Logarithmic temperature dependence of conductivity in a random quasi-two dimensional assembly of gold nanoclusters

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Abstract
Electrical conductivity measurements on a two-dimensional random assembly of Au nanoclusters of an average size 5 nm and an average inter-cluster separation of 12 nm show logarithmic temperature dependence of conductivity in the temperature range 205–229 K followed by an activated nearest neighbour hopping conduction in the temperature range 230–340 K. The activation energy for hopping was found to be approximately equal to the Coulomb charging energy of a cluster. The charge transport between clusters in the logarithmic regime is shown to take place by a random walk of step size equal to the average inter-cluster separation.

1. Introduction
Electrical transport measurements in granular films [1], doped systems of self-assembled quantum dots [2], thin films of Cu–SiO₂ [3] and several such systems [4] have revealed interesting properties due to quantum confinement effects and an interplay of competing length and energy scales. Therefore it is of interest to study the transport in an assembly of metal nanoclusters since this forms a simple system where the effects of grain boundaries and interfaces would not be present. This study focuses on a metal nanocluster assemblage where the electrons are localised in individual clusters that are isolated from each other by a large distance. Electron transport in the cluster assemblage occurs by the intra-grain diffusive electron motion and the electron tunnelling between clusters which results in their sequential charging [5]. Therefore the interplay of the coupling between the clusters and the electron–electron Coulomb interaction that originates from the charging of the clusters controls the transport properties of this system [6]. The discreteness of the electronic levels in these nanoclusters also plays an important role, especially at low temperatures. The studies on electron transport and the localisation effects in these artificially controlled systems are described in this paper.

2. Experimental methods
Electrical conductivity measurements were carried out on cluster assembled films deposited between two electrodes for electrical contacts. To increase the measured current, the clusters were deposited between the fingers of an inter-digitated electrode structure made by e-beam lithography. Each finger was 11 μm long and 200 nm broad, and the average spacing between the fingers was 86 nm. An SEM micrograph of the electrode structure is shown in figure 1 (a).

The Au clusters were deposited using a NANODEP60 cluster deposition system from Oxford Applied Research, UK. This deposition system is based on the principle of inert gas phase condensation. Atoms are sputtered using a DC magnetron source and are made to move under an inert gas flow in an agglomeration zone where they coalesce to form clusters whose size depends on the length of the agglomeration zone, the gas flow rate, the temperature of the chamber, and the magnetron power. The clusters then move into the deposition chamber through an aperture and get deposited onto the substrate. The deposition chamber is maintained at a lower pressure as compared to the agglomeration chamber using a turbo pump of higher pumping rate as compared to the turbo pump of the agglomeration chamber, thus providing a differential...
pressure for the flow gas together with the agglomerated clusters to flow towards the deposition chamber. The deposition conditions are described in table 1 and the microstructure of the electrode plus nanocluster system is shown in figure 1 (b).

The current versus voltage IV measurements were carried out using an Agilent model B1500A Semiconductor Device Analyser with the sample temperature varied in a Cryogenic Probe Station (Lake Shore Cryotronics Model CRX-4K). The sample chamber had a vacuum of at $10^{-6}$ Torr or better. The electrodes used in the probe station were of Be–Cu. The substrate was Silicon with SiO$_2$ gate oxide and the interdigitated electrodes were made out of silver.

One can observe some aggregated nanoclusters at the periphery of the electrodes. However these are in contact or very close to the electrodes. Since the conduction process is by hopping between the isolated clusters as discussed later in this work, the clusters in contact with the electrodes will not contribute as the resistance between the electrodes and the resistance contribution would be very small as compared to the resistance between the isolated clusters. We do not expect the results to be affected by these clusters very close to the electrodes.

### 3. Results

The size distribution of the clusters was a lognormal distribution as shown in figure 2(a). However the distribution of inter-cluster distance (figure 2(b)) was Gaussian. The average clusters size was $(4.8 \pm 0.2)$ nm whereas the average inter-cluster spacing was determined to be $(12.3 \pm 0.6)$ nm.

Figure 3 shows the measured resistance in the temperature range 205–340 K for the nanocluster assemblage described above. There is a rapid increase of resistance with decrease in temperature which suggests that an activated conduction is taking place in the system. This type of activated behaviour has also been reported in granular metals [7] and in gold nanocrystalline arrays at temperatures above 100 K [8, 9]. In an earlier study on

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**Table 1.** Deposition conditions used for cluster deposition using NANODEP60 system.

| Sample description                                      | Isolated Au clusters between inter-digitated electrodes |
|---------------------------------------------------------|--------------------------------------------------------|
| Argon gas flow                                          | 60 sccm                                                |
| Aggregation distance                                    | 140 mm                                                 |
| Base pressure                                           | $8 \times 10^{-7}$ mbar                                 |
| Working pressure                                         | $2 \times 10^{-5}$ mbar                                 |
| Power                                                   | 125 watts                                               |
| Duration of deposition                                  | 3 min                                                  |

