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Rapid communication

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Patterning nonanethiol protected gold films by barium atoms

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ABSTRACT Self assembled monolayers (SAM) formed from nonanethiols on thin gold films were exposed to a beam of ground state and metastable neutral barium atoms through a nickel mask. The interaction of the Ba atoms with the nonanethiol layer, followed by an etching process, creates well defined structures on the gold film, with features below 100 nm. We compared the interaction of ground state Ba atoms and SAM molecules with respect to metastable Ba atoms, finding that by using metastable atoms the Ba dose per SAM molecule is reduced. The results indicate that nanofabrication in the nanometer range with barium atoms is feasible.

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1 Introduction

During the last decade the use of neutral atomic beams to produce nanostructured patterns has been implemented in several experiments of atom lithography [1, 2]. The so called atom nanofabrication has the advantages of a parallel lithographic process and of a negligible contribution by diffraction phenomena due to the short de Broglie wavelength of the atoms. The internal degree of freedom of the atoms can be used to engineer specific processes. Furthermore, both mechanical and optical masks can be used. In the second case one or more standing waves of near resonant light are utilized as lenses for atoms and can produce periodical arrays spaced by a fraction (usually a half) of the laser wavelength. The neutral atoms can be either directly deposited on a surface or they can be used as a lithography tool. The first case has been demonstrated for some atomic species including sodium, chromium and aluminum [1]. However the formation of permanent structures requires stability of the deposited species upon exposure to air, a crucial problem for many species as alkali atoms, which are easily laser manipulated. For these species a more traditional lithographic technique has been developed. In this method a film of gold or silicon is coated with a SAM of alkanethiols or organosilicon, utilized as a resist. Once exposed to the atomic beam through a mechanical or light mask, the so produced pattern is transferred to the underlying film through an etching process as in conventional optical lithography. The demonstration of this technique has firstly been done using metastable argon atoms [3] and later extended to other metastable noble gas atoms, to alkali atoms, with cesium first [4, 5] and to highly charged ions [6]. The main difference between these atomic species is in the number of deposited monolayers (i.e. number of incident atoms per organic molecules) required to damage the resist, which reflects in different exposure times. In fact metastable noble gas atoms and highly charged ions have a large internal energy (e.g., 20 eV for He* and 51,000 eV for Xe^{44+}) that can be released in the collisional process, resulting in shorter exposure times with respect to alkali atoms.

In this communication we introduce a new atomic species, barium, into the realm of lithography. The barium case is an interesting one because it has also metastable states, having about 1.5 eV of internal energy, available for damaging the SAM layer. Therefore lithography is here tested for barium atoms with and without internal energy. We found that the use of mestastable Ba atoms reduces the dose of Ba atoms needed to damage a nonanethiol molecule.

2 Experimental set-up

The experimental set-up we exploited is schematically shown in Fig. 1a. The Ba atom source is an effusive cell mounted in a stainless steel vacuum chamber divided in two parts with differential pumping. The first side, with a pressure around 10^{-7} Torr, contains the barium oven made out of tantalum. The oven, heated up to 800 K creates a collimated barium atomic beam. The atoms enter the second part of the chamber, with vacuum in the 10^{-8} Torr range, through a 1.5 mm diameter skimmer producing a final divergence of 5 mrad (FWHM) for the atomic beam. This chamber equipped with viewports, manipulators and entry is used to probe the atomic beam and to hold the substrate holder. The substrate is clamped on a stainless steel holder and can be positioned on the beam path or outside by a manipulator.

The silicon substrate is covered by a sputtered 30 nm thick gold layer, with an adhesion layer (5 nm thick) of chro-

