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Microstructure and photoluminescence of Er-doped SiO_x films synthesized by ion beam assisted deposition*

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Er-doped SiO_x films were synthesized at 500°C by ion beam assisted deposition technique and annealed at 800 and 1100°C for 2h in the air atmosphere. The analysis by using energy dispersive x-ray spectroscopy showed that the ratio of Si to O decreased from 3 in the as-deposited films to about 1 in the annealed films. The investigation by using transmission electron microscopy and x-ray diffraction indicated that annealing induces a microstructure change from amorphous to crystalline. The grain sizes in the films were about 10 and 40nm when annealed at 800 and 1100°C, respectively. The films annealed at temperatures of 800 and 1100°C exhibited a sharp photoluminescence (PL) at 1.533μm from the Er centres when pumped by 980nm laser. The influence of microstructure and grain size on the PL from Er-doped SiO_x films has been studied and discussed.

Keywords: ion beam assisted deposition, Er-doped SiO_x film, microstructure, photoluminescence
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1. Introduction

Due to the transition of Er^{3+} from $^4I_{13/2} \rightarrow ^4I_{15/2}$, corresponding to the wavelength of maximum transparency of standard silica-based optical fibres, Er-doped materials have played an important role in the development of optical communication technology in the past decade.[1−4] Because silicon is the dominant semiconductor material in the micro-electronic industry, Er-doped Si-based materials have attracted much attention since Ennen *et al* observed the light emission at 1.54μm and electro-luminescence (EL) in Er-doped silicon.[5,6]

Si-rich silica (SRSO) or SiO_x (x <2) is an attractive host material for Er^{3+} because the PL observed from Er-doped SRSO is two orders of magnitude higher than that from Er-doped SiO_2.[7] In 1998, Fuji *et al*[8] found that Si nanocrystals (nc-Si) strongly enhanced PL of Er^{3+} at 1.54μm and the PL intensity at 1.54μm increases about two orders of magnitude with the decrease of grain size from 3.8 to 2.7nm. The improvement of PL efficiency of Er^{3+} with the decrease of nc-Si grain size was attributed to the quantum size effects of nc-Si. However, the measurements of PL spectra in the Er-doped SRSO films annealed at various temperatures revealed that there is a best annealing temperature between 800 and 1000°C, in which the maximum PL intensities were detected.[9−11] These results show that the behaviour of PL emission in Er-doped SRSO films annealed at different temperatures is similar to that in other Er-doped materials.[4] Unfortunately, the correlations between grain size and annealing temperature have not been reported in their researches.

As is known in material research, the grains in materials can grow up with the increase of annealing temperature. Annealing is an effective method to control the grain size in films. In this study, ion beam assisted deposition (IBAD) has been employed to synthesize the Er-doped SiO_x films. The microstructure and grain size of the films as-deposited and annealed at 800 and 1100°C have been characterized using x-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) in detail. The influence of the microstructure and grain size on the PL from Er-doped

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SiO_x films has been studied and discussed.

2. Experiment

2.1. Film deposition and annealing treatment

The Er-doped SiO_x films were deposited on Si (100) and GaAs (100) chips by using an IBAD system, which has been described in our previous paper in detail.[12] In general, the IBAD system consists of a sputtering ion source, an assisted ion source and a low-energy ion source used mainly to clean the substrate. Er-doped SiO_x film can be synthesized by co-sputtering a Si target and Er rods and assisted by low-energy oxygen ion beam irradiation simultaneously. The chips were placed about 100mm far from the target which was a low-doped n-type Si (100) wafer. Over the target, aluminum strips embedded with metal erbium rods with a diameter of 2mm were fixed. The purity of Er rods is 98%, and the sputtered area of erbium rods was about 5% of the total sputtered area.

The chips were cleaned by the standard cleaning method before loading-in the chamber. The base vacuum of the system was in the order of 10^{-3} Pa. Before deposition, Ar ion sputtering was used to clean the surfaces of the samples for 15min. During deposition, the oxygen flow was 1.1 sccm and the argon flow was 0.5 sccm. The working pressure was 3.0×10^{-2}Pa. The current of Ar ion beam used for sputtering was 50mA and the energy of Ar ions was 3keV. The current of O ion beam used for irradiation was 50mA and the energy of O ions was 500eV. The substrate was heated to 500°C by a filament heater.

