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INSTRUMENTS AND METHODS OF INVESTIGATION

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Controlled ion-beam transformation of electrical, magnetic, and optical materials properties

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Contents

Abstract. The key condition for radical progress in technology in the 21th century is the availability of a technique for the controlled production in a solid of 3D patterns incorporating regions of desired physical and chemical properties, with the possibility of downsizing pattern elements to the nanometer scale being a crucial requirement. In this paper, a method for changing the electrical, magnetic, optical and other key physical properties in a direct and deliberate manner by radically modifying the solid's atomic composition is proposed for the first time. The physical foundation of the new nonlithography technology is the observation — thoroughly investigated and well verified in our numerous experiments — that accelerated particle beams can be used to selectively remove atoms from thin films of di- or polyatomic compounds. It is shown, in particular, that by selectively removing atoms of a given sort, dielectrics can be transformed into metals or semiconductors, nonmagnetic materials into magnetic ones, and the optical and other properties of materials can be changed radically. The selective removal of atoms of a specified sort from a material is of great interest for future technologies, especially for those relevant to nanoelectronics and, more broadly, to the numerous 'nanoproblems' ahead in the third millennium.

1. Introduction

Traditional methods for sweeping changes of the physical properties of substances (considered as compounds of different atoms) are based on chemical synthesis resulting in a principal change of the combination of physical properties of final products compared with those of the interacting initial reagents. An analogous transformation of properties is possible through chemical decomposition of di- or polyatomic compounds. Similar processes can be accompanied by radical modification of the electrical conductivity, magnetic or optical properties and other physical and chemical qualities of a material, and have long been used in practice. In addition to chemical and phase reactions leading to sweeping changes of the atomic composition of substances, there is another method associated with nuclear reactions of different kinds. The first of these methods (chemical) has such a wide field of applications that they could not even be enumerated. As for the second, the field of its use is quite narrow and is often of exotic character.

It is essential that none of these methods can provide *controlled spatial modulation* of the transformation process of atomic composition in the body volume (first of all, in solids). In other words, those methods do not allow one to produce a *desired 3D 'pattern'* of local atomic composition variations in *a controllable* way.

Developing such a method could result in the production of materials with controlled spatial modulation of needed physical and chemical properties. Something like this is now realized in lithographic production of metal layers in microprocessors. However, in this case the desired result is reached not by means of changing the atomic composition of the starting compound but through a complex multistage physicochemical (and even mechanical) treatment of consecutively used different materials. Such a situation is also typical of producing arbitrary structures by methods of molecular beam epitaxy (MBE) [1], direct ion deposition [2, 3] and so on.

A somewhat different situation arises in the event of spontaneously forming nanostructures produced, for example, by special chemical techniques and MBE methods or as a result of the silicon matrix exposure to electron beams [4 – 9]. However, effects of self-organization do not allow the production of nanostructures of arbitrary geometry.

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This study demonstrates the possibility of purposeful and radical single-stage change of atomic composition of solids by the action of accelerated beams of certain energies. That transformation of atomic composition is not associated with the proceeding of some chemical or nuclear reactions but is fully connected with the *selective removal of atoms of a given sort* from di- or polyatomic compounds as a result of atomic displacements by the beam of accelerated particles. Such variations of atomic composition can lead to sweeping changes of the physical properties of substances and, in particular, to the transformation of insulators into metals or semiconductors and nonmagnetic materials into magnetic ones, to the modification of optical properties and so on.

2. Physical foundation for selective removal of atoms of a given sort from di- or polyatomic compounds through the atomic displacements

Let us consider the situation which arises during the interaction of a monoenergetic beam of nonrelativistic particles of energy E and mass m with a diatomic crystalline solid consisting of atoms with masses M_1 and M_2. The maximum energy transferred by beam particles to the atoms of the solid is [10]

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

where $E_{\max}^{(1)}$ and $E_{\max}^{(2)}$ are the maximum energies which accelerated particles could transfer to atoms with masses M_1 or M_2. The displacement of atoms out of lattice sites to form stable Frenkel pairs is a threshold effect and occurs in the case when the energy transferred to crystal atoms is more than the threshold displacement energy $E_{\rm d}$ [11] [1]. If the crystal consists of atoms of only one sort, $E_{\rm d}$ has a single value for each crystallographic direction. As a rule, the $E_{\rm d}$ value is a few tens of electron-volts, i.e. an order of magnitude higher than the sublimation energy. Such a high value could be explained as follows. To generate a stable Frenkel pair, the knocked-on interstitial atom has to be removed from the vacancy over a distance of ~ 5 lattice periods. During this transfer, the interstitial atom interacts with crystal atoms positioned close to its trajectory. That needs a certain energy input depending on the number of atoms which interact with the interstitial atom in the course of its transfer from the own vacancy to the nearest stable position and on the coordination of those atoms, which is determined by the trajectory of the interstitial atom motion relative to one or another lattice crystallographic directions.

From the preceding it is clear that threshold energies for atoms of different sorts in di- or polyatomic crystals will, in general, differ for various crystallographic directions. In addition, it follows from relationship (1) that on irradiation of di- or polyatomic crystals, the maximum energies transferred to dissimilar atoms by accelerated particles are also different. The stronger the difference of atomic masses, the higher is that distinction. If $m < M_1 < M_2$, then $E_{\max}^{(1)} > E_{\max}^{(2)}$, and if $M_1 < M_2 < m$, then $E_{\max}^{(1)} < E_{\max}^{(2)}$.

Therefore, varying the mass and the energy of beam particles one can attain conditions when the higher energy will be transferred to lighter (if $m < M_1 < M_2$) or heavier (if $M_1 < M_2 < m$) atoms in the di- or polyatomic crystal. That opens up a new possibility of *selective removal* of only light (or only heavy) atoms from the di- or polyatomic crystal. Such selective removal of atoms of a single sort under exposure to particle beam is possible in the case when the maximum energy transferred to atoms exceeds the threshold energy $E_{\rm d}$ for atoms of that sort only.

These considerations concerning displacements of different atoms in *single crystals* are applicable, in great part, to the same compounds resided in an *amorphous state*. In conformity with the problem at hand, the most significant distinction of amorphous materials from single crystals lies in the fact that there is no spatial anisotropy of the displacement threshold energy in amorphous substances. However, the above distinction is not an obstacle for selective removal of atoms, if the conditions mentioned are fulfilled.

Thus, it is clear that for a particle beam incident normal to the crystal surface, conditions could be built up to displace atoms of a single sort in the direction of the incident beam through a crystal thickness comparable with the projective range of beam particles in the di- or polyatomic crystal. In doing so, other atoms would not be subjected to any directed transfer. This allows one to diminish significantly the concentration of selected atoms in the corresponding crystal layer or remove them completely by varying the incident particle fluence. As a result, one can cause efficient modification of physical and chemical properties in the relevant crystal layer or thin films. Such a transformation can occur in layers whose thickness is comparable with the projective range of beam particles in the irradiated material.

Some obvious features of the considered mechanism of selective removal of atoms may be formulated as follows:

(1) The rate of selective atomic removal is proportional to the flux density of incident beam particles.

(2) The process of selective atomic removal under the action of the incident beam is, in nature, nonthermal over a wide range of irradiation temperatures that distinguishes such a process principally from chemical reactions and processes of substance transformation according to phase diagrams.

