Eur. Phys. J. D **24**, 291–294 (2003)
DOI: 10.1140/epjd/e2003-00144-3

THE EUROPEAN PHYSICAL JOURNAL D

Electrical measurements of nanoscale bismuth cluster films

M. Schulze[1,2], S. Gourley[1,2], S.A. Brown[1,2,a], A. Dunbar[1,2], J. Partridge[1,2], and R.J. Blaikie[1,3]

[1] Nanostructure Engineering Science and Technology (NEST) Group and The MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Canterbury, Christchurch, New Zealand
[2] Department of Physics & Astronomy, University of Canterbury, Christchurch, New Zealand
[3] Department of Electrical & Computer Engineering, University of Canterbury, Christchurch, New Zealand

Received 10 September 2002
Published online 3 July 2003 –

Abstract. A range of percolating atomic cluster films, with nanoscale overall dimensions, have been studied using a combination of *in situ* and *ex situ* electrical transport measurements, together with field emission electron microscopy and atomic force microscopy. Bismuth clusters with mean diameter 20 nm were deposited between electrical contacts defined by electron beam lithography. The morphology of the films can be understood within percolation theory, and the electrical measurements show complex behaviour characteristic of both percolation effects and modification of the cluster films by current flow and by oxidation.

PACS. 73.63.-b Electronic transport in nanoscale materials and structures – 36.40.-c Atomic and molecular clusters – 64.60.Ak Renormalization-group, fractal, and percolation studies of phase transitions
81.07.-b Nanoscale materials and structures: fabrication and characterization

1 Introduction

Atomic clusters can be seen as nanoscale building blocks which might eventually be useful for the fabrication of nanoelectronic devices [1,2]. While there have been some significant efforts to incorporate nanoscale particles into devices [3–5], research in this field is still in its infancy. This is especially true for the case of atomic clusters, which we define to be nanoparticles produced in the gas phase by techniques such as inert gas aggregation [1].

The simplest cluster-based devices that can be imagined are those with a pair of electrical contacts on a planar insulating substrate between which clusters are deposited [2,6]. The random nature of the deposition process suggests that such cluster assembled films might be understood within percolation theory [7,8]. Indeed, finite size effects in the percolation threshold have recently been observed [6]: the surface coverage, p, at which the cluster film becomes conducting is found to decrease to values as low as $p \sim 0.2$ when the spacing between the contacts is $L \sim 5$, and the width of the contacts, w, is large (where L and w are measured in units of the cluster's diameter). In comparison, the percolation threshold is $p_c = 0.5927461$ [7] for infinite 2D square lattices, while in the more realistic 2D continuum percolation model (where the positions of the clusters are not restricted to a lattice) $p_c \sim 0.68$ [9].

Since the correlation length (in broad terms, the mean size of the connected structures formed by the clusters) exhibits power law behaviour it turns out [6] that the onset of conductivity also follows a power law

$$p_{\text{onset}}(L) - p_c \propto L^{-z} \tag{1}$$

where $z = 0.75$ is the inverse of the power law exponent for the correlation length in a 2D system [7]. The low surface coverages at which the contacts can be connected for sufficiently small L leads to the observation that the connection can only be formed by a wire-like structure.

In this paper we investigate the morphology and electrical characteristics of atomic cluster films with rather larger L than in our previous work [6], using a combination of *in situ* and *ex situ* techniques. The objective of this study was to correlate the electrical resistance of the cluster films with the structure of the films, but as will be seen below, a number of interesting new effects make the correlation of conductance and morphology a complex task.

