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Role of amorphous silicon domains on Er^{3+} emission in the Er-doped hydrogenated amorphous silicon suboxide film*

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An investigation on the correlation between amorphous Si (a-Si) domains and Er^{3+} emission in the Er-doped hydrogenated amorphous silicon suboxide (a-Si:O:H<Er>) film is presented. On one hand, a-Si domains provide sufficient carriers for Er^{3+} carrier-mediated excitation which has been proved to be the highest excitation path for Er^{3+} ion; on the other hand, hydrogen diffusion from a-Si domains to amorphous silicon oxide (a-SiO_x) matrix during annealing has been found and this possibly decreases the number of nonradiative centres around Er^{3+} ions. This study provides a better understanding of the role of a-Si domains on Er^{3+} emission in a-Si:O:H<Er> films.

Keywords: a-Si domain, erbium, photoluminescence
PACC: 7855, 6170A, 3520G

1. Introduction

The rare earth erbium in its trivalent state is well known to emit photons at λ=1.54μm after excitation. This wavelength coincides with the absorption minimum of silica-based fibres. Therefore, erbium-doped emitters or amplifiers are of considerable interest. The silicon-rich silicon dioxide (SRSO), which consists of nanocrystalline silicon (nc-Si) domains embedded in a SiO_2 matrix, is a desirable host in which the doped Er^{3+} ions can be excited efficiently by the transfer of energy from nc-Si domains.[1−5] Room-temperature Er^{3+} photoluminescence (PL) from Er-doped SRSO has been found to be two orders of magnitude higher than that of Er-doped SiO_2.[1] Another desirable host, the a-Si:O:H film, has also received much attention because a strong room-temperature Er^{3+} emission from the film doped with Er has been observed.[6−8] The a-Si:O:H film usually consists of two phases: amorphous silicon (a-Si) domains embedded in a-SiO_x matrix.[9] Therefore, a-Si:O:H is virtually a silicon-rich silicon suboxide film. This microstructure is very similar to that of SRSO. However, compared with the intensive research on the correlation between nc-Si and Er^{3+} emissions in Er-doped SRSO,[2−5] little investigation is related to the effect of a-Si domains on Er^{3+} emission in the a-Si:O:H <Er> film. In this paper, we present a study on the correlation between a-Si domains and Er^{3+} emission in the a-Si:O:H<Er> film. We find that the reconstruction of the microstructure of a-Si domains and hydrogen diffusion during annealing have significant effects on Er^{3+} emission. In addition to the improvement of Er^{3+} emission, a-Si domains in the a-Si:O:H<Er> film shows some different behaviours from the nc-Si domains in Er-doped SRSO.

2. Experiment

The a-Si:O:H films were deposited by plasma-enhanced chemical vapour deposition (PECVD) with a background pressure equal to 130Pa, onto c-Si(100) substrates maintained at 250°C. By varying the deposition rates of SiH_4 and N_2O, the samples were prepared with different stoichiometries. The film deposited at the N_2O/SiH_4 flow ratio (γ) of 5/5 was implanted with erbium ions at an energy of 500keV to

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a dose of $3\times10^{15}/cm^2$. After implantation, the film was divided into pieces which were then annealed under N_2 for 30s at T_a=308, 430, 535, 650, 727, 840, 935°C respectively.

The Er^{3+} PL spectra for the samples were measured using an Ar^+ laser(514.5nm), a grating monochromator, a liquid-nitrogen-cooled InGaAs detector, and a standard lock-in amplifier. The nominal laser power was 200mW. The visible PL (400–900nm) and Raman scattering measurements were conducted using a Dilor XY-800 triple grating spectrometer with a charge-coupled device (CCD) detector. The samples were excited by the 514.5nm line of Ar^+ laser. Infrared absorption spectra (400–4000cm^{-1}) were measured using a Perkin Elmer 2000 Fourier Transform IR (FTIR) system. The spectral response of the detection system was calibrated using a standard lamp. The evolution of bonded hydrogen with annealing temperature can be determined from the FTIR spectra. X-ray photoemission spectroscopy (XPS) was measured using the ESCALAB MK-II. The incident source was MgKα x-ray beam. The spectra were corrected for system response and sample charging by referencing to the adventitious carbon peak at 284.5eV. High resolution transmission–electron microscopy (HRTEM) analyses were carried out with a 200keV CM200/FEG microscope to determine the presence of nanocrystal silicon in our sample.

