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Core-level and valence-band photoemission study of granular platinum films

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Photoemission and resistivity measurements have been made on Pt clusters imbedded in an amorphous silicon dioxide matrix. No significant changes in the Pt $4f_{7/2}$ or $5d_{5/2}$ core-level shifts or in the density of states per Pt atom at the Fermi level are seen at the percolation threshold. Most of the Pt $4f_{7/2}$ core-level shift can be explained as a Coulomb effect due to finite cluster size. We speculate that because of the unusually large core-level shifts there may also be charge transfer from the Pt clusters to the silica matrix.

INTRODUCTION

Considerable interest has recently been focused on extracting chemical[1] and thermodynamic[2,15] information from shifts in the measured binding energy in photoemission from core levels. In small clusters, which are of interest here, such a determination involves separating out the contributions of screening and relaxation effects from the initial-state change in the core-level binding energy. One approach is to look at core-level and valence-band photoemission while going from small clusters, or preferably an atom to large clusters of metal atoms. The usual method has been to support the clusters on or in a weakly conducting or insulating substrate such as carbon,[1] SiO_2,[1] or a rare-gas matrix.[3,4] In the system studied here, Pt in SiO_2, the problem of the metal-to-insulator transition as the metal concentration changes makes the system even more interesting. Previous work on a similar system, Pd in SiO_2,[5] only looked at the valence band. We have extended these measurements to the case of Pt clusters in an amorphous silicon oxide matrix where one can simultaneously measure a $4f$ core level and the valence band, including the $5d$ levels as a function of cluster size. The photoemission process will be seen to be a local probe—the breakdown of macroscopic metallic conductivity at the percolation limit for granular materials does not result in a major decrease in screening and large core-level shifts. The evolution of metallic behavior in the density of states at the Fermi level, broadening and movement of the Pt $5d_{5/2}$ level towards the Fermi level, the corresponding motion of the $4f$ core levels towards the Fermi level, and correlations between these quantities are discussed.

EXPERIMENTAL

The experiments were performed at the U7 beamline on the vacuum-ultraviolet ring at the National Synchrotron Light Source at Brookhaven National Laboratory. The granular Pt films were prepared by Ar^+ cosputtering from Pt and Si targets, separated by about 2 in., onto a 4-cm-long Ta or sapphire substrate in the top level of a three-level ultrahigh-vacuum (UHV) chamber. The result was a gradient of Pt concentration along the length of the sample, with the sample being most Pt-rich near the Pt target. Approximately 1% O_2 was added to the sputter gas to ensure formation of silicon oxides rather than platinum silicides. A thin Cu strip was evaporated lengthwise on half of the sapphire substrate prior to sputtering to avoid charging problems during photoemission and Auger electron spectroscopy measurements. The top level of the chamber, where the sputtering was performed, was separated from the lower levels by a UHV valve and was pumped separately before transferring the sample to the lower levels to perform Auger spectroscopy with a Physical Electronics model No. 10-155 cylindrical mirror analyzer (CMA). The photon resolution of the plane-grating monochromator combined with the Physical Electronics model No. 15-255 double-pass CMA, used for electron energy analysis, resulted in an overall resolution of ≈ 0.5 eV at $h\nu = 60$ eV and ≈ 1.5 eV at $h\nu = 185$ eV, the two photon energies used. Resistivity measurements were performed after removing the sample from the UHV chamber by standard four-probe techniques at room temperature and liquid-nitrogen temperature. The volume concentration x of Pt as a function of position along the sample was calculated using Auger spectra and found to vary between 0.8 and 0.05 for the sample with the sapphire substrate and between 0.5 and 0.07 for the Ta substrate. The thickness of the film was estimated to be between 10 and 20 nm by measuring the attenuation of the substrate Auger signal for thinner films and extrapolating to longer sputtering times.