(3) The process of selective atomic removal from crystals could be realized through an upper (relative to the beam) additional layer of another material if its thickness is less than the projective range of beam particles in the layer. Moreover, if the threshold energy of atomic displacement in the additional layer is higher than the maximum energy transferred to them from beam particles, then directed displacement of atoms in that material does not occur. Otherwise, the implantation of atoms of the material to the underlying layer and their transfer in the beam direction could occur over a distance comparable with the projective range of beam particles in the 'sandwich' considered.

The above-mentioned features of the proposed method of action on thin films or layers indicate its perspective for the efficient, purposeful and spatially modulated modification of

[1] In some cases, the generation of Frenkel pairs (radiation defects) on irradiation could be associated not only with threshold effects which are specific to atomic displacements out of lattice sites due to *elastic* (quasi-elastic) scattering of incident particles by atoms. In insulators, Frenkel pairs can arise owing to the excitation of the electron subsystem of a crystal due to *inelastic* interaction of incident particles with solid atoms. This phenomenon is well known for wide-gap ion insulators of which typical examples are alkali-halide crystals [12]. In the present work this effect is not considered as: (1) in every case, the classic threshold generation of radiation defects has been observed with all studied compounds, and (2) it is impossible to produce *directed* displacements of interstitial atoms as a result of Frenkel pair generation due to excitation of the electron subsystem in quasi-amorphous or fine-crystalline solids.

the composition and structure of the materials as well as their physical and chemical properties.

3. Modification of structural, electrical, magnetic and optical properties by selective atomic removal

In deciding on a particular material for selective removal of atoms, metal compounds which in the initial state are insulators hold the greatest practical interest. Among diatomic compounds, these are, for example, many metal oxides as well as some metal hydrides and nitrides. Though in the course of this work experiments were performed with compounds of all above-mentioned types, metal oxides along with certain semiconductor oxides were investigated most thoroughly. The qualitative features of the effects accompanying selective atomic removal are identical in all the above-mentioned compounds. The aim of the experiments was to selectively remove oxygen (nitrogen or hydrogen) atoms by irradiation of the original insulator and to obtain, finally, a metal or semiconductor. Experiments were performed with thin films of a different thickness, which were fabricated by reactive sputtering of metals in an atmosphere of relevant gases (oxygen, nitrogen or hydrogen) [13].

In most cases, the films were irradiated by protons with energies from ~ 150 up to ~ 1200 eV. In addition, in some experiments, films were irradiated in an electron microscope column by electrons with an energy of 100 – 200 keV and by helium ions with energies ranging from 200 to 300 eV.

In the work, complex investigations of initial and irradiated films were performed, which included: measurements of electrical conductivity within the temperature range 4.2 – 300 K, magnetic and optical properties [13], structural measurements by means of transmission electron microscopy and electron diffraction analysis [14], the tunnel microscopy technique [15] and by methods of X-ray photoelectron spectroscopy [16].

To measure the electrical conductivity of films in the course of the proton irradiation, special electrical through contacts were built into the film substrates. One of the contact ends was polished level with the surface of the substrate on which the film studied was deposited later.

Films were deposited on substrates of different insulators with high electrical conductivity (higher than $10^9\,\Omega\cdot$cm), for instance, on a diamond-like covering or glass. Check experiments on substrate irradiation showed that radiation-induced effects changing electrical resistance of substrates are not significant compared with the observed effects of changing the properties of the studied films themselves.

Investigating films of different di- and polyatomic dielectric materials shows that their behavior on irradiation strongly depends on the energy of beam protons, all other factors being the same. Observed radiation-induced modification of thin-film properties was of a clearly defined threshold character [2]. No modifications of the structure, composition, electrical or magnetic properties of the thin films were detected until the proton energy reached a certain minimum value (which is individual for each of the materials studied). According to the preceding, this means that as long as the energy E_{max} transferred to material atoms by protons is low ($E_{max} < E_{d1}$, E_{d2}, where E_{d1}, E_{d2} are the displacement threshold energies for atoms of the first and second kinds, respectively), atomic displacements from lattice sites do not take place. With increasing proton energy, conditions appear when $E_{d1} \leqslant E_{max} < E_{d2}$. Then principal variations of structure, composition, electrical, magnetic and optical properties of materials begin to be observed. As shown below, all these variations are connected with selective removal of oxygen, nitrogen or hydrogen atoms from the studied compounds (oxides, nitrides or hydrides, respectively). On further increasing the proton energy, the condition $E_{d1} < E_{d2} < E_{max}$ is reached and atoms of both sorts in diatomic compounds begin to be displaced from lattice sites. Within the relevant energy range, the selectivity of atomic displacements diminishes with increasing E_{max}. Such a regime is not considered below, being less interesting.

Now we consider in detail experimental results on selective atomic removal for diatomic compounds in the regime when the condition $E_{d1} \leqslant E_{max} < E_{d2}$ is fulfilled. Investigations show that initial dielectric films of different materials reside in one of three structural states:

(1) a polycrystalline state with grains of 10 – 100 nm;

(2) an amorphous state;

(3) a combined state with variously oriented grains distributed in an amorphous matrix or separated by thin amorphous interlayers.

The electron diffraction patterns of all the above-mentioned types of films correspond to the annular diffraction specific to polycrystals, or look like a diffuse halo, or appear to be a composition of both those types of diffraction. It should be also noticed that most of the studied films had crystal structures which did not correspond to the handbook data for the equilibrium compounds of the same composition. It is known that a similar situation is characteristic of thin films and is associated with their intrinsic inclination to form nonequilibrium and polymorphous phases [13, 17]; the same circumstance could lead to different anomalies in thin-film properties.

Experiments show that, independently of the structure of original insulators, the films involved behave equally in the course of selective atomic removal. At the first stage of irradiation of insulators (of polycrystalline or combined structure), amorphization of crystallites takes place. This effect is detected clearly by a disappearance of crystal contrast in the dark-field electron microscope images (see Fig. 1a). With this, a significant reduction of the intensity and broadening of point reflexes (lines) in annular electron diffraction patterns (up to their complete transformation into a diffuse halo characteristic of amorphous materials) are observed (see Fig. 1b, c).

Further irradiation is accompanied by yet another phase transformation corresponding to the transition from the amorphous state to the crystal one. This is evident from the appearing crystal contrast in the dark-field electron microscope images associated with newly generated grains (see Fig. 1a). Simultaneously, complete or partial (depending on original material) disappearance of the diffuse halo, increase in intensity and the appearance of a new system of diffraction rings in the electron diffraction patterns occur, testifying the appearance of a new (metallic) phase (see Fig. 1c, d). The possibility for the formation of a metallic phase after irradiation with a high fluence is demonstrated below when presenting the results of investigations.

[2] In what follows, basic effects are predominately demonstrated for diatomic metal oxides (because of their essential qualitative similarity for all compounds).

