PHYSICAL REVIEW B VOLUME 49, NUMBER 3 15 JANUARY 1994-I

Intermixing at Au-In and Pd-In interfaces at 90 K as observed by *in situ* Auger-electron and electron-energy-loss spectroscopy

Th. Koch, A. Siber, J. Marien, and P. Ziemann
Fakultät für Physik, Universität Konstanz, P.O. Box 5560, D-78434 Konstanz, Federal Republic of Germany
(Received 28 June 1993)

Auger-electron spectroscopy and electron-energy-loss spectroscopy methods have been employed to study the growth process and possible intermixing of Au and Pd films on top of polycrystalline In at 90 K. To accomplish this, In films (thickness 30 nm) were deposited by ion-beam sputtering onto fused-quartz substrates and then stepwise covered by Au or Pd up to a total coverage of 5 nm. During this process, the intensities of the Auger emission lines and the accompanying plasmon loss lines of In were measured as a function of the increasing Au or Pd coverage. Additional information was extracted by *in situ* comparison of energy-loss spectra of Pd/In interfaces obtained with 120-eV electrons to those of bulk In_3Pd and In_3Pd_5 alloys as well as of pure In and Pd. The results indicate that during the deposition of Au or Pd onto In intermixed phases are formed even at 90 K. This intermixing is restricted to a coverage of 1.5 nm for Au and 0.4 nm for Pd corresponding to mixed layer thicknesses of 6.0 and 2.8 nm, respectively. For higher coverages, growth of the pure metals is observed.

I. INTRODUCTION

The ability to grow high-quality ultrathin multilayers has led to a remarkable upsurge in interest and activity in the field of surface and interface properties. For layered systems, the behavior of the interfaces are both of practical and fundamental importance. In *A-B* bilayers, a special feature is the possible occurrence of interface reactions. In some metallic multilayers of (*AB*) type, the formation of amorphous binary phases has been observed due to long-range interdiffusion accompanied by a solid-state reaction.[1,2] An additional route into the amorphous phase was reported recently for the Au/In system.[3] Here, at 85 K, a reaction is found into the amorphous phase, which is restricted to the interface to within approximately 6.0 nm, while the interdiffusion observed at higher temperatures always results in a crystalline phase.[4] Exploiting the above interface reaction, thick amorphous Au/In films can be prepared by stacking Au/In layers with individual layer thicknesses below the threshold values of 1.5 nm for Au, and 4.5 nm for In. Similar interface reactions have been found for In/Pd layers and were used to prepare amorphous films of the nominal composition In_3Pd.[5] In both systems, the interface behavior was characterized by *in situ* resistance measurements during layer deposition. Though this technique is highly sensitive,[6] one cannot definitely exclude possible misinterpretations due to the influence of surface scattering on the resistance, which in turn depends on the roughness or the specularity of the surface and its vibrational behavior,[7] i.e., on quantities which are difficult to determine experimentally. Thus, in the present context, resistance measurements become conclusive only in those cases where the concentration dependence of the resistivities and recrystallization temperatures of existing amorphous phases are quantitatively known. As a consequence, additional analytical tools are needed to arrive at an unequivocal conclusion about the occurrence of an interface reaction into an amorphous phase. In Ref. 5, the perturbed angular $\gamma\gamma$ correlation (PAC) had been applied for this purpose. Based on the high sensitivity of the hyperfine interaction of the radioactive isotope ^{111}In on the local atomic environment, this technique allows us to distinguish between an interface reaction resulting in a crystalline or amorphous phase. But the applicability of PAC to the present aim hinges on the requirement that the probe atoms occupy well-defined sites at or close to the surface prior to the interface reaction, which is not granted in many cases. Thus it appears quite natural to apply a well-established electron spectroscopy like Auger-electron spectroscopy (AES) to analyze for interface reactions. However, by considering the deposition of *B* atoms on top of a thick *A* film, and performing *in situ* AES to measure, e.g., the intensity of an Auger line of atom *A* as a function of the coverage of *B* atoms, it is immediately clear that AES by itself is not sufficient to distinguish between, e.g., the occurrence of an interface reaction and island growth of *B* [Volmer-Weber (VW) growth]. It is the aim of the present paper to demonstrate that by combining the standard AES technique with electron-energy-loss spectroscopy (EELS) using low energies of the primary beam (typically 100–500 eV), clear experimental evidence can be provided for the occurrence of an interface reaction in the Au/In and In/Pd systems. Unfortunately, this combination does not allow us to distinguish between an amorphous or crystalline phase as a result of such a reaction. To accomplish this distinction, a further *in situ* technique needs to be combined with the spectroscopy. However, in many cases, the experimental establishment of the occurrence of an interface reaction is already of considerable importance. In the following examples of Au/In and In/Pd layers, the above-mentioned resistance measurements can provide additional information on amorphousness.

