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Controlling surface states and photoluminescence of porous silicon by low-energy-ion irradiation

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Abstract

Porous silicon (PS) was irradiated by three kinds of low-energy ions with different chemical activity, namely argon ions, nitrogen ions and oxygen ions. The chemical activity of ions has significant effect on the surface states and photoluminescence (PL) properties of PS, The photoluminescence quenching after argon ions and nitrogen ions irradiation is ascribed to the broken Si–Si bonds, while the PL recovery is attributed to the oxidation of Si–H back bonds. Oxygen ions irradiation leads to the formation of a SiO_x layer with oxygen defects and PS shows different PL evolution than PS irradiated by argon ions and nitrogen ions.
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1. Introduction

Porous silicon (PS) shows strong visible luminescence and is regarded as a potential material for illumination and optic-electrical integration [1]; however, the instability of luminescence intensity must be solved before PS could be employed for the practical application [2,3]. As an effective technique to improve photoluminescence (PL) stability and intensity [4,5], ion irradiation has been investigated intensively. For example, in the case of active-ions irradiation, Si ions with the energy of 10 MeV caused maximum increase in the PL intensity of PS by 20 times, whereas O ions of 14 MeV resulted in a PL improvement by 6 times [4]. However, in the case of inert-ions irradiation, the PL intensity of PS was reduced controllably after 250 keV Ne ion irradiation, which was attributed to the creation of defects that act as nonradiative recombination centers [5]. The energy of ions used for irradiation is usually higher than 5 keV [6], few works were performed on the ultra-low-energy (less than 5 keV) ions modifying the PL properties of PS [7].

As compared with high-energy-ions irradiation, low-energy-ions irradiation does not change the crystal structure of PS, however, low-energy ions may react with the surface bonds and modify the surface states of PS. In previous work, we presented low-energy-nitrogen-ions (800 eV) irradiation on PS [7], herein, we compare three kind of low-energy ions with different activity (argon ions, nitrogen ions and oxygen ions) to investigate the effect of chemical activity on the PL properties of PS, the results show surface states and PL properties of PS could be modified significantly by low-energy-ions irradiation.

2. Experiment

PS samples were prepared by electrochemically etching p-type (B-doped), (1 0 0)-oriented Si wafers ($\rho = 3 \, \Omega \, cm$) in a 1:1.5:2 ($HF:H_2O$:ethanol) solution at current density of 40 mA/cm^2 for 5 min. Ions irradiation experiments were performed in vacuum chamber of magnetron sputter equipment, the chamber was evacuated to 7.0×10^{-5} Pa before ion irradiation, and the gas pressure in the chamber was kept 2.5 Pa during ion irradiation. The PS samples were irradiated by 800 eV argon ions or nitrogen ions or oxygen ions with a dose of $3 \times 10^{16} \, cm^{-2}$. The penetration depth of 800 eV ions into bulk silicon was estimated by using the software SRIM2003 [8]; the results are 3 ± 2 nm for argon ions and 3.9 ± 3 nm for

nitrogen ions and 3.7 ± 2 nm for oxygen ions. PL spectra were collected by using a Hitachi F-4500 fluorescence spectroscope at excitation wavelength of 365 nm. The FTIR spectra were measured by using a Nicolet 560 FTIR spectrometer.

3. Results and discussion

PL spectra before and after irradiation are shown in Fig. 1. The as-etched PS exhibits a broad PL band with the main peak at 570 nm and a shoulder at 610 nm. After argon-ion irradiation, PL is completely quenched. The recovery of PL is observed after 2 days. The PL intensity increases gradually and reaches a maximum which is still lower than that of as-etched PS after 14 days. The PL quenching and recovery also occur after nitrogen ions irradiation. The maximum PL intensity of nitrogen ions irradiated PS is higher than that of as-etched PS after 14 days. After oxygen ion irradiation, the shoulder at 610 nm disappears immediately, while the PL peak at 570 nm decreases gradually as stored in air.

Raman spectra were taken both on as-etched PS and argon-ion-irradiated PS, as shown in Fig. 2. Both spectra exhibit a sharp TO phonon peak centered at about 520 cm^{-1} [9], and no obvious change was found after irradiation. Especially, the characteristic peak of amorphous silicon at 480 cm^{-1} did not appear after ion irradiation [10]. Same results were found for samples irradiated by nitrogen and oxygen ions. Above results indicate the amorphization did not occur during the irradiation of low-energy ions with energy of 800 eV and dose of 3×10^{16} cm^{-2}.

