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Cluster growth and core-electron binding energies in supported metal clusters

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Examination of the coverage dependence of the core-electron photoemission intensity and binding energy for simple, noble, and transition-metal clusters supported on amorphous carbon reveals three distinct, cluster-size-dependent regimes. In very small clusters, containing fewer than ~30 atoms, the final-state hole is screened by the polarization of the neighboring atoms, and the binding energy depends only weakly on cluster size. In larger, metallic clusters the hole is screened by conduction electrons, with the missing charge appearing at the surface of the cluster. In this regime, the core-electron binding-energy shifts vary inversely with the one-third power of the coverage, confirming that they are dominated by the Coulomb energy of the charged final-state cluster. In the third regime the clusters begin to coalesce, forming a contiguous metallic layer in which the binding energy rapidly approaches that of the bulk metal.

I. INTRODUCTION

During the past ten years a great deal of effort has been devoted to the study of supported metal clusters. Photoemission is well suited to study the electronic properties of supported clusters, because it offers sufficient sensitivity to detect a small fraction of a monolayer of atoms. Amorphous carbon has been the most widely used support because it has a relatively weak interaction with most metals, allowing clusters to grow as well-formed entities. It also has significant advantages in x-ray photoelectron spectroscopy (XPS) studies because the signal from the carbon valence electrons is relatively weak and featureless, making it simple to separate the signal of the clusters from that of the substrate.

Although there is general agreement regarding the nature of the photoemission data for clusters of many different metals supported on amorphous carbon,[1-18] their interpretation remains controversial. Of course, a single mechanism is not likely to account for all phenomena, for all materials and all cluster sizes. Rather, one must determine which mechanisms are important in any particular case. While the positive core-level shifts observed for all metal clusters on carbon have been attributed by some to size-induced changes in band structure, we have suggested[12,17] that they are due primarily to the Coulomb energy of the cluster's positive charge, which results from the emission of the photoelectron. The most direct evidence in favor of the cluster-charge interpretation of core-electron binding-energy shifts is the simultaneous shift of the clusters' Fermi cutoff,[12,17] for which no alternative explanation has been offered. In this paper we will show that the coverage dependence of the core-level shifts also offers strong support for our model.

Let us begin by describing the experimental situation. The experiments have generally been done with random-sized clusters on substrates of amorphous carbon, carefully cleaned by sputtering in vacuum. The clusters are grown by depositing metal vapor from a hot furnace onto the substrate, where they grow at fixed nucleation sites.[16,19] Electron microscopy has shown that the resulting clusters are faceted solids of compact shape, indicating that the cohesive interactions among the cluster atoms are much greater than their adhesive interaction with amorphous carbon. The observed size distribution is in accord with model calculations of this growth process.[16] Cluster size is typically not a well-determined quantity. It is usually estimated from the flux from the deposition furnace, an assumed unity sticking coefficient, and a nucleation site density determined by others[19] for similar substrates. Photoemission data are typically reported for a range of metal coverages from 3×10^{13} up to 10^{17} cm^{-2}. Since the nucleation site density is typically 3×10^{12} cm^{-2}, these coverages range from clusters containing as few as ten atoms on the average up to the percolation limit where the clusters have formed a contiguous metallic layer, though generally not without holes.

II. RESULTS AND DISCUSSION

A. Core-electron binding-energy shifts

Core-electron binding energies, measured relative to the Fermi level of a thick layer of metal later deposited on the same substrate, have been reported for clusters of simple, noble, transition, and rare-earth metals. The remarkable fact is that in every case the core-electron binding energy is larger in the cluster than in the metal, and increases monotonically with decreasing cluster size. This fact by itself has inspired many different interpretations of the shift. Prominent among the proposed mechanisms are (1) size-induced changes in band structure resulting in flow of charge between orbitally distinct bands, (2) an increasing role of the substrate interaction, and (3) a reduction in final-state screening. Unfortunately these mechanisms have not been subjected to a quantitative test because the computational costs are prohibitive. The calculations that are required to minimize the energy of a 100-atom cluster and to obtain its band structure, even without including the support interaction, are beyond current means.

