Three-dimensional percolation effect on electrical conductivity in films of metal nanoparticles linked by organic molecules

K. -H. Müller,* G. Wei, B. Raguse, and J. Myers

Commonwealth Scientific and Industrial Research Organization, Telecommunications and Industrial Physics, Sydney 2070, Australia
(Received 1 August 2003; published 9 October 2003)

We study experimentally and theoretically the electrical conductivity of films made of gold nanoparticles linked by alkanedithiol molecules. The dependence of the conductivity on the length of the alkanedithiol molecule and on the thickness of the nanoparticle films at room temperature is investigated. We describe theoretically conductance between adjacent metal nanoparticles in terms of single electron tunneling along the linker molecules. Due to variations in the separation gaps between neighboring nanoparticles a film can be approximated by a network of widely varying tunnel conductances and the film conductivity can be described in terms of percolation theory. We demonstrate that the expected exponential decrease of the conductivity with increasing length of linker molecules is weakened by the presence of high conductance percolation pathways and we show that due to three-dimensional current percolation the conductivity of the nanoparticle films becomes film thickness dependent.

I. INTRODUCTION

It has been shown in previous investigations that the electrical conductivity in films of metal nanoparticles linked by organic molecules can be understood as being due to single electron tunneling between neighboring nanoparticles along the linker molecules.[1–5] The theoretical description of the conductance of a realistic nanoparticle film becomes intricate because of the inherently strong disorder present in most nanoparticle assemblies. At least three types of disorder can be distinguished. First, the overall global structural disorder in the topology of the assembly; second, the local structural disorder due to nanoparticle size variations and fluctuations in the separation gaps between adjacent nanoparticles; and third, possible local charge disorder due to random immobile offset charges in the substrate and in the linker molecules. The most important disorder affecting the conductivity of the film at room temperature is the separation gap disorder[5] because the tunnel conductance between adjacent nanoparticles depends exponentially on the separation gap. Monte Carlo simulations have been used to study the effects of certain types of disorder on the conductance in one-dimensional (1D) and 2D nanoparticle arrays.[6–10] Disorder was taken into account in the form of variations in particle size, capacitative coupling between particles, and offset charges. Unfortunately, these calculations can only be applied to relatively small particle assemblies which poorly resemble a real nanoparticle film. We have shown in previous work[5] that the temperature dependence of the electrical conductance of gold nanoparticle films linked by alkanedithiol molecules can be well understood in terms of bond percolation theory where the film is approximated by a random network of widely varying tunnel conductances.

In this paper we use the percolation approach to demonstrate that local disorder in the form of fluctuations in the separation gaps between adjacent nanoparticles can enhance the film conductivity and reduce the dependence of the conductivity on the length of the linker molecule. We further show that separation gap disorder causes the conductivity of the film to become film thickness dependent. Our percolation approach to model the conductivity of nanoparticle films has a resemblance to the description of the conductivity of doped semiconductors where conductivity is described in terms of variable range hopping.[11] 2D to 3D crossover of conductivity has been investigated previously in granular metal-insulator thin films by Kapitulnik and Deutscher.[12] The importance of 2D percolation in thin metal films was first shown by Voss *et al.*[13] as well as Kapitulnik and Deutscher.[14]

This paper is organized as follows: In Sec. II we develop a theoretical model for the electrical conductivity of a disordered metal nanoparticle film linked by organic molecules by using the bond percolation approach, describing the films as networks of widely varying tunnel conductances. In Sec. III we describe our gold nanoparticle film preparation procedure and conductivity measurements. In Sec. IV we compare the experimental and theoretical conductivities of films with different alkanedithiol linkers and different thicknesses. The conclusion is given in Sec. V.

