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ETCHED TRACK MORPHOLOGY IN SiO_2 IRRADIATED WITH SWIFT HEAVY IONS *

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We examined pore formation in thermally oxidized silicon wafers (SiO_2 / Si) by means of swift heavy ion irradiation followed by chemical etching of latent track zones in SiO_2 matrix. The samples were irradiated with 710 MeV Bi up to the fluences of (1–5)$\cdot 10^8$ and $5\cdot 10^{10}$ cm^{-2}. Afterwards the targets were etched in the dilute solutions of hydrofluoric acid for various durations. Scanning electron microscopy was used to probe the processed samples. From the geometric parameters of the pores the etch rate V_t of the tracks and the etch rate V_b of bulk a-SiO_2 were estimated. The etching behaviour and morphology of the etched tracks has been found to change markedly with fluence. Mutual influence of tracks at their higher densities was analysed in terms of radiation-induced modifications of material around the ion path. It was shown that the morphology of etched tracks did not change after the annealing at 900 °C for 30 min.

Keywords: swift ion irradiation, silicon dioxide, latent track etching, SEM

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1. Introduction

In most dielectric targets, swift heavy ions create irreversible material degradation along the ion trajectories [1, 2] whenever the electronic stopping power S_e is above a certain threshold value S_{th}. These damaged regions, so called "latent tracks", extend from the sample surface to the major part of the ion ranges. The track diameters vary typically between 5 and 50 nm. Different calculations based on a thermal spike approach have been developed to account for track formation as well as to predict the nanometre track radius [3, 4]. It is necessary to know the information on morphology and depth profile of the tracks to test theoretical models. On the other hand, the tracks can be etched in a suitable chemical agent to produce pores or nanochannels that, in turn, can be refilled with inorganic or organic substances. There is a number of applications of the ion track technology developed, going from fission-fragment dosimetry, to molecular sieves, and to a variety of electronic and magnetic devices [5–8]. Porous layers of SiO_2, a thermally stable and chemically resistant material, can find applications in environments where plastic membranes are not applicable.

The purpose of this work was to investigate the topography and depth profile of the etched tracks in SiO_2 irradiated with high and low fluence of swift heavy ions. We have estimated the influence of high-temperature treatment on the porous SiO_2 morphology, too.

2. Experimental details

Samples used in this work were cut from the thermally oxidized n-doped (100) Si wafer. The thickness of SiO_2 layer was evaluated from Rutherford backscattering spectrometry and transmission electron microscopy measurements and was equal to 600 nm. SiO_2 / Si structures were irradiated normally to the surface with 710 MeV Bi ions up to the fluence of $(1-5)\cdot 10^8$ and $5\cdot 10^{10}$ cm^{-2} at the Joint Institute for Nuclear Research (Dubna, Russia). The ion flux was kept constant and equal to $2\cdot 10^8$ cm^{-2}s^{-1}. To provide reliable thermal contacts the samples were fixed on a

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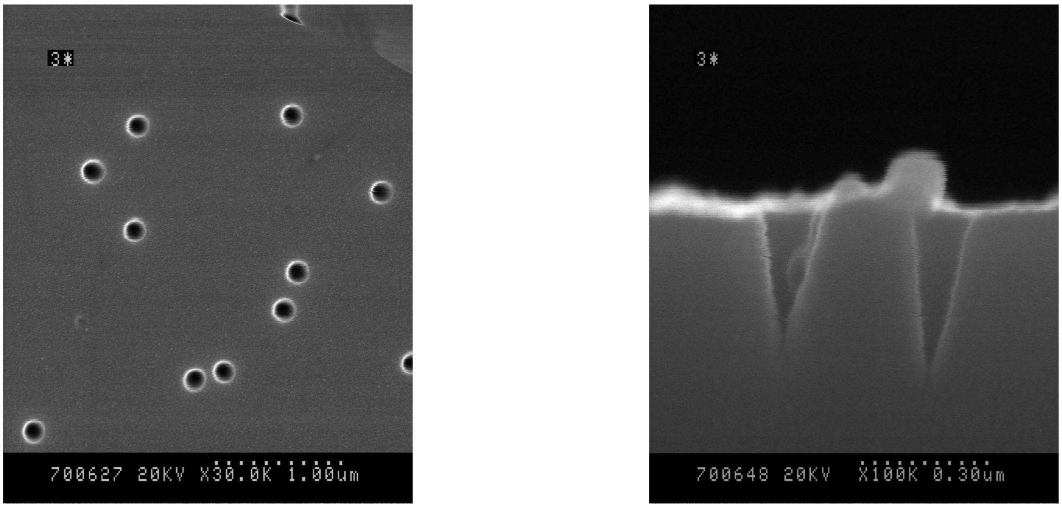


