Controlling single cluster dynamics at the nanoscale

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(Received 8 June 2009; accepted 2 September 2009; published online 8 October 2009)

Gold nanoclusters deposited on highly oriented pyrolytic graphite are selectively detached and moved as a function of their size using the atomic force microscope. Control is obtained working in amplitude modulation and by tuning the interaction strength between oscillating tip and clusters. We show that fundamental controlling parameter is the energy dissipation that can be adjusted varying the tip amplitude oscillation and monitoring the phase shift signal. We characterize the energy detachment threshold of nanoclusters with sizes of 24 and 42 nm of diameter, then we precisely induce and control the movement of clusters with diameter below 40 nm within a mixed deposition. © 2009 American Institute of Physics. [doi:10.1063/1.3238320]

Understanding different regimes of friction for nano-sized contacting objects and achieving the ability of tuning their dynamics represent a subject of fundamental interest1–3 and a formidable technological task.4,5 In this letter, we present an atomic force microscopy (AFM) experimental method allowing us to perform controlled movements and reproducible particle size selection down to the nanometer scale on surface deposited clusters. The method relies on using the AFM tip oscillations, and its periodic interaction with the substrate, to induce cluster’s movements. The extreme control of the excitation strength, obtained by tuning the tip oscillation amplitude, and the variation of friction forces as function of cluster size, are key points for the success of this method.

The amplitude modulation feedback method (AMAFM), routinely used to perform imaging from soft to hard materials, can be extended to measure different material properties up to the atomic resolution by recording the phase shift signal over the standard height measurement.6 Phase variation is connected to the energy dissipation processes taking place during tip-sample interaction7 and, even if the tip experiences a strong nonlinear force field along its periodic trajectories, it is exclusively related to inelastic interaction process.8,9 In particular during AM-AFM operations, where amplitude oscillations and frequency are kept constant, phase shift is the only observable where inelastic effects can manifest themselves. The energy dissipated per cycle E is related to physical measurable quantities and it corresponds to phase variations through the relation

$$E = \frac{\pi k A}{Q} [A_0 \sin(\varphi) - A],$$

(1)

where $A_0$ is the “free” amplitude oscillation and $A$ is the amplitude during imaging, $k$ is the elastic constant of the cantilever, $Q$ is its quality factor, and $\varphi$ is the phase shift between the external driving oscillation and the tip response.

Recently, combining AM-AFM and phase shift measurements and according to Eq. (1), energy dissipation values corresponding to detachment and movement of clusters on surfaces in different environment conditions have been determined.2–4 These values will be denoted as detachment energies in the following. Exploiting this mechanism, we will show how to repeatable detach and manipulate clusters with size in the tenth nanometer range for a slippery system like gold on highly oriented pyrolytic graphite (HOPG).10–12 The phenomenon has been modeled13 for example as a momentum exchange between tip and cluster following two basic assumptions: (a) tip induced detachment is a non adiabatic transition between two energy minima and (b) during a tip oscillation period the cluster, eventually detached, stabilizes into a new minimum.

Experiments have been performed on Au nanoclusters deposited in air, from an aqueous solution, on freshly cleaved HOPG graphite. We have used two different gold nanocluster sizes: with diameters of $24 \pm 3$ and $42 \pm 4$ nm, respectively. Their distribution has been checked by transmission electron microscopy and scanning electron microscopy and confirmed by AFM heights analysis showing that clusters have nearly spherical shape. Details of cluster production can be found in Ref. 3. Measurements have been done under ambient conditions ($T \approx 25^\circ$C, relative humidity 40%) using a commercial AFM microscope (mod. Enviroscope by VEECO) with cantilevers characterized by nominal spring constants between 5 and 50 N/m.