We have proposed[12] a simple mechanism to account for the ubiquitous positive core-level shift. We identify the shift with the Coulomb energy of the cluster in the photoemission final state. Photoemission leaves a cluster with a net unit positive charge, which is eventually neutralized by an electron from the substrate. The charge neutralization time of supported clusters is an important question. If the cluster is in contact with a metallic substrate, this charge may be neutralized within the lifetime of a typical core-hole state, i.e., within 10^{-15} sec. In accord with this, experiments show very small shifts for clusters supported on metals. On insulating or semiconducting substrates neutralization may require tunneling through a barrier and could be quite slow. Although it is known experimentally that on amorphous carbon the charge-neutralization time is much shorter than the typical interval between photoemission events from a single cluster, we believe that it is much longer than the core-hole lifetime. By contrast to the band-structure-based models, our cluster-charge model makes a simple, material-independent prediction for the size dependence of the binding-energy shift, which for a free, spherical cluster of radius r is $e^2/2r$. Below we will consider the complications introduced by the problem of supported, nonspherical clusters and we will comment on the range of applicability of this simple model.

In order to test the cluster-charge model[12] we will assume that each cluster's mass is proportional to the amount of material deposited per unit area of the substrate. The cluster radius then varies as the cube root of the coverage, Θ, and the Coulomb energy of the charged final state varies as

$$E_{\text{Coul}} \propto e^2/2r \propto \Theta^{-1/3} \ . \tag{1}$$

A log-log plot of the shift of the core-electron binding energy from the value in the bulk metal against coverage should then have a slope of $-\frac{1}{3}$. Figures 1–4 show data for clusters of Ag,[17] Sn,[15] Pd,[17,18] and Pt (Ref. 14) plotted in this way. In every case a region with a slope of $-\frac{1}{3}$ is found at low coverage, followed by a drop that begins at a coverage of one or two monolayers. Although abrupt changes at monolayer coverage are characteristic of layerwise growth, here the observed increase in slope is a result of the coalescence of clusters. That it occurs at a coverage near one monolayer is a fortuitous result of the density of nucleation sites on amorphous carbon. We will now examine both the binding-energy shifts and the photoemission intensities for evidence of the evolution of cluster morphology.

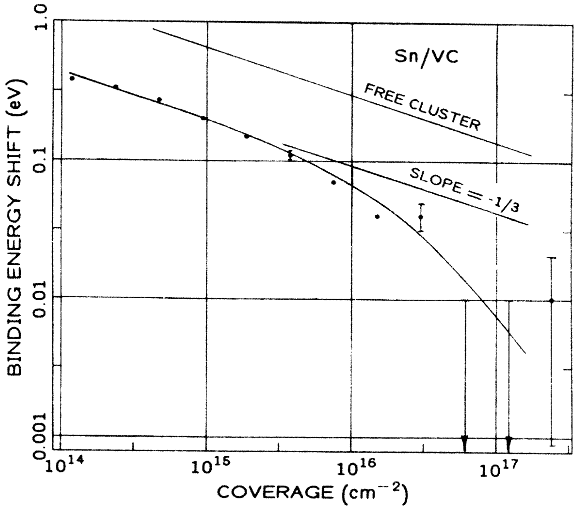

FIG. 1. Core-electron binding-energy shift of tin clusters on vitreous carbon plotted against coverage. For coverages less than 3×10^{15} cm^{-2} the data exhibit a slope of $-\frac{1}{3}$, indicating that the shift is inversely proportional to the linear dimension of the clusters. At higher coverage the shift drops rapidly below this line, indicating that the clusters have begun to coalesce. The Coulomb shift for free clusters of the same diameter is also indicated.