3. Results

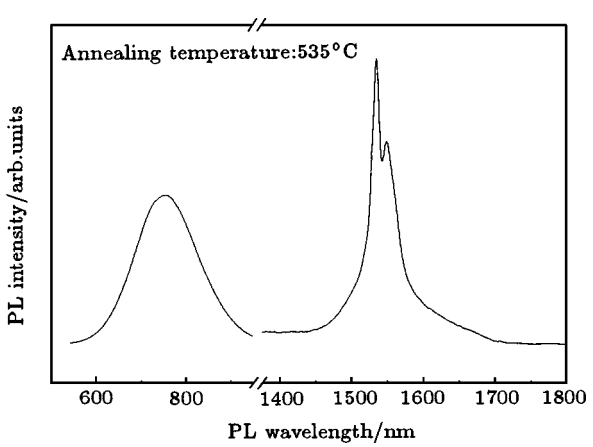


Fig.1. A typical PL spectrum from the a-Si:O:H<Er> film.

Figure 1 shows a typical PL spectrum of the a-Si:O:H<Er> film. Two PL signals at around 750nm and 1.54μm are observed. The 750nm band is correlated to a-Si domains in the film,[10] and the 1.54μm band is from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ intra-4f-shell Er^{3+} transition. Figure 2 indicates the variation of the intensity of the two luminescence bands as a function of annealing temperature in the range from 308 to 935°C. It is clearly seen that the 750nm PL and Er^{3+} PL follow the same trend with annealing temperature and the optimum temperature corresponding to the maximum PL for them is 535°C (Fig.2 only shows their main trend upon annealing temperature).

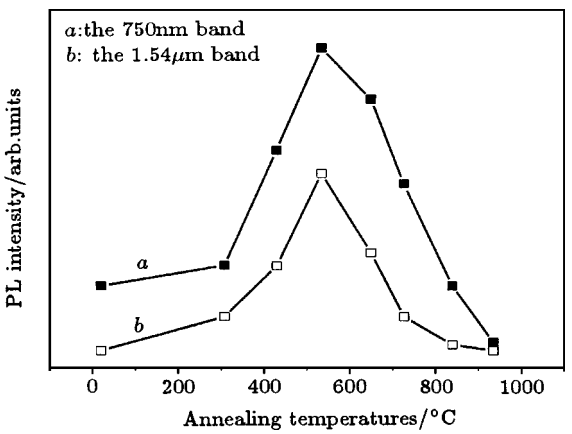


Fig.2. Dependence of visible and IR PL intensities on annealing temperature.

The XPS spectra of the unannealed and the annealed samples at 535°C in the energy range of the Si-2p core level are shown in Fig.3. The peaks at 101.16eV and 102.05eV for both of the samples can be ascribed to SiO_x; the shoulders at 98.85eV and 99.08eV correspond to Si-Si_4.[10] The shoulder at 98.85eV in Fig.3(a) indicates that the silicon domains are present even in the unannealed sample. Annealing at 535°C improves the S-O binding energy from 101.16eV to 102.05eV; while the shoulder, besides a slight shift from 98.85eV to 99.09eV, seems to be more intense than that for the unannealed sample. These results suggest that annealing induces a phase-separation process. Raman spectra for the unannealed sample and the annealed samples at 535° and 935° are presented in Fig.4. The two bands centred at 480cm^{-1} and 170cm^{-1} indicate that the silicon domains in our a-Si:O:H<Er> films are mainly amorphous. Raman spectrum of the unannealed sample indicates that amorphous silicon domains are present even in the unannealed sample; this coincides with the XPS result of the sample (see Fig.3(a)). It is worth mentioning that we do not succeed in resolving any response in the Raman spectra in the region of 510–520cm^{-1}, which signals the presence of silicon crystallites in the amorphous network. This has been further

confirmed by HRTEM observation for the sample annealed at 535°C that no crystalline phase has been found. Figure 5 presents a typical HRTEM photograph for the sample annealed at 535°C. It suggests that the sample be completely amorphous. It is not surprising because the crystallization is more difficult for small-dimension clusters embedded in a dielectric matrix.[11] Based on the XPS, TEM and Raman results, a two-phase structure model that the a-Si domains are embedded in a-SiO_x matrix can be confirmed.

