Photoemission study of the transition from the insulating to metallic state in ultrathin layers

D. J. Huang, G. Reisfeld, and M. Strongin
Department of Physics, Brookhaven National Laboratory, Upton, New York, 11973-5000
(Received 18 October 1996)

The transition from the insulating to metallic state in ultrathin Pb films was studied using high-resolution photoemission. The states near E_F were probed as Pb was deposited onto a thin insulating layer, thin enough to reduce macroscopic charging. The results, which experimentally show a vanishing of states at E_F, are consistent with the arguments of Efros and Shklovskii based on electron-electron interactions, and as far as we know are the first *in situ* study of the electronic properties as one goes from the insulating to metallic state in a two-dimensional system. [S0163-1829(97)50804-6]

The properties of ultrathin metallic layers and the effects of correlation and localization near the metal-to-insulator transition in this system has been an active subject over many years.[1–4] It is important to note that in the most disordered of these thin layers, localization effects become dominant, the Ioffe-Regal condition (i.e., the mean free path in a metal cannot exceed $2\pi/k_F$) is not obeyed and the usual quasiparticle picture breaks down,[5] as does the superconducting state. In this ''insulating'' or localized regime, the conduction becomes activated and the resistance per square area $R_\square$ is of the order of 5–10 kΩ, which is close to $h/4e^2$, the quantum unit of resistance at the insulator-to-metal transition. Previous tunneling measurements in such layers on the metallic side of the transition have already shown that correlation effects are important[6,7] and they have shown a Coulomb anomaly in the states near E_F predicted by Altschuler and Aronov.[8] Hence, it is not unreasonable to expect that correlated behavior will dominate the localized regime studied in this work. It is also interesting that another class of materials called ''bad metals''[5] also violate the Ioffe-Regal condition and the quasiparticle picture, but remain metals. These conductors include the high-temperature oxide conductors, organic conductors, and other recently discovered ''synthetic systems.'' Furthermore, it is thought that correlated behavior due to weakened screening dominates both the linear behavior in the normal-state resistivity, as well as the yet unexplained superconductivity in the oxide conductors.

To better understand the nature of the electronic states in a metal where there is localization and the Ioffe-Regal condition is violated, this present work on ultrathin Pb films uses photoemission to study the electronic states on the insulating side of the transition. Traditionally the resistivity of ultrathin Pb films has been studied by evaporating the metal onto cryogenically cooled substrates, usually glass. Even with evaporation onto surfaces below 10 K, continuity is not achieved on glass until the film thickness is of the order of 50 Å. It has usually been assumed that even at this low temperature, because of the weak interaction of Pb with the substrate, the metal agglomerates and the clusters connect at a relatively large average thickness. On the other hand, it was found that by predepositing Ge or SiO,[1] continuity could be achieved at average thicknesses approaching a monolayer. The films studied in this work are of this latter type. Because continuity is evident near a ''monolayer'' coverage, these films are generally called homogenous. Superconductivity in this system shows that the range of coherence extends over many microscopic grains,[1] which further justifies the assumption of homogeneity. In the present case we show below that the relevant range of the Coulomb interaction is large enough to average over microscopic inhomogeneities.

The angle-integrated photoemission experiments were performed using a standard He discharge lamp and a 200-mm hemispherical analyzer. The energy resolution in these experiments is about 40 meV. Some runs have been taken in the traditional way of predepositing leads on glass slides and measuring both photoemission and the electrical resistance as small amounts of Pb are evaporated. In these experiments about two layers of Ge were deposited onto the glass slide after it was cooled to about 10 K. This technique provides conditions for the growth of a two-dimensional metal, since electrical continuity is attained at about a monolayer of metal. Although this traditional technique is excellent for conductivity measurements, it is limited for photoemission studies on the insulating side of the transition due to charging. To circumvent this problem, Ta substrates were heated in O_2 to produce an oxide from 10 to 50 Å thick. The oxide thickness was confirmed by the reduction of Ta d states in the photoemission spectrum, due to the attenuation of the Ta photoelectrons in passing through the oxide. However, the oxide layer was thin enough so that some charge could be transferred from the underlying metal to neutralize static charges from the photoemission experiment.

