Self-Assembled Cluster Nanostructures and Nanodevices

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ABSTRACT

This paper reviews the achievement of *contacted* electronic nanowire-based devices which are self-assembled from atomic clusters. The focus is on the assembly of nanowires but many aspects of controlled cluster assembly are under investigation. In all cases, simple cluster deposition and standard nanofabrication techniques are used. The self-assembly of nanowires between contacts, avoiding the more usual slow manipulation of wires into position, means that these devices show a great deal of promise for commercial applications.

Keywords: Nanowires, Atomic Clusters, Self Assembly, Nanostructures, Deposition Control

1 INTRODUCTION

Atomic clusters can be conveniently made in a size range (100nm to 0.5nm) that bridges the gap between the limits of current lithographic fabrication technologies for integrated circuits and the atomic/molecular regime which is the ultimate future of electronic devices. Hence, devices fabricated from atomic clusters offer the opportunity to continuously scale between the devices of the present and future, using a single technology. In addition, the fundamental physics and chemistry of atomic clusters changes dramatically over the same size range, offering an opportunity for fabrication of devices with remarkable new properties. [1,2]

Nanowires have been previously demonstrated by many groups to be effective components in devices ranging from chemical sensors to transistors, but difficulties in the assembly of wires between contacts have so far remained unsolved. In this work, two different methods of formation of contacted nanowires are demonstrated based on self-assembly of cluster chains.

Chains resembling wires have been previously achieved through diffusion to the naturally occurring step-edges on highly oriented pyrolitic graphite (HOPG) [3,4]. However, since the position of these surface defects is random, the placement of the wires cannot be controlled. In addition, graphite is not a microelectronics compatible substrate. Several attempts have been made to use cluster diffusion in conjunction with surface patterning techniques to control cluster assembly. In one study, a regular array of cluster structures was created by diffusion to an array of focused ion beam engraved defects on a graphite substrate [5]. Clusters have also been aligned along the edges of optical photoresist templates on Si [6] and SiO_2 [7] to form uncontacted wire-like chains. Previously, contacting to cluster-assembled wires has only been achieved using a relatively complex electrodeposition / lift-off technique [8]

The final part of this paper discusses the assembly of a range of structures through atomic / cluster diffusion. These structures include compact and highly ramified islands, as well as unusual rectangular nanorods.

2 EXPERIMENTAL

The experiments discussed here can be divided into 2 distinct groups. In the first, lithography is used to produce samples on to which clusters are deposited with the aim of producing contacted nanowires. In the second, extremely smooth surfaces on HOPG are used to allow atomic material (or small clusters) to diffuse and aggregate into novel nanostructures.

The focus in this work is on Sb and Bi nanostructures. This is because these semi-metallic materials have very interesting electronic properties, and because cluster production is straightforward. We note however that clusters of a very wide range of materials can be produced using a variety of standard techniques. [9]

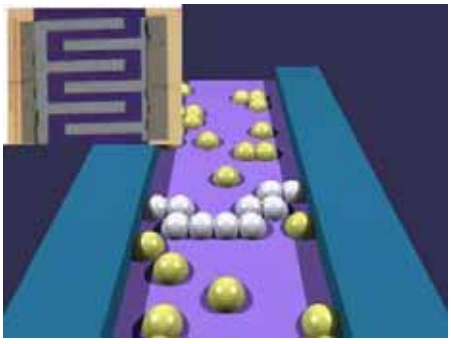

Fig. 1. Schematic of clusters assembled into a nanowire between a pair of contacts with (inset) a micrograph of a pair of the interdigitated contacts used in the percolation experiments.

2.1 Percolation and Templated Assembly

Prior to cluster deposition, contacts and templates for the cluster assembled wires were prepared using standard optical lithography techniques. [10] For the percolating devices, interdigitated NiCr/Au contacts are prepared on SiN substrates. For templated devices, both passivated and unpassivated V-grooved Si <100> substrates are utilized. Electrical contacts are defined at the ends of passivated V-grooves. Clusters are produced in an inert gas aggregation source [9], that generates a molecular beam of clusters. Wires are produced when the clusters impinge on the lithographically patterned substrates. The wires are characterized by *in situ* electrical conductivity measurements and *ex situ* scanning electron microscopy (SEM), and field emission SEM (FE-SEM).