0163-1829/94/49(3)/1996(5)/$06.00 ©1994 The American Physical Society

Using EELS, main emphasis is placed on losses due to the excitation of bulk plasmons either by the primary beam (extrinsic excitation) or accompanying an Auger event (extrinsic and intrinsic excitations). For the present purpose, the principal distinction between intrinsic and extrinsic excitations of plasmons[8] is not important. Though the analysis of plasmon losses has been used previously to study equilibrium reactions at interfaces such as oxidations[9,10] and the formation of silicides,[11,12] or to exclude interface reactions as in the case of Pb/Ni(001),[13] we are not aware of an application of this technique to detect an interface reaction into a metastable metallic phase, which is restricted to a certain length. Furthermore, the previous electron loss studies placed emphasis on the energy of the plasmon under study to extract information about chemical reactions. On the other hand, from x-ray photoemission spectroscopy (XPS) results it is well known,[14–16] that the intensity of a plasmon loss structure also can be dramatically reduced by alloying, especially in alloys containing a *3d* element as in the present examples. It is this special feature which is exploited in combination with standard AES to extract information about the existence of an interface reaction and its reaction depth.

II. EXPERIMENT

The experiments were performed in a stainless-steel UHV system consisting of two separate chambers for sample preparation and analysis, respectively, which are connected via a load lock system to allow sample transfer. The residual gas pressure is less than 3×10^{-9} mbar in the preparation chamber, and less then 2×10^{-10} mbar in the analysis chamber.

The samples were prepared by ion beam sputtering of elemental targets using 1-keV Ar^+ ions extracted from a Kaufmann-type ion source. In this way, a 30-nm-thick In film is deposited onto fused-quartz substrates kept at 90 K. Subsequently, this In surface is stepwise covered at the same temperature with Au or Pd, respectively, again by ion-beam sputtering. After each deposition step producing a coverage of 0.1 nm, the covering process is interrupted and the sample, still kept at 90 K, is transferred into the analysis chamber for the electron spectroscopy measurements. Au or Pd deposition is performed at a rate of 0.015 nm/sec as monitored by a quartz microbalance, which is also used to determine the total thickness of the In film and the coverage.

For the electron spectroscopy, the analysis chamber is equipped with a commercial cylindrical mirror analyzer (CMA) with an internal coaxial electron gun (Omicron). The Auger spectra were recorded using an electron beam with a primary energy of 3 keV, and the EEL spectra were taken with an energy of 120 eV of the primary beam. Its angle was 30° relative to the sample surface normal, and its current was 2 μA. The electron-energy-distribution curves were recorded in the derivative mode by using lock-in technique, while the negative second derivatives for the EEL spectra were obtained by numerical methods. Sinusoidal modulation voltages of 0.5 and 2.0 V_{pp} were applied to the CMA when recording EEL and Auger spectra, respectively. The peak-to-peak distance of the first derivative signals are taken as a measure for the AES line intensities.

To provide an additional possibility for identifying phases produced by interface reactions, reference samples of the crystalline In_3Pd and In_3Pd_5 alloys were prepared by thermally reacting In/Pd multilayers of appropriate composition at 390 K.

