# Photoemission and Transport Studies of the Metal-Insulator Transition in Granular Palladium Films

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Photoemission and resistivity measurements of granular Pd samples are reported which exhibit a metal-insulator transition with decreasing metal fraction. As the net metallic concentration is reduced the resistivity passes through $\sqrt{T}$, $\ln T$, $\exp\{+(A/T)^{1/4}\}$, and insulating $\exp\{+(B/T)^{1/2}\}$ temperature dependences while the photoemission results show a continuous reduction in the Pd local density of states within 1 eV of the Fermi level. In the insulating regime a gap is observed in the photoemission spectrum.

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One central problem in the metal-insulator transition[1] concerns the relative importance of disorder-induced localization[2] and many-body electron-correlation effects.[3] McMillan[4] has recently proposed a scaling theory which includes both effects on an equal footing and makes a number of specific predictions. Both the zero-temperature conductivity and the tunneling density of states at the Fermi level, $N_t(E_F)$, are expected to decrease continuously to zero as the metal fraction is reduced to a critical concentration. $N_t(E)$ is predicted to exhibit a square-root anomaly near $E_F$ with a gap finally opening in the insulating phase. Tunneling experiments[5-8] have confirmed most of these predictions. Most notably, a recent experiment[8] has demonstrated that $N_t(E_F)$ vanishes at precisely the same metallic concentration where the extrapolated zero-temperature conductivity becomes zero. However, because of complexities of the field penetration into the insulator, tunneling experiments[5-8] have been unable to show the existence of a true energy gap.[4]

In this work we report measurements which correlate the Pd local density of states, $N(E)$, as measured by photoemission energy distribution curves (EDC's), with the metal-insulator transition observed in resistivity measurements of a granular Pd system. As the metal content of the sample is reduced the temperature dependence of the resistivity changes from metallic character to insulating behaviors. Through the same regimes of concentration the photoemission EDC's show a continuous and gradual reduction of the local density of states of the Pd system within 1 eV below the Fermi level with a small energy gap opening finally when the resistivity suggests insulating behavior.

The granular Pd films were prepared by $Ar^+$ cosputtering from a Pd and a Si target directly onto a $3\times1$-in.$^2$ glass substrate in the top level of a three-level ultrahigh vacuum (UHV) system. The glass substrate had been presputtered with connected Nb strips in order to avoid the charging problem in photoemission and Auger measurements. The top level was separated from the lower levels by a UHV valve, and could be separately pumped after sputtering. The sputtered sample could be transferred by a manipulator to the lower levels, where both Auger and photoemission measurements, with the He I line, were performed as a function of position on the sample. The resistance measurements were performed in a separate liquid-He Dewar vessel with a four-probe technique. The volume concentration, $x$, of Pd as a function of position along the sample was calculated from the Auger spectra and found to vary between approximately 0.5 and 0.1, consistent with the reports of Abeles *et al.*[9] for other metal-$SiO_2$ granular films. X-ray diffraction data on the samples were consistent with Pd grains embedded in an insulating matrix of amorphous $SiO_2$ and were similar to data[9] on granular Pt and Ni. Specifically, the particle size of these granular metals was found[9] to vary linearly between 40 and 20 Å for $x$ between 0.5 and 0.2. Pure Pd films ($x=1$) were obtained in a sample where $Pd_2Si$ was formed and was not otherwise used in these studies.

Figure 1 shows the variation of $N(E_F)$ obtained

 

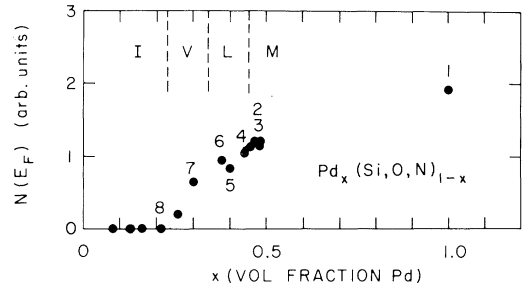


FIG. 1. The density of states at $E_F$, measured from photoemission, plotted as a function of $x$. The regions indicated by $M$, $L$, $V$, $I$, represent where metallic, log$T$, variable-range hopping, and insulator behavior appears, respectively. The numbers indicated in the figure represent the specimen reference number discussed in the text.

