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Swift heavy ion irradiation reduces porous silicon thermal conductivity

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M. Massoud^a, B. Canut^a, P. Newby^b, L. Frechette^b, P.O. Chapuis^c, J.M. Bluet^{a,*}

^a Université de Lyon, Institut des Nanotechnologies de Lyon INL-UMR5270, CNRS, INSA de Lyon, F-69621 Villeurbanne, France ^b Centre de Recherche en Nanofabrication et Nanocaractérisation (CNR2), Université de Sherbrooke, Sherbrooke, Québec, Canada ^c Université de Lyon, Centre de Thermique de Lyon CETHIL-UMR5008, CNRS, INSA de Lyon, F-69621 Villeurbanne, France

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ABSTRACT

While the electrical conductivity of semiconductors can be easily changed over order of magnitudes (8 in silicon) by playing on the doping, the thermal conductivity (TC) control is a challenging issue. Nevertheless, numerous applications require TC control in Si down to 1 W m⁻¹ K⁻¹. Among them, there are thermal insulation requirements in MEMS, thermal management issues in 3D packaging or TC reduction for thermoelectric applications. Towards this end, the formation of nanoporous Si by electrochemical anodisation is efficient. Nevertheless, in this case the material is too fragile for MEMS application or even to withstand CMOS technological processes. In this work, we show that ion irradiation in the electronic regime is efficient for reducing TC in meso-porous Si (PSi), which is more mechanically robust than the nanoporous PSi. We have studied three different mass to energy ratios (²³⁸U at 110 MeV and ¹³⁰Xe at 91 MeV and 29 MeV) with fluences ranging from 10¹² cm⁻² to 7 × 10¹³ cm⁻². The sample properties, after irradiation, have been measured by infrared spectroscopy, Raman spectroscopy and scanning electron microscopy. The TC has been measured using scanning thermal microscopy. Although, bulk Si is insensitive to ion interaction in the electronic regime, we have observed the amorphisation of the PSi resulting in a TC reduction even for the low dose and energy. For the highest irradiation dose a very important reduction factor of four was obtained.

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1. Introduction

Crystalline silicon is the material of choice for fabrication in the majority of micro-electro-mechanical systems (MEMS) and sensors. Among MEMS, energy harvesting devices are intensively studied nowadays due to the development of wireless applications. One of the main issues, to get suitable yields in these devices, is to be able to separate hot points from cold points. Toward this end, tuning of Si thermal conductivity (TC) from the high bulk value of 156 W m⁻¹ K⁻¹ down to the very low values of insulating materials like glass $(1-2 \text{ W m}^{-1} \text{ K}^{-1})$ is a challenging issue. One of the most efficient approaches is to fabricate porous silicon (PSi). Indeed, (PSi) made by electrochemical etching of single crystal silicon wafers (c-Si), has a TC which is 2-3 orders of magnitude lower than that of bulk c-Si [1,2]. However, there is a limit to the reduction in TC which can be obtained by increasing porosity, as porosification also has a detrimental effect on the mechanical properties of PSi [3].

A trade-off must therefore be found between TC and mechanical performance. An approach is to perform a slight oxidation of the PSi. By this way, a reduction of TC by a factor of two has been achieved [4,5]. Further oxidation is not useful as, from one hand, it causes swelling and stress in the PSi layer which are detrimental for MEMS processing [6,7], and from the other hand, as oxygen incorporation reduces porosity, TC increases again beyond a given limit [4,5]. Consequently, alternative techniques for reducing the TC of PSi without increasing its porosity or damaging it, are desirable. One way is to amorphise Si as disorder reduces thermal transport in crystalline solids [8]. In the case of Si this gives a two order of magnitude reduction with values ranging between 1 and 5 W m⁻¹ K⁻¹ depending on the fabrication process [9].