II. THEORY

Consider two adjacent metal nanoparticles in a nanoparticle film, each surrounded by organic linker molecules (see Fig. 1). The electrostatic potential difference between the metal nanoparticles is eV and the separation gap is L. The electrical current I which flows between the two metal nanoparticles due to single electron tunneling is given by[5,15]

$$I = \frac{8\pi^2 e}{h} \sum_{r,l} \{ f(E_l - eV)[1 - f(E_r - E_c)] - f(E_r)$$
$$\times [1 - f(E_l - eV - E_c)] \} |M_{lr}|^2 \delta(E_r - E_l). \quad (1)$$

Here e is the electron charge and h is the Planck constant. The sum is over all single electron states l and r of the left and right nanoparticle, respectively. In our case the metal nanoparticles are sufficiently large so that the single electron
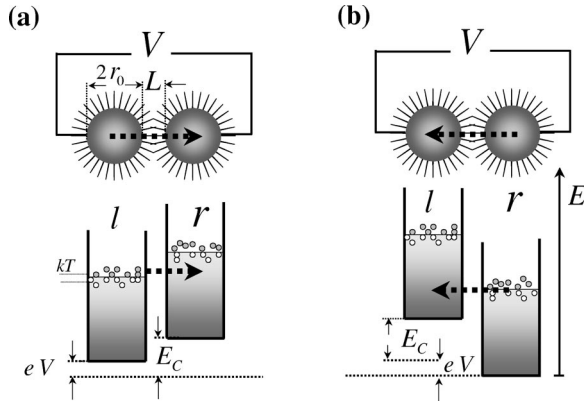
(a)   **(b)**

FIG. 1. Schematic energy diagram of two neighboring metal nanoparticles of size $2r_0$ with separation gap L. The electrons in the normal-metal nanoparticles are described in terms of free electron Fermi gases. The electrostatic potential between the nanoparticles is eV. (a) When an electron tunnels from the left (l) to the right (r) nanoparticle it has to overcome the energy $E_c - eV$. (b) When an electron tunnels from the right (r) to the left (l) nanoparticle it has to overcome the energy $E_c + eV$.

level spacing is negligibly small. The function f is the Fermi-Dirac distribution, $f(x) = (1 + e^{(x-E_F)/kT})^{-1}$, where T is the absolute temperature, k is the Boltzmann constant, and E_F is the Fermi energy of the electron gas in the metal nanoparticles. The quantities M_{lr} are the tunneling matrix elements and E_l and E_r are the energy levels of the single electron states. E_c is the Coulomb blockade energy (Coulomb charging energy) required to move an electron from one nanoparticle to a neighboring one.[16] Figures 1 (a) and (b) show energy diagrams illustrating the tunneling of electrons from the left (l) metal nanoparticle to its neighbor nanoparticle on the right (r) and vise versa. The roles of the electrostatic potential difference eV and the Coulomb blockade energy E_c are indicated in Fig. 1. In Eq. (1) the first part in the curly brackets describes tunneling from left to right [Fig. 1(a)] and the second part the tunneling from right to left [Fig. 1(b)]. The Coulomb blockade energy E_c in a film of nanoparticles can be estimated by the expression[3]

$$E_c = \frac{e^2}{8\pi\epsilon_0\epsilon_r} \frac{L}{r_0(r_0 + L)}, \tag{2}$$

where ϵ_0 is the permittivity of free space, ϵ_r the relative dielectric constant of the molecules surrounding the nanoparticles, and r_0 is the radius of the nanoparticles. The average size of our gold nanoparticles is $2r_0 = 8$ nm with $\sim 20\%$ size fluctuations. The separation gap formed by the shortest alkanedithiol linker molecules is $L = 0.81$ nm and the relative dielectric constant of these molecules is $\epsilon_r = 2.2$ (hydrocarbons).[17] Using Eq. (2) one finds the value $E_c = 13.6$ meV. In our case $eV \ll E_c \ll E_F$ as $eV \simeq 0.1$ mV, which enables us to simplify Eq. (1). One derives[5]

$$I = G_T V, \tag{3}$$

where G_T is the tunnel conductance

$$G_T \propto e^{-\beta L} \frac{1 - (1 - E_c/kT)e^{E_c/kT}}{(1 - e^{E_c/kT})^2}. \tag{4}$$

