CPC(HEP & NP), 2011, **35**(9): 885–889 Chinese Physics C Vol. 35, No. 9, Sep., 2011

Raman scattering investigation of C-doped a-SiO_2 after high energy heavy ion irradiations*

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Abstract: Thermally grown amorphous SiO_2 films were implanted at room temperature with 100 keV C-ions to 5.0×10^{17} or 1.2×10^{18} ions/cm^2. These samples were irradiated at room temperature with 853 MeV Pb-ions to 5.0×10^{11}, 1.0×10^{12}, 5.0×10^{12} ions/cm^2, or with 308 MeV Xe-ions to 1.0×10^{12}, 1.0×10^{13}, 1.0×10^{14} ions/cm^2, respectively. Then the samples were investigated using micro-Raman spectroscopy. From the obtained Raman spectra, we deduced that Si–C bonds and sp^2 carbon sites were created and nano-inclusions may also be produced in the heavy ion irradiated C-doped SiO_2. Furthermore, some results show that Pb ion irradiations could produce larger size inclusions than Xe ions and the inclusion size decreased with increasing the irradiation fluence. The possible modification process of C-doped a-SiO_2 under swift heavy ion irradiations was briefly discussed.

Key words: swift heavy ion irradiation, C-doped SiO_2, Raman spectroscopy

PACS: 61.72.Ww, 61.80.Jh, 78.30.-j **DOI:** 10.1088/1674-1137/35/9/019

1 Introduction

Silicon or silicon dioxide based light-emitting material is compatible with modern silicon planar techniques and can be applied for highly luminescent solid electro-optical displays and light-emitting diodes. As a processing technique to significantly modify the surfaces and near-surface properties of materials, ion implantation had been widely used to modify the properties of silicon-based materials. For instance, Ge, C, or Si ions implanted into amorphous SiO_2 (a-SiO_2) could be used in the synthesis of ultra fine clusters that can show unique electrical and optical properties [1–6]. In recent years, swift heavy ion irradiations have also been used to investigate the modification of silicon-based materials and various phenomena such as swift heavy ion irradiations induced blue-violet photoluminescence [7] and new chemical bonds formation [8] in C-doped a-SiO_2 were reported.

In the present work, we aim to experimentally study the structural transformation in C-doped a-SiO_2 films after swift heavy ion irradiations. For this purpose, high energy Pb and Xe ion irradiations were performed and Raman spectroscopy was mainly used in the sample analysis. Combined with other analyse, the structural modifications in C-doped a-SiO_2 films induced by swift heavy ion irradiations were investigated, and then possible mechanism was briefly discussed.

2 Experiment

Amorphous SiO_2 (a-SiO_2) films with about 500 nm in thickness were thermally grown on silicon (111) wafers by wet oxidation at 1050 ℃. These samples were first implanted at room temperature (RT) with 100 keV C-ions from LC-4 High Energy Ion Implanter (Institute of Semiconductors, CAS), then irradiated at RT by Pb- (CIRIL-GANIL, Caen) or Xe- (HIRFL, Lanzhou) ions. The detailed parameters of ion implantation and irradiations were listed in Table 1, in which E, S_e, S_n, R_p and Φ are respectively the ion

Received 12 February 2011

* Supported by NSFC (10475102), Scientific Research Foundation of Heze University, China (XY09WL02) and Heze University Doctoral Foundation (XY10BS02)

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energy, the electronic energy loss, the nuclear energy loss, the projected range and the implantation/irradiation fluence and S_e, S_n and R_p were estimated by SRIM 2003. From Table 1 we know that the implanted carbon atoms stopped into the a-SiO_2 films. Because of that R_p (Pb or Xe) >> 500 nm > R_p (C-ion) and S_e (Pb or Xe) >> S_n (Pb or Xe), all the incident Pb or Xe ions could penetrate and stop far from the C-doped region and the a-SiO_2 film and thus the S_e plays an important role in the irradiation effects. In other words, the observed modification of the C-doped a-SiO_2 films after Pb or Xe ion irradiations should be mainly due to the electronic energy loss effects.

Table 1. Parameters of C-ion implantation and heavy ion irradiations.

ion	E/MeV	S_e/(keV/nm)	S_n/(keV/nm)	R_p/nm	Φ/(ions/cm^2)
C	0.1	0.28	0.05	286	(5.0, 12) × 10^{17}
Pb	853	26.1	0.05	44.0 × 10^3	(5.0, 10, 50) × 10^{11}
Xe	308	17.8	0.04	25.4 × 10^3	(0.10, 1.0, 10) × 10^{13}

After C-ion implantation and swift heavy ion irradiation, the samples were investigated at RT using a JOBIN YVON HR-800 micro-Raman spectrometry. The excitation light was 532 nm lasers with 0.3 mW and the beam spot size was less than ϕ2 mm. Some of the samples were also analyzed using fluorescent spectroscopy for comparison.

