Subsurface core-level shifts for an Au monolayer buried in Ag(111)

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The Au $4f_{7/2}$ core-level energy has been measured using photoemission for an Au(111) monolayer buried in Ag(111). The measured core-level energy as a function of the distance between the Au monolayer and the sample surface shows that the effective spatial range of surface effects is about three atomic layers. This range is significantly larger than what is expected from a simple model for the screening of potential changes in jellium. The result implies that significant subsurface core-level shifts can occur for close-packed metal surfaces.

Generally speaking, surface effects on localized electronic excitations in metals are nearly completely damped out for regions just a few atomic layers below the surface. This is because electronic screening of potential changes is extremely short-ranged in metals, being on the order of atomic dimensions.¹ The manner in which the electronic properties change below the surface, i.e., the subsurface electronic relaxation, has been studied theoretically. For example, layer-by-layer variations in the local density of states, the one-electron eigenvalue, the electrostatic potential, the effective one-electron potential, etc., have been calculated for a number of surfaces.¹⁻⁴ Experimentally, it is quite difficult to obtain similar information about subsurface electronic relaxation with atomic-layer resolution, because essentially all surface-sensitive techniques probe several atomic layers simultaneously with signals from different atomic layers not (well) resolved in general.

This paper reports a photoemission study of the layerresolved core-level binding energy shifts near the surface for a metal system. Core-hole excitations are highly localized, and the measured core-level binding energies provide a direct measure of the local electrostatic potential to the first-order approximation (i.e., within the one-electron picture). The system under investigation is Ag(111) fabricated by molecular-beam epitaxy with one atomic layer substituted by a well-matched Au(111) atomic layer at various depths below the surface. Au and Ag have very similar valence electronic structure.⁵ The lattice mismatch between Ag and Au is practically zero. Thus, the Ag-Au system is a nearly ideal model system; to a good approximation, an Au atom can be thought of as an Ag atom with just different core levels.

In our experiment, the Au $4f_{7/2}$ core-level binding energy was measured as a function of the distance between the (buried) substitute Au monolayer and the sample surface. Since there are no Ag core levels to interfere with the measurement, the Au $4f_{7/2}$ core level provides a convenient local probe. Significant surface-induced shifts in core-level energies have been observed for the Au monolayer occupying the first (top), second, or third atomic plane. The measured Au $4f_{7/2}$ binding energy converges asymptotically to a constant value for increasing depth below the surface, as expected. The overall direction of the core-level energy shift is consistent with what is expected from a simple model for the screening of surface potential in jellium,⁶ but the measured spatial range of the surface effect is much larger than what is expected from the same model. The present result implies that significant subsurface core-level shifts can exist for close-packed surfaces of metal single crystals. Previous experimental studies of the core-level line shapes for surfaces of metal single crystals typically ignored the subsurface core-level shift in the data analysis.⁷

The photoemission measurements were performed at the Synchrotron Radiation Center of the University of Wisconsin-Madison. Synchrotron radiation from the Tantalus storage ring, monochromatized by the Mark-V Grasshopper monochromator, was used as the light source. The photoelectrons were analyzed by a cylindrical-mirror analyzer. The Ag(111) substrate was prepared by sputtering with Ar⁺ and annealing in the usual manner. Ag(111) samples with one specific (111) atomic layer below the surface substituted by an equivalent Au atomic layer were prepared by molecular-beam epitaxy. High-energy electron diffraction from all samples showed sharp unreconstructed (1×1) patterns. The surface cleanliness was verified with Auger spectroscopy.

It has been demonstrated by electron diffraction, corelevel photoemission studies, and ion scattering studies that Au-Ag(111) interfaces formed at room temperature are abrupt with little strain and few stacking faults, and that the overlayers are smooth without clumping.^{8,9} This observation is further supported by the present data, to be discussed below.

