Dislocation of antimony clusters on graphite by means of dynamic plowing nanolithography

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Abstract

Antimony clusters of different shapes and dimensions have been obtained by evaporating antimony on graphite. The dependence of the shape and dimensions of the particles on the evaporation parameters (effective layer thickness, temperature, pressure) is discussed. A characterisation of the different structures is presented. In particular, the decoration of graphite steps is discussed. Clusters have been dislocated by means of dynamic plowing nanolithography, both in vector and in image pattern mode. The dependence of the energy needed to dislocate a cluster on its dimensions and position is discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

There is a growing interest in the study of clusters, i.e., mesoscopic structures having a structural size of a few nanometres. Since such particles have physico-chemical properties differing from usual bulk properties, the growth of thin films and nanostuctures on different substrates represents a powerful way to synthesise new materials with interesting properties. As a general rule, when a cluster is deposited on a substrate, it may either meet another cluster, diffuse on the surface and form an island (nucleation event), or be captured by an already existing island (growth process). Also graphite steps or surface defects, e.g., nanometre-sized pits produced in the first monolayer of the highly oriented pyrolytic graphite (HOPG) surface by oxidation, are possible nucleation centres [1].

A fractal island morphology can be preferentially obtained instead of a compact morphology if the rate of hopping diffusion of atoms on the substrate is larger than the rate of edge diffusion of adatoms along islands [2,3]. At low temperature the edge diffusion coefficient can be lower than the surface diffusion coefficient and fractal islands have been observed [4–7]. Moreover, by increasing the surface defect density on HOPG, a continuous variation of the island morphology is obtained, from extended ramified shapes to small compact shapes. An evolution from compact to ramified shapes can also occur on graphite surfaces as the mean size of deposited clusters increases. The diffusion and aggregation of large antimony clusters

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deposited on graphite is described in the literature [8–12].

The atomic force microscope (AFM) is able to modify samples not only by cutting and engraving different surfaces, but also by dislocating and repositioning surface structures [13–17].

The dislocation of surface structures can be achieved in different ways. Stiff well anchored structures on hard substrates may be dislocated in contact mode by increasing the force between the tip and sample during pushing. Applying the same method to weakly anchored structures, also with small repulsive forces, results in a “cleaning up” of the scanned area, because all the structures in the scanned surface are pushed outside or adhere to the tip. Further, depending on their stiffness, such structures can be damaged and altered. In order to avoid damages to the sample due to high interaction forces, images of soft samples and of weakly adhering particles are obtained in tapping mode. When the microscope is operated in tapping mode, a dither piezo vibrates the cantilever near its resonance frequency. The oscillation amplitude, that depends on the distance between the cantilever and sample, is kept constant by means of a feedback loop that changes the extension of the Z piezo, and hence the distance between the sample surface and the cantilever. The changes of the Z piezo extension are used to reconstruct the topography of the sample. Tapping mode may also be employed to cut and emboss the surface by dynamic plowing lithography (DPL) [18–20]. In DPL, modifications of the sample are obtained by changing the modulation amplitude applied to the dither piezo that drives the cantilever. On soft samples, the tip is likely to indent the sample surface and to induce elastic and plastic deformations. This technique, as well as the microscope employed in the experiments, is presented in details in a previous article [20].

On graphite, the vibrating amplitude is chosen in a way that no modifications (except elastic deformations) occur. Nevertheless, such amplitudes can be employed to displace weakly anchored structures on the surface.

In this article we present the results obtained with antimony clusters on graphite. These results show the capability of changing the position of such structures and provide some information about the adhesive energy between the structures and the substrate.

In Section 2, we present the samples and discuss the shape and dimensions of the antimony structures; in Section 3 we show the results obtained by dislocating such structures and discuss the dependence of the energy needed to dislocate them on their dimensions and position. The final Section 4 gives some concluding remarks.

2. Experimental set-up

Samples have been prepared by evaporating antimony molecules of Sb₂ on a freshly cleaved HOPG surface in a vacuum evaporation chamber (Edwards Vacuum Technology, Kirchheim, Germany). The deposited antimony had an effective layer thickness of about 3 nm. The deposition process was checked by a movable crystal quartz microbalance. A PT100 sensor, whose thermal properties are similar to those of the sample, has given a temperature reading of 35°C during evaporation. The mean pressure in the vacuum evaporation chamber was about 10⁻⁶ mbar.