To evaluate the size dependence of detachment energy we follow a detailed measurement protocol composed by an alternation of imaging and manipulation steps (see Fig. 1). We select an area, typically $1 \mu$m$^2$, and perform a first image with optimized AM-AFM parameters Fig. 1(a). In the following image [Fig. 1(b)] we intentionally increase the free amplitude oscillation $A_0$, keeping it fixed along the complete scan, so that the raise in the tip oscillation mechanical energy eventually induce some cluster detachments. Within a manipulation step we evaluate the maximum dissipated energy on each cluster from the phase shift signal (not shown) by means of Eq. (1) and we record the number of detachment events by comparison with the subsequent imaging step [Fig. 1(c)]. The procedure is repeated until any movement appears during two subsequent manipulation steps.

The experimental data in Fig. 2 summarize the size selectivity of detachment energy measurements. Panels (a) and
FIG. 1. (Color online) Manipulation sequence relative to 24 nm gold clusters. (a) AFM scan directions superimposed to the initial topographic image; (b) manipulation scan: two single clusters are detached and pushed along the slow scan direction; (c) final topographic image: cluster on the right has left the scan area, cluster on the center now sits on the right upper corner. Note the large jump at the end of its trajectory (120 nm long) and the deflection effect due to the presence of graphite edge; (d) interaction scheme between tip and cluster. Both tip apex and cluster are represented by a sphere, the repulsive force $F$ is along the line connecting the two centers and decomposed along the surface plane ($F_x, F_y$) and the tip oscillation directions ($F_z$).

FIG. 2. (Color online) Panels (a) and (b), referring to 24 and 42 nm diameter clusters respectively, show the number of detachment events (normalized to the total number of single clusters) and their associated detachment energy. Data are sorted by increasing energy and represent the collection of a number of manipulation sequences containing about 140 single clusters each, covering an equivalent area of 10 $\mu$m². Panel (c) contains the same data but presented as the incremental sum of detachments events. The linear increase of incremental sum represents regions where detachment occurrence has random uniform probability. Detachment energy thresholds are located in the center of these regions, while their width corresponds to the maximum associated errors ($E_{24}=67 \pm 30$ eV and $E_{42}=130 \pm 55$ eV).

(b) show the raw data representing detachments events sorted by increasing energy. They correspond to the collection of a number of manipulation sequences containing about 140 single clusters each and covering an equivalent area of 10 $\mu$m². Panel (c) contains the same data but presented as the incremental sum of detachments events. Curves are normalized to the total number of single clusters.

The overall behavior is similar for both cluster families but the energy regions, where detachments occur, are clearly different and well identifiable. The curve representing the incremental sum consists of a region where detachments occurrence increases linearly followed by an almost flat plateau indicating that all the detachment events have already taken place. The linear increase typically represents a random uniform probability so the detachment energy threshold can be conveniently located in the center of this region, while its width corresponds to the maximum associated error. The detachment energy thresholds result in $E_{24}=68 \pm 30$ eV for 24 nm particles and $E_{42}=130 \pm 55$ eV for 42 nm particles.

The clusters dynamic behavior during a forced movement is highlighted in Fig. 1. Typical clusters trajectories are those visible in panel (b) resulting on the movements evidenced on panel (c). About 95% of detachments and forced movements (over a total of about 200 classified events) show this behavior. The underlying mechanism can be described as follow. Cluster trajectory corresponds to a succession of partial cluster profiles indicating a series of depinning and displacement events where the movements are oriented toward the slow scan direction and their length is small compared to the AFM step (about 2 nm in this case). These results are consistent with the momentum exchange model and can be described equivalently with a simple scheme of the interaction between the AFM oscillating tip and the cluster where only the final repulsive force acting during the contact is considered [Fig. 1, panel (d)]. The repulsive force $F$ between two hard bodies is directed along the normal to the contact surface and, if we assume a spherical shape for both the cluster and tip apex, this corresponds to the segment connecting the centers of the two spheres. Under such hypothesis the problem becomes intrinsically anisotropic respect to the substrate surface normal and sensitive to the two force components ($F_x, F_y$) coplanar to the graphite surface; the effect of the cantilever tilting, particularly important to analyze flat anisotropic surfaces, may slightly contribute as well. Averaging over all the possible contact points between ideal tip and cluster during the fast scans and considering the friction isotropy on HOPG terraces, one expects an overall translation parallel to the slow scan direction. The exact trajectory angle depends on the real shape and size of both tip and cluster, and on the steps of AFM scan movements. Since the analysis of a number of images reveals that trajectories within the same sequence are parallel, tip morphology seems to prevails over cluster shape and the trajectory direction could be aligned to the requested translation movement. Our procedure samples a set of possible impact angles. This effect helps to induce a preferred movement direction but it may cause errors in determining the detachment energy thresholds because of different imparted momenta responsible of depinning.