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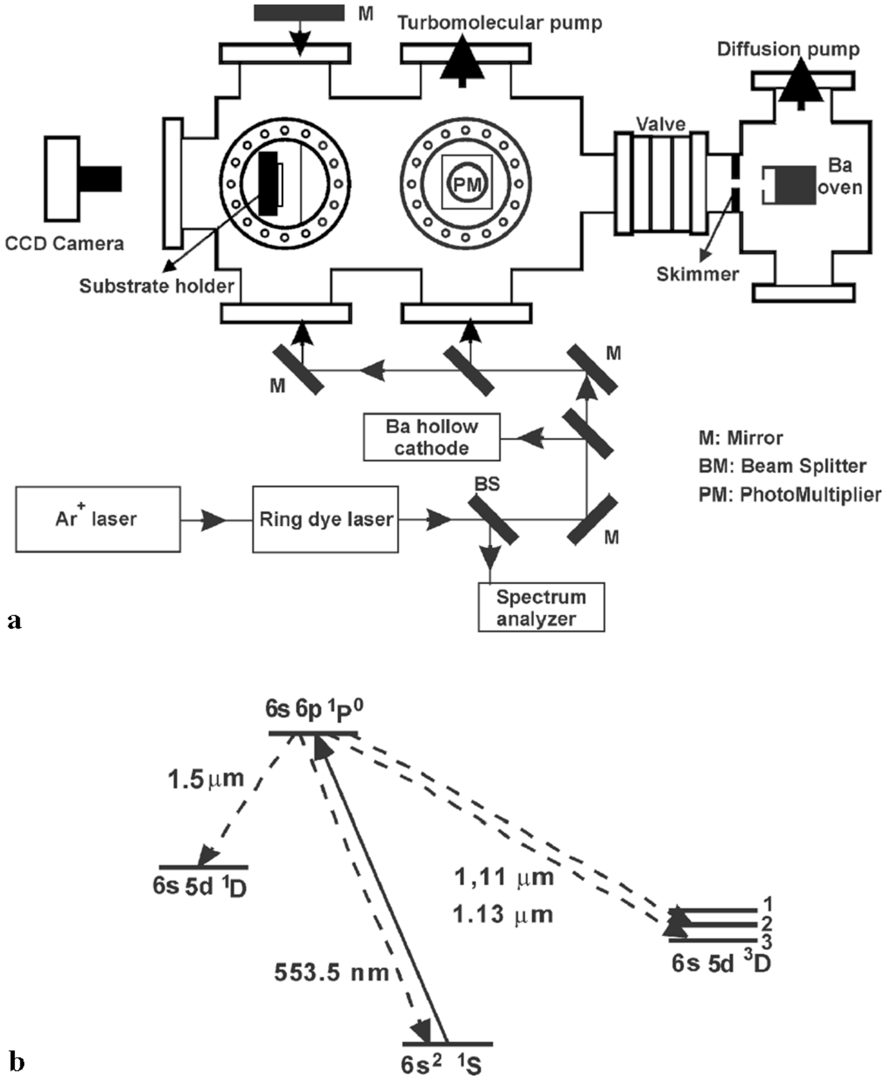

FIGURE 1 **a** Sketch of the experimental set-up. **b** Lower energy levels of the barium atom driven by the 553.5 nm laser (*continuous line*) and populated by optical pumping (*dashed lines*)

mium. The monolayer of nonanethiol molecules ($CH_3(CH_2)_8SH$) is formed on top of the substrate by dipping into a 2 mM ethanol solution for 24 hours. Before SAM growth, the gold substrates were cleaned with piranha solution. In order to pattern the substrate with the barium atoms different physical masks can be mounted, in particular results obtained using a bidimensional nickel mesh with 16.5 μm period and 11.5 μm square openings will be presented in the following. After exposure to the barium beam the samples are removed from the vacuum chamber and immersed in a wet chemical etching solution [7] that completely removes the gold layer, where it is no more protected by the SAM, in about 10 minutes.

Barium atoms were probed by excitation with light tuned to the $^1S_0 - {}^1P_1$ transition at 553.5 nm, as shown in Fig. 1b. The light was provided by a c.w. single mode ring dye laser. The barium atoms, excited by the same dye laser, were monitored by light induced fluorescence using a photomultiplier and a CCD camera. The camera allows also for investigating the atomic beam spatial profile. Laser light is resonant with the most abundant isotope ^{138}Ba (72% of natural barium). A Ba hollow cathode lamp was used as a reference. By sending the laser at a small angle with respect to the atomic beam direction and by scanning its frequency, the velocity profile of the beam was reconstructed [8]. In typical operating conditions the beam had a flux of about 5×10^{11} atoms $s^{-1}cm^{-2}$, the maximum of the atomic velocity distribution equal to 290 m/s and a spatial width of 5.7 mm at the substrate position, that is located at 1 m distance from the oven.

The total flux of barium atoms (atoms $s^{-1}cm^{-2}$) is obtained by a LIF measurement, where a σ^+ polarized, resonant probe laser is sent perpendicular to the atomic beam. The fluorescence is collected on photon multiplier tube with a green passband filter. The flux calculation accounts for collection angle, PMT response, optical saturation and pumping effects in the interaction volume.