In this article three characteristic types of antimony islands are presented: the isolated compact islands (Fig. 1a), the flower-shaped islands (Fig. 1b), and the ramified structures (Fig. 1c). These different structures were obtained under nearly the same evaporation conditions. We have observed a very sensitive dependence of the island morphology on the evaporation parameters and on the HOPG surface defect density. It might be possible that the growth of antimony molecules on the surface is influenced by the formation of superperiodic patterns [21] or by different electrical conductivity on HOPG terraces. These structures may also be contiguous.

The area of the isolated compact islands is in the range 0.01–0.04 μm². The area of the flower-shaped islands is in the range 0.01–0.3 μm², with a peak on 0.06 μm² for the sample presented in Fig. 1b. An histogram of about 900 islands is presented. In other cases the peak is around 0.15 μm², but islands larger than 0.3 μm² have never been observed. The volume is in the range 10⁻⁵–3 × 10⁻⁴ μm³, with
Fig. 1. (a) Isolated compact islands (scan range 6 × 6 μm², 512 × 512 pixels, height scale 61 nm). (b) Flower-shaped islands (scan range 15 × 15 μm², 512 × 512 pixels, height scale 36 nm); the insert (750 × 750 nm²) shows a single flower-shaped island. The plot of \( \log(S) = v \log(P) - K \), where \( P \) and \( S \) are the perimeter and the area of the flower-shaped islands, is presented. The coefficient \( v \) is 2.26 ± 0.03. Histograms of the area and of the volume are shown. (c) A ramified structure (scan range 1.5 × 1.5 μm², 100 × 100 pixels, height scale 26 nm) and the plot of \( \log(S) = v \log(P) - K \), where \( P \) and \( S \) are the perimeter and the area of the ramified structures. The coefficient \( v \) is 2.93 ± 0.02.
a peak on $6 \times 10^{-5} \, \mu m^3$. The average height is in the range 7–12 nm. The area of the ramified structures is in the range 0.15–1.5 $\mu m^2$. The volume is in the range $10^{-3}$–1.5 $\times 10^{-2}$ $\mu m^3$. The average height is in the range 7–10 nm.

The plot of log$(S)$ vs. log$(P)$ in the form log$(S) = v \log(P) - K$, where $S$ is the surface area, $P$ the perimeter, and $v$ and $K$ are constants, has been calculated for the flower-shaped islands and for the ramified structures. The constants $v$ and $K$ are related to the usual fractal dimension $D$ and the shape coefficient $\rho = P^{D}/S^{1/2}$; in particular, $v = 2D$ and $K = 2 \log(\rho)$ (see Ref. [22]). For the flower-shaped islands $v$ is $2.26 \pm 0.03$ (calculated over 900 islands) and for the ramified structures it is $2.93 \pm 0.02$ (calculated over 90 structures). Both plots are shown in Fig. 1b and c. Flower-shaped islands are quite 2D structures, while ramified structures are fractals. $\rho$ is 10 for the flower-shaped islands. This rather high value shows that these structures have a very complicated shape ($\rho$ is $\approx 10$ for an hexagon with six squares around, touching each side with only one point). Such a comparison cannot be drawn for the fractal ramified structures [22].

All structures show decoration effects of graphite steps. This can be observed in Fig. 1a and b.

The experimental set-up of the DPL using an AFM has been described in a previous article [20]. In this case the DPL is used to control and manipulate individual nanometre-sized antimony particles on HOPG surface. An interactive user interface has been added to the lithography software mode. Unlike surface imaging, where the tip movement is typically operated in a raster scan mode, lithography can also be operated in a vector scan mode. The lithography software provides a set of commands that permits line scans of arbitrary length and direction under defined scan speed and tapping force. Obviously this procedure is faster than the image pattern mode. To get an overview on the area of interest a normal scan can be performed. Afterwards the tip movement is controlled by a small mouse panel which allows the user to move the tip across the visualised topography area. Thanks to the hardware linearised
scanner unit the desired particle can be directly addressed. Within a negligible thermal drift and the accuracy of the scanner linearisation the repositioning can be performed very well. Both the vector and the image pattern lithography are presented.