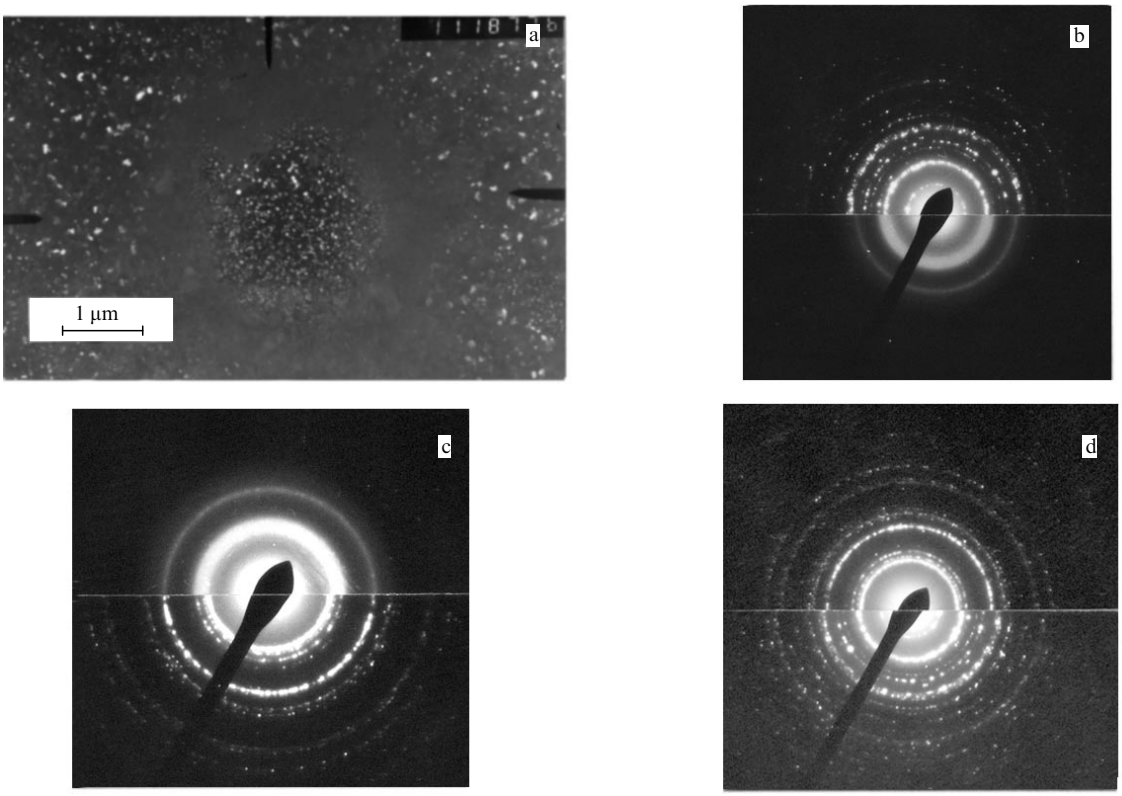

Figure 1. Typical variations of the microstructure and diffraction patterns in the course of selective removal of atoms of one sort from the compound. (a) Dark-field image of a thin-film microstructure fragment for a diatomic compound after electron irradiation ($E = 200$ keV). Seen is the nonsimultaneity of the structural transformations over the irradiated area due to the Gaussian distribution of the electron beam intensity. In the center, there are crystallites of a new phase surrounded by an amorphous phase, while in the periphery, there are original phase crystallites not subjected to irradiation. (b) Combined diffraction pattern: at the top — from the original polycrystal phase (before irradiation); at the bottom — from the intermediate amorphous phase. (c) Combined diffraction pattern: at the top — from the intermediate amorphous phase; at the bottom — from the crystallites of a new phase formed in the course of irradiation. (d) Combined diffraction pattern: at the top — from the original polycrystal phase (before irradiation); at the bottom — from the crystallites of a new phase formed in the course of irradiation.

In most cases, diffraction in crystallites of the newly generated metallic phase does not correspond to those types of crystal lattices which are cited in reference books for the relevant pure bulk metals. At the same time, diffraction in crystallites of the new crystalline phase (produced from insulators due to selective atomic removal) in some instances corresponds to diffraction data which have been obtained for thin films of the relevant pure metals. For example, with selective removal of oxygen atoms from the oxide WO_3, metallic tungsten has been generated in an fcc lattice of period $a = 4.19 \pm 0.02$ Å instead of the bcc lattice typical for bulk tungsten. As mentioned above, this could be associated with the polymorphism characteristic of thin films. However, in some works (see, for instance, Ref.[18]) the formation of thin W-films in an fcc lattice of period $a = 4.15$ Å has been observed on sputtering pure tungsten. Taking into account that these authors estimated the accuracy of their electron diffraction measurements to be within $\sim 2\%$ [18], one should consider the coincidence of lattice parameters as very good.

Nevertheless, in some cases the metal film with crystal lattice identical to the proper bulk metal is produced on selective atomic removal. For instance, copper was produced on selective removal of oxygen atoms from CuO oxide, exhibiting diffraction pattern characteristic of the fcc lattice. Measured value of the lattice parameter a was found therewith to be 3.60 ± 0.02 Å, whereas the known reference magnitude of the same parameter for copper is 3.615 Å.

Experiments show that variation of the irradiation temperature (from -198 up to 300 °C) does not influence the rate of phase transformations (amorphization and subsequent crystallization).

In spite of some distinctions, the dependences of electrical resistance of different films on the proton fluence have common features. As a rule, at the initial stage of selective removal of atoms of a certain kind (for instance, oxygen atoms), a sharp reduction (up to $\sim 10^{10}$ times) of the film electrical resistance is observed (see Fig. 2, curve *1*). However, for compounds with low starting resistivity, a temporary increase of resistivity is at first observed during the initial stage of irradiation with a subsequent sharp reduction (cf. Fig. 3). Further, on increasing the irradiation dose from ~ 10 up to ~ 400 dpa [3], the resistivity continues to slowly reduce or asymptotically approaches a limiting minimum value. The latter is defined by properties of the metal whose oxide is subjected to irradiation. In the long run the irradiation reduces the electrical resistivity by a factor of 10^{12} at room temperature, and even more at lower temperatures.

In the proton energy range $E_{d1} \leqslant E_{max} < E_{d2}$, the shape of fluence dependences of resistivity is qualitatively and quantitatively similar for equivalent irradiation times.

At higher proton energies, when $E_{max} > E_{d2}$, the character of fluence dependences of resistance is changed due to

[3] Abbreviation 'dpa' means the number of displacements per atom.

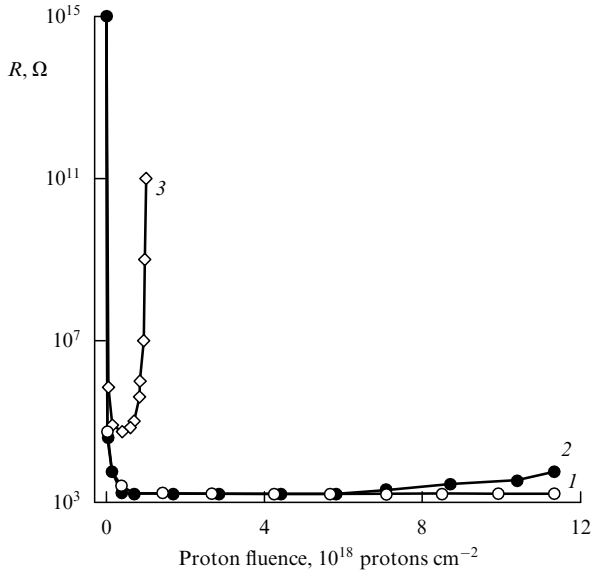

Figure 2. Fluence dependence of the electrical resistance of WO_3 film (of 10 nm in thickness) on proton irradiation: *1*, $E = 100$ eV; *2*, $E = 1050$ eV ($E_{max} - E_{d2} \approx 2$ eV); *3*, $E = 5000$ eV ($E_{max} - E_{d2} \approx 85$ eV).

