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Selective removal of atoms as a new method for fabrication of nanoscale patterned media

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Abstract

The method of 'selective removal of atoms' is proposed for purposeful efficient modification of a solid atomic composition under exposure to an accelerated ion beam of a certain energy. Such modification can dramatically change the physical properties of a thin material layer. This method could be used to create directly the needed spatial modulation of atomic composition and physical properties of a material, i.e. to produce a nanoscale patterned media for various applications (magnetic storage media, GaAs Schottky diodes and field effect transistors, optical structures, nanoscale biochips, and many others).

Keywords: Selective removal of atoms; Patterned media; Nanoscale structure; Ion irradiation; Nanodevices

1. Introduction

The objective of this paper is to demonstrate the practical opportunities of the recently discovered phenomenon of 'selective removal of atoms' [1] for producing nanoscale patterned media. It is well known that many actual practical tasks demand a production of composite materials consisting of areas with preset geometry and with different physical properties. Such materials are most prominent for applications in microelectronics and nanotechnology.

Traditionally, materials with different physical properties are those with various chemical compositions. We have experimentally demonstrated the possibility of direct alteration of a solid atomic composition under exposure to an accelerated ion beam of a specific energy. This modification of atomic composition is not a result of any chemical or nuclear reaction, but is completely caused by the selective removal of atoms of a specific type from two- or multi-atomic compounds as a result of atomic displacements induced by the accelerated ions. Such modification can result in a radical change of the material's physical properties and, in particular, to the transformation of insulators into metals or semiconductors, nonmagnetic materials into magnetic ones, changing optical properties, etc. [1]. It means that there is an opportunity to produce in thin films a desirable pattern in local areas having various atomic compositions.

The physical basis of the method is as follows. Let us consider a situation that arises during interaction

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of a monochromatic ion beam of energy E and mass m with a two-atomic crystal consisting of atoms of different masses M_1 and M_2. The maximum energy transferred by the ions to atoms of a crystal is [2]:

$$E_{\max}^{(1,2)} = \frac{4mM_{1,2}}{(M_{1,2}+m)^2} E \quad (1)$$

where $E_{\max}^{(1)}$ and $E_{\max}^{(2)}$ are maximum energies which could be transferred by the accelerated ions to atoms with masses M_1 and M_2.

The displacement of atoms from their equilibrium crystal lattice sites is a threshold effect, which occurs when the transferred energy exceeds the threshold displacement energy E_d [3]. As a rule, this energy $E_d \approx 20–25$ eV, which exceeds considerably the sublimation energy [4]. It follows from Eq. (1), that during the irradiation of two- or multi-atomic crystals, the maximum transferred energies are different for different kinds of atoms. The larger the atomic mass difference, the stronger is the difference in the transferred energies.

Thus, by varying the mass and the energy of ions, it is possible to achieve the situation in a two- or a multi-atomic crystal when the higher energy would be transferred to the atoms of low or high masses. If the maximum transferred energy exceeds the threshold value E_d for atoms of only one kind, then there exists a method of selective removal of only light (or only heavy) atoms from two- or a multi-atomic crystal [1]. The considered mechanism regarding the displacement of atoms of different kinds in a crystal refers equally to the same compounds in an amorphous state. Thus, it is clear that at the normal incident of the ion beam on a crystal surface, it is possible to achieve conditions whereby atoms of one kind only would move in the direction of the incident beam within a layer of a thickness comparable with the ion projective length in a two- or a multi-atomic crystal. At the same time the atoms of other kinds would not undergo any directed movement. Thus one can reduce the concentration or remove completely atoms of the desired kind in the proper layer of a crystal by selecting a necessary dose of irradiation. As a result, it is possible to get dramatic modifications of chemical and physical properties in the proper layer of a crystal or within a thin film.

Let us formulate some obvious features of the considered physical mechanism of selective removal of atoms:

- The rate of the process is proportional to the flux density of the incident ion beam.
- The process is naturally a non-thermal one over a wide range of irradiation temperatures; this distinguishes it principally from a chemical reaction.
- The process can be proceed in a layer below the surface even if covered by another material, if its thickness is less than the ion projective length in the layer. If, in addition, the threshold energy of atomic displacement in the additional layer is higher than the transferred energy from the ions, the directed displacement of atoms in that material will not occur. Otherwise, the atoms of material penetrate in the underlying layer and their transfer in the beam direction occurs over a distance comparable with the ion projective length in the 'sandwich' considered.