III. RESULTS AND DISCUSSION

AES was used to determine the Au and Pd film growth mode at 90 K on top of polycrystalline In. For this purpose, the intensity (peak to peak) of the In *MNN* Auger line at 404 eV has been determined as a function of the coverage with Au or Pd atoms, respectively. For pure In, an additional line of significant intensity can be detected at 392 eV. The observed shift to lower energies by 12 eV exactly fits the well-known excitation energy of an In bulk plasmon.[17] Thus this line can be identified as a satellite of the 404-eV Auger transition due to In bulk-plasmon losses. This feature is clearly visible in the Auger spectrum of pure In shown in Fig. 1. Due to the overlap with the 404-eV line, the analog plasmon loss satellite of the In 410-eV Auger transition can be seen only as a shoulder at 398 eV. Added to Fig. 1 are the corresponding spectra obtained for crystalline In_2Au and In_3Pd alloys. Here the most important feature is the

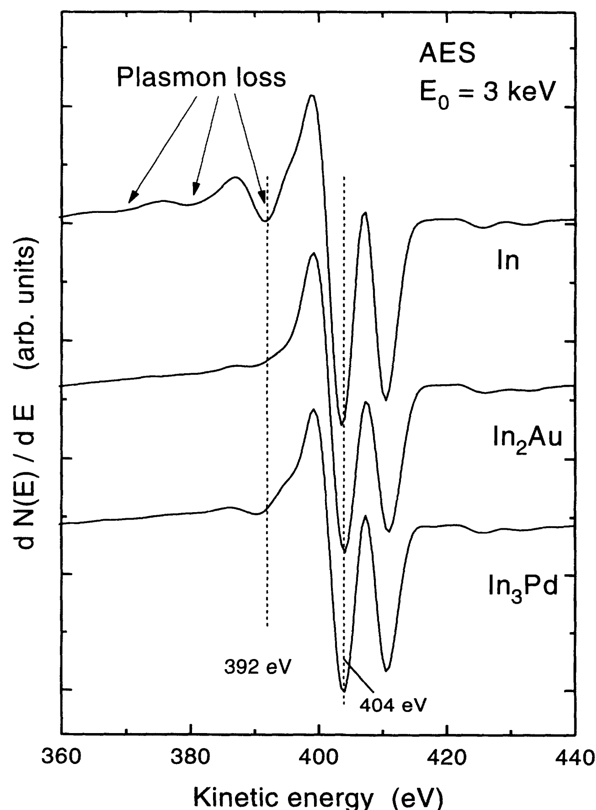

FIG. 1. Auger spectra of pure In and of In_2Au and In_3Pd alloys resulting from In *MNN* transitions (404 and 410 eV) and plasmon loss satellites as indicated by arrows.

drastic reduction of plasmon loss signals at 392 eV, which become hardly detectable in first derivative spectra. In contrast, the 404-eV Auger transition of In is practically not affected by alloying. It is this dramatic change of the plasmon loss intensity, which is exploited in the following to characterize the Au/In and Pd/In interfaces.

A. The Au/In system

To study the In/Au interface, the intensity of the 404-eV In Auger line is measured as a function of the Au coverage. The results are shown in Fig. 2, where the intensities are normalized to the starting value prior to Au deposition. For clarity, these intensities are plotted logarithmically [Fig. 2(a)] as well as linearly [Fig. 2(b)] versus the Au thickness as independently determined by a quartz microbalance. Assuming a layer-by-layer growth [Frank–van der Merwe (FvM) growth], the AES signal of the In film at the monolayer (ML) end points would be given by

$$I/I_0=\exp(-nd/\lambda\cos\varphi) , \qquad (1)$$

where I_0 is the signal of the clean In surface without attenuation, d is the thickness of 1 ML of deposited material, and λ is the inelastic mean free path (IMFP) of the In

