Unit Charge on Supported Gold Clusters in Photoemission Final State

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Positive binding-energy shifts in small metallic clusters supported on poorly conducting substrates are shown to arise from the unit positive charge remaining on the cluster in the photoemission final state.

We have found that the ubiquitous shift to larger electron binding energy[1-9] reported for small metallic clusters supported on poorly conducting substrates has its origin in the positive charge of the cluster in the photoemission final state. This interpretation of the shift removes the apparent contradiction between the negative shift of the core-electron binding energy of gold surface atoms[10,11] and the positive shift found in small gold clusters. It also leads in general to a reevaluation of the effect of cluster size on electronic structure.

The experiment consists of a comparison of photoemission from similar clusters on different substrates. We have chosen to examine gold clusters on two amorphous substrates, vitreous carbon and Metglas,[12] a commerical metallic glass. Argon-ion sputtering produced clean surfaces on both substrates and removed the oxide from the Metglas. The gold was then deposited from a Knudsen cell at a deposition rate of 0.2 Å/sec, as determined by a quartz-crystal microbalance. This deposition rate was confirmed by the amount of attenuation of the carbon substrate signal at low gold coverage. The samples were transferred between the spectrometer chamber and the preparation chamber under vacuum. Data were taken with monochromatized Al $K\alpha$ radiation in a HP 5950A spectrometer modified for ultrahigh-vacuum operation. For the vitreous carbon substrate, spectra of the C $1s$, Au $4f$, and valence-band regions were recorded. For the Metglas substrate the Ni $2p_{3/2}$ was used to monitor the substrate. Various other scans, e.g., Ar $2p$ and O $1s$, were also taken to monitor the condition of the substrate.

The core-level spectra were analyzed by least-squares fitting, with use of a Doniach-Sunjic[13] line shape. The Au contribution to each valence-band spectrum was obtained by subtracting the spectrum obtained on the clean carbon surface, with the amplitude determined by the attenuation of the C $1s$ signal by the overlayer. The location of the gold Fermi edge was then precisely deter-

mined, also by least-squares fitting.

Figure 1 shows the net gold valence-band spectra for a series of Au exposures on vitreous carbon. The narrowing and the decreased spin-orbit splitting of the Au $5d$ levels at low coverages have been noted elsewhere,[1,7-9,14,15] and are understood to result from the finite size of the Au clusters.[2] The most important aspect of this figure is the appearance of the Au Fermi level at progressively higher binding energy with decreasing coverage. All spectral features of the substrate are unchanged by the adsorption of gold, and the Au Fermi-level shift noted above is measured relative to these features. We note that this shift is a final-state effect, since in the initial state the Fermi edges of the gold, of the substrate, and of the spectrometer (to which the sample is grounded) are aligned. We further assert that this is indeed the Au Fermi edge and not simply an atomiclike s level, as this effect is present at coverages at which the Au valence-band spectra clearly indicate metallic behavior in the clusters.