We have found few exceptions to the regular behavior we have previously discussed. Clusters initially sitting on a graphite step remain pinned on their positions. Clusters usually do not cross the steps and their trajectories are modified [Fig. 1, panel (b)] indicating that graphite steps correspond to...
higher friction zones.\textsuperscript{17} Last, we have observed few events where large jumps appear [Fig. 1(c) left movement, final part]. Even if the occurrence is very rare, this result seems to agree with recent measurements by Dietzel \textit{et al.}\textsuperscript{1} who observed, by contact AFM, superlubric translations of antimony islands on HOPG graphite, even in ambient condition.

The ability to move selectively nanoclusters characterized by different nominal sizes is tested on a deposition containing both 24 and 42 diameter particles obtained by stirring equal volumes of the two original liquids. A protocol aiming at separate the 24 and 42 nanoclusters, based on a delicate calibration procedure and on a particular manipulation sequence, has been optimized. First we make a complete calibration of the cantilever stiffness\textsuperscript{18} and of the AFM sensitivity to calculate from Eq. (1) the maximum available energy for dissipation ($\phi=90^\circ$) as a function of $A$ and $A_p$. Then, we evaluate the correspondence between $A_0$ and the applied voltage on the driving piezo ($V_d$) at the resonance frequency so that we can easily adjust the oscillation energy just above a given detachment threshold. The overall results obtained on a $4 \times 4$ $\mu$m$^2$ area are summarized in the histogram plot on panel (b) of Fig. 3. The initial particles size distribution was almost uniform between 20 and 50 nm (not shown) while, after a single upward scan above the $E_{24}$ threshold, a large fraction of particles with diameter below 40 nm have been pushed out. The histogram represents the difference between the initial and final particle distribution. Values around zero (between 40 and 60 nm) corresponds to clusters unaffected by the manipulation scan while values above zero (between 20 to 40 nm) reveal clusters dragged out during the scan. On panel (a) of Fig. 3 a detail of cluster movements during the manipulation scan is presented. On the top image two large clusters (more than 40 nm high) are clearly visible in the left corner, while eight smaller clusters (between 15 and 30 nm high) are dispersed on the remaining area. The central image shows clusters movements induced along the slow scan direction with an energy just above the $E_{24}$ detachment threshold. Finally the lower image shows the selection effect of this action.

The mechanical energy stored in the AFM tip oscillation is transfer to clusters bounded on a surface and it may cause their detachments and movements. This is usually a non controlled effect. Here we show that the energy dissipation signal obtained in AM-AFM and a proper averaging and calibration procedure allow to obtain selected detachments and controlled movements of cluster in the tenth nanometer range, as proved for 24 and 42 Au cluster on HOPG. The evaluation of the fraction of mechanical energy effectively used to start sliding during a single stroke require further dedicated measurements and modeling.

Research partially supported by Net-Laboratory INTERMECH-SUP&amp;RMAN (PRRITT Emilia Romagna) and by ACOF, and AFRI projects (FANAS-ESF). Thanks to K. Mougin for providing gold nanoclusters.

\begin{figure}
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\includegraphics[width=\textwidth]{Figure3}
\caption{(Color online) Panel (a). Top: initial topographic image showing two clusters more than 40 nm high, plus eight smaller clusters, between 15 and 30 nm high (blue plane is a 10 nm cutoff introduced for graphical reason). Central: cluster’s movements induced using an oscillation energy just above the $E_{24}$ detachment threshold. Lower: selection effect and trajectories, deduced from the central image, aligned along the slow scan direction. Panel (b): difference between the initial and final particle size distribution (normalized to the total number of clusters), after a single scan above the $E_{24}$ threshold.}
\end{figure}