The average size of the Pt clusters was estimated to be ≈ 10 Å in diameter for the smallest concentration of Pt using results of measurements of cluster size versus metal volume fraction from Abeles, Sheng, Coutts, and Arie[6] who prepared granular metal films in a similar fashion. The Auger spectra showed no platinum silicides which have a characteristic signature.[7] In fact, the Auger spectra for the Ta substrate show the characteristic signature of SiO_2.[8] In the case of the sapphire substrate we see a slightly shifted SiO_2 Auger signal with no presence of elemental Si.

DATA

Figures 1 and 2 show the valence-band and core-level spectra as a function of position along the sapphire-substrate sample. The valence-band spectra in Fig. 1 from the Pt-poor end are consistent with the valence-band spectra of polycrystalline amorphous silicon oxide films.[9,10] The Si $2p$ spectra are also consistent with this interpretation.[9] Macroscopic charging was not found to occur in almost all the spectra taken. Such charging would have been reflected in a uniform shift of all features in a spectrum and was not observed in most of the spectra. In the two instances where such charging was seen on the Pt-poor end, the entire spectra were shifted uniformly.

From Figs. 1 and 2 we see the general results of this work. In Fig. 1 we see a decrease in the density of states at the Fermi level as the Pt content decreases and the Pt d density of states moves away from the Fermi level. Figure 2 shows the shifting of the Pt $4f$ core levels towards higher binding energy with decreasing Pt content. The Pt $4f$ core levels were fit with Doniach-Sunjic line shapes[11] to determine the binding energy and width of the core levels. The separation of the $4f_{5/2}$ and $4f_{7/2}$ levels and their widths do not change within the limits of the resolution. This is indicative of all the Pt atoms being in the same set of states, i.e., a state for "surface" atoms and a state for bulk atoms. No surface-bulk core-level shift could be resolved.

Returning to the valence-band spectra, in Fig. 3 we have plotted some difference spectra to show the development of the Pt $5d$ states with increasing cluster size. Basically we see that the Pt $5d_{5/2}$ level broadens as it moves towards the Fermi level with increasing cluster size. Tentatively, we can also see the increase in the spin-orbit splitting between the Pt $5d_{3/2}$ and $5d_{5/2}$ levels with increasing cluster size. The presence of an overlapping silicon-oxide feature prevents us from making a definite measurement of this splitting. The trend is seen clearly for Pt clusters in a solid Xe matrix[4] as well as for Au clusters on a carbon substrate.[12]

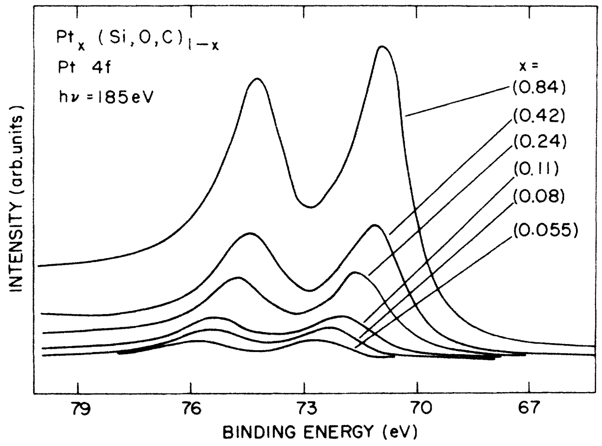

FIG. 2. Pt $4f$ electron distribution curves as a function of Pt volume fraction in $Pt_x(Si,O,C)_{1-x}$ at a photon energy of 180 eV.

The binding energies of the Pt $5d_{5/2}$ and $4f_{7/2}$ core levels as well as the density of states per Pt atom at the Fermi level as a function of Pt volume fraction is shown in Fig. 4. The data for the Ta substrates are plotted as +. Note that

