Creation of atomic and molecular nanostructures of arbitrary shape on a surface

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Abstracts

We present experimental research of a method for nanostructures creation, based on the idea of object imaging in atom optics via atom pinhole camera. Possibility of atom nanolithography based on atom pinhole camera is explored focused on key features of the lithography for creation of atomic and molecular nanostructures of prearranged shape and factors limiting its resolution. We show that the concept of atom pinhole camera as a novel tool for atom nano-fabrication is offering the following merits: (1) it makes possible nanostructures with typical size down to 30 nm; (2) the nanostructures can have an arbitrary prearranged shape; (3) size and form of nanostructures are determined by well controlled parameters; (4) creation of the great number of identical nanostructures is possible; (5) a variety of materials for nanostructures (atoms, molecules, clusters) is feasible; (6) the method is free from use of a chemically selective etching; (7) in the process of nanostructures creation no destruction of the substrate surface happens.

1. Introduction

Atomic and molecular nanostructures on a surface are key components in modern technologies [1-4]. Semiconductor devices are currently constructed on a microscopic scale, predominately using optical lithography. The fabrication of structures at scales smaller than the current limits is a technological goal of great practical, but also fundamental interest: material structures with dimensions in the 10 nm range represent a bridge between the classical and the quantum mechanical world.

In practice, it is desirable to have the ability to build any nanostructures with atomic precision using any atomic species. To date, no single approach meets this demand. Rather, there are a number of techniques, each of them possessing some advantages and having some drawbacks.

At present, the most developed method for surface nanostructure creation is optical photolithography [5]. Photolithography, or exposure to light of a photosensitive material through a photomask, is a widespread technique used to replicate patterns. It is highly developed and well-suited for applications in microelectronics [1]. Today, photolithography makes possible nanostructures with minimum lateral dimensions down to 45 nm. It is, however, limited to photosensitive materials and is suitable only for fabrication on planar surfaces. Another problem is that in all conventional optical techniques the resolution is restricted by diffraction.

Many other approaches to nanolithography are actively developing nowadays: electron beam lithography [6], nanoimprint lithography [3], surface self-assembly of atoms [7]. The above-listed methods have several restrictions on material, form and linear dimensions reproduction accuracy of nanostructures to be created.

There are investigations of number of alternative approaches to nanolithography: stencil mask nanolithography [8-10], individual atoms control on a surface through the use of a tunnel microscope [11], ink jet lithography [3].

An alternative tool for nanotechnology is atom optics [12-15]. Among many applications of atom-optics, a potentially important one is micro- and nanofabrication of material structures, usually referred to as atom nanolithography [13,16]. Methods of atom nanolithography are founded on deposition of atoms from a beam sharply focused by an atom lens, generated by a spatially inhomogeneous field of laser radiation [17,18]. Despite numerous suggestions and experimental studies in atom beam focusing [19], the issue has not been resolved technologically. The central problem is generation of an atom-electromagnetic field interaction potential, which in properties would be close to «ideal» lens for atoms: with minimum chromatic aberration and compensated astigmatism while permitting to focus the atom beam into a spot, diffractionally limited in space.

Recently new approach for nanostructures creation, based on the idea of object imaging in atom optics via atom pinhole camera was demonstrated (APC nanolithography) [20,21,22]. In this paper we present study of key features of the lithography in application to creation of atomic and molecular nanostructures of prearranged shape.

2. Experiment

2.1 Atom Pinhole camera imagery

A new approach in atom nanolithography [20,21] has its origin in idea of object imaging with *pinhole camera*. In modern experimental physics the pinhole camera is used when the creation of focusing element (lens) is difficult [23]. In an *atom pinhole camera*, atoms act as photons in an optical pinhole camera and therefore the main principles of imaging by an atom pinhole are akin to those used in light optics of a pinhole camera. As is generally known from light optics, a pinhole camera is capable of producing high-quality (distortion free, high resolution) object images.