The above-mentioned features of the proposed method determine its potential for efficient, purposeful, and spatially modulated modification of the composition, structure, physical, and chemical properties of materials. It will be shown below that such a modification of chemical composition can dramatically change the physical properties of a thin material layer, e.g. to produce an insulator–metal transition, to change magnetic or optical properties and so on. Thus a possibility exists to create a controlled volume 'pattern' of areas with different physical properties. As to the materials for selective removal of atoms, the metal oxides, hydrides and nitrides that are insulators in the initial state hold the greatest practical interest.

2. Experimental results and discussion

During our studies we tested all the above-mentioned compounds, with metal oxides being investigated most thoroughly. It should be noted that the qualitative features of the effects accompanying selective removal of atoms are identical in all the types of compounds studied. Experiments have been performed with thin films of different thicknesses, produced by reactive sputtering of metals in the

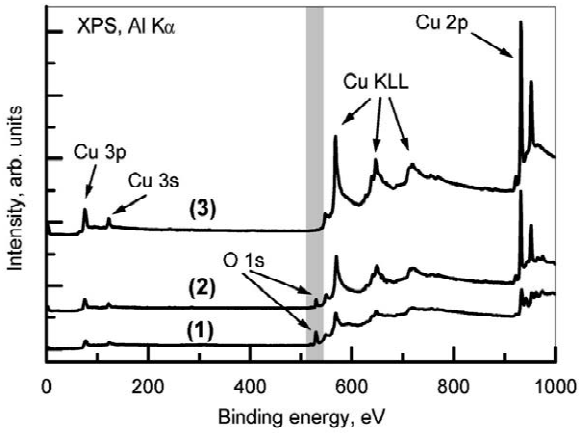

Fig. 1. XPS-spectra for CuO-film in the initial state (1) and after proton irradiation of various doses (2,3). They demonstrate the reduction of oxygen concentration in the film during irradiation.

atmosphere of relevant gases (oxygen, nitrogen or hydrogen). The irradiation was performed by proton beam, with the needed energy being dependent on the material (for oxides it makes 1–5 keV).

During the process of selective removal of atoms from the various compounds, the material volume can change. It is clear that such a process will result in a decrease in material volume (as compared to the original volume) due to a bulk relaxation of metal atoms into voids created by removal of atoms. The measurements show that after irradiation the thickness reduction of an irradiated section is about 40–60% (depending on the chemical composition of the compound). It is essential that in spite of such a significant film thickness reduction, there are no changes of linear film dimensions in the plane. The latter is in agreement with the fact that in our numerous experiments we observed neither film exfoliation nor violation of its continuity. It is caused by radiation creep of the irradiated film [5].

Fig. 1 illustrates typical changes of a chemical composition during the selective removal of atoms. Fig. 2 shows the typical experimental results on both electric (a) and magnetic (b) property modifications of metal oxides during the proton irradiation. As a result, the insulator (MoO_3) transforms into metal (Mo), and non-magnetic material (Co_3O_4) becomes magnetic (Co).

It is important to note that selective removal of atoms allows one to simultaneously change the physical properties of separate layers in a multi-layer

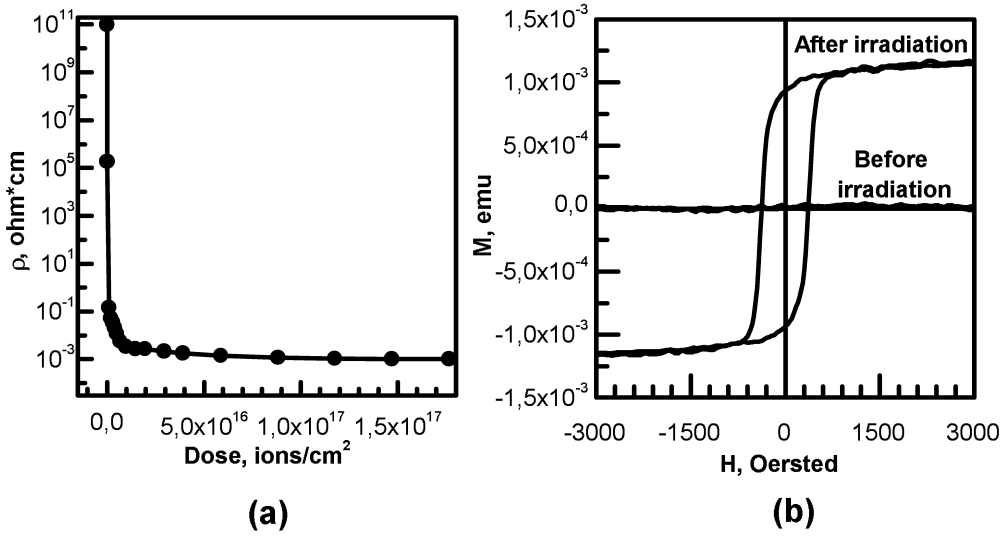

Fig. 2. Typical behavior of electrical resistivity (a) and of hysteresis loop (b) of metal oxides during proton irradiation. It demonstrates the transition of insulators into metals (a), and non-magnetic materials into magnetic ones (b).