2 Experimental

A beam of bismuth clusters with a mean diameter of 20 ± 5 nm is generated in an inert-gas aggregation source [1]. Deposition onto a substrate with prefabricated contacts is controlled by a shutter. Typically six pairs of NiCr/Au contacts are defined on each substrate, using a combination of standard optical and electron beam lithography (EBL) techniques. For these electrical measurements

[a] e-mail: simon.brown@canterbury.ac.nz

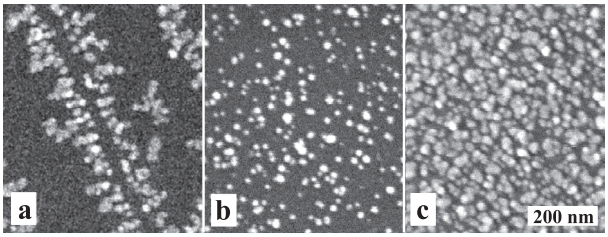

Fig. 1. Field emission SEM images of cluster films (a) at low coverage on HOPG, (b) at low coverage on SiN, and (c) at higher coverage on SiN. Note that the 20 nm Bi clusters used in these experiments diffuse on HOPG but not on SiN.

the substrate is the highly insulating and flat surface of a 200 nm SiN layer grown on a Si wafer, although microscopy has also been performed on cluster films deposited on unpatterned SiN and highly oriented pyrolitic graphite (HOPG). The non-uniform cluster beam together with the six contact pairs allows a number of films with slightly different coverages to be prepared simultaneously. Interdigitated contacts allow for a high w/L ratio in a compact area [6]. Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FE-SEM) have been used to characterise the samples after deposition.

During deposition a DC bias (5 mV with a 1 GΩ series resistance to limit the current flow) is applied between one or more pairs of contacts and the current is measured as a function of deposition time. At a clearly defined time during the deposition the cluster network becomes conducting over the length scale defined by the separation of the contacts and the current increases over several orders of magnitude. After the onset of conduction the current increases only slowly. Each contact pair is placed far enough from its neighbours so that it is effectively isolated from them (see Eq. (1)) *i.e.* conduction between any pair of contacts ($L \sim 10{-}20$) begins long before conduction between neighbouring pairs of contacts ($L \sim 5000$).

3 Results and analysis

3.1 Morphology of cluster films

Bismuth clusters have been deposited onto both HOPG and unpatterned SiN. Examples of FE-SEM images of cluster films are shown in Figure 1. In Figure 1a the ~ 20 nm bismuth clusters deposited have aggregated into islands at step edges and defects through diffusion on the atomicly smooth HOPG surface. The diffusion of such large bismuth clusters on HOPG will be discussed elsewhere. In contrast, Figure 1b shows that there is no evidence that clusters of the same size diffuse on SiN: they stick where they land. The immobility of clusters on the SiN surface allows the use of simple percolation models to describe low density cluster films.

Figure 1c shows a higher coverage cluster film on SiN. It can clearly be seen that the mean cluster size is comparable to that of the low density film, but that there is a degree of coalescence between neighbouring particles, and that a conducting path is likely to have formed. Note however that both with AFM and FE-SEM it is difficult to distinguish whether neighbouring clusters are in electrical contact or whether there is a small gap or non-conducting "neck" between particles [10].

Clearly in the higher density example shown in Figure 1c the simple 2D lattice and continuum models of percolation become less appropriate because the cluster film is only quasi 2-dimensional. When the density of clusters in the *first* layer on the surface (p_1) becomes significant the probability that an incoming cluster arrives in a second or higher layer (equal to p_1) also becomes significant. It is straightforward to set up differential equations describing the probabilities that a newly arriving cluster arrives in the first layer or in any higher layer. The solution of these equations is

$$p = -\ln(1 - p_1) \tag{2}$$

where p is the total coverage. Note that p can take values greater than 1, but that $0 \leq p_1 \leq 1$. As p_1 increases toward 1 the likelihood that a newly arriving cluster lands in the first layer becomes vanishingly small. Equation (2) indicates that in the real (quasi-2D) cluster film, the total coverage needed to achieve a conducting path through the first layer is $p = -\ln(1 - p_c) = 1.13$ in the continuum model ($p_c \sim 0.68$). Thus, in cluster deposited films, a total coverage equivalent to more than one monolayer is needed to achieve percolation in the first layer. Note however that this correction is approximately linear at low coverages and therefore it does not significantly affect the power law of equation (1).