2.2 Self-Assembly: fractals, stars and rods

Both Bi and Sb nanostructures were grown on HOPG (grade ZYB) in an ultrahigh vacuum environment and characterized *ex situ* with SEM, FE-SEM, atomic force microscopy (AFM), and electron backscatter diffraction (EBSD). The substrates were cleaved in air then heated overnight at 650K under UHV to remove adsorbed contaminants. Bismuth (Bi_2) and Antimony (Sb_4) were thermally evaporated and deposited at room temperature. The flux and coverage were monitored with a calibrated quartz crystal microbalance. The coverage is described in monolayers (ML), where we define 1ML=3.4Å, the average distance between atoms in bulk Bi.

3 RESULTS AND DISCUSSION

Percolating nanowire devices are discussed first, followed by templated devices. We then turn to a discussion of self-assembled fractals, stars and rods.

3.1 Percolation

The simplest possible cluster assembled device consists of a random assembly of clusters between a pair of electrical contacts. Such an assembly of clusters is well described by percolation theory [11], which is a well-established method of understanding the properties of randomly interconnected sites. In infinite two dimensional systems there is a well-defined percolation threshold for a surface coverage of 0.5927. In small square systems (i.e. spaces between electrical contacts) the percolation threshold remains substantially unchanged but it broadens dramatically, ensuring that measurements on a single device will yield essentially random results. It turns out [12], however, that the choice of interdigitated contact geometries (Fig. 1. (inset)) causes the percolation threshold to shift to very low coverages. We have demonstrated this effect experimentally and shown that there is a clear onset of conductivity in the cluster system at the percolation threshold. [12] Importantly, in small systems the percolation threshold occurs for coverages of around 0.2 when the contact spacing is ~6 cluster diameters. In this case, the connection between the contacts must consist of an approximately linear chain of clusters, as shown schematically in Fig. 1.

We note that the rapid shift of the percolation threshold with the spacing between the contacts, described above, provides an unusual and useful technique to control the deposition of nanoparticles. By selecting a particular contact spacing, and terminating deposition at the percolation threshold (onset of conduction), it is possible to engineer cluster films with precisely defined surface coverages.

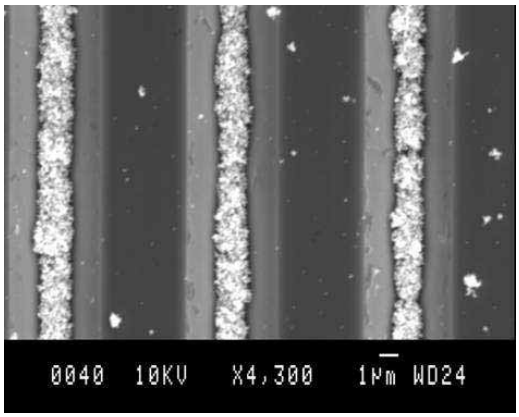

Fig. 2. Sb wires self-assembled at the apexes of three V-grooves. Note the almost total absence of clusters from the plateaus between the V-grooves.

3.2 Templated Assembly

The percolating nanodevices described in the previous section may well prove useful in applications such as gas sensors, where the properties of nanowires allow dramatically increased sensitivity and functionality, but the placement of the nanowire is not important. In many devices, for example transistors, precise placement of the nanowire in the device is critical. For this reason we have developed a templating technique which achieves this objective.