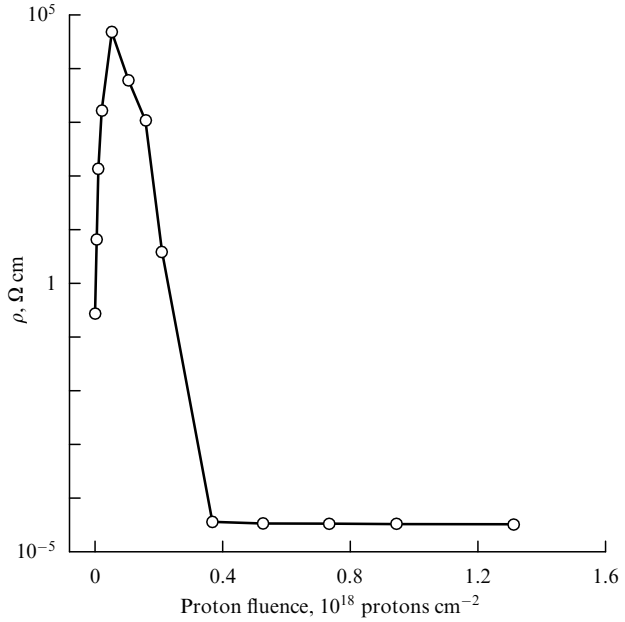

Figure 3. Fluence dependence of the electrical resistivity for CuO films (of 100 Å in thickness) on proton irradiation ($E = 450$ eV).

displacements of metal atoms (cf. Fig. 2, curves *2*, *3*). In the case when $(E_{max} - E_{d2}) \leqslant 3-5$ eV, only a weak increase in the resistance of the film material is observed at high proton fluences (cf. Fig. 2, curve *2*). But if the maximum transferred and threshold energies differ significantly ($E_{max} - E_{d2} \geqslant 50-80$ eV), the character of fluence-dependent resistance is changed sharply (cf. Fig. 2, curve *3*). Our investigations show that the pronounced increase in the electrical resistance for high proton fluences (cf. Fig. 2, curve *3*) arises from the physical sputtering of a film material, and the respective reduction of its thickness due to metal atom sputtering. In this connection, the experimental results cited below refer to the film irradiation by protons of an energy which is only sufficient for the displacement of light atoms in studied di- or polyatomic materials.

X-ray photoelectron spectroscopy of the film material irradiated by proton beams of different fluences shows that an increase in the fluence of protons whose energy corresponds to the condition $E_{d1} \leqslant E_{max} < E_{d2}$ is accompanied by a monotonic reduction of oxygen concentration in the film material (see Fig. 4). After proton irradiation with high fluences (~ 400 dpa for oxygen atoms), one is left with only traces of oxygen in the films. Then the electrical resistivity of the films takes values typical for metal films ($\sim 10^{-3}-10^{-5}$ Ω·cm) but distinctly exceeding the reference values for bulk materials. Thus, the energy E_{d1} corresponds to the threshold displacement energy of oxygen atoms in the studied diatomic compounds. It should be noticed that for the investigated oxides this energy varies within wide limits: from ~ 35 eV (Fe_2O_3) up to ~ 100 eV (TiO_2) (in some events the threshold energy for oxygen atoms exceeds 100 eV).

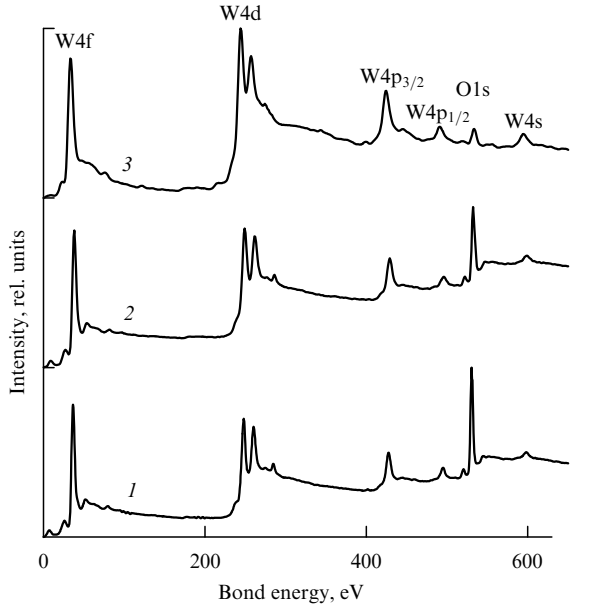

Figure 4. X-ray photoelectron spectra for WO_3 films (of 100 Å in thickness) in the initial state and after proton irradiation ($E = 1000$ eV) of various doses: *1* — before irradiation; *2* — the fluence of 7×10^{16} protons cm^{-2}; *3* — the fluence of 7×10^{17} protons cm^{-2}.

The fluence dependences depicted in Fig. 2 demonstrate that the energy E_{d2} corresponds to the threshold displacement energy of metal atoms. The increasing resistivity at high proton fluences, when $E_{max} > E_{d2}$, is conditioned by reducing film thickness due to metal atom displacements, which could be readily detected experimentally. The threshold displacement energy of metal atoms varies from ~ 20 eV (for W in WO_3) up to ~ 70 eV (for Ti in TiO_2).

To ensure that the conductance of the materials produced by the bombardment is of the metal type, we studied the electrical resistivity temperature dependences of selected materials. In Fig. 5 are shown the temperature dependences of electrical resistance for (1) the original CoO-oxide film (curve *1*); (2) the same film irradiated with two different proton fluences (curves *2*, *3*), and also (3) a film of the same thickness obtained by ion sputtering of the pure metal (curve *4*). For the sake of clearness, the dependences of the reduced resistance $R(T)/R(300\ \mathrm{K})$ are represented in the figure. It is

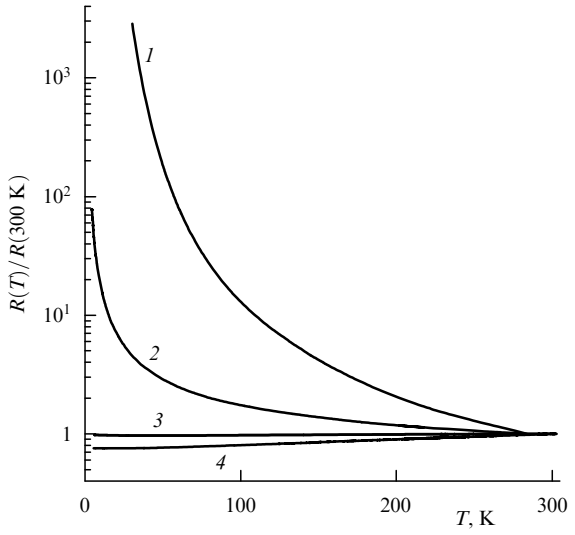

Figure 5. Temperature dependences of the reduced resistance $R(T)/R(300\ \mathrm{K})$ for Co films of 100 Å in thickness: *1* — CoO oxide before irradiation; *2* — CoO oxide after irradiation up to a fluence of 0.5×10^{18} protons cm^{-2}; *3* – CoO oxide after irradiation up to a fluence of 10×10^{18} protons cm^{-2}; *4* — Co obtained by ion sputtering of the pure metal.