structure. This is a principal advantage of the proposed technology compared to any other known technology or physical principle. As a result it enables the simultaneous (in parallel) production of structures with different shapes and properties in various layers by ion irradiation through the same mask. Such a procedure allows one to get an overlapping of the structure elements in various layers with an accuracy of about 1 nm. The latter feature is a crucial point in the production of multilayer nanostructures.

Another important advantage of this method is a possibility of producing hybrid electronic devices in combination with traditional CMOS-technology, the nanostructures being prepared by the proposed technology.

In Fig. 3, the experimental results are shown which demonstrate the possibility of simultaneous changes of physical properties in various multilayered structures with alternating functional and auxiliary layers (the scheme of the sandwich with different layers irradiated through the same mask (a, b). Also shown in Fig. 3 is the dose dependence of Co_3O_4 and CuO layer resistances in the sandwich during their consecutive transformation under irradiation into Co and Cu, respectively (c).

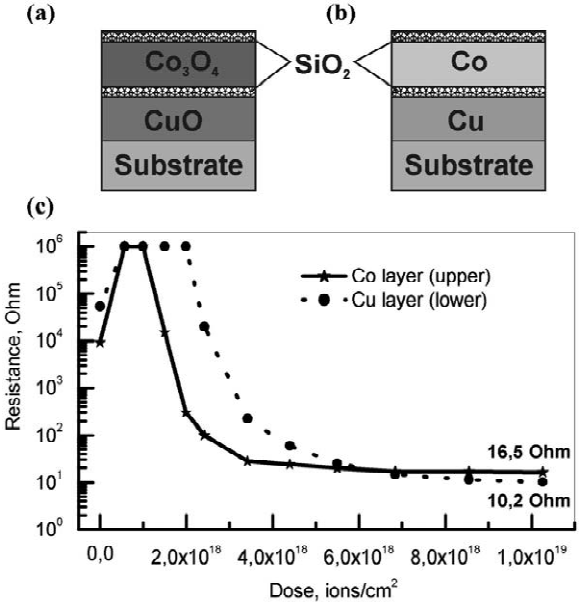

Fig. 3. Schemes of multilayer structure in the initial state (a), after proton irradiation (b) and the dose dependence of Co_3O_4 and CuO layer resistances in the sandwich during their consecutive transformation under irradiation into Co and Cu, respectively.

It is very promising to use the proposed method for formation of magnetic patterned media with high areal density. To attain an extreme density of data storage with magnetic recording media, it is necessary to use the patterned media consisting of regularly positioned magnetic nanogranules of identical form and orientation. The smallest possible size of the granules is defined by the so-called superparamagnetic limit. The minimum distance between the granules depends on dipole–dipole intergranular interaction and can not be less than the lesser granule size.

Elongated (anisotropic) single-domain Co bits of a small size (from 320×1600 nm down to 15×45 nm) in Co_3O_4 matrix have been produced through a mask prepared by electron lithography. Examples of the structures are shown in Figs. 4 and 5. These images were obtained by atomic and magnetic force microscopy. For the moment, the best resolution and, accordingly, the smallest bit size is 15×45 nm.

Fig. 6 shows a GaAs Schottky diode and field effect transistor with the gate produced by selective removal of atoms. The current–voltage characteristics of these structures demonstrate the well-pronounced field effect (transistor behavior) of the same quality as for transistors obtained by conventional technologies. It was also shown that after ion irradiation the carrier mobility of GaAs does not change. In other words, the carrier mobilities in the structures obtained by conventional and by the new method differ by less than 5%.

We are also planning to apply our technology for developing a new generation of nanoscale biosensors for a fast and detailed on-site identification of both the pathogen or virus and its possible modifications. This task seems very important because the limit parameters of traditional biochips are already reached and their characteristics cannot be essentially improved. In fact, the proposed technology provides a possibility for a real breakthrough in biochips due to a change to nano-detectors having an element size comparable with a molecule itself and, correspondingly, to electro–physical registration of individual molecules.

