Modification of Nanostructured Materials by High-Power Ion Beam Treatment

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Abstract – The influence of high power proton-carbon ion beam treatment on nanostructured materials (por-Si, nanoporous SiO\textsubscript{2}, amorphous carbon films) was investigated by scanning electron and atom force microscopies. The melting of nanoporous Si and SiO\textsubscript{2} under high-power ion beam (HPIB) irradiation of nanosecond duration was observed. The sizes of ellipsoidal particles formed in Si and those of holes formed in SiO\textsubscript{2} under irradiation were determined. The possible origin of these morphology features was discussed. The influence of high power ion beam treatment on surface morphology and resistance of carbon films synthesized by PE CVD was investigated also. Possible mechanisms of surface morphology changes and increasing of carbon film resistance after irradiation was discussed.

1. Introduction

Nanomaterials are a class of materials the modification of which by high-power ion beams of nanosecond duration has been studied insufficiently. This concerns nanoporous Si and SiO\textsubscript{2}, nanostructured carbon which are promising for the formation of various nanocomposites, including the creation of chemical and gas sensors [1]. In most cases nanocomposites are formed by the deposition of a thin layer of a chemical compound on the developed surface of the nanostructured medium with its subsequent activation under temperature or ion beam impact [2]. It is obviously important to study the features of the effect of a high-power ion beam on nanostructured medium – nanoporous Si and SiO\textsubscript{2}, carbon film having different thermodynamic parameters. The low heat conductivity of porous media along with the higher ion ranges in them should lead to considerable differences in the morphology of the irradiated surface if compared with a continuous medium of the same material.

2. Experiment methods

In this study, the surface morphology of nanostructured inorganic materials – porous silicon, industrial KSKG silica gel (GOST 3956-76) and carbon films was investigated under a high-power ion beam (HPIB) irradiation of nanosecond duration. Layers of porous silicon were obtained by anode etching of a monocrystal Si (KDB-0.005) of p-type with the (111) orientation in solution of HF (40%): C\textsubscript{2}H\textsubscript{5}OH (1:1) at a current density of 60 mA/cm\textsuperscript{2}. The thickness of the porous layer set by the time of anode etching varied from 2.8 to 6.0 μm and was determined by studying the cross-section of the sample on an atomic-force microscope. The characteristic porous size was about 20 nm and the porosity size was about 50%. A flat region was formed on KSKG silica gel samples having a spherical or ellipsoidal form by polishing with a finely dispersed abrasive. Then samples were exposed to ultrasonic cleaning in dehydrated acetone to remove abrasive particles and thermal vacuum drying before irradiation. The characteristic porous size was from 2 to 15 nm, and the porosity size was from 60 to 80%.

Amorphous carbon films was deposited on glass ceramic substrates (ST-50) with using PE CVD method. Working gas was mixture C\textsubscript{2}H\textsubscript{2} and H\textsubscript{2}. The substrate was heated up to 400 °C before carbon film deposition.

The materials under study were irradiated on a Temp accelerator with a proton-carbon beam (30% H\textsuperscript{+} and 70% C\textsuperscript{+}) with an average energy of 300 keV, duration of beam pulse of 60 ns, and current density from 5 to 150 A/cm\textsuperscript{2}. Both the average current density of the beam and the irradiation pulse number were varied in experiments. All samples of Si and SiO\textsubscript{2} had a porous layer thickness exceeding the ion range of the beam used. Carbon films had thickness up to 4 μm.

The surface morphology of the nanostructured layers before and after HPIB irradiation was studied by atomic-force microscopy (AFM) on a scanning probe Solver PRO (NT-MDT) microscope in the semiconductor mode in air with the use of the NSG10 probe and scanning electron microscope Philips SEM-515.

3. Results and discussion

Figure 1, a shows the AFM image of the initial surface of a porous silicon layer. The roughness height does not exceed 1.5 nm, and the characteristic pore diameter is about 20 nm. A single HPIB exposure with the average density \( j = 10 \text{ A/cm}^2 \) on such a porous silicon layer results in the formation of ellipsoidal silicon particles (Fig. 1, b). The characteristic diameter of the particles is 190 nm, their height is up to 45 nm, and the surface density of particles reaches \( 4 \cdot 10^7 \text{ cm}^{-2} \). The increase in the number of irradiation pulses up to three with the same beam current density \( (j = 10 \text{ A/cm}^2) \) leads to an increase in the characteristic diameter of particles up to 980 nm and their heights up to 460 nm. However, the surface density of the parti-
The holes formed upon irradiation have an irregular form with a characteristic size of 128 nm and depth of up to 200 nm (Fig. 2, b). The average height of ledges in this case is 88 nm, and, according to the data of reference [3], the average height of ledges decreases to 40 nm, the characteristic cross section of the ellipsoidal particles is 250 nm, and their concentration reaches $6.4 \cdot 10^7$ cm$^{-2}$. The holes formed upon irradiation have an irregular form with a characteristic size of 128 nm and depth of 80 nm, their concentration being $1.3 \cdot 10^8$ cm$^{-2}$. The increase in the number of irradiation pulses up to five for the same current density of the ion beam leads to an increase in the average height of ledges of up to 118 nm, the characteristic size of holes of up to 470 nm, and their depths of up to 200 nm (Fig. 2, c). The concentration of holes is $1.6 \cdot 10^8$ cm$^{-2}$. At this irradiation mode, a small amount of holes with a diameter of up to 1.5 μm and depth of up to 1 μm is observed.

