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Swift heavy ion irradiation reduces porous silicon thermal conductivity

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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 (^{238}U at 110 MeV and ^{130}Xe at 91 MeV and 29 MeV) with fluences ranging from 10^{12} cm^{-2} to 7×10^{13} 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.

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 W m^{-1} 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 $^{4}He^{+}$ 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].

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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 ^{238}U 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 ^{238}U and ^{130}Xe 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 μm) 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 ^{130}Xe ions (91 MeV and 29 MeV energies) or ^{238}U 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 ^{130}Xe 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 cm^{-2} 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 × 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 the sample depends on the sample's TC. This procedure is exploited for determining k after calibration with samples of well-known TC [19].

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_p (nm)	S_e (keV nm^{-1})	S_n (keV nm^{-1})
^{130}Xe	29	6.8	6.4	0.24
^{130}Xe	91	13.7	10.9	0.1
^{238}U	110	14.2	12.3	0.35

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 SiH_2 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, SiH_2 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 (3×10^{13} cm^{-2} and 7×10^{13} 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

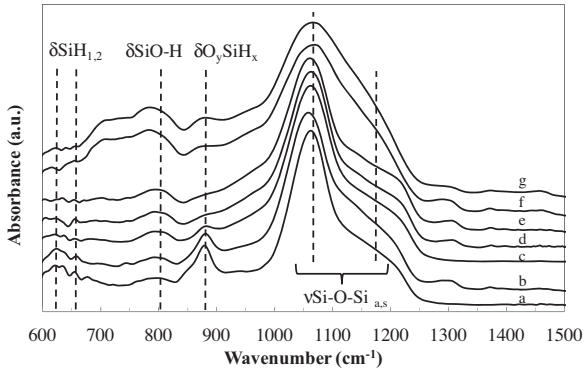

Fig. 1. Infrared absorbance spectra obtained in ATR mode for 56% porosity Si irradiated with ^{238}U at 110 MeV. For easier observation, the spectra have been shifted vertically starting from the non irradiated sample up to the sample irradiated with the highest fluence (a: non irradiated; b: 10^{12}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