(a) (b)

Fig. 1. Scanning electron microscopy (SEM) images of (a) the surface and (b) the cross-section of the SiO_2 / Si irradiated with 710 MeV-Bi up to the fluence of (1–5)$\cdot 10^8$ cm^{-2} and afterwards etched in 1.2% HF for 20 min.

massive metallic holder with a heat conducting paste. The irradiated samples were treated in hydrofluoric acid (HF) dilute aqueous solutions at room temperature. Then the samples were investigated using the scanning electron microscope Hitachi S-806. A part of samples was probed by means of Talystep profilometer to evaluate the etch rate of SiO_2 in HF solution. To estimate the morphological stability of etched tracks during heating a part of $SiO_{2\,\mathrm{por}}$ / Si samples was annealed in resistance furnace in inert atmosphere at 900 °C during 30 min.

3. Results and discussion

Figure 1 shows the holes in SiO_2 irradiated with the low fluence of Bi ions and etched in 1.2% HF solution for 20 min. Their density, calculated from the SEM image, was equal to $2.3\cdot 10^8$ cm^{-2}. This value coincides with Bi ion fluence. It was shown that each ion impact at the surface of amorphous SiO_2 leads to an etchable track provided that the electronic stopping power S_e of the ion exceeds 4.0 keV/nm [9]. In our experiment this criterion is fulfilled, as $S_\mathrm{e} = 23.8$ keV/nm for 710 MeV Bi ions in a-SiO_2 according to SRIM'2003 code [10]. Figure 1(b) represents depth profile of etched tracks. One can clearly see the conical shape of holes resulted from the limited ratio between the etch rate V_t of the tracks and the etch rate V_b of bulk a-SiO_2. The half cone angle, β, obtained from SEM image was 15°. From the values of the depths, z, the etching duration, t_e, and the half cone angle of the holes, the track and bulk etch rates (V_t and V_b) can be determined using the relations: $z = (V_\mathrm{t} - V_\mathrm{b})t_\mathrm{e}$ and $\sin\beta = V_\mathrm{b}/V_\mathrm{t}$ [1, 2]. For 1.2% HF solution at room temperature $V_\mathrm{t}/V_\mathrm{b} = 3.9$. Accordingly, V_b and V_t are 6.3 and 25.5 nm/min. It should be noted that V_b and V_t values are in a reasonable correlation with the estimations of ones given in the papers [11, 12]. Complementary measurements by means of profilometer were performed on virgin SiO_2 layers etched in 1.5% HF solution. By measuring of the step height between etched and un-etched regions of SiO_2 surface $V_\mathrm{b} = 7.7$ nm/min was found. This value is in agreement with the V_b estimation obtained from the pore geometry data.

As can be seen from Fig. 1, etched tracks have minor dispersion of diameter and depth. On this condition the knowledge of V_b and V_t values allows one to predict etching time necessary for the formation of through channels in the track region. If V_b and V_t are 6.3 and 25.5 nm/min, correspondingly, during the 20-minute etching of the irradiated sample in 1.2% HF solution, the layer of bulk material with the thickness of 126 nm is dissolved. In the track region, the removed material thickness is equal to 510 nm. SiO_2 thickness before etching was equal to 600 nm. Therefore, after such treatment the pore bottom does not reach silicon and etched tracks look like sharp-pointed cones. Simple calculation shows that for the formation of through channels in the form of truncated cones the etching time should exceed 24 min.

The evolution of opening diameter versus the etching time is presented in Fig. 2. An extrapolation of the data to zero etching time intercepts the vertical axes at the value $D_0 \approx 20$ nm. This value can be interpreted as the diameter of the track core at the surface of the SiO_2 target irradiated under the conditions of our experiment.