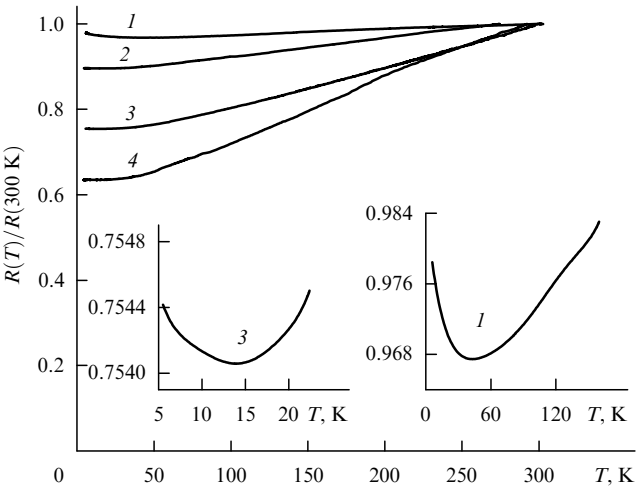

Figure 6. Temperature dependences of the reduced resistance $R(T)/R(300\ \mathrm{K})$ for Co and Cu films of 100 Å in thickness: *1* — Co film produced by selective atomic removal from an oxide; *2* — Cu produced by selective atomic removal from an oxide; *3* — Co obtained by ion sputtering of the pure metal; *4* — Cu obtained by ion sputtering of the pure metal. In the insets, curves of enlarged scale for pure Co (*3*) and Co produced from an oxide (*1*) demonstrate minima at low temperatures. At the same time, the same curves for Cu are practically monotonic.

seen that with increasing proton fluence the temperature coefficient of resistance $\mathrm{d}R/\mathrm{d}T$ increases and even changes its sign from the negative one, typical for insulators (Fig. 5, curves *1*, *2*), to a positive one (curves *3*, *4* in Fig. 5) corresponding to metal conductivity. For metal films obtained by selective atomic removal, extrapolation of the temperature resistivity dependences to $T = 0$ results in a clearly nonzero residual conductivity that unambiguously indicates their metal character of conductivity. More detailed analysis shows that the resistivity of the original insulator and that of the material obtained at low irradiation doses are well described by the relationship $\rho \propto \exp[(T_0/T)^{1/2}]$ known for hopping conductivity, where the parameter T_0 diminishes with increasing irradiation dose. Such dependence is well known and describes the conductivity of systems where charge transfer occurs via electron tunneling. On further increasing irradiation dose, the conductivity – temperature dependence of the studied materials develops an appearance typical for metal glasses or amorphous and quasi-amorphous metals and looks like a similar dependence for a deposited film of pure metal (see Fig. 6 and the insets to it). Indeed, at relatively high temperatures the temperature coefficient of resistance demonstrates positive sign and the dependence $R(T)$ is approximately linear; at lower temperatures there appears a characteristic minimum on the $R(T)$ curve (cf. Fig. 6), and at even lower temperatures $R \propto \ln T$ that is in good agreement with known results for metallic glasses [19].

In some cases (as an example, for copper produced by selective removal of oxygen atoms from CuO oxide), this dependence is practically monotonic and looks analogous to that corresponding to a metal film obtained by ion sputtering of pure copper (cf. Fig. 6, curves *2*, *4*).

Apart from the above-cited features, some characteristic properties should be noted which confirm the resemblance of the materials obtained to quasi-amorphous (ultradisperse) metals. Firstly, the characteristic values of the residual resistivity for the materials obtained and quasi-amorphous metals are similar and much higher than those of crystal analogs. Secondly, in both cases the values of the temperature coefficient of resistance are of the order of several percent per Kelvin [19]. Finally, there is a weak dependence of the resistivity on the film thickness, associated with the significant role of electron scattering from intergrain boundaries, within crystal grains and in the amorphous phase. (The thickness dependence of film conductivity is discussed below in more detail.) Estimates of the electron mean free path l in the material give a value of $\sim (0.3-10) \times 10^{-7}$ cm, so in the case considered $l \sim 1\ \mathrm{nm} \ll d \sim 10\ \mathrm{nm}$ that excludes the manifestation of classical size effects [20]. Irradiating the oxide of mostly refractory metal — tungsten, we did not succeed in obtaining a positive temperature coefficient of resistance, but even in that case there was a nonzero residual resistivity of $\sim 8 \times 10^{-4}\ \Omega\,\mathrm{cm}$ and, hence, the metallic conductivity of the material produced is not in doubt. At helium temperatures, the sign of the temperature coefficient of resistance becomes positive and experimental results could be described by the relationship $\sigma = 1/\rho \propto \ln T$ characteristic of quasi-two-dimensional disordered metals [21].

Experiments demonstrate that on varying the thickness d of irradiated films over a wide range (but, naturally, with d not exceeding the projective proton range in the relevant material), the resistance R of metal films (obtained under identical irradiation conditions) changes according to the relationship $R \propto \rho/d$, where ρ is the electrical resistivity of the film material.

In Table 1, the results of electrical resistivity measurements on metal films produced by ion sputtering of pure metal targets and the same metals obtained by selective removal of oxygen atoms from oxide with proton irradiation are shown. For comparison, reference values of electrical resistivity for bulk metals are also presented.

The results compiled in Table 1 show that the electrical resistivity of thin metal films is strongly dependent on their

Table 1. Electrical resistivity (μΩ cm) of metal films produced by various methods as a function of their thickness ($T_{meas} = 20°C$): (a) film obtained by reactive ion sputtering of the pure metal target; (b) film produced by selective removal of oxygen atoms from the oxide on proton bombardment; (c) reference value for bulk metal.

Material	Film thickness, nm				
	5	10	20	50	100
Cu[a]	44	14	9.3	7.4	6.2
Cu[b]	—	27	19	—	—
Cu[c]			1.68		
W[a]	163	133	—	105	65
W[b]	—	800	—	960	700
W[c]			5.39		
Co[b]	—	120	—	—	—
Co[c]			6.24		
Fe[a]	75	35	26	—	—
Fe[b]	—	368	—	—	—
Fe[c]			9.72		
Al[a]	134	16.9	—	11.1	10.1
Al[b]			2.73		

thickness. Furthermore, the smaller the film thickness, the greater the distinctions from the reference values for bulk samples. For films of 10 nm in thickness, these distinctions are about an order of magnitude, and for films of 5 nm in thickness they are generally even more. As has been mentioned, this is probably associated with the classical size effect [20]. There is no escape from noticing that in metal films generated by selective oxygen atom removal from oxides (in the same thickness range of 10 – 100 nm), the electrical resistivity practically does not depend on the thickness (see Table 1). It has been noticed to be associated with a small value of the electron mean free path as compared with the film thickness. Electron-microscopy investigations demonstrate that significant distinctions in the electrical resistivity for films of minimum thickness produced from pure metals are most likely connected with the occurrence of amorphous component in the film structure. In such films (especially, in the thinnest of them) the volumes of amorphous and crystalline phases are comparable, which is clear, for instance, from the corresponding electron diffraction patterns. With increasing thickness of pure metal films, the volume fraction of amorphous phase sharply diminishes and for the thickness of 50 – 100 nm it disappears completely. Simultaneously with lowering the fraction of the amorphous phase, an enlarging of the mean crystallite size in pure metal films is observed. Effects of thickness on the film structure are most likely conditioned by the difficulty of grain growth in the course of film deposition due to surface proximity that promotes conservation of the amorphous phase in such films. Besides, it is known that crystallite growth in thin films strongly depends on the conditions of their condensation (firstly, on the temperature and the rate of deposition) [13, 17].