All experiments have been performed at room temperature in air. Commercially available cantilevers (Pointprobe NCL-50, Nanosensors, Wetzlar-Blankenfeld, Germany) with length \( L = 225 \, \mu m \), width \( W = 38 \, \mu m \), thickness \( T = 7 \, \mu m \), resonance frequency \( F \approx 150 \, kHz \), and spring constant \( K = 31–71 \, N/m \) have been used. Since the silicon tip of these cantilevers is damaged after some hours of lithography, a cantilever with tungsten carbide coated tip (NT-MDT NSC12/W2C, Moscow, Russia, \( L = 90 \, \mu m \), \( W = 35 \, \mu m \), \( T = 2 \, \mu m \), \( F = 350 \, kHz \), \( K = 12–16 \, N/m \)) has been used for the last experiment (see below), where lithography has been being performed for longer times and forces were higher.

3. Results and discussion

We have operated DPL on graphite surfaces covered with flower-shaped islands. Fig. 2 shows a 10 \times 10 \, \mu m^2 area before (Fig. 2a) and after (Fig. 2b) DPL. The surface shown in Fig. 2 is roughly divided in two parts: the upper left part contains “well structured” flower-shaped islands, the bottom-right part several isolated clusters. The two parts are divided by a graphite step decorated with antimony clusters along the diagonal. Also the isolated clusters have been moved. Since it is rather difficult to single out the isolated clusters before and after the dislocation and to follow their movement, only the dislocation of flower-shaped islands is shown by means of white arrows. The result of the dislocation is shown in Fig. 2b.

The mask of the DPL, i.e., a grey scale pixel image encoding the manipulation amplitudes, contains four vertical “white” stripes, whose position is indicated by arrows outside the figure. In correspondence of these stripes, the vibration amplitude of the cantilever is increased of a 10-fold factor (writing amplitude), with respect to the “reading” regions (5 V instead of 0.5 V). When the tip is vibrating with the smaller “reading” amplitude, the clusters do not move. At the larger “writing” amplitude, the tip has enough energy to move the clusters.
The movement of the flower-shaped islands is influenced by the presence of other clusters or surface structures. In the experiment shown in Fig. 2, all flower-shaped islands move aside, till they are outside the modification zone. In other experiments with more stripes, flower-shaped islands have been moved all along the scanned area. The shape of the islands, and the mutual position of the single clusters is not altered, when the surface around is free from other clusters or surface structures. Only when the islands are pushed against some other islands, their shape is altered. Not compact islands may also be split up, usually in two parts, but this has happened very seldom.

In order to address a single flower-shaped island, and to control the movement more precisely, islands have been dislocated also in vector mode DPL. Fig. 3 shows a $3 \times 3$ $\mu m^2$ area with some flower-shaped Sb clusters. In Fig. 3b the little movement towards the right of the island “a”, obtained in vector mode DPL, is shown by means of a white arrow. Islands $r'$ and $r''$ have been used as reference. The beginning and the end of the arrow indicate the position of the centre of the island before and after the lithography. The movement is proportional to the length of the lithography vector. In Fig. 3c the movement, always towards the right, is larger. In Fig. 3d both “a”

![Dislocation by means of vector mode DPL. Differences in the shape of the islands and in the Y distances are due to thermal drift. All images have a scan range of $3 \times 3$ $\mu m^2$, a height scale of 40 nm and a scan resolution of 512 $\times$ 512 pixels. (a) Graphite surface covered with flower-shaped islands, whose position has been changed by means of vector mode DPL. (b) A white arrow indicates the performed little dislocation towards the right of the island “a”. The beginning and the end of the arrow indicate the position of the centre of the island before and after the lithography. Islands $r'$ and $r''$ have been used as reference. (c) The island “a” has been dislocated again towards the right. (d) Both “a” and “b” have been moved towards the left.](image-url)
and “b” have been moved towards the left. Note that this technique can be used to separate previously grouped clusters, as in the case of “b”.

Also ramified structures have been dislocated, but these larger structures do not keep their shape. The movement is very irregular. Fig. 4 shows a $8 \times 8 \, \mu m^2$ area modified with image pattern lithography. The arrows indicate the movement, when possible. Fig. 4b shows the result of the dislocation. Even if all structures are addressed by a stripe, islands A, B, C, and D do not move. Islands E, F, G, H, and K are split up into several parts. These parts, as well as the whole island, move in a very irregular way, and rotate sometimes. Only island J has been moved along the slow scan direction without altering its shape. This result shows that the ramified structures are not very compact, and that single parts are not strongly connected to the rest of the structure. Also the adhesion to the substrate is very different within different structures and within different dendritic arms of one structure.

