

Conference Paper

Formation of High-quality Aluminum Oxide under Ion Beam Irradiation

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Abstract

In this work we used the radiation-induced technique of selective association of atoms (SAA) to create the aluminum oxide layer on the surface of metallic Al under oxygen ion beam irradiation. Optimal conditions for carrying out the radiation-induced aluminum oxidation process were established to minimize the target sputtering. An aluminum oxide layer of 20 nm thickness was obtained after irradiation of aluminum target with oxygen ions with 0.2 keV energy up to a dose of $\sim 2.6 \cdot 10^{18}$ ions/cm² at room temperature. HRTEM and EELS techniques were used to characterize the chemical compositional changes after irradiation. It was found that aluminum oxide layer after irradiation contained an excessive amount (~ 10 at.%) of implanted oxygen.

Keywords: ion beam irradiation, aluminum thin films, EELS, HRTEM

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1. Introduction

The radiation techniques of direct modifications of thin-film materials atomic composition and properties under low-energy ion-beam irradiation were developed in the National Research Centre «Kurchatov Institute» [1–3]. In recent years these techniques allowed to achieve new results in their application in the field of nanotechnology.

One of the last examples of application of selective displacement of atoms technique (SDA) was the development a controlled way of decreasing the thickness of superconducting ultrathin (5 nm) NbN films. These NbN films were irradiated with low-energy oxygen ions and the process was accompanied by substitution of nitrogen atoms with oxygen atoms in the irradiation zone [4]. The depth of radiation-induced replacement of nitrogen atoms by oxygen atoms was controlled by the value of the full projected range of oxygen ions in the target material. The values of full projected range of oxygen ions in NbN reached (2–3) nm at (100–300) eV energies [4].

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In this paper we proposed the use of selective association of atoms (SAA) technique [1] to create an alumina layer on the surface of a thin metallic Al film. Aluminum is a traditional material for creating commutation wiring for integrated circuits, while Al is simultaneously a contact material to the semiconductor and an interconnect material. The use of aluminum as a contact material is due to a number of valuable properties: low resistivity ($2.65 \mu\Omega \cdot \text{cm}$), significant adhesion to dielectrics, high corrosion resistance, due to low solubility in Si, forms in its band gap only small acceptor energy levels [5]. Low-energy oxygen ions (0.2 and 0.5 keV) irradiation was used to realize aluminum radiation-induced oxidation. Low energies were chosen to form a high-quality alumina that was capable to perform an interlayer insulator function in the integrated circuit metallization, and, on the other hand, minimized the sputtering of aluminum under oxygen ion beam irradiation.

The results obtained in this work can find wide application in the creation of electrical insulation of metallic conductors as an alternative technique to methods of dielectric layers deposition in both traditional microelectronics and nanotechnologies. The main advantages of this technique were the precision of aluminum oxidation in depth, the high dielectric properties of the formed alumina and the possibility of reducing the number of technological operations in the process of creating devices.

2. Experiments

Samples of metallic thin Al films were produced by cathode sputtering of aluminum target at Kr 3.5 kV discharge voltage at a pressure of 10^{-8} Torr at room temperature. Metallic Al thin films with thickness of 40 nm were deposited on a single-crystal substrate coated with a thin layer of natural SiO_2 oxide.

Irradiation of the samples was carried out on a "Copra Cube" irradiation facility with a high-frequency plasma source of oxygen plasma. Subsequent ions extraction on the sample was realized by applying a pulse bias potential to the substrate with the sample. Every negative bias pulse was accompanied by the positive pulse (to extract electrons from the plasma) to minimize the charging of the target during irradiation. The value and duration of the positive bias pulse were chosen to compensate the positive charge of ions after negative bias pulse. The Al films were irradiated at room temperature at 0.2 keV ion oxygen energy up to fluencies $(0.66-2.6) \cdot 10^{18}$ ions/cm² and at an energy 0.5 keV up to fluencies of $(0.94-5.6) \cdot 10^{18}$ ions/cm².