Here, the attenuation parameter β is a constant which describes the tunneling of electrons along the organic linker molecules. The value of β can be obtained either by estimating the matrix elements M_{lr} using a tight-binding model[18,19] or directly from experiment.[5,20]

Our nanoparticle films are strongly disordered because the films are formed from fractal-like nanoparticle aggregates.[21] In such strongly disordered nanoparticle films, the separation gaps L and the Coulomb blockade energies E_c fluctuate strongly and thus the tunnel conductances G_T between neighboring pairs of nanoparticles in the film vary over many orders of magnitude. Therefore, our films can be viewed as networks of widely varying tunnel conductors where the behavior of the network can be described in terms of percolation theory.[11,22,23] In percolation theory the conductivity σ of a network of widely varying conductors is given by

$$\sigma = \sigma_0 e^{-\xi_{cd}}. \tag{5}$$

Here, σ_0 is a constant and ξ_{cd} is determined by

$$p_{cd} = \int_0^{\xi_{cd}} h(\xi)d\xi, \tag{6}$$

where p_{cd} is the bond percolation threshold for a film conductor network of thickness d and $h(\xi)$ is the probability density distribution of finding, anywhere in the film, a pair of adjacent nanoparticles connected by a tunnel conductance $G_T \propto e^{-\xi}$, where

$$\xi = \beta L - \ln\frac{1 - (1 - E_c/kT)e^{E_c/kT}}{(1 - e^{E_c/kT})^2}. \tag{7}$$

We have shown in a previous paper[5] that at room temperature the fluctuations in E_c can be neglected against fluctuations in L since the thermal energy kT is sufficiently large compared to E_c. Equation (6) then simplifies and becomes

$$p_{cd} = \int_0^{L_{cd}} h_L(L)dL. \tag{8}$$

$h_L(L)$ is the probability density distribution of finding a gap of size L between a pair of adjacent nanoparticles and $L_{cd} = \xi_{cd}/\beta$. Since details of the $h_L(L)$ distribution of our films are unknown, we assume for simplicity that $h_L(L)$ is composed of two distributions. First, a square distribution of width ΔL centered around L_0 where L_0 is equal to the length of the linker molecule, and second, a distribution at very large L corresponding to the wide separation gaps across voids. Separation gaps L which are smaller than the linker length L_0 ($L < L_0$) are formed if during the film formation process insufficient amounts of linker molecules are present while a nanoparticle attaches to another nanoparticle. The case $L > L_0$ arises because the nanoparticle films are composed of aggregates of irregular fractal-like structures. Using Eq. (8) and denoting the volume fraction of voids by f_v, we find
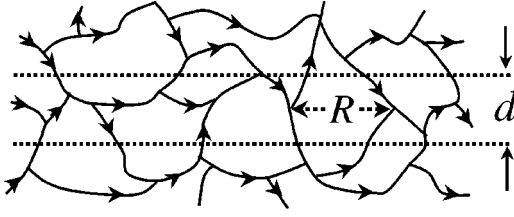
FIG. 2. Schematic view of the skeleton network of the percolating current (Ref. 26). $\mathcal{R}$ is the correlation radius. Dashed lines show the boundaries of the film of thickness d.