3 Results and discussion

3.1 C-ion implantation effect

Figure 1 shows the typical micro-Raman spectra of C-ion implanted a-SiO_2 films. For the non-implanted a-SiO_2 films, three peaks located at 300, 520 and 960 cm^{-1} originate respectively from Si–O bonds of SiO_2, the first and second Raman shift peaks of crystal silicon. With increasing the C-ion implantation fluence, three contributions can be seen: (1) A broad band centered at about 1520 cm^{-1} relates to the implanted carbon. (2) A peak is located at 708 cm^{-1} which roots of Si–C bonds. (3) The peaks at 300, 520 and 960 cm^{-1} disappear while a new peak at 404 cm^{-1} appears.

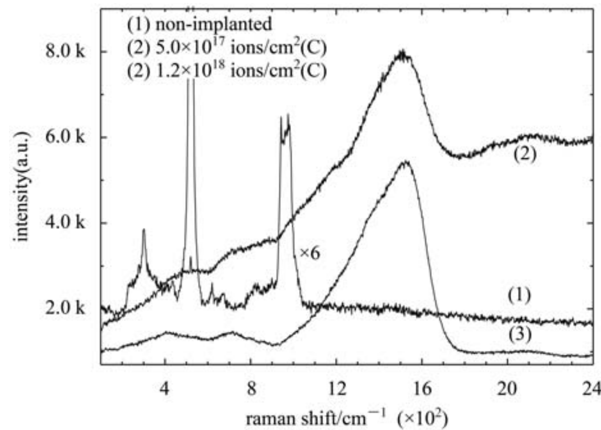

Fig. 1. The micro-Raman spectra of 100 keV C-implanted a-SiO_2 samples.

The appearance of a band at about 905–1735 cm^{-1} shows that large amounts of carbon related bonds are formed. The disappearance of the peaks at about 300, 520 and 960 cm^{-1} for the sample implanted with C ions revealed that the SiO_2 structure becomes distorted greatly. And the more the C-ion implantation doses the more the SiO_2 structures are modified.

Another characteristic is the base line height varying with C-ion implantation fluence. This may be from some light emission centers such as the point defects produced by C ion implantations. With increasing the C-implantation fluence, the doped carbon atoms could combine with the previously produced light emission centers, thus leading to the decrease of the background luminescent intensity.

3.2 Swift heavy ion irradiation effect

Figure 2 shows the typical micro-Raman spectra of Xe- and Pb-ion irradiated C-ion implanted a-SiO_2 films in which four light emission bands centered at about 410–450 (Ⅰ), 700–750 (Ⅱ), 1360–1580 (Ⅲ) and 2100–2130 (Ⅳ) cm^{-1} are observed. With increasing the Xe- or Pb-ion irradiation fluence, the positions of Band-Ⅲ and Band-Ⅳ nearly have no change, whereas a low frequency shoulder appears in Band-Ⅲ and the intensity of Band-Ⅳ is reduced until it can be neglected. For the given C-doped samples, the positions of Band Ⅰ and Ⅱ are shifted slightly toward larger wave numbers.

In the 600–1000 cm^{-1} region, Si–C stretching modes of amorphous and crystalline silicon carbides are reported [9–11] and the band located at 750 cm^{-1} is attributed to the optical-like modes of hetero-polar Si–C bonds [10] or can be partially assigned to Si–C

vibration and the second order Si–Si LO mode [12]. It can also be deduced that the Pb-ion irradiations produced much more Si–C bonds than the Xe-ion irradiations. In addition, Band-Ⅰ may originate from amorphous silicon and Band-Ⅳ could be assigned to –SiH_2 units [13].

