Core-level shifts in trimetallic systems

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Trimetallic systems prepared by the deposition of monolayers of two different metals (Cu, Pd, Ag, and Au) on a Mo(110) single crystal have been studied using x-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS). Because the dissimilar second layer can be resolved from the bulk substrate with XPS, this approach allows the core-level shifts (CLSs) for the first and second layers in the trimetallic system to be measured. ISS was employed to measure the relative surface composition of the sample in order to identify those systems in which no significant mixing of the admetals takes place at room temperature. The Cu/Pd/Mo(110), Au/Pd/Mo(110), and Ag/Cu/Mo(110) systems were determined to exist as segregated monolayers at room temperature. Initial ISS studies showed that a He$^+$ ion beam with an energy of 475 eV was sufficient to induce alloying between Cu and Pd monolayers. The CLSs for the Au/Pd/Mo(110) and Cu/Pd/Mo(110) systems indicate changes in the $d$-electron populations of Au, Pd, and Cu. In the case of the Cu/Pd/Mo(110), the CLSs cannot be explained in terms of a simple charge transfer between metals. © 1995 American Vacuum Society.

I. INTRODUCTION

Because of the implications for heterogeneous catalysis, the study of the physical and chemical properties of mixed metal systems has recently elicited a great deal of interest. The characterization of electronic properties by x-ray photoelectron spectroscopy (XPS) has garnered particular attention.1–3 Redistribution of charge between the constituent metals in a mixed metal system as well as orbital rehybridization, may be manifested in a core-level binding energy shift from that of the pure bulk metal. Recent studies of various metal overlayer systems have demonstrated correlations between the magnitude and direction of the core-level shift (CLS) in the deposited overlayer and the fraction of filled/unfilled states in the valence band of the substrate.3,4 Furthermore, a relationship between these CLS’s with chemisorptive behavior towards CO, as determined by temperature-programmed desorption (TPD) and infrared spectroscopy at surfaces (IRAS)5 has been reported. An obstacle confronting this type of study is the difficulty associated with deconvoluting the XPS spectral components arising from the topmost interfacial layer of the substrate from that of the bulk metal below.

Recent work in our laboratory has focused on trimetallic systems obtained by sequentially vapor depositing various combinations of Pd, Cu, Au, and Ag on a Mo(110) single crystal. The advantage of this approach is that the dissimilar second layer can be easily resolved from the bulk substrate underneath in XPS, thereby allowing the CLS in both metals to be monitored simultaneously. Care must be taken to confirm that significant alloying does not take place for this approach to be valid.

With its superb surface sensitivity, ion scattering spectroscopy (ISS) was employed to determine the degree, if any, to which the deposited metals mixed. This allowed those systems which were deposited as discrete monolayers with minimal alloying to be identified and treated as such in the CLS determination. Several potential systems were disquali-

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II. EXPERIMENT

The experiments were performed in a conventional ultrahigh vacuum (UHV) chamber, described previously5 with a base operating pressure of $\sim 5 \times 10^{-10}$ Torr. The system was equipped with instrumentation to perform XPS, ISS, TPD, Auger electron spectroscopy (AES), and low energy electron diffraction (LEED).

The sample was mounted on a transferable probe that allowed for liquid nitrogen cooling down to 90 K and for resistive heating up to 1600 K. The sample temperature was monitored with a W-5%Re/W-26%Re thermocouple spot-welded to the edge of the crystal. Additionally, the sample could be flashed to 2300 K using an electron beam assembly. The sample was cleaned by oxidation and electron beam heating cycles, and also by He$^+$ sputtering at 700 K with a beam energy of 3.0 keV. The sample cleanliness was confirmed by XPS and ISS, and the long-range order by LEED.

Metal vapor deposition was accomplished by resistively heating a Ta filament wrapped with a high purity wire (99.999%) of the desired metal. All coverages are reported in monolayers (ML) equivalencies, based on the TPD peak area of 1.0 ML of the metal on the bare Mo(110) surface with an accuracy of ±0.05 ML. The TPD experiments were conducted with a linear heating rate of 10 K/s.