$$L_{cd} = \frac{p_{cd}\Delta L}{1-f_v} + L_0 - \frac{\Delta L}{2}. \qquad (9)$$

In order to estimate the percolation threshold p_{cd} we employ the concept of the correlation radius $\mathcal{R}$, where[11,12,24,25]

$$\mathcal{R}(p_{cd}) = (2r_0 + L_0)(p_{cd} - p_c)^{-\nu} \qquad (10)$$

and $p_{cd} > p_c$. Here, p_c is the bond percolation threshold of an infinitely thick dense film (bulk material) and ν is the critical parameter,[25] $\nu = 0.9$. The percolation radius $\mathcal{R}$ represents the average distance between the nodes of the skeleton (or backbone) network, shown in Fig. 2, which embodies the major current pathways, neglecting dead ends and redundant current loops.[11] If p_{cd} is close to p_c then the correlation radius $\mathcal{R}$ largely exceeds the film thickness d and the major current pathways within the film break into isolated parts that are not connected to each other. By increasing p_{cd} gradually one can make $\mathcal{R}$ smaller than the film thickness d such that fully connected current pathways fall within the film. Thus, a rough estimate of p_{cd} can be obtained by equating the correlation radius to the film thickness[26,27]

$$\mathcal{R} = Ad, \qquad (11)$$

where A is a constant expected to be of the order of unity. Finally, from Eqs. (5), (9), (10), and (11) one obtains the following expression for the electrical conductivity of a disordered film of metal nanoparticles linked by organic molecules

$$\ln \frac{\sigma}{\sigma_0} = -\beta \left(L_o - \frac{\Delta L}{2} + \frac{\Delta L}{1-f_v} \left[p_c + \left(\frac{2r_0 + L_0}{Ad} \right)^{1/\nu} \right] \right). \qquad (12)$$

Equation (12) reveals that the electrical conductivity σ of a nanoparticle film depends on the parameter β which is a measure of the conductance of the organic molecules, the separation gap probability distribution characterized by L_0, ΔL, and the volume fraction of voids f_v, the percolation threshold p_c of the infinitely thick film, the average size $2r_0$ of the nanoparticles, the factor A defined by Eq. (11), and the thickness d of the film. Instead of estimating p_{cd} using Eqs. (10) and (11), one can also employ the method of percolation renormalization as outlined by Neimark.[24] This leads to the same expression (12) with $A \simeq 4$ where the value of A arises from the difference between the 2D and 3D percolation thresholds of triangular (fcc) lattices.[25]

III. NANOPARTICLE FILM PREPARATION AND EXPERIMENT

Suspensions of gold nanoparticles in toluene were prepared by reducing hydrogen tetrachloroaurate with sodium borohydrate as described by Brust et al.[28,29] Small amounts of alkanedithiol linker molecules, i.e., $HS(CH_2)_n SH$, $n = 2,4,8,12$ or 15, were added to the suspensions which caused the nanoparticles to form fractal-like aggregates.[21] The resultant mixture was diluted with n-hexane followed by filtration through an Isopore membrane filter under vacuum to form nanoparticle films on the Isopore membrane.[30] The concentration of linker molecules and the time for nanoparticle aggregation were chosen such that the nanoparticle aggregates were large enough not to pass through the <200 nm wide pores of the membrane. More details regarding the film preparation are described by Raguse et al.[31] The final films had the form of disks of radius $b = 9.6$ mm. The thickness of the films could be varied by adjusting the total number of gold atoms initially contained in the mixture. The average thickness d of a film was estimated by using the expression

$$d = \frac{N_{Au}a_0^3(r_0 + L_0)^3}{4\pi b^2 f_p(1-f_v)r_0^3}, \qquad (13)$$

where N_{Au} is the number of gold atoms in the gold nanoparticle suspension before filtering. N_{Au} was determined from the chemical preparation procedure. In Eq. (13) a_0 is the lattice constant of bulk gold, $a_0 = 0.407$ nm; r_0 is the average radius of our nanoparticles, $r_0 = 4$ nm; f_p is the filling fraction of densely packed nanoparticles (fcc lattice), $f_p = 0.74$. Using a Powerlab/4SP potentiostat from ADinstruments, the conductances G_{tot} of our films were measured at room temperature by contacting 40 mm long, closely-spaced gold contacts, separated by the distance $w = 0.85$ mm, onto the disk-shaped nanoparticle films. The total applied voltage was less that 10 V which ensured that the average voltage drop between adjacent nanoparticles in the film was much less than E_c/e. Finally, the conductivities σ of the films were determined by applying the expression