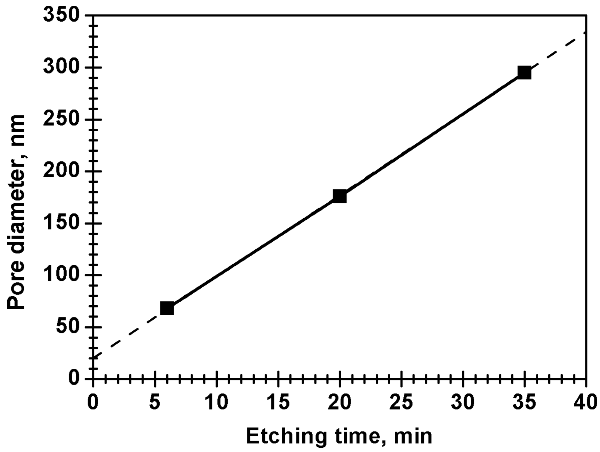
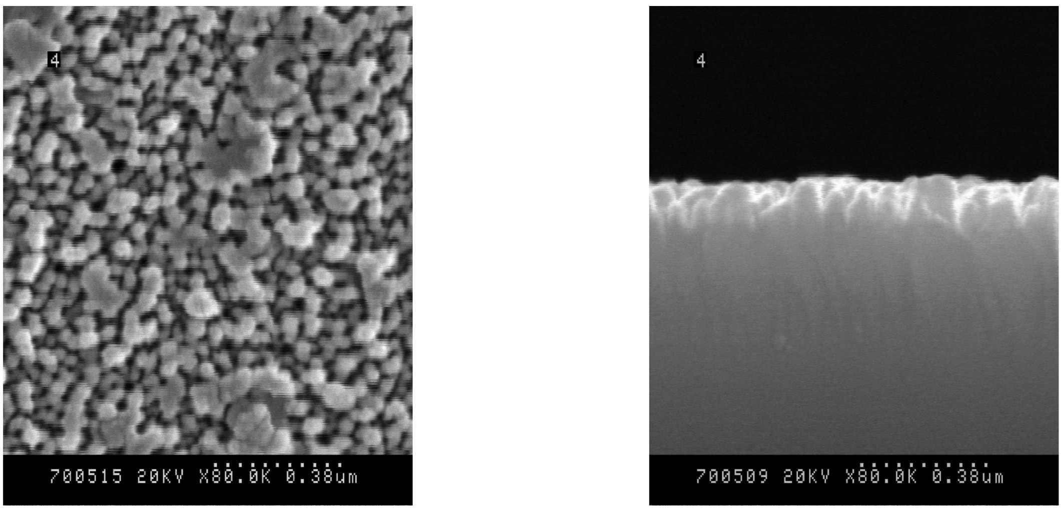


Fig. 2. Mean diameter of the tracks versus the etching time. The straight line is the linear fit to the data.

The diameter of the track core in a-SiO_2 has been estimated in [12], too. In accordance with [12], D_0 is equal to about 10 nm for 200 MeV Au ion irradiation.

In order to calculate the diameter of molten phase in the track region and its lifetime for SiO_2 irradiated with 710 MeV Bi ions, the thermal spike model [3] has been used. Molten region diameter is equal to 15.6 nm, lifetime of the molten region is equal to 37.5 ps. Calculated lifetime of the molten region allows one to speak about the presence of the liquid phase and its subsequent solidification. Calculated diameter of the track region coincides with the etching data.

