Noble- and transition-metal clusters: The d bands of silver and palladium

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A comparison of x-ray photoemission from Ag and Pd clusters grown on amorphous carbon substrates highlights the importance of the unfilled $4d$ band in Pd clusters. In both cases, the valence-band spectra show the d-band narrowing with decreasing cluster size, as expected. In both cases, also, there is a positive shift of the binding energies of the d-band centroids and of the core levels, primarily due to the unit positive charge that remains on the cluster in the photoemission final state, as occurs for other metal clusters on amorphous carbon. In Ag clusters the core-level shift is smaller than the valence-band shift because in small clusters the Coulomb energy of the charged cluster suppresses the conduction electron screening of the core hole. By contrast, in Pd clusters the increased localization causes a reduction in the d-electron density of states at E_F, resulting in a transition to s-electron screening and hence a core-level shift that is larger than the valence-band shift.

INTRODUCTION

Information about changes in electronic structure with cluster size should contribute to our understanding of the unusual electronic and catalytic properties of small metal clusters. Photoemission is an especially useful probe of electronic structure and has naturally been applied to supported metal clusters in many studies reported in the literature.[1-12] Valence-band spectra have generally exhibited the band-narrowing expected due to the increased localization in small clusters. Core-level photoemission studies have also produced consistent phenomena, showing core-electron binding-energy shifts to larger values for small clusters of many different metals supported on amorphous carbon. However, there has been disagreement as to whether these shifts reflect changes in the occupancy of the bands in the initial state or changes in final-state screening. In our recent work with noble[10] and sp metals[12] we have shown that neither of these mechanisms is responsible for the ubiquitous positive shifts. Rather, they arise from the charge left on the cluster in the final state, and the self-energy, $e^2/2r$, of this charge can have an overriding influence on final-state processes in smaller clusters.[13]

An initial motivation for our studies of core-electron spectra of small clusters was our interest in observing the change, with decreasing cluster size, in the response of the cluster's conduction electrons to the core hole created by photoemission. This screening response depends on the nature of both the occupied and the empty states near the Fermi level of a metal system, and should be a major factor in the sensitivity of core-electron photoemission to the transition from the bulk metal to clusters too small to be consider metallic.

The number of atoms required to give a cluster metallic properties is usually estimated in the following manner. For simplicity consider alkali or noble-metal atoms, which have one outer s electron. In an n-atom cluster there will be $2n$ s states, within an interval comparable to the width of the s band of the infinite solid. When n becomes so large that the separation between these states becomes comparable to the thermal energy kT, then the electrons are no longer localized and the cluster has metallic properties. At room temperature, in a metal with a bandwidth of 5 eV, this transition takes place when n exceeds 100 atoms, corresponding to a spherical cluster with a diameter of 15 Å.

Unfortunately, the final-state charge on the cluster has frustrated our attempts to study screening changes, by suppressing the metallic screening response in clusters that are actually metallic. The suppression occurs because the energy reduction that results from metallic screening of the core hole in a grounded (charge-neutral) system would in the *charged* cluster be more than offset by the Coulomb energy cost of that arrangement of conduction electrons.

In this paper we report our studies comparing Ag clusters and Pd clusters. The clusters were prepared on identical substrates under identical conditions, in order to investigate the contribution of changes in the d-band to the core-level shifts. The silver clusters exhibit behavior similar to that previously observed for noble and sp-band metals. We present these data both to provide further support for our contentions regarding the final-state charge and to provide a framework for a discussion of photoemission from clusters. We also present results for clusters of the transition metal Pd, and demonstrate that for this material we are able to observe a band-structure-induced change in the screening behavior of small clusters.

EXPERIMENTAL DETAILS

The clusters were prepared by deposition of metal atoms from a Knudsen cell onto amorphous carbon substrates at room temperature. The deposition rates were monitored with a quartz-crystal microbalance. The substrates consisted of amorphous carbon deposited on polished Si slabs from a carbon arc. All subsequent sample preparation took place in a chamber with a base pressure

in the 10^{-10}-torr range, attached to a Hewlett-Packard HP-5950A ESCA (electron spectroscopy for chemical analysis) spectrometer. The carbon substrates were sputtered with Ar ions just prior to the metal deposition. The samples were transferred directly into the spectrometer chamber without exposure to higher pressure, and were found by x-ray photoelectron spectroscopy (XPS) to have negligible oxygen contamination. For each run, a variety of valence-band and core-electron spectra were taken using monochromatized Al $K\alpha$ radiation. The metal-atom coverage was typically increased by a factor of 2 between successive runs.