$$\sigma = \frac{G_{tot}w}{2bd}. \qquad (14)$$

Figure 3 shows a scanning electron microscope (SEM) image of one of the nanoparticle films. The image reveals strong structural disorder and indicates that our films are composed of nanoparticle aggregates. The film in Fig. 3 is made of nanoparticles of size $2r_0 \simeq 15$ nm in order to show the structure more clearly by SEM. The film has an average thickness of only about four nanoparticle diameters and the filter membrane (substrate) is visible as dark regions.

IV. RESULTS AND DISCUSSIONS

Instead of determining the attenuation parameter β in Eq. (4) from a complicated tight-binding model calculation we take β directly from conductance measurements on self-assembled monolayers of alkanethiol molecules of different lengths formed on gold substrates.[20] For our calculations we
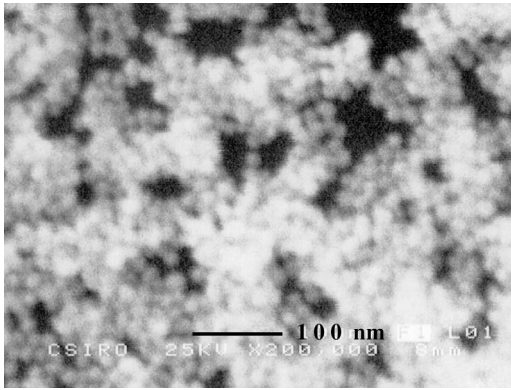
FIG. 3. SEM image (top view) of a thin Au nanoparticle film where the Au nanoparticles are about 15 nm in size. Dark areas show the membrane substrate.

use the value $\beta = 11.5$ nm^{-1}. The separation gap L_0 between nanoparticles was taken as the length of the alkanedithiol molecule plus the average length of the sulphur-gold bonds at both ends of the linker molecule[32] assuming an angle of 30^0 between molecule and normal of the nanoparticle surface. We find $L_0(n=2) = 0.81$ nm, $L_0(n=4) = 1.02$ nm, $L_0(n=8) = 1.46$ nm, $L_0(n=12) = 1.89$ nm, and $L_0(n=15) = 2.23$ nm. The average size of our gold nanoparticles is $2r_0 = 8$ nm and we roughly estimated the volume fraction of voids f_v from SEM images and found $f_v \approx 0.3$. The percolation threshold for the infinitely thick film was taken as $p_c = 0.119$ which is the bond percolation threshold of an fcc lattice (densely packed nanoparticles).[25] For the constant A in Eq. (11) we used $A = 0.45$. A similar value for A was previously found in investigations on granular metal-insulator thin films by Kapitulnik and Deutscher.[12] In order to estimate the degree of separation gap disorder in our films, the relative width $\Delta L/L_0$ of the $P_L(L)$ distribution was varied and the measured and calculated conductivities were compared.

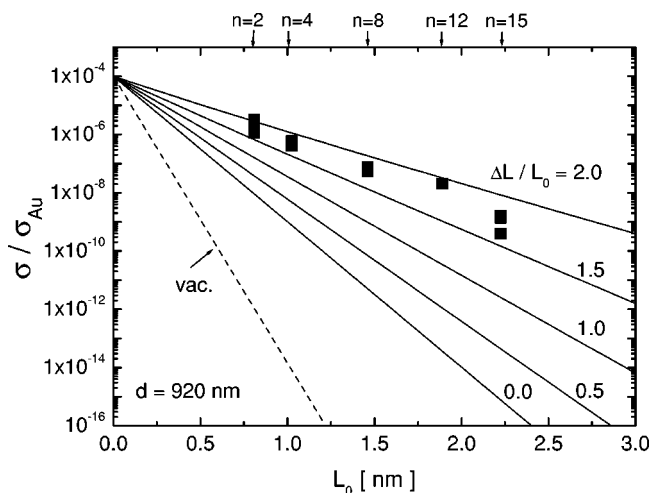The squares in Fig. 4 show the measured conductivity of

