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THE ELECTRONIC STRUCTURE OF Ag/Cu(100) AND Pd/Cu(100) SURFACE ALLOYS STUDIED BY AUGER-PHOTOELECTRON COINCIDENCE SPECTROSCOPY

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Key words: APECS, Auger-photoelectron coincidence spectroscopy, Ag/Cu(100), Pd/Cu(100), surface alloy, photoemission, electronic structure.

Abstract: We have measured the Ag and Pd M_5VV Auger spectrum in coincidence with Ag and Pd $4d_{5/2}$ photoelectrons for the Ag/Cu(100) and Pd/Cu(100) systems, respectively, as a function of admetal coverage. These systems form surface alloys (i.e. random substitutional alloys in the first atomic layer) for impurity concentrations in the 0.1 monolayer range. For these systems, the centroid of the impurity $4d$ levels is expected to shift away from the Fermi level by ~ 1 eV [Ruban *et al.*, Journal of Molecular Catalysis. A **115** (1997) 421], an effect that should be easily seen in coincidence core-valence-valence Auger spectra. We find that the impurity Auger spectra of both systems shift in a manner that is consistent with d -band moving away from E_F . However, the shift for Pd is considerably smaller than expected, and a shift almost absent for Ag. The disagreement between theory and experiment is most likely caused by the neglect of lattice relaxations in the calculations.

In recent years, there has been increasing interest in the subset of bimetallic systems known as surface alloys.[1-14] These are systems where an impurity metal atom intermixes with a metallic host, but only in the first or first few atomic layers. The presence of a surface modifies the thermodynamic variables allowing new structural phases to be stabilized in the near-surface region. As a result, there can be surface alloys that have no bulk alloy counterparts. Surface alloys also exhibit a number of intriguing physical properties both from a technological and fundamental perspective.

Some surface alloys exhibit important catalytic[11, 15, 16] and magnetic properties[13] only seen otherwise in multilayer structures. Others exhibit completely new behavior. For example, MnNi, which is antiferromagnetic as a bulk alloy, is ferromagnetic as a surface alloy[12].

Two prototypical random surface alloys that have received considerable attention in the literature are Ag/Cu(100) and Pd/Cu(100).[7, 10, 17, 18] However, these studies have largely been confined to elucidating their surface structure. At room temperature and at low concentration (few percent), these systems tend to form random surface alloys as confirmed by scanning tunneling microscopy studies[18]. Many important physical properties of surface alloys, however, are directly related to their electronic structure. It is well known that the constituent atoms of bulk alloy systems often have unique electronic properties[19-26]. Most of the progress in understanding the electronic structure of surface alloys, however, has been on the theoretical side. Ruban *et al.*[16] have conducted a comprehensive theoretical investigation of transition metal binary surface alloys. Their study focussed on the shift in the centroid of the impurity metal d -bands (referred to as ϵ_d) as the impurity is incorporated into the close-packed surface of the host. For the late $4d$ transition metals alloyed in the Cu(111) surface, they found that the d -band of the impurity atom shifts away from the Fermi energy (E_F). Furthermore, the magnitude of this shift increases monotonically as one moves from Ru to Ag in the Periodic Table. Pd and Ag were found to have largest d -band shifts, on the order of 1 eV. Similar to the notion of surface core levels, the direction of this shift can be understood in terms of d -band filling. The magnitude of the shift, on the other hand, is less well understood.

As mentioned above, there has been relatively little experimental work on the electronic structure of surface alloys. This is in part because they tend to form at extremely low impurity concentrations ($\lesssim 0.1$ monolayer [ML]), making it very difficult to use conventional techniques such as photoelectron spectroscopy. In an effort to overcome these difficulties, we have studied the Ag/Cu(100) and Pd/Cu(100) surface alloy systems using Auger-photoelectron coincidence spectroscopy (APECS). We have measured the Ag and Pd M_5VV Auger spectrum in coincidence with Ag and Pd $4d_{5/2}$ photoelectrons for the Ag/Cu(100) and Pd/Cu(100) systems, respectively, as a function of admetal coverage. Our main goal is to use these core-valence-valence (CVV) Auger spectra to determine whether the predicted changes in the impurity $4d$ levels exist, and if so, how do they depend on impurity metal concentration.