from the photoemission EDC's as a function of metal concentration. Also indicated are four regimes, denoted $M$, $L$, $V$, and $I$, wherein the temperature dependence of the resistivity exhibits the distinctive behavior discussed below. In the $M$ regime ($x > 0.46$) the resistivity increases with decreasing temperature with a $\sqrt{T}$ dependence. Two examples are shown in Fig. 2(a). [The resistivity of the pure metallic specimen (No. 1) remains constant for $T < 10$ K.] The $\sqrt{T}$ dependence of $\sigma$ in a granular metallic system has been predicted in the electron-electron interaction theory of Al'tshuler and Aronov.[3] In the $L$ regime ($0.38 < x < 0.46$) the resistivity is best fitted by a ln$T$ temperature dependence. Two examples are shown in Fig. 2(b). A ln$T$ dependence of $\sigma$ is predicted for a two-dimensional disordered system[10] and is not expected for systems that are manifestly three dimensional such as this one. Although this logarithmic behavior has also been observed and discussed in a granular aluminum system,[11] our temperature range is probably not large enough to reach a definite conclusion. In the $V$ regime ($0.24 < x < 0.38$) the low-temperature resistivity shows a distinctive behavior of variable-range hopping.[1] As illustrated in Fig. 3 for specimen No. 7, the resistivity increases with decreasing temperature, first following an $\exp\{+A'/T\}$ dependence at high temperatures and then an $\exp\{+(A/T)^{1/4}\}$ dependence at low temperatures. As the metal concentration, $x$, moves further into the $I$ region ($x < 0.24$) the resistivity rises following an $\exp\{+(B/T)^{1/2}\}$ temperature dependence in accord with previous observations in many insulating granular systems.[9,12]

Figure 4 illustrates the local density of states as reflected in a photoemission EDC of the granular Pd system over the concentration range discussed above. The continuous decrease in $N(E_F)$ is readily apparent. Of particular note, here and in Fig. 1, is the fact that variable-range hopping type behavior occurs when a nonzero value of $N(E_F)$ is observed. When $N(E_F)$ does vanish and a gap opens,[13] true insulating behavior ensues. As discussed below, in tunneling experiments, a zero $N_t(E_F)$ would be observed at the $V$ region where localization of current carrying states occurs. Our combined photoemission and resistivity measurements therefore provide additional information not accessible to a transport measurement which averages over the entire sample. In what follows we describe an intuitive picture of granular metals within which both the tunneling and photoemission results are explicable.

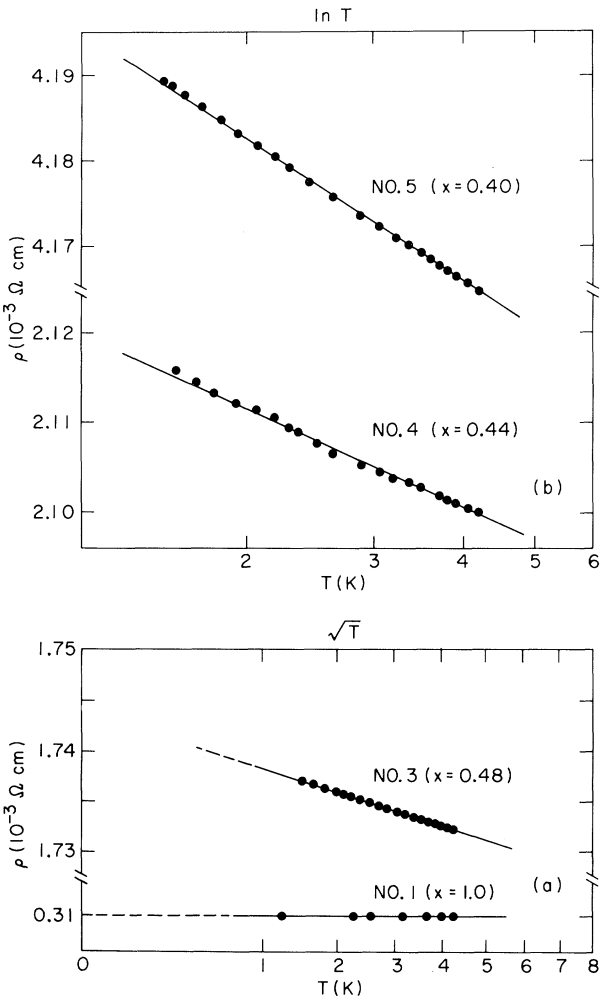


FIG. 2. (a) Resistivity plotted as a function of $\sqrt{T}$ for two specimens. (b) Resistivity plotted as a function of ln$T$ for two specimens.

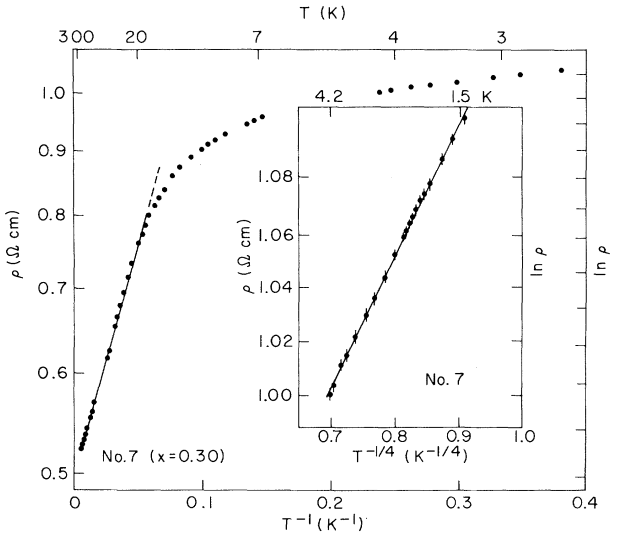


FIG. 3. Ln$\rho$ vs $T^{-1}$ for $x = 0.30$ specimen. The inset shows ln$\rho$ vs $T^{-1/4}$.