We have used AFM to measure the cluster film thicknesses as near as possible to various pairs of contacts. We have developed a technique whereby one AFM tip is used to make a scratch in the surface of the cluster film and a second (undamaged) tip is used to measure the thickness. In this way we are able to compare the measured film thickness with the estimated critical film thickness (see below). Conduction is observed only for films which exceed the critical thickness (except in rare cases which can be attributed to the random/statistical nature of the deposition process).

Figure 2 shows a plot of the critical film thickness obtained from AFM measurements *versus* the inverse of the deposition rate. It is clear that the measured film thickness at the onset of conduction increases with decreasing deposition rates. We believe this to be due to a deterioration of the film which takes place during (and after) deposition of the clusters. This is likely to be due to the effects of residual oxygen in our high vacuum system (pressure around 10^{-6} torr) and/or to the presence of a thin film of water on the surface of the substrate.

If the oxidation rate is R_0 and the flux of arriving particles is Φ (both R_0 and Φ in nm/s), then the actual thickness at the percolation threshold d_a is related to the nominal critical thickness d_c by

$$(\Phi - R_0)d_a = \Phi d_c \tag{3}$$

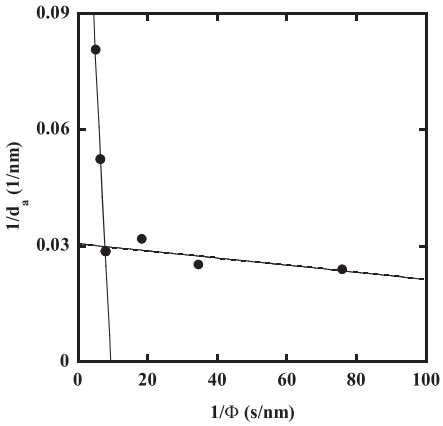

Fig. 2. Actual critical thickness d_a obtained from AFM data as a function of the deposition rate Φ. d_a is the critical thickness for an infinite 2D system obtained from the measured critical thickness for systems with 200 nm and 400 nm contact separations using a correction based on the data in Figure 5b in reference [6]. Inverse quantities have been plotted to allow comparison with equation (4).

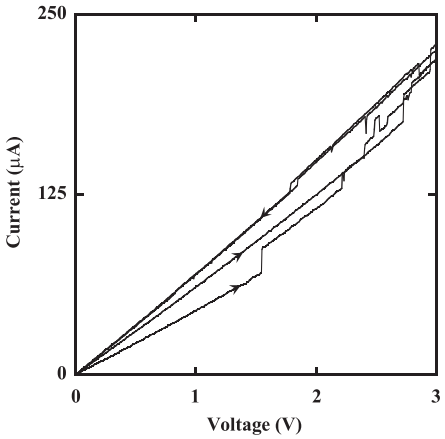

Fig. 3. Typical $I(V)$ data for a cluster film at 300 K showing an initial ohmic low voltage curve with steps in the conductance at higher voltages. Two complete voltage cycles are shown, with the first following the higher resistance, lower current path for increasing bias. For decreasing bias the path followed is almost the same for both cycles.

and if $\Phi < R_0$ a conducting film will not be obtained: at sufficiently low Φ this is indeed found to be the case in the experiments. From equation (3) we would expect

$$1/d_a = 1/d_c - (R_0/d_c)1/\Phi \tag{4}$$

and so the slope and intercept of a straight line in Figure 2 would give R_0, and the critical thickness in the absence of oxidation d_c. However, Figure 2 shows that the actual behaviour is more complex than in the simple model of equation (4). The best interpretation of Figure 2 at present is that there might be two *effective* deterioration rates, perhaps due to the different effects of oxidation on the cluster film as a whole and on certain critical parts of the film such as narrow 'necks' between clusters.