APECS is ideally suited to investigate the electronic structure of these systems for a number of reasons. As the Auger transition is an atomic process, APECS is chemically specific and the CVV transitions should

respond to changes in the valence band. Furthermore, the technique is extremely surface sensitive and eliminates the unwanted background from the host[27, 28], so an undistorted signal from the impurity metal is easily detected, even at concentrations of 0.1 ML or less. We find that the Auger spectra of the impurity atoms in both systems exhibit shifts consistent with the centroid of their $4d$ -band shifts away from E_F , as predicted by the theory. However, the shift for Pd is considerably smaller than expected, and the shift is almost nonexistent for Ag. The disagreement between theory and experiment most likely arises because lattice relaxation about the impurity atom is not considered in the calculations.

All APECS and soft X-ray photoemission spectroscopy (SXPS) measurements reported here were carried out at beamline U16B at the National Synchrotron Light Source at Brookhaven National Laboratory (NSLS). Details of the coincidence spectrometer are presented elsewhere.[27] Briefly, the coincidence spectra were acquired by using two cylindrical mirror analyzers (CMAs), one held fixed at the core level of interest, while the other scanned through the energy range of the corresponding Auger spectrum. Counts occurring in each analyzer within 20 ns of each other were considered coincidence events. We also monitored events where a count in one analyzer occurred 180 ns (the orbit period of the synchrotron) after a count in the other analyzer. This gave us a measure of the accidental coincidence rate. Only true coincidence spectra, which were generated by subtracting the accidental spectrum from the coincidence spectrum, are presented here. Coincidence spectra were acquired at $h\nu = 470$ eV for the Ag/Cu(100) data and at 440 eV for Pd/Cu(100). In both cases, the total energy resolution was 1.0 eV (photons + electrons). In addition to the coincidence spectra, we simultaneously acquired conventional photoemission spectra, which are referred to as singles spectra. Conventional SXPS spectra were also collected for the valence band of the substrate and the alloy systems. The total resolution for these data was 0.12 eV.

Two different Cu crystals with a (100) surface orientation were used for the measurements. Both crystals were known to produce sharp (1×1) LEED patterns which are appropriate for a fcc(100) surface. The samples were cleaned in a standard fashion with cycles of sputtering (500 eV Ar⁺ ions) and annealing (740 K for 15 minutes) until no contamination from the deposited metal could be detected by SXPS. Deposition of the transition metal adsorbates was done with a thermal evaporation source located *in situ*. Base pressure in the UHV chamber was $\sim 8 \times 10^{-11}$ torr; the pressure rose to 4×10^{-10} Torr during deposition of the metal films. Film thickness was calibrated *ex situ* with Rutherford backscattering spectroscopy and cross referenced with the deposition time and the spectral intensity of the Ag or Pd $3d$ core levels

relative to the emission from the substrate Cu 3*p* core lines. As Pd readily forms a surface alloy with Cu[2, 18], the Pd/Cu(100) samples did not undergo any further treatment before acquisition of the APECS data. The formation of the Ag/Cu(100) surface alloy, on the other hand, seems to be a thermally activated process[10] and therefore the samples were annealed to 150° C after deposition of the Ag films. After deposition, the samples were checked for contamination with SXPS before acquisition of the APECS data. In all cases, high-resolution valence band spectra were also acquired immediately before collecting the APECS data.

