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Photoluminescence from Magnetron Sputtered SiO_2 Films Co-doped with (Er, Ge) under Excitation of a 325 nm He-Cd Laser Line

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We have studied photoluminescence (PL) from SiO_2 films co-doped with (Er, Ge) deposited by magnetron sputtering of an Er+Ge+SiO_2 composite target in pure Ar ambient. Under excitation of a 325 nm He-Cd laser line, blue emission bands around 400 nm and near infrared bands around 800 nm have been observed, which are attributed to Ge-related defects and Ge nanoclusters (Ge-ncls), respectively. Strong Er^{3+} PL at 1.54 μm was also observed from the films, while the Er PL intensity of a control Er-doped SiO_2 film (i.e., without Ge), is negligible under the same excitation. All the PL intensities vary as functions of thermal annealing temperatures. The results demonstrate that the significant enhancement of Er PL in the (Er, Ge) co-doped SiO_2 films are due to the incorporation of Ge. The roles of Ge-ncls and Ge-related defects to the Er^{3+} excitation are discussed.

Introduction

During the past decade, the Er^{3+} photoluminescence (PL) at 1.54 μm from Er-doped Si-rich Si oxide (Er-SRSO) films has been studied intensively for the development of light sources or small-sized and Si-compatible optical amplifiers (1-3). A major driving force behind this is the requirement for a wide range of low-cost and compact optical components for implementation of wavelength division multiplexing (WDM) in fiber-to-the-home systems (4-6). On the other hand, light emission from the SRSO matrix of the films has also been studied not only for the fundamental study of energy transfer mechanism, but also for the applications in displays or in integrated circuits as a light source. Compared to the Er-doped SRSO system, the emission from Ge nanoclusters (Ge-ncls) and/or Ge-related defects is quite different, which may result in different luminescence properties when co-doped with Er ions (7).

Recently, studies of the PL from (Er, Ge) co-doped or (Er, Ge, Yb) co-doped SiO_2 systems have also attracted much interest (8-10). In a previous study, we have reported on the PL from an (Er, Ge) co-doped SiO_2 film excited by a 488 nm Ar-ion laser line, and found that the Er PL intensity was strongest after annealing the film at 700 °C in N_2 for 30 minutes (9). Since the excitation wavelength was resonant with the Er^{3+} $^4F_{7/2}$ energy level, direct excitation of Er^{3+} by the laser line was not negligible. The direct excitation of Er^{3+} has been studied for a magnetron sputtered Er_2O_3 film on a thermally oxidized Si substrate by Miritello *et al.* (11). However, in the present work, we report on the PL properties of SiO_2 films co-doped with (Er, Ge) under the non-resonant excitation of a 325 nm He-Cd laser line, and study the effects of Er concentrations on the Er PL. The energy transfer from Ge-ncls to Er ions will also be discussed.

Experimental details

The (Er, Ge) co-doped SiO_2 films were deposited on single crystal n-type Si substrates by rf magnetron sputtering of a Ge+Er+SiO_2 composite target in a pure Ar plasma. The concentrations of Ge and Er in the films were controlled by changing the area ratios of small pieces of Ge or Er plates to the SiO_2 matrix in the target. The base vacuum of the chamber was less than $1x10^{-7}$ Torr. During sputtering, the plasma power was kept at 130 W with a working gas pressure of $5.0x10^{-3}$ Torr. Two types of films were deposited and labeled as A and B, respectively. The films were characterized and studied by using transmission electron microscopy (TEM) with a Philips CM12 microscope operating at 120 keV. The thickness of film A was 1.95 μm, and the Ge and Er concentrations were 7.4 at.% and 1.3 at.%, respectively. Film B had a thickness of 1.54 μm, with Ge and Er concentrations of 7.0 at.% and 2.82 at.%, respectively. For comparison, two control structures were also deposited on identical substrates under identical sputtering conditions: (i) an Er-doped SiO_2 film was deposited by sputtering an Er+SiO_2 composite target. The thickness of the film was 1.5 μm and the Er concentration was similar to that in film B; (ii) a Ge-doped SiO_2 film was deposited by sputtering a Ge+SiO_2 composite target. The thickness of the film was 1.4 μm, with a Ge concentration slightly higher than that in films A and B.

All of the films with the substrates were then cleaved into small pieces and subjected to thermal treatments in flowing N_2 ambient for 30 minutes at different temperatures, as is indicated in the text. The PL setup for the Er^{3+} 1.54 μm PL measurements comprised a 325 nm line of a He-Cd laser, a grating monochromator with an InGaAs detector, and a lock-in amplifier with a chopper working at 40 Hz. The visible to near infrared PL from the films was detected by a spectrometer employing a charge-coupled device array, and the spectra were corrected for system response and optics transmission and subsequently converted to normalized photon flux (12).