3.2 Conductivity measurements

As noted above, the electrical conductivity of the cluster films were measured during deposition in order to observe the onset of conduction and the formation of a percolating path through the film. Immediately after the onset of conduction low bias $I(V)$ measurements were performed on each of the six pairs of electrical contacts. (Initially the voltage was restricted to the range 0–100 mV). When a finite conductance (*i.e.* $10^{10}\ \Omega > R > 10^3\ \Omega$) was observed the $I(V)$ curves were generally linear, or nearly linear, indicating predominantly ohmic conduction. Contact pairs with resistance values greater than $10^{10}\ \Omega$ were deemed to be open circuit and the $I(V)$ curves showed capacitive/charging behaviour (to be discussed elsewhere). There is a strong correlation between the measured film resistance and the degree to which the critical film thickness has been exceeded, *i.e.*, thicker films have higher conductivity (as is expected).

Following the initial $I(V)$ measurements samples were transferred to a liquid helium cryostat (as quickly as possible to minimise oxidation) for more extensive conductivity measurements as a function of both voltage and temperature. Figure 3 shows $I(V)$ data for a typical sample at 300 K and biases up to 3 V. As the voltage reaches $\sim$ 1 V a series of steps in the $I(V)$ curve become apparent. These steps appear to occur randomly (the positions of the steps are not reproducible) however there are a number of features of Figure 3 that are observed quite generally both at room temperature and low temperatures (down to 4 K). Firstly, the samples start out with relatively high resistances and on repeated cycling of the bias voltage the majority of the steps increase the conductance of the sample. Once a sufficient number of steps have occurred at low biases, steps are only observed when the voltage range is extended beyond that which has been used previously. Another consistent feature is that between the random steps some resistance values (*i.e.* the slopes of the $I(V)$ curves) are repeated on successive voltage cycles (although not necessarily in the same voltage range) *i.e.* there are preferred conductance values which are consistently achieved on repeated cycles. This is particularly the case when ramping the voltage downwards: in Figure 3 the slope of the $I(V)$ curve for decreasing bias is almost unchanged over the full range of voltages used, and for both cycles shown.

We have also monitored the conductance of many samples over long time periods, after the deposition of clusters has ended. A fixed bias (usually 5–30 mV) is applied and the current monitored as in Figures 4 and 5. In general, a slow increase in the resistance of the film is observed, which can be attributed to a gradual oxidation process similar to that discussed above. After sufficiently long periods in vacuum, or if samples are exposed to air for periods longer than one day, films that initially showed strong

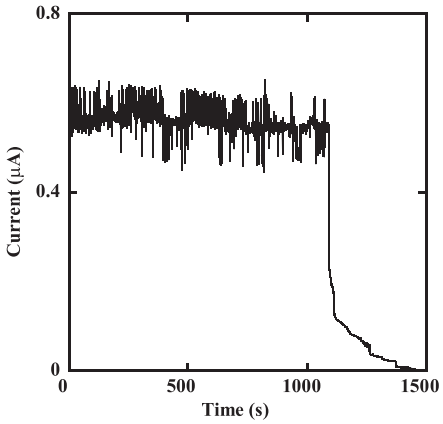

Fig. 4. Current as a function of time for a typical cluster film. $V = 30$ mV, $T = 300$ K. In this case there is a slow decrease in current along with random telegraph noise, before a dramatic change in resistance on exposure of the cluster film to nitrogen gas with some oxygen contamination.

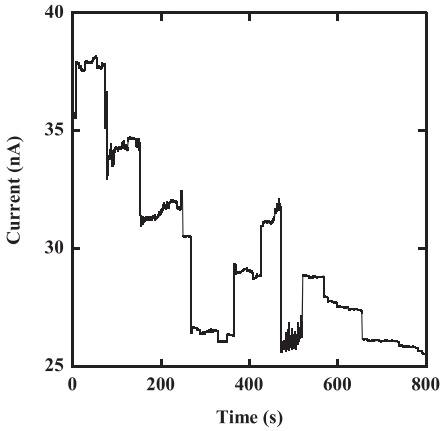

Fig. 5. Current as a function of time for a typical cluster film. $V = 5$ mV, $T = 300$ K. In this case there are a series of random steps superimposed on a slow decrease in current.

connections and relatively low resistances (~ 20 kΩ) became highly resistive ($R > 10^{10}$ Ω).

