

Nanopatterning by atomic nanofabrication: Interaction of laser cooled atoms with surfaces

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Received 7 May 2006; received in revised form 23 August 2006; accepted 23 August 2006

Available online 17 October 2006

Abstract

By using laser manipulation techniques, we have produced a cesium beam with sub-thermal velocity; atoms of the beam have then been deposited onto graphite substrates. Analyses of the samples, carried out in vacuum by tunneling microscopy, demonstrate that, at reduced surface coverage rates, isolated atom-sized structures are formed on the substrate. Results are of interest for the development of an atomic nanofabrication approach exploitable also with soft materials.

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Keywords: Atomic nanofabrication; Nanopatterning; Laser cooling; Laser manipulation

1. Introduction

Relentless efforts are being devoted to develop new approaches for controlled nanopatterning of both inorganic and organic materials, with outcomes not only in electronics, where lateral definition is an essential step to realize miniaturized devices [1], but also in other areas, including tissue engineering, where the availability of suitable regularly ordered nanosized templates can promote growth of structures with a predefined spatial ordering. The ability to produce nanosized patterns has been a strong driving force for the advancements of conventional microelectronics, but application of high resolution techniques (e.g., electron or ion beam lithography) to organics is often cumbersome due to the soft nature of such materials.

In the last decade, a nanofabrication method based on laser-controlled deposition of atoms, the so-called Atomic NanoFabrication (ANF) [2], has been developed, with the original aim to

overcome diffraction-based limitations typical of optical lithography [3]. The key ingredient of ANF is a neutral atom beam, dynamically conditioned through standard laser manipulation methods [4] and made to interact with a quasi-resonant standing wave acting like an immaterial mask (optical mask). Similarly to optical lithography, parallel processing is preserved, while diffraction effects are pushed down to the range of the de Broglie wavelength of the atom beam, well below 1 nm. In spite of drawbacks in view of large-scale exploitations, including limitations in the choice of the laser-manipulated atomic species and a poor flexibility in the definition of pattern geometry (but more complex schemes have been proposed in order to overcome this problem [5,6]), ANF holds appealing promises for use with organic substrates, allowing their patterning without collateral effects thanks to the reduced kinetic energy of the impinging particles. This feature is particularly important in the apparatus we have developed, where a laser cooled cesium atom beam is used leading to sub-thermal particle velocity.

The present paper addresses one specific issue specifically relevant in the conditions of our experiment, dealing with the possible occurrence of peculiar self-organization and growth mechanisms after the arrival of laser cooled atoms onto a flat

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surface. The issue has been investigated by using scanning tunneling microscopy (STM) to image atomic details of substrates exposed to the laser cooled cesium beam; in this stage of our research, conductive crystalline substrates (graphite) have been employed instead of organic layers, whose properties are often strongly dependent on the fabrication procedures and on the features of the underlying layers [7]. Furthermore, in order to better clarify possible effects which can be ascribed solely to the peculiar dynamical properties of our atom beam, non-structured deposits have been produced by switching off the optical mask.

2. Experimental

The experimental setup, which has been already described in details elsewhere [8,9], comprises of an ultra-high vacuum (UHV) apparatus divided into four parts (see Fig. 1 for a sketch of the overall system). The most distinctive part is devoted to produce the laser cooled atom beam; to this aim, we exploit a “pyramidal atomic funnel” [10], a mirror and prism ensemble, which, upon illumination by a single, large sized, laser beam, is able to reproduce the beam configuration of a standard magneto-optical trap (MOT). Due to the presence of a hole at the pyramid apex, atoms captured from the background and magneto-optically cooled down to temperatures in the 0.1–0.3 mK range feel a radiation force unbalanced along the pyramid axis direction. As a consequence, they leave the pyramid, producing a continuous beam with a longitudinal velocity on the order of 10 m/s [8], well below the conventional (thermal) conditions. Right after the pyramid hole, the atom beam encounters two pairs of counter-