In this work, we propose to use ion irradiation to render PSi amorphous in order to combine the TC reduction due to porosity and amorphisation. As we aim to keep the PSi material structure, nuclear interactions which are known to cause amorphisation, are nevertheless not desired. Indeed, in this regime crush down of the PSi material occurs. For instance, a previous study on the irradiation of PSi in the nuclear regime showed that irradiation with 4 MeV ⁴He⁺ ions caused a densification of the porous layer [10]. Consequently we use swift heavy ion irradiation. Indeed, in most of covalent insulating materials and in given binary semiconductors this irradiation causes the creation of a cylindrical damaged zone ("latent track") along the path of the ions [11,12].

^{*} Corresponding author.

In the case of PSi, irradiation with swift heavy ions has also been carried out in order to improve its photoluminescence efficiency [13–15] but these studies lacked a structural analysis of the irradiation-induced effects.

In a previous work [16], we have shown amorphisation and TC reduction of PSi after irradiation with ²³⁸U at 110 MeV. In this work, extended results for different energy and mass ion at various doses are presented. Toward this end, we fabricated PSi with 56% porosity and we have irradiated it with ²³⁸U and ¹³⁰Xe ions at different energies and fluences. The samples properties have been investigated using infrared and Raman spectroscopy, scanning electron microscopy (SEM) and their TC was evaluated by scanning thermal microscopy (SThM).

2. Material and methods

The porous silicon (PSi) samples were obtained by electrochemical etching of p+ (ρ = 0.01–0.02 Ω cm) monocrystalline (100) Si wafers. The etching process was carried out in a Teflon cell, using a (1:1) HF (48%) – ethanol mixture. A pulsed current was used, with zero-current etch-stop periods (4 s stop for 1 s on) to improve uniformity of the thick (10 μ m) PSi layers [17]. The current density amplitude during the pulse, was fixed to 150 mA cm⁻² which gave a porosity of 56% for all the samples studied here. This porosity was measured by infrared reflectivity using an effective medium model for the refractive index. The PSi targets were irradiated at the SME and IRRSUD beam lines of the GANIL accelerator (Grand Accélérateur National d'Ions Lourds, CAEN France), using ¹³⁰Xe ions (91 MeV and 29 MeV energies) or ²³⁸U ions (110 MeV energy). In all cases, the nuclear stopping power is far below the electronic one calculated in bulk Si from the SRIM2013 code [18] and the projected range exceeds the PSi thickness except for 29 MeV ¹³⁰Xe irradiation. Considering that the calculation was done for bulk Si we can assume by simple density consideration that in 56% PSi the projected range might double. These parameters are listed in Table 1. The ion fluence ranged between 10^{12} and 7×10^{13} cm⁻². All irradiations were performed at room temperature with a flux limited to $10^9 \text{ cm}^{-2} \text{ s}^{-1}$ in order to avoid any overheating of the targets. The samples composition and surface chemistry were studied by infrared spectroscopy (Bruker Vertex 80 spectrometer) in attenuated total reflectance (ATR) mode using a Ge prism (Specac). Their morphology was evaluated using SEM in cross section on cleaved samples and Raman spectroscopy (Renishaw RM 1000 spectrometer) in micro Raman mode (objective magnification \times 50) with a laser excitation at 532 nm. During the Raman experiment, the laser power was reduced in order to prevent sample heating by the laser beam. Indeed, as the 56% PSi TC is about 20 times lower than the one of bulk material, usual laser powers in the 10 mW range cause heating and consequently spectral shifting to lower energies and broadening. Finally, TC was measured using the SThM technique, which is based on atomic force microscopy (AFM). For the measurement, a thermoresistive wire probe mounted on the AFM cantilever is excited by a DC current. The probe is then heated by Joule effect. When this probe is brought to contact with the sample, it locally delivers heat to the sample and consequently cools down. The electrical power required for maintaining the probe's temperature constant while it contacts

Table 1

Main characteristics of the ion irradiations calculated for bulk Si for the different projectiles and incident energy (*E*): projected range (R_p), electronic (S_e) and nuclear (S_n) stopping powers at the incident surface.