Experimental results and discussions

Figure 1 shows the Er PL spectra for the control Er-doped SiO_2 film annealed at three different temperatures, 600, 800 and 1000 °C, respectively. There is no evidence for Er^{3+} emission near 1.54 μm at 600 and 1000 °C annealing temperatures. The film annealed at 800 °C seems have a very weak broad band at about 1550 nm, but whether there is weak Er^{3+} emission is uncertain. The results demonstrate that the direct excitation of Er^{3+} ions is weak under the non-resonant 325 nm line illumination.

Figure 2 shows the PL spectra for the control Ge+SiO_2 film in the range 340-850 nm. The samples were annealed at temperatures in the range 500-900 °C. It can be seen that under excitation by the 325 nm line, there are blue and near-infrared emission bands present in each PL spectrum. The 500 °C anneal yields the highest PL intensity. The origin of the blue emission band is normally attributed to Ge-related defects (13). It has been reported that Ge+SiO_2 films can emit light with peak wavelengths at around 370, 396 and 415 nm, respectively. The 370 and 415 nm bands have been attributed to Ge-associated neutral oxygen vacancies, and the 396 nm band to GeO color centers (14, 15). The emissions in the near infrared regions are normally attributed to radiative

recombination within Ge-ncls, but some authors also attribute an emission at around 780 nm to the optical transition in the GeO color center (15). We believe however that the peaks superimposed on the blue and near- infrared bands are due to multiple interference effects on the reflectivity (16). With increasing the annealing temperature from 500 to 900 °C, the PL intensity decreases gradually. From Fig. 2, it is noted that the emissions from the Ge-related defects are much stronger than those from the Ge-ncls. This signifies the efficiency of the short-wavelength excitation of defects.

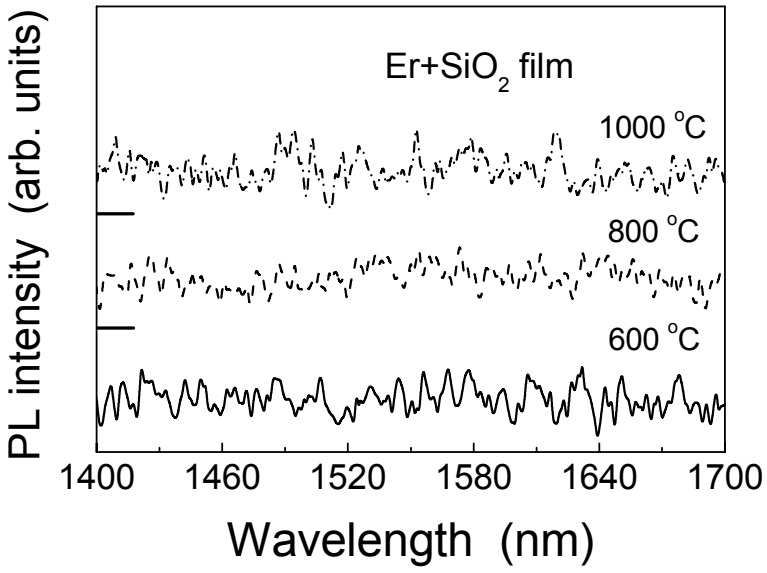

Figure 1. The Er PL spectra at 1.54 μm for the pure Er-doped SiO_2 film, which has been annealed in N_2 for 30 minutes at 600, 800 and 1000 °C, respectively.

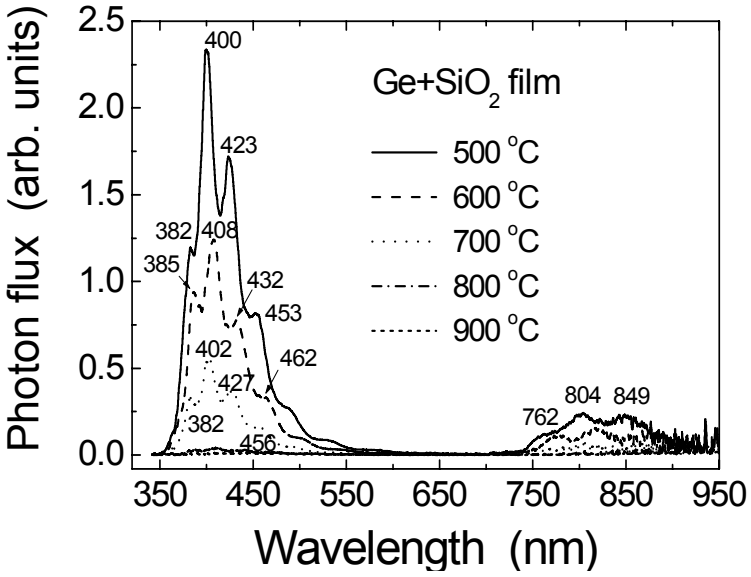

Figure 2. The PL spectra of the Ge-doped SiO_2 film which has been annealed in N_2 for 30 minutes at 500, 600, 700, 800 and 900 °C, respectively.

