



# Size-dependent changes in the electronic structure of metal clusters as investigated by scanning tunneling spectroscopy

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## Abstract

Pd, Ag, Cd and Au clusters of varying sizes have been investigated by scanning tunneling spectroscopy under ultra-high vacuum. The conductance of the clusters decreases markedly when the cluster diameter is  $\leq 1$  nm. A plot of the density of states at the Fermi level against the cluster volume varies nearly linearly up to a cluster volume of  $4 \text{ nm}^3$  (diameter  $\sim 2$  nm). Below a cluster diameter of 1 nm, an energy gap occurs, the value of which increases with the decrease in cluster size, reaching values up to 70 meV at small sizes. Clearly, the very small clusters tend to become non-metallic. © 1998 Published by Elsevier Science B.V. All rights reserved.

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## 1. Introduction

One of the fundamental problems in condensed matter science relates to the metallicity of divided metals. To this end, it is of considerable interest to investigate the electronic properties of metal clusters as a function of size [1]. With the advent of the scanning tunneling microscope (STM), which provides the desired sensitivity and spatial resolution for such studies, tunneling spectroscopy has become an indispensable and unique tool for the investigation of small clusters [2–4]. A few years ago, First et al. [5] reported non-metallicity and gap states in small Fe clusters supported on GaAs (110) using scanning tunneling spectroscopy (STS) and estimated a band gap of 0.1 eV in a  $\text{Fe}_{13}$  cluster. STS measurements

on Au and Pd clusters in air indicated the occurrence of a metal–nonmetal transition as the cluster size is decreased [6,7], but the results were subject to some doubt because of the ambient atmosphere in the measurements. In an interesting study, Bifone and co-workers [8] have recently carried out STS measurements on Pd clusters supported on highly oriented pyrolytic graphite (HOPG) in ultra-high vacuum (UHV) and found that the surface density of electronic states at the Fermi level has a strong size dependence for small Pd clusters, becoming size-independent in clusters larger than a critical volume. These workers interpret the results in terms of the size-dependent electronic structure of the particles. Wawro et al. [9] have studied the electronic structure of Sb, Ni and Au clusters deposited on HOPG substrates in UHV using STM and attribute the disappearance of the clusters in the STM images at

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certain ranges of the bias voltage as due to the occurrence of small energy gaps in the electronic structure of the clusters. In view of the importance of the problem, we decided to carefully investigate the size-dependent conductance and energy gap in metallic clusters.

We have carried out a systematic study of Pd, Ag, Cd and Au clusters of varying sizes by STS under UHV conditions after having characterized the clusters by photoelectron spectroscopy and STM. The purpose of choosing these four metals was to explore whether the size effect is found universal in metals of widely differing electronic configuration. As we know, the atomic electronic configurations in Pd, Ag, Cd and Au are  $4d^{10} 5s^0$ ,  $4d^{10} 5s^1$ ,  $4d^{10} 5s^2$  and  $5d^{10} 6s^1$ , respectively, whereas the Engel–Brewer configuration in small clusters of Pd, Ag, Cd and Au are  $d^7 s^1 p^2$ ,  $d^8 s^1 p^2$ ,  $d^{10} s^1 p^1$  and  $d^8 s^1 p^2$ , respectively. The study has indeed shown that the tunneling conductance of the clusters generally decreases with the decrease in size below  $\sim 1$  nm diameter, accompanied by a widening gap. The results establish the occurrence of a non-metallic state in small clusters ( $< 1$  nm) in all the four metals studied.

## 2. Experimental

Clusters were deposited on freshly cleaved HOPG substrate by resistive evaporation of the metal using a tungsten filament in the preparation chamber of a multi-purpose surface spectrometer (base pressure  $\sim 10^{-10}$  Torr). High-purity metals (Pd, Ag, Cd, Au) from Aldrich Chemical Co. were used after thorough degassing. Prior to deposition, the HOPG wafers were mounted on a molybdenum stub using silver glue. X-ray photoelectron spectroscopy measurements were carried out (with Al  $K_{\alpha}$  radiation, 1486.6 eV), both before and after the metal deposition, using a VSW EA45 analyzer at 100 eV pass energy. In the case of each metal, deposition [10] of  $\sim 0.5 \times 10^{15}$  atoms/cm<sup>2</sup> was obtained. The core level binding energies of the deposited metal clusters, were higher with respect to the bulk metal values by  $\sim 0.2$  eV due to the size effect, arising from the decrease in core–hole screening in small metal clusters [6].