Projectile E (MeV) $R_{\rm p}$ (nm) $S_{\rm e}$ (keV nm ⁻¹)	S_n (keV nm ⁻¹)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.24 0.1 0.35

the sample depends on the sample's TC. This procedure is exploited for determining k after calibration with samples of well-known TC [19].

3. Results and discussion

3.1. Surface chemistry

The infrared absorbance in the middle infrared range is displayed in Fig. 1 for 238 U irradiation. The same features are observed in the case of 130 Xe irradiation and are summarized below. As the ion fluence increases:

- (i) The SiH and SiH₂ bending modes at 625 cm⁻¹ and 660 cm⁻¹ respectively vanish for fluencies higher than 10^{12} cm⁻². The same is observed for the SiH, SiH₂ stretching modes at 2082 cm⁻¹ and 2112 cm⁻¹ (not presented in Fig. 1).
- (ii) In the same way a pronounced peak at 880 cm⁻¹ attributed to O_ySiH_x bending mode in PSi [20] also vanishes quickly. For the highest fluence, a broad peak with small low energy shift, which may be due to Si–O–Si bending, seems to reappear.
- (iii) The broad peak at 800 cm⁻¹ attributed to SiO-H bending slightly increases with irradiation fluence. The same is observed for the broad stretching mode band of SiO-H between 3100 cm⁻¹ and 3600 cm⁻¹ (not presented in Fig. 1).
- (iv) The well known symmetric and asymmetric Si–O–Si stretching modes at 1070 cm⁻¹ and 1180 cm⁻¹ respectively are broadening especially for the highest fluences $(3 \times 10^{13} \text{ cm}^{-2} \text{ and } 7 \times 10^{13} \text{ cm}^{-2})$.

Globally the observed features indicate a reduction but not total disappearance of the surface H bonding accompanied by a slight oxidation of the sample for all fluences higher than 10^{12} cm⁻². The Si–O–Si stretching bands are not growing in intensity as it would be expected for a volume oxidation of the crystallites but are broadening due to the formation of Si–O surface modes and maybe also due to partial amorphisation of the sample. This possible amorphisation of the sample is most probable for the 3×10^{13} cm⁻² and 7×10^{13} cm⁻² fluences, for which all of the spectra peaks are broadened.

3.2. Morphology



Fig. 2a presents SEM image of non-irradiated PSi also in the case of ^{238}U irradiation. The formed PS is mesoporous (pore width

Fig. 1. Infrared absorbance spectra obtained in ATR mode for 56% porosity Si irradiated with ²³⁸U at 110 MeV. For easier observation, the spectra have been shifted vertically starting from the non irradiated sample up to the sample irradiated with the highest fluence (a: non irradiated; b: 10^{12} cm^{-2} ; c: $3 \times 10^{12} \text{ cm}^{-2}$; d: $7 \times 10^{12} \text{ cm}^{-2}$; e: 10^{13} cm^{-2} ; f: $3 \times 10^{13} \text{ cm}^{-2}$ and g: $7 \times 10^{13} \text{ cm}^{-2}$;

a) <u>100 nm</u> c) <u>100 nm</u> <u>100 nm</u> <u>100 nm</u>

Fig. 2. Cross-section SEM images of 56% porosity Si. (a) Non irradiated sample. (b–d) Samples irradiated with 238 U at 110 MeV with respective ion fluences of 3 × 10¹² cm⁻², 10¹³ cm⁻² and 3 × 10¹³ cm⁻².