Photoemission results from ultrathin Pb films of various thickness deposited on such an oxidized Ta foil are shown in Fig. 1. Two layers of Ge were deposited over the oxide to provide a surface similar to previous transport measurements. Initially, the photoemission energy distribution curve (EDC) from the oxide shows the large insulating gap of Ta oxide. As we have mentioned above, the thinness of the oxide grown on Ta allows for charge transfer from the Ta substrate to neutralize static charging. In the EDC obtained from 4 Å of Ge on the oxide, the gap is much smaller and is probably characteristic of α-Ge, which is a band gap of $\sim$0.66 eV at 300 K. This leaves a region near 0.5 eV below E_F where there are still no significant states and thus we can still monitor the development of Pb states with deposition. The initial deposition of Pb was a film with a nominal thick-

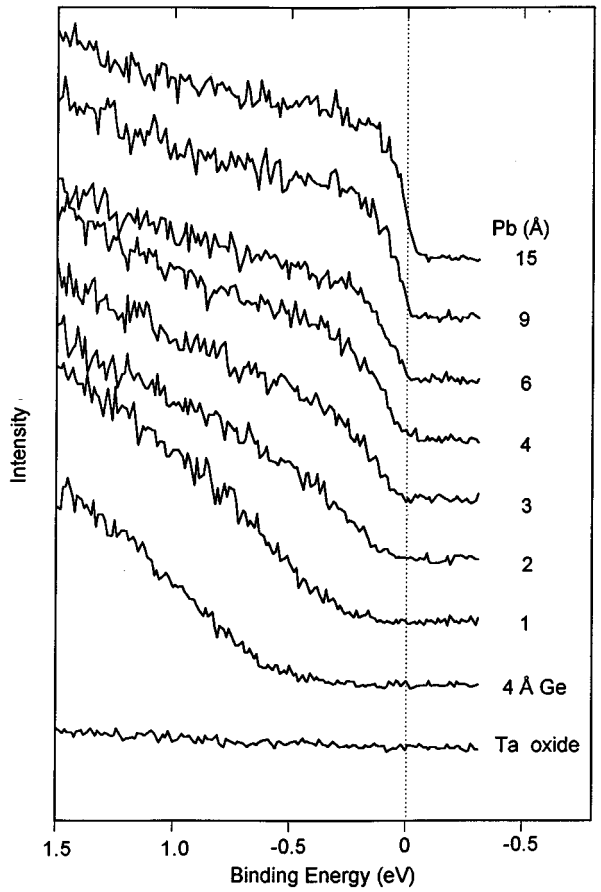

FIG. 1. Photoemission spectra in a small region around E_F. The numbers to the right of the curves are the approximate amounts of Pb deposited as measured on a quartz crystal thickness monitor. In this series of runs around 4 Å of Ge was deposited onto the 10 K substrate before the deposition of metal at about 10 K. The curve marked Ta oxide shows no states in the regime around E_F and is consistent with the gap of the insulator. Amorphous Ge shows a much smaller gap around E_F than the oxide, as expected. Resistance values from the data on glass substrates indicate some continuity at about 4–5 Å in the 50-M Ω range. By 6 Å the resistance is in the 50 000-Ω range by 15 Å, normal metallic resistivities are observed. These values are meant to be representative and vary from run to run.

ness of 1 Å. In this submonolayer regime it is reasonable to argue that the Pb bonds with the Ge and it can be seen that the gap becomes significantly reduced. With the next deposition of an additional 1 Å of Pb, the gap in the states near E_F is only in a very small region, and then there is a linear increase in the number of states as the binding energy increases below E_F. With subsequent depositions, the gap is gone and the density of states linearly decreases to zero as the Fermi level is approached. With increasing deposition of metal, the slope of this falloff in electron states, as E_F is approached, becomes greater and approaches that of the pure metal. It will be argued below that this change in slope is consistent with the Coulomb gap[9,10] and an increasing dielectric constant as more metal is deposited. Resistance measurements during deposition on glass surfaces indicate that the resistance in the layer becomes detectable (about 20 MΩ) at about 5 Å of Pb, and by about 7 Å of metal the resistance per square area $R_\square$ is about 20 000 Ω. Hence, the data presented here are for Pb films where the conduction states are still localized. We emphasize again that the detection of some conductivity after deposition of one or two monolayers of metal indicates that the growth is two dimensional and involves relatively small nuclei of metal whose number grow on the substrate surface[11] in the submonolayer regime, and finally start to coalesce as the monolayer regime is approached. As we have already mentioned, this submonolayer regime is characterized by the absence of measurable conductivity and an energy gap in the states around E_F. We have also made measurements for Pb deposited directly on Ta oxide formed *in situ*, but without Ge. In this case the photoemission spectra, shown in Fig. 2, are similar to the Ge coated oxide in Fig. 1. This implies two-dimensional growth for Pd on Ta oxide at 10 K and we have used this substrate for most studies. We emphasize that on a ''dirty'' oxide surface or glass, agglomeration occurs, and there is ''three-dimensional'' growth; a gap in the states is seen and states do not appear at E_F until ~30 Å of metal are deposited. This is contrasted to the ''two-dimensional'' case where the insulating gap disappears near 5 Å of metal.

