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Core-level shifts for Au epitaxial overlayers on Ag

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The Au $4f_{7/2}$ core-level binding energies for epitaxial Au films on Ag(111) and Ag(100) and Ag-covered Au films have been determined from photoemission measurements. The surface and subsurface contributions can be separated, and the evolution of binding energies as a function of Au film thickness provides useful information about the one-electron potential variation within the film. The mode of initial film growth is determined by the core-level intensities from different layers.

Core-level binding energies of surface atoms are often shifted relative to bulk atoms for crystalline materials. Citrin, Wertheim, and Baer[1] reported a surface shift of -0.4 eV for polycrystalline Au; since then, a number of studies of single-crystal materials including metals, semiconductors, and insulators have been reported.[2,3] Connections can be made between the experimentally determined core shifts and the surface atomic structure; thus, for example, the various surfaces of Au including the (111)-(1×1), (110)-(2×1), (100)-(1×1), and (100)-(5×20) all show different surface shifts.[2,4] The measured surface core-level shifts can also provide useful information about the surface electronic properties.[2,5] An important relationship between the surface core shifts and the surface-impurity segregation energies has been established theoretically by Johansson and coworkers,[6] and has been exploited experimentally by Egelhoff.[7]

There also exist many experimental studies of core-level shifts in atomic clusters and thin films on substrates for the purpose of understanding the interfacial electronic and thermochemical properties.[2,8,9] For these systems, the atomic structure is generally either so complex or insufficiently determined that a detailed understanding becomes difficult. Even for the simple case of a smooth epitaxial overlayer, the atomic spacing and lateral strain and registry at the interface are often unknown, but are, however, important input parameters for theoretical calculations. In this paper we report the first high-resolution photoemission measurement of the Au $4f$ core-level shifts for the Au-Ag system, a nearly ideal model system for overlayer core shift studies. Ag and Au have a very small lattice mismatch, 0.2%, which is negligible for many purposes. Au grows on Ag(111) epitaxially in a smooth layer-by-layer fashion continuing the fcc sequence with few stacking faults and little strain at room temperature as determined by ion scattering.[10] The valence electronic properties of these two materials are also quite similar. The intention of this work was to measure the layer-by-layer core-level shifts for increasing Au overlayer thickness on both Ag(111) and Ag(100), in order to determine the one-electron potential variation within these films. Interestingly, Ag(100) as well as Au(111) and Ag(111) shows no reconstruction, while Au(100) shows either the (5×20) structure obtained by sputtering with Ar^+ or the metastable (1×1) structure obtained by sputtering with O^+ at room temperature.[11] The important question here is how the surface structure and core shifts evolve as a function of Au overlayer thickness on Ag(100). This information can help understanding of the perturbation induced by surface reconstruction and bimetallic contact as well as quantum-mechanical effects associated with restricted geometry. We have also investigated the behavior of the complimentary systems of Ag-covered Au(111) and Au(100).

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 substrates, Ag(111) and Ag(100), were prepared by sputtering with Ar^+ and annealing; a layer of Ag about a few hundred angstroms thick was then autoepitaxially grown on each substrate at 320 °C to smooth out residual surface roughness. Subsequent deposition of Au followed by Ag was done at room temperature to avoid any intermixing.[10] High-energy electron diffraction (HEED) patterns from the samples prepared *in situ* were very sharp indicating good atomic order; the overlayers appeared to be smooth even for very thick films deposited at room temperature during test runs. The HEED results were also reproduced in a different vacuum chamber. The film thickness was determined from the evaporation rate measured with a quartz thickness monitor. The surface cleanliness was checked with Auger spectroscopy.

The Au $4f_{7/2}$ core-level spectra for various overlayers on Ag(111) taken with a photon energy of 110 eV are shown in Fig. 1 with dots; the results of a least-squares fit and the decomposition of the spectra into the contributions of various components are shown as solid curves. At the selected photon energy, the photoelectrons have a rather short electron escape depth of about 5 Å.[4] The spectrum for 10 monolayers (ML) of Au on Ag(111) in Fig. 1 should be essentially the same as that for bulk Au(111). Indeed, it resembles very much the spectrum for bulk Au(111) in Ref. 4; the asymmetric line shape is due to a surface shift. Our spectrum in Fig. 1 was fitted by assuming a Voigt line shape (convolution of a Gaussian and a Lorentzian) for both the surface and bulk contributions on top of a quadratic polynomial background function. It is not necessary to use the Doniach-Šunjic line shape at this energy.[4] The full width at half maximum (FWHM) of the Lorentzian was taken to be 0.32 eV.[1] The FWHM of the Gaussian is about 0.33 eV from our fit, which includes instrumental resolution and other broadening factors. The surface (S) and bulk (B) contributions are indicated in Fig. 1; the surface-to-bulk

