Influence of Implantation Process Mode and Reactivity of the Implanted Ions on the Surface Properties of Insulators

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Abstract – Analysis of experimental output of the various ions exposure to the surface properties of inorganic dielectric materials was carried out. It is shown that the ion-thermal modification of all investigated materials leads to the dramatically decrease of their sheet resistance. Properties of the modified layer are defined by the radiation defect formed during the implantation and by the chemical activity of alloying elements. The significant changes of the electrophysical properties of surface are realized by ion modification with weight elements (Li, C). Increase of ion mass (Al, Fe, Mo, W) make worse efficacy of modification. Maximum change of electrophysical properties of the dielectrics surface are reached by the ion-beam mixing. The resistance of modified layer can be controlled within 10^{15}–10^{3} ohm by varying of the irradiation and thermal treatment parameters.

1. Introduction

The modification of surface properties of heat-resistant inorganic materials on the basis of carbides, oxides and nitrides by ion implantation has a significant scientific and practical interest. At present, ion implantation is extensively used for introduction the impurities into crystals. The other areas of application the ion-thermal modification is optics and machine-building, where it is used to increase a microhardness, durability and corrosion stability of materials and the like.

Ion beams exposure to the solid produces the changes complex into a nuclear and electronic subsystem. The elastic and inelastic collisions between the alloying particles and atoms and electrons of substrate lattice arise from ion bombardment on materials surface. As a result of this interaction, the making vacancy and more difficult defects, excitation of an electronic subsystem and, as a consequence, change in structures of material surface up to fully amorphization. Furthermore, impurity introduction into sample surface at ion modification can be accompanied the new chemical compounds formation. High concentration of induced defects, phase distortions, and structural changes distort the electron structure of the band gap of modified layers. These changes of electron structure influence the optical, mechanical, and electrophysical properties of material surface.

Purpose of this work is investigation of the changes of electrophysical properties of dielectric after ion-thermal modification; determination of the influence of implanted species and chemical activity between impurity atoms and substrate matrix on the surface properties of modified materials; realization of the comparative analysis of the various modification conditions (ion implantation and ion-beam mixing).

2. Experimental details

Investigations of the changes of electrophysical properties of dielectric surface after ion-thermal modification was accomplished on the oxides (Al_2O_3, Al_2O_3–SiO_2 and MgO–SiO_2) and nitrides (BN, AlN, Si_3N_4) ceramics, leucosapphire single crystal and fused quartz. Irradiation was realized by pulse-frequency arc-plasmous particle accelerator allowed to get the wide-aperture ion beams of various metals and alloys [1]. The principle of operation accelerator founded on the plasma forming from cathode material by pulsed current arc discharge in vacuum with previous discharge between the cathode and keep-alive electrode ones microsecond duration and following the extraction and acceleration of ions.

The implanted ions were Fe^+, Ti^+, Cu^+, Mo^+, W^+, Li^+, C^+, and Al^+. The energies of implanted ions were 80–120 keV, the current density 10^{-3}–10^{-2} A/cm^2, pulse duration 250 μs, pulse-repetition frequency 50 Hz, and fluence 10^{13}–10^{18} ions/cm^2. Annealing after ion implantation was realized either in vacuum or in the nitrogen atmosphere in order to exclude of the electrons interchange between sample surface and active reagents of atmosphere promotional the reduction of properties due to the electron-ion reactions between the induced defects [2].

The resistance measurement of surface layers was carried out at a constant voltage in the temperature range between 300 and 2000 K by diode system composed of the potential (ring-type) electrode and measuring electrode. This system was described more fully in [3]. For determination of electrical transport mechanism, the $\sigma_s(T)$ was approximated according to the expression

$$\sigma_s(T) = \sigma_0 \exp\left(\frac{T_0'}{T}\right)^{1/n}, \quad (1)$$

where T_0' and $1/n$ depend on density of localized states about either the Fermi level or the permitted bands ($n = 1$ correspond to the activated behavior of conductivity, $n = 4$ correspond to the jumping transport within the framework of Mott model).

Investigation of the structure, phase composition and surface morphology of inorganic dielectric materials after ion-thermal modification was carried out by transmission electron microscopy and electron diffraction investigation and described in [4].