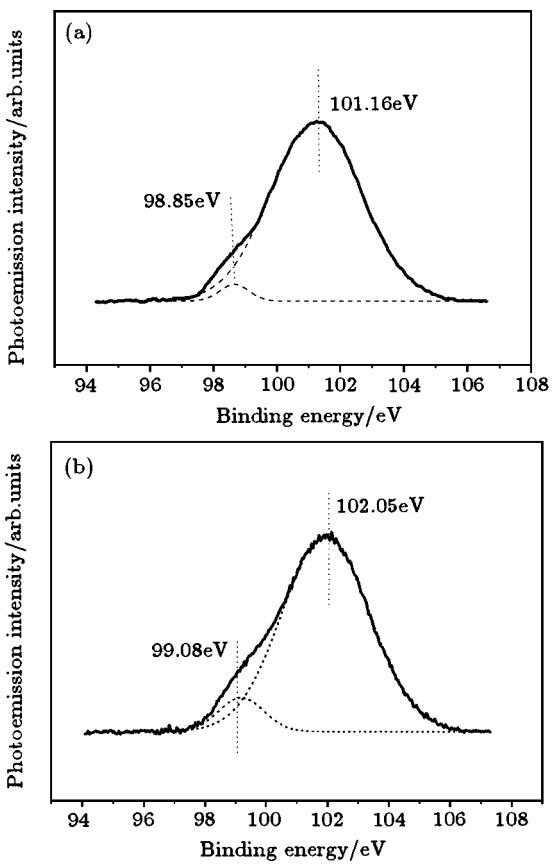


Fig.3. x-ray photoemission spectra of the unannealed sample(a) and the annealed sample at 535°C (b).

Infrared absorption spectra for the samples are displayed in Fig.6. The absorption band is attributed to the stretching mode of monohydride Si-H bonds with one, two and three oxygen atoms backbonded to the silicon atom.[12] Two pronounced features in Fig.6 should be noted. One is decreasing the absorption bands for the samples, which is evident at higher annealing temperature, suggesting the hydrogen release from the films. The other is decreasing the absorption intensity for each of the samples annealed above 308°C, which is much larger in low wavenumber than in high wavenumber. This is in agreement with the theoretical work of Jing *et al*[13] who demonstrate that the dissociation energy of the Si-H bond increases from 3.55eV for Si_3-Si-H groups to 4.11eV for O_3-Si-H groups. These results mean that the break of Si-H bond due to annealing mainly occurs in a-Si domains at relative low temperatures (<=535°C) and then in a-SiO_x matrix at higher temperature. Therefore, the free atomic hydrogen is more in a-Si domains than in a-SiO_x matrix at relative low annealing temperatures. This will lead to atomic hydrogen diffusion from a-Si domains into a-SiO_x matrix. We can clearly see such diffusion from the FTIR spectrum of the sample annealed at 535°C. The sharp increase of the absorption at around 2250cm^{-1}, attributed to the O_3-Si-H group, is the result of more atomic hydrogen diffusion into SiO_x matrix.

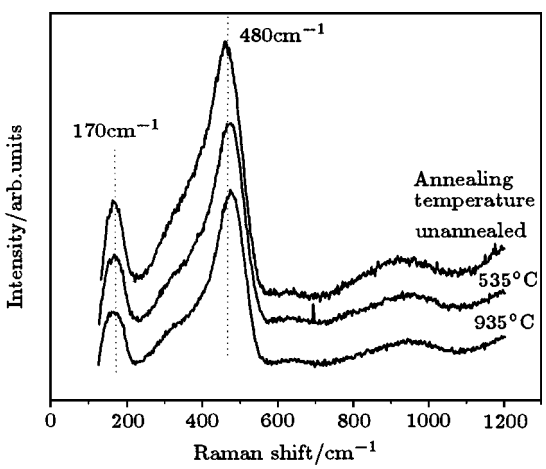


Fig.4. Raman spectra for the unannealed sample and the samples annealed at 535 and 935°C.

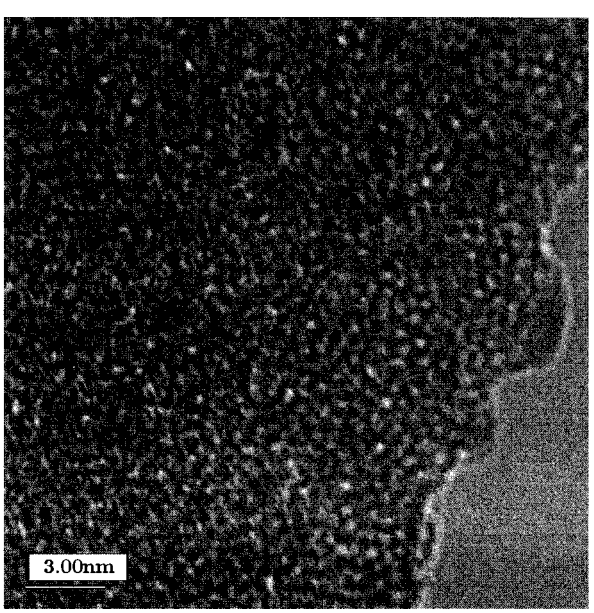


Fig.5. A typical HTEM photograph of the sample annealed 535°C.