FIG. 4. Measured and calculated conductivity of gold nanoparticle films of the same thickness d normalized to the conductivity of bulk gold vs the separation gap L_0.
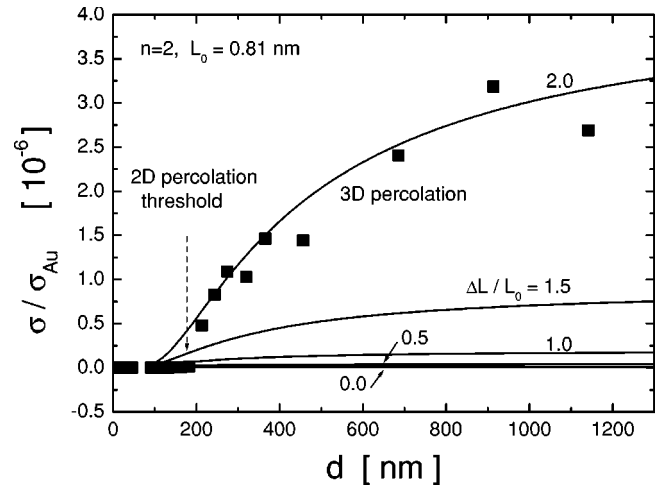

FIG. 5. Measured and calculated conductivity of gold nanoparticle films normalized to the conductivity of bulk gold vs the film thickness d for $n=2$ alkanedithiol linker molecules.

several gold nanoparticle films of estimated thickness $d = 920$ nm [Eq. (13)], normalized to the conductivity of bulk gold ($\sigma_{Au} = 4.55 \times 10^7 \Omega^{-1}$ m^{-1}) for alkanedithiol linker molecules, HS(CH$_2$)$_n$SH, of different length, where $n = 2$, 4, 8, 12, and 15. As can be seen from Fig. 4, the measured film conductivity decreases by about three orders of magnitude when the length of the linker molecule is increased from $n = 2$ to $n = 15$. The experimental data can be fitted by $\ln(\sigma/\sigma_0) = -\beta_{\text{eff}} L_0$, where $\beta_{\text{eff}} = 5$ nm^{-1} which is significantly smaller that the attenuation parameter $\beta = 11.5$ nm^{-1}. The full curves in Fig. 4 show the calculated values of σ/σ_{Au} obtained from Eq. (12). The value for σ_0 in Eq. (12) was determined from the experimental data by extrapolating σ/σ_{Au} to $L_0 = 0$ which gives $\sigma_0 = 10^{-4}\sigma_{Au}$. In the calculation the relative width $\Delta L/L_0$ of the $P_L(L)$ distribution [Eq. (8)] was varied from 0 to 2. As can be seen from Fig. 4, the calculation agrees well with the experimental data if a wide $P_L(L)$ distribution is chosen, i.e., $1.5 < \Delta L/L_0 < 2$. The calculation displayed in Fig. 4 reveals that the presence of separation gap disorder in the film enhances the conductivity as the current is able to find percolation pathways of larger tunnel conductances. The calculation predicts (Fig. 4) that in the case of no separation gap disorder, i.e., $\Delta L/L_0 = 0$ and $\ln(\sigma/\sigma_0) = -\beta L_0$, the conductivity changes over seven orders of magnitude when the linker molecule is varied from $n = 2$ to $n = 15$. The dashed curve in Fig. 4 corresponds to vacuum tunneling without linker molecules for a hypothetical film with $\Delta L/L_0 = 0$, using the work function of gold as the tunnel barrier. This demonstrates that the linker molecules assist single electron tunneling which, together with current percolation, dramatically enhances the conductivity of the films.