There is only one characteristic peak at 1332 cm^{-1} in Raman spectra of diamond built completely with sp^3 atoms and there is a sharp peak at about 1580 cm^{-1} named G (Graphic) line in Raman spectra of large crystal graphite built completely with sp^2 atoms. When the crystal graphite is destroyed, a peak located at 1350 cm^{-1} named D (Disorder) line would appear. Compared with diamond, graphite, carbon black and glass carbon, the characteristic of Raman spectra of amorphous carbon films is the broad band from 1100 cm^{-1} to 1700 cm^{-1}. According to Reference [14], the G line would shift to low frequency if the sp^3 atoms in the film are increased. So the shifting to the high frequency of G line is likely to indicate

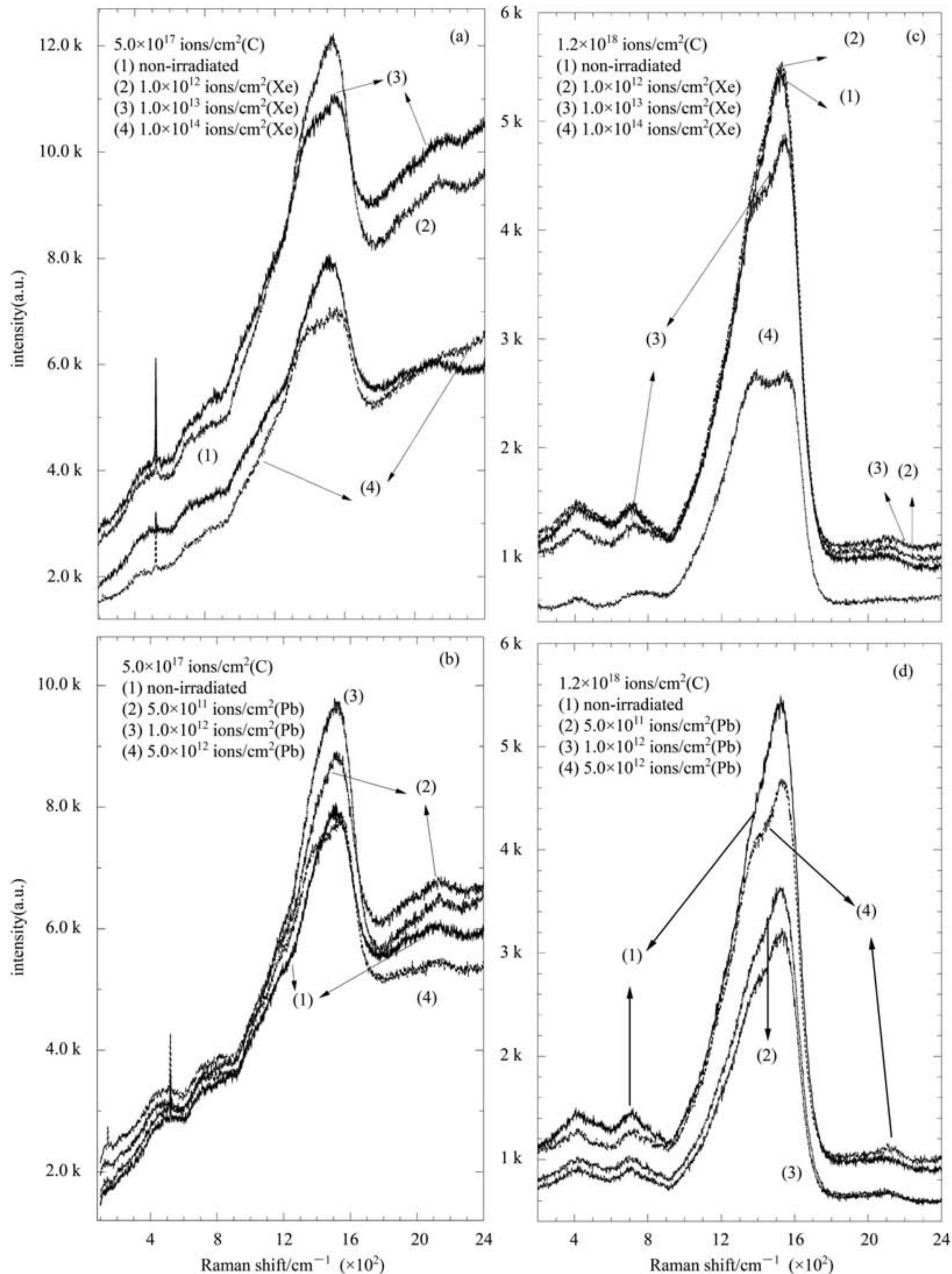

Fig. 2. The micro-Raman spectra of Xe- and Pb-ion irradiated C-doped a-SiO_2 films.