Figure 1. SEM picture of the electrodes across which the isolated Au nanoclusters were deposited. (a) Image showing the interdigitated fingers of electrodes. (b) A higher resolution picture revealing the individual electrodes and the small clusters between the electrodes.
Fe–X (X = Au, Pd, and Pt) nanocluster films that consisted of mutually separated nanoclusters due to surface oxidation, it was shown that the electrons in the clusters can be considered to be localised due to Anderson localisation \[^{[10]}\]. The transport of current between the clusters was due to near neighbour hopping or variable range hopping. A similar situation exists for the present system where there is a large separation between the metal clusters and there is little or no overlap between the wave functions of the clusters.

Assuming that the resistance data follows the general hopping law:

\[
R(T) = B T^{-m} \exp \left( \frac{T_0}{T} \right)^x,
\]

where \(R\) is the resistance, \(T_0\) is a characteristic temperature and \(B\) and \(m\) are material dependent constants, the analysis was carried out using Zabrodskii and Zinov’eva method of analysis \[^{[11]}\]. This method gives an estimate of the exponent \(x\) which decides whether the hopping is due to near neighbour hopping (NNH), \((x = 1)\), Mott Variable Range Hopping, \((x = 1/2)\) or Efros Shklowski Variable Range Hopping, \((x = 1/4)\). Equation (1) can be written in the form:

\[
\ln [W(T)] = \ln (x T_0^x) - x \ln (T),
\]

where

\[
W(T) = - (\partial \ln R / \partial \ln T).
\]
The slope of the straight line obtained by plotting ln \((W)\) and ln \((T)\) yields an approximate value of the exponent \(x\). The inset of figure 3 shows this plot and reveals two regions with different slopes exhibiting a crossover between two different resistance behaviours. The slope for the data between 230 and 340 K was determined to be \(0.96 \pm 0.31\). The lower temperature part from 205 to 229 K displayed a very high value of slope which is explained later as due to a different conduction mechanism.

Having obtained a value of the exponent \(x\) close to 1, we take the applicable hopping mechanism in this system to be a near neighbour hopping and fit the observed resistance directly to the NNH activated behaviour

\[
R(T) = R_0 \exp\left(\frac{T_0}{T}\right).
\] (4)

The fits are shown in figure 4 and a comparison of the parameters obtained from Zabrodskii and Zinov’eva method and those obtained from the fit using equation (4) is given in table 2.

| Method          | \(x\)         | \(T_0\) (K) |
|-----------------|---------------|-------------|
| Z–Z method      | 0.96 \(\pm\) 0.31 | 1762 \(\pm\) 10 |
| Fit to \(R(T) = R_0 \exp(T_0/T)\) | 0.98 \(\pm\) 0.11 | 1516 \(\pm\) 10 |

The activation energy \(T_0\) for metallic clusters has been shown to coincide with the Coulomb blockade energy in the limit of small tunnelling conductance [12], and this condition is found to be applicable since the inter-cluster separation is large. A spherical cluster of radius \(r\) has a capacitance given by \(C = 4\pi \varepsilon r\). For the electron to hop to a cluster of capacitance \(C\), it requires charging energy \(e^2/2 C\). The average cluster size for this system was 4.8 nm \(\pm\) 0.2 nm. The temperature corresponding to the average charging energy is then estimated to be 1738 K. This agrees reasonably well with the value of \(T_0\) that was obtained from the fits to the resistance data. This shows that NNH with an activation energy due to Coulomb blockade effect [13] plays a major role in determining the properties of the system between 230 and 340 K.

The value of the exponent \((x)\) for the data in between 205 and 230 K obtained was 11.18 \(\pm\) 0.68. This value is extremely high in the context of electron hopping mechanisms for which the exponents usually lie between 0 and 1. So it was clear that the hopping may not be the appropriate electron transport mechanism in this temperature region. The observed behaviour in our system was identified as a logarithmic temperature dependence of conductance given by \(\sigma = a + b \ln T\), where \(a\) and \(b\) are material dependent constants. This temperature dependence is similar to that observed in certain granular metals [14].
3.1. Origin of logarithmic temperature dependence

The exact origins of the logarithmic dependence of conductivity are still being debated and are a subject of current interest \[15\]. The application of Ambegaokar–Eckern–Schoen (AES) model \[16\] to a system with local fluctuations of inter cluster voltages leads to logarithmic temperature dependence of the effective conductance. Efetov and Tschersich have shown that this logarithmic dependence is valid in any dimension \[17\]. According to this model, important physical properties of such systems are described in terms of a parameter called the dimensionless tunnelling conductance, \( g_0 = G/(e^2/\hbar) \), where \( G \) is the average tunnelling conductance between neighbouring clusters and \( e^2/\hbar \) is the quantum of conductance. The temperature dependence of conductivity has been shown \[4\] to be given by:

\[
\sigma(T) = \sigma_0 [1 - (1/\pi z g_0) \ln (g_0 E_c/T)],
\]

where \( E_c \) is the charging energy of an individual grain and \( z \) is the coordination number i.e. the number of neighbours for a single site on the array. The data in the temperature region 205–229 K was fitted to this model (figure 5). From the value of the slope, an estimate of the dimensionless tunnelling conductance comes out to be \( g_0 = 9.85 \times 10^{-4} \). This small value of the tunnelling conductance is consistent with the large average inert-cluster separation of 12 nm between clusters.

