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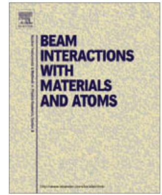

Radiation effect on the photoluminescence properties of Si/SiO_2 thin films

Kun Zhong [a], Zhisong Xiao [b,*], Xiangqian Cheng [a], Fang Zhu [b], Lu Yan [b], Feng Zhang [b], Guoan Cheng [a]

[a] Department of Materials Science and Engineering, Beijing Normal University, Beijing 100875, China
[b] Department of Physics, School of Science, Beihang University, Beijing 100191, China

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ABSTRACT

Silicon ions were implanted into SiO_2 thin films with various doses and energies. For the films implanted with various ion doses the photoluminescence (PL) intensity of 470 nm firstly increased with the increase of Si ion dose, which is similar to the variation trend of displacement per atom (DPA) number during ion radiation. Further increasing Si ion dose the PL intensity of 470 nm decreased gradually since the neutral oxygen vacancy centers were destroyed. For the samples implanted with different energy the variation trend of PL intensity for 470 nm peak is similar to the result of DPA under different radiation energy according to SRIM2006 simulation. With the increase of radiation energy a new PL peak at 550 nm appeared because of the variation of defect type. Combining with the simulation results and PL spectra the radiation effect on Si/SiO_2 thin films were proposed.

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1. Introduction

Strong visible photoluminescence (PL) was observed from Si-riched SiO_2 at room temperature [1]. As a consequence, this material system is of considerable technological interest for opto-electronic device applications [2]. Such PL was associated with the effect of quantum confinement in the quantum dots surrounded by the high potential barriers of SiO_2 or with radiative recombination between electron energy levers localized in the structural defects in the SiO_2 [3]. It is well-known that defects can be created by ion bombardment and high energy ray irradiation [4].

The generation of point defects in SiO_2 under irradiation has been the subject of intensive study, but the formation mechanisms of these point defects under irradiation need to be clarified. In fact, it is still not clear if they originated from precursors or from regular structure. Tanabe et al. performed in situ analyses of ion-induced luminescence of silica glasses under D and He ion irradiation to investigate the mechanism of the luminescence and the influence of the implanted hydrogen and helium [5]. Nuccio et al. reported an experimental study of the effects of γ and β irradiation on the generation of a point defect known as ODC (II) in various types of commercial silica (a-SiO_2) [6]. Silicon implantation introduces several types of point defects in SiO_2, such as the E′ center ($O_3\equiv Si\cdot$, E′), the neutral oxygen vacancy ($O_3\equiv Si–Si\equiv O_3$, NOV), the nonbridging oxygen hole center ($O_3\equiv Si–O\cdot$, NBOHC), the small peroxy radical ($O_3\equiv Si-\overset{O}{\overset{|}{O}}-Si\equiv O_3$, SPR), and other interstitial defects [7–9]. Some Si–O related species in SiO_2 can induce optical absorption in the UV range and give rise to a visible PL emission [7].

In the present work, we observed PL from Si implanted SiO_2 layers and studied the ion irradiation effect on PL response in terms of incident ion energy and dose. Since the lattice damage is generally related with DPA, the DPA of various ion irradiation energy and dose has been calculated by means of SRIM2006 code. By comparing the observed spectra and calculation results the detailed mechanisms of the luminescence are discussed.

2. Experiment

300-nm-thick SiO_2 lays were thermally grown at 1100 °C by dry oxidation of (100) n-type Si substrates (2–5 Ω cm). Silicon were implanted with ion dose of 1×10^{15}–1×10^{17} cm^{-2} at the energy of 30 keV. In another sample series Si ions were implanted into SiO_2 films at room temperature at energy of 20–70 keV with the constant ion dose of 5×10^{16} cm^{-2}. PL spectra were measured using Fluorolog-Tau-3 photo-spectrometer with R928P photomultiplier at room temperature. The excitation wavelength was 250 nm. X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM) was performed to determine the chemical state of elements in film. Before XPS measurement the sample surface was cleaned by Ar^+ sputtering.

3. Result and discussion

Fig. 1 shows observed luminescence spectra of the Si ion irradiation silica with doses ranging from 1×10^{15} to 1×10^{17} cm^{-2} with the same energy of 30 keV. All spectra exhibited a PL band centered at 470 nm, which is very similar with the emission reported by Prucnal et al. [1]. When the samples were pumped with varying

* Corresponding author.
E-mail address: zsxiao@buaa.edu.cn (Z. Xiao).