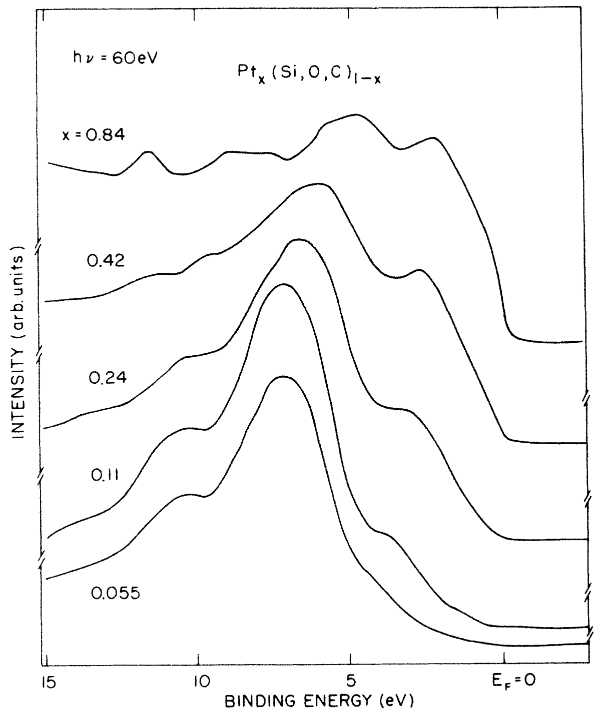

FIG. 1. Valence-band electron distribution curves for some volume fractions of Pt in $Pt_x(Si,O,C)_{1-x}$. Photon energy is 60 eV.

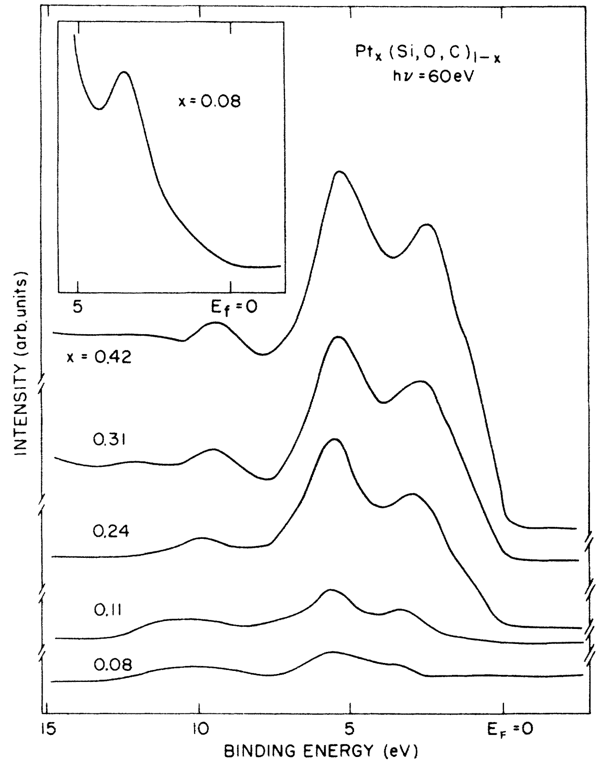

FIG. 3. Valence-band difference curves with respect to $x \approx 0.03$ for various Pt volume fractions for 60 eV photons. Inset shows $x = 0.08$ on an expanded scale to show relative sharpness of Pt $5d_{5/2}$ level.