To investigate the variations of microstructure and PL properties of Er-doped SiO_x films with annealing temperature, we annealed the films at temperatures of 800 and 1100°C for 2h in the air atmosphere.

2.2. Characterization of structure and PL measurement

The microstructure of Er-doped SiO_x films was determined using XRD and TEM. TEM observation was carried out with a JEOL-100CX electron microscope to examine the plane-view morphology and to determine the crystal structure of the films. XRD was used for phase analysis of the films. The composition analysis was performed by using the energy dispersion x-ray spectrum (EDX). To eliminate the influence of substrates on the film compositions, the films deposited on the GaAs substrates were used for the determination of composition of the films.

PL spectroscopy measurement was used to optically characterize the PL spectra of Er-doped SiO_x films at room temperature. A chopped 980 nm line from a diode laser was used to excite the PL. The maximum output power of the laser is 1 W. The PL spectra of the films around 1.53μm was amplified by a lock-in amplifier and detected by a semiconductor detector.

3. Results and discussion

3.1. Composition and microstructure of Er-doped SiO_x films

Table 1 lists the compositions determined using EDX for the Er-doped SiO_x films as-deposited and annealed at 800 and 1100°C. As can be seen in the table, there is a small amount of aluminum in the films except for Si, O, and Er. The concentration of oxygen is about 20 at% in the as-deposited film and increases to above 40 at% after annealed at 800 and 1100°C, which is much lower than the concentration of oxygen in SiO_2 and also in the Er-doped SRSO films synthesized by Han *et al.*[11] According to Ref.[11], Si concentration in the range of 34 to 44 at% does not influence PL intensity considerably. It should be noticed that the concentration of oxygen in the film annealed at 1100°C is not much higher than that annealed at 800°C. The ratio of Si to O decreases from about 3 in the as-deposited film to about 1 in the annealed films. This implies that the annealing temperature plays the main role in the effects on microstructure and the PL of the annealed films.

Table 1. The compositions of the as-deposited films and the films annealed at 800 and 1100°C.

	O/at%	Al/at%	Si/at%	Er/at%
As-deposited	21.71	14.14	63.82	0.33
800°C annealed	40.96	12.11	46.58	0.35
1100°C annealed	43.57	13.73	42.36	0.34

The PL spectrum of Er-doped materials is sensitive to the thermal annealing process. The annealing temperature influences both the grain size in the films and the local environment of Er^{3+}. In this work, the influence of annealing temperature on the microstructure of the film was investigated by using TEM and XRD. XRD patterns of the Er-doped SiO_x films as-deposited and annealed at 800 and 1100°C are shown in Fig.1, which shows that the film as-deposited by IBAD at 500°C is typically amorphous. This result is in agreement with that in Ref.[13] observed in the films obtained by reactive magnetron sputtering. After annealing at 800 and 1100°C for 2h, the films become polycrystalline. By indexing the XRD patterns, we can conclude that the diffraction peaks result from Si polycrystals in the films and neither silicon oxides nor aluminum oxides can be observed. The results suggest that the oxides in the film do not show strong enough diffraction.

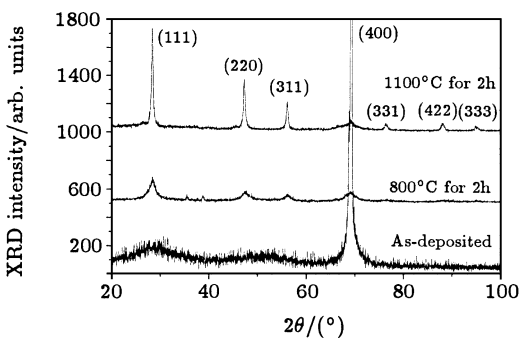


Fig.1. XRD patterns of Er-doped SiO_x films in the as-deposited state and after annealed at 800 and 1100°C.