The ultimate resolution and imaging properties of optical pinhole camera can be derived from the diffraction theory and one can safely apply the diffraction theory for atomic de Broglie wave in atom optics. For practical application the essentials regarding the optics of atom pinhole camera can be obtained from qualitative physical considerations. It is obvious that, at given distance to the image plane, a large pinhole does not allow to gain an image of high quality. On the other hand, with far too small an aperture the diffraction of atoms also hinders an image construction. The standard approach to imagery through the use of pinhole camera is to consider a point object image construction at infinity. In this case a plane wave is incident on a screen with pinhole of radius s and at distance l (focal length of the pinhole camera) a spot of radius r is created. The best pinhole camera is the one producing the smallest spot. When the pinhole is large, the spot presents its geometrical shadow, and the image radius equals that of the pinhole. As the pinhole decreases, the image spot must be described by physical optics and diffraction pattern of the pinhole. In this case, for a circular pinhole the spot radius $r = 0.61(\lambda/s)\ l$. Hence the radius R of the image spot made by pinhole camera is roughly the sum of the image geometrical radius r and the radius of the diffraction pattern caused by the aperture:

$$R = r + 0.61\lambda(l/s) \tag{1}$$

where l is the distance between the pinhole and the image plane. The smallest image is achieved when geometrical optics and theory of diffraction give the same results. Closer examination based on theory of diffraction shows that the resolution of a pinhole camera can be even better than the geometrical one. Precise calculations show that the image spot diameter at the optimum distance is three times smaller than the pinhole diameter [24]. The optimum aperture then includes more than the half and less than the whole of the zone.

As is generally known from light optics, a pinhole camera is capable of producing high- quality object images and the same is true for atom pinhole camera. An atom pinhole camera is free from linear distortion aberration. The lack of linear distortion follows from the argument based on Fermat's principle (for small aperture) and from ray optics treatment (in geometrical approximation). Another attractive feature of atom pinhole camera is its very large depth of field.

The inherent astigmatism of all types of pinhole camera comes about because the pinhole aperture appears as an ellipse when viewed not at right angle. The optimum focal length in one plane then differs from that in the perpendicular plane. An atom pinhole camera is also prone to chromatic aberration. This is evident from the relationship between focal distance and wavelength: $l \sim s^2/\lambda_{dB}$. In material particles optics, for the lenses based on electromagnetic interaction potentials the relationship between chromatic aberration and velocity of particles is quadratic. In an atom pinhole camera by virtue of linear relationship between optimum focal length and velocity of an atom, chromatic aberration is linear with respect to the atom velocity, i.e. for atom pinhole cameras this type of aberration is of lesser importance.

The preceding analysis of atom pinhole camera presupposes an infinitely thin screen. In a real experiment the screen thickness is finite, and at sufficiently small aperture the action of van der Waals forces takes effect in atom's motion through the pinhole. Trajectories of atom’s motion are changed by the action of attractive forces to the nanopinhole channel walls. In the paraxial approximation the process can be looked upon as an atom beam being defocused by a diverging lens with focal distance:

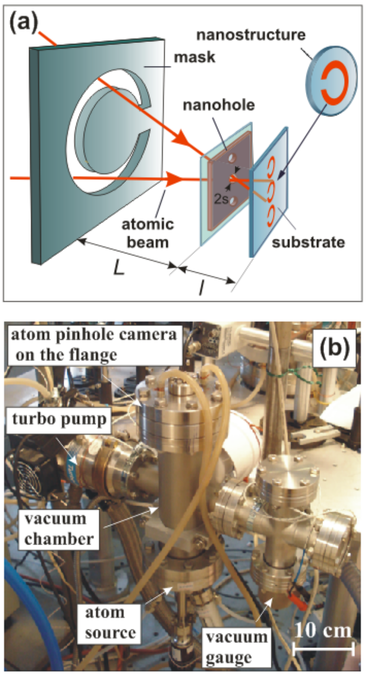

Fig.1(a). Schematic drawing of an atom pinhole camera. The atoms having passed through the mask form, by analogy with light optics, a "luminous object" of prearranged geometry. An atom nanostructure with the shape of the mask's scaled down image is generated on the substrate. (b) Photo of the atom pinhole camera nanolithography experimental setup.