Barium atoms can be efficiently pumped into metastable states by resonant laser light. As in the energy scheme of barium shown in Fig. 1b, atoms, laser excited into the $^1P_1$ state, decay not only to the ground $^1S_0$ state but also to the $^1D_2$ and to the ^3D_J states [9, 10]. The absorption/spontaneous emission cycles accumulated a large population mainly the $^1D_2$ state that is metastable with a lifetime of about 0.5 s. For the optical pump into those metastable states the laser radiation, retroreflected in order to avoid the atom deflection, excited transversally to the atomic beam direction. By using a laser intensity of 700 mW cm^{-2} and an interaction time of 20 μs, more than 80% of the atoms are pumped into metastable states, as measured by the decrease in the atomic fluorescence detected downstream.

3 Results and discussion

Once exposed to the atomic beam and after 10 minutes of wet etching, the patterned gold samples were then analyzed by both an optical microscope and by an atomic force microscope (AFM). Figure 2a shows a typical optical microscope image of a patterned gold sample (a nickel mask with 16.5 μm period used). The pattern of the mask is well transferred to the gold layer; the presence of a well defined structure shows that barium atoms can be used to impress nonanethiols molecules in an atom lithography setup. The AFM image Fig. 2b shows a well defined pattern with sharp edges. Figure 2c shows an AFM scan line profile, and the edge resolution (calculated from the 10 to the 90% of the total height) is of 70 nm. In fact the grain size of the gold film is around 100 nm and the presence of such grains affects the edge resolution. This edge reso-

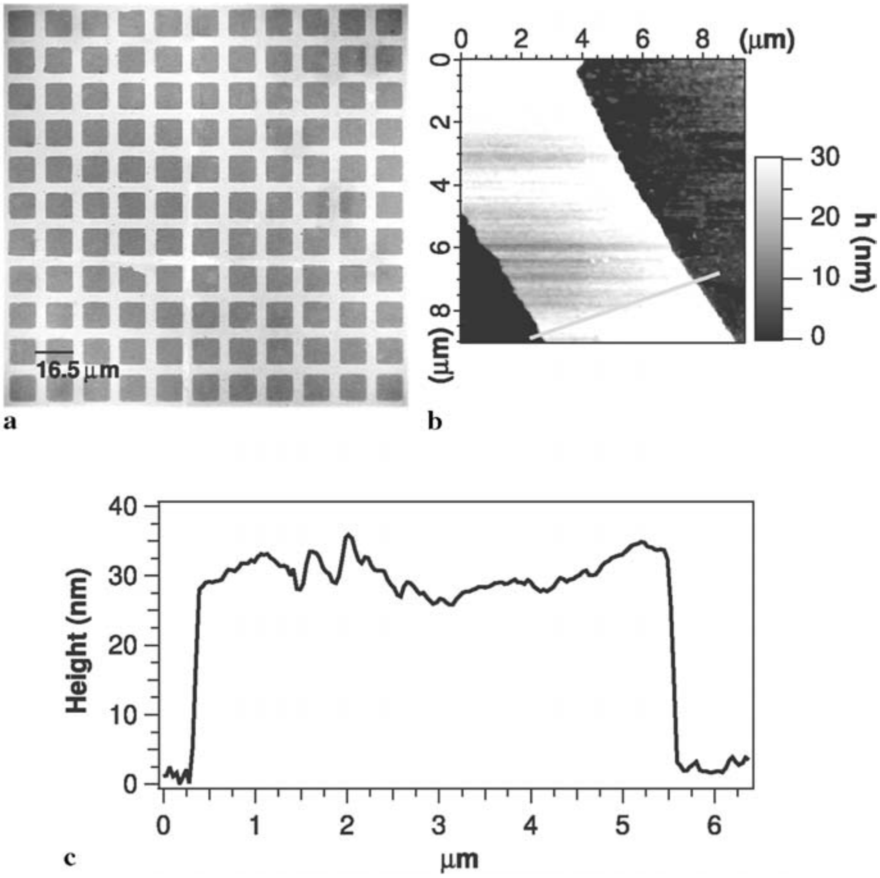

FIGURE 2 Optical and AFM images of an exposed and etched gold sample. The bright regions are the ones where the gold film was not removed. **a** Optical microscope image (500x) of a sample exposed for 3 hours to a beam of metastable barium atoms, with a flux equal to 4×10^{11} atoms $s^{-1}cm^{-2}$. **b** AFM image of the same sample (9.37×9.37 µm). **c** Line profile of the AFM picture along the path reported in picture **b**

lution can be in principle improved by using anisotropic etching solution, thiols molecules with a shorter alkyl chain and flatter substrates.