FTIR spectra at different stages after argon-ion irradiation are shown in Fig. 3a and b. The spectrum at 2 days after argon-ion irradiation shows Si–H peaks at 2100 and 890 cm^{-1}, Si–O–Si peaks at 1080–1010 and 820–800 cm^{-1} [11,12]. 7 days after irradiation, the peak of Si–H stretching vibration mode shifts to higher wavenumber and Si–H deformation mode disappeared, meanwhile, some new absorption peaks are observed, the peaks are assigned to HSi–O_3 (2265–2240, 927–881 cm^{-1}), H_2Si–O_2 (2196–2180, 973 cm^{-1}), HSi–Si_2O (2145–2110 cm^{-1}) [12–14]. These results suggest the oxidation of the Si–H back-bond occurs at the PS surface. 14 days after irradiation, the peak of HSi–O_3 bond increases and the peak of HSi–Si_2O bond decreases, which suggests the oxidation degree of the Si–H back-bond increases.

Fig. 3c and d shows the FTIR spectra of PS irradiated by nitrogen ions. As compared with that irradiated by argon ions, the oxidation of the Si–H back-bond occurs at the PS surface, too. A new peak at 848 cm^{-1} can be attributed to Si–N bonds [15,16] which could be cross-checked by XPS result [7].

Fig. 3e and f shows the FTIR spectra of PS irradiated by oxygen ions. As compared with that irradiated by argon ions, the Si–H peaks are rather weak, a new peak appears at 1260–1020 cm^{-1}, which can be attributed to the stretching mode of Si–O bonds in oxygen-deficient silicon oxide, SiO_x ($1 < x < 2$) [17]. As stored in air, the Si–O peak heightens slightly, whereas the Si–H peak lowers significantly. On the other hand, the HSi–O_3 bond appears just after oxygen ions irradiation. This means the oxidation of Si–H back-bond occurs during oxygen ions irradiation.
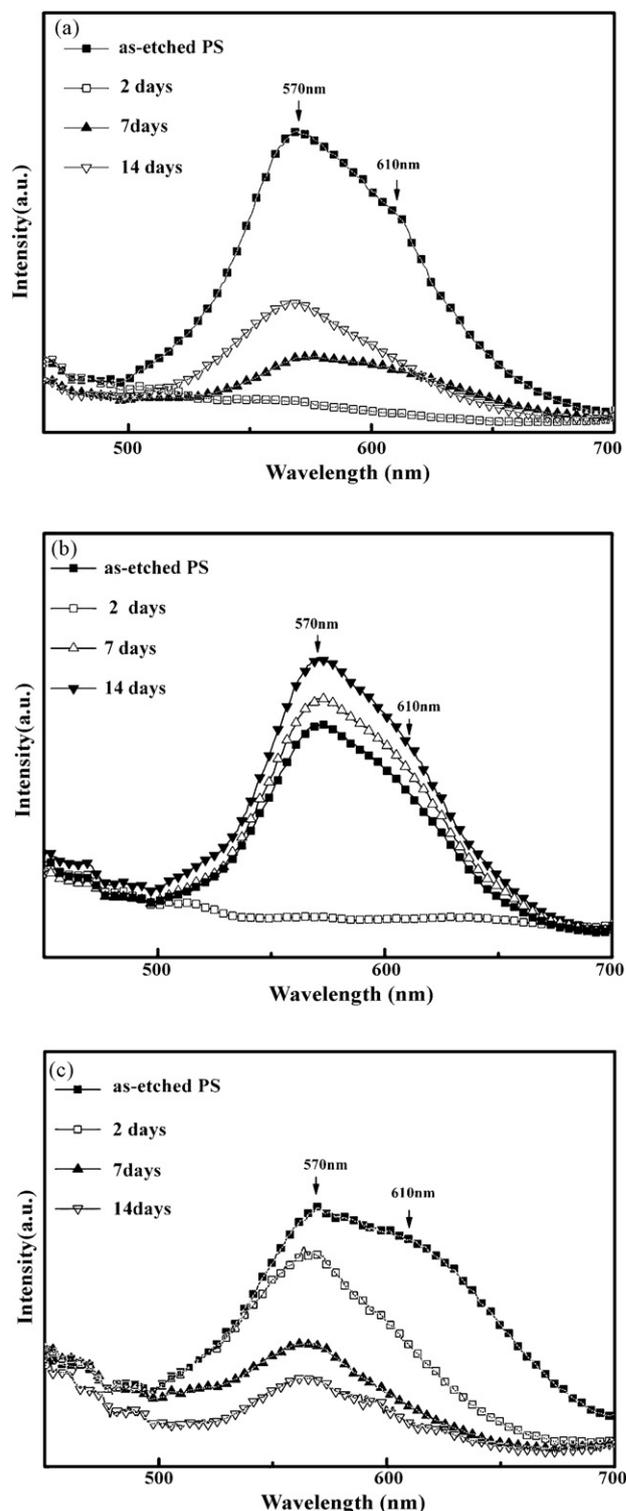

Fig. 1. The evolution of PL intensity of PS irradiated by (a) argon ions, (b) nitrogen ions and (c) oxygen ions.