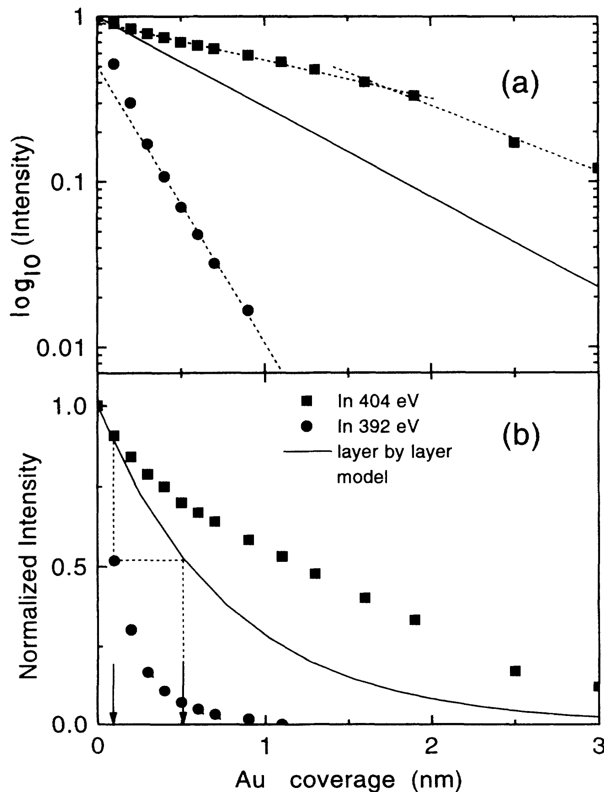

FIG. 2. Attenuation of the normalized intensity of the In 404-eV AES signal and its plasmon loss satellite at 392 eV due to a stepwise coverage of an In film by Au atoms: (a) logarithmic scale (arb. units); (b) linear intensity scale. The solid curves are calculated assuming a layer-by-layer growth (cf. text); the dashed lines in (a) represent exponential least-squares fits to the data.

Auger electrons escaping through the deposited overlayer with a total number of n ML. To obtain the effective escape depth, the thickness is corrected by the inverse cosine of the spectrometer takeoff angle φ (42° for the CMA). Based on Eq. (1), the solid curves in Figs. 2(a) and 2(b) were calculated using $\lambda_{\mathrm{Au}}=1.07$ nm from Ref. 18, and $d_{\mathrm{Au}}=0.256$ nm as deduced from the Au density.

The intensity of the In 404-eV Auger line exhibits a clear deviation from the calculated ideal layer-by-layer growth. All data points lie significantly above the solid curves in Fig. 2. Such behavior can be explained by different models. Either the Au atoms have a tendency to form islands if deposited on top of In (VW growth), or an intermixing of In and Au atoms takes place due to an alloy formation at the interface. To decide between these possibilities, the intensity behavior of the plasmon loss line at 392 eV has to be taken into account. As also demonstrated in Fig. 2, the intensities of this line are strongly attenuated by the Au coverage, leading to its disappearance at approximately 1 nm. Since the kinetic energies of the detected electrons from both In lines differ by only 3%, identical values of the corresponding inelastic mean free paths are expected.[18] Thus the dramatic difference of the observed attenuation behavior of both lines cannot be interpreted as an IMFP effect. As a consequence, both lines should exhibit the same intensity versus coverage relation for VW growth in contrast to the experimental result. In this way, one is led to the conclusion that the deposited Au atoms react with the underlying In film to form an alloy with a composition which can be quantitatively estimated in the following way. Figure 2(a) gives a slope of the exponential decay of the plasmon loss line at 392 eV, which is larger than the corresponding value calculated for layer-by-layer growth by approximately a factor of 5. Furthermore, from the reference spectra shown in Fig. 1 it is obvious that the plasmon excitation probability is strongly reduced after alloy formation. Combining both informations, one concludes that, e.g., an overlayer of 0.1-nm Au results in an attenuation of the loss line corresponding to a 0.5-nm-thick layer of a supposed alloy [this estimate is indicated in Fig. 2(b) by dashed lines]. Here a homogeneous lateral growth of the alloy has been assumed. The 0.5 nm compares very well with the value of 0.4 nm calculated for the formation of In_2Au by the reaction of 0.1-nm Au with In, where available densities have been used. Thus the formation of this alloy is assumed to be the dominating interface reaction, though the somewhat steeper slope observed for the first 0.2 nm of Au (cf. Fig. 2) indicate a more In-rich composition at the beginning of the deposition.