Figure 1 shows the photoemission spectra of the Au $4f_{7/2}$ core level for Ag(111) covered by 1 monolayer (ML) of Au (bottom spectrum) and for the same sample further covered by 1-4 ML of Ag as indicated. The curves are the result of a least-squares fit to the data obtained by assuming a Voigt line shape (convolution of a Lorentzian and a Gaussian) for the core level and a smooth cubic polynomial function for the background.^{8,10} The initial energy is defined to be the difference between the photoelectron kinetic energy referred to the Fermi level and the photon energy. The origin of the abscissa in Fig. 1 is chosen to be at the line center of the Au $4f_{1/2}$ peak for Ag(111) covered by 1 ML of Au. Clearly, the Au $4f_{7/2}$ line center shifts as increasing amounts of Ag are laid on top of the Au monolayer. Within our experimental uncertainty, the photoemission intensity of the Au $4f_{7/2}$ peak decays exponentially for increasing Ag overlayer thickness. From the data, we obtained an effective angleaveraged electron escape depth of 4.7 Å.¹¹ This value is consistent with earlier experimental values when differences



FIG. 1. Photoemission spectra of the Au $4f_{7/2}$ core level taken with a photon energy of 110 eV for Ag(111) covered by 1 ML of Au (bottom spectrum) and the same sample further covered by 1-4 ML of Ag (upper four spectra). The dashed vertical line passing through the origin of the abscissa indicates the core-level peak position for the bottom spectrum.

in the photoemission geometry and the photon energies used are considered.^{8, 10} This result supports the evidence mentioned above that the overlayers are indeed smooth, pinhole-free, and without clumping.

The Au $4f_{7/2}$ peak positions obtained from the leastsquares fit are plotted in Fig. 2 as dots for different sample configurations. The upper horizontal scale shows the position of the substitute Au monolayer relative to the sample surface with the first atomic layer being the surface layer. The vertical scale in Fig. 2 shows the relative initial energy of the core level with the origin chosen to correspond to an Au layer deep inside the Ag(111) crystal.

If the minor differences between the Au and Ag valence electronic structures are neglected, the data shown in Fig. 2 simply give the layer-by-layer variation in the core-level energy for Ag(111). The measured core-level energy shifts relative to the bulk are roughly in the ratios of $1:\frac{1}{2}:\frac{1}{4}:0:0$ for layers 1-5; namely, significant shifts exist for the top three atomic layers. This result has important impact on the analysis of core-level photoemission line shape for singlecrystal surfaces.⁷ Typically, subsurface shifts have been ignored in this kind of analysis, because different layer contributions are not sufficiently resolved to permit a reliable deconvolution of the data.

From the data in Fig. 2, the overall shift of the Au core level is about 0.27 eV for the substitute Au monolayer at the surface relative to deep inside Ag(111). This is roughly comparable to the measured surface-to-bulk core-level shift



FIG. 2. Relative core-level energies (dots) determined from the data in Fig. 1 plotted as a function of the substitute Au monolayer location relative to the surface. The lower horizontal scale is the distance measured from the positive background edge, and the upper scale shows the atomic-layer locations with the first atomic layer being the surface layer. The solid curve is the electrostatic potential energy for Ag(111) estimated from a jellium calculation.

of 0.33 eV for pure Au(111).^{8,10} Note that this value of 0.33 eV was deduced from photoemission results from Au(111) by assuming negligible subsurface shifts; thus, it may have a non-negligible uncertainty. Although no surface core shift data exist for Ag(111), they are expected to be similar in magnitude to that for Au(111).

The core-level energy shifts measured by photoemission has contributions from both the initial- and final-state effects.³ The initial-state shift reflects the change in the oneelectron eigenvalue in the ground state, and the final-state shift corresponds to the difference in screening energy. The relative importance of the two contributions has been a subject of great interest and controversy.^{3,7} Note that there are actually no unique and mutually independent definitions for the initial- and final-state shifts. In a suitably chosen oneelectron theoretical model, the final-state effect can be negligible and the measured core-level shift is mainly the one-electron eigenvalue difference.