A molybdenum stub containing the HOPG sub-

strate was transferred to a UHV STM stage (Omicron Vakumphysik) attached to the main spectrometer chamber, using a combination of a magnetic manipulator and a wobble stick. The cylindrical piezo has a sensitivity of 10 nm/V in all X, Y and Z directions. The whole setup is placed on an eddy current dampener in order to minimize noise. Nanotips used in our measurements were prepared by electrochemical etching of a thin tungsten wire.

STM imaging was initially carried out using the forward  $I$  channel over large areas (typically  $200 \times 200$  nm) with a bias voltage of  $\sim 0.1$  V, feed back current of  $\sim 3$  nA and a scan speed of 1000 nm/s. Scanning tunneling spectroscopy (STS) measurements were then made on selected areas ( $15 \times 15$  nm) as a  $250 \times 250$  grid with the feed back loop off. At each grid point, 50  $I$ – $V$  points were collected each with an acquisition time of 640  $\mu$ s and a delay of 50  $\mu$ s. The sweep range in voltage was  $\pm 0.5$  or  $\pm 0.05$  V. Data analysis was carried out in two ways. First, the average slope of an  $I$ – $V$  data of a cluster was obtained from the linear part of the curve in both the positive and the negative regions and was normalized with respect to the average slope of the corresponding HOPG data. In addition, we have obtained the  $dI/dV$  curves for the clusters, after

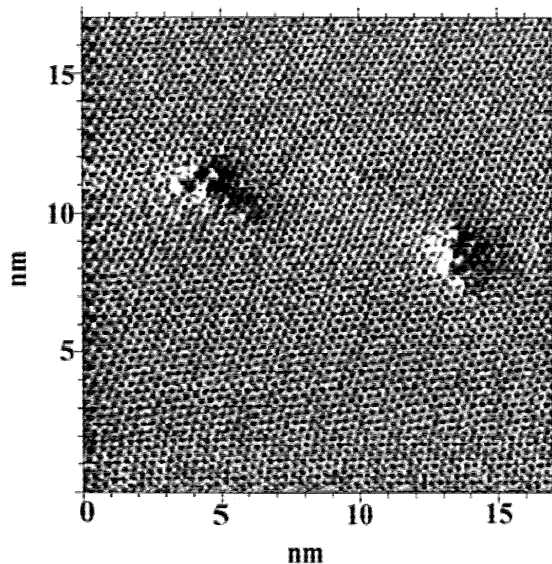


Fig. 1. Small-area STM image of Au clusters at a bias voltage of 0.03 V. Atomic resolution is achieved in these images as seen from the background lattice of the HOPG.

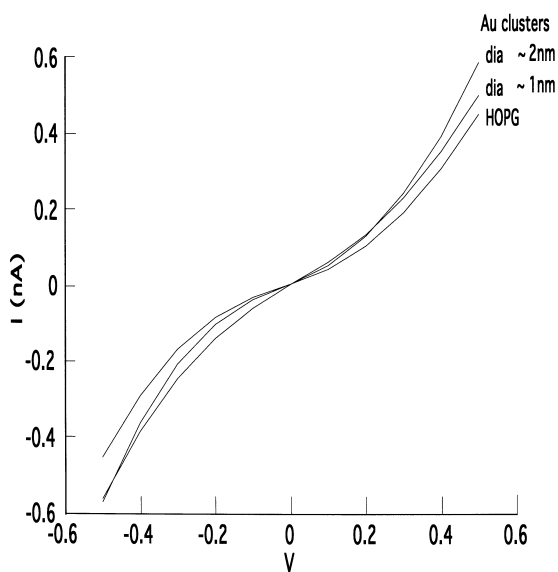


Fig. 2. Typical  $I$ - $V$  curves in the voltage range of  $\pm 0.5$  V of Au clusters along with that of the substrate HOPG.

subtracting the  $I$ - $V$  data of the HOPG from those of the clusters.