The average grain size in the films can be estimated by the Debye–Sherrer formula:

$$D = \frac{0.94\lambda}{B\cos\theta}, \qquad (1)$$

where D is the average diameter of grains in the films, $B = \Delta 2\theta$ is the full width at half-maximum (FWHM) of the diffraction peak, λ is the wavelength of x-ray, and θ is the Bragg angle. According to formula (1) and the FWHM of (111) diffraction peaks, the average diameters of the crystals in the films annealed at 800 and 1100°C are 7 and 23nm, respectively. In other words, the films annealed at 800 and 1100°C are nc-Si. It should be pointed out that the average grain size in the film calculated with the Debye–Sherrer formula is less than the true grain size in the film because there are two main factors broadening the diffraction peaks: the grain size and the stress in the film. In our calculation, the broadening from the stress in the film was not separated.

Figure 2 shows the selected area diffraction (SAD) patterns and the bright field images of TEM of Er-doped SiO_x films as-deposited and annealed at 800 and 1100°C. As can be seen in the figures, the SAD pattern of the film as-deposited (Fig.2(a)) shows that the film is amorphous. The film annealed at 800°C is nc-Si and no other phase can be observed. The grain size in the film annealed at 800°C is about 10nm, which is about the same as that calculated from XRD. After annealed at 1100°C for 2h, the film still mainly consists of nc-Si and the grain size in the film is about 40nm, which is a little larger than that calculated by using XRD result and is similar to that of the sample with the stronger PL intensity reported in Ref.[13]. Furthermore, the SAD pattern of the film annealed at 1100°C shows that some new phases besides silicon appear in the film. Because the grain size of the new phases is similar to that of nc-Si and too few to be identified, we cannot give more information about them. We suggest that the new phases are possibly oxides.

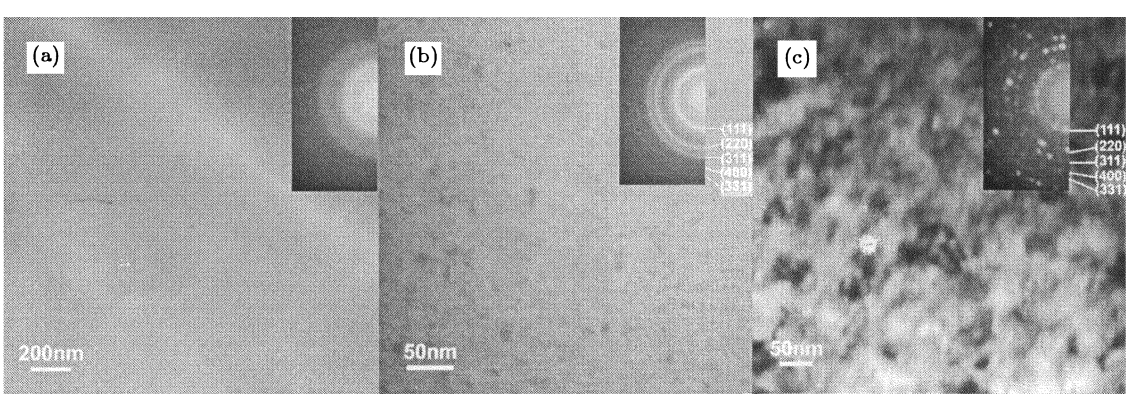


Fig.2. TEM bright-field images and electron diffraction patterns of Er-doped SiO_x films: (a) as-deposited, (b) annealed at 800°C, (c) annealed at 1100°C.

3.2. The PL of Er-doped SiO_x films

No PL spectrum had been detected from the Er-doped SiO_x film as-deposited at 500°C until the excitation laser power reached 1W. After the films had been annealed at 800 and 1100°C separately for 2h, however, stronger PL spectra were detected, as shown in Fig.3. We can see that the peak at 1.533μm does not shift obviously but the FWHM of the peak increases from about 30 to 40nm with the increase of annealing temperature from 800 to 1100°C. As can be seen in the figure, the increase of FWHM results from the increase of sub-transition at 1.55μm. This result indicates that the local environment of Er^{3+} in the Er-doped films annealed at 1100°C is not the same as that at 800°C.