The interpretation of photoemission spectra from insulators is extremely difficult for several reasons. First there is the problem of macroscopically charging the sample due to the inability of the insulator to replenish the charge left on the sample during the photoemission process. This kind of charging can cause a shift in the spectra, similar to the spectra observed for the submonolayer coverages of Pb, such as in Figs. 1 and 2(a). We have ruled out this possibility by changing the photon flux and observing that there is no change in the spectra of Pb on the Ta oxide. Hence, the oxide on Ta is thin enough to serve as a drain for the static charge. On glass, which is an excellent insulator, no spectra could be obtained in this regime due to charging. Another plausible explanation for the observed depletion of states below E_F in these submonolayer Pb films is an actual gap in the density of states of the dilute assembly of microclusters which have quantized levels and have only a small overlap with neighboring clusters. This is confirmed by the absence of any observable conductivity.

Another issue that impacts the interpretation is the so-called ''final-state'' effect and the screening of the valence-band hole caused by the photoemission process. The relaxation problem affects all photoemission experiments on samples where the resistance is very high. A crude estimate of the response time for a film with 1 MΩ resistance per square area is about 10^{-14} sec, which is longer than the time of a photoemission event. It is this slow response that allows one to observe the unrelaxed state when an electron is removed from the system. This problem of rapidly adding or removing an electron from a localized system has been theoretically discussed by Efros and Shklovskii[9] from a somewhat different point of view, and we return to this picture below. To experimentally investigate this relaxation problem during the photoemission process we have varied the connection of the sample to the electron ''bath'' in the metallic Ta substrate. In these measurements the oxide thickness was changed so that metallic Ta states could be observed through the oxide layer. Because electrons can now tunnel rapidly from the underlying Ta to the Pb layer, the relaxation process is greatly affected and, furthermore, the Pb microclusters are

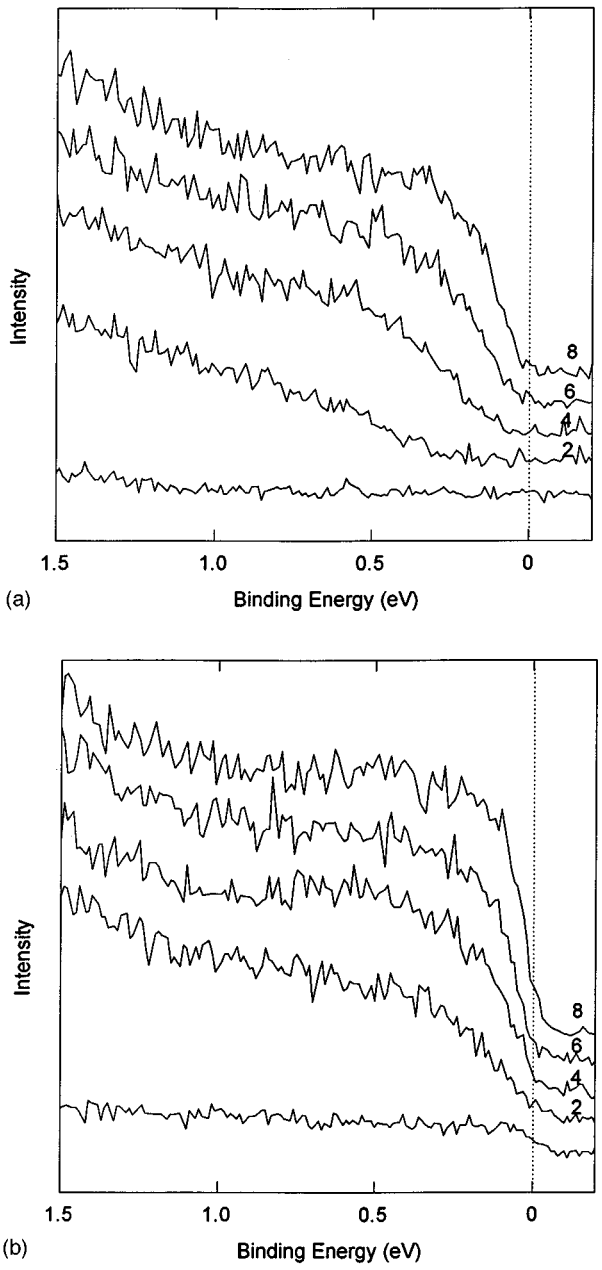

FIG. 2. (a) Photoemission spectra near E_F for Pb deposited directly onto the oxide surface at 10 K. The absence of Ta states indicates that the oxide thickness was significantly greater than 20 Å. The numbers on the right indicate the nominal Pb thickness in Å. (b) In this series of spectra the oxide layer is of the order of 20 Å and Ta d states can be seen at E_F in the bottom spectrum. This allows some relaxation of the photoemission hole and the spectra are much sharper for the same thickness than those shown in (a). The connectivity through the substrate will also increase the effective dielectric constant of the film.