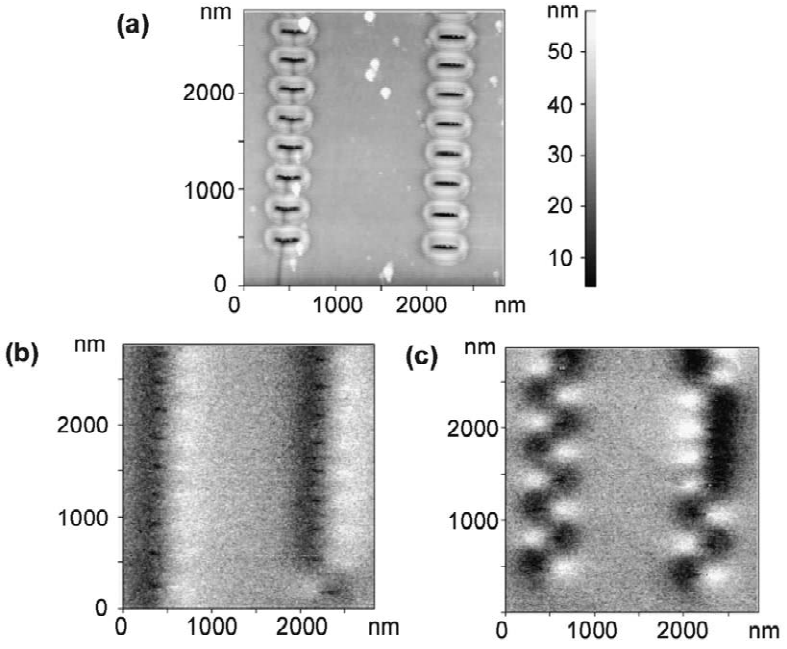

Fig. 4. Examples of patterned magnetic media with areal densitiy 1.2 Gb/in.^{2} (bit size 80×400 nm^2). (a) AFM topography image and (b,c) magnetic force microscopy images with the different magnetization direction in single domain bits.

3. Perspectives and conclusions

In the present paper, the physical principles are described and the conditions are formulated which allow for selective removal of certain atoms from multiatomic solids by their thin films or thin multilayers irradiation with accelerated ions. The essential features of the process that are originated from the

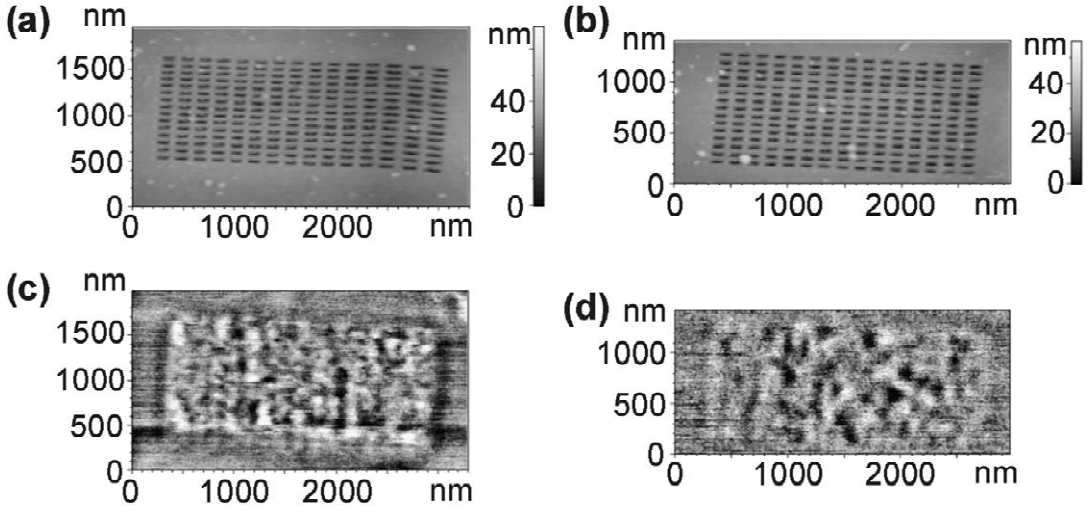

Fig. 5. Examples of patterned magnetic media with areal densities: 45 Gb/in.^{2} (bit size 25×125 nm^2) (a, c) and 57 Gb/in.^{2} (bit size 20×100 nm^2) (b, d). (a, b) AFM topography images, (c, d) magnetic force microscopy images.