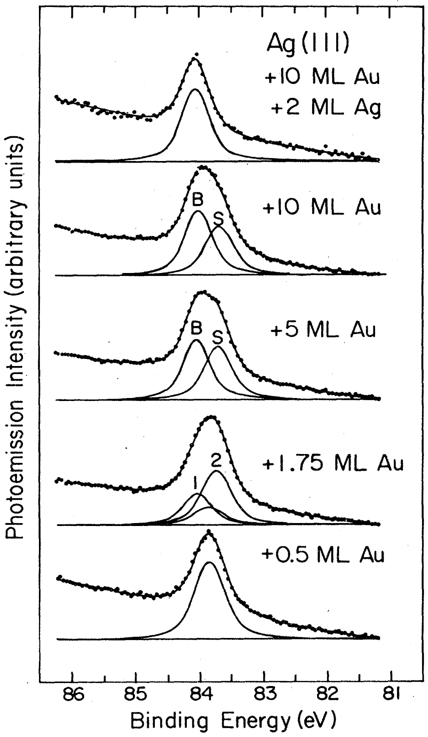

FIG. 1. Au $4f_{7/2}$ core-level photoemission spectra (dots) for 0.5, 1.75, 5, and 10 ML of Au and for 2 ML of Ag on 10 ML of Au prepared on an Ag(111) substrate. The binding-energy scale is referred to the Fermi edge. The solid curves are the results of a fit and decomposition of the spectra into various contributions.

binding energy shift is -0.33 eV which is close to the value of -0.35 eV cited in Ref. 4 for bulk Au(111). If the projection of the electron escape depth along the surface normal is λ, the intensity ratio of the surface layer contribution to the bulk contribution is

$$R=[\exp(d/\lambda)-1]/\{1-\exp[-(n-1)d/\lambda]\}\ , \qquad (1)$$

where d is the inter-atomic-layer spacing, and n the number of atomic layers in the film. For the present case $n=10$, and the value of R is essentially the same as for $n=\infty$. From the fit $R=0.8$, we obtain $\lambda=4.0$ Å from Eq. (1). Since the electron emission angle is about 42° with respect to the surface normal in our experiment, the electron escape depth itself is about 5 Å in agreement with Ref. 4. Therefore, our present result for the 10-layer film is in close agreement with that for bulk Au(111).

The other spectra in Fig. 1 were analyzed similarly. Each spectrum was fitted by the smallest number of components leading to a reasonable fit. The details will be published elsewhere. For 5 ML of Au on Ag(111), the spectrum is similar to that for 10-ML Au on Ag(111) except that the surface-to-bulk intensity ratio R is slightly larger because the film is thinner. The experimental value of R exactly equals the value calculated using Eq. (1) and $n=5$. For 0.5 ML of Au on Ag(111), the spectrum shows just one peak indicating that one-atomic-layer-thick islands are formed in agreement with a smooth layer-by-layer growth mode. For 1.75 ML of Au on Ag(111), 25% of the surface is covered by just one atomic layer giving rise to the smallest of the three peaks seen in Fig. 1. 75% of that surface is covered by two atomic layers; the contributions from the first (bottom) layer and the second layer are labeled by 1 and 2, respectively, in Fig. 1. The relative intensities of the three peaks are described well by Eq. (1) and the above model. Finally, the spectrum for 10 ML of Au covered by 2 ML of Ag shows just one peak with a binding energy somewhat larger than the bulk value of the 10-ML Au film.

Our results provide convincing evidence that the initial growth of Au on Ag(111) is indeed layer by layer. The Au $4f_{7/2}$ binding energies for various layer configurations are summarized in Fig. 2(a), where all energies are referred to the bulk value for the 10-layer film; the estimated uncertainty is about ± 0.01 eV. The data points for the bilayer of Au on Ag(111) are deduced from the spectrum for 1.75 ML of Au in Fig. 1 by ignoring the peak corresponding to monolayer coverage. The dashed lines are just a guide to the eye to indicate the evolution of the peak positions.