This is the first observation of logarithmic temperature dependence in a nanocluster assembled structure. Logarithmic temperature dependence was observed in disordered systems as well as systems with reduced dimensions. These were systems exhibiting weak localisation or electron–electron interaction effects \[15\]. There are reports on granular metals exhibiting this behaviour by Simon et al \[15\] and Gerber et al \[19\]. The logarithmic dependence was observed in disconnected Pb films from 77 to 0.05 K \[20\], in under-doped \( La_{2-x}Sr_xCuO_4 \) crystals \[21\], granular niobium nitride films \[15\] and in some of the nanocrystalline samples earlier. This behaviour has been observed in some cermet systems \[24, 25\] also. In these systems it is observed that the logarithmic temperature dependence is very weak and occurs over a limited temperature range only \[17\].

It may be mentioned here that some of the above experimental results \[15, 18, 19\] show the logarithmic temperature dependence of resistivity rather than conductivity whereas the theoretical models developed for understanding this mechanism show that the conductivity, and not the resistivity should follow a logarithmic dependence (please see the discussion on page 510 of the review paper by Beloborodov et al \[4\]). In Au nanocluster assemblage we have observed a logarithmic dependence of conductance which is according to the theoretical models.

3.2. I–V Characteristics of the nanocluster assemblage

Nonlinear I–V characteristics as well as nonzero threshold voltages may emerge as a consequence of the Coulomb blockade in a system \[4, 22\]. So I–V measurements were also carried out on the gold nanocluster assembly.

Figure 5. The resistance versus temperature data showing fit to the equation \( 1/R(T) = a + b \ln T \). Inset showing the linearity of the conductance data when plotted with \( \ln T \).
In I–V measurements recorded in figure 6, the nonlinear increase of current with voltage is evident, showing the presence of Coulomb blockade in the system. The differential conductance ($\frac{dI}{dV}$) is obtained from the I–V characteristics and is found to reveal a dip in the conductance. This dip is found to increase with the decreasing temperature. Figure 7 shows the ($\frac{dI}{dV}$) versus $V$ plot at 240 K revealing the dip at zero-bias. This dip is attributed to the presence of Coulomb blockade and the full width at half minimum of the conductance dip is given by [23]:

$$V_{1/2} = \frac{5.439 N K_B T}{e}, \quad (6)$$

where $N$ is the number of uniform junctions in series, in a symmetric linear array.

The dip in conductance is fitted to a Gaussian curve and the value of full width at half minimum $V_{1/2}$ is found to be 5.2 V. The value of $V_{1/2}$ does not depend on any of the system parameter other than the number of junctions $N$. Substituting the values for $V_{1/2}$ and $T$ in equation (6) the number of junctions $N$ in the system is estimated to be 46. The calculation [23] is based on a uniform array of junctions whereas in our system we have a
A random array of nanoclusters. So we apply a random walk model to estimate the number of junctions. The average distance \(D\) between the interdigitated electrodes is 86 nm. Considering the electron makes a random walk from one electrode to the other with the step \(l\) being the average inter-cluster distance of 12.3 nm the number of junctions can be estimated using the equation:

\[
D = \frac{l}{N},
\]

where \(D\) is the distance travelled, \(l\) is the step size and \(N\) is the number of steps. Substituting the value of \(D\) and \(l\) the number of steps in travelling from one electrode to the other comes out to be 49. Excluding the first and the last step the number of hopping steps in our system would be 47 which is in agreement with the number of junctions estimated from \(V_{1/2}\).

4. Conclusions

In conclusion, an assemblage of isolated Au nanocluster was successfully prepared between inter-digitated electrodes using a nanocluster deposition system. Transport measurements revealed a nearest neighbour hopping conductivity in the temperatures range 230–340 K with an activation energy equal to the average cluster Coulomb charging energy. Between 205 and 229 K the conductivity behaviour was identified as logarithmic, with a temperature dependence given by \(\sigma = a + b \ln T\) as suggested by the AES model. The presence of Coulomb Blockade was also confirmed from the nonlinear \(I–V\) characteristics. The number of random hopping steps between nanoclusters that an electron takes in going from one electrode to the other comes out to be in good agreement with the estimated number of junctions in a linear array of junctions.

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