Noble- or transition-metal atoms are mobile on amorphous carbon at room temperature and form clusters because the cohesive energy of these metals is much larger than the adsorption enthalpy. Clusters grow at nucleation sites,[14] which typically have a density of the order of 3×10^{12} cm^{-2}. The clusters begin to coalesce at a coverage of $\sim 10^{16}$ cm^{-2}, when they contain 3×10^3 atoms.

A calibration of the average cluster size of the Pd particles was obtained from the work of Takasu et al.,[6] who report an average diameter of 12 Å for a coverage of 1.6×10^{15} atoms/cm^2 on carbon. They find that the core-electron shift saturates at coverages just below 10^{15} atoms/cm^2, while our data place saturation at 3×10^{14}, suggesting that our clusters are slightly larger for the same coverage. The estimated cluster size for a coverage of 1.5×10^{14} atoms/cm^2, the lowest coverage reported here, is then 10 Å.

For the Ag data both the location of E_F in each valence-band spectrum and the binding energy of the $3d$ core level were determined by least-squares fitting, using techniques previously described.[15] Satisfactory fits to the $3d$ spectra were obtained with the many-body line shape,[16] even though at low coverages the asymmetry of the peak is not due to the final-state screening process. Rather, as will be discussed below, the $3d$ peak is distorted by the distribution of cluster sizes. The location of the $4d$ band in the valence region is specified by the midpoint of a line drawn at half height. Calculated centroids were found to be so seriously affected by changes in the high-energy tail of the d band as not to be representative of the position of the main part of the band.

In the Pd valence band, the $4d$ density of states has a sharp peak just below E_F; consequently, fitting the Fermi cutoff in the valence band requires an explicit representation of the density of states even for the bulk metal, whereas for Ag the flat density of states of the s band can be represented analytically. Furthermore, the density of states of bulk Pd, which is known, will be modified by the finite size of the clusters, with results that can at best be only roughly estimated from ultraviolet photoemission spectroscopy (UPS) data.[1,2] The complicated density of states also inhibits analysis of the core-level spectrum of bulk Pd. Because the d band ends just above E_F, the core-electron spectrum for bulk Pd deviates strongly from the power-law line shape obtained in a simple metal.[16] At all coverages, then, we simply use the position of the maximum of the Pd $3d_{5/2}$ peak as a measure of the binding energy, while we monitor the valence band by tracking the centroid of the $4d$ band.

RESULTS AND DISCUSSION

Simple arguments suggest that the behavior of small clusters should be related to those of the surface atoms of the bulk solid.[17] The cluster, viewed as a core of bulk atoms surrounded by surface atoms, should exhibit an average core-electron binding energy that can be calculated from the bulk binding energy, the surface-atom shift, and the surface-to-bulk atomic ratio. The sign and magnitude of the cluster shift should approach that of the surface atoms when the size is reduced to the point where most of the atoms are on the surface. The shift may actually exceed the surface shift, because atoms in the cluster surface are similar to atoms at steps and corners, and such atoms have shifts larger than those of the planar surface.[18,19]

From this point of view, Ag clusters should have a small, negative shift because the surface-atom core-level shift of Ag is only -0.08 eV.[20] In the case of Pd the surface-atom core-level shift has not been reliably determined. It has been theoretically estimated to be -0.2 eV (Ref. 17) and -0.4 eV (Ref. 21), but has been measured to be 0.25 eV (Ref. 22). We have attempted to measure the surface shift of polycrystalline bulk Pd, both by varying the takeoff angle in one set of measurements and by covering the Pd with Cu. Neither procedure produced a measurable change in line shape or position, thus establishing limits of ± 0.1 eV for the surface-atom core-level shift in Pd. Considering the fact that both Ni (Ref. 23) and Pt (Ref. 24) have negative surface shifts, a small negative value seems most likely for Pd. As will be discussed below, the shifts in cluster experiments are large and positive, demonstrating that they are not related to surface effects.