3. Results and discussion

Figure 1 displays the surface conductance of fused quartz, alumina, magnesium oxide and pyrolytic boron nitride irradiated with carbon ions at the fluence of 10^{17} cm^{-2} as a function of the postimplantation annealing temperature.

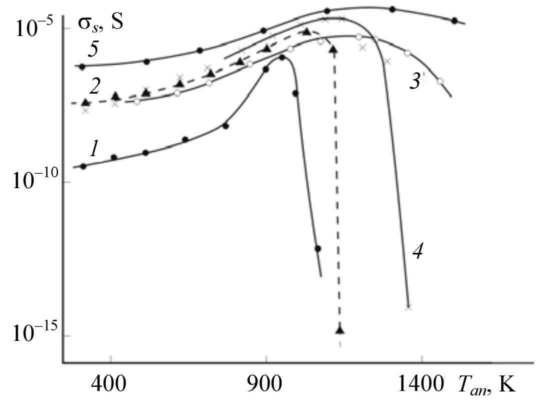

Fig. 1. Annealing effect on the surface conductance σ_s in the fused quartz (*1*), mono- (*2*) and polycrystalline Al_2O_3 (*3*), MgO single crystal (*4*), and pyrolytic boron nitride (*5*) irradiated with carbon ions at fluence of 10^{17} cm^{-2}

As can be seen from Fig. 1, the ion-thermal treatment of all investigated materials leads to the same effect – the significant increase of surface conductance. The each following heating cycle during the thermal treatment increases and stabilizes of the σ_s. The author's investigations show the stabilization of the properties attained after irradiation began after annealing under T_{an} = 950–1200 and 1100–1500 K for the oxide and nitride ceramics respectively. The temperature coefficient of sheet resistance of the modified samples (TC ρ_s) cannot exceed the 10^{-4} – 10^{-3} deg^{-1} (Table).

It is known that the induced defects (impurity vacancy complexes) and precipitate induced during ion implantation determine the surface properties of modified dielectric in many respects. However, the chemical interaction between impurity atoms and atoms in substrate lattice plays an important role in the making the heat-resistant semiconducting layer into near surface region of dielectrics as well. The correlation between chemical activity of alloying elements and properties of modified surface is observed well from irradiation of fused quartz with titanium, copper, iron ions [5] and xenon and carbon ions [6]. Thus, modification of fused quartz with titanium ions leads to the significant decrease of sheet resistance (lowest achieved resistance is 70 ohm). By contrast the modification with copper and iron ions (which are known not to react chemically with SiO_2) under the same conditions has caused an only a change in surface color of irradiated samples (brownish after irradiation with iron ions, pink after irradiation with copper ions). This result suggests about a significant influence of chemical activity of impurity atoms on the properties of modified surface.

Investigations of the boron nitride modification with various ions in the ion implantation and ion-beam mixing modes and the optimum post-implantation annealing temperature are summarized in Table.

The sheet resistance magnitude of modified layer (ρ_s), temperature coefficient (TC ρ_s) and heat resistance of modified layer is defined by implanted species, irradiation and thermal treatment conditions.

The boron nitride irradiation with ions and subsequent thermal treatment decreased sheet resistance to 10^3–10^5 ohm in all cases. Our investigations show the maximum changes of electrophysical properties of surface are reached by modification with weight elements ions (Li^+, C^+) and by ion-beam mixing as well.

Table. Optimum annealing temperature of ion-irradiated PNB and its surface resistive properties

Ion	Thermal treatment range, K	Properties				
		ρ_s (300 K), ohm	TC $\rho_s \cdot 10^3$, deg^{-1}	Temperature, K	T [ρ_s (min)], K	ρ_s (min), ohm
Ion implantation						
Li	1050–1500	(3–10) · 10^4	–0.62	300–1200	1250	1.1 · 10^4
C	1000–1600	(2–9) · 10^4	–0.37	300–1200	1300	1.2 · 10^4
Al	1070–1250	(2–5) · 10^6	–1.3	300–1000	1200	6.8 · 10^4
Mo	1050–1150	(7–12) · 10^6	–1.7	300–800	1150	11 · 10^4
W	1000–1200	(2–10) · 10^7	–2.5	300–600	1150	11 · 10^4
Ion-beam mixing						
Al	1100–1750	(1–5) · 10^4	–0.72	300–1500	1170–1250	(7–11) · 10^3
Fe	1130–1400	(7–24) · 10^4	–0.63	300–1370	1200	2.3 · 10^4
Cu	1100–1750	(2–6) · 10^4	–0.45	300–1550	1350–1500	8 · 10^3
W	1100–1750	(2–5) · 10^4	–0.57	300–1500	1170–1500	(6–9) · 10^3