$$f_{vdW} \approx -\frac{1}{12}\frac{E_k}{C_3 d}s^5, \qquad (2)$$

where C_3 is the van der Waals coeffcient, d is the thickness of the screen, E_k is the atom's kinetic energy. The van der Waals's interaction does not limit the resolution of an atom pinhole camera when the condition $|f_{vdW}| >> l$ is fulfilled. This relationship defines minimum sport size as:

$$s >> a_{\min} = \sqrt[5]{\frac{12C_3 d}{E_k}}, \qquad (3)$$

For example, for atoms of Cs and a silicon screen 50 nm thick the minimum pinhole radius a_{min}= 55 nm, for atoms of He the pinhole radius a_{min} = 1 nm.

2.2 Experimental setup

The above consideration of atom pinhole camera's optics show that its realization calls for a nanometer diameter pinhole in a screen of nanometer thickness. Schematic diagram of the atom pinhole camera is shown in Fig.1. Besides the pinhole itself it includes: an atom beam, a mask, a nanoaperture and a substrate on which the nanostructures were created. The atoms having passed through the mask form, by analogy with ray optics, a "luminous object" of prearranged geometry. Parameters of the atom pinhole camera were chosen for reason of gaining camera's maximum resolution and a possibility to construct large arrays of surface nanostructures. As already noted, when employing thermal atom beams with characteristic de Broglie wavelength of the order of 0.01 nm and the pinhole diameter 20 nm, optimum focal distance is in the range of $l_{opt} \approx 10 \div 30$ µm. This determines the distance between the pinhole and the substrate where the nanostructures are created $l = l_{opt}$. At given value l, the distance from the pinhole to the mask governs "reduction" of the atom pinhole camera's object, and consequently the size of the mask itself.

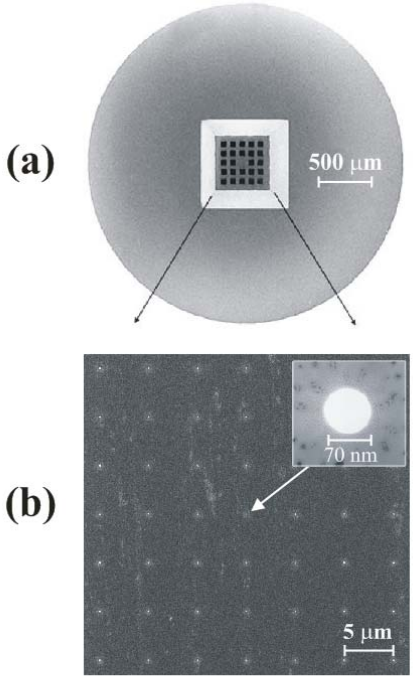

Fig. 2. (a) Photo of membrane for the atom pinhole camera. The membrane holder is in the form of a disc 3 mm in diameter and 200 µm in thickness, with a membrane 0.5× 0.5 mm in size at the centre. The membrane is made of 50 nm thick SiO_2 (white square marks the field with nanoapertures); (b) electron image of the membrane portion with nanoapertures 70 nm in diameter.

The analysis of the above considerations has shown that optimum distance from the pinhole to the mask falls in the range L = 1 - 10 cm. The "reducing power" of the atom pinhole camera $M = L/l$ in this case is 10^3 -10^4. For this geometry of atom pinhole camera, typical dimensions of the mask lie within the range of micrometers, and typical dimensions of the structures created on a surface - within the range of nanometers; i.e. atom pinhole camera provides a transformation of *microscopic* objects into *nanoscopic* one. Another important outcome of the atom pinhole camera "scaling geometry" is the possibility to use in one device not a single pinhole, but their large array. In this case each pinhole generates its own image, which does not intersect the neighboring ones, i.e. the realization of an "atom multiple pinhole camera" (AMPC) is possible. "Atom multiple pinhole camera" opens up wide opportunities for simultaneous generation of great numbers of identical nanostructures because even at significant quantity of pinholes (up to 10 million ones) inclined-beams aberrations (beginning to show up in the outermost pinholes) are not that restrictive for the resolution of an "atom multiple pinhole camera".