In the usual self-consistent local-density-functional formalism, the initial-state contribution to the core-level energy is just the electronic electrostatic potential energy ϕ ;^{1,6} the final-state contribution appears to be generally smaller for metals.^{3,7} Thus, the variation of ϕ near the surface is expected to roughly describe the core-level shift data in Fig. 2, at least for the overall direction of the shift.¹² The solid curve shown in Fig. 2 is ϕ obtained from a jellium calculation for $r_s = 2.07.^{6,13}$ In the jellium model, the atomic cores in the solid are replaced by a uniform positive background; the edge of the positive background is at a distance of onehalf of the interlayer spacing beyond the surface atomic plane. The lower horizontal scale in Fig. 2 is the distance measured from the edge of the positive background. The calculated ϕ shows a rapid rise near the surface with a net step height of about 6 eV. The oscillations of ϕ inside the solid are the Friedel oscillations. The atomistic effects associated with the lattice are totally ignored in the jellium calculation. Although this approximation may not be satisfactory, there are no better theoretical results available in the literature. The curve of ϕ in Fig. 2 is plotted such that it coincides with the two leftmost data points.

The curve of ϕ in Fig. 2 correctly describes the general direction of shift in core-level energy at the surface. For the Au monolayer at the surface, the measured shift relative to the bulk value, about 0.27 eV, has the same sign as ϕ , but about 2.6 times as large. The numerical discrepancy is not surprising and is likely due to the final-state shift and the jellium approximation.^{2, 3, 7}

The most significant difference between the core-level energy shift and ϕ in Fig. 2 is in the spatial extent of the variation. Apart from the small Friedel oscillations, the surface-induced shift in ϕ is significant only for the first (surface) atomic layer, whereas the measured core-level energies show significant shifts for up to three atomic layers near the surface. This discrepancy is most likely due to the atomistic effects neglected in the jellium approximation. For example, in the case of Al(001) for which state-of-theart calculations exist, it has been found that proper account of the atomic potential is extremely important in determining the (sub)surface core-level shifts. In a linearized augmented plane-wave calculation with spherically averaged atomic potential, Al(001) showed negligibly small surface and subsurface core shifts, while in a full-potential calculation with the same method, but without the spherical averaging of the atomic potential, Al(001) showed significant core shifts for the top two layers of a nine-layer slab.² In light of these calculations (although the final-state effects were totally ignored), the jellium results cannot be expected to describe the data in Fig. 2 quantitatively.

To summarize, we have determined the core-level shifts for a substitute Au(111) monolayer as a function of the depth of the Au monolayer below the surface. The purpose is to determine experimentally the manner in which the surface effect decays for increasing depth below the surface. The spatial extent of the surface effect has been found to be significantly larger than what is expected from a simple model for the screening of surface potential in jellium, although the overall direction of the shift is consistent with the prediction of this model. The measured core-level shifts should correspond approximately to the layer-resolved core-level shifts in pure Ag(111), but we cannot give a reliable estimate of the uncertainty introduced by the difference in Ag and Au. The phenomenon of subsurface multilayer relaxation is of importance to the understanding of surface properties. In light of the present results, it will be illuminating to reexamine the theoretical ideas using stateof-the-art computational methods, especially in the area of final-state screening effects for which few calculations exist. We have also tried to prepare other similar systems including Ag(111) with one subsurface layer selectively doped with impurity atoms, but none of the systems tried so far could be fabricated with the same level of atomic precision as in the case of Au in Ag(111). It appears that several semiconductor systems (such as GaAs-AlAs and alloys) and insulator systems (such as rare-gas solids)¹⁴ are promising candidates for this type of experiment. This report should stimulate further interest in the studies of material properties with the use of samples with tailored atomic configurations.

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