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Temperature-dependent top-layer composition of ultrathin Pd films on Cu(100)

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Positron-annihilation-induced Auger electron spectroscopy (PAES), electron-induced Auger electron spectroscopy, and low-energy electron diffraction have been used to study the composition and structure of vapor-deposited Pd films on Cu(100). Our results show that the PAES intensity from Pd saturates while that from Cu attenuates to near zero by one monolayer of Pd deposition at 173 K. This is confirmation of the top-layer selectivity of PAES in metal-on-metal systems. Changes in the PAES intensities provide a direct indication of the intermixing of Cu and Pd in the topmost layer as a Pd film deposited at 173 K is warmed to 303 K, and of the formation of a Cu overlayer upon further warming to 423 K. Lack of agreement between model calculations which assume delocalized positron states and measured PAES intensities at 173 K suggests that positrons are localized at sites containing Pd atoms.

Work on artificial multilayer materials, as well as studies of chemical, electronic, and magnetic properties of ultrathin metal films have prompted interest in the development of a detailed understanding of the factors involved in the growth of thin metal films. For a given film-substrate combination the necessary conditions for desired growth modes must be determined experimentally.[1] For example, surface segregation of the substrate material [as in the case of Fe on Cu(100) (Ref. 2)], or surface-alloy formation [as in the case of Pd (Refs. 3–6) and Au (Refs. 7 and 8) on Cu(100)], has been observed to inhibit layer-by-layer growth, even at room temperature.

Ideally, an experimental probe of ultrathin film growth would be able to resolve the chemical composition of a single layer. Previous experimental[9,10] and theoretical work[11] strongly suggests that positron-annihilation-induced Auger electron spectroscopy (PAES) should be able to obtain information selectively from the topmost layer of metal-on-metal systems. The enhanced surface selectivity of PAES stems from the fact that the positron becomes localized just outside the surface before it annihilates. As a result almost all of the Auger electrons originate from the topmost atomic layer.[9–11] This is in contrast to conventional Auger techniques in which the Auger electrons originate from an excitation volume which extends hundreds of atomic layers below the surface. The surface selectivity in conventional Auger spectroscopy is therefore limited to the 4–20-Å escape depth of the Auger electrons. In this paper, we present the results of our study of the temperature-dependent top-layer composition of submonolayer Pd films deposited on Cu(100) using PAES, electron-induced Auger electron spectroscopy (EAES), and low-energy electron diffraction (LEED). The relative PAES intensities of Pd and Cu were measured at different substrate temperatures with varying amounts of Pd deposition in order to observe directly the surface alloy formation and to determine the Pd surface coverage. The results confirm the top-layer selectivity of PAES in metal-on-metal systems and demonstrate that overlayer growth can be distinguished from surface segregation due to dramatic changes in Pd and Cu PAES intensities in the submonolayer coverage range. In addition, a comparison of our experimental results with model calculations suggests that positrons are sensitive to surface defects such as adatom islands and step edges. Such defect sensitivity has also been shown in previous research on Ni(100).[14] This could imply that information derived from PAES is representative of the atomic species in the vicinity of defects or step edges.

The room-temperature ($\sim$300 K) deposition of Pd on Cu(100) has been studied by several authors.[3–6] Pd deposition on Cu(100) at 300 K results in a $c(2\times2)$ LEED pattern at submonolayer coverages. With increasing coverage the $c(2\times2)$ LEED pattern reaches a maximum in intensity and then starts to fade out, leaving a diffuse $p(1\times1)$ LEED pattern. It is well established that the maximum intensity of the $c(2\times2)$ LEED pattern corresponds to the formation of an ordered 50:50 surface alloy of Pd and Cu.[12] The structure of this 50:50 Cu(100)$c(2\times2)$-Pd surface alloy is thought to be similar to the (100) face of ordered Cu_3Pd. An ordered surface alloy is distinguished from an ordered bulk alloy by the fact that it is limited to the top sample layer with no Pd atoms found in the bulk of the substrate. However, it

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should also be mentioned that some of the previous results indicated that small amounts of disordered Pd atoms may be dissolved in the Cu below the $c(2\times2)$ surface at 300 K.[4,6] Recently, Pope *et al.*[13] confirmed the Pd coverage associated with the maximum $c(2\times2)$ intensity to be between 0.5 and 0.6 monolayers (ML) using Rutherford backscattering spectroscopy (RBS), EAES, and LEED.