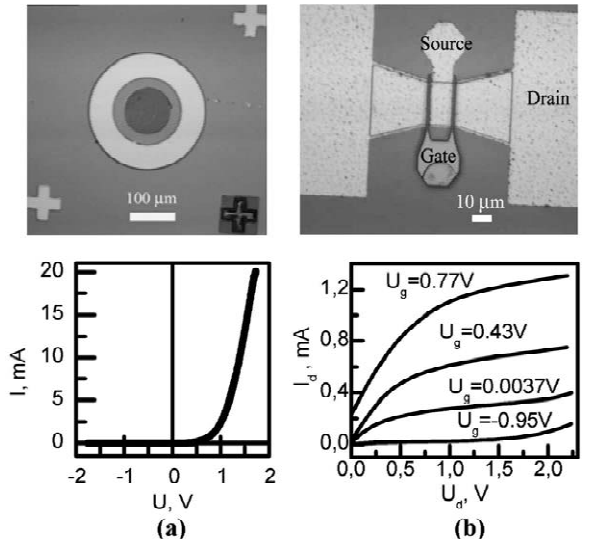

Fig. 6. A picture of a GaAs Schottky diode and its current–voltage characteristic (a) and the same for a GaAs field effect transistor with a Schottky barrier (b). The gates were produced by the method of selective removal of atoms.

proposed physical mechanism were listed. We demonstrated experimentally the possibility of selective atom removal, confirmed the process mechanism, and investigated its most essential features. In the course of these experiments, we revealed that selective atom removal from multiatomic compounds is accompanied by radical alterations of the most important physical properties of materials, such as electrical, magnetic and optical. Investigations show that the modification of a material's properties is a result of changes in their atomic composition and structural transformations (phase transitions), which accompany the process. Besides, we have shown some prospective applications of the given method for production of multilayer nanostructures for various purposes.

Nowadays there is only submicron industrial technology for microelectronic device production (with the minimum design standards 0.07–0.1 μm) based on optical lithography. There is the absolute necessity in industrial lithography for producing devices with smaller element size. Many experts consider nanoimprint lithography as the most realistic alternative to optical methods [6–10].

But even nanoimprint lithography itself implies production of multilayer devices in a consecutive manner similar to optical lithography (i.e. consecutive creation of metal, dielectric and other layers and intermediate structures). Extending traditional consecutive principles of microdevice manufacturing to multilayer nanodevices demands the solution of two basic problems: a creation of structural elements with the sizes of 10 nm and less, and ensuring the overlapping of the structure elements in various layers with accuracy of 1–2 nm. Within the frameworks of optical lithography and of traditional consecutive layering principles, the solution of these problems is not obvious now, nor will it be in the foreseeable future.

Nanoimprint lithography allows one to solve the first problem just now: the single-layered nanostructures with the element size of less than 10 nm [6,7], and with the areal density of elements ~700 Gb/in.^{2} [11] have already been produced.

To solve the second problem within the framework of traditional consecutive manufacturing methods is not possible now. It can be done by only the combination of nanoimprint lithography and the method of selective removal of atoms. The latter allows one to create various patterns simultaneously in several layers through the same mask. As a result, self-overlapping with ~1 nm accuracy can be obtained.

Besides this practical reason the application prospectives of ion-beam atom removal are conditioned by a number of other reasons:

1. Ion beams have a few important advantages:
   - Effects of back-scattering inherent (for ion beams could be practically eliminated) that results in increasing spatial resolution of patterns on usual thin films deposited on massive substrates or thin layers on/in massive samples.
   - Short wavelengths of incident particles important for high resolution, could be obtained with low accelerating voltages.
2. The method could be used to create directly the needed spatial modulations of atomic composition and physical properties of a material, such as metal or semiconductor 'patterns' in insulators, magnetic drawings in nonmagnetic substances, light guides in opaque media, etc.

3. It is important that during proton irradiation they (protons) could leave the material due to diffusion without any negative influence on material properties.

In conclusion, a new method for fabrication of nanoscale patterned media is proposed based on the effect of selective removal of atoms from multi-atomic compounds under exposure to an accelerated ion beam of a specific energy. The main advantages of the proposed technology are as follows:

- It is a parallel processing technique with respective high throughput.
- Possibility exists to form the various nanopatterns with needed physical properties in different layers through the same mask.
- An intrinsic feature of the method is the self-overlapping (~1 nm) of elements in different layers of the structure.
- The method can be easily combined with traditional CMOS technology to produce hybrid devices.

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