The templates used in this work are V-grooves etched into silicon substrates using standard lithographic processes. Figure 2 shows three wires assembled at the apexes of the grooves. In this case the wires are about 1 μm in width, but using 20-30nm clusters we have demonstrated single wires as small as 50nm in 5μm V-grooves [14]. If, as expected, this 1:100 ratio can be maintained when both smaller clusters and smaller V-grooves are used, this technique should allow high precision placement of extremely narrow nanowires. This is a necessary enabling step along the path to working self-assembled nanoelectronic devices (such as transistors)

which are much smaller than will be achievable by even the most sophisticated lithographic technologies of the future. It should be emphasized that the wire width is controlled simply by the number of clusters deposited (time of deposition).

One of the most extraordinary features of Fig. 2 is the almost total absence of clusters from the plateaus between the V-grooves. This is obviously extremely beneficial since the possibility of parallel conduction paths is eliminated. The absence of the clusters from the plateaus has been shown to be because the clusters bounce away from them. The same bouncing effect is responsible for the absence of clusters from the upper parts of the V-groove walls – the clusters simply bounce (or slide) to the apex.

The bouncing / sliding effect can be controlled by the velocity of the clusters [10], which itself is determined by the flow rate of the inert gas that is supplied to the cluster source. The effect can be understood, at least qualitatively, within a model developed to describe bouncing liquid droplets [13]. It has been shown [10,13] that Bi clusters, which wet the surface of the substrate much more than Sb clusters, require higher velocities or larger cluster sizes in order to increase the incident kinetic energy sufficiently to allow the clusters to bounce. Bi clusters are therefore significantly 'stickier'.

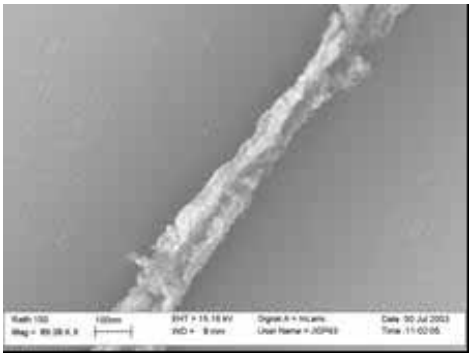

Fig. 3. 100nm wide Au wire at the apex of a V-groove formed by using an Sb cluster-assembled nanowire as an etch mask.

The placement of electrical contacts at the ends of the V-grooves prior to cluster deposition allows an onset of conduction to be observed and subsequent electrical characterization to be performed *in situ*. Sb nanowire resistances of ~10-20kΩ at room temperature are routinely obtained for Sb wire widths ~400nm. [13] The low electrical conductivity of bulk antimony is largely responsible for these relatively high resistances, but the granular nature of the wires means that there is more scattering of carriers than in single crystal wires. It has been shown that annealing, by passing an electric current, can significantly increase the conductivity of the wires. The current fuses clusters together and allows control over the granularity of the wire. Highly granular wires are preferred in some gas sensing applications [8], but crystalline wires are preferred in most electronic devices.

Finally, it has been shown that the templating technique can be used to produce wires of materials other than the cluster material. In Fig. 3 a ~100nm Sb wire has been used as an etch mask to achieve pattern transfer into a gold film that was evaporated onto the V-grooved substrate prior to cluster deposition. [14] The Au wire is still ~100nm wide.

3.3 Self-Assembly: fractals, stars and rods

Sb_4 tetramers diffuse on HOPG either until they aggregate by colliding with one another or until they reach a step edge on the graphite surface [15]. Fig. 4 shows typical fractal islands (upper two thirds of the image) which have grown by diffusion limited aggregation [16]. In the lower part of the image, a step edge can be clearly seen, decorated by a series of islands which have grown outwards away from the step edge. All these structures have heights in the region of 10-40nm, and typical overall lengths (branch widths) on the scale of ~1μm (~100nm). These structures result from a balance between thermodynamic and kinetic contributions to the growth process [17]. A detailed understanding of the assembly of these structures requires modeling of diffusion of tetramers both upwards and around the edges of the structures.