### 3. Results and discussion

Large-area STM images showed metal clusters of varying sizes ranging from 1 to 5 nm as estimated by quantitative analysis of the distribution. In order to obtain the  $I$ - $V$  characteristics of the small metal clusters, the scan areas were restricted to  $15 \times 15$  nm and the images were collected in the spectroscopy mode (see Section 2). As an example, we show in Fig. 1 an STM image obtained with small Au clusters at a bias voltage of 0.03 V. Tiny clusters in the diameter range of 0.5–1 nm situated on top of the HOPG lattice are clearly seen from this figure. A specific region of interest was identified using the spectroscopy menu and the  $I$ - $V$  data from that region was averaged. Typical  $I$ - $V$  curves of the Au

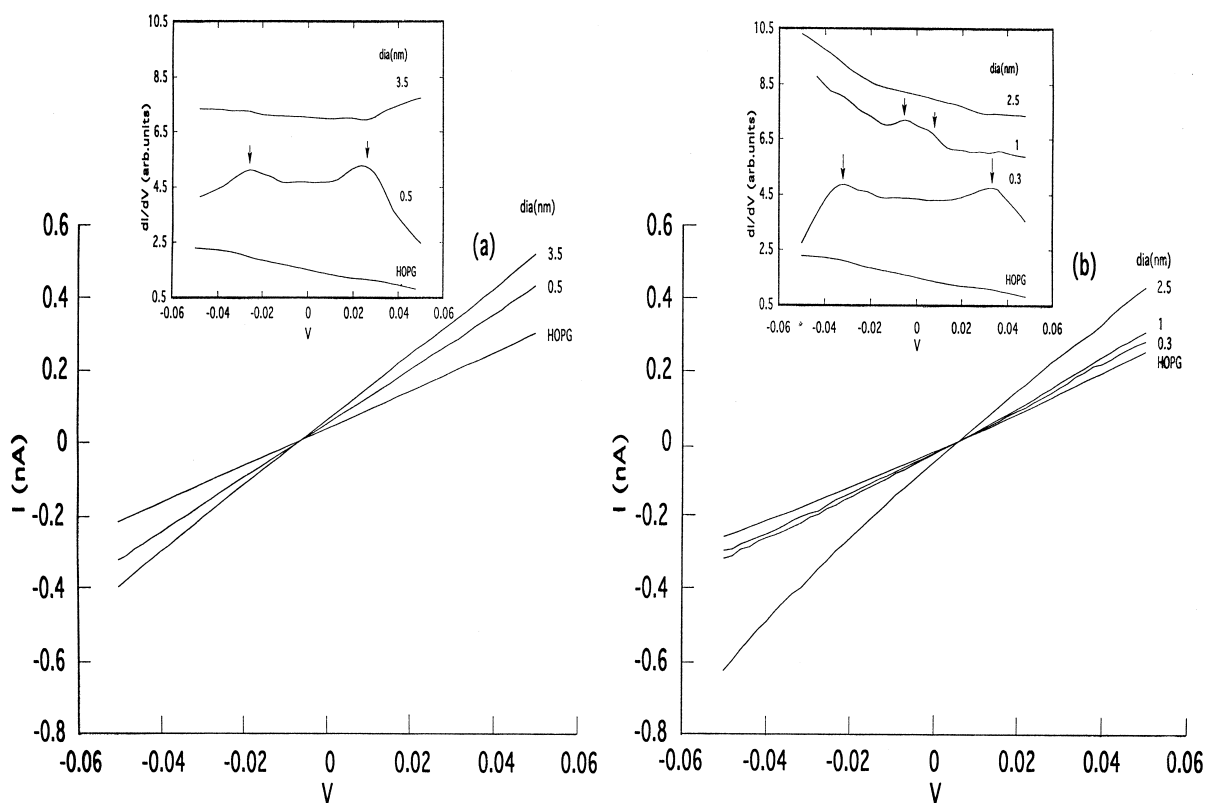


Fig. 3. Typical  $I$ - $V$  curves of small metal clusters of (a) Pd and (b) Cd in a voltage range of  $\pm 0.05$  V along with that of the substrate HOPG. Insets show the corresponding derivative curves. The gap features are marked by arrows.

