This implies that reconstruction of the Au surface does not take place until several layers have developed. The TEM methods of Yagi and co-workers[14] provided them with a direct view of a Au(111) reconstruction during the first stages of epitaxy and they found that it does not form until about four layers of Au are deposited on Ag or Pd. This supports the conclusions that the Au(111) double peak, which does not form until several layers of Au are deposited, is due to surface reconstruction, the details of which are yet to be determined.

For layer-by-layer growth, the theory of epitaxy developed by Frank and van der Merwe[17,18] is appropriate. On the basis of intermetallic binding energies and strain energy they predict that for lattice mismatches of less than about 9% the initial growth phase will be pseudomorphic, i.e., the overlayer lattice will conform to the lattice structure of the substrate, and will continue to grow this way until a critical thickness is reached. Above this thickness misfit dislocations will begin to form and the film will gradually shift to the bulk lattice constant. For Au on Pd the critical thickness was estimated by Kuk et al.[15] to be about 6 Å. Both the ion-backscattering experiments and the present work are in agreement that the observed critical thickness is close to this value. For Au on Ag, the critical thickness is very large, while for Au on Ni, with a 13.6% mismatch, no pseudomorphic growth behavior is predicted and is not observed. Further experimental details about the growth behavior for Au on Ni are needed but this work indicates that growth is layer-by-layer epitaxy in combination with possible strain and dislocations or other defects due to the large lattice mismatch.

CONCLUSIONS

Electron reflection has been applied to the study of the initial growth stages of epitaxy. Both pseudomorphic and nonpseudomorphic growth behavior are observed and other details of growth can be seen. Only a few monolayers of Au are sufficient to cause extinction of the substrate signal indicating that layer-by-layer growth is occurring in all three cases. Comparison of these results with those obtained from LEED, Auger spectroscopy, TEM, and ion-backscattering experiments corroborate the conclusions, and both the direction and magnitude of the peak shifts occurring during epitaxy are in agreement with the theoretical predictions of band theory. The ability of the method to see layer-by-layer growth in the early stages is somewhat qualitative. For thicker films the QSE oscillations provide striking evidence for the nearly atom-

ic uniformity in thickness of the Au films on Pd over macroscopically large areas.

This technique is simple, relatively easy to use, and with some modifications can be used continuously during film growth. Since electronic states peculiar to the first few atomic layers are probed by low-energy electrons, the intensity and position of the Γ_2' peak provides a sensitive monitoring tool to keep track of film thickness, film quality, surface cleanliness, and degree of annealing. The method so far has been used only for fcc metals but there is hope that it can be extended to other metal and semiconductor systems.

ACKNOWLEDGMENTS

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