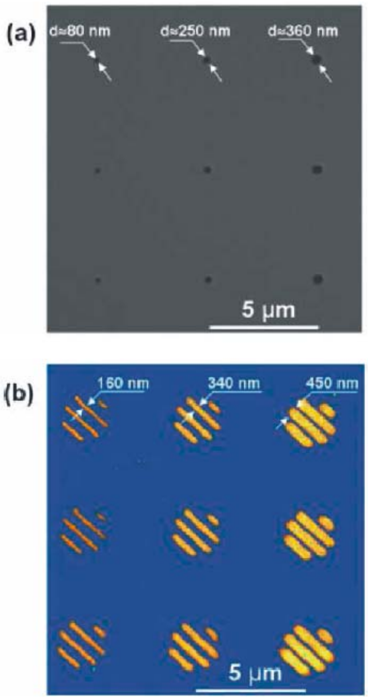

Fig.3. Nanostructures made with the atom pinhole camera. (a) the electron image of membranes with the nanoapertures of different diameters: d = 80 *nm*, 250 *nm* and 360 *nm*; (b) the AFM-images of nanostructures built up from atoms of In on a silicon surface using the pinholes of the membrane (a).

The essential feature of the atom pinhole camera is its nano-pinhole. We have used a nano- pinhole manufactured by method of ion beam milling (FEI Quanta 200 3D dual beam) suitable to the problem of nanometer-range holes (down to molecular size) fabrication in a nanometer-thin membrane produced in a solid [25]. In this method massive ions with energies of thousands electron-volts impinge on a substrate surface and an atomic scale process starts. In this process approximately one atom is removed from the surface for every incident atom. The method enables us to make apertures with diameters down to several nanometers [26]. To produce nanoapertures for atom pinhole camera, membranes of the company Ted Pella Inc. have been used. The membranes represent an ultra low stress 50 nm thin Silicon Nitride film. The film is mounted in the center of a cylindrical disc 3 mm in diameter and 0,2 mm thickness, Fig.2(a). Fig.2(b) shows a SEM image of such a membrane with apertures (diameter d = 120 nm) arranged in rows.

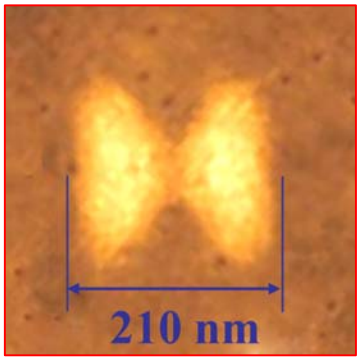

Fig. 4. A single gold bow-tie shaped nanostructure build up on a glass cover slip (AFM-image).

An AMPC with the above parameters has been realized and employed for fabrication of nanostructures made of In, Au and Ag on a silicon surface. AMPC has been placed into a vacuum chamber with the residual vapor pressure in the order of 2×10^{-7} mBar. As a source of atomic beam a high temperature effusion cell was used, providing rates of nanostructures growth up to 0.3 Å/s. The production time for a nanostructures series on one substrate has been determined by atom beam intensity and desired value of nanostructures height. Typical time of exposure in the experiment has been t ~ 10 min. for nanostructures of height h ~ 25 nm. The geometry of nanostructures has been studied by means of atomic force microscope CP-II of the Veeco company.