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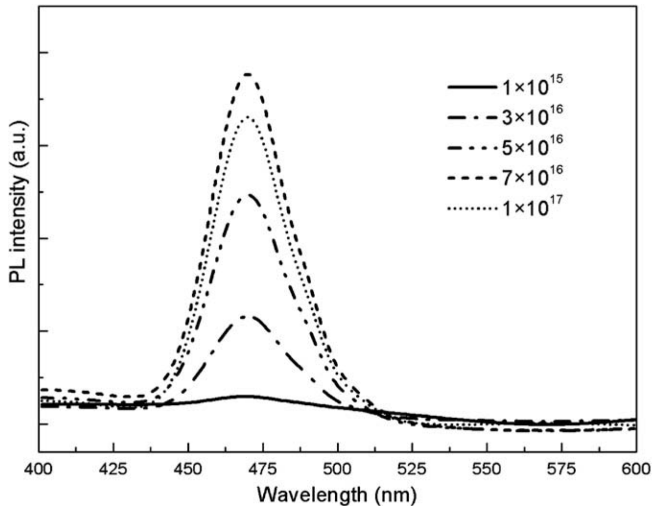

Fig. 1. PL spectra of the Si ion implanted silica films with doses ranging from 1×10^{15} to 1×10^{17} cm^{-2}.

wavelength, the shape of PL is stable except the intensity (was shown in other paper), which indicates that the 470 nm PL is a single PL peak. The PL band was attributed to oxygen deficiency center, referred as NOV centers [1,7]. The intensity of 470 nm band increases gradually with the ion dose increasing and is saturated at the ion dose of 7×10^{16} cm^{-2} as shown in Fig. 2(a). It was suggested that the dynamical change of the luminescence intensity is attributed to the point defects and the oxygen deficiency related with atomic displacement [5]. Thus DPA number dependence on irradiation dose can be obtained by the SRIM2006 code assuming the Kinchin–Pease model [5], which is linearly increase with the increase of ion dose as shown in Fig. 2(a). It also shows in low ion dose range the slope of PL intensity curve is consistent with the slope of DPA curve. This initial linear increase of the 470 nm PL intensity is attributed to the increase in number of point defects associated with oxygen deficiency resulted from the displacement effect. With irradiation dose increasing above 3×10^{16} cm^{-2} the slope of PL intensity curve is less than that of DPA curve, which indicates that the initial increase of PL intensity is attributed to the increase of newly produced defect centers by atomic displacements. But further increase of ion dose induced clustering of the point defects like Si precipitation and forming of oxygen bubbles, which deteriorates the luminescence performance.

Fig. 3 shows PL spectra of Si implanted silica films with the energy varied from 20 to 70 keV. As the ion-irradiated energy increases the 470 nm PL intensity increases continuously. When the irradiated energy is 40 keV, a new 550 nm PL band appears. Mutti and Ghislotti observed stable PL band at 540 nm for this material after 1000 °C annealing, and they think it resulted from PL quantum confinement effect [10]. Nevertheless, this PL band is observed in this case without thermal treatment at high temperature, the origin from nano-particles can be eliminated. The 550 nm PL band is due to some defects in SiO_2. Under 30–70 keV irradiation energies, a surplus of oxygen defects formed by the small "peroxy radical" (SPR) is found in our samples by ESR spectrum (reported in other paper), which is though to be responsible for the 550 nm PL [9,11].

The 470 nm PL intensity reaches its maximum value at the irradiated energy of 50 keV. The dependence of PL intensity on ion energy was also showed in Fig. 2(b). As mentioned above the 470 nm PL band is ascribed to NOV center and is related with atomic displacements. The energy is converted to DPA by the SRIM code assuming the Kinchin–Pease model. In Fig. 2(b), At the energy range of 20–30 keV the slope of PL intensity curve is consistent with the slope of DPA curve. When the energy is above 30 keV, the slope of DPA curve is larger than that of the PL intensity curve. At the same time, the discrepancy between those two curves increases gradually with the irradiative energies increasing. At the energy of 50 and 60 keV the PL intensity and DPA number reach theirs maximum value, respectively.