The PL evolution after low-energy-ion irradiation can be understood based on the above results. It was reported that PL band at 500–700 nm is related to Si–H and Si–O bonds [13], the peaks of as-etched PS at 570 nm and that at 610 nm could be attributed to Si–O bonds and Si–H bonds at the surface of the silicon nanocrystals in PS, respectively [18].
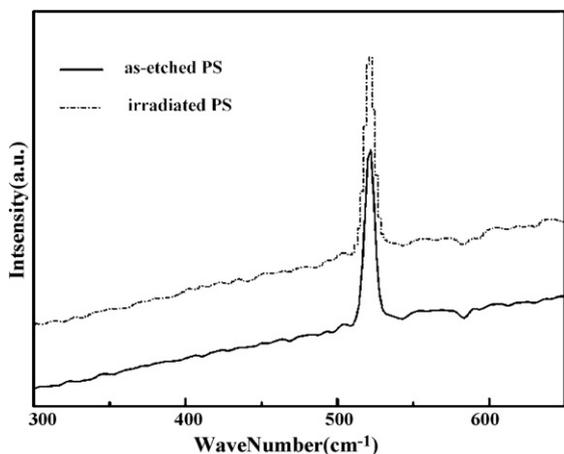
Fig. 2. Raman spectra of as-etched PS and PS irradiated by argon ions.

After argon ions and nitrogen-ions irradiation the PL is quenched. Raman results demonstrate the crystal structure did not change during the irradiation of argon ions and nitrogen. Therefore, the destruction due to ions irradiation should be limited in surface layer of the nanocrystals in PS, on the other hand, FTIR results indicate Si–H bonds still remain after ion irradiation, it is reported that the bonding energy of Si–H bonds (3.05 eV) is stronger than that of Si–Si bonds (1.83 eV) [19], hence, we propose the back bonds of Si–H bonds, Si–Si bonds, were broken during irradiation, which creates many nonirradiative recombination centers responsible for the PL quenching. As for the PL recovery after argon and nitrogen-ions irradiation, FTIR results indicate Si–O bonds related to the peak at 570 nm increase obviously, and PL intensity is consistent with the extent of the oxidation of Si–H back bonds. The result suggests the oxygen in air reacts easily with the broken Si–Si bonds, and the
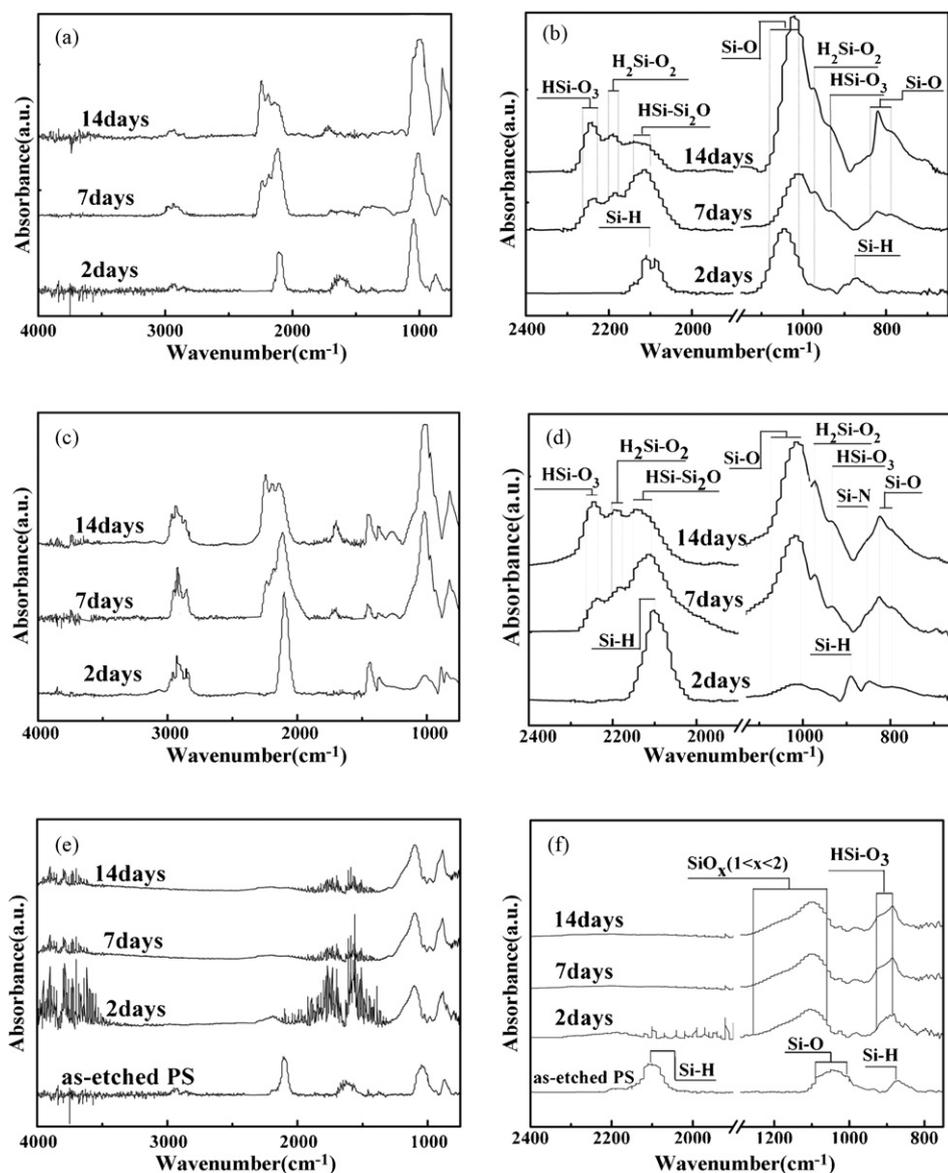