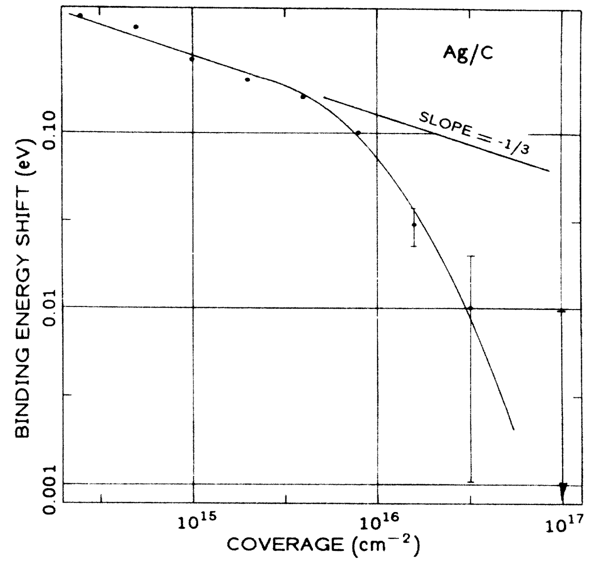

FIG. 2. Core-electron binding-energy shift for silver clusters on amorphous carbon, from Ref. 17, replotted as in Fig. 1.

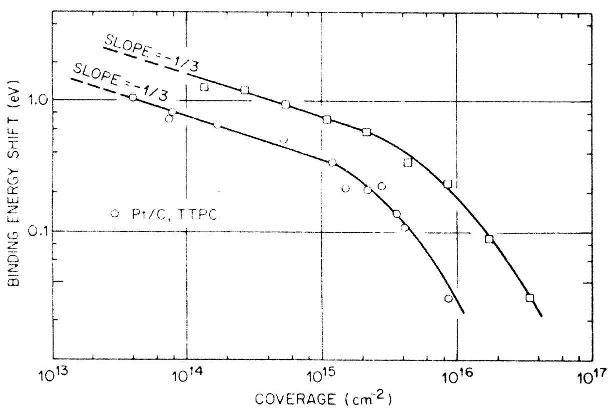

FIG. 3. Core-electron binding-energy shifts for clusters of Pd, from Ref. 17, and Pt, from Ref. 13, replotted as in Fig. 1.

It is generally agreed that on amorphous carbon there are 3×10^{12} nucleation sites per square centimeter. Independent determinations agree within about a factor of 2. The average area per nucleation site is then 3.3×10^{-13} cm^2, and the diameter of an average site is 65 Å. For sites placed randomly in a plane, we expect most of the site diameters to lie between 23 and 95 Å. Consider hemispherical clusters of silver atoms (for which the atomic volume is 16.94 Å^3), and assume that the number of atoms in a cluster is proportional to the Wigner-Seitz area of its nucleation site. At a Ag coverage of 3×10^{15} cm^{-2}, then, the clusters on the sites mentioned range from 20 to 52 Å in diameter, so that the smallest clusters will begin to coalesce with their neighbors. The cluster shift drops precipitously as as coalescence changes the cluster size distribution in favor of larger clusters. Finally, when the diameter of the average cluster reaches the diameter of the average nucleation site, the clusters form a contiguous metallic layer. For our hemispherical Ag clusters this point corresponds to a coverage Θ of 1.3×10^{16} cm^{-2}.

Corroboration of this change in the cluster morphology is readily obtained from the coverage dependence of the core-electron photoemission signal strength. In Fig. 5 we show a log-log plot of intensity data obtained from tin clusters grown on vitreous carbon. The interesting observation is that the intensity begins to deviate from a line with unit slope at a coverage well below 1 ML (monolayer), but saturates only at a coverage about 100 times greater. For layerwise growth, by contrast, the turnover would be quite abrupt. The intensity of photoemission from a single spherical clusters can be calculated as