The experiments were performed using the University of Texas at Arlington PAES system which has been described in detail previously.[16] The PAES system consists of a magnetically guided positron beam, a trochoidal energy analyzer, and a UHV sample chamber equipped with EAES, LEED, and an ion gun for sample preparation and characterization. The Cu(100) single crystal was mechanically polished using standard techniques and oriented parallel to the (100) face to within ±1° by Laue diffraction. The sample was cleaned by multiple Ne^+ sputtering (3 keV) and annealing (873 K) cycles. A liquid-nitrogen cooling stage and a button heater was attached to the sample holder and the sample temperature was held constant using a computerized control system. The positron beam was incident onto the sample surface at $\sim$20 eV. Auger electrons were detected using a microchannel plate in coincidence with the annihilation γ rays, detected using three NaI(Tl) scintillators.

Pd overlayers were deposited onto the Cu(100) surface at 173 K using a Pd evaporator consisting of a pure 1-mm-thick Pd foil wrapped onto a Ta foil which was heated resistively. After outgassing, the pressure in the chamber stayed at $\sim 5\times10^{-10}$ Torr during evaporation and at $\sim 2\times10^{-10}$ Torr during the PAES measurements. A quartz crystal thickness monitor was used to control the evaporation rate of the Pd. As verified by EAES, atomically clean Pd films were deposited at 173 K onto the Cu(100) surface. Data were taken at each Pd coverage at 173 K using PAES, EAES, and LEED and then repeated after warming the sample to 303 and 423 K without changing the amount of Pd deposited.

PAES spectra at three different temperatures for 360-sec deposition of Pd on Cu(100) at 173 K are shown in Fig. 1. This time corresponds to the deposition which gave the best $c(2\times2)$ LEED pattern at 303 K. PAES spectrum for the as-deposited surface at 173 K [Fig. 1(a)] shows predominantly the Pd, $N_{23}VV$ (40 eV) Auger peak. Figure 1(b) shows the PAES spectrum after the sample was heated to 303 K without further Pd deposition. Here the appearance of the Cu $M_{23}VV$ (60 eV) Auger peak is clearly observed as well as the decrease in the Pd Auger peak. As shown in Fig. 1(c), upon heating the sample to 423 K the Pd Auger peak mostly disappears and the Cu Auger peak gets larger, showing that Pd is moving below the top surface layer. The corresponding EAES spectra associated with the PAES spectra in Fig. 1 show only small variation with temperature as reported elsewhere.[17] Using the PAES and EAES results together, we can infer that the Pd atoms move only one atomic layer down. The large reduction of the Pd 40-eV Auger peak in the PAES spectrum at 423 K indicates that the Pd atoms move below the top layer. At the same time, the small changes observed in the EAES intensities indicate that the Pd atoms do not diffuse deep into the bulk. Specifically, the ratio R of the Pd to Cu EAES intensities (defined[18] as $R=[\mathrm{Pd}(MNN)]/[\mathrm{Cu}(MVV)]$ where the square brackets indicate the peak-to-peak intensities of the derivative EAES spectra shown in Ref. 17), changes from $R=0.92$ to 0.57. This is consistent with the Pd atoms moving down one atomic layer if we assume an electron exit angle of 42.6° (appropriate for our EAES analyzer) and a physically reasonable attenuation length of 3.8 ML.[19] Hence this shows that no bulk diffusion processes are involved in this case as would be expected from the low activation temperatures necessary.

A two-parameter linear least-squares fit was used to extract the relative contributions of Pd and Cu contributing to the PAES spectra.[17] First, fitting functions for clean Cu and a thick layer of Pd were obtained by convoluting EAES spectra for these elements with the resolution function of our spectrometer. Next a new function was obtained from a linear combination of these two functions, where the two coefficients were taken as fitting parameters. The Pd and Cu PAES intensities, normalized to the intensities for the thick Pd layer and clean Cu surface, respectively, were taken to be the values of these parameters determined from the least-squares fit. The fit to each spectrum in Fig. 1 is shown as a solid line and the normalized Pd and Cu PAES intensities at the surface ob-

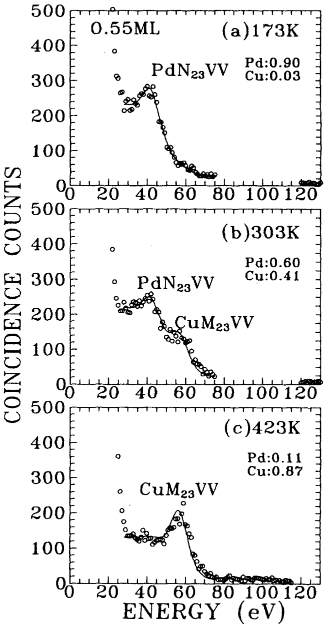

FIG. 1. Positron-annihilation-induced Auger electron spectra for 360 sec of deposition time of Pd on Cu(100) [this time corresponds to the coverage that gave us the sharpest $c(2\times2)$ LEED pattern at 303 K]. (a) shows the "as-deposited" spectrum at 173 K. (b) shows the Auger spectrum after the sample was heated to 303 K. (c) shows the Auger spectrum after the sample was heated to 423 K. The 40-eV Pd $N_{23}VV$ and the 60-eV Cu $M_{23}VV$ peaks are also identified in (a)–(c). The solid lines were obtained by fitting the data as described in the text. The normalized intensity of Pd and Cu as obtained from the fit are also shown on the right-hand side of each spectrum.

tained from the fit are also shown in the upper-right corner of each spectrum.