Preparation of cross-section samples was performed at FIB "Helios Nanolab" facility. Analytical scanning transmission electron microscopy (STEM) was used to study oxidation degree in depth of initial aluminum after irradiation. The main advantage of this

technique is the possibility of local chemical analysis on cross-section specimens. In this paper, chemical composition of initial and irradiation samples were studied using electron energy loss spectroscopy (EELS) in core loss region (line $L_{2,3}$ for Al (73 eV) and K-line O (532 eV)). EEL spectra were recorded with transmission electron microscope "Titan 80-300" operated at 200 kV, equipped with energy loss spectrometer "GIF-2001" in STEM mode. EEL spectra acquisition conditions were: a half convergence angle $\alpha = 10$ mrad, a half collection angle $\beta = 14.8$ mrad and energy dispersion 1 eV/channel. Al and O profiles of concentration changes in depth were calculated by the relative concentrations method.

3. Results and discussion.

Successful solution of the problem relating to the aluminum oxide layer formation on the surface of metallic Al film using SAA method suggested determination of irradiation parameters. One of the most important parameters was the energy range of oxygen ions, allowing to form oxide layer with sufficient thickness and to prevent significant sputtering of aluminum at used irradiation doses.

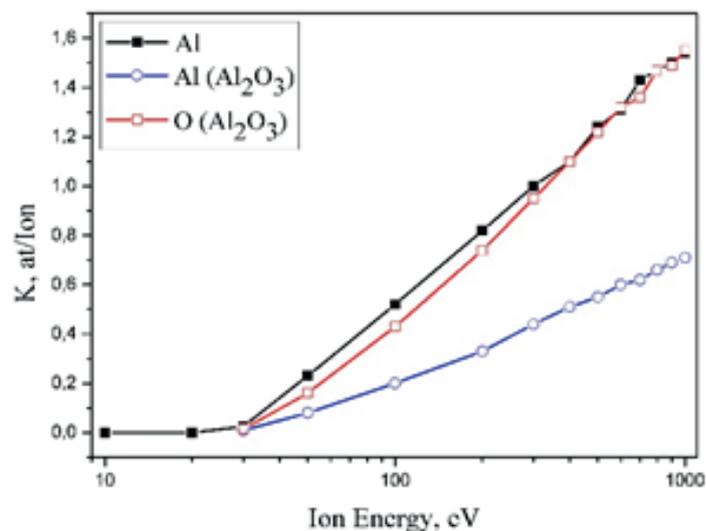


Figure 1: Calculated sputtering coefficient for Al (black line), for Al in Al_2O_3 (blue line) and for O in Al_2O_3 (red line) as a function of oxygen ions energy.

Figure 1 illustrates the calculated dependencies of the aluminum and oxygen atoms sputtering coefficients as a function of oxygen ions energy, performed using SRIM code [6]. Notice that at an ion energy above 300 eV, a significant sputtering of the substrate

during irradiation is observed, since the sputtering yield of aluminum atoms becomes greater than 1.

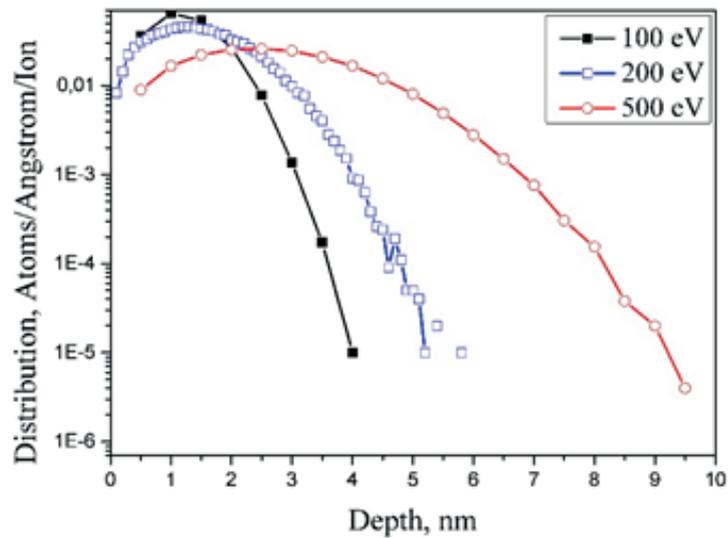


Figure 2: Calculated distribution profiles of oxygen atoms in Al target under oxygen irradiation with different energies.