propagating laser beams, directed orthogonally with respect to the beam axis, which, for a suitable choice of the operating parameters, lead to further decrease the atom kinetic energy associated with the transverse direction (transverse 2-D cooling, [4]). As a result, the atom beam is collimated with a residual divergence in the mrad range [8]. After traveling for around 30 cm, the atom beam enters the deposition region, where it can interact with a 1-D standing wave, playing the role of optical mask, prior to impinging onto the substrate. Beam features at this region have been carefully ascertained through spectroscopy measurements [8,9]. In particular, the beam diameter is around 3 mm (FWHM), and atom fluxes in excess of 10^9 atoms/s can be typically achieved. Thanks to the reduced divergence of the particle beam, interaction with the optical mask is highly effective in terms of space segregation. Since in the present paper we report only on experiments carried out by switching off the standing wave, we will not enter here into the description of the processes underlying the atom guiding (i.e., focusing) onto the surface. However, we point out that numerical simulations of the atom trajectories [11] suggest that, during interaction with the optical mask, atoms are channeled, i.e., their transverse position is oscillating in a channel a few tens nm wide. As a consequence, a lateral space definition below 50 nm can be achieved in the produced nanostructures, as demonstrated in [7]. Due to the space segregation effect, the beam intensity is locally increased at the node (or anti-node) positions; numerical evaluations indicate that nanostructures one monolayer thick can be deposited in few minutes, or tens of minutes, depending on the experimental parameters. We remark that, though similar performances are not suitable for an industrially-oriented exploitation of the technique, they are sufficient for

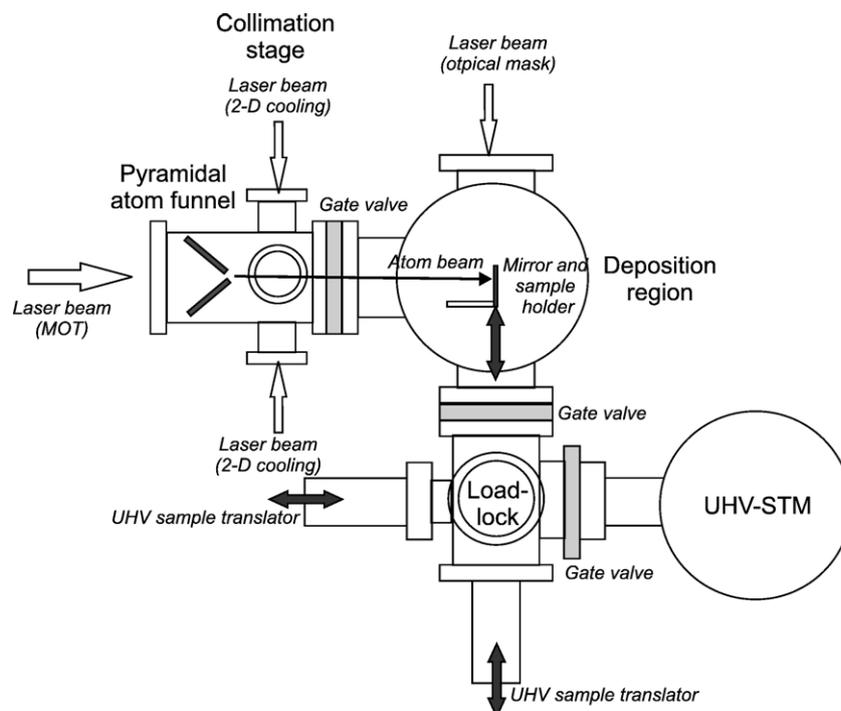


Fig. 1. Sketch of the experimental apparatus; the whole system consists of a set of interconnected UHV chambers separated by gate valves and evacuated by ion pumps (base pressure below 10^{-9} mbar), except the load-lock region, which is pumped by turbo dry pumps. Magnetic translators are used to transfer the sample from the deposition to the investigation (STM) region.

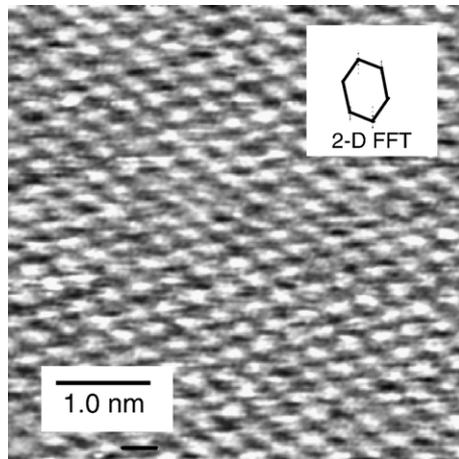


Fig. 2. STM image (scan size 5.0×5.0 nm) of a fresh, unexposed HOPG surface; raw data are shown. In the inset: 2-D FFT map of the STM image; peaks are located at the vertices of a hexagon, in agreement with the graphite lattice structure (lines connecting data points are guides to the eye).

laboratory-scale experiments. Special care, however, must be used in order to ensure stability of the experimental parameters during the deposition time, as accomplished by using a specific substrate holder system [8]. Furthermore, the radiation needed for beam production and conditioning, generated by diode lasers in external cavity configuration (the D2 resonance cesium line is concerned, lying around 852 nm, a wavelength accessible by standard diode lasers), is continuously controlled in terms of frequency and intensity by suitable feedback systems.