These features of the morphology of the surface of porous Si and SiO$_2$ under the high power proton-carbon beam of nanosecond duration can be interpreted from the point of view of features of the spatial energy release of such an ion beam in porous media. The calculation data of reference [3] can be used to estimate the ion ranges in porous Si and SiO$_2$ at the energy used. They were larger than those in the continuous Si and SiO$_2$ medium by approximately three times. The penetration of the high-energy ion into the target lattice is accompanied by the local heating and melting of substance in the ion track resulting in large temperature, surface tension, and local pressure gradients, thus causing mass flow [4]. The size of the melting zone formed in the region of the ion track of the beam in the materials under investigation is of the order of several nanometers. This favors the effective melting of the porous medium skeleton at temperatures lower than those in the case of the bulk material. Since the Si and SiO$_2$ melts formed upon irradiation strongly differ in the series of the thermodynamic parameters, the morphology change of the surface of these materials under the HPIB exposure should differ as well. The increase in the sizes and the decrease in the concentration of the ellipsoidal particles formed on the porous silicon surface upon repeated irradiation can be due to the association of the nearby particles formed earlier at the subsequent irradiation pulses. At the increase in the current density, the area of the porous layer in which the temperature exceeds that of porous silicon melting increases. As a result, the size of the larger-diameter ellipsoidal particles formed of the material of the above area increases. The heat sink from the bottom border of this area to the nearby porous silicon layers or the near-surface layers of the monocrystal substrate limits the association of the melt skeleton elements because of their fast hardening and leads to the formation of the second layer of the smaller-diameter particles. Due to the high viscosity of the SiO$_2$ melt and its low heat conductivity (approximately ten times smaller than that of porous silicon), the relief of the polished silicon gel surface is mainly smoothed, with the smoothing proceeding after the termination of the irradiation pulse as well. In the locations of local ledges (or conglomerates of the spherelike silica gel particles), ellipsoidal SiO$_2$ particles can be formed. The near-surface character of the energy release of the ion beam results in strong heating of the material at some distance from the surface, desorption of the residual water and gas molecules in the SiO$_2$ pores, increase in their pressure, breaking of the top layer of the SiO$_2$ melt, and, finally, to the formation of holes. Upon repeated irradiation of nanoporous SiO$_2$, there occurs a gradual accumulation of water vapors and desorbed gases due to their diffusion from the deeper layers and their subsequent emission with the formation of the large-diameter holes.

In work was investigated also one more nanostructural material – carbon film. Typical ACM image of a surface film is presented in Figure 3, a.

The film has globular structure with the characteristic sizes of globule: height is 17 nm, diameter is 50 nm. After HPIB irradiation one impulse with ion current density 20 A/cm$^2$ the surface morphology of the film changes considerably (Fig. 3, b). Together with initial globule there are larger globular conglomerates. In this case the average height of particles increases to 67 nm and their cross-section size to 142 nm. The increasing of ion current density to 40 A/cm$^2$ lead to still considerable change of the surface relief of a (Fig. 3, c). The surface of the big conglomerates becomes more developed. The average height of particles reaches 219 nm and their cross-section size increases to 1080 nm. Carbon film thickness was decreased on 0.15–0.4 μm for one pulse of
Fig. 1. AFM image of the por-Si surface: (a) the initial sample; after the HPIB treatment with: (b) $j = 10 \text{ A/cm}^2$, $n = 1$; (c) $j = 50 \text{ A/cm}^2$, $n = 1$

Fig. 2. AFM image of the por-SiO$_2$ surface: (a) the initial sample; after the HPIB treatment with (b) $j = 20 \text{ A/cm}^2$, $n = 1$; (c) $j = 20 \text{ A/cm}^2$, $n = 5$
Fig. 3. AFM image of the carbon film: (a) the initial surface; after the HPIB treatment with (b) $j = 20 \text{ A/cm}^2$, $n = 1$; (c) $j = 40 \text{ A/cm}^2$, $n = 1$.

HPIB at the investigated range of ion current density. The change of surface carbon under HPIB treatment can be caused by melting, ablation and scattering of carbon by ion beam. In our experiments the ion current density was insufficient for carbon melting because of high melting point (4371 K) [5]. Scattering factor of carbon by ions was small. Possibly the formation of conglomerates at HPIB treatment is caused by presence at a carbon film of hydrocarboxonic compound (for example, transe-polyacetylene) which promote the association of small carbon particles in larger globule at heating film by ion beam. These conglomerates influence on resistance carbon film after HPIB irradiation.

4. Conclusions

Thus, the character of the surface changes of nanoporous Si and SiO$_2$ upon HPIB exposure is determined not only by the pore sizes and the total porosity of the material, but to a great extent by the thermodynamic properties of the melt of these materials. The surface changes of carbon films at HPIB treatment depend on chemical compound of film to a considerable degree.

References