Lithography experiments may be performed with different “writing” amplitudes. When writing with different amplitudes, it is evident that there is a threshold amplitude, below which certain flower-shaped islands are not moved. Such threshold amplitude depends (a) on the area of the island and (b) on its position (whether the island is on a graphite step or not). Fig. 5 shows the dependence of the threshold amplitude on island area for 54 flower-shaped clusters. Data have been collected by repeating lithography experiments with different amplitudes on the same scanning area. Each area value is the average of 14 measurements. The “reading” amplitude was 0.5 V. The plot suggests a linear dependence of the threshold amplitude on the area. The threshold amplitude has been plotted also as a function of the volume. In this case there is no clear dependence.

According to the Bowden and Tabor adhesion model, in the case of single asperities, the friction force is proportional to the contact area, i.e., $F^S = \tau S$, where the shear strength $\tau$ depends on the materials [23]. Since $\tau$ is the same for every island, the force needed to displace an island is proportional to the contact area. The elastic force of the cantilever is $F^E = k\delta$, where $\delta$ is the cantilever

Fig. 4. (a) Graphite surface covered with ramified structures (scan range $8 \times 8 \, \mu m^2$, 512 x 512 pixels, height scale 30 nm) modified with image pattern mode DPL. White arrows indicate the movement. (b) Result of the dislocation. A, B, C, and D do not move. Islands E, F, G, H, and K are split up into several parts that move in a very irregular way, and rotate sometimes. Only J moves along the slow scan direction and keeps its shape.
deflection. Hence, when the elastic force $F^E$ exceeds the friction force $F^S$, the island is displaced. The deflection of the cantilever, and hence the elastic force, depend in turn on the vibration amplitude $A$.

The threshold amplitude is additive with the area. When two flower-shaped islands are one under the other, the tip, scanning from the top to the bottom and pushing towards the bottom, “sees” a single island, whose area is the sum of the areas of the two islands. Let us assume that $A$ is the actual amplitude of the vibrating cantilever and that $A_t$ and $A_b$ are the threshold amplitudes of the top and the bottom island, respectively. If $A < A_b$, no movement is obtained. If $A_b \leq A < A_b + A_t$, only the bottom island is moved, because at the beginning the cantilever is pushing the two islands together, but, as soon as the top island has been scanned, the tip pushes only the bottom island. If $A \geq A_b + A_t$, the whole block is moved. The additivity of the thresholds has been verified for several couples of islands.

The threshold amplitude depends also on the position of the flower-shaped island. If the island lies on a graphite step, the amplitude needed to displace it is higher than the amplitude needed to displace an island with the same area that is not lying on the graphite step. Fig. 6 shows the dependence of the threshold amplitude on island area for 72 flower-shaped islands. 12 flower-shaped islands are on a graphite step (open circles), 60 are “free” on the graphite surface (full black circles). The slow scan direction, and hence the direction of displacement, is perpendicular to the step. The amplitude needed to displace an island on the step is a 2.5-fold factor higher than the amplitude needed to displace a free island with the same area. This shows that the adhesion of the island on the step is higher than the adhesion of the islands on the flat surface. Once the islands have been displaced from the step, the amplitude needed to move them further is lower. The threshold amplitude does not depend on the direction of the displacement.

4. Conclusions

Antimony has been evaporated on HOPG. Three fundamental structures have been characterised: isolated clusters, flower-shaped islands, and ramified structures. In particular, the fractal dimension has been calculated for flower-shaped islands and ramified structures, showing that the ramified structures are fractals.
The three structures can be dislocated by means of DPL. Isolated clusters cannot be singled out and their movement cannot be followed. Ramified structures happen to be split up when displaced. The dislocation of flower-shaped islands turns out to be very interesting. Islands can be manipulated and displaced with a precision corresponding to 20% of their dimensions. Groups of clusters can be separated and areas can be cleaned up.

Further, the relationship between the island area and the vibration amplitude needed to move it can be used as a tool to study the adhesion between the clusters and the substrate. Not only the adhesion of different materials can be studied, but also differences in the adhesion between the clusters and the substrate due to surface structures, e.g. graphite steps. Additional work is needed, in order to quantify the deflection of the cantilever during displacement and hence the force employed to dislocate the cluster. By measuring the actual force applied, since the area can be simultaneously measured, the shear strength $\tau$ can be calculated.

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