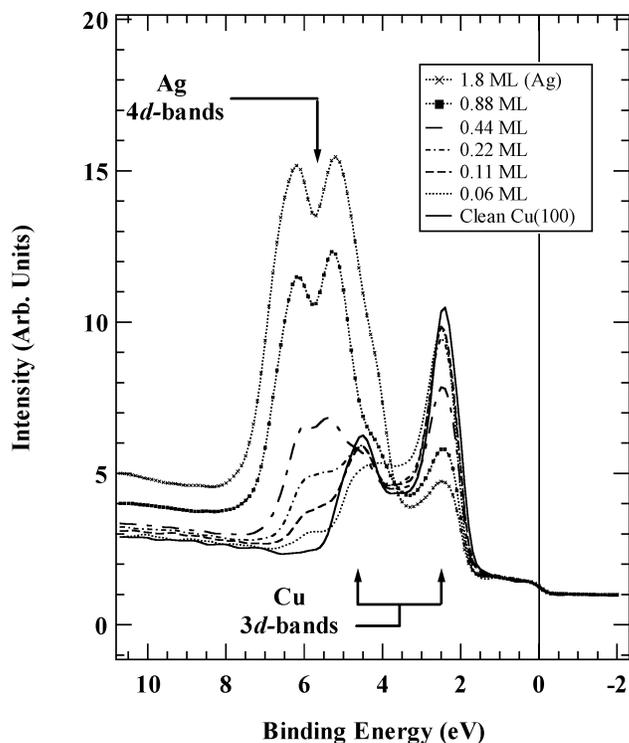


Figure 1. UPS valence band spectra acquired at $h\nu = 50$ eV for ultrathin films of Ag deposited on Cu(100). The Ag/Cu(100) random surface alloy will only form in the low coverage films of 0.11 ML and 0.06 ML.

Before examining the Auger spectra, we first consider what can be concluded using valence band photoemission spectroscopy. Fig. 1 shows a series of spectra from the Ag/Cu(100) system as the concentration of Ag is varied. The Cu 3*d*-bands dominate the binding energy region between 2 and 5.5 eV. As small amounts of Ag are deposited onto the surface, the Ag 4*d*-bands begin to develop at about 6 eV below E_F . The random surface alloy

phase, which occurs for Ag coverages less than 0.13 ML[10], is present only in the 0.06 ML and 0.11 ML data sets. As the Cu 3d band emission overwhelms that of the Ag 4d levels, it is almost impossible to discern between a shift in the Ag 4d band and an attenuation of the Cu 3d emission. This figure clearly demonstrates the difficulty in using photoemission to study the electronic structure of surface alloys.

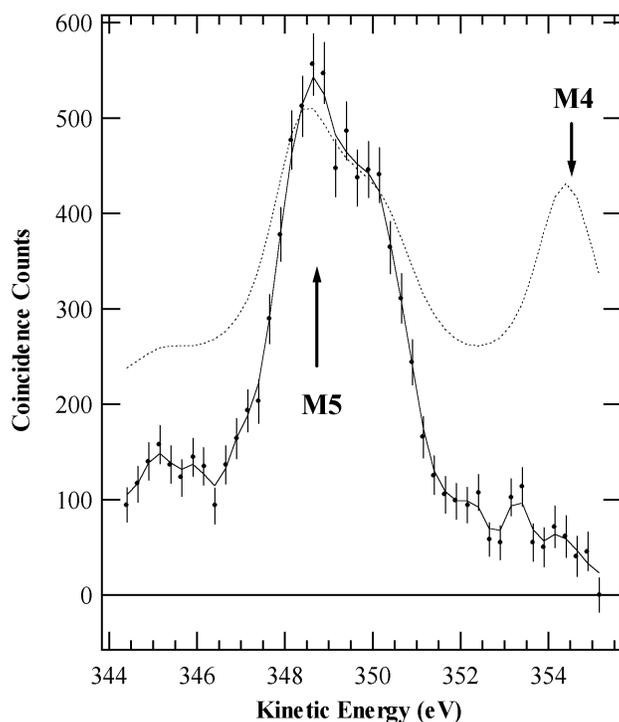


Figure 2. The Ag M_{5VV} Auger line for 0.88 ML of Ag on a Cu(100) acquired in coincidence with emission from the Ag $3d_{5/2}$ core level. The excitation energy was 470 eV. The filled circles with error bars are the coincidence data, the solid black line is a smooth fit to the coincidence data, and the dotted line is the singles spectrum acquired simultaneously. Note that the large background from Cu and the contribution from the Ag M_{4VV} Auger line are completely eliminated in the coincidence measurement.