between 2 and 50 nm). It is formed of dendritic silicon quasi-columns, with a diameter on the order of 10 nm, perpendicular to the wafer surface, and separated by pores. These quasi-columns remain monocrystalline and retain the crystalline orientation of the substrate. For the non-irradiated sample, the ramification of the dendritic structure ends with small spike structures with a width of few nanometers. As the fluence is increased up to 7×10^{13} cm⁻² the PSi skeleton remains unchanged and the sample porosity does not change. As stated in the experimental part from the calculated values of S_e and S_n (see Table 1), this proves that the dominant interaction regime is the electronic one. Indeed, in the case of nuclear interaction with such heavy ions like ²³⁸U. the cascade of collisional damages is expected to crush down the porous structure as was observed for 4 MeV ⁴He⁺ irradiation [10]. Neverthe less, for 3×10^{13} cm⁻² and 7×10^{13} cm⁻² fluences, small ramifications are turning into beads. This morphology at the ramification ending calls to mind solidification of molten Si droplet which may have been formed during irradiation. Indeed, according to the thermal spike model [21], the target electrons, previously excited by the incoming ions in the first 10^{-15} s following their passage, transfer their energy to the crystal lattice via electronphonon coupling (10^{-12} s) . This in turn can cause the target to melt locally, if the deposited energy density is high enough. If PSi crystallites are not totally melted, liquid phase epitaxial regrowth could occur during cooling down. In the opposite case, amorphous Si will form as it appears in infrared measurement for the highest fluences. In order to obtain a more accurate evaluation of the amorphous fraction present in the sample, Raman spectroscopy was used.

Indeed, Si amorphisation results in selection rules breakdown, which makes all phonon modes observable in Raman spectroscopy and not only the optical mode in Brillouin zone center (k = 0). Consequently a complex spectrum in which intensity is mainly proportional to phonon density of states, as all phonons can be seen, is extending from 0 to 521 cm⁻¹. One empirical way to determine the amorphous fraction from this spectrum is to compare the Si crystalline Raman peak area to the area of the TO branch peak appearing at 480 cm⁻¹ in amorphous material [22]. The amorphous fraction can be obtained directly, this way, if Raman cross sections of amorphous and crystalline (or porous) Si are considered

equal. As the ratio of these cross sections spreads from 0.1 to 1.7 in the literature [22–27] we have chosen the simple value of 1 as our goal is more to show a trend with increasing fluence than to obtain



Fig. 3. Raman spectra of 56% porosity Si irradiated with 29 and 91 MeV ¹³⁰Xe for different fluences. The red spectra are for the 29 MeV energy and the blue ones for the 91 MeV energy. The vertical dashed lines at 480 cm⁻¹ and 520 cm⁻¹ are guide for the eyes to follow the intensity evolution of amorphous Si Raman peak and porous Si Raman peak respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Amorphous fraction (left hand axis) and thermal conductivity (right hand axis) variation as a function of the ¹³⁰Xe ion fluence. Black lines with filled symbols stand for 91 MeV energy ions, while gray lines with open symbols correspond to the 29 MeV energy.

an absolute value of amorphous fraction. The Raman spectra for 29 MeV and 91 MeV ¹²⁹Xe irradiation at different fluences are shown in Fig. 3. As can be observed for the non irradiated sample, the PS peak is asymmetrically broadened towards lower wavenumbers. Its position is also shifted by a few cm⁻¹ to lower wavenumbers in comparison to bulk Si. These changes are usually ascribed to phonon confinement in the PSi crystallites [28,29]. After irradiation, for an increasing dose, the broad band centered at 480 cm⁻¹, typical of amorphous Si is clearly increasing. At equivalent fluence, the intensity of this band is higher for the higher irradiation energy (higher electronic stopping power, see Table 1). The evolution of the amorphous fraction with ion fluence is shown in Fig. 4 on a logarithmic scale. The linear trend of these curves shows that the damage creation kinetics follows a classical Poisson's law. In the case of ²³⁸U irradiation at 110 MeV, the electronic stopping power (12.3 keV nm⁻¹) is higher, and full amorphisation (disappearance of the PS Raman Peak) is observed at 3×10^{13} cm⁻² fluence. Nevertheless we have to notice that in the case of bulk Si the only known method for creating amorphous tracks is to irradiate the sample with fullerenes [30], which have a much higher electronic stopping power than uranium and other single ions [31]. Comparing PS properties to the bulk material ones, it appears that the main reason for amorphous track creation by swift heavy ions irradiation is the considerably lower TC of the porous material. Indeed, in the case of 56% porosity, the TC $(6-7 \text{ W m}^{-1} \text{ K}^{-1})$ is approximately 25 times lower than the one of bulk Si. With this TC approaching the one of dielectric materials, according to the thermal spike model, the target temperature after electron-phonon coupling reaches the melting temperature thus inducing amorphous track formation along the projectile path. In order to verify this low TC value and to study the impact of ion irradiation on this material property we have measured this parameter.