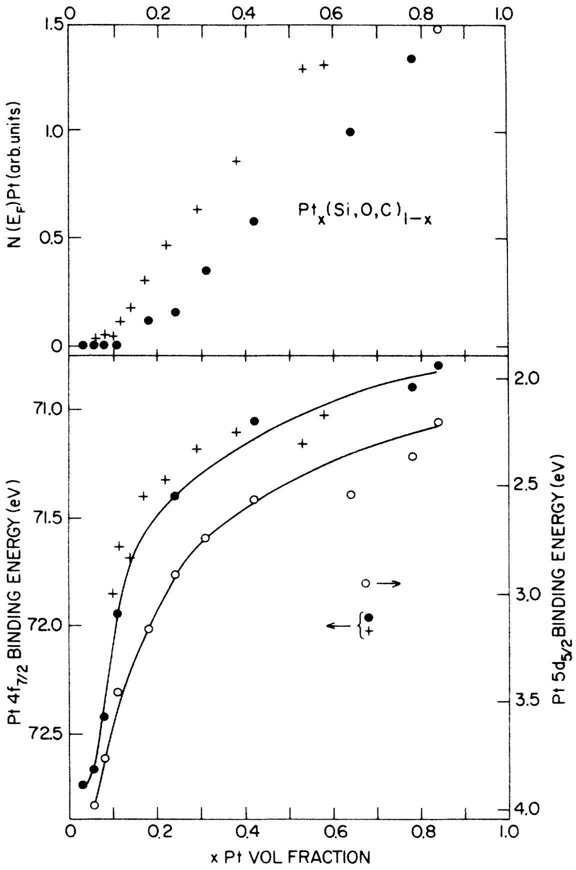

FIG. 4. Top portion of figure shows density of states per Pt at the Fermi level as a function of Pt volume fraction. Bottom portion shows the binding energy change of the Pt $4f_{7/2}$ and Pt $5d_{5/2}$ levels with Pt volume fraction. + is for the sample on the Ta substrate, closed circles for the sapphire substrate, and open circles for the Pt $5d_{5/2}$ on the sapphire substrate. The lines are a guide to the eye.

there essentially is qualitative agreement between the results for the two substrates. The differences are within the experimental noise.

DISCUSSION

An interesting feature of Fig. 4 is that there is no significant change in the density of states per Pt atom at the Fermi level, the binding energy of the Pt $4f_{7/2}$ core level, or the binding energy of the Pt $5d_{5/2}$ core level at the percolation threshold at $x \approx 0.6$, where the conductivity changes by two orders of magnitude. The concentration for the percolation threshold, which was determined from resistivity measurements, agrees approximately with that obtained for granular films by Abeles *et al.*[6] and McAlister, Inglis, and Kayll.[13] Resistivity is clearly a macroscopic measurement as it requires connectivity between the Pt grains or aggregates of Pt grains to enable high conductance. The breakdown of this connectivity at the percolation threshold is not accompanied by abrupt changes in cluster size or the properties of groups of metal clusters. If one assumes that the particles in the aggregates are still connected, as before the transition, one would not expect any change in the core levels at the percolation transition. Clearly, as the Pt becomes more dilute, the aggregates of clusters break up into single particles, and large core-level shifts are observed. Thus, we have a confirmation for what one intuitively expects—that the photoemission process is a local one not affected by macroscopic connectivity, assuming of course that the macroscopic conductivity is high enough so that charging of the whole medium does not occur.

Continuing to look at Fig. 4 we see that the Pt $4f_{7/2}$ and Pt $5d_{5/2}$ levels track each other so that each moves ≈ 1.8 eV from the Pt-rich end to the Pt-poor end. The picture emerging is the growth of a metal with increasing cluster size imbedded in an insulating matrix. The growth in metallic behavior is seen in the increasing density of states per Pt atom at the Fermi level as well as in the behavior of the Pt $5d_{5/2}$ level which broadens as it moves towards the Fermi level with increasing cluster size indicating increased hybridization with the $6s$ electrons and a corresponding delocalization of the $5d$ electrons. Of course we have to confirm that we do actually have Pt clusters in a silica matrix and not, say, a platinum oxide or silicide causing the core-level shifts. As the largest $4f_{7/2}$ core-level shift is ≈ 1.9 eV and the shift of any platinum oxide is at least 3 eV, we can rule out the presence of platinum oxide. The possibility of platinum silicides has already been discounted from the absence of a characteristic platinum silicide signal.[7] Further confirmation is seen in the work of Rossi *et al.*[14] on Pt on Si(111), where they find silicidelike valence-band photoemission spectra for low Pt coverages, but a Pt $4f_{7/2}$ shift of only ≈ 0.3 eV. Thus, combined with our discussion earlier of the Auger spectra, Si $2p$ core-level shifts, and valence photoemission spectra on the Pt-poor end of the sample, we believe that we have Pt clusters in an amorphous silicon oxide or dioxide matrix.