Silver clusters

The valence-band spectra of silver clusters in Fig. 1 show band narrowing and a centroid shift to greater binding energy with decreasing cluster size. The data differ significantly from those obtained by XPS for air-exposed clusters,[25] but are in better agreement with a UPS study of clean silver clusters.[26] Band narrowing is expected based on the loss of long-range periodicity in small clusters. A crude estimate of the relationship between bandwidth and cluster size can be obtained by assuming that the width is proportional to the square root of the coordination number. Then the bandwidth of the smallest clusters in Fig. 1 corresponds to an average coordination number of 6, or equivalently to a cluster of ~ 20 atoms.[7] The molecular orbital calculations of Baetzold[27] yield bandwidths in good agreement with the coordination number estimate. Even making the above assumption, one must recall that there are other contributions to the bandwidth: (i) the $4d$ spin-orbit splitting of 0.4 eV, (ii) the broadening due to the distribution of cluster sizes, and (iii) the instrumental resolution function. Neglecting these other contributions tends to increase the estimated cluster size.

The midpoint of the d band of the smallest clusters is shifted ~ 0.6 eV from the bulk value. If this shift were due to charge redistribution between the $4d$ and $5s$ bands, the sign would imply a substantial flow of charge from
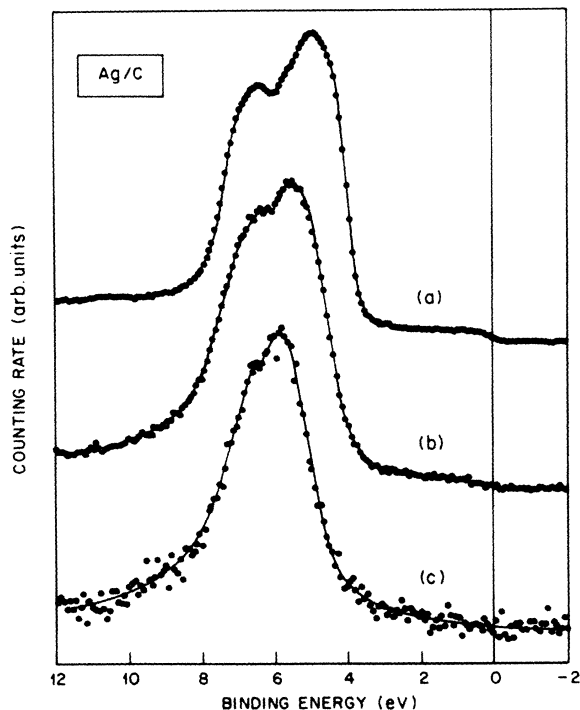
FIG. 1. X-ray photoelectron spectra of the valence band of (a) bulk Ag, and (b) and (c) Ag clusters on sputtered carbon substrates. The coverages for (b) and (c) are 1.0×10^{15} and 2.5×10^{14} atoms/cm^2, respectively. The response of the carbon substrate has been subtracted from the spectra of the clusters.

FIG. 2. Region of the Fermi cutoff for (a) bulk Ag, and (b)—(d) Ag clusters on amorphous carbon. The coverages for (b), (c), and (d) are, respectively, 4.0×10^{15}, 2.0×10^{15}, and 1.0×10^{15} atoms/cm^2.

the spatially compact $4d$ wave functions to the more extended $5s$ band. However, band narrowing should have the opposite effect, with the $5d$ states becoming more atomic in character and reducing their hybridization with the $5s$ band. Even this effect should be small since the $4d$ band lies well below E_F, so that there is little unoccupied d character even in bulk Ag. The effect of band narrowing should then be a small shift to lower binding energy, as is observed for the surface atoms of Ag; however, the observed shift for clusters is large and positive.