The squares in Fig. 5 show the measured electrical conductivity of gold nanoparticle films normalized to the conductivity of bulk gold versus the film thickness d for $n=2$ alkanedithiol linker molecules. The experimental data reveals a 2D percolation threshold below $d = 200$ nm where the nanoparticle aggregates (average diameter ~ 200 nm)

have formed a 2D connected network. For an average film thickness d larger than 200 nm the conductivity increases rapidly as 3D percolation takes over. The full lines in Fig. 4 are the calculated σ/σ_{Au} values resulting from Eq. (12) where the relative width $\Delta L/L_0$ of the $P_L(L)$ distribution is varied from 0 to 2. A wide $P_L(L)$ distribution with $\Delta L/L_0 \approx 2$ fits the experimental data best. If $\Delta L/L_0 = 0$, i.e., if the film has no separation gap disorder, the conductivity is independent of the film thickness d [see Eq. (12)] and $\sigma/\sigma_{Au} \approx 10^{-8}$. For a film thickness greater than 1200 nm (not shown here) the measured conductivity decreased due to the formation of microcracks observable under SEM.

The conductivity of most materials is independent of the size and shape of the material. In the case of our nanoparticle films, where 3D current percolation takes place, the conductivity becomes film thickness dependent as an increase in film thickness enhances the chance that the current will find pathways of higher conduction along the third dimension, i.e., the thickness direction.

V. CONCLUSION

The electron transport mechanism in films of metal nanoparticles linked by organic molecules is due to single electron tunneling. Electron tunneling takes place along the linker molecules across the separation gap L between adjacent nanoparticles. At low temperatures tunneling becomes partially impaired by the repulsive Coulomb blockade energy. Our gold nanoparticle films are strongly disordered as they are composed of fractal-like nanoparticle aggregates in which the separation gaps L vary. These separation gap variations cause strong fluctuations of the tunnel conductances between adjacent nanoparticles which allows us to view our films as networks made up of widely varying tunnel conductances. Such networks can be described by bond percolation theory where the conductivity of the system is determined by the tunnel conductance at the percolation threshold. The dependence of the percolation threshold on the film thickness can be estimated from the correlation radius of percolation.

Experimentally, we have found that at room temperature the conductivity of our films decreases exponentially with increasing length of the linker molecule. The observed decrease of the conductivity is much weaker than expected from the β parameter of the alkanethiol molecule. Our theoretical investigations have revealed that at room temperature the fluctuations in the Coulomb blockade energies can be neglected and that the weak exponential dependence of the conductivity on L_0 can be well explained by our model if a wide separation gap distribution with $\Delta L/L_0 \approx 2$ is assumed. Separation gap disorder enhances the conductivity because the electrical current is able to find percolation pathways which are made up of large tunnel conductances.

When the thickness of our nanoparticle films is increased new percolation pathways for electron tunneling become available which results in an increase in conductivity. We have shown that the experimentally observed increase in conductivity with thickness can be well modeled in terms of percolation theory using the concept of the correlation radius and assuming a wide separation gap distribution with $\Delta L/L_0 \approx 2$. Whereas most materials do not show conductivity which depends on thickness, by utilizing the disorder of our nanoparticle films we are able to produce materials with thickness dependent conductivity and defined 2D or 3D current percolation behavior.

*Electronic address: karl.muller@csiro.au

[1] R.M. Hill, Proc. R. Soc. London, Ser. A **309**, 377 (1969).

[2] R. Kiernan and D.W. Stops, Nature (London) **224**, 907 (1969).

[3] B. Abeles, P. Sheng, M.D. Coutts, and Y. Arie, Adv. Phys. **24**, 407 (1975).