In that case, the basic question of what the various contributions to the core-level shifts are, remains to be answered. One contribution clearly is a reconfiguration *cum* relaxation effect on going from an atomic configuration for the free atom ($5d^96s$ for Pt) to that in the metal ($\approx 5d^{8.5}6s^{1.5}$ for Pt). A free-atom–to–metal core-level shift of the order of 4 or 5 eV, with core levels referenced to the vacuum level, is expected from the arguments and calculations of Johansson and Martensson[15] and has actually been measured for some metals (see references in Johansson and Martensson[15]). Our largest core-level shift is 1.8 eV which is more than two times smaller than the atom-to-metal shift mentioned. This is to be expected as our smallest clusters are of diameter ≈ 10 Å corresponding to ~ 50 atoms, so that we are closer to the metallic rather than atomic limit. Hence, in the discussion to follow, the atomic case will not be considered again. It should be mentioned that extended x-ray absorption fine-structure measurements on small Pt clusters ≈ 10 Å average diameter dispersed on silica[16,17] show that there is no nearest-neighbor distance contraction or expansion relative to bulk metal though there is considerably more atomic disorder for the small clusters. Thus, it appears that there is no sizable shift due to lattice parameter changes in the density. It appears more likely that the largest contribution to the core-level shift is from the electrostatic contribution caused by the hole left on the cluster by the photoemission process. If the neutralization of the hole is slow, on the scale of a photoemission event, there will be a shift from the bulk metal value by a Coulomb energy given by $e^2/2r$ where r is the cluster radius. Such a contribution was stressed, for example, by Wertheim, DiCenzo, and

Youngquist[12] for Au clusters on carbon. Actually the magnitude of the Coulomb shift would be reduced by the dielectric response of the amorphous silicon dioxide so that the disagreement of data and the $e^2/2r$ approximation would increase. It is interesting that at the larger cluster end, say at Pt concentration $x = 0.42$, we estimate from Abeles *et al.*'s[6] data an average cluster diameter of 35 Å, giving $e^2/2r = 0.41$ eV. Subtracting this value from the measured $4f_{7/2}$ binding energy yields 70.6 eV compared with a $4f_{7/2}$ binding energy of 70.8 eV for the Pt-rich end. Hence, the actual core-level shift is somewhat smaller than expected from the $e^2/2r$ term, thereby indicating, for example, either the effect of the dielectric or the agglomeration of clusters. On the other hand, for the smallest particles, the shift is greater than one would expect from the $e^2/2r$ term. For example, for a 10-Å particle $e^2/2r$ yields a shift of 1.44 eV, whereas the observed shift is near 2 eV. Thus, we are led to speculate that there is some charge transfer between the Pt and silica, particularly at the end containing smaller clusters where the discrepancy between an $e^2/2r$ approximation reduced by dielectric response is greatest. Such a charge transfer is clearly of interest technologically due to the great use of small Pt clusters supported on silica as a catalyst.[18] The charge transfer could be due to dangling bonds and defects in the amorphous silicon oxide matrix. The charge transfer to the silica leaves a net positive charge on the small Pt clusters resulting in a larger apparent binding energy for the $4f_{7/2}$ analogous to what happens from the charge transfer in platinum oxides. A uniform shift for all the Pt atoms is reasonable as a large percentage (80%–90% for the 10-Å-diameter clusters studied by Marques *et al.*[16]) of the atoms are "surface" atoms. (One way to separate the contribution of the charge transfer to the silica from the $e^2/2r$ term is to look for materials such as, say, Au where there is considerably less likelihood of such a transfer.)

SUMMARY

Summarizing our results, we see the development of bulk metallic properties with increasing Pt cluster size by the shift of the $4f$ and $5d$ levels towards the Fermi level with increasing cluster size as well as the broadening of the $5d$ levels with increasing hybridization. No significant effects are seen at the percolation threshold. The magnitude of the Pt $4f_{7/2}$ level shift is shown to be possibly due to a Coulomb shift combined with some atomic reconfiguration. We also speculate that some of the Pt $4f_{7/2}$ core-level shift may be due to charge transfer to the silica matrix.

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