To explain the variation in the position of the Au Fermi edge we propose that in the final state the gold cluster is not neutralized during the time scale relevant to photoemission. That is, because of the weak cluster-substrate interaction[16] which is due perhaps to the low density of states in the semimetallic carbon substrate, there is *not* a rapid transfer of an electron to the cluster as there would be on a metallic surface. Thus, although the relaxation response within the cluster may otherwise proceed normally, there will remain an excess unit positive charge on the cluster. The Au conduction-electron charge will be attracted towards the core hole, leaving the excess positive charge distributed over the cluster's surface. The resulting Coulomb attraction will therefore increase the apparent binding energy of the Au electrons by $\sim e^2/R$, where R is the cluster radius. This R dependence accounts for the observed decrease in the shift as the coverage, and hence the aver-
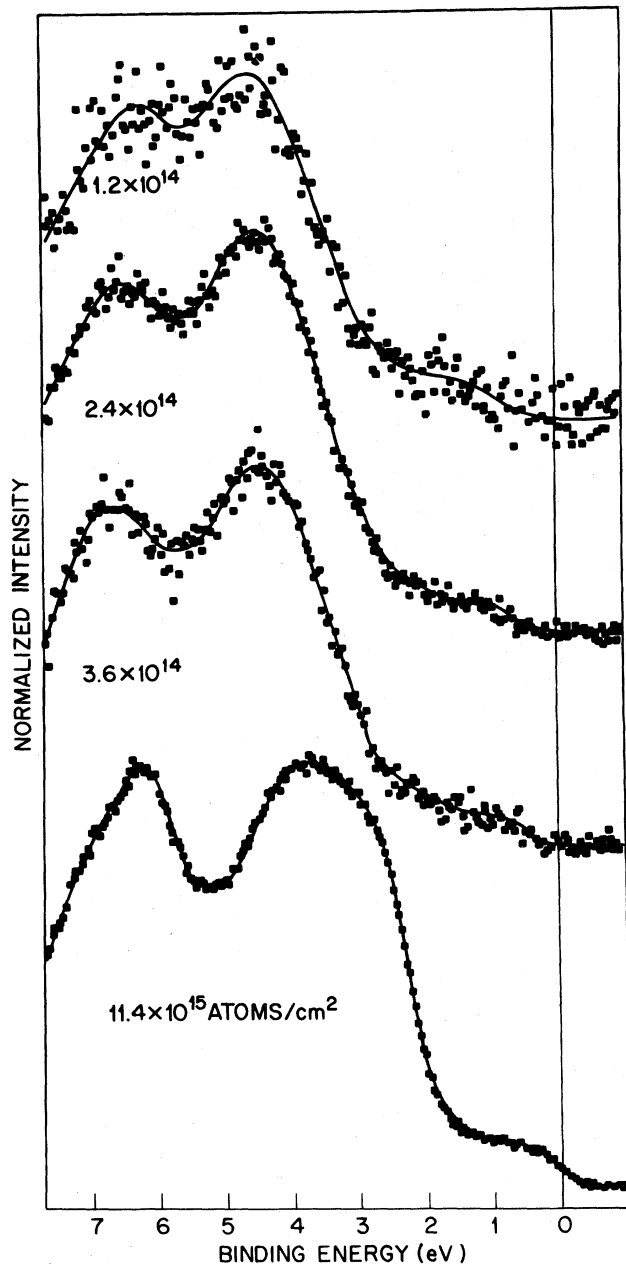
FIG. 1. Valence-band spectra of gold clusters on a vitreous carbon substrate. The substrate's contribution to each spectrum has been subtracted.
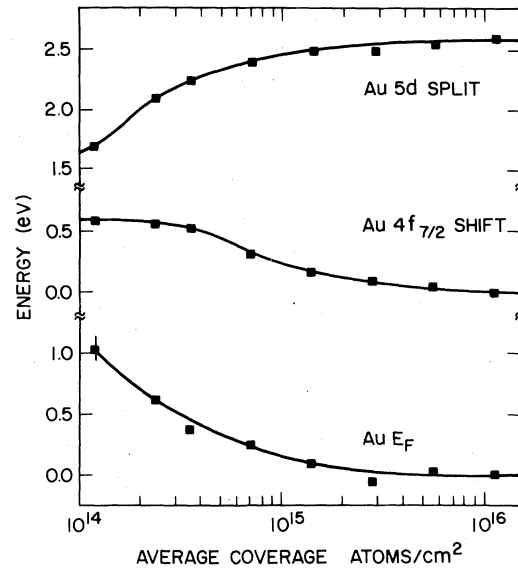

FIG. 2. Coverage dependence of the Au $4f$ binding energy, of the observed position of the Au Fermi edge, and of the Au $5d$ splitting.

ized in the final state.

We can use the Au Fermi-level shifts to estimate the mean cluster size. We assume spherical clusters, in which case the cluster radius R is simply $e^2/\Delta BE$, where ΔBE is the Fermi-level shift. Using the Au $5d$ spin-orbit splitting to match Au coverages in our data and in the data of Lee et al.,[14] we infer cluster sizes that are 2 or 3 times as big as those measured by Lee et al. using electron microscopy. Granted that the substrate will contribute relaxation terms that tend to decrease the shift and hence to increase our inferred radius, this approximate agreement reinforces our interpretation of the data.