There occurs a different situation if one obtains metal films by selective atomic removal from insulators — in this case, the grain growth is conditioned by crystallite generation during phase transition from the amorphous state. Our experiments show that the mean crystallite size and the existence (or absence) of an amorphous component do not practically depend on the thickness of irradiated dielectric films. There appears a clear tendency: the lower the melting temperature of the metal produced by dielectric film irradiation, the larger the crystallite size (and, respectively, the lesser the volume fraction of the amorphous phase). There are metals with a relatively low melting temperature (for example, Cu, Co and Fe), where the distinction between the measured electrical resistivity and the reference one is an order of magnitude less than for W (see Table 1). The same reason could, probably, explain the distinctions between temperature dependences of the conductivity for films produced using Cu, Co and W. The effect of melting temperature on the resistivity and its temperature dependence, crystallite size and absence of the amorphous phase is most evident for copper produced by selective removal of oxygen atoms from the oxide. Copper has the lowest melting temperature among all the studied metals. That is probably the reason for the closeness of all its properties to that of copper films produced by ion sputtering of pure metal.

It follows from experimental results obtained with films of various thicknesses (at a given proton energy) that the projective range l_p of protons with the energy of ~ 1 keV equals ~ 100 nm for WO_3 films. When the thickness of films irradiated by protons of this energy becomes more than l_p, the measured resistance turns out to be higher than that calculated with the relationship $R \propto 1/d$, assuming that the transformation from insulator to metal occurs over the whole film thickness.

It appears to be of interest to investigate the influence of proton flux density on the rate of resistivity variation during selective atomic removal from oxides and their transformation into metal. Experiments demonstrate that the rate of insulator transformation into metal increases proportionally to the proton flux density. This effect is readily seen on the analysis of fluence dependences of the electrical resistance, obtained with different proton flux densities for the same materials.

There are works where a giant conductance increase has been observed after the ion irradiation of insulators [22 – 25]. In particular, in paper [22] a conductivity increase of about eight orders of magnitude was registered in the course of Fe^+-ion irradiation of magnesium oxide. Moreover, on irradiation by O^+, N^+, Ar^+ gaseous ions and Si^+ ions, the conductivity increase was as great as eleven orders of magnitude [23, 24]. However, these effects were conditioned, in authors' opinion, by some specific radiation defects appearing in the course of the ion bombardment. Those defects could lead to changing energy levels and a reconstruction of the density of electron states in the forbidden gap [22 – 24]. In spite of the giant conductance increase through the ion bombardment, all the studied samples remained insulators as evidenced by the temperature dependence of the conductivity being close to the Arrhenius one, and by optical absorption experiments as well. In these experiments, there are no pronounced effects of selective removal of oxygen atoms to produce metal, as governed, primarily, by the high energy and relatively heavy mass of the ions used. As follows from the above, in this case the difference between the energies transferred by the ions to various atoms of the irradiated substance becomes negligible. The latter is the most plausible reason for the lack of material

transformation producing metal in the course of the procedure described in Refs [22 – 25].

Special experiments have also confirmed the possibility of selectively removing atoms from insulators (and transforming them into metals) in the case when the surface irradiated by the charged particle beam is covered by an additional thin layer of another material. These experiments have been performed in two, principally different, variants.

In the first one, the insulator was covered with a thin film of a substance whose atoms had been subjected to displacement in the course of the irradiation (like atoms selectively removed from the insulator). In that case, the fluence dependences of the electrical resistivity (see Fig. 7) demonstrate that the transformation of the insulator into metal occurs in the same way as in the case when the additional layer between the beam and the insulator is absent (compare Fig. 2 and Fig. 7). However, in the initial portions of the resistivity – fluence dependences, peculiarities appear which are connected with the transportation of atoms of the additional layer through the dielectric layer under the action of the proton beam (see Fig. 7). In effect, in that case the atoms of the additional layer (in this instance, carbon atoms) are sputtered in the direction of the incident beam. It is of value to take into account this somewhat unusual mode of sputtering in irradiating thin films.

The presence of atoms of the additional layer material in the transformed insulator increases, to some extent, its resistivity and thus assists in lowering the rate of the dielectric – metal transformation. Increasing the additional layer thickness prolongs the transformation time (see Fig. 7, curves *1* and *2*). However, the additional layer has practically no effect on the final resistance of the metal film originating from an insulator. This results from the fact that for a high irradiation dose the additional layer completely disappears — partly, owing to the usual physical sputtering but, mainly, due to the transportation of atoms of that layer through the insulator/metal layer under the action of protons. Eventually, atoms of the additional layer material are removed from the insulator/metal into the substrate. In order for this to happen, some requirements have to be met: the irradiation dose must be high enough and, in addition, the projective range of beam ions has to be comparable with the total thickness of the irradiated 'sandwich'.

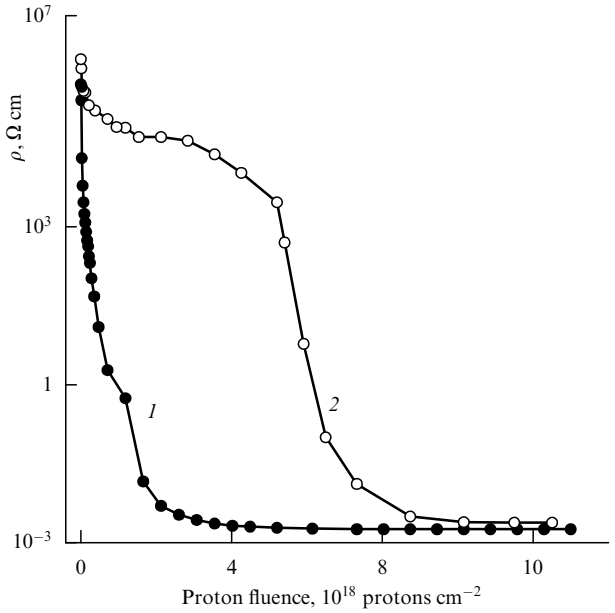

Figure 7. Fluence dependence of the electrical resistivity for a sandwich carbon – WO_3 film of 100 Å in thickness on proton irradiation ($E = 600$ eV): *1* — additional carbon layer of 50 Å in thickness; *2* — additional carbon layer of 400 Å in thickness.

In the second variant of the experiment, an additional rhenium layer was used, whose atoms had not been displaced by beam protons of a given energy (due to the large rhenium atomic mass). This fact has been confirmed in special preliminary experiments in which rhenium films were irradiated by protons under the same conditions and the rhenium resistance appeared to be unchanged. The thickness of the additional rhenium layer was selected so that its resistance R was 9 times higher than that of the Co film, r_∞, produced by selective removal of oxygen atoms from cobalt oxide at high irradiation doses and at the same geometry but without the additional rhenium layer, i.e. $R = 9r_\infty$.

Let $r(t)$ be the fluence dependence of the oxide film electrical resistance in the course of proton irradiation under conditions considered and without rhenium film. In a test experiment, one third of the oxide film surface (between contacts to measure resistance) was covered by an additional thin rhenium layer. At the early irradiation stage, when $r(t) \gg R$, the resistance R_s of the sandwich with the rhenium layer equals $R_s = (1/3)R + (2/3)r(t) \approx (2/3)r(t)$. If the additional rhenium layer prevents selective atomic removal from the oxide, then under high fluences R_s could be represented as the sum of the resistance $(2/3)r_\infty$ of the film portion not covered by rhenium and the series resistance of a rhenium segment. In this case, as mentioned above, the latter equals $3r_\infty$ and is well below the resistance of oxide film lying beneath the rhenium layer. Thus, one finds $R_s = (2/3)r_\infty + 3r_\infty = (11/3)r_\infty$. If the additional rhenium layer does not affect the selective removal of atoms from the insulator, then under high irradiation doses one obtains $R_s = (2/3)r_\infty + (1/3)r_\infty \times 3r_\infty/[(1/3)r_\infty + 3r_\infty] = (29/30)r_\infty$. Therefore, under high irradiation doses, the sandwich resistances should differ by a factor of about 3.8 for the two cases considered.