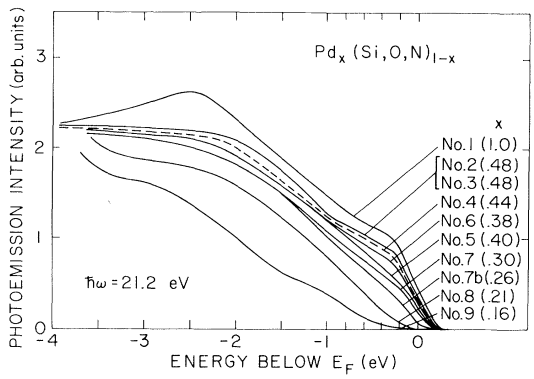


FIG. 4. Photoemission energy distribution curves for specimens No. 1 through No. 9.

It is useful first to consider two limiting cases. In the metallic regime, the states at the Fermi level are extended and free-electron conduction is expected. Both tunneling and photoemission reflect the bulk density of states. In the opposite regime the sample consists of small metal grains, say of 10 Å diam, completely surrounded and isolated by the insulating matrix. Tunneling between small grains requires a finite charging energy to be overcome as discussed by Abeles *et al.*[9] so that no current flows at zero bias, i.e., $N_t(E_F)$ goes to zero. Conversely, photoemission should be sensitive to the local properties of a single grain which, at this size, will yield an essentially bulklike density of states.[14-16] However, if the electrons liberated by the photoelectric effect are not efficiently resupplied to the grain, a macroscopic charging occurs which produces gross distortions of the spectrum. This is commonly seen when photoemission is attempted from bulk insulators.

Now consider the passage between these two extreme situations. As the metal fraction is reduced somewhat below unity the morphology becomes a collection of rather large (50–100 Å) metal particles separated by small insulating regimes. Free-electron motion between grains is hindered by disorder scattering and the motion of a typical Fermi-level wave packet is best described as diffusive. Such states will ultimately acquire finite amplitude throughout the sample although the propagation will be more difficult than in the metallic limit. The system appears homogeneous and a tunneling current will be supported. Of course these states will also be seen in the photoemission spectrum. However, according to recent ideas,[3,4] the diffusive motion has a profound effect on the density of states. In addition to a square-root anomaly near the Fermi level,[3] the magnitude of the contribution to $N(E_F)$ from these diffusive states is expected[4] to decline to zero with decreasing metal fraction. The physical idea is that the screening capability of the metal breaks down so that poorly screened charge fluctuations begin to appear. The resulting charging energies inhibit electron motion and shift the energy of the diffusing wave packets. Eventually these states localize to one or several grains and the normal tunneling current shuts off as the metal fraction is reduced further and the morphology becomes a collection of inhomogeneous small (~10–30 Å) particles.

Bulk conduction in this inhomogeneous regime can only proceed via hopping between the grains and a variable-range hopping mechanism is expected and is observed by us. However, the bulklike density of states of the wave functions limited to an isolated particle (~10–30 Å) revealed by photoemission is strongly affected by Coulomb interactions with the fluctuating charges on *neighboring* particles. Indeed, it is the disappearance of the extended diffusing states which otherwise replenish the photoemitted charge which leads to this situation. A suppression of $N(E_F)$ relative to the noninteracting-particles form is expected by extension of the work of Efros and Shklovskii and Davies, Lee, and Rice[17] on the opening of a Coulomb gap. The charging energies at issue here are exactly the same sort which cut off the extended states earlier. The

hindered tunneling between grains is presumably sufficient to prevent the macroscopic charging characteristic of the extreme insulating limit.

In conclusion, the morphological variation of the granular metal (decreasing mean particle size and increasing intergrain distance) with decreasing metallic fraction leads to various phenomena revealed by resistivity and photoemission measurements. The density of states at $E_F$ measured by photoemission diminishes as conducting diffusive electronic states are shifted by local charge fluctuations. When localization of these states occurs variable-range hopping ensues with the local $N(E_F)$ of individual grains modified by the persistence of charging effects. The variation in electronic structure is continuous with a small Coulomb gap at $E_F$ finally opening in the insulating regime.

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