[4] R.H. Terrill *et al.*, J. Am. Chem. Soc. **117**, 12 537 (1995).

[5] K.-H. Müller, J. Herrmann, B. Raguse, G. Baxter, and T. Reda, Phys. Rev. B **66**, 075417 (2002).

[6] A.A. Middleton and N.S. Wingreen, Phys. Rev. Lett. **71**, 3198 (1993).

[7] A.S. Cordan, A. Goltzené, Y. Hervé, M. Mejias, C. Vieu, and H. Launois, J. Appl. Phys. **84**, 3756 (1998).

[8] H.-O. Müller, K. Katayama, and H. Mizuta, J. Appl. Phys. **84**, 5603 (1998).

[9] A.S. Cordan, Y. Leroy, A. Goltzené, A. Pépin, C. Vieu, M. Mejias, and H. Launois, J. Appl. Phys. **87**, 345 (2000).

[10] J. Johansson and D.B. Haviland, Phys. Rev. B **63**, 014201 (2000).

[11] B.I. Shklovskii and A.L. Efros, *Electronic Properties of Doped Semiconductors, Springer Series in Solid-State Sciences*, Vol. 45 (Springer-Verlag, Berlin, 1984).

[12] A. Kapitulnik and G. Deutscher, J. Phys. A **16**, L255 (1983).

[13] R.F. Voss, R.B. Laibowitz, and E.I. Alessandrini, Phys. Rev. Lett. **49**, 1441 (1982).

[14] A. Kapitulnik and G. Deutscher, Phys. Rev. Lett. **49**, 1444 (1982).

[15] A. Nitzan, Annu. Rev. Phys. Chem. **52**, 681 (2001).

[16] K.K. Likharev, Proc. IEEE **87**, 606 (1999).

[17] *CRC Handbook of Chemistry and Physics*, 75th ed., edited by D.R. Lide (CRC Press, Boca Raton, 1994).

[18] V. Mujica, M. Kemp, and M.A. Ratner, J. Chem. Phys. **101**, 6849 (1994).

[19] A. Onipko, Y. Klymenko, L. Malysheva, and S. Stafström, Solid State Commun. **108**, 555 (1998).

[20] R.E. Holmlin, R. Haag, M.L. Chabinyc, R.F. Ismagilov, A.E. Cohen, A. Terfort, M.A. Rampi, and G.M. Whitesides, J. Am. Chem. Soc. **123**, 5075 (2001).

[21] D.A. Weitz and M. Oliveria, Phys. Rev. Lett. **52**, 1433 (1984).

[22] V. Ambegaokar, B.I. Halperin, and J.S. Langer, Phys. Rev. B **4**, 2612 (1971).

[23] M. Pollak, J. Non-Cryst. Solids **11**, 1 (1972).

[24] A.V. Neimark, Zh. Eksp. Teor. Fiz. **98**, 611 (1990) [Sov. Phys. JETP **71**, 341 (1990)].

[25] M.B. Isichenko, Rev. Mod. Phys. **64**, 961 (1992).

[26] B.I. Shklovskii, Phys. Lett. **51A**, 289 (1975).

[27] B.I. Shklovskii, Phys. Status Solidi B **83**, K11 (1977).

[28] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, and R. Whyman,

J. Chem. Soc., Chem. Commun. **7**, 801 (1994).

[29] M. Brust, D. Bethell, D.J. Schiffrin, and C.J. Kiely, Adv. Mater. **7**, 795 (1995).

[30] Isopore membrane filter, Millipore Co.

[31] B. Raguse, J. Herrmann, G. Stevens, J. Myers, G. Baxter, K.-H. Müller, T. Reda, A. Molodyk, and V. Braach-Maksvytis, J. Nanopart. Res. **4**, 137 (2002).

[32] S.N. Yaliraki, M. Kemp, and M.A. Ratner, J. Am. Chem. Soc. **121**, 3428 (1999).