connected through the substrate which greatly reduces any charging effects. The results are shown in Fig. 2(b), where for the same thickness of deposited Pb, there is no insulating gap and the states are now linear below E_F and there is a greater slope. By providing more coupling of the clusters through the thin insulator, the assumption of a uniform medium becomes plausible at these submonolayer coverages. We, of course, do not know exactly how the thin oxide changes the nature of the system, but it is possible that the connection of the clusters through the substrate both smears out the quantized levels and increases the effective dielectric constant. This effectively reduces the charging energies and affinity levels in the grains so that the observed gap disappears.

A matter that deserves further attention is the extreme submonolayer regime (1 Å Pb), where there is a complete depletion of states near E_F [Figs. 1 and 2(a)]. We have already mentioned quantized levels in the individual grains as a possible explanation. However, another plausible explanation is also related to the shift in energy due to the poor neutralization of charge left on an independent grain in the time of a photoemission event.[12] The charging energy is $e^2/2\kappa r$ and could cause a shift in the spectra away from the Fermi energy defined by the Ta substrate, as observed in Figs. 1 and 2(a) for the smallest amounts of Pb. Of course as continuity is achieved, or the clusters are connected through the substrate, the effect would vanish, as observed in Fig. 2. Intuitively, there must be some transition from the independent cluster regime to the regime where the approximation of a uniform medium is valid, as in the Efros and Shklovskii picture. Another issue which deserves a brief discussion is whether a distribution of inhomogeneous grains can account for the smearing in the data. If this was the case, sharp states at E_F might be expected from the larger clusters and the states at E_F would be expected to grow with subsequent depositions. We observe no states at E_F and with subsequent depositions the slope of the linear dropoff in states increases, as E_F is approached.

In general, this development of the states near E_F in these thin layers is consistent with a Coulomb gap in a disordered film that finally evolves into true metallic states with increasing amounts of metal. Previous measurements on three-dimensional oxide and semiconducting systems have provided some experimental information about the Coulomb gap.[13,14] In two dimensions the result Efros and Shklovskii[9] give for the density of single electron states $g(\varepsilon)$ is

$$g(\varepsilon)=\alpha\kappa^2|\varepsilon-\mu|/e^4, \tag{1}$$

where $\varepsilon=E-\mu$, μ is the chemical potential, α is a numerical constant, and κ is the dielectric constant. Thus the data in Figs. 1 and 2 can be understood by associating the observed linear regime near E_F with the behavior predicted in Eq. (1). It is interesting that no specific material parameters appear here except the dielectric constant. The Coulomb gap may be defined as the absolute value of $\varepsilon-\mu$ corresponding to the crossing of $g(\varepsilon)$ predicted by Eq. (1) and the constant two-dimensional quasiparticle density of states g_0. The gap is then given as $\Delta=g_0e^4/\kappa^2\alpha$, and for the observed $\Delta\sim0.2$ eV and using $g_0=10^{14}$ cm^{-2} eV^{-1}, implies $\kappa\sim4$. The r given by $e^2/\kappa\Delta$ is about 20 Å, and since this value is larger than the film thickness and is also larger than the microclusters of metal, the general use of the Efros and Shklovskii picture should be valid. Note that Eq. (1) shows that the slope of $g(\varepsilon)$ changes as the dielectric constant increases with metal deposition, as seen in the data of Figs. 1 and 2. In their picture of a grandular material, Sheng and Abeles[15] give an expression like $\kappa=\kappa_0(1+d/2s)$, where d is the particle diameter and s is the spacing between particles. Although in

this limit of quasiatomic clusters one cannot expect this result to be valid, it is reasonable that $\kappa=\kappa_0 f(d/s)$ and the observed initial $\kappa\sim 4$ is not unreasonable. In the simplest model of what happens with increasing metal deposition, one can argue that initially the number of clusters or nuclei, which probably contain several atoms, grows and the spacing between clusters decreases and thus the dielectric constant increases. In the regime where the clusters coalesce the analysis is too complex, but of course it is clear that the dielectric constant must approach that of a metal.