clusters deposited on the HOPG substrate, measured in the voltage range of  $-0.5$  to  $+0.5$  V, are shown in Fig. 2, along with the  $I$ - $V$  curve of HOPG itself. At smaller voltages, the curves are nearly linear, with the increase in  $I$  becoming more rapid at voltages beyond  $\pm 0.1$  V. Thus, these curves are typical of metal-insulator(vacuum)-metal (MIM) tunneling junctions [4]. The tunneling current typically obtained in the regions of the clusters is significantly larger than that directly from the HOPG surface.

The measurements discussed above are not due to Coulomb blockade. Supported metal clusters have been investigated in the literature by STS in reference to the Coulomb blockade process [11–13]. When the surface of the cluster is covered with an oxide or when the clusters are supported on a dielectric layer that forms a tunneling barrier between the metal cluster and the support, the  $I$ - $V$  data generally exhibit rectification due to charging. In the present measurements, the deposition of clusters was performed in UHV with the XPS and other measurements confirming that the surfaces of the clusters were devoid of any oxygen. We have carried out further careful measurements near the zero-bias region with a reduced voltage scan range of  $\pm 0.05$  V keeping the rest of the parameters the same as described earlier. In Fig. 3, we show typical  $I$ - $V$  curves over the  $-0.05$  to  $+0.05$  V range for Pd and Cd clusters. Again the  $I$ - $V$  data from the metal clusters vary nearly linearly and the regions containing the metal clusters give higher tunneling currents compared to HOPG (akin to the behaviour in Fig. 2).

We have examined the cluster size dependence of the slope of the  $I$ - $V$  curves in some detail. For this purpose, we found it convenient to take the average of the slopes from the positive and negative lobes. After normalization with respect to HOPG, the slope was plotted against the volume of the cluster as shown in Fig. 4. We see that as the cluster size increases the slope of the curve increase linearly up to a volume of  $4 \text{ nm}^3$  ( $d \approx 2 \text{ nm}$ ) and reaches a constant value for bigger clusters. This observation suggests that the slope of the  $I$ - $V$  curves near the zero-bias region is related to the DOS near the bulk Fermi level (FLDOS) [8]. Accordingly, the FLDOS reaches saturation when the cluster size enters the bulk regime ( $> 2 \text{ nm}$ ).

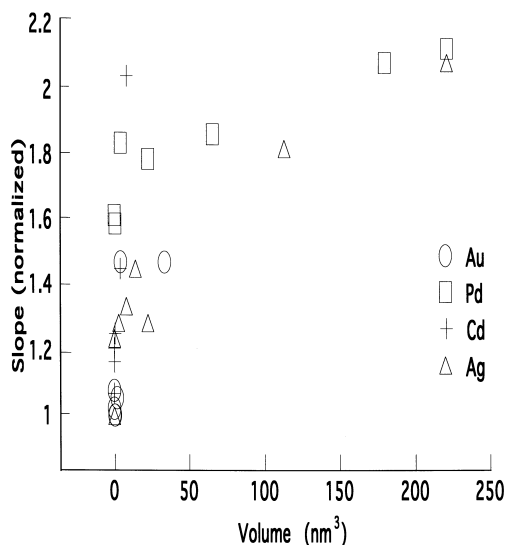


Fig. 4. Normalized slope of the  $I$ - $V$  curves (conductance) as a function of the cluster-volume for the four metals studied. Above a critical volume ( $\sim 4 \text{ nm}^3$ ), the slope becomes size independent.