These changes are related with the formation a high concentration of induced defects and ability for impurity atoms to replace the substrate lattices atoms along with the formation a semiconducting solid solutions. Increase of ion mass (Al, Fe, Mo, W) make worse efficacy of modification. Influence of ion mass on the properties of modified layers at modification in the ion-beam mixing condition is traces less than at modification in the ion implantation condition (Table).

It is known that the increase of implanted ion fluence allows getting the modified layer with higher impurity concentration which is well correlated with the changes of electrophysical properties surface in accordance with [5]. Investigations of the nitrides ceramics modification with carbon ions at variety ion fluence is shown in Fig. 2.

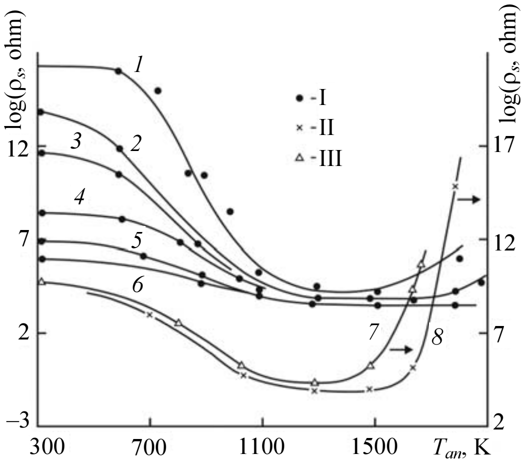

Fig. 2. Annealing effect on the sheet resistance in the nitrides ceramics at 300 K. Fluence (cm^{-2}): *1* – 10^{13}; *2* – 10^{14}; *3* – 10^{15}; *4*, *8* – 10^{16}; *5* – 10^{18}; *6*, *7* – 10^{17} (I – pyrolytic boron nitride, II – silicon nitride, III – aluminium nitride)

The increase of ion fluence leads to the greater decrease of sheet resistance and the range extension of optimum post-implantation thermal treatment, as can be seen in Fig. 2.

However, the impurity accumulation in the samples during ion irradiation is accompanied, as it is known, by the sputtering process of substrate surface and removal of already implanted impurity. The fluence increase leads to the transformation of implanted impurity distribution profile as a result of impurity accumulation dynamics taking into account a sputtering process, and when a fluence reaches a critical value, defined by modified material characteristics (for pyrolytic boron nitride this value is 10^{17} cm^{-2} [7]), the equilibrium between the impurity introduction and the sputtering is established. This leads to the saturation of ion-implanted impurity concentration [5, 8]. The highest impurity concentration can be obtained by modification in the ion-beam mixing condition. This modification mode is realized either by the thin film evaporation on a substrate surface before ion irradiation (static mixing) or by the matching of atoms deposition and the ion bombardment (dynamic mixing) [9]. Increase of impurity concentration in this modification mode is accomplished by the accessory insertion of recoil atoms into substrate. The physical-chemical composition of the surface can be controlled by varying of the irradiation and sputtering parameters and the impurity concentration can reach to 100% under the certain conditions [8]. Investigations of the boron nitride modification in various implantation conditions show the semiconducting layer formed by ion-beam mixing have a lower sheet resistance, higher thermostability and smaller temperature coefficient as compared with ion implantation [10]. This improvement of electrophysical properties connected perhaps, as noted above, with a higher concentration of impurity and induced defects.

4. Conclusions

The investigations of the inorganic dielectric materials modification show the ion irradiation and subsequent thermal treatment significantly change the energy characteristic of surface layer. The resistance of modified surface is defined by the modification conditions. The implanted species and their chemical activity against modified materials play an important role in making a semiconducting layer causing the forming of solid solution and intermetallides. Maximum changes of the electrophysical properties are reached after modification in ion-beam mixing mode. A semiconducting layer formed in this mode have a high thermostability and low temperature coefficient of resistance.

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