The next point we wish to make is that, as may be seen in Fig. 2, the Au $4f$ shift is quite similar to the Au Fermi-level shift, deviating only at very low coverage. Thus the previously reported shift to higher binding energy of core levels in Au clusters on amorphous carbon[8,9] is due to the positive charge on the cluster in the final state. This resolves the apparent conflict between the small-cluster data and expectations based on the known negative surface-atom core-level shift of gold[10,11]; in this view the high surface-to-bulk ratio in small clusters should yield Au core levels with a lower average binding energy. The Au surface-atom core-level shift has been attributed to a transfer of charge from the s band to the d bands,[10,17-19] resulting from narrowing of

age cluster radius, increases. It is presumed that at some point the average cluster radius increases more rapidly because of coalescence of clusters. Coverages $> \sim 2$ monolayers correspond to clusters large enough to show no Fermi-level shift. It is unclear whether this is due to the effect's $1/R$ dependence, or whether the larger clusters, perhaps because of increased contact area with the substrate, are now being neutral-

the d bands due to the greater localization at the surface; such effects are naturally expected to occur in small clusters. However, since the surface-atom core-level shift on clean polycrystalline gold is only -0.4 eV, this initial-state effect would clearly be overwhelmed by the large positive shift induced by the final-state charge. It is tempting, in fact, to ascribe the discrepancy between the $4f$ shift and the Au Fermi-level shift at the lowest coverages to just such an initial-state effect; however, the data are not conclusive.

Although a cluster carries a positive charge during the time relevant to photoemission (10^{-16} sec), it is neutralized within a time which is short compared with the rate of photoemission from the overlayer, that is, there is no buildup of positive charge on the sample surface. Such a buildup would be evident in the substrate spectra, which on the contrary do not change as gold is adsorbed, as we emphasized above. Such long-term charge buildup is known to occur on insulating substrates.

The core-electron binding-energy shifts of supported clusters must be distinguished from the changes in threshold ionization potential of free clusters, which have been observed[20,21] and calculated.[22,23] The threshold change contains two terms: an increase due to the attraction of the unit charge left behind by photoemission, and a reduction due to the weaker image potential of a sphere compared to that of a plane, giving a net increase of $3e^2/8R$ in the threshold ionization potential. However, it is well known that when a sample is grounded to the spectrometer, changes in the threshold do not affect the measured kinetic energy of the photoelectron. This is not contradicted by the fact that the core-level shifts that we report here have the same form as the first of the two terms in the threshold change, and likewise result from the unit charge on the cluster in the final state. By contrast, the image-charge interaction, despite its importance for the photoemission threshold, has no influence on our data. This is confirmed by our data for clusters on a metallic substrate.

We expect that on a metal substrate the high density of states at and near the Fermi energy will speed charge transfer to a supported cluster, leaving no macroscopic charge during the photoemission final state. Indeed, for Au clusters on Metglas the Au $4f$ level exhibits only a very small (< 0.2 eV), negative shift at the lowest coverages, although the valence-band spectrum clearly shows the narrowing of the $5d$ band characteristic of the formation of small clusters. The absence of a substantial binding-energy shift confirms not only the neutrality of the cluster in the final state but also the irrelevance of threshold effects in our measurements: The first term in the threshold change, being due to the net cluster charge, vanishes, but the image-charge interaction for a neutral spherical cluster would decrease the photoemission threshold by $5e^2/R$, which is nearly an order of magnitude greater than our observed shift. The small negative shift we observe may be due to an increased contribution from surface atoms with smaller electron binding energy. The Fermi level of the gold is unfortunately not directly measurable because of the high density of states of the Metglas.

We have shown that the large positive core-level shifts seen in photoemission from Au clusters on poorly conducting substrates result from a unit positive charge left on a cluster during the photoemission final state. We find that the case of clusters supported on a (poorly conducting) amorphous carbon subrate is intermediate between the case of free clusters (which remain charged on a macroscopic time scale) and that of clusters supported on metallic substrates. On metallic substrates the high density of states at the Fermi energy facilitates charge transfer and hence neutralization of the cluster in the final state. Consequently we observe no large, positive shift of the Au $4f$ binding energy for small clusters of Au on Metglas. This in turn implies that the shifts observed for clusters on carbon do not result from a size-induced decrease in metallic screening,[6,8,24,25] nor are they due to band-structure effects, nor do they contain a contribution from the image charge interaction, which helps determine the photoemission threshold. Our identification of this macroscopic Coulomb effect removes the apparent conflict between positive core-level shifts and the expected initial-state band-structure effect, whereby increased localization in small clusters should increase the d density in gold,[10,17,18] thereby decreasing the Au core electron binding energy. We do in fact tentatively identify very small negative core-level shifts, relative to the Fermi level, at the lowest gold coverages on both substrates which may confirm these expectations.

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