When the cluster size is very small (say  $< 1 \text{ nm}$ ), it is likely that the regions of HOPG in the immediate surroundings of the cluster contribute to the tunneling current apart from the cluster itself and the electronic nature of the small clusters is therefore not easily discernible [14]. The thermal broadening at room temperature ( $\sim 50 \text{ meV}$ ) also limits the resolution of the measurements. In order to enhance the features of the  $I$ - $V$  curves we have obtained the derivative at each data point. Typical derivative curves are shown in the inset of Fig. 3a and b. The derivative curve from HOPG as well as from a  $3.5 \text{ nm}$  Pd cluster are featureless while that from a  $0.5 \text{ nm}$  Pd cluster shows well-defined peaks at  $-0.024$  and  $+0.025 \text{ mV}$  (Fig. 3a). These features seem to originate from a conduction gap, expected in small metal clusters due to the depletion of electronic states near the bulk Fermi level. Although the resolution of the measurements does not permit us to probe the discretization of the electronic levels in small clusters, it has been possible to observe the presence of a gap by means of the small changes in the tunneling current. Such a gap is found to occur in a small Cd cluster ( $\sim 0.3 \text{ nm}$ ) which exhibits features separated by  $65 \text{ mV}$ , a  $1 \text{ nm}$  Cd cluster showing closely spaced features ( $12 \text{ mV}$ ), characteristic of the

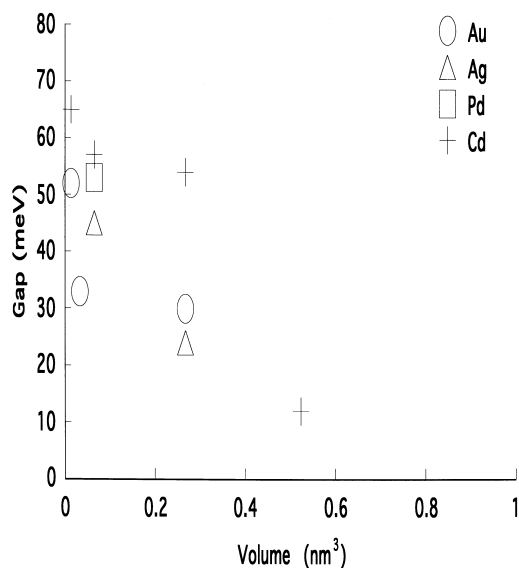


Fig. 5. The conduction gap observed in small clusters of the four metals as a function of the cluster-volume.

vanishing conduction gap in the bigger clusters (Fig. 3b). We have carried out such gap measurements on clusters of varying sizes of all the four metals and find that the measured value of the gap lies between 10 and 70 mV. These results are depicted in Fig. 5. The conduction gap decreases with the increase in cluster volume and there is no gap in clusters larger than  $\sim 1$  nm. This observation suggests that small metal clusters ( $\leq 1$  nm) are indeed non-metallic. The present study is in agreement with the earlier photoemission studies [15–17] which indicated the expected changes in the electronic structure near the Fermi level in small clusters of  $\leq 1$  nm, compared to the bulk metal. The present study is also consistent with a recent theoretical study [18] of a model metal cluster which predicts electron localization to occur around a cluster diameter of 0.6 nm.

In conclusion, the present scanning tunneling spectroscopy study of clusters of four metals, Pd, Ag, Cd and Au, under ultra-high vacuum conditions establishes that the tunneling conductance of the clusters decreases markedly with the decrease in cluster size, when the cluster size is  $\leq 1$  nm. In this small cluster regime, the density of states near the Fermi level is linear with cluster volume, reaching saturation when the volume is higher. Interestingly,

as the cluster size decreases below 1 nm dia, there is emergence of an energy gap. The gap increases with the decrease in cluster size going up to 70 meV in very small clusters. The present results may be taken as clear evidence for the occurrence of a size-dependent metal–nonmetal transition in metal clusters with the decrease in cluster size.

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