The discussion above makes it clear that initial-state band-structure changes cannot account for the positive core-electron binding-energy shift observed in Ag clusters; rather, this is a final-state effect, as we shall now show. We begin with an examination of the Fermi cutoff of the valence-band data shown in Fig. 2. As was previously found for Au clusters,[10] the Fermi level of the clusters moves away from that of the substrate, shifting toward larger binding energy with decreasing cluster size. This is easily understood if one assumes the emitted photoelectron is not quickly replaced, so that the cluster is left with a unit positive charge during the photoemission final state.[10] The final-state energy is then increased by the Coulomb energy, which for a charged conducting sphere is $e^2/2r$. Since this final-state charge occurs whenever a photoelectron is emitted, the entire spectrum, core levels as well as the Fermi edge, appears shifted to higher binding energy by this Coulomb energy. We note that the cluster remains positively charged during the core-hole
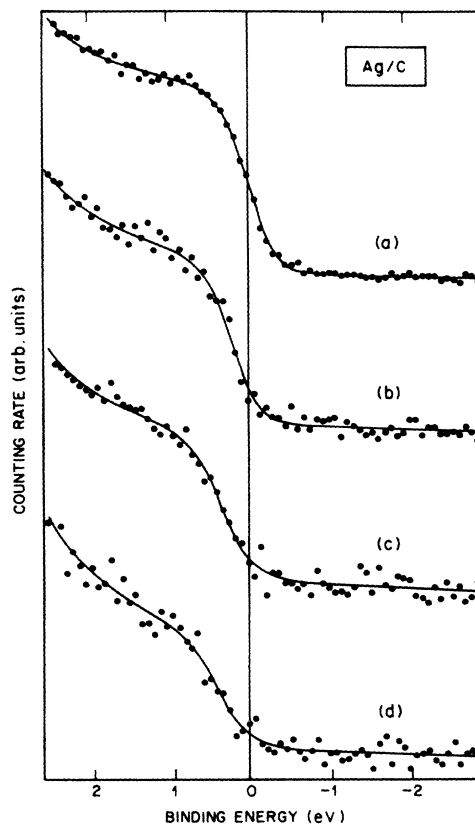
lifetime, but is clearly neutralized in a time shorter than the average time between photoemission events in a cluster; otherwise, the long-term buildup of charge would cause substantial shifts in the substrate spectrum.

In Fig. 3 the $3d_{5/2}$ core-electron spectra of the Ag clusters show the expected shift to greater binding energy with decreasing cluster size. A detailed comparison of the shifts of the Fermi edge, $4d$ band, and $3d$ core level is presented in Fig. 4. The agreement between the shifts of the Fermi edge and the $4d$ band is striking and confirms their common origin. The shift of the core level tends to be somewhat smaller in the smallest clusters, because of the suppression of screening mentioned in the Introduction. To explain this process, we begin by noting that in a large cluster the core hole is screened by the cluster's conduction electrons, much as it would be in bulk Ag. However, whereas in a grounded system such as bulk Ag, the screening charge that is concentrated near the core hole is replaced, a cluster on amorphous carbon is effectively not grounded. Thus, the formation of the screening state induces a net positive charge on the cluster surface, this being the final-state charge discussed above. The binding-energy shift we observe is the energy difference between the final state in the cluster and that of a core hole in the bulk material and is, as above, just the Coulomb energy of the charged cluster. In smaller clusters, however, the increased Coulomb energy of the surface charge can exceed
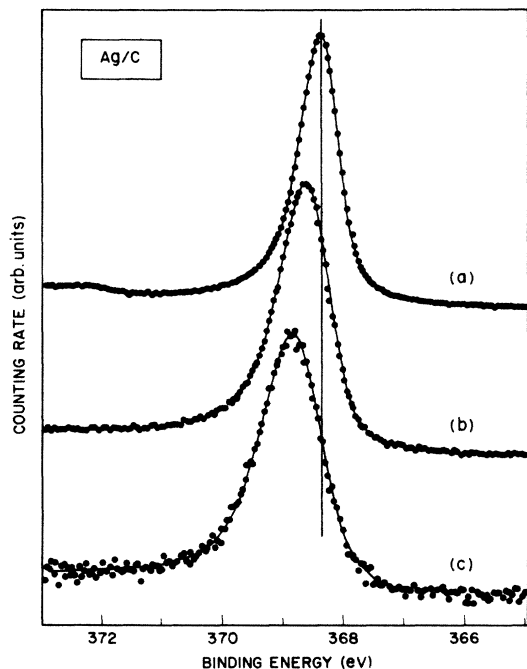
FIG. 3. Ag $3d_{5/2}$ core-electron spectra of (a) bulk Ag, and (b)—(c) Ag clusters on amorphous carbon substrates. The coverages are the same as in Fig. 1.

the screening energy, so that the metallic screening response of the cluster is suppressed, even if the cluster still has a metallic band structure that could otherwise support conduction-electron screening. The core hole is then screened locally and the Coulomb potential of the charged cluster is reduced. In Fig. 4 the observed agreement of all three shifts at high coverage confirms the final-state cluster charge model, while the divergence of the core-level shift at low coverages marks the crossover to a regime in which the conduction-electron screening response is suppressed by the self-energy of the charged cluster.[12]

At this point we emphasize again that the shift in the larger clusters is not the result of a decline in the screening response. First, metallic screening is a response to a localized core hole and as such cannot account for the shift of the cluster's Fermi edge. Second, the shift is observed, for core and valence electrons, in clusters containing 10^4 atoms, which we judge to be fully metallic given the absence of valence-band narrowing.