In Fig. 2 we focus our attention on the Ag $M_{4,5VV}$ Auger spectrum of the 0.88 ML Ag/Cu(100) system. Both conventional (singles) and coincidence spectra are shown. In the singles spectrum, the Ag M_{5VV} and M_{4VV} Auger lines are clearly visible. In contrast, since it was acquired in coincidence with Ag $3d_{5/2}$ photoelectrons, only the Ag M_{5VV} Auger line appears in the APECS spectrum. The APECS data reveal the intrinsic line shape of the Ag

M_5VV transition from the surface alloy, free of contributions from the closely spaced M_4VV Auger line or the inelastic background. With a strong atomic-like multiplet structure in a main peak at 348.6 eV and a pronounced shoulder at 350.2 eV, the line shape is very similar to the M_5VV spectrum from elemental Ag.[29-32] We attribute these features to the 1G_4 and the 3F_4 multiplet components of the two-hole Auger final state, respectively. Also similar to the elemental Ag spectrum, there is a pronounced band-like part of the emission that extends from about 351 eV up to 355 eV.

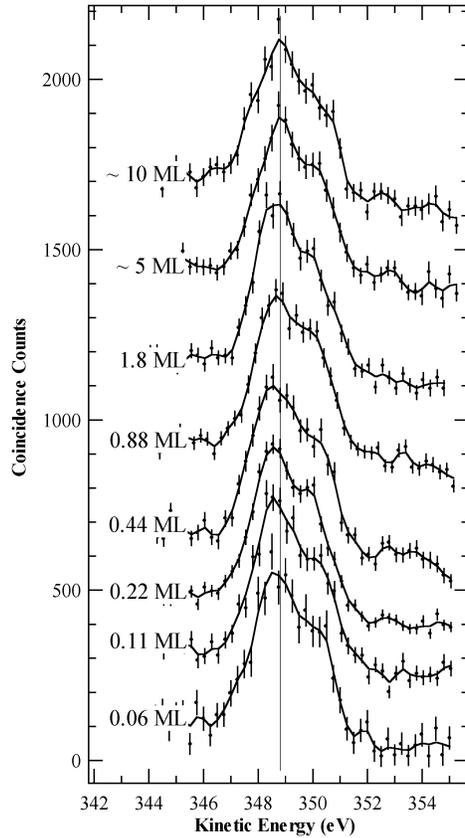


Figure 3. The Ag M_5VV Auger line for various coverages of Ag on Cu(100) as measured with APECS. The incident photon energy is again 470 eV. The filled circles with error bars are the APECS data and the solid black curves are a smooth fit to the APECS data. The vertical black line is a guide to the eye.

As opposed to what was found for valence band photoemission, changes in the Ag M_5VV Auger line shape can be tracked easily with APECS as the Ag concentration in the Ag/Cu(100) system is varied. Spectra acquired for

different Ag film thicknesses are presented in Fig. 3. The surface alloy occurs in the two thinnest films (0.11 ML and 0.06 ML). The vertical line in the figure, intended to serve as a guide to the eye, indicates the position of the M_5VV peak for the 10 ML thick Ag film. It is clear from this figure that any changes which occur to the Ag M_5VV line shape as a function of Ag coverage are very small. The M_5VV peak shifts by about 0.25 eV towards lower kinetic energy as the coverage decreases from 5 ML to 1.8 ML. Below 1.8 ML, the spectra do not change appreciably either in the energy position of the main peak nor in the shape of the peak. In other words, the APECS data in the coverage range of the random surface alloy phase do not show any significant differences with the spectra for the thicker films. Apparently, the process of forming the Ag/Cu(100) surface alloy does not change the Ag M_5VV line to an appreciable degree.