The Mg $K\alpha$ XPS spectra of the deposited overlayers were referenced against the substrate Mo 3$d_{5/2}$ transition at 227.7 eV, and the binding energy peak positions were determined to within ±0.03 eV. ISS was performed using He$^+$ ions at 475 and 220 eV. The ion beam incidence angle with the surface was 45° and the scattering angle was 60°. The beam was rastered 7 mm × 7 mm to minimize beam damage. The rate of sputter depletion during ISS was found to be negligible for the extraordinarily low beam energies used in all of the systems studied.

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III. RESULTS

A. Ion-beam-induced alloying of Cu–Pd

ISS is not a totally nondestructive technique, and may give rise to sample beam damage. Although an uncharacteristically low beam energy of 475 eV was used, as well as employing He$^+$ ions to minimize beam effects, evidence for ion induced alloying of Cu–Pd was observed. A film consisting of Cu$^{1.7 \text{ ML}/}$Pd$^{1.0 \text{ ML}/}$Mo$^{110}$ was vapor deposited and the ISS signal was recorded as a function of beam exposure. The resulting spectra from sequential scans are shown in Fig. 1. With increasing ion beam exposure (each scan was 50 s), the higher kinetic energy peak, attributed to Pd, begins to grow as the lower kinetic energy peak, which arises from Cu, begins to decrease. (It should be noted that the elemental sensitivity for Cu is not equivalent to that of Pd as will be discussed in Sec. III B.) Even at this relatively low beam energy, it can clearly be seen that the degree of mixing on the surface is increasing as a function of exposure time to the beam. This result is not surprising seeing that Pd and Cu are readily miscible and form bulk alloys.6,7

Atomic displacement and diffusion frequently occur within the collision cascade created by an impinging ion. This is most often observed for higher beam energies, yet, as we have shown, this effect may also play a role at relatively low energies as well. The experiment was repeated with an ion beam energy of 220 eV, yielding negligible changes in sequential ISS spectra. Based on these results, all ISS data were taken at a beam energy of 220 eV to minimize ion-beam-induced alloying.

B. Pd and Cu on Mo(110)

Figure 2 shows ISS spectra for 1.0 ML of Pd vapor deposited on a 10.0-ML-thick film of Cu on Mo(110), as a function of annealing temperature. In the initial run, before the Pd is added, only a single peak is registered at 177 eV kinetic energy, corresponding to Cu. Upon deposition of 1.0 ML Pd at room temperature, a larger feature appears at 190 eV corresponding to surface Pd, and some Cu signal is still present. This indicates that either some mixing of Pd with Cu has already occurred, or that the Pd has experienced some three-dimensional (3D) growth. Upon annealing to higher temperatures the ratio of Cu to Pd signal increases until the Cu peak is about three times as intense as the Pd peak. The ISS sensitivity for Pd, based on comparisons of ISS intensities of single constituent films, is about six times that of Cu. If the two peaks were normalized for this, the Cu signal would be about 18 times as intense as the Pd signal. This suggests that Pd has diffused into the thick Cu film. Further annealing does not change this ratio appreciably. If the Pd and Cu were randomly, homogeneously mixed, the normalized ISS ratio of Cu to Pd would be expected to be about 9:1 rather than 18:1. This Cu to Pd signal enhancement is consistent with preferential segregation of Cu to the surface.9
The Cu 2p peak more intense. Based on the relative intensities of the normalized peaks, this indicates about 90% Cu on the surface when deposited with Pd in monolayer quantities on Mo(110). This is consistent with the fact that Pd binds more strongly to Mo(110) than does Cu, as is shown in the TPD desorption temperatures in Table I, and also consistent with results from bulk alloys described above.

The XPS spectra for Pd and Cu in Cu(1.0 ML)/Pd(10.0 ML)/Mo(110) are presented in Fig. 4(B). The shift in the Cu 2p/2 BE increases negatively as the Cu:Pd ISS ratio decreases. For the highest annealing temperature, the Cu 2p/2 BE is found to be shifted -0.97 eV from that for the bulk, again consistent with previous work for a 10% Cu–Pd alloy. The shift in the Pd 3d/2 peak in this system at 350 K is +0.10 eV and does not change significantly with annealing.