A further conclusion can be drawn from the two significantly different logarithmic slopes observed for the intensity decay of the Auger line at 404 eV in Fig. 2(a). At an Au coverage of 1.5 nm, the attenuation of this line becomes stronger, and the logarithmic slope is not too far from the value expected for a layer-by-layer growth. For this reason, it is concluded that up to a thickness of 1.5-nm Au on top of In, an alloy forms at the interface with an average composition of In_2Au and a total thickness of approximately 6.0 nm. For larger Au thicknesses, its

growth seems to be appropriately described by the FvM model. These results and conclusions are in excellent agreement with those reported in Ref. 4, which were obtained by measuring the electrical resistance during Au deposition onto In at 90 K.

B. The Pd/In system

As in the case of In/Au, the In/Pd interface has been studied by analyzing the same In Auger lines as above during the deposition of Pd on top of In at 90 K. To emphasize the similarity to the In/Au data, the In/Pd results are presented in Figs. 3(a) and 3(b) in total analogy to Figs. 2(a) and 2(b). Again, the solid lines represent the expected behavior for a layer-by-layer growth calculated with $\lambda_{Pd}=1.01$ nm,[18] and $d_{Pd}=0.245$ nm. During the Pd deposition, the presence of some oxygen could be observed in the Auger spectrum. This contamination leads to the scattering of the experimental intensities of the Auger line at 404 eV, as can be seen in Fig. 3. However, the results still clearly demonstrate that all data points lie above the solid lines, as found before for In/Au. Also, the much steeper intensity decay of the plasmon loss line at observed 392 eV is in close analogy to the In/Au results. Quantitatively, in the present In/Pd case, the slope of this exponential decay is larger than the calculated FvM slope by a factor of 7. Thus, applying the same arguments as above for the In/Au system, it is concluded that during the deposition of Pd on top of In an interface reaction takes place leading to the formation of an alloy. The composition of this alloy is estimated as indicated by the dashed lines in Fig. 3(b). Here, 0.1-nm Pd reacts to form a 0.7-nm-thick layer of reduced plasmon excitation probability. This result fits nicely with the calculated reaction of 0.1-nm Pd with 0.6-nm In to form 0.7-nm In_3Pd. This conclusion is in excellent agreement with a recent study of the (100)-Pd surface covered with In atoms using the PAC technique, which also reported the formation of In_3Pd at the interface.[5]

Due to the higher noise level of the Auger intensities, in the present case a well-defined distinction of two different logarithmic slopes is not possible. However, assuming a behavior as indicated by the dashed line in Fig. 3(a), one can at least estimate that a layer-by-layer growth starts at a Pd coverage of 0.4 nm. Thus, assuming the formation of In_3Pd, one concludes that the thickness of the reaction zone is approximately 2.8 nm. This estimate will be confirmed by the analysis of EELS measurements described in the following.

To further corroborate the conclusions drawn from the intensity decay of the In Auger line at 404 eV, and its

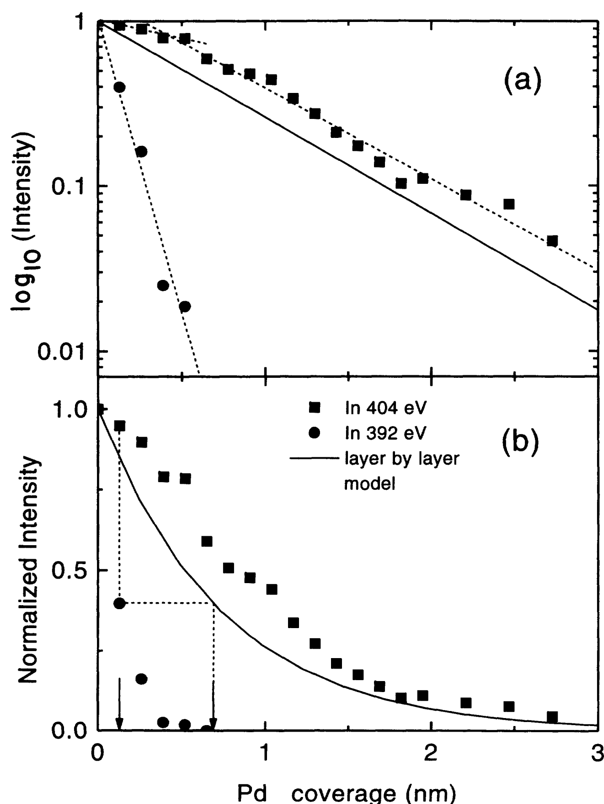

FIG. 3. Attenuation of the normalized intensity of the In 404-eV AES signal and its plasmon loss satellite at 392 eV due to a stepwise coverage of an In film by Pd atoms: (a) logarithmic scale (arb. units); (b) linear intensity scale. The solid curves are calculated assuming a layer-by-layer growth (cf. text); the dashed lines in (a) represent exponential least-squares fits to the data.