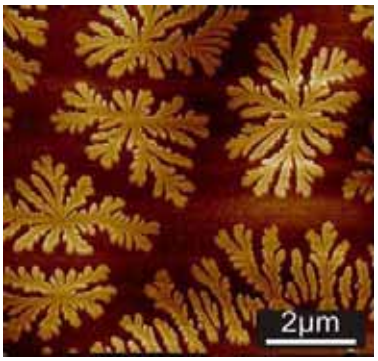

Fig. 4. AFM image of typical Sb structures on HOPG.

Bismuth produces very different nanostructures on HOPG as shown in Fig. 5. On HOPG terraces, bismuth dimers typically diffuse until they aggregate together, producing elongated star structures with a clear central axis. Unlike the case of Sb, the aggregates have a clear symmetry, which is a result of the crystal symmetry of the Bi nanostructures. The main axes of neighboring islands are also aligned with one another at 60 degree angles, indicating that the hexagonal symmetry of the HOPG surface plays an important role in the assembly of these structures.

In the case of the step-edge nucleation, the structures produced are nanorods, which are also oriented with the high symmetry directions of the substrate (Fig. 5, bottom). These structures result from a combination of the effects of

a highly anisotropic diffusion field and of edge diffusion, which ensures the transport of material to the tips of the rods.

Detailed EBSD studies of both stars and nanorods show that all these Bi structures grow with {01-12} planes of Bi parallel to the {0001} HOPG surface and that <11-20> directions of the Bi crystals are aligned with the <10-10> directions on the graphite surface.

AFM studies show that the stars and rods occur with mean heights that are always within a narrow range (1.0±0.3 nm and 2.0±0.3nm respectively). This indicates that the growth mode is highly two dimensional, again in strong contrast to the case of Sb.

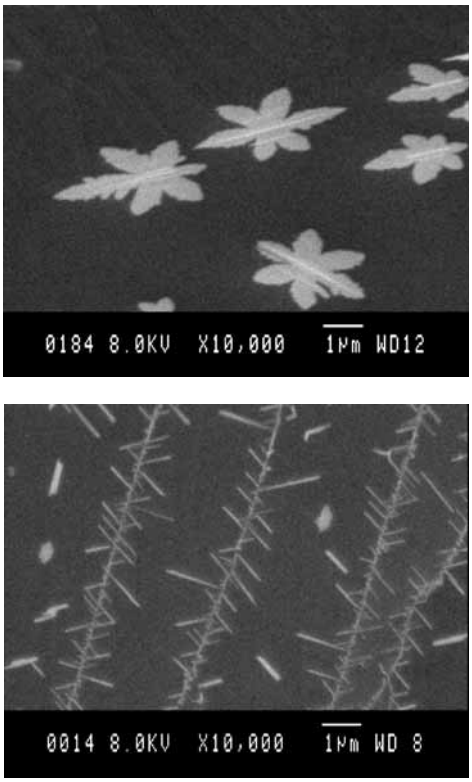

Fig. 5. SEM images of typical Bi structures on HOPG. Top: Aligned Bi stars on HOPG terraces. Bottom: aligned Bi nanorods at HOPG step edges.

It is important to emphasise that the images presented here provide only typical examples of the predominant Sb and Bi structures produced [18]. Control of the type of structure is achieved by varying the flux and total dose of deposited material.

4 CONCLUSIONS

Two different methods of formation of contacted cluster nanowires have been presented. The first technique relies on a deep understanding of percolation theory and detailed simulations. [12] The second relies on surface texturing and self-assembly techniques. [10] Crucially, both technologies result in nanowires that are self-contacting and where electrical current can be passed through the wire as soon as it is formed. These techniques have been used successfully to produce Ag, Si, Bi and Sb nanowires. The smallest widths achieved are below 50nm, which is $1/100^{th}$ of the smallest lithographic features on the same devices. We have also demonstrated that cluster assembled nanowires can be used as etch masks to produce narrow wires of materials other than the cluster material. [14]

Growth of Sb and Bi islands on graphite provides a fascinating model system for the study of diffusion limited aggregation and related effects, and for the production of nanostructures that could have a variety of applications. In the medium term we expect that such studies will have an important impact on the production of useful nano-electronic devices, such as the nanowires discussed here.

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