Fig. 3. FTIR spectra of the post-irradiated PS stored in air at different stages. the whole spectra in the wavenumber range of 750–4000 cm^{-1} of (a) argon-ions irradiation, (c) nitrogen-ions irradiation and (e) oxygen ions irradiation; the enlarged spectra in the wave number range of 1800–2400 and 750–1150 cm^{-1} of (b) argon-ions irradiation and (d) nitrogen-ions irradiation and (f) oxygen ions irradiation.

Si–O bonds are formed. The generated Si–O bonds could eliminate broken Si–Si bonds and act as irradiative recombination centers, which is responsible for the recovery of the PL peak at 570 nm related to Si–O bonds.

In the case of nitrogen-ions irradiation, the Si–N bond is formed during nitrogen-ions irradiation according to FTIR result, correspondingly, the sample irradiated by nitrogen ions realizes higher PL intensity than that irradiated by argon ions, which suggests that the formation of Si–N bonds contributes to the final PL intensity.

As for oxygen ions irradiation, a strong PL peak at 570 nm can be still detected just after the irradiation. Since the energy and dose of oxygen ions are same as those of argon ions and nitrogen ions, the Si–Si bonds should be broken too, however, the oxygen ions with energy reacted with broken Si–Si bonds effectively, and a large amount of Si–O bonds constitute a SiO_x layer, which gives a strong peak at 1260–1020 cm^{-1} in FTIR spectrum. Moreover, Si–H bonds may react with active oxygen ions, and lead to the reduction of Si–H peak in FTIR spectrum compared with as-prepared PS. Therefore, the Si–H bonds and Si–H back bonds were oxidized during the oxygen ions irradiation rather than after irradiation. It was reported a kind of oxygen defects (dangling nonbriging oxygen ions) in SiO_x can act as irradiative recombination center, which gives 564 nm (2.2 eV) light emission [20]. Therefore, we propose that the PL peak at 570 nm (2.18 eV) is related with oxygen defects. As stored in air, the SiO_x layer is oxidized continuatively by oxygen and the number of oxygen defects is decreased, which leads to the PL bleaching.

4. Conclusion

By adopting low-energy ions with different chemical activity, the surface state and photoluminescence of PS could be significantly modified. The low-energy-ions irradiation breaks Si–H back bonds on the surface of PS, the broken Si–Si bonds could react with oxygen either after ions irradiation or during irradiation depending on the ions type used for irradiation. The PL quenching is ascribed to the broken Si–Si bonds, while the PL recovery is attributed to the formation of new radiative recombination centers due to the oxidation of Si–H back bonds. Moreover, nitrogen ions can react to form Si–N bonds, which are responsible for the enhancement of PL intensity. Oxygen ions irradiation leads to the formation of a SiO_x layer with oxygen defects and PS shows different PL evolution with that irradiated by argon ions and nitrogen ions.

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