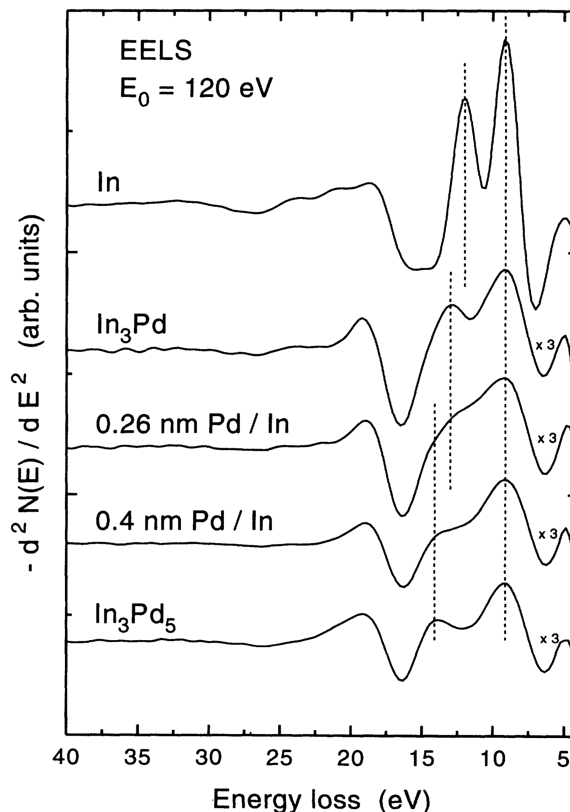

FIG. 4. Second derivative electron-loss spectra (normalized to the intensity of the elastic peak in the corresponding first derivative spectra) obtained for pure In, crystalline In_3Pd, and In_3Pd_5 reference samples, and an In film covered at 90 K with Pd layers of 0.26- and 0.4-nm thickness, respectively. Note the enlargement factors times 3 for the alloys and interfaces. The energy of the primary electron beam in all cases is $E_0 = 120$ eV.

plasmon loss satellite at 392 eV due to the Pd deposition, additional EELS measurements were performed using a primary electron beam with an energy of 120 eV. To enlarge the essential characteristic features, the corresponding results are presented in Fig. 4 in the form of second derivative loss spectra. The idea is to compare the loss spectra obtained after deposition of a thin Pd layer onto In at 90 K with the spectrum of pure In as well as with the reference spectra observed for crystalline In_3Pd and In_3Pd_5 alloys. For the pure In sample, one finds pronounced structures due to interband transitions at 5.0 and 9.1 eV, and to the bulk plasmon loss at 12.0 eV. Less pronounced structures are seen at 18.7, 21.1, 24.2, and 32.4 eV. All these positions of structures are in very good agreement with previous experimental data.[17,19] The second spectrum in Fig. 4 corresponds to In_3Pd. Besides an overall loss of intensity (all spectra in Fig. 4 are normalized to the intensity of the elastic peak in the first derivative spectra; note the enlargement factor times 3), a clear shift of the bulk-plasmon energy of 0.9 eV relative to the position in pure In is found. An identical shift can be recovered as a shoulder in the third spectrum in Fig. 4, which is observed after coverage of an In film with a 0.26-nm-thick layer of Pd. Also, the strongly reduced overall intensity is comparable to the In_3 Pd spectrum. Both features clearly suggest that the deposited Pd reacts with the underlying In to form a thin In_3 Pd alloy. This view is supported by the additional shoulder at 14.1 eV in the 0.26-nm Pd/In spectrum. This specific structure becomes much more pronounced by adding more Pd on top of In, increasing its total thickness up to 0.4 nm (cf. Fig. 4), while the shoulder at 12.9 eV disappears. In the case of an interface reaction, the additional Pd may lead to the formation of a more Pd-rich alloy. Comparison to the lowest spectrum obtained for In_3Pd_5 in Fig. 4 confirms this interpretation.