Figure 2 shows the SRIM [6] calculated distribution profiles of oxygen atoms in Al target under oxygen irradiation with different energies. The film volume changes accompanying radiation-induced oxidation of aluminum could reach several times, according to the literature data about the average atomic density of aluminum oxide in some crystal modifications [7]. For example, an increase of film thickness during the aluminum transformation to oxide could be reached ~ 4 times for aluminum oxide with a low atomic density $0.0394 \text{ at}/\text{A}^3$. Taking into account the latter, the thicknesses of aluminum layers oxidized under irradiation will be in the corresponding number of times exceed the depth of the projective range of oxygen ions in aluminum, shown in Figure 2.

Samples of initial metallic aluminum were characterized by a cubic structure and a large grain size (Figure 3).

Figure 4 shows the depth distribution of the elements after Al film irradiation with oxygen ions with energy of 0.5 keV up to different doses. It is clear from the Figure 4 that irradiation of aluminum has led to the formation of the aluminum oxide on the surface of the target. Figure 4 shows that the depth of aluminum oxide formation corresponded to 4 nm at a dose of $9.4 \cdot 10^{17} \text{ ions}/\text{cm}^2$ and 6 nm at a dose of $1.9 \cdot 10^{18} \text{ ions}/\text{cm}^2$. At the same time, the thicknesses of aluminum oxide and aluminum films were very low at a dose of $5.6 \cdot 10^{18} \text{ ions}/\text{cm}^2$ (see Fig. 4,c). A small oxidation

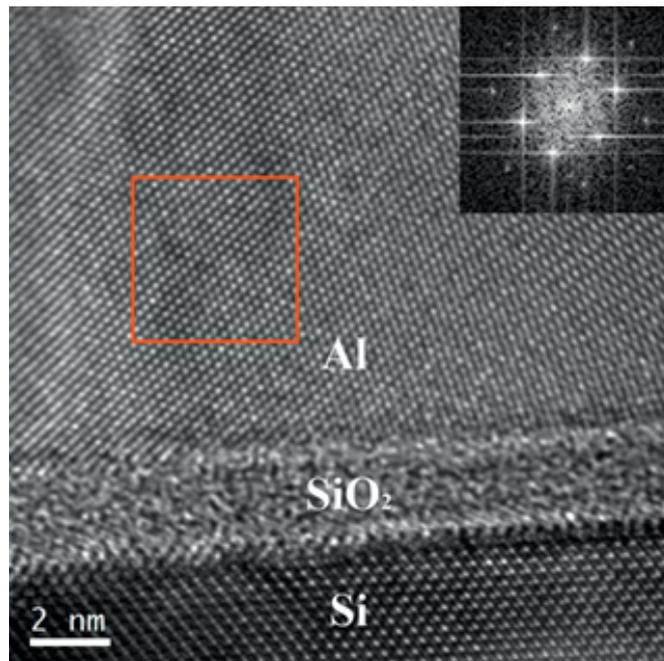
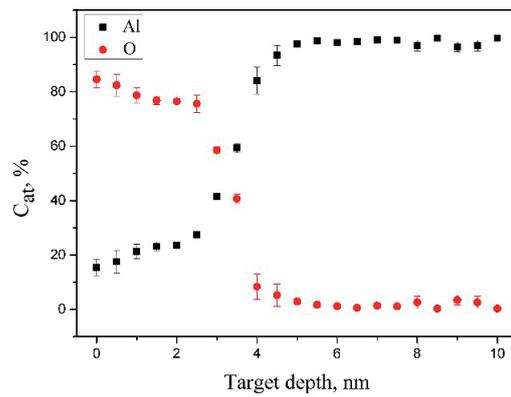


Figure 3: Bright-field HRTEM image of initial Al film cross section, synthesized on a monocrystalline silicon substrate coated with a thin layer of SiO_2 , diffraction (inset).