For silica the fundamental defect centers are considered to be related with the micro-structure of matrix. XPS were used to investigate the surface chemical state as a function of irradiation energy. Fig. 4 shows the analytical result of XPS of sample with 50 keV irradiated energy at a dose of 5×10^{16} cm^{-2}. Five oxidation states Si^{n+} ($n = 0–4$) could exist in the Si implanted SiO_2 films. Si_{2p} spectrum can be fitted with five Gaussian functions centered at 99.00,

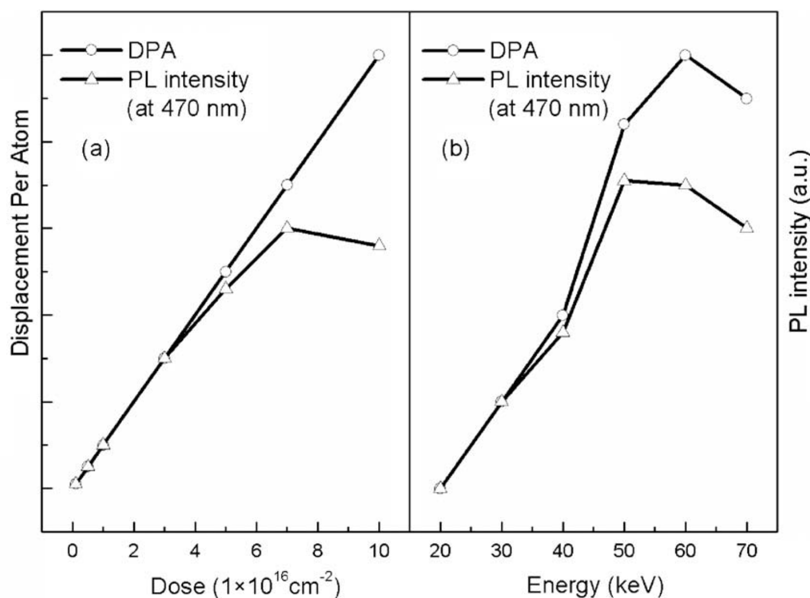

Fig. 2. The dependence of DPA and PL intensity on (a) ion dose and (b) energy.

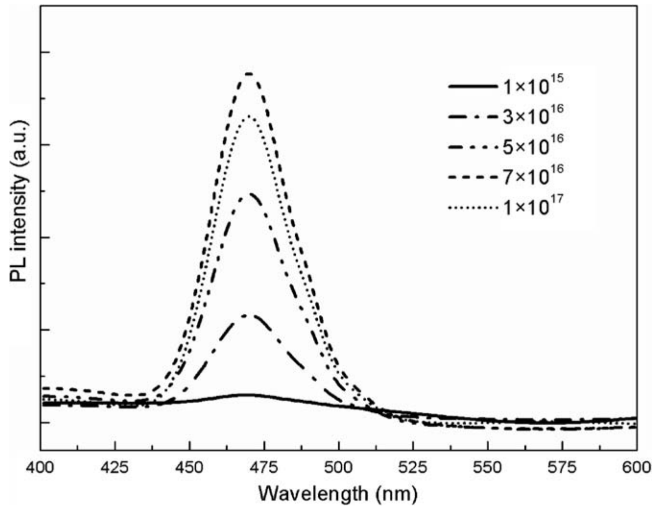

Fig. 3. PL spectra of Si implanted silica films with the energy varied from 20 to 70 keV with ion dose fixed at $5 \times 10^{16}\,cm^{-2}$.

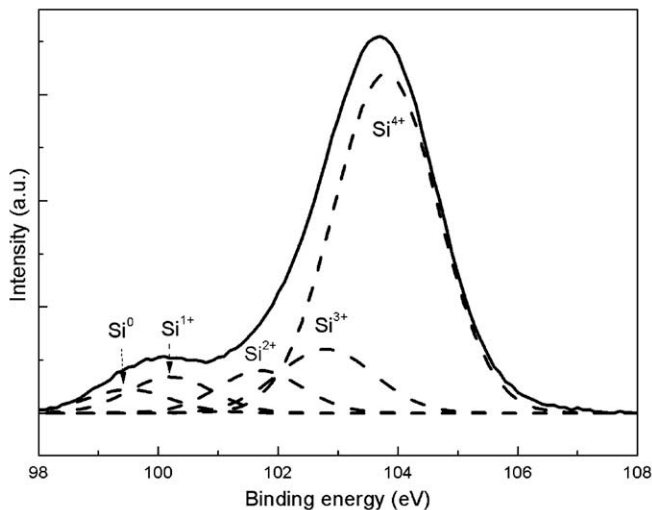

Fig. 4. The XPS spectra of sample with an energy of 50 keV at ion dose of $5 \times 10^{16}\,cm^{-2}$.