$$S=\pi\lambda^3\{x^2+[(2x+1)e^{-2x}-1]/2\}\ , \qquad (2)$$

where λ is the escape depth, $x=r/\lambda$, and r is the radius of the cluster. For small r, the right-hand side of (2) reduces to the cluster volume $4\pi r^3/3$, and the photoemission intensity is proportional to the number of atoms. For $r\gg\lambda$, S tends to $\pi r^2\lambda$, and the signal is proportional to the cluster's projected area, as only the photoelectrons from the surface region of the cluster are detected. Since the cluster volume is a linear function of the coverage, a log-log plot of S versus Θ, which allows comparison with Fig. 5, should have a slope of 1 at small Θ, decreasing to a slope of $\frac{2}{3}$ at high coverage. Experimentally, this decrease in slope can be seen in Fig. 5, but it is followed by a gradual decrease to zero slope. This saturation of the intensity occurs when the clusters have grown to the point where they touch and can no longer increase their projected area, a phenomenon not included in Eq. (2), which describes an *isolated* cluster. The slope of log intensity versus log coverage becomes less than $\frac{2}{3}$ only when the clusters coalesce, so that it is easy experimentally to identify the coverage where deviations from the $\Theta^{-1/3}$ behavior of the binding-energy shift are expected. A comparison with the data in Fig. 1 shows good agreement between these two points, confirming that coalescence, and the resulting abrupt increase in cluster size, is responsible for the abrupt drop in binding-energy shift.

We now consider whether the *magnitude* of the observed binding-energy shift is in accord with the cluster-charge model. For spherical clusters, screened by an image charge in the substrate, simple electrostatic calculations show that the core-electron binding-energy shift is reduced to about one-half of the free-cluster shift in Eq. (1). In Figs. 1–4 the Coulomb shift for free spherical clusters is shown passing through 0.3 eV for a coverage of 10^{16} cm^{-2}, corresponding to an assumed nucleation site density of 3×10^{12} cm^{-2}. The observed shifts are reduced from the free-cluster value, and range from 30% for Ag and Sn to 70% for Pd. The range of this reduction seems reasonable, allowing that the clusters are not spheres and that the nucleation site density is not the same for all metals. For example, there is evidence[19] that, on identically prepared carbon substrates, silver has a lower nucleation site density than platinum. Figures 2 and 4 show that Ag clusters have a smaller shift than Pt clusters at the same coverage and that coalescence, as indicated by the falloff in the shift, occurs at a higher cov-

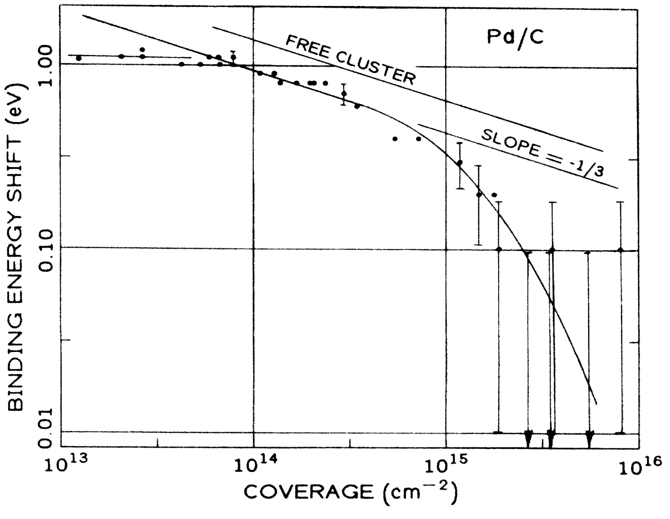

FIG. 4. Core-electron binding-energy shift for Pd clusters, from Ref. 18, replotted as in Fig. 1. Note the saturation of the shift below a coverage of 10^{14} cm^{-2}, where the average cluster contains fewer than 30 atoms.