The spectra of Au $4f_{7/2}$ core levels for various layer configurations on Ag(100) are shown in Fig. 3; they have been analyzed similarly and checked against Eq. (1). For 0.75 ML of Au on Ag(100), two peaks were observed. Peak 1 is derived from Au atoms in direct contact with the substrate, and peak 2 is derived from Au atoms in the second (top) layer. Peak 2 is much less intense than peak 1; therefore, the growth mode of the Au overlayer is close to but not quite smooth layer by layer. The interpretation of the other

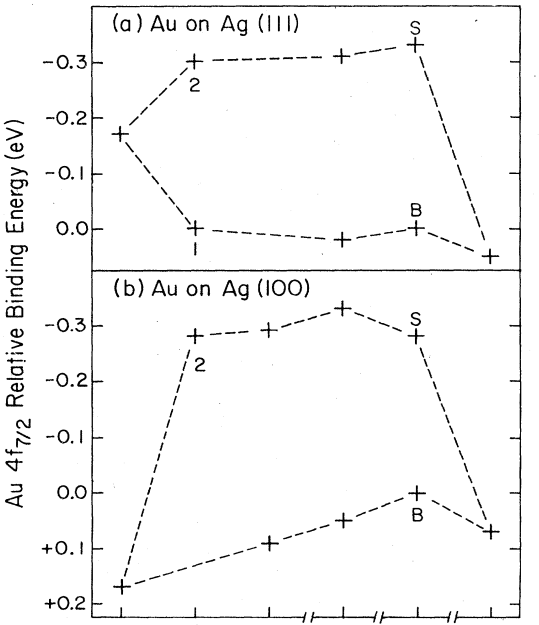

FIG. 2. Relative Au $4f_{7/2}$ core-level binding energies for (a) Au on Ag(111) and (b) Au on Ag(100) as a function of Au overlayer thickness. For 2-ML Au coverage, the first- (bottom-) layer and the second-layer contributions are labeled 1 and 2, respectively. For 10-ML Au coverage, the surface and bulk contributions are labeled S and B, respectively. The rightmost data point for each case labeled Ag/Au corresponds to 10 ML of Au on the substrate further covered by 2 ML of Ag. The binding-energy scale is referred to the bulk contribution of the uncovered 10-ML Au film. The dashed lines are just a guide to the eye.

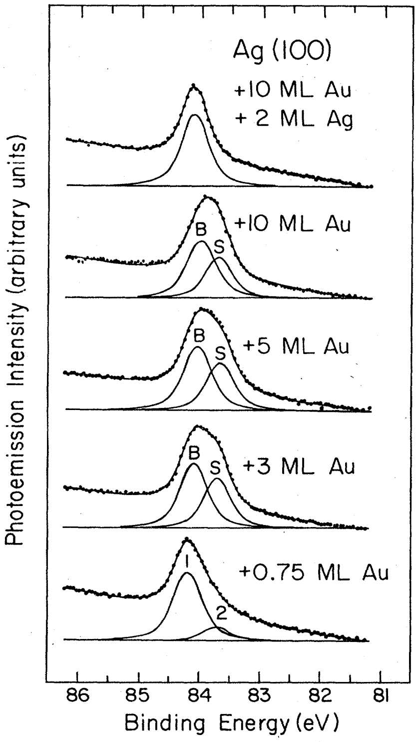

FIG. 3. Same as Fig. 1 except that the spectra are for 0.75, 3, 5, and 10 ML of Au and for 2 ML of Ag on 10 ML of Au prepared on an Ag(100) substrate.

spectra is straightforward. The Au $4f_{7/2}$ core-level binding energies for various layer configurations are summarized in Fig. 2(b); they are referred to the bulk contribution of thick film Au(100).

The HEED patterns for Au on Ag(100) indicate a fairly smooth (1×1) surface for Au coverages up to almost 5 ML. At 5-ML coverage the diffraction streaks begin to split but no $\frac{1}{20}$th order spots can be seen, indicating a partial conversion of the surface structure from (1×1) to (5×20). At 10-ML Au coverage, the pattern becomes a sharp (5×20). With further coverage of just ML of Ag, the pattern converts back to a sharp (1×1). Palmberg and Rhodin also studied Au on Ag(100) using low-energy electron diffraction techniques and found a (1×1) to (5×20) transition occurring at an Au coverage of 3 ML.[12] The discrepancy may be due to differences in the sample preparation conditions. During growth, the Au atoms first form large two-dimensional islands; Au atoms falling on these islands may combine to form two-dimensional islands in the second layer before the completion of the first layer. The islands in the second layer are too massive to move as a whole; rather, individual Au atoms moving away from the perimeter may find the first-layer island boundary and become part of the first-layer island. The resulting morphology depends on the growth kinetics, evaporation rate, sample temperature, and the number of surface defects which may hinder the diffusion of atoms. Most probably the Au overlayers on Ag films deposited on KCl and MgO of Palmberg and Rhodin showed more three-dimensional character, and therefore the (5×20) reconstruction was first detected at a smaller average Au coverage. For bulk Au(100), the (1×1) surface converts into (5×20) at just 100 °C,[11] indicating a small margin of metastability.