Figure 3 represents the surface of SiO_2 irradiated with the high Bi ions' fluence and etched in 2% HF solution for 6 min. As figure shows, SiO_2 surface is essentially different from the surface of the sample irradiated with low fluence of Bi ions. Low-fluence irradiation leads to formation of a system of pores with right conical shape in SiO_2. The pore sizes are practically equal, and their density corresponds to the fluence. Under the high-fluence irradiation the pores in the form of wide near the surface asymmetrical cones, with more deep narrow pore in the centre, are formed. Their sizes differ very much, and the density is essentially (up to one order of magnitude) less than the fluence. Cross-section of etched sample shows that SiO_2 region with etched tracks represents complicated system of multistep cones with different height and diameter (see Fig. 3(b)). Measurement of separate pores' geometrical characteristics in such samples is complicated by their confluence. The track overlapping effects cause these morphological changes. For the purposes of nanotechnology, the smaller the diameter of the latent track, the better. In an ideal scenario the latent track could be a linear trail of damage, while the material between the tracks remains unaltered. However, the radial extension of ion tracks in solids is finite, and depends on the type of solid and on the energy density deposited around the track trajectory. The dissipated energy initiates radiation-induced modifications of material which become evident during the etching of irradiated material. For the random distribution of tracks the mean distance between neighbours is $\langle a \rangle = 1/2\sqrt{n}$, where n is the mean track density [13]. It has been shown above that in the conditions of our experiment the latent track density is proportional to the current fluence and for the fluence of $5{\cdot}10^{10}$ cm^{-2} $\langle a \rangle \approx 22$ nm. The track core diameter at the surface of the SiO_2 target, D_0, obtained from the etching data (Fig. 2) is equal to $\approx$20 nm. Thus, $\langle a \rangle \approx D_0$. Previous study of polymers, alkali halides and A^3B^5 semi-

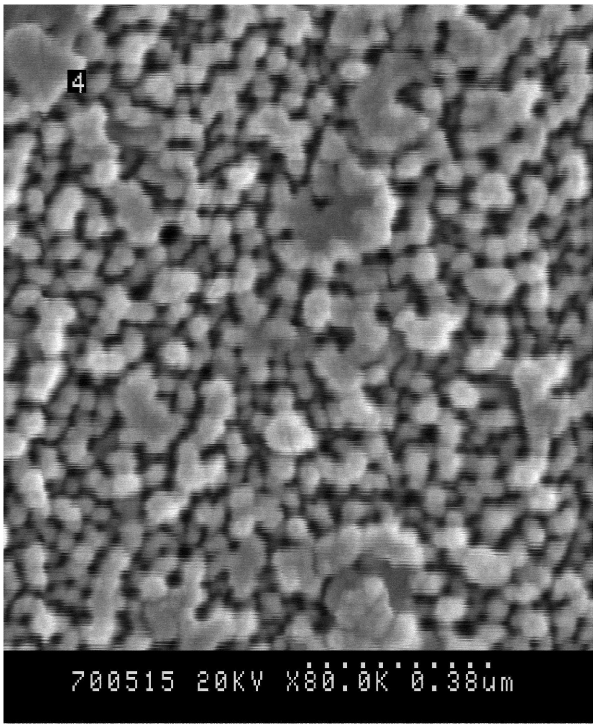


(a) (b)

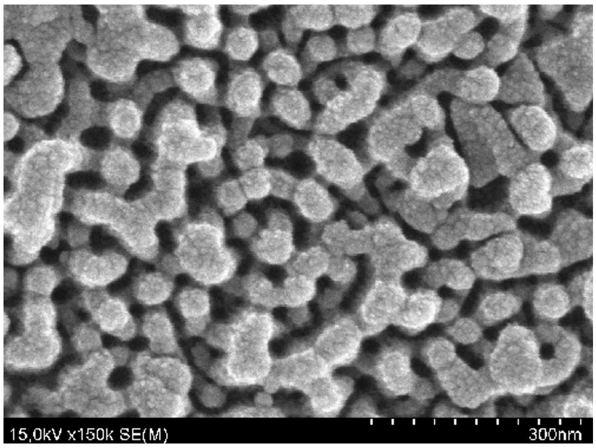
Fig. 3. (a) SEM images of the surface and (b) the cross-section of the SiO_2 / Si irradiated with 710 MeV-Bi up to the fluence of $5{\cdot}10^{10}$ cm^{-2} and afterwards etched in 2% HF for 6 min.

conductors showed that ion tracks in solids typically have a narrow core surrounded by a halo of larger radius [14–16]. Supposedly, distorted chemical bonds and the smaller density in comparison with the virgin matrix characterize the material in the halo region. Hence, the etch rate of material in the halo may differ from the etch rate of undamaged bulk material. One can conclude that for the track density of $5{\cdot}10^{10}$ cm^{-2} the neighbouring tracks influence each other because of the overlapping of halos and partial overlapping of track cores. For the track density of $2.3{\cdot}10^{8}$ cm^{-2} (in the case of samples irradiated with low fluence of Bi ions) $\langle a \rangle$ is $\approx$330 nm. The latter is much more than D_0. Accordingly, for the samples irradiated with low fluence no interactions between the tracks were revealed.