We have compared the efficiency in the lithography procedure based on metastable Ba atoms compared to that with ground state barium atoms. In order to investigate the damage to the surface as a function of the dose of ground state and metastable atoms, samples were exposed to the atomic beam without using a mask. Using the known flux profile of the atomic beam and the measured reflectivity profile of the exposed region to normally incident light at 632 nm, the damage of the surface can be determined as a function of the ground state/metastable Ba covering, as applied previously in [5] for cesium atoms. The results are shown in Fig. 3, where the dose is calculated from the measured flux and the exposure time. We should remark that the absolute flux is known with an accuracy of 60%, but the relative error between the dose of ground and metastable state atoms is of the order of 5%. Data show the threshold feature of the lithographic process, i.e. the presence of a region below 2 monolayers (<1 monolayer for metastable atoms) where no etching of the gold layer was observed. The main finding is that the dose necessary to damage the resist is lower for metastable atoms (about a factor 2), showing that the possibility of playing with the internal degrees of freedom (or internal states) of the atoms leads to a more efficient lithographic process.

An interpretation of the physical and chemical processes which change the properties of the nanonethiols layer after the interaction with Ba atoms (ground state or metastable) cannot be easily derived from the present work. The energies involved (typically of the order of few tens of meV for ground state atoms and 1.5 eV for the metastable ones) are lower than the typical binding energy of the thiol molecule with Au surface which is around 3 eV [11]. Contrary to the metastable noble gas atoms and highly charged ions where the large internal energy suggests that the most likely mechanism is a direct physical damage of the SAM layer [12, 13], for the case here considered we believe that a chemical interaction is the main damaging mechanism. One hypothesis is that Ba atoms can reach, through the open defects of the SAM layer, the bottom of the SAM layer having access to the sulfur-gold bond, a suggestion supported by the observation that less ordered SAM layers produce better defined structures [4, 14] and that the exposed regions show an increased degree of disorder [13]. Because the energies associated with the van der Waals interactions between the alkyl chains are less than 0.5 eV [11], the metastable

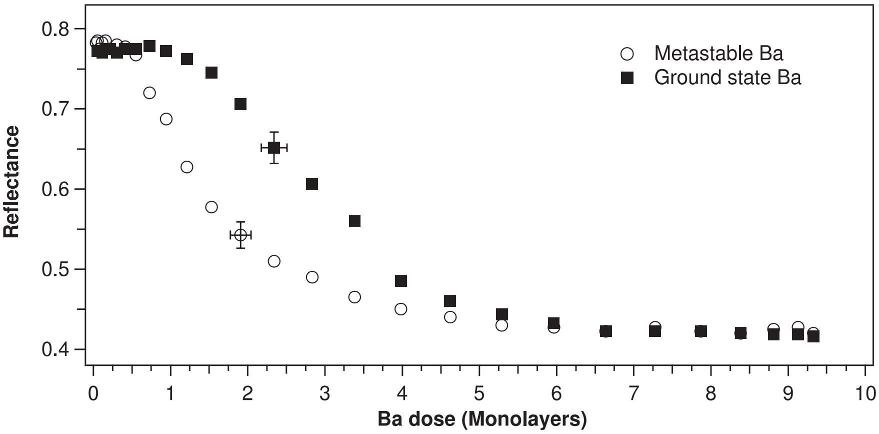

FIGURE 3 Reflectance of an etched gold surface after exposure and etching as a function of the dose of ground state and metastable Ba atoms. A monolayer is defined to have the surface density of the SAM (4.6×10^{14} atoms/cm^2)

atoms should be favored by the fact that 1.5 eV internal energy released on the SAM surface may increase the number of surface defects. We can not exclude the formation of an ionic species Ba^+ as a consequence of the interaction between the Ba atom and the Au surface as reported for other species (Ag, W, Si, and Cu) [15] and an interaction of the ionic species with the thiol molecule, as recently suggested for the cesium case [16]. Further work has to be done in order to fully clarify the interaction mechanism.

4 Conclusions

In conclusion we have demonstrated that a neutral barium beam can be used as a tool for patterning SAM layer and gold films through atom lithography. The comparison between the ground state and the metastable atoms, show a significant decrease of the Ba dose necessary to damage the SAM layer. Further work will be devoted to the understanding of the Ba-SAM molecule interaction processes and to the use of optical masks, in order to focus the Ba atoms in nanometer scaled ordered structures.

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