3. Results & Discussion

The great merit of atom pinhole is its ability to produce nanostructures from different atomic, molecular and even biological materials. Of particular interest is the nanostructures from noble metal (Au and Ag) for their various applications in nanoplasmonics. We have produced with atom pinhole camera nanostructures made of In, Au and Ag atoms on a silicon and glass surface. The Fig. 3 shows an example of such nanostructures in shape of nanorods on a silicon surface. The nanostructures have been constructed by means of an atom pinhole camera containing an array of nanoapertures of various sizes, see Fig.3(a). The nanoapertures have been arranged in matrix order 3×3, each column having apertures of particular diameter: d_1 = 80 nm, d_2 = 250 nm and d_3= 360 nm, see Fig.3(a). The nanostructures created are shown in Fig.3(b). The AMPC's reduction coefficient has been chosen $M \approx 3000$. From Fig.3 can be seen that the arrangement of nanostructures on the substrate correlates with that of nanoapertures in the membrane of the AMPC. Nanostructures created by the apertures with different diameters are distinguished by the width of the strips Δ, forming a nanostructure, and its height h. The relationship between the width of the strips and the diameter of nanoapertures is consistent with the optics of the pinhole camera, the corresponding values of the width of the strips are: Δ_1= 160 nm, Δ_2= 340 nm and Δ_3= 450 nm. The measured values of the nanostructures' height equal respectively to: h_1 = 9 *nm* for the aperture with the diameter of d_1 = 80 *nm*, h_2 = 12 nm for the aperture with the diameter of d_2 = 250 nm, and h_3 = 17 nm for the aperture with the diameter of d_3 = 360 nm. In this geometry the relationship between the height of the created nanostructures and the diameter of AMPC's apertures is determined by three processes: (1) dependence of the intensity of the atom beam from the nanoaperture diameter; (2) absorption of atoms by the walls of the membrane's nanoaperture channel; and (3) influence of van der Waals forces on the atom trajectory.

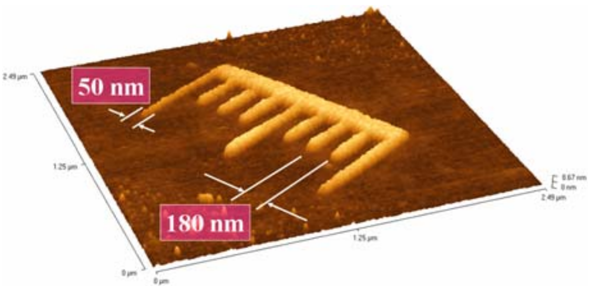

Fig. 5. AFM-image of a nanostructure built up from atoms of In on a silicon surface.

Fig. 4 presents nanostructure made with use of APC nanolithography. The nanostructure has a shape of the bow-tie nanoantenna widely used in nanoplasmonics applications. The experiment has been performed with a pinhole with the diameter of 45 nm. This nanostructure was made by Au atoms forming atomic beam in the APC. The APC mask had the openings in a shape of a bow-tie made by a focused ion beam. Use of an ion beam guarantees sharpness of corners of triangles forming the bow-tie configuration. Corresponding curvature angle radius was 500 nm while triangle side was 250 μm. The geometry of the nanostructure is similar to the topology of the utilized APC mask. It is important in many applications that the created nanostructure has a proper sharpness of its corners and a small surface roughness. As we can see from Fig. 4 in the current experiment the nanostructure's corners sharpness corresponds to diameter of the nanohole used. Nanostructure surface roughness is limited by diffusion of Au atoms adsorbed on the surface. This problem is well known in technology of thin film production and can be solved by proper treatment of the used substrate, so that as low as 0.15 nm roughness can be reached [27].

As an example of practical application of the APC nanolithography we have created a nanostructure presented on Fig. 5. This nanostructure was made with use of a mask in the form of a ruler.

In addition to the limitations listed above, creation of nanostructures with the typical size under 50 nm by means of an atom pinhole camera may be complicated by a variety of technical reasons, such as (1) mechanical instability of the membrane with nanoapertures [28]; (2) thermal drift of the holder of the mask and the membrane with the substrate; (3) clogging of the membrane's smaller-diameter nanoapertures [15]; (4) atoms' surface diffusion [29].

4. Conclusions

In conclusion, we have successfully implemented the concept of atom pinhole camera as a novel tool for atom nano-fabrication offering the following merits: (1) it makes possible nanostructures with typical size down to 30 nm and with theoretical resolution limit down to 6 nm; (2) the nanostructures can be of an arbitrary prearranged shape; (3) size and form of nanostructures are determined by well controlled parameters; (4) creation of the great number of identical nanostructures is possible; (5) a variety of materials for nanostructures (atoms, molecules, clusters) is feasible; (6) the method is free from use of a chemically selective etching; (7) in the process of nanostructures creation no destruction of the substrate surface happens. Such technique may find application in production of elements for nanoelectronics, plasmonics, spintronics, bio-nano-sensors and metamaterials.

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