Figure 2(a) shows the variation of the Pd and Cu PAES intensities with deposition time, where Pd was deposited onto a Cu(100) surface held at 173 K and the PAES measurements were also performed at this temperature. Figure 2(b) shows the PAES measurements repeated at each Pd coverage after the sample was heated to 303 K. The horizontal axis for both figures is the Pd deposition time for the cold (173 K) Cu(100) surface. The vertical axis indicates the normalized intensities for Pd and Cu as determined from the least-squares fit to the data described above.

The results of theoretical calculations for the Pd overlayer on Cu and the Pd-Cu surface alloy are shown by the dark symbols in Figs. 2(a) and 2(b), respectively. The calculations were performed using the method outlined in Ref. 11, except that the surface dipole term was approximated using the approach of Weinert and Watson[20] in which a correction is applied to the atomic charge densities used in the superposition rather than in the final positron surface potential. Total annihilation probabilities for the Cu($3s+3p$) and Pd($4s+4p$) core levels were calculated for the two different cases of Pd overlayers on Cu(100) and the Pd-Cu surface alloy on Cu(100). In the case of the Pd overlayers the calculations were done for ordered coverages of Pd on top of the Cu(100) surface. The Pd/Cu surface alloy was modeled by replacing the appropriate number of Cu atoms from the top layer with Pd atoms without changing the crystal structure of the surface and assuming that the second and third layers are undisturbed.

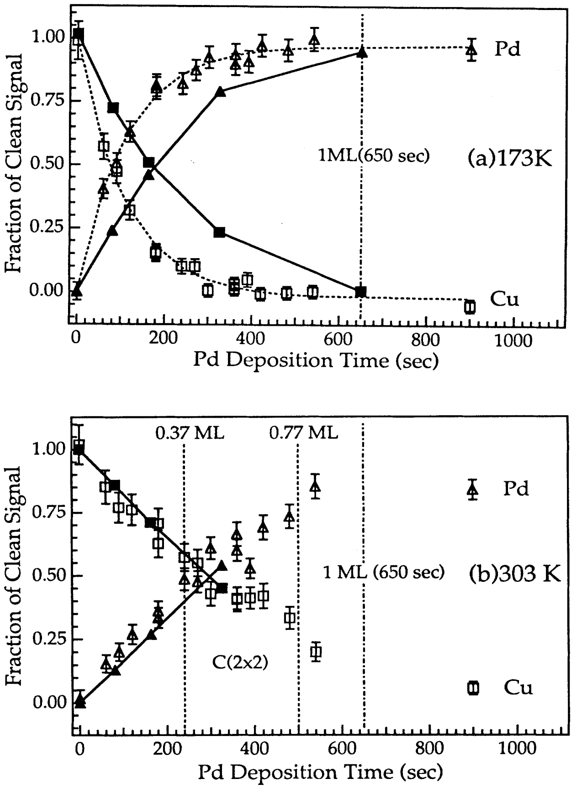

FIG. 2. Normalized PAES intensity vs deposition time of Pd on Cu(100) at 173 K is shown in (a). The dashed lines are fits to functions of the form $A+Be^{Ct}$ and are intended as a guide for the eye. (b) shows the PAES intensity after the sample was heated to 303 K. The horizontal axis for both figures is the Pd deposition time at 173 K. Open triangles and squares correspond to measured Pd and Cu intensities, respectively. Solid triangles and squares correspond to the calculated Pd and Cu PAES intensities, respectively, which are connected by solid lines. In (b) the dashed lines show the coverage range between which a $c(2\times2)$ LEED pattern was observed. The sharpest pattern was observed at 360±30 sec of Pd deposition time. Following Ref. 12, we take this deposition to be 0.55 ML.

The first thing to note is the dramatic difference between Figs. 2(a) and 2(b) indicating a change in the Pd/Cu(100) surface structure with temperature. At 173 K the Cu PAES intensity drops rapidly while the Pd PAES intensity increases in a corresponding fashion with increasing Pd deposition time. In contrast, at 303 K, the PAES intensities for Pd (Cu) increase (decrease) linearly and there are indications of a plateau region in the range of the 250–450-sec deposition time with the surface composition approximately 50% Pd and 50% Cu. Beyond 450-sec deposition time the data show that the Pd covers the surface with a corresponding decrease in the Cu PAES intensity to zero.