Experiments showed that on irradiation of such a sandwich up to high doses, its measured electrical resistance agrees with the latter relationship with an accuracy of ~ 15 – 20%. Hence, the conclusion could be made that the additional rhenium layer does not prevent oxide transformation into metal by means of selective atomic removal and does not affect the resistance of the metal film produced under high proton fluences.

One could also expect that with selective removal of oxygen atoms from initially nonmagnetic (or weakly magnetic) oxides of ferromagnetic metals, the nonmagnetic films could transform into a ferromagnetic state. It is clear that in the relevant experiments other di- or polyatomic compounds of ferromagnetic metals could be employed along with oxides. Part of our results concerning experiments performed with some di- and polyatomic systems are presented below.

Magnetization of films deposited on nonmagnetic substrates has been measured with a special magnetometer designed for thin-film measurements. Selective atomic removal was induced by proton irradiation of differing energy. In addition to the fluence resistivity dependences (cited in part above), in the course of these experiments the threshold displacement energies E_{d1}, E_{d2} and projective ranges for protons of selected energies were also determined.

Investigations of dielectric films CoO, Fe_2O_3 and Fe–Co–V–O showed that the original states of first two of them were nonmagnetic (cf. Fig. 8a, curve *1*) and the third film possessed a weak magnetization (cf. Fig. 8b, curve *3*). In bulk, these oxides are weak ferromagnetics. However, as has been mentioned above, the structure of thin films produced by reactive sputtering is distinct from the bulk sample structure. Probably, the same circumstance leads to the difference between the magnetic properties of films and bulky bodies.

After irradiation by protons with energies meeting the requirement $E_{d1} \leqslant E_{max} < E_{d2}$ (for each of the above-mentioned oxides), the transformation of all these insulators into respective metals resulted (see Fig. 9). Subsequent measurements showed that all metals generated as a result of selective removal of oxygen atoms from oxides became ferromagnetic. Thus, in the case of CoO and Fe_2O_3 oxides, selective atomic removal induced not only the transformation of the insulator to a metal but the transition from a nonmagnetic material into a ferromagnetic one as well (cf. Fig. 8a, curve *2*). In the case of the Fe–Co–V–O oxide, irradiation resulted in increasing the saturation magnetization by an order of magnitude (Fig. 8b, curve *4*). It should be noticed that the specific magnetization of metal films produced by this means is several times (1.5–3) lower than the reference values for bulk materials or thin films obtained by ion sputtering of the respective pure metals. The reasons for this are likely the same as those which lead to the distinction between electrical resistivities of bulk metals and that of the same metals produced by selective atomic removal from insulators.

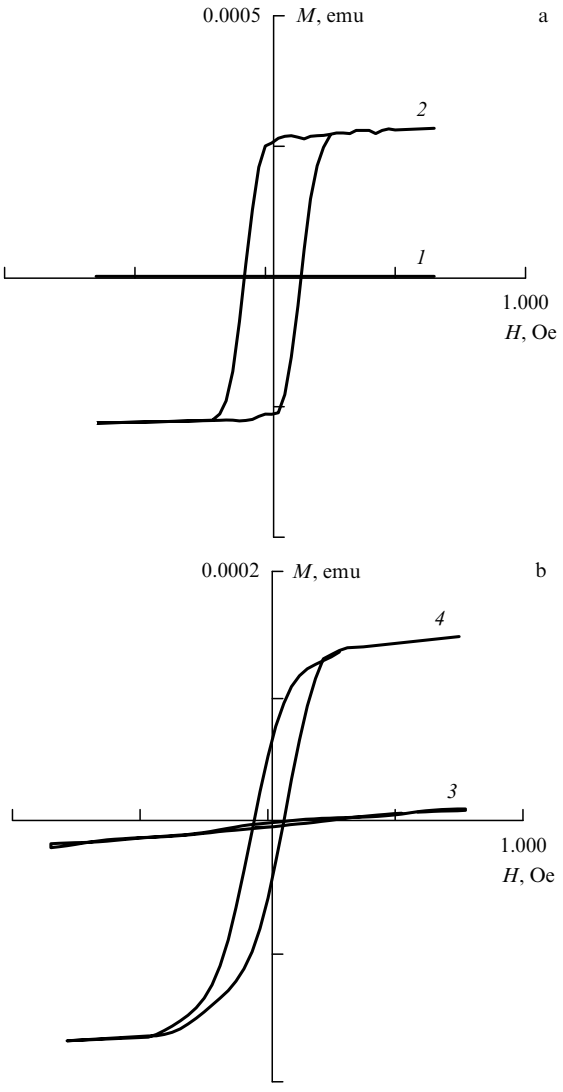

Figure 8. Magnetization curves for original dielectric films and metals produced from them by selective atomic removal: (a) *1* — CoO film (50 nm) before irradiation; *2* — Co film produced by proton irradiation ($E = 600$ eV) of CoO film (50 nm); (b) *3* — Fe–Co–V–O film (10 nm) before irradiation; *4* — Fe–Co–V film produced by proton irradiation ($E = 400$ eV) of Fe–Co–V–O film (10 nm).

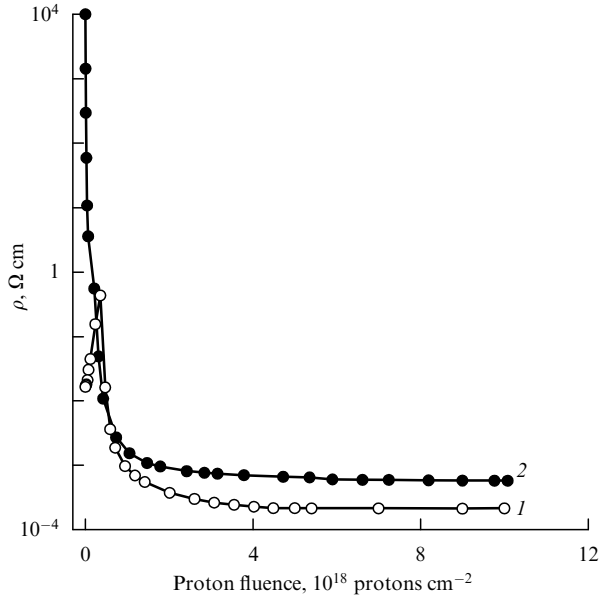

Figure 9. Fluence dependence of the electrical resistivity for ferromagnetic metal oxide films: *1* — CoO film (100 Å) under proton irradiation ($E = 600$ eV); *2* — Fe_2O_3 film (100 Å) under proton irradiation ($E = 400$ eV).

During the process of selective atomic removal from various compounds, the volume of a material can change. It is clear that such a process has to result in decreasing the material volume (as compared with the original one) due to the bulk relaxation of metal atoms into voids appearing after the removal of oxygen atoms from oxides (or some different atoms from compounds of other types).