A quantitative check of the cluster charge model might begin with a comparison of cluster size and binding-energy shift, which should be $e^2/2r$ for isolated clusters. For supported clusters, however, the observed shift is significantly reduced by the screening response of the substrate, i.e., even in a poorly conducting material like amorphous carbon an image of the cluster charge will be formed in the substrate. The reduction will vary from metal to metal and will depend on the cluster-substrate geometry—the shape of the cluster, the contact area, etc. Obviously, equating the measured shift with the Coulomb energy of an isolated sphere will always result in a serious overestimate of the cluster size. This is apparent in the case of Ag, where a shift of 0.6 eV is measured for clusters estimated to be 9 Å in diameter on the basis of the d-band width. For a free metallic cluster, that shift corresponds to a diameter of 24 Å.

In addition to the binding-energy shift, the Ag core-level spectra show an increase in the asymmetry and the width of the peak, as is also observed in the core-level spectra of Sn clusters.[12] These line-shape changes reflect the size distribution of clusters prepared by evaporation onto a substrate. We have calculated[13] the distribution of cluster sizes for nucleation sites randomly distributed over a substrate's surface. The resulting Gaussian distribution of cluster radii was combined with the cluster's Coulomb energies and, with the escape depth of the photoelectrons taken into account, predicts an asymmetric distribution of binding-energy shifts, whose width and mean vary with the amount of metal deposited, in good qualitative agreement with experiment.

The width at half height of the $3d_{5/2}$ line and the $4d$ band are compared in Fig. 5. With decreasing cluster size
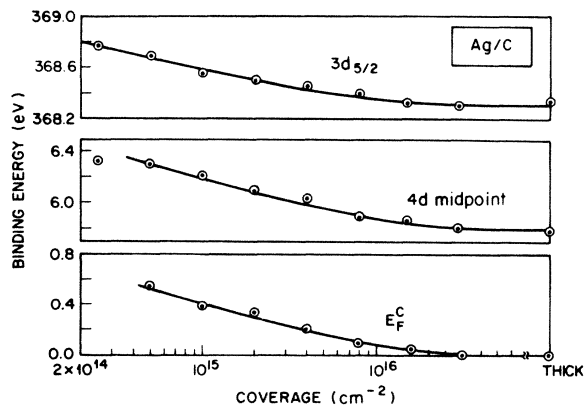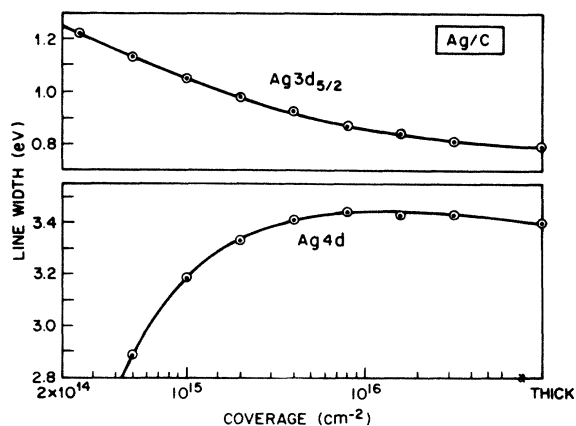

FIG. 4. Coverage dependence of the binding energies of the $3d_{5/2}$ core electrons, the $4d$ band, and the Fermi cutoff of Ag clusters on amorphous carbon substrates.

FIG. 5. Coverage dependence of the widths of Ag $3d_{5/2}$ and $4d$ spectra, measured at half height.

the 4d band initially shows a slight tendency to broaden, but then the decrease in the bandwidth itself becomes dominant. The broadening seen in the 3d line is difficult to detect in the 4d band because, even at the lowest coverages, the 4d bandwidth is much greater than the size-related broadening.

Pd clusters

The valence-band data for the Pd clusters shown in Fig. 6 exhibit band narrowing and a centroid shift not unlike those of the Ag clusters. The data are qualitatively similar to valence bands obtained by UPS,[1] and yield bandwidths in agreement with those previously obtained by XPS.[28] The behavior of Pd is, however, more complicated than that of Ag because the Pd 4d band is broader and intersects E_F. Compared to the spectrum of bulk Pd, the larger clusters show a rounding off at the upper edge of the band, indicating that the d band has lost the high-density-of-states peak at E_F, due to the loss of long-range periodicity. The weakening of the peak near E_F does not imply a loss of *occupied* d states, but only a redistribution of states within the band. For the smaller clusters the d-band cutoff moves away from the Fermi level of the substrate but, as in the Ag clusters, this must correspond to a shift of the Fermi level of the clusters and does not imply that the d band has been filled.