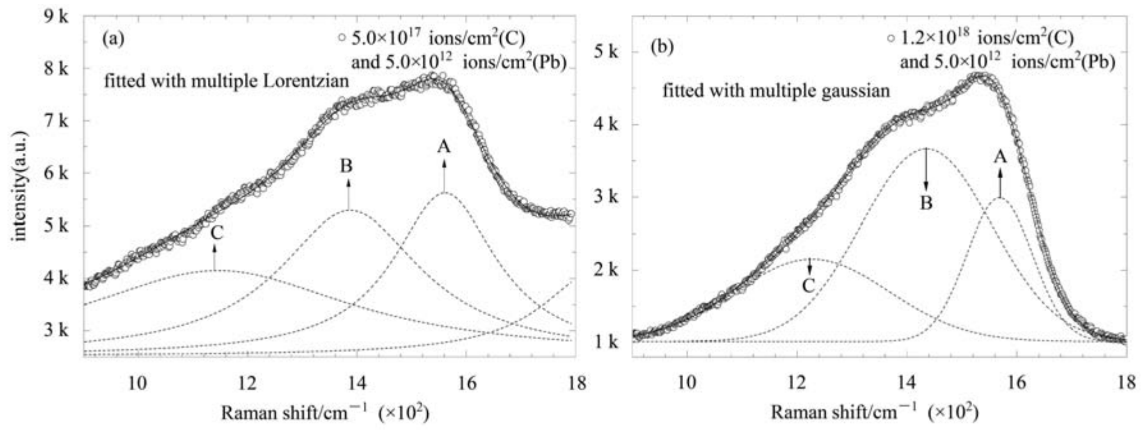

Fig. 3. The examples of Lorentzian and Gaussian multi-peaks fitting.

Fig. 4. The fitting parameters versus the energy deposition density, the (a), (b) and (c) are the 1.2×10^{18} ions/cm^2 and the (d), (e) and (f) are the 5.0×10^{17} ions/cm^2 implantation film.

that there is some change of the proportion between the sp^3 atoms and the sp^2 atoms.

In order to investigate clearly the modification of C-doped a-SiO_2 after swift heavy ion irradiations, the spectra within 900–1800 cm^{-1} were fitted with multi-peaks (Lorentzian or Gaussian) and, as examples, two pictures are showed in Fig. 3. Suitable fitting can be seen with four Lorentzian functions for spectra of 5.0×10^{17} ions/cm^2 C-ion implanted a-SiO_2 samples and three Gaussian functions for spectra of 1.2×10^{18} ions/cm^2 C-ion implanted a-SiO_2 samples. We define the bands at 1550 (G peak), 1380 (D peak) and 1175 cm^{-1} as A, B and C bands in Fig. 3(a) and the bands at 1570 (G peak), 1430 (D peak) and 1220 cm^{-1} as A, B and C bands in Fig. 3(b) respectively.

Figure 4 shows the I_D/I_G (I_D/I_G is the radio of integral area between D peak and G peak), the G peak position and the G peak width versus the energy deposition density (ΦS_e) of high energy Pb and Xe ion irradiations. For the spectra of 5.0×10^{17}ions/cm^2 C-ion implantation, with the increase of the ΦS_e, the increase of the I_D/I_G is nonlinear (rough exponential) and the position of G peak is closed to 1580 cm^{-1} and G peak width is reduced. It should be noted that Pb-ion irradiation has a larger change rate than that of Xe ions.

According to Ref. [15], the value of I_D/I_G is associated with the increase of the number or/and the size of graphite particle. So these experiment results imply that the carbon related domains may form in the samples [16, 17] and the new inclusions created by Pb-ions are more than those by Xe-ions. With increasing ΦS_e, the sizes of inclusions are decreased and the structures may be transferred to sp^2C sites or clusters. This is also evidenced by PL measurements [18].

4 Concluding remarks

Modification of the C-doped a-SiO_2 after high energy heavy ion irradiations has been studied using micro-Raman spectroscopy. It is evidenced from the obtained experimental results that Si–C bonds and carbon sites are created in heavy ion irradiated C-doped a-SiO_2. Pb and Xe ion irradiations could produce inclusions in C-doped a-SiO_2 and the size of the inclusions is augmented with the increase of irradiation fluence. Furthermore, Pb-ions irradiations could produce larger size and more stable inclusions than Xe-ions. All of these phenomena may be strongly linked to the intense electronic excitations induced by high energy Pb and Xe ions. The intense electronic excitations lead to a transient thermal spike process that drives the reactions of the implanted carbon atoms with a-SiO_2, as well as the diffusion and aggregation of the doped carbon atoms. As S_e(Pb)> S_e(Xe), Pb ion irradiation is more efficient in the modification of the C-doped a-SiO_2 films.

We are very grateful to all staff of CIRL-GANIL (Caen, France) and HIRFL-SFC (IMP, Lanzhou) for their help during the Pb- and Xe-ion irradiation experiments.

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