That assumption has been verified by special experiments which have been performed in the following way. The surface of the dielectric film was covered by a mask with regular through holes and then the film was bombarded by protons with energies providing selective atomic removal from the insulator. Hence, only open sections of the film were irradiated. The proton fluence was high enough and provided obtaining transformed metal films with a resistance close to the minimum. After irradiation, the relief generated at the film surface was studied with the help of tunnel microscope. Measurements showed that the thickness reduction of the irradiated film sections was 20–50 % (depending on the chemical composition of insulators). It is essential that in spite of such a significant film thickness reduction, there are no changes of linear dimensions in the film plane. This conclusion is confirmed by the following fact: in our numerous experiments, we never observed either film exfoliation or violation of its continuity. This fact is especially

remarkable as the transformation into metal through selective atomic removal experiences the amorphization stage. For this reason, variations of linear dimensions leading to film volume changes would be isotropic. The observed strong anisotropy of the linear dimension variations (with diminishing film volume after irradiation) could be explained as follows. With reducing film volume, mechanical stresses arise on the film – substrate interphase boundary. The impossibility of film deformations in the boundary plane results in tensile stresses which act on the film from the substrate side and could reduce the film's linear dimensions (that is to deform the film) along the direction perpendicular to its surface. It is likely that the deformation is realized through the mechanism of radiation creep [26] rather than plastic deformation. The point is that at room temperature (where the most of experiments were performed), the capacity of oxides to usual plastic deformation, as a rule, is rather low and the rate of atomic displacements (in the process of their selective removal) in our experiments was very high and equaled $\sim 10^{-2}$ dpa s^{-1}.

In addition, a special experiment confirmed the generation of stresses at the film – substrate interphase boundary in the course of uniform irradiations of two different samples, when the dielectric films of identical compositions underwent transformations into metal. The first sample was a film without a substrate, and the second one was a film on a substrate. The study of electron diffraction in irradiated films (for the film on a substrate, reflection electron diffraction was measured) showed that the diffraction pattern for the film on a substrate was similar to that for materials under a load. Therefore, the above-mentioned assumption concerning the causes leading to the anisotropy of linear dimension variations with diminishing film volume via selective atomic removal seems to be quite probable.

All the experiments aimed at selective atomic removal from insulators were accompanied by essential variations in the optical properties of films undergoing transformation into metals. Firstly, the transition led to the appearance of a characteristic metallic luster on the irradiated sections of films. To estimate the variation of optical properties quantitatively, measurements of the film absorption coefficient S were carried out (in the visible light) with the help of a microphotometer.

In the course of these measurements, a dielectric film of a given thickness was deposited onto a glass substrate. Then the absorption coefficient of that sandwich was measured before irradiation and after selective atomic removal and transformation of the insulator into metal. For comparison, analogous measurements (but without irradiation) were taken with films of various thicknesses produced by ion sputtering of the same pure metal on glass.

The results obtained with cobalt oxide (CoO) present a typical example which demonstrates the variation of the S quantity. The initial absorption of a dielectric CoO film of 10 nm in thickness is characterized by the value of $S = 0$ — that is, the film is transparent. Comparison shows that the optical transmittance of the cobalt film (obtained by selective atomic removal from cobalt oxide) with a final thickness of about 8 nm and resistivity $\rho \approx 1.3 \times 10^{-4}$ Ω cm corresponds to that of a pure cobalt film with a close thickness of 7.5 nm. Hence, these measurements indicate that the optical properties of metals produced by selective atomic removal from insulators and pure metals produced by ion sputtering are virtually coincided.

4. Conclusions

In the present paper, physical principles are described and conditions are formulated, allowing one to remove selectively atoms of a certain sort from di- or polyatomic solids by means of irradiation with accelerated particles. All the salient features of the selective atomic removal, following from the physical mechanism through which that process is realized, are noted. We experimentally demonstrated the possibility of such selective atomic removal, confirmed the process mechanism and investigated its most essential features. In the course of experiments, we revealed that the selective removal of atoms from di- and polycomponent compounds is accompanied by radical variations of some of the most important physical properties of the materials, such as electrical, magnetic and optical properties. Investigations showed that the modification of the materials' properties is a consequence of their atomic composition variations and those structural transformations (phase transitions) that accompany selective atomic removal from materials.

Our experiments allowed us to outline the basic phenomena accompanying selective atomic removal. However, many details of the physical processes leading to observed radical variations of material physical properties remained beyond the scope of our work. First of all, they are associated with the complexity and unusual character of the phenomena which accompany selective removal of atoms. In the experiments performed, 50 – 75% atoms were removed from the material volume! That is why we have no detailed explanation of the observed distinctions between the properties of thin metal films produced by selective atomic removal and those produced by sputtering pure metals, or of the distinctions between thin film properties and those of bulk materials.

However, this circumstance, which arises over and over again in science and technology history, is not an insuperable obstacle for the practical utilization of physical phenomena or processes which seem to be perspective for solving important practical problems. This is undoubtedly true in the case discussed. At the moment, it is more or less clear how to reduce significantly the distinctions between the properties of thin metal films produced by the above-described transformation process and those of bulk materials. However, these items are far beyond the scope of the present paper whose aim is, first of all, to demonstrate the principally new opportunities given by the method of selective atomic removal from di- or multicomponent compounds with the help of accelerated particle beams. Evidently it is presently impossible to outline clearly and completely the universe of potential compounds which are the best objects for selective atomic removal from the practical standpoint. In addition, it is clear that simultaneous removal of atoms of several sorts is possible in polyatomic compounds. In doing so, the relative rates of their removal could vary. We observed similar effects when dealing with some polyatomic substances. All this indicates the high potential and very wide application field for the selective atomic removal technique aimed to obtain local spatial variations of atomic composition in thin films or material layers.

The mere fact of selective removal of atoms of a certain sort from di- or polyatomic compounds is of great interest for creating future technology aimed, primarily, at the needs of micro- or, more precisely, nanoelectronics and numerous other problems. At present, there are installations which generate ion beams of dimensions as low as 10 nm.

However, the realization of a lithographic process with such a resolution is limited by effects of (back and forward) scattering [27]. Taking into account the threshold character of the atomic displacement during their selective removal, forward scattering effects and the respective loss of resolution could be reduced to a minimum. This is possible in the case when the maximum energy transferred from beam ions to selectively removed atoms only slightly exceeds their threshold displacement energy. In the case of selective atomic displacement by an ion (atomic) beam, back scattering effects are negligible and their influence on the loss of resolution could be neglected. Our estimates show that for mentioned above conditions concerning ion (atom) energies, attainable (nanometer) resolution in selective removal of atoms is limited solely by the beam diameter.

Practical applications of the selective atomic removal method are conditioned by a number of factors:

(1) Employing ion beams has some important advantages and allows:

• the avoidance of back scattering effects (inherent to electron beams) and, hence, a significant reduction of the loss in resolution for thin layers of the material or thin films on substrates;

• the use of low acceleration voltages providing a short wavelength of beam ions that is essential for producing patterns of high resolution.

(2) The method of interest could be used to directly create (avoiding lithography) needed spatial modulations of atomic composition and physical properties of a material, say, metallic or semiconductive 'patterns' in insulators, magnetic drawings in nonmagnetic substances, light guides in opaque media, etc.

(3) Calculations show that with proton beams (of the parameters which are needed for effective realization of the selective atomic removal process) an ion-projective system with a scaling projective factor of 5 could be designed that produces a pattern of 1-cm^2 area with a resolution of about 3 nm. In doing so, upon termination of the process, protons (hydrogen) could leave the material due to diffusion without any negative influence on the materials' properties.

(4) The one-stage character and simplicity of the selective atomic removal process opens a potential opportunity to create plain and cheap technology for obtaining multilayer bulk nanostructures of various applications. It is essential that in contrast to modern lithographic microtechnologies, here we could limit ourselves to two in-vacuum operations only — successive depositions of the required matrix films and the drawing of a given bulk picture (by selective atomic removal) with the required spatial localization of certain physical properties.

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