Two main conclusions can be drawn from this lack of significant change in the Ag M_5VV Auger line. First, the centroid of the Ag $4d$ -bands, ϵ_d , is not moving to higher binding energy as the amount of Ag is reduced. Second, the hole-hole interaction energy, U , is not increasing as the Ag concentration becomes more dilute. In order to observe a fixed energy position of the Ag M_5VV Auger line, ϵ_d and U would have to move in opposite directions. However, it is difficult to argue that the hole-hole interaction energy of the Auger final state should decrease as the Ag atoms become more isolated. Indeed, one would expect that U should increase as the Ag becomes more dilute. If that were the case, the multiplet peaks in the Auger line should become more prominent at the expense of the high kinetic energy band-like emission above ~ 351 eV. We do not observe such a change in the APECS data and therefore we conclude that the hole-hole interaction energy is not increasing with decreasing Ag thickness. The associated implication is that ϵ_d is not changing by more than 0.125 eV. We arrive at this number because in the simplest picture, the CVV Auger spectrum will reflect the self-convolution of the valence band density of states (SCDOS). Hence, the center of the Auger spectrum should shift by at most twice the shift of the centroid of the DOS (*i.e.*, by $2\epsilon_d$).

The situation for the Pd/Cu(100) system is quite different. A series of Pd M_5VV Auger spectra obtained in coincidence with Pd $3d_{5/2}$ photoelectrons for different Pd coverages is presented in Fig. 4. For the thicker films of 2 ML and 1 ML, there is little difference between the APECS spectra. As the coverage is decreased below 1 ML, however, the M_5VV peak shifts to lower kinetic energy by almost 1 eV. In addition, at the lowest coverage of 0.25 ML, the entire spectrum is skewed slightly to lower kinetic energy. As with the Ag data, there are two possible reasons for these changes. Either there is an increase in the hole-hole interaction energy, or spectral weight in the valence band shifts away from E_F as the Pd concentration becomes more

dilute. The former possibility is inconsistent with an earlier study[30] where the peak energy and line shape of the M_5VV spectrum from the 0.25 ML surface alloy was compared to the Pd SCDOS calculated of a bulk $\text{Pd}_{0.25}\text{Cu}_{0.75}$ alloy.[33]. Remarkably good agreement was found,[30] indicating that the observed shifts are most likely associated with shifts in the Pd d -levels.

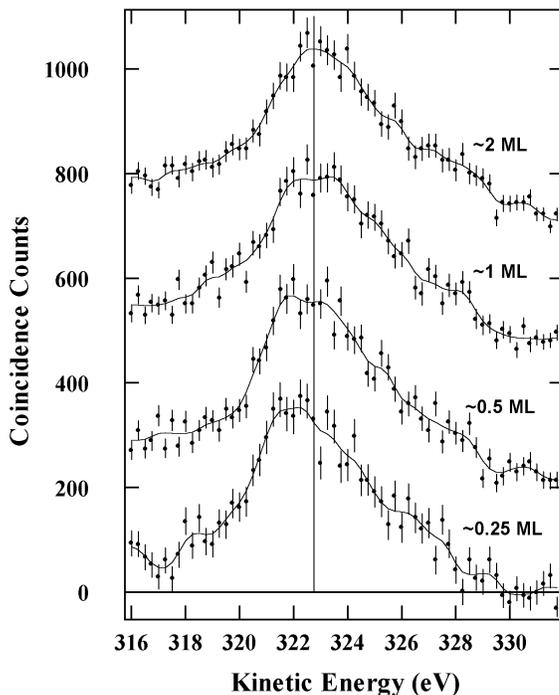


Figure 4. The Pd M_5VV Auger line for various coverages of Pd on Cu(100) as measured with APECS. The incident photon energy is 440 eV. The filled circles with error bars are the APECS data and the solid black curves are smooth fits of the APECS data. The vertical black line is a guide to the eye.