In bulk Pd the Fermi level intersects the d band, leaving ~0.6 empty d states and, since Pd has 10 valence electrons, 0.6 occupied 5s states. (In the free Pd atom the d states are filled and the 5s level is empty.) Charge flow between the bands depends on the overlap between the s and d bands, rather than on the width of the d band alone. The d band can be filled only by emptying the s band and, as long as the two bands overlap, there will be empty d states at E_F. As the d band narrows, the Fermi level must stay below the d band's upper edge, until the s band narrows sufficiently to separate from the d band. In fact, it is clear that the 4$d^{10}5s^0$ configuration of the isolated Pd atom is inappropriate even for a few-atom cluster.

The Pd 3$d_{5/2}$ core-electron spectra in Fig. 7 show a pronounced shift to larger binding energy with decreasing cluster size. The shift tends to saturate at 1.3 eV for coverages less than 2×10^{14} atoms/cm^2. These results are in good agreement with earlier work on clusters prepared in vacuum,[7,9] but are distinctly different from those obtained for air-exposed clusters, which have much larger shifts at saturation.[29] The sign of the shift is opposite to that expected for d-band filling. As with the Ag data discussed above, and as with data on other metal clusters, we believe that both the shift and the broadening of the core-electron spectrum and the shift of the Fermi cutoff and the valence-band centroid, are due mainly to a final-state cluster charge.

In the discussion of Ag clusters we showed that the core-electron binding-energy shift is due to the self-energy
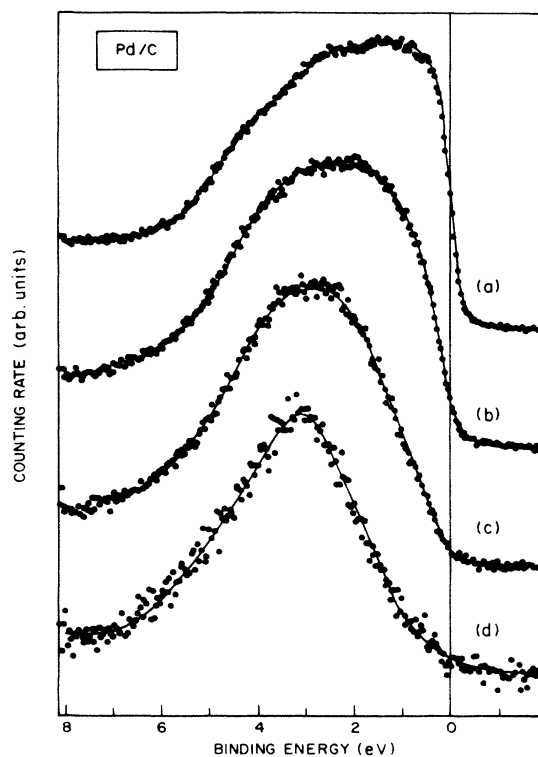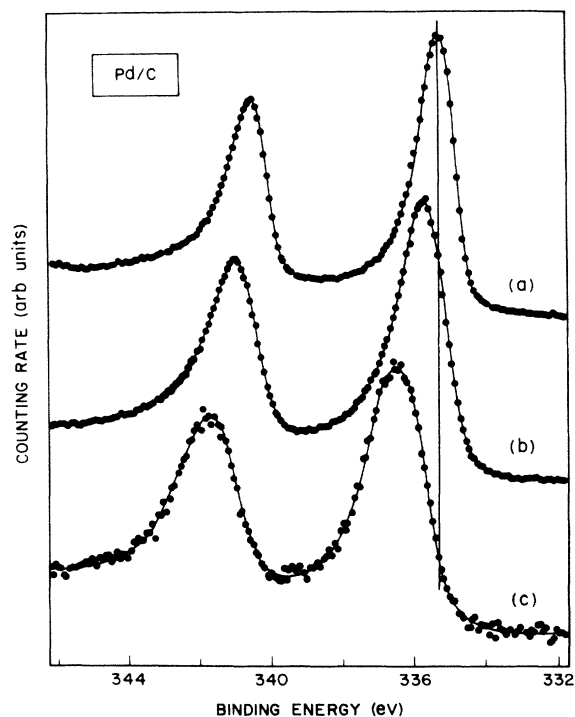

FIG. 6. X-ray photoelectron spectra of the valence band of (a) bulk Pd, and (b)—(d) of Pd clusters on sputtered carbon substrates. The coverages for (b), (c), and (d) are, respectively, 4.0×10^{15}, 1.0×10^{15}, and 3.0×10^{14} atoms/cm^2. The response of the carbon substrate has been subtracted from the spectra of the clusters.