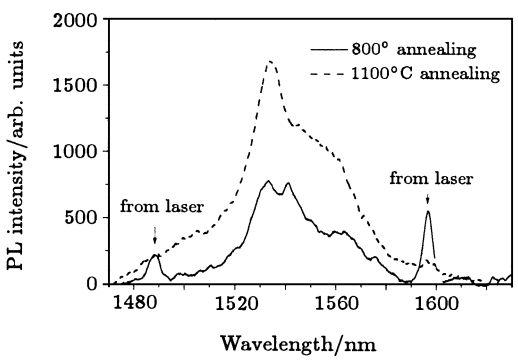


Fig.3. PL spectra of Er-doped SiO_x films annealed at 800 and 1100°C, pumped with 980 nm laser.

According to our analysis about the microstructure of the Er-doped films as-deposited at 500°C and annealed at 800 and 1100°C, we can conclude that the silicon amorphous matrix is not beneficial to the PL of the Er-doped films. The result is similar to that observed in Ref.[13], where much weaker PL spectra were detected in the films with silicon amorphous matrix, compared with the PL spectra observed in the crystalline matrix. Cerqueira *et al*[13] suggested that the increase of PL intensity observed in the annealed samples could be due to the formation of nc-Si, to the annealing of some structure defects or to the decrease of hydrogen or oxygen concentration during the annealing process.

According to Fuji *et al*'s investigation on the PL from SiO_2 films containing nc-Si, the presence of nc-Si can strongly enhance the PL of Er^{3+} at 1.54μm and this PL intensity increases by about two orders of magnitude with the decrease of grain size from 3.8 to 2.7nm. In our experiment, however, the PL intensity at 1.54μm increases by about one order with the increase of grain size from 10 to 40nm. This result agrees with the observation of PL emission in the Er-doped films annealed at different temperatures,[9–11] where no detailed information about grain size was reported. Based on our results of PL emission at 800 and 1100°C and the behaviour of PL emission with annealing temperature reported in Refs.[9–11], the thermal activation of Er^{3+} ions and the annealing of some structure defects, such as non-radiative defects, may play the main roles in the improvement of PL intensity in our Er-doped films. The reason why no obvious quantum enhancement was observed may come from the fact that the grain size in our samples is larger than 10nm, which is much larger than the exciton Bohr radius of Si (about 5nm). Therefore, the quantum size effect in our samples is very weak.

Figure 4 shows the dependence of PL intensities at 1.53μm on the excitation laser power in the Er-doped films annealed at 800 and 1100°C. As can be seen from the figure, the PL intensities in the Er-doped films annealed at 800 and 1100°C increase with the increase of excitation laser power and there is no obvious power saturation when the laser power is up to 1W. The results are different from Fuji *et al*'s observation in the Er-doped films with nc-Si grain size of 2.7nm and Er concentrations of 0.02 and 0.07 at%. Because Er concentration in our films is much higher than that in Fuji *et al*'s films, we suppose that the saturation of PL intensity with the increase of excitation laser power depends on the concentration of Er^{3+} ions in the films.

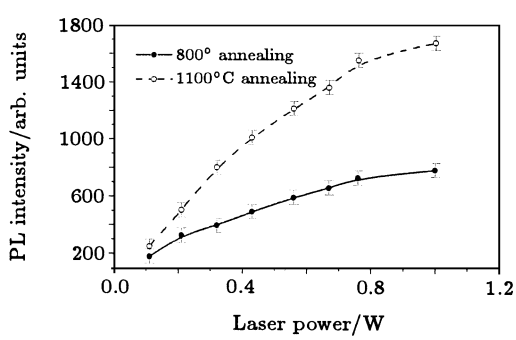


Fig.4. Dependence of PL intensities from Er-doped SiO_x films annealed at 800 and 1100°C on the excitation power of laser.

4. Conclusions

(1) In the Er^{3+}-doped SiO_x films synthesized by IBAD, the ratio of Si to O decreases from about 3 in the as-deposited film to about 1 in the annealed films.

(2) The film as-deposited at 500 °C is amorphous. After annealed at 800 and 1100°C for 2h, the film

structure changes into nc-Si, and the average grain size increases from 10 to 40nm estimated from TEM.

(3) No PL spectrum was detected from the Er-doped SiO_x film as-deposited. The PL intensity increases by about one order with the increase of the annealing temperature up to 800 and 1100°C.

(4) No obvious saturation of PL intensity can be observed in Er-doped SiO_x films when the laser power increases up to 1W. We suppose that the saturation of PL intensity depends on the concentration of Er^{3+} ions in the films.

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