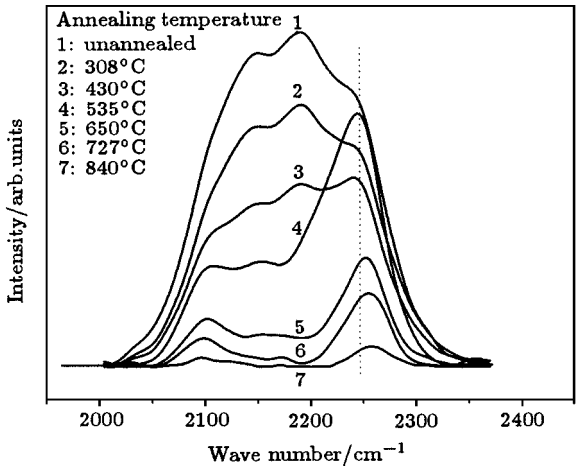


Fig.6. FTIR spectra for the samples annealed at various temperatures.

4. Discussion

According to the microstructure of the a-Si:O:H<Er> film, Er^{3+} ions may exist in three kinds of structural environments: within the a-Si domains, within the a-SiO_x matrix while far away from the a-Si/SiO_x interface, and within the a-SiO_x matrix while close to the a-Si/SiO_x interface. It is known that the pure a-Si film doped with Er shows a near complete suppression of Er^{3+} luminescence.[14] Therefore, the Er^{3+} ions within the a-Si domains are not efficient emitting centres. The Er^{3+} ions within the a-SiO_x matrix while far away from a-Si domains cannot contribute to strong Er^{3+} emission because of no sufficient photogenerated carriers necessary for Er^{3+} carrier-mediated excitation. Only the Er^{3+} ions within the a-SiO_x matrix while close to the a-Si/SiO_x interface (denoted as $Er^{3+}(i)$ below) are likely to contribute significantly to the strong Er^{3+} emission from the a-Si:O:H<Er> film. The $Er^{3+}(i)$ ions have two principal advantages for contributing to the intensive Er^{3+} emission: (1) a very weak thermal quenching due to the wide band gap of a-SiO_x matrix; (2) the formation of more optimal Er-O emitting centres due to sufficient oxygen atoms in the a-SiO_x matrix.

A-Si has a larger absorption coefficient than c-Si, as a result a great number of carriers are generated in a-Si under light incidence. However, these carriers are localized due to a great number of defects such as dangling bonds in a-Si.[15] Only those carriers generated near the Si/SiO_x interfaces are likely to contribute significantly to the Er^{3+} (i) carrier-mediated excitation. From the discussion on Fig.6, we have known that hydrogen evolution occurs mainly in a-Si domains at annealing temperatures up to 535°C, therefore the reconstruction of the microstructure of the a-Si:O:H<Er> film occurs in a-Si domains. The variation of 750nm PL intensity with annealing temperature is related to such a change in a-Si domains. The increase of the 750nm PL intensity at temperatures up to 535°C demonstrates decreasing the nonradiative defects in a-Si domains after annealing. However, with most hydrogen released from the film at higher temperatures, the number of nonradiative defects rises, leading to decreasing 750nm PL intensity. In fact, similar variation of nonradiative defects with annealing temperature has been observed in the a-Si:O:H film.[16] In addition, atomic hydrogen diffusion from a-Si domains into a-SiO_x matrix during annealing up to 535°C possibly saturates the nonradiative defects around $Er^{3+}(i)$ ions. The nonradiative centres existing around Er^{3+} ions have been proved to decrease the Er^{3+} emission in Er^{3+}-doped SRSO.[17,18] The nonradiative centres around $Er^{3+}(i)$ ions will increase with more atomic hydrogen release from the a-SiO_x matrix at higher temperatures. The same trend of the 750nm and 1.54μm PL intensities with annealing temperature originates from these changes associated with a-Si domains during annealing.

5. Conclusion

We have studied the role played by a-Si domains on the Er^{3+} emission in the a-Si:O:H<Er> film. Annealing up to 535°C lowers the number of defects in a-Si domains and causes hydrogen diffusion from a-Si domains into a-SiO_x matrix, thus increases the number of carriers tunnelling to $Er^{3+}(i)$ ions. On the other hand, nonradiative centres will rise with more hydrogen release from the a-Si:O:H<Er> film at higher annealing temperatures, leading to a decrease of $Er^{3+}(i)$ excitation possibility.

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