FIG. 7. 3$d_{5/2}$ core-electron spectra of (a) bulk Pd, and (b) and (c) Pd clusters on amorphous carbon substrates. The coverages for (b) and (c) are, respectively, 2.0×10^{15} and 3.0×10^{14} atoms/cm^2.
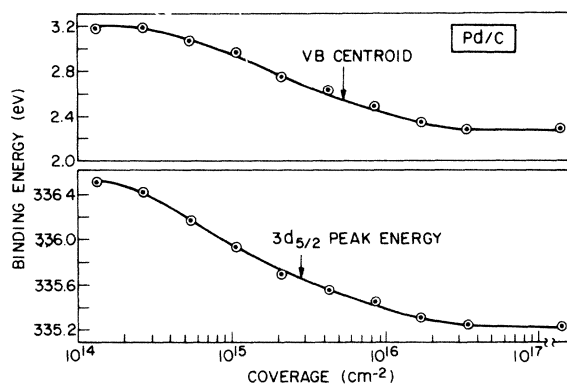
FIG. 8. Coverage dependence of the binding energies of the centroid of the $4d$ band and of the $3d_{5/2}$ core electrons of Pd clusters on amorphous carbon.

of the charged cluster, and that the saturation of the shift is not due to decreased metallic character of the cluster but arises when the Coulomb energy of the cluster charge surpasses the screening energy. One motivation for studying transition-metal clusters is the larger screening energies that result from the participation of d electrons. In Fig. 8 we compare the shifts of the $3d$ core-electron binding energy with that of the centroid of the $4d$ band. Unlike the results for Ag, where the core-electron shift is smaller than that of the valence-band features, for Pd the core-electron binding-energy shift is larger than the valence-band shift. For photoemission from the Fermi level, the shift is simply the cluster's Coulomb energy. For the core levels, as explained above, the charge appears on the cluster surface as a result of the concentration of screening charge around the core hole; if the Coulomb energy would be larger than the screening energy, screening does not occur and there is no surface charge. Therefore, the core-level shift cannot exceed the metallic screening energy or, more precisely, the energy difference between metallic screening and a local response to the core hole.

The Ag data show just this saturation of the core-level shift. In the Pd data at high coverage and large cluster size, there is no change in screening and, as expected, the core-level shift tracks the valence-band centroid. For smaller clusters, the core-level shift exceeds the valence-band shift, indicating that metallic screening, and the resulting cluster surface charge, still occurs but that the screening is less effective. One could have predicted the screening to be less effective, because the decrease in the density of states decreases the screening by d electrons. Any changes in core-hole screening are dominated by changes in the d band near E_F; screening by the more diffuse s orbitals is known to be less effective in reducing the final-state energy. Note that the decrease in the d density is due to a band-structure change; in particular, the rounding off of the peak just below E_F. Of course, if the d occupancy had increased, this would move the Fermi level closer to the top of the d band and would also contribute to the decreased density of states.

CONCLUSIONS

Both Ag and Pd clusters exhibit shifts to higher binding energies for both core electrons and valence-band features. These shifts are due primarily to the charge left on the cluster in the final state by the photoemission process. The narrowing of the Ag $4d$ band in the valence region provides the only direct information about the cluster-size-related changes of the electronic structure of Ag. Localization induces a similar narrowing of the d band in Pd clusters; however, in this case the band narrowing also alters the d-electron density of states at E_F. This causes a shift from mainly d-electron screening of the core hole to a screening response that is more dominated by the (less effective) s electrons, resulting in a positive core-electron binding-energy shift in addition to the positive shift due to the final-state cluster charge. Thus, the discrepancy between the core-level and the valence-band shifts in Pd clusters has allowed us to observe one aspect of the Pd cluster metallic nature changing as the clusters become smaller and less bulklike.

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