Results of ISS indicate that Cu preferentially segregates to the surface when deposited with Pd in monolayer (1.0 ML each) quantities on Mo(110). This is consistent with the fact that Pd binds more strongly to Mo(110) than does Cu, as is shown in the TPD desorption temperatures in Table I, and also consistent with results from bulk alloys described above. Figures 5(A) and 5(B) show ISS spectra from each deposition sequence. For the system where Pd is deposited first, followed by Cu [represented in Fig. 5(A)], peaks for both Pd and Cu can clearly be seen at room temperature, with the Cu peak more intense. Based on the relative intensities of the normalized peaks, this indicates about 90% Cu on the surface. This could reflect surface alloying or three dimensional island growth of Cu. Upon annealing to progressively higher temperatures, the spectrum for the initial deposition of Cu exhibits a Cu peak with an intensity roughly corresponding to a monolayer of Cu and a Pd peak with an intensity of less than 10% of the average signal for pure Pd. This seems to indicate that the Cu has largely wet the surface. The Cu 2p peak BE for this arrangement is 931.95 eV. Corrected for the established Cu surface CLS on Cu(100) of -0.17 eV,10 this represents a shift of -0.38 eV from the bulk value. As the annealing temperature is driven progressively higher, the Pd-to-Cu ratio increases dramatically, again indicating diffusion of the admetal into the bulk film.

Figure 4(A) shows the ISS spectra for 1.0 ML Cu deposited on a 10.0-ML-thick film of Pd on Mo(110) at room temperature, and subsequently annealed to higher temperatures. The spectrum for the initial deposition of Cu exhibits a Cu peak with an intensity roughly corresponding to a monolayer of Cu and a Pd peak with an intensity of less than 10% of the average signal for pure Pd. This seems to indicate that the Cu has largely wet the surface. The Cu 2p BE for this arrangement is 931.95 eV. Corrected for the established Cu surface CLS on Cu(100) of -0.17 eV,10 this represents a shift of -0.38 eV from the bulk value. As the annealing temperature is driven progressively higher, the Pd-to-Cu ratio increases dramatically, again indicating diffusion of the admetal into the bulk film.

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temperature, the Pd peak is enhanced and the Cu peak is attenuated as the two metals mix on the surface to a greater degree. For the system where Cu monolayer is laid down on Pd at 750 K resulting in Ag segregation to the surface. Impact collision ion scattering spectroscopy (ICISS) has been employed by Nakanishi et al. to study Ag deposited on Cu(001), and no surface exchange was determined to have taken place. 

The ISS results for monolayer quantities of Cu and Ag deposited on Mo(110) at room temperature in this experiment are consistent with these findings. Regardless of the deposition sequence, ISS shows that Ag preferentially covers the surface. Annealing up to 900 K does not change this. For the Ag(1.0 ML)/Cu(1.0 ML)/Mo(110) system, the SCLS corrected Ag 3d_{5/2} BE does not shift from the bulk value within experimental error. The Cu 2p_{3/2} BE is 932.55 eV, exhibiting no shift from that observed in Cu(1.0 ML)/Mo(110) within experimental error. This seems to imply very little electronic modification of either constituent in the dual overlayer by the other, though this conclusion cannot be drawn on the basis of core-level shifts alone.

For monolayer Ag deposited on a thick Cu film, ISS reveals that Ag wets the surface. Additionally, if the Ag mono-

### Table II. CLS’s in trimetallics.

<table>
<thead>
<tr>
<th>Overlayer on Mo(110) (values in MLs)</th>
<th>Cu 2p_{3/2} BE (eV)</th>
<th>Pd 3d_{5/2} BE (eV)</th>
<th>Au 4f_{7/2} BE (eV)</th>
<th>Ag 3d_{5/2} BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1.0)/Pd(10.0)</td>
<td>931.95</td>
<td>-0.38</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Cu(1.0)/Pd(1.0)</td>
<td>932.15</td>
<td>-0.18</td>
<td>340.81</td>
<td>+0.56</td>
</tr>
<tr>
<td>Au(1.0)/Pd(20.0)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Au(1.0)/Pd(1.0)</td>
<td>...</td>
<td>...</td>
<td>83.39</td>
<td>+0.14</td>
</tr>
<tr>
<td>Ag(1.0)/Cu(7.0)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>368.06</td>
</tr>
<tr>
<td>Ag(1.0)/Cu(1.0)</td>
<td>932.55</td>
<td>+0.05</td>
<td>...</td>
<td>367.97</td>
</tr>
</tbody>
</table>