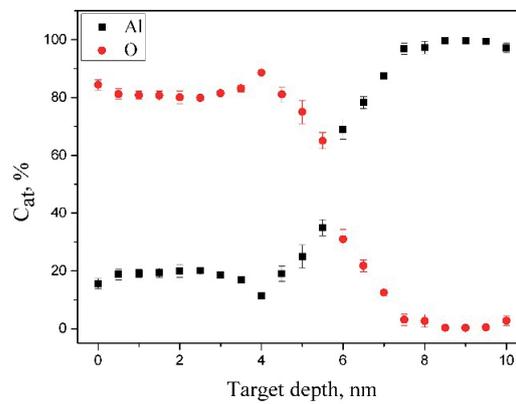
depth, as well as significant decrease of film thickness at high radiation dose, indicated that the process of intensive surface sputtering of the formed alumina took place during irradiation with 0.5 keV oxygen ions. These data qualitatively corresponded to the calculated data shown on Fig.1. It should also be noted that the concentration of oxygen atoms in the irradiated layer of aluminum at dose of $1.9 \cdot 10^{18}$ ions/cm² was ~ 80 at.%. This high concentration of oxygen could be explained by implantation of oxygen atoms to the substrate during irradiation.

Decreasing the energy of oxygen ions up to 0.2 keV made it possible to reduce significantly the surface sputtering effect, without reducing the efficiency of the aluminum oxide formation process at the Al target surface.

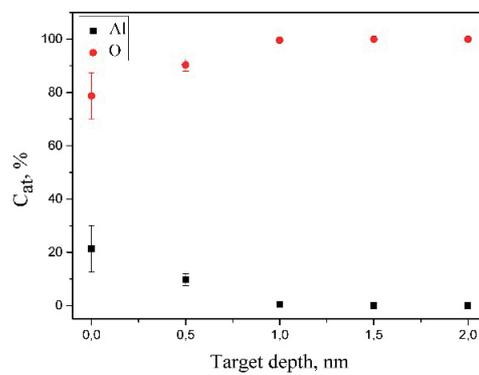
Figure 5 shows the depth elements distribution profiles on aluminum film irradiated with 0.2 keV oxygen ions in dose range $(0.66-2.6) \cdot 10^{18}$ ions/cm². It is clear from Figure 5 that the thickness of aluminum oxide layer increased with increasing of radiation dose and reached a value of ~ 20 nm at a dose 2.6×10^{18} ions/cm². At the same time, we can see the presence of residual layer of metallic aluminum under the oxide layer (see Fig.5). During Al irradiation with 0.2 keV ions, the oxygen implantation process have also took place. Taking into account the latter, it should be noted that the resulting concentration of oxygen atoms in the transformed layer is about 10 at.% higher than the characteristic stoichiometric oxygen concentration for Al_2O_3 . Excess oxygen atoms were impurity and occupied interstitial positions in the crystal structure of aluminum



(a)



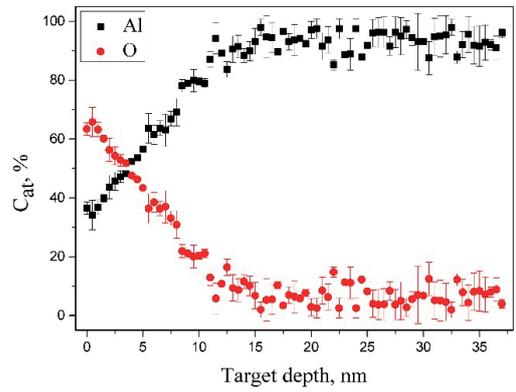
(b)



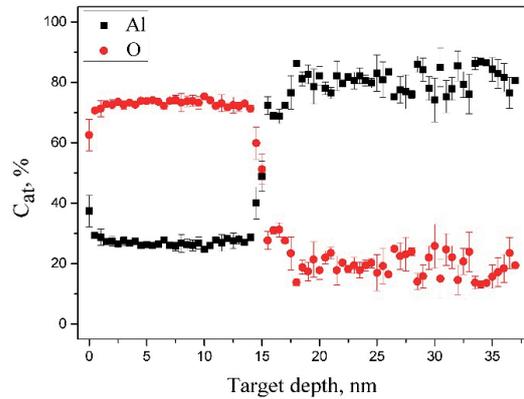
(c)

Figure 4: Elements depth distribution profiles of the Al film irradiated with 0.5 keV oxygen ions (calculated from EELS data) for doses: (a)– $9.4 \cdot 10^{17}$ ions/cm²; (b)– $1.9 \cdot 10^{18}$ ions/cm²; (c)– $5.6 \cdot 10^{18}$ ions/cm².