The fourth region of our setup hosts a sample analysis facility, based on STM. In order to prevent cesium reactions with the laboratory atmosphere, which might destroy the produced nanostructures, an UHV head (Omicron LS-STM, with Nanotec Dulcinea controller) is implemented in the same vacuum chamber used for the deposition, allowing on-line investigations. A specifically designed set of sample manipulators and translators is used to transfer samples from the deposition to the investigation

regions. Data presented in this paper have been acquired by using highly oriented pyrolytic graphite (HOPG) as the substrate, a conductive material whose atomic properties have been widely investigated in the past by STM.

3. Results and discussion

The system has been already successfully used to produce an array of parallel nanotrenches in a gold layer [7]. In those experiments, a resist-assisted approach has been used: to this aim, a self-assembled monolayer (SAM) consisting of alkanethiols (nonanethiol molecules) has been grown by dipping Au/Cr/Si substrates (gold nominal thickness 30 nm) into a SAM/ethanol solution. Though the involved mechanisms are still matter of debate [12], alkanethiol SAMs are known to be sensitive on the arrival of alkali atoms. In particular, the exposed regions turn out to be no longer protected against wet etching; thus, after exposure of the SAM layer to the space segregated laser cooled cesium beam, a wet etching process has been used to transfer the pattern (an array of parallel lines, spaced exactly 425 nm) onto the gold layer.

Sample investigations show the occurrence of the expected array of parallel nanotrenches; their lateral definition, typically in the 40–50 nm range, turns out to be strongly affected by local SAM defects induced by the morphology of the underlying gold layer. As a matter of fact, atomic force microscopy shows irregular features at the trench borders, reflecting the gold grain structure. Hence space resolution in ANF is affected by the resist features, suggesting a minimum measurable value which, in the best operating conditions, can be estimated around 20 nm [7].

This circumstance provided us with a first motivation for direct deposition experiments: indeed, by avoiding the use of a resist and of chemical etching steps, genuine features of ANF can be more clearly analyzed, including those possibly associated with the sub-thermal nature of the atom beam. The kinetic energy of the impinging particles in our experiment is remarkably smaller than in conventional deposition schemes, where effusive beams, or

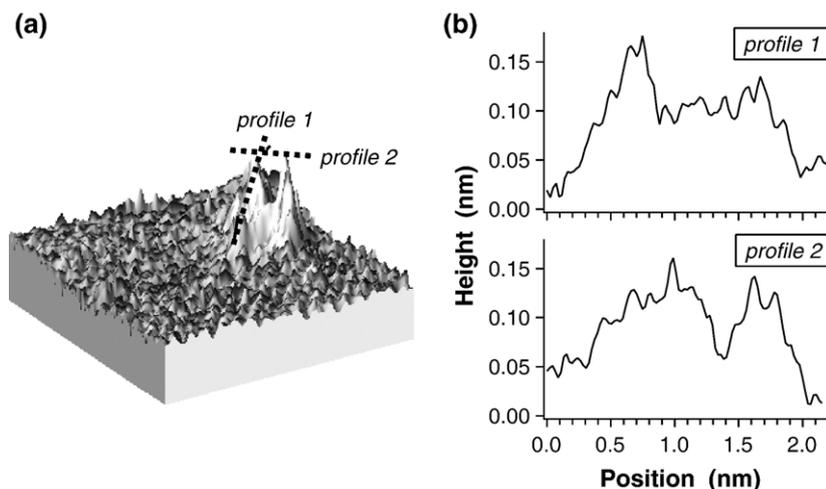


Fig. 3. 3-D view of an STM image acquired on an HOPG surface exposed to the laser cooled cesium beam (scan size 6.0×6.0 nm); cesium structures are clearly visible, superimposed to the ripples representing the graphite lattice structure (a); line profile analyses along the two directions marked by dotted lines in the left panel (b).