*Corrected where appropriate for SCLS exhibited in Cu/Cu(100), −0.17 eV (Ref. 10); Pd/Pd(100), −0.3 eV (Ref. 11); polycrystalline Au, −0.3 eV (Ref. 12); polycrystalline Ag, −0.1 eV (Ref. 12).
layer is deposited first, followed by multilayer Cu deposition at room temperature, the Ag will still segregate to the surface. At 325 K, the normalized ISS intensities indicate a Cu:Ag ratio on the surface of about 1:1. Upon annealing to 500 K, the Cu peak is completely attenuated. The Ag 3d5/2 BE for this Ag(1.0 ML)/Cu (7.0 ML)/Mo(110) system is 368.06, representing a +0.08 eV CLS.

IV. DISCUSSION

Interpreting the CLS’s reported in Table II is not straightforward. Core-level BE shifts in bimetallic and trimetallic systems can variably be attributed to charge transfer between the constituent metals, changes in the admetal–admetal interactions resulting from the overlayer adopting the lattice parameters of the substrate, and orbital rehybridization. Modifications in the final state screening may also be manifested in CLS’s.

A simple model has been advanced by Rodriguez and Goodman that correlates the CLS’s in bimetallic systems with the fraction of filled and unfilled states in the valence d band. It has been suggested that orbital rehybridization that changes the valence d-band electronic densities, as well as simple charge transfer mechanisms to unfilled d-band states, play a role in the CLS’s. In general, the core levels of a metal are very sensitive to changes in its d orbital population produced by interatomic and intra-atomic electron transfers.

Applying this simple model to the CLS’s in Table II, the negative shifts for Cu indicate a gain of Cu 3d electrons, whereas the positive shifts for Pd and Au suggest a decrease in the Pd 4d and Au 5d electron populations. This type of behavior is consistent with results of L-edge x-ray absorption near-edge structure (XANES) experiments for bulk alloys that show similar changes in the d population of Cu, Pd, and Au. For the Ag(1.0 ML)/Cu(1.0 ML)/Mo(110) system, the CLS’s of Ag and Cu are very small, suggesting that no significant redistribution of d electrons [with respect to Cu/Cu(100) and Ag/Ag] has taken place.

For Cu(1.0 ML)/Pd(1.0 ML)/Mo(110), the Pd CLS is +0.56 eV with an associated shift of −0.18 eV for the SCLS corrected Cu value. For Cu, the CLS’s could be interpreted to be consistent with a charge transfer model. The negative CLS for the Cu on bulk Pd is greater than for the Cu on Pd(1.0 ML)/Mo(110), where the Pd CLS is itself shifted positively with respect to the bulk. However, in the Cu(1.0 ML)/Pd(1.0 ML)/Mo(110) system the Pd CLS is actually reduced with respect to that of Pd(1.0 ML)/Mo(110). These results are summarized schematically in Fig. 6. If charge transfer played the only, or dominant, role in the CLS’s observed, the Pd CLS would be expected to be greater in the trimetallic system as a result of charge transfer to both the Mo(110) substrate and the Cu overlayer. This indicates that charge transfer alone cannot explain the CLSs observed in this system.

V. CONCLUSIONS

Trimetallic surfaces of Pd, Cu, Au, and Ag were prepared on Mo(110) in an attempt to resolve the XPS CLS’s of both constituents in the bimetallic overlayers. The composition of the films was monitored with ISS for evidence of alloys or discrete overlayers. It was found that with a He+ beam energy of 475 eV, alloying was induced between Pd and Cu monolayers at room temperature. The CLS’s for the Au/Pd/Mo(110) and Cu/Pd/Mo(110) systems indicate change in the d-electron populations of the admetals. In the case of Cu/Pd/Mo(110), the CLS’s cannot be explained by simple charge transfer between the metals.

ACKNOWLEDGMENTS

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