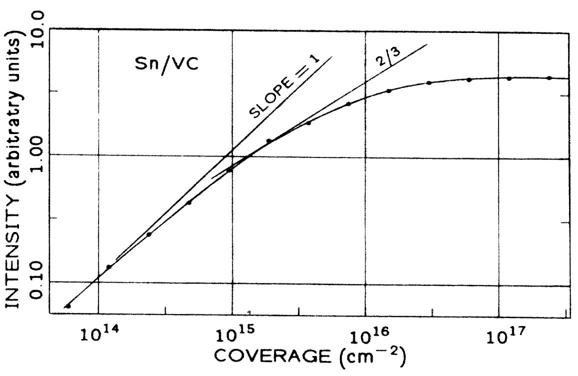

FIG. 5. Core-electron photoemission signal intensity for the tin clusters of Fig. 1 plotted as a function of coverage. Note that the slope falls below $\frac{2}{3}$ above a coverage of 2×10^{15} cm^{-2}, where coalescence becomes significant.

erage of Ag than of Pt; both phenomena are expected if Ag has the lower site density.

We now turn from consideration of the large-cluster regime to that of the small-cluster limit of our model. Identifying the cluster shift with the Coulomb energy of a charged cluster implies that the photoemission final state is otherwise identical to that for the bulk metal. This will obviously not be true for clusters small enough that the core-hole screening process changes. There are two possible causes of a change in screening. (1) The cluster becomes nonmetallic (or nearly so) and there is no conduction charge available for screening. (2) The cluster may still be metallic and normal screening may still be possible, except that the reduction in energy obtained by metallic screening is less than the Coulomb energy of the resultant surface charge.[15,16] The first condition *must* obtain for small enough clusters (in which case the implied band-structure changes will also make initial-state contributions to the shift), while the second may or may not occur. In either case metallic screening is replaced by local screening (polarization of the substrate and the neighboring atoms), and the final-state contribution to the cluster shift falls gradually to that of the isolated adatom. These limits are reached below coverages of 10^{14} cm^{-2}, where the average cluster contains fewer than 30 atoms, and the Coulomb energy exceeds 1.5 eV. The data of Kohiki and Ikeda,[18] for Pd on amorphous carbon, are unusual in that they extend to this low coverage range. As seen in Fig. 4, these data do show the expected leveling off of the binding-energy shift at coverages between 10^{13} and 10^{14} cm^{-2}.

Finally, we investigate whether there is any contact between the core-level data and the theoretical work on metal clusters. There have been few attempts to calculate core-electron binding-energy shifts in clusters. The majority of theoretical work has been concerned with the threshold ionization potential of alkali metal and jellium clusters, but the core-electron binding energy is a different physical quantity. The ionization potential is the minimum energy required to remove an electron from the cluster, whereas the binding energy is the difference between the energy of the unionized cluster and the cluster in the final state with the photoelectron far away. Thus a change in one quantity does not imply a change in the other. Core-electron binding-energy shifts have been calculated for small, free clusters, by taking the difference between the total energy of the cluster with one hole-state atom in the final state and its energy with all atoms in the ground state. In the final state the theoretical cluster has unit positive charge, as do the experimental clusters according to the model we have been discussing. Such calculations should therefore make it possible to investigate the transition from molecular to metallic behavior with increasing cluster size. To date such calculations have been reported for small cubical Li clusters,[20] and do show some of the expected behavior.

III. CONCLUSIONS

We have demonstrated that the final-state cluster-charge model accounts for the coverage dependence of the photoemission data for a wide variety of supported metal clusters. The Coulomb energy of the charged clusters produces the observed $\Theta^{-1/3}$ variation of the core-electron binding-energy shifts at low coverage. This coverage dependence changes at higher coverage when the clusters begin to coalesce, as confirmed by the disappearance of the cluster shift and the simultaneous change in the coverage dependence of the photoemission intensity. The saturation of the shifts observed at the very lowest metal coverages results from the breakdown of metallic screening in the photoemission final state in very small clusters; this marks the boundary between a regime where the simple cluster-charge model is applicable and a regime dominated by dramatic changes in band structure. No other model has enjoyed a comparable success, particularly in the regime where clusters are large enough to be metallic but small enough to avoid coalescence, and no other model accounts for the observed shift of the Fermi edge.

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