IV. CONCLUSION

It has been demonstrated that a combination of the standard Auger technique with an analysis of the intensity decay of a plasmon loss line brought about by stepwise covering a metal A with another metal B, can be used to decide whether an interface reaction occurs leading to the formation of an $A_{1-x}B_x$ alloy. An estimate of x is obtained by comparing the experimental intensity decrease of the loss line to that expected for an ideal layer-by-layer coverage of A by B and relying on available densities. Additional information about the extension of the interface reaction can be extracted from the logarithmic slopes of the coverage dependence of the Auger intensities.

This combined technique has been applied to the A/B interfaces In/Au and In/Pd, which are prepared and analyzed at 90 K. In both cases the occurrence of an interface reaction could be detected. For In/Au, the deposition of the first 1.5-nm Au leads to an In_2Au alloy approximately 6.0 nm thick. For In/Pd, during the coverage of the first 0.26-nm Pd, a predominantly In_3Pd alloy is formed with a transition to a more Pd-rich composition (In_3Pd_5) for Pd thicknesses up to 0.4 nm. The reaction zone is restricted to approximately 2.8 nm in this case. The results for both systems are in excellent agreement with those reported previously based on electrical resistivity measurements[4] and PAC.[5]

ACKNOWLEDGMENTS

This work has been continuously supported by Deutsche Forschungsgemeinschaft (DFG), Sonderforschungsbereich 306.

[1] W. L. Johnson, Prog. Mater. Sci. **30**, 81 (1986).
[2] K. Samwer, Phys. Rep. **161**, 1 (1988).
[3] M. Seyffert, A. Siber, and P. Ziemann, Phys. Rev. Lett. **67**, 3792 (1991).
[4] M. Seyffert, A. Siber, and P. Ziemann, Thin Solid Films **207**, 197 (1992).
[5] R. Fink, T. Koch, G. Krausch, J. Marien, A. Plewnia, B.-U. Runge, G. Schatz, A. Siber, and P. Ziemann, Phys. Rev. B **47**, 10 048 (1993).
[6] D. Dayal, H.-U. Finzel, and P. Wißmann, in *Thin Metal Films and Gas Chemisorption,* edited by P. Wißmann (Elsevier, Amsterdam, 1987), p. 53.
[7] D. Schumacher, *Surface Scattering Experiments with Conduction Electrons,* Springer Tracts in Modern Physics Vol. 128 (Springer, Berlin, 1993).
[8] P. Steiner, H. Höchst, and S. Hüfner, Z. Phys. B **30**, 129 (1978).
[9] P. Sen, M. S. Hedge, and C. N. R. Rao, Appl. Surf. Sci. **10**, 63 (1982).
[10] S. M. Rossnagel, H. F. Dylla, and S. A. Cohen, J. Vac. Sci. Technol. **16**, 558 (1978).
[11] R. Anton, U. Neukirch, and M. Harsdorf, Phys. Rev. B **36**, 7422 (1987).
[12] P. J. W. Weijs, J. C. Fuggle, and P. A. M. van der Heide, Surf. Sci. **269**, 97 (1992).
[13] Zhao Ruguang and Yang Weisheng, Acta Phys. Sin. **41**, 1125 (1992).
[14] B. M. Hartley and J. B. Swan, Aust. J. Phys. **23**, 655 (1970).
[15] S. A. Abo-Namous, P. T. Andrews, and C. E. Johnson, J. Phys. F. **9**, 61 (1979).
[16] H.-G. Boyen and P. Oelhafen (private communication).
[17] M. Scrocco, Phys. Status Solidi B **125**, 713 (1984).
[18] M. P. Seah and W. A. Dench, Surf. Inter. Anal. **1**, 2 (1979).
[19] R. A. Pollak, L. Ley, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, J. Electron Spectrosc. **3**, 381 (1974).