In addition to the long-term drift upwards in the resistance *versus* time data, it is frequently observed that there are step-wise changes in resistance. These steps take two forms. Firstly, as shown in Figure 4, there may be repeated high frequency steps in resistance between relatively well defined levels (in Fig. 4 there are three levels but in other cases there are only two levels, in others there are more). This behaviour is characteristic of random telegraph noise and is often associated with systems in which random oscillations of the state of the system can occur. One such example is the oscillations in the resistance of a Si-MOSFET that occur due to tunneling of charge onto defects in an oxide layer (see for example [11] and references therein).

The second form of step-wise behaviour is shown in Figure 5. Random steps occur between relatively well defined levels, but on a much longer timescale than in Figure 4, and are mainly decreases in current. These steps are similar to the steps in resistance observed in the $I(V)$ curves shown in Figure 3, except in this case the deterioration of the film generally causes steps upwards in resistance, whereas steps induced by current flow are generally decreases in resistance.

4 Discussion and conclusions

The steps in resistance induced by either current flow, random telegraph noise, or oxidation of the cluster films can be understood if it is first noted that there are two distinct kinds of step-wise behaviour *i.e.* some resistance levels are reproducible and others irreproducible. Some resistance levels can be achieved repeatedly, and in this case the appropriate model is similar to that of reference [11]: tunneling of carriers from a conducting path onto a nearby defect or island, and subsequent perturbation of current flow in the original path by the charged defect or island, will lead to reproducible resistance levels for each specific charge state of the island. The irreproducible step-wise behaviour is best considered as being due to current driven changes in the morphology of the films, such as coalescence of clusters due to resistive heating of a narrow "neck" between clusters, or electro-migration of atoms between clusters. In general, any set of $I(V)$ or $I(t)$ data result from a combination of both reproducible and irreproducible effects and it is only by performing repeated measurements that the two effects can be distinguished.

In summary, the electrical characteristics of bismuth cluster films have been studied in conjunction with SEM and AFM measurements and a consideration of percolation theory. The results indicate that a modified version of the continuum percolation model can account for the structure of the films, and that steps in the resistance of the films can be accounted for in a model which includes both tunneling and current-driven changes in the film morphology. Oxidation of the films is an important issue, even in a high vacuum environment, but it is expected that a new ultra-high vacuum deposition system will eliminate this complication.

References

1. P. Milani, S. Iannotta, *Cluster Beam Synthesis of Nanostructured Materials* (Springer, Berlin, 1999)
2. P. Melinon *et al.*, Int. J. Mod. Phys. B **9**, 339 (1995)
3. W. Chen *et al.*, Appl. Phys. Lett. **66**, 3383 (1995)
4. D. Ralph *et al.*, Phys. Rev. Lett. **78**, 4087 (1997)
5. C. Thelander *et al.*, Appl. Phys. Lett. **79**, 2106 (2001)
6. J. Schmelzer *et al.*, Phys. Rev. Lett. **88**, 226802 (2002)
7. D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, 1985)
8. H.E. Stanley, Rev. Mod. Phys. **71**, s358 (1999)
9. A. Okazaki *et al.*, Phys. Rev. E **54**, 3389 (1996)
10. The coalescence of clusters is in itself an interesting phenomenon and molecular dynamics simulations will be discussed elsewhere: S. Hendy, S.A. Brown (submitted)
11. D.H. Cobden, B.A. Muzykantski, Phys. Rev. Lett. **75**, 4274 (1995)