Referring to Fig. 2, the main observations for Au on Ag(111) are as follows. (1) A monolayer of Au(111) on Ag(111) has a core binding energy larger than that for the surface layer of bulk Au(111), by 0.16 eV. Note that the crystal potentials of Au and Ag are different;[13] therefore, the Ag-Au interface can support a potential variation causing the contacting layers to exhibit shifted core-level binding energies. The effect is nevertheless small. (2) With just 2 ML of Au on Ag(111), the top and the bottom layers already have core binding energies very close to those of the surface and bulk of thick Au films. One might think intuitively that the interfacial perturbation is screened within one atomic layer distance; therefore, the top layer does not sense the presence of the Ag substrate and the bottom layer sees a more bulk-Au-like environment. [But see (4) below.] (3) For thicker films (5–10 ML) the relative shifts among subsurface atomic layers are small and cannot be resolved experimentally,[4] indicating a rapid decay of the surface perturbation in the bulk. (4) A thick film of Au(111) covered by 2 ML of Ag shows just one unresolved peak with a small positive relative binding energy; therefore, the top layer(s) of the Ag-covered Au film does not see exactly a bulk-Au-like environment. [See (2) above.] This result indicates a nontrivial interface potential variation; the core-level binding energies for a given layer are not just determined by the identity of its nearest-neighbor layers.

More interesting behaviors are observed for overlayers on Ag(100). (1) A monolayer of Au(100) on Ag(100) has a core binding energy 0.55 eV larger than that for the surface layer of bulk Au(100)-(1×1), taking the surface core shift for bulk Au(100)-(1×1) to be -0.38 eV.[4] A similar but much smaller effect was discussed above for Au on Ag(111). (2) The potential variation near the interface is expected to be mostly limited within the first layer since the metallic screening length is very short. For 3 and 5 ML of Au on Ag(100), the surface-to-bulk shift, -0.38 eV from Fig. 2, is exactly the same as for bulk Au(100)-(1×1), although at 5-ML coverage the surface already shows partial conversion toward the (5×20) structure. The peculiar behavior is that the bulk contribution in each case shows a binding energy positive relative to the bulk of thick film Au(100), indicating a measurable overall shift in potential throughout the thin film. This shift in potential becomes smaller as the film thickness is increased. If the substrate had no effect for the 3- and 5-ML Au films, the surface core level would have a relative binding energy of about -0.38 eV rather than the experimentally determined values of -0.29 and -0.33 eV, respectively. (3) At 10-ML Au coverage, the film should be like bulk Au(100)-(5×20). Indeed, the measured surface-to-bulk core shift, -0.28 eV, is identical to that for bulk Au(100)-(5×20).[4] (4) With 2-ML Ag on thick-film Au(100), the top layer(s) of the Au film shows a binding energy larger than that of the bulk, similar to what has been seen for Ag-Au(111).

To summarize, we have demonstrated that high-resolution core-level measurements can provide very useful information about one-electron potential variations in thin films and near interfaces and about initial film-growth modes, etc. The system Au-Ag(100) also provides an interesting case for the investigation of surface transition. The Au-Ag interface has very simple atomic structure, and, therefore, theoretical calculations can be made without the usual ambiguity about the interface atomic structure. However, such calculations are not available yet. Qualitatively, we notice that even for this relatively simple system, Au-Ag, the behavior can be nontrivial. Thus, for example, a monolayer of Au on Ag does not behave the same as a monolayer of Au on Au, etc. Owing to the very short screening length in metals, it is unlikely for any appreciable potential gradient from atom to atom to exist within the bulk part of the Au overlayers; experimentally, the bulk core-level peaks are not appreciably broadened. However, we found a measurable overall shift in potential for 3–5 ML of Au on Ag(100), but not for Au on Ag(111). A possible explanation is as follows. Owing to the restricted geometry and different boundary conditions, the valence levels in the film can be altered leading to a modified one-electron potential and hence possibly to an overall shift in the potential. The difference between Au-Ag(111) and Au-Ag(100) must have its origin in the different boundary conditions at the interface. Clearly, the Ag(100) substrate has an effect on the surface structure of the Au film, as the (1×1) to (5×20) transition commences at an Au coverage of 5 ML. In this sense, the range of the interface perturbation is quite long in producing noticeable physical effects.

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