The LEED measurements at 173 K show that there is an increase in the background in the $p(1\times1)$ LEED pattern up to approximately 180 sec of deposition time. From this point on, the LEED pattern gets more diffuse with increasing deposition time, indicating disorder at the surface. At still higher deposition times (beyond 500 sec) we observe diffuse streaks between the spots in addition to the increased background. At 303 K a $c(2\times2)$ LEED pattern appears approximately in the range of the 300–500-sec deposition time. We observed that the $c(2\times2)$ LEED pattern reached maximum intensity at 360±30-sec deposition time before starting to fade out. These results are in agreement with previous LEED work done on the same system at room temperature.[3–6] More recently, the Pd coverage associated with the maximum $c(2\times2)$ LEED intensity was confirmed to be 0.55±0.05 ML using RBS, which gives reliable information on the amount of deposited material at the surface.[13] Using the RBS measurement as a reference point we estimate from our LEED observations that approximately 650±60 sec of deposition time corresponds to 1 ML Pd. This is shown in Figs. 2(a) and 2(b) as the dotted-dashed line.

As shown in Fig. 2(a), by a deposition time corresponding to 1 ML Pd, the Cu PAES intensity attenuates to zero, while the Pd PAES intensity saturates. This demonstrates that the Pd stays as an overlayer. It also provides a dramatic demonstration of the top-layer selectivity of PAES as compared to other core-level spectroscopies. Upon heating the surface to 303 K [Fig. 2(b)] one can directly observe the change in the surface morphology and the formation of the 50:50 Cu(100)$c(2\times2)$-Pd surface alloy at approximately 0.5 ML of Pd coverage.

Figure 2(a) also shows the theoretical core annihilation probabilities for Cu(100) covered by ordered overlayers of Pd at coverages $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, and 1 ML [$c(4\times4)$, $p(2\times2)$,

$c(2\times2)$, and $p(1\times1)$ structures, respectively] with 1 ML Pd coverage taken to be 650 sec. The experimental PAES intensities of Pd increase and the Cu intensities decrease much faster than is predicted by the model calculations indicating that the positrons sample the Pd ion cores to a much larger degree than is predicted by the model. For example, at 180 sec of Pd deposition time ($\sim\frac{1}{4}$ ML) the PAES intensity of Pd grows to approximately 80% of the pure Pd signal while the PAES intensity of Cu drops to approximately 15% of the clean Cu signal. The discrepancy between theory and experiment indicates that the assumptions in the model that the positron is in a delocalized surface state on an ordered overlayer are not sufficient and that a more realistic model that includes the effects of islanding,[1] and positron trapping at surface defects and step edges[14,15] is necessary. The preferential sampling of the overlayer by the positrons is currently being investigated in our laboratory for other overlayer-substrate systems.

In contrast to the low-temperature case, the calculated total core annihilation probabilities for ordered Cu/Pd surface alloy structures [$c(4\times4)$, $p(2\times2)$, and $c(2\times2)$ corresponding to coverages $\frac{1}{8}$, $\frac{1}{4}$, and $\frac{1}{2}$, respectively] are in good agreement with the experimental results. The Pd and Cu PAES intensities are approximately proportional to Θ and $(1-\Theta)$, respectively (where Θ is the Pd coverage in ML's), as can be seen by comparing the experimental results with theory [Fig. 2(b)]. This is exactly the behavior expected for a surface alloy in which most of the Pd is in the topmost layer intermixed with Cu atoms. It is reasonable to expect that the model calculations should be in better agreement with the 303-K data since effects due an inhomogeneous distribution of Pd (such as Pd islands) are probably washed out by the mixing that takes place during the alloy formation. It is important to note that the model calculations indicate a large change in PAES intensities as the structure of the top layer changes from Pd atoms sitting on top of a Cu surface to a mixed Pd/Cu alloy layer in agreement with the experimental trends.

In conclusion, this application of PAES to thin-film growth demonstrates the ability of PAES to directly monitor temperature-dependent compositional changes at submonolayer coverages in the topmost atomic layer. Upon deposition of Pd on Cu(100) at 173 K the overlayer Auger intensity saturates while the substrate Auger intensity attenuates to zero within 1-ML coverage. Large changes in the PAES intensities as the sample is warmed from 173 to 303 K provide a direct indication that the surface structure is changing from one in which the Pd atoms are on top of the Cu surface to one in which the Pd atoms are in a mixed alloy layer. At 423 K the PAES signal from Cu grows to a value very close to that of a clean Cu surface and the signal from Pd almost disappears indicating that the Pd is going below the surface. The EAES signal from Pd at 423 K is attenuated by a small amount compared to 173 K consistent with the Pd atoms moving below one atomic layer of Cu. Comparison of our experimental results at 173 K with theoretical calculations suggests that positrons are localized at sites containing Pd atoms.

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