even accelerated charges, are used. This gives our apparatus the unique ability to access “unconventional” and rather unexplored deposition regimes. For instance, in similar conditions the role of atom diffusion, a relevant process in defining the ultimate space resolution in ANF (see, for instance, [13]), might be modified. It must be noted that we keep the substrate at room temperature, hence atoms are expected to lose any memory of their dynamical status right after their impact onto the surface; further work will be devoted in the future to compare in details depositions with effusive and laser cooled atoms, with the aim to confirm this expectation from the experimental point of view. Interaction between sub-thermal atoms and surfaces is an issue relevant also in view of ANF applications to soft materials, which is our final goal: preventing the occurrence of any kinetic damage of the layer might be relevant in designing new local surface functionalization processes.

As already mentioned, we have carried out experiments where we have deposited laser cooled cesium atoms onto HOPG and we have analyzed the sample morphology at the atomic scale by STM. Surface exposure to both non-segregated and segregated atom beams (i.e., without and with the optical mask radiation) has been performed. In the present paper, we restrict ourselves to samples produced without the optical mask; data pertaining to nanostructured samples will be published and discussed elsewhere.

Prior to deposition, HOPG surface has been prepared by simply peeling out the uppermost layers. This procedure is known to lead to fresh graphite surfaces, atomically flat on a typical size of a few squared microns: flat regions turn out to be more frequently found close to terrace steps. Fig. 2 shows a typical STM image of a fresh, unexposed, HOPG surface. According to the literature [14], topographical features can be readily interpreted in terms of the graphite lattice structure, as demonstrated by the space distribution of the peaks in the corresponding FFT map (inset), situated at the vertices of a hexagon.

Fig. 3a reports an example of STM imaging of an exposed sample. Since our aim was to investigate the features of isolated atom-sized structures, we carefully avoided any possibility of continuous layer formation by appropriately choosing the deposition time. In the example shown in the figure, the estimated relative coverage of the graphite surface by cesium atoms was on the order of 0.1. By repeating investigations over larger surface area, we could conclude that the actual surface coverage was smaller than expected (by a factor of 2–4), indicating a non-negligible contribution of surface scattering and re-evaporation processes, probably enhanced by the high vapor pressure of cesium.

When compared with the images of unexposed surfaces (see Fig. 2), results clearly indicate occurrence of island-like structures following exposure to the laser cooled cesium beam. A variety of island morphologies has been detected; typically, their lateral size is in the nm range, whereas their height, as demonstrated by the line profiles in Fig. 3b, is a few Ångström. Sometimes, in large scale images not reported here, a mutual organization between neighboring islands can be identified, leading to elongated structures roughly mutually aligned to each other. This can be probably ascribed to diffusion of cesium atoms

occurring along preferential directions of the graphite plane associated with the stresses suffered by HOPG during the peeling process.

The nature of the bonding between the cesium atoms and the graphite surface requires further investigations aimed, in particular, at clarifying the possible role of defective graphite sites in promoting cesium atom sticking. The topic of alkali/graphite interaction has been in the past of particular interest in view of intercalation purposes; the relevant literature [15] reports phase diagrams, obtained in effusive depositions, demonstrating growth of stable cesium structures under suitable conditions. We note that our cesium islands, produced through deposition of a laser cooled beam, exhibit a remarkable stability: they are still detected in measurements repeated several hours after the deposition, while keeping samples in UHV conditions. The morphology of the observed islands suggests achievement of (partially) ordered structures, in agreement with the above-mentioned phase diagrams. Depositions with larger coverage ratio will be carried out in order to ascertain the eventual transition to disordered morphologies and/or to assess details of the island growth.

4. Conclusions

We have developed an atomic nanofabrication apparatus which exploits a laser cooled cesium beam. Extensive application of laser manipulation techniques enables to efficiently control dynamical and spatial features of neutral atoms impinging onto a surface, opening the way for applications in a variety of nanotechnological fields. In particular, the low kinetic energy of the deposited species promises to be a key point in applications aimed at nanopatterning soft organic layers. Preliminary results presented here, which have been attained using a crystalline model substrate, demonstrate feasibility of atom-sized structure fabrication by using our approach.

Acknowledgments

Financial support by Fondazione Cassa di Risparmio di Pisa, through the Research Project “Nanodeposizione atomica su substrati soft”, is gratefully acknowledged.

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