In order to use porous SiO_2 as a template for nanocomposite material deposition, it is necessary for $SiO_{2\,por}$ to stand high-temperature treatment without pore geometry changes. To check the influence of the annealing on $SiO_{2\,por}$ morphology, the SiO_2 / Si samples irradiated with Bi and treated in 2% HF for 6 min were annealed in resistance furnace in inert atmosphere at 900 °C for 30 min. Figure 4 represents photographs of SiO_2 surface with etched tracks before and after annealing. As figure shows, there are no pore geometry changes after the annealing. Thus, porous silicon dioxide can stand high-temperature annealing without etched pore geometry changes.



(a)



(b)

Fig. 4. SEM images of the porous SiO_2 surface for (a) un-annealed sample and (b) for the same sample annealed in inert atmosphere at 900 °C during 30 min. Note that image (b) is obtained at higher magnification.

4. Conclusion

The morphology of pores in porous SiO_2 layers obtained by 710 MeV Bi irradiation of thermally oxidized silicon wafers (SiO_2 / Si) followed by etching in the dilute HF solutions has been studied. It has been shown that for samples irradiated with fluence of $(1-5){\cdot}10^{8}$ cm^{-2}, pores have right conical shape. Their sizes are practically equal, and their density corresponds to the fluence. The etch rate V_t of the tracks and the etch rate V_b of bulk a-SiO_2 have been calculated using geometric parameters of conical pores. Accordingly, V_t and V_b are 25.5 and 6.3 nm/min. Track core diameter for 710 MeV Bi ion at the surface of the SiO_2 target has been estimated using pore diameter dependence on etching time. This value is of about 20 nm.

Fluence increase up to $5{\cdot}10^{10}$ cm^{-2} changes porous layer morphology, leading to the formation of system of multistep cones with different height and diameter. Their sizes differ very much, and the density is essentially (up to one order of magnitude) less than the fluence. Comparison of track core diameter for 710 MeV Bi ion at SiO_2 surface and mean distance between neighbouring tracks, calculated for the fluence of $5{\cdot}10^{10}$ cm^{-2}, allows one to conclude that observed changes in pore morphology are caused by track overlapping effects.

Thermal stability of porous SiO_2 has been estimated. It is shown that heating in inert atmosphere at 900 °C for 30 min does not lead to pore morphology changes.

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ĖSDINTŲ GRIOVELIŲ MORFOLOGIJA GREITAIS SUNKIAISIAIS JONAIS ŠVITINTAME SiO_2

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Santrauka

Tirtas pórų radimasis termiškai oksiduotuose silicio bandiniuose, juos apšvitinus greitais sunkiaisiais jonais ir po to chemiškai ėsdinant liekamųjų trekų sritis SiO_2 matricoje. Pavyzdėliai švitinti 710 MeV Bi $(1–5)\cdot10^8$ ir $5\cdot10^{10}$ cm^{-2} srautais. Vėliau jie ėsdinti skiestu vandenilio fluorido tirpalu įvairų laiką. Apdoroti bandiniai tirti skenuojančiu elektroniniu mikroskopu. Pagal geometrinius pórų parametrus įvertinta trekų ėsdinimo sparta V_t bei ištisinio a-SiO_2 ėsdinimo sparta V_b. Nustatyta, kad ėsdinimas ir griovelių morfologija labai priklauso nuo švitinimo srauto. Analizuota trekų, kai jie tankūs, savitarpio įtakos priklausomybė nuo apšvitos indukuotų medžiagos pokyčių aplink jonų takus. Parodyta, kad ėsdintų trekų morfologija nepasikeičia po 30 min trunkančio atkaitinimo 900 °C temperatūroje.