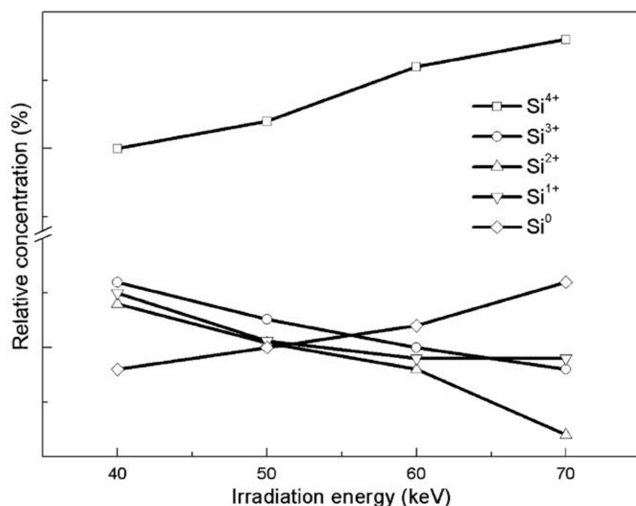

Fig. 5. The variation trend of five states Si^{n+} (n = 0–4) with the irradiation energy.

100.19, 101.61, 102.87 and 103.73 eV which correspond to Si^0, Si^{1+}, Si^{2+}, Si^{3+} and Si^{4+}, respectively [4]. The peak areas of the five oxidation states change with irradiation energy are shown in Fig. 5. When irradiation energy is above 40 keV the SiO_2 (Si^{4+}) concentration increases, while the concentrations of the Si suboxides (Si^{1+}, Si^{2+} and Si^{3+}) decrease. The reduction is due to the decomposition of the suboxides. This is a multi-steps process where the number of Si^{2+} and Si^{1+} states decreases by processes as

$$Si^{2+} + Si^{2+} = Si^{1+} + Si^{3+}, \quad (1)$$

and

$$Si^{1+} + Si^{3+} = Si^{0} + Si^{4+}, \quad (2)$$

respectively. The process is activated by the ion irradiation and the XPS measurement has proved the increasing of the Si^0 and Si^{4+} contribution to the material composition. Similar chemical state separations of SiO_x material have been induced by UV photon irradiation [4]. It should be noted that the decomposition of SiO_x occurred during the deposition process after energetic particle (ions, electrons and photons) bombarding.

NOV center [12] is formed by the jointing of two Si^{3+} and SPR structure composed by two Si^{4+} [11]. PL intensity from NOV centers should be in proportional to the amount of Si^{3+}, and PL intensity from SPR centers should be in proportional to the amount of Si^{4+}. When irradiation energy is less than 40 keV, reaction (1) dominates, resulting in more Si^{3+}, that is, more oxygen vacancies are formed. These oxygen vacancies enhance the PL intensity of 470 nm. When irradiation energy is above 40 keV, reaction (2) start to occur, more Si^{3+} will turn into Si^{4+} and SPR centers are formed, which is verified also by ESR spectra. At the energy of 50 keV the 470 nm PL intensity decreased and the 550 nm PL band appeared upon the change of defects. Although the variation of NBOH centers is similar to that of Si^{4+}, the NBOH center emits light with the wavelength at around 630 nm [7,12]. The origin of the 550 nm is thought to be due to the SPR rather than the NBOH centers.

4. Conclusions

Si/SiO_2 thin films were prepared by ion implantation of silicon ions into silica films with various doses and energies. Both series of samples exhibited PL peak at 470 nm originated from neutral oxygen vacancy centers. The variation trend of PL intensity is similar to that of DPA number during ion radiation. With further increasing Si ion dose, the PL intensity of 470 nm peak decreases since the neutral oxygen vacancy centers are destroyed. For the samples implanted with different energy, when irradiation energy is above 40 keV, more Si^{3+} will turn into Si^{4+} and SPR centers are formed by the ion irradiation. A new PL peak at 550 nm appeared upon the change of defects. Combining with the XPS spectra 550 nm PL is assigned to the SPR centers.

Acknowledgements

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