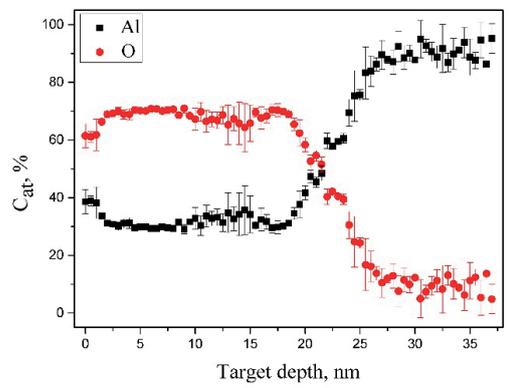
oxide. If necessary, it is possible to use thermal annealing to activate the process of excess oxygen release from the alumina lattice.



(a)



(b)



(c)

Figure 5: Elements depth distribution profiles of the Al film irradiated with 0.2 keV oxygen ions (calculated from EELS data) for doses: (a)– $6.6 \cdot 10^{17}$ ions/cm²; (b)– $1.3 \cdot 10^{18}$ ions/cm²; (c)– $2.6 \cdot 10^{18}$ ions/cm².

It is clear from Fig.5 that irradiation of Al target with oxygen low-energy ions leads to the formation of aluminum oxide layer of 20 nm thickness on the surface of metallic

Al. Thus, it confirmed the possibility of using the radiation technique of selective association of atoms to create an interlayer insulating dielectric in metallization formation of multilayer circuits.

4. Conclusions

We have demonstrated using of oxygen ion beam irradiation to form aluminum oxide layer of 20 nm thickness on the surface of metallic Al at room temperature. We have found the optimal irradiation conditions to eliminate unwanted surface sputtering effect and get high-quality alumina at the surface: energy of oxygen ions 0.2 keV and dose $\sim 2.6 \cdot 10^{18}$ ions/cm².

References

- [1] B.A. Gurovich, K.E. Prikhodko, E.A. Kuleshova et al., «Use of radiation effects for a controlled change in the chemical composition and properties of materials by intentional addition or substitution of atoms of a certain kind», *Journal of Experimental and Theoretical Physics* v.116(6), pp. 916-927, 2013.
- [2] B.A. Gurovich, K.E. Prikhod'ko, A.N. Taldenkov et al., «Fabrication of metal nanowires by ion-beam irradiation of oxides through high aspect ratio resist masks», *Journal of Vacuum Science and Technology B*; v. 29(2), pp.021013-1 - 021013-5, 2011.
- [3] B.A. Gurovich, K.E. Prikhod'ko, D.A. Komarov, A.N. Taldenkov, «Formation of monocrystalline silicon nanowires using low-energy ion irradiation», *Nanotechnologies in Russia* V. 8, No 3, pp. 199-204, 2013.
- [4] B.A. Gurovich, K.E. Prikhodko, D.A. Komarov, M.A. Dement'eva, L.V. Kutuzov, «The use of ion irradiation to control the thickness of thin superconducting films», *Nuclear Instruments and Methods B*, to be published, 2017.
- [5] M.A. Korolev, T.Yu. Krupkina, M.G. Putrya, «Technology, designs and methods for modeling silicon integrated circuits», part 2, 424 p., 2009, Binom.
- [6] J.F. Ziegler, J.P. Biersack, M.D. Ziegler, «The Stopping and Range of Ions in Matter», Lulu Press Co., Morrisville, 2008. <http://www.srim.org>.
- [7] JCPDS № 3-1033