It is evident that these measurements are basically consistent with a picture of an absence of single electron states at the Fermi level in the insulating state, and the fact that the long-range Coulomb energy from the hole perturbs the electronic states in a small region near E_F. We emphasize that as the film becomes more metallic, single electron states do not grow at E_F, as might be expected from localized states with no Coulomb interaction, but instead near E_F the slope of $g(\varepsilon)$ becomes greater as $R_\square$ decreases and the film becomes more metallic. Hence, within the resolution of these experiments, the Coulomb gap decreases with increasing metal deposition, but remains finite until the metallic state.

It should be mentioned that the present studies are for very disordered systems; however, it is possible that features such as those observed here are more general properties of any two-dimensional correlated system where screening starts to become ineffective. For example, a broadening is seen in photoemission spectra of the high-T_c superconductors as they are disordered and the conduction becomes activated. We speculate that the behavior observed in these experiments and those by Almèras *et al.*[16] are characteristic of any quasi-two-dimensional metal where $R_\square$ becomes above the $h/4e^2$ (about 6500 Ω), and where screening and Coulomb effects become important. In fact on the level of a few meV, even at an $R_\square$ of several hundreds of ohms some effects might well be observable. It is interesting that in the very recent work of Carpinelli *et al.*[17] there is a charge density wave for epitaxial Pb on Ge and the authors already argue that this may be associated with correlation effects. In these layers of ordered Pb on Ge, as well as the case here for disordered layers of Pb on Ge, the breakdown of metallic screening leads to correlated behavior. This phenomena must be considered carefully in discussions of two-dimensional metals.

In summary, the present results give some introduction to the complexity of investigating systems with strong localization. In addition to the effects of localization itself, the photoemission technique, as well as tunneling, involve highly correlated behavior because of the hole or electron left in the system and this greatly affects the interpretation of the measurements. However, in this present case the interpretation of the results in terms of the Coulomb gap is credible and photoemission is an excellent probe.

We have benefitted enormously from discussions with many colleagues. Professor M. Kastner, Professor S. Kivelson, and Professor Z. Ovadyahu have clarified the physics of the Coulomb gap. Our Brookhaven colleagues D. Basov, V. J. Emery, P. D. Johnson, J.-H. Park, Mark W. Ruckman, and M. Weinert have also clarified many points and have made numerous suggestions. This work was supported by the U.S. Department of Energy, Division of Materials Science, under Contract No. DE-AC02-76CH00016.

[1] M. Strongin, R. S. Thompson, O. F. Kammerer, and J. E. Crow, Phys. Rev. B **1**, 1078 (1970).
[2] J. M. Graybeal and M. R. Beasley, Phys. Rev. B **29**, 4167 (1984).
[3] R. C. Dynes, A. E. White, J. M. Graybeal, and J. P. Garno, Phys. Rev. Lett. **57**, 2195 (1986).
[4] D. B. Haviland, Y. Liu, and A. M. Goldman, Phys. Rev. Lett. **62**, 2180 (1989).
[5] V. J. Emery and S. A. Kivelson, Phys. Rev. Lett. **74**, 3253 (1995).
[6] A. E. White, R. C. Dynes, and J. P. Garno, Phys. Rev. B **31**, 1174 (1985).
[7] S. Y. Hsu and J. M. Valles, Jr., Phys. Rev. B **49**, 16 600 (1994).
[8] B. L. Altshuler and A. G. Aronov, Solid State Commun. **30**, 115 (1979)].
[9] A. L. Efros and B. I. Shklovskii, J. Phys. C **8**, 149 (1975).
[10] We emphasize that in previous references to the gap we are referring to the usual absence of states in a region around E_F. The Coulomb gap is not a ground state property and states are only absent at E_F.
[11] See, for example, C. Neugebauer, in *Handbook of Thin Film Technology*, edited by L. I. Maissel and R. Glang (McGraw-Hill, New York, 1970).
[12] See, for example, S. B. DiCenzo and G. K. Wertheim, Comments Solid State Phys. **11**, 203 (1985); S. L. Qiu, X. Pan, M. Strongin, and P. H. Citrin, Phys. Rev. B **36**, 1292 (1987).
[13] J. H. Davies and J. R. Franz, Phys. Rev. Lett. **57**, 475 (1986).
[14] J. G. Massey and M. Lee, Phys. Rev. Lett. **75**, 4266 (1995).
[15] P. Sheng and B. Abeles, Phys. Rev. Lett. **28**, 34 (1972).
[16] P. Almèras, H. Berger, G. Margaritundo, J. Ma, C. Quitmann, R. J. Kelley, and M. Onellion, Solid State Commun. **91**, 535 (1994).
[17] J. N. Carpinelli, H. Weitering, E. W. Plummer, and R. Stumpf, Nature (London) **381**, 398 (1996).