3.3. Thermal conductivity

The samples' TC was estimated from the SThM measurements, as exposed in Section 2, using interpolation between well-known TC of calibrated samples. Note that the surface state of these bulk reference materials can be different from the PSi one. Consequently, the real TC values may depart slightly from the estimated ones. The results are presented in Fig. 4 (right hand axis) as a function of the fluence on a logarithmic scale. As can be observed, the TC for both irradiation energies decreases almost linearly with the logarithm of the fluence down to a very low value of

1.7 W m⁻¹ K⁻¹. This represents a 4 times reduction in comparison to the non-irradiated sample. On the same figure (left hand axis) is represented the evolution of the amorphous fraction with the fluence which clearly demonstrates that damage caused by irradiation in the electronic regime causes amorphisation. Additionally, FTIR measurements have shown that irradiation results in a surface oxidation of the nanocrystallite. This oxidation occurs at the lower doses (between 10^{12} cm⁻² and 3×10^{12} cm⁻²). Consequently both surface oxidation and amorphisation (as amorphous Si has lower TC than crystalline Si) can explain the strong reduction observed in TC for the irradiated samples. Since H related peaks in FTIR measurements disappear for all fluences higher than 10^{12} cm⁻², we can consider that the surface oxidation is the same for all the fluences higher than 10^{12} cm^{-2} and, consequently, that the role of surface oxidation is also the same. The main factor of TC reduction with increasing the irradiation fluence, is then the amorphisation. This is confirmed by the linear dependence between TC and amorphous fraction as can be observed in Fig. 5. From an applicative point of view, this graph shows the possibility to adjust the TC by varying the amorphous fraction (i.e. by varying the fluence for a given ion and energy). Towards this end, it will be interesting in future work to reduce both the ion irradiation energy and the ion mass in order to investigate if amorphisation by electronic interaction still occurs in PSi for more usual irradiation conditions than the one used in this work.



Fig. 5. Thermal conductivity as a function of amorphous fraction. The straight lines are linear fits to the data. As in Fig. 4, black lines with filled symbols stand for 91 MeV energy ions, while gray lines with open symbols correspond to the 29 MeV energy.

4. Conclusion

We have shown that swift heavy ion irradiation with 110 MeV ^{238}U ions and also 91 MeV and 29 MeV ^{129}Xe ions can create an amorphous phase in mesoporous silicon, while no effect is observed in bulk material. Combined with a partial surface oxidation observed in FTIR, this amorphisation results in a considerable reduction of the PSi TC. This amorphisation is assumed to result from the following mechanism: the PSi small ramification melt due to electronic interaction, as can be explained by the thermal spike model, and lose their crystallinity during re-solidification. Nevertheless, the PSi keeps its global structure with no change in porosity. As a consequence, it is possible to adjust the amorphous volume fraction and therefore the TC by varying the ion fluence. We have shown that this value can be reduced by a factor of 4 in comparison to the non-irradiated PSi, down to $1.7 \text{ W m}^{-1} \text{ K}^{-1}$ for a porosity of 56%. To obtain such a low value without irradiation, processes involving much higher porosity and/or an oxidation step would be needed. In these cases, the sample mechanical properties are degraded which makes it less suitable for micro-technological processing. From this applicative point of view, we plan to try more conventional irradiation with lighter ions at lower ion energy. As, partial surface oxidation also occurred after irradiation, the pore chemical stability with time and consequently the TC value stability (i.e. aging of the sample) is also an issue to be addressed in future work regarding device application.

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