In Fig. 5 we summarise our findings for the shift in the position of the Ag (filled circles) and Pd (filled triangles) M_5VV peaks. Here, zero is the Auger peak position in the thickest films. As noted above, the direction of the measured shifts is consistent with the results of Ruban *et al.*[16] Those calculations, however, predicted that ϵ_d for Ag and Pd should be comparable, or, if anything, larger for Ag. Our results indicate that ϵ_d for Pd is much larger than ϵ_d for Ag. One possible source of this discrepancy is that our experiments were done on a different crystal face of Cu than was used in the calculations. Ruban *et al.*[16] argue, however, that the energy differences

between different facets of the same crystal could change their predictions for ϵ_d by about 0.2 eV. As the changes in going from a Cu(111) substrate to a Cu(100) substrate should be in the same direction for both Pd and Ag, this effect cannot account for the relative discrepancy (Ag vs. Pd) between the predictions and the experimental data.

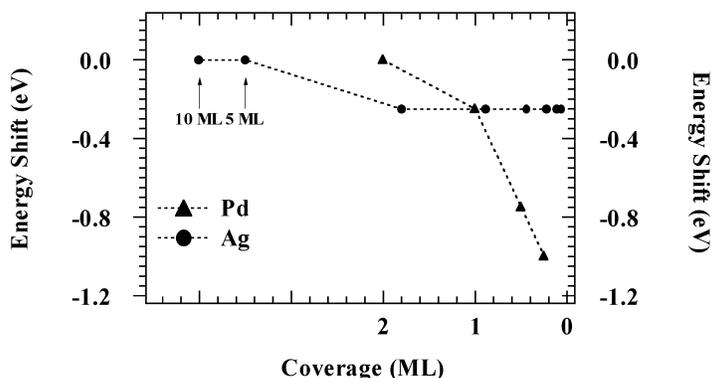


Figure 5. Measured shift in the Ag and Pd M_5VV Auger line on Cu(100) as a function of admetal coverage. Contrary to theoretical predictions, the Pd shift is much larger than Ag.

A potentially more significant point is that the theoretical calculations neglect to include lattice relaxations in the alloy phase. As the lattice constants of Ag (4.08 Å) and Pd (3.89 Å) are significantly different than that of the Cu host (3.61 Å), it is reasonable to expect that the Cu neighbors surrounding the Ag or Pd impurities will adjust to accommodate the larger atoms into the surface plane. Indeed, EXAFS studies for dilute ($Pd_{0.05}Cu_{0.95}$) bulk alloys[34] indicate that there is a local lattice expansion on the order of 2%. Similar structural data are not available on the lattice expansions for Ag in Cu as the two metals do not have a bulk alloy phase. It is reasonable to expect, however, that the Cu lattice would relax in some fashion to accommodate the larger Ag atom. In fact, an STM study of Ag/Cu(100) indicates that the dealloying of Ag and Cu at concentrations above 0.13 ML is driven by the strain field in the substrate as the Cu lattice relaxes to accommodate the larger Ag adsorbate[10]. The inclusion of such lattice relaxations might have a significant effect on calculations of the electronic structure of surface alloys, which could reduce the discrepancies with our experimental measurements. This would be particularly true for Ag in Cu as the Ag d -band shift results from a change in the exchange-correlation potential when the Ag is incorporated into the Cu lattice[35]. The exchange-correlation potential is a sensitive function of the lattice spacing and the

associated changes in the embedding density. Therefore the net shift in the *d*-bands of Ag might be small when these corrections are taken into account.

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