Figures 3(a) and 3(b) show the PL spectra for film A which has been annealed at 540, 625, 712, 750, 800, 850 and 900 °C, respectively. In Fig. 3(a), the PL spectra were

recorded in the same range as that in Fig. 2, indicating the emissions from the Ge+SiO_2 matrix of the film. It can be seen that after annealing the film at 540 °C, the shapes of the PL spectra are similar to those in Fig. 2. The PL intensity increases when the annealing temperature increases from 540 to 625 °C, but decreases as the temperature increases further to 712 and then to 750 °C. The peak positions in each spectrum are also quite different. The PL intensity recovers to increase after an 800 °C annealing and reaches its highest level after a 850 °C anneal, then decreases with increasing the temperature to 900 °C. This dependency of the PL on annealing temperature is different from that shown in Fig. 2. This is related to the concentrations of the Ge and Er dopants which are beneficial to the precipitation of Ge-ncls.

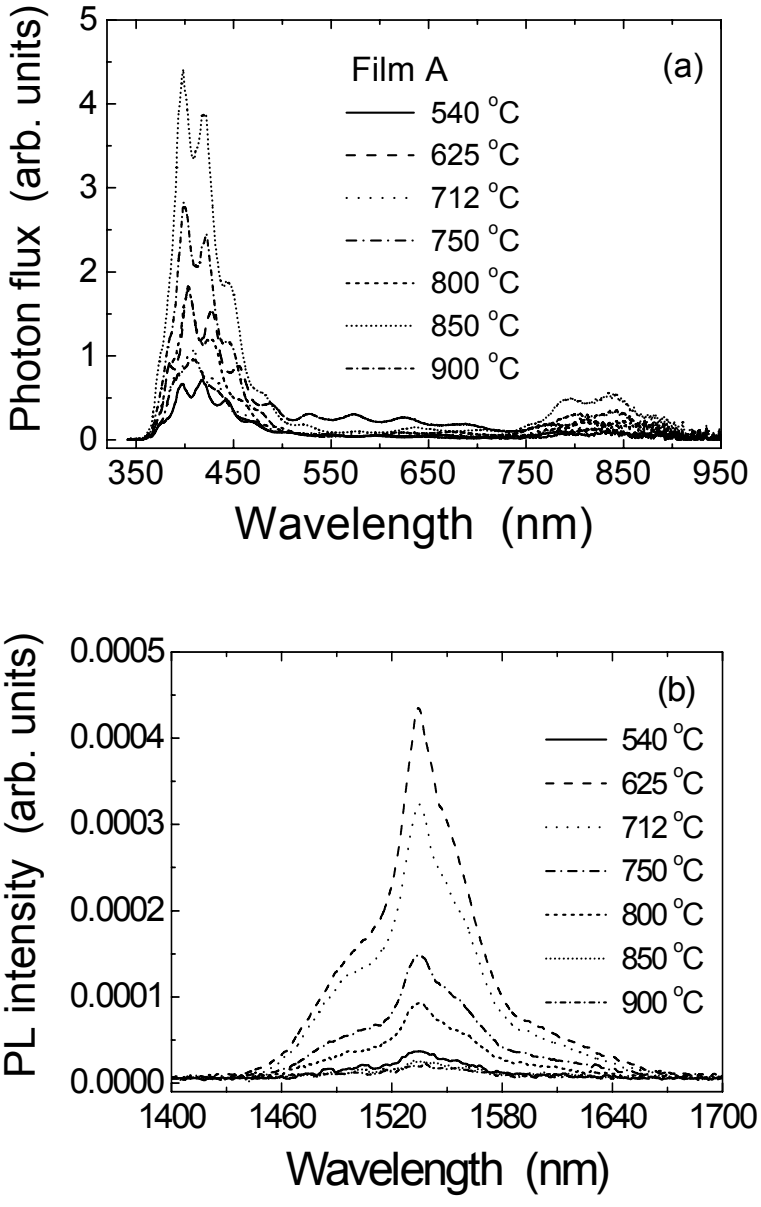

Figure 3. The PL spectra of film A after annealing in N_2 for 30 minutes at 540, 625, 712, 750, 800, 850 and 900 °C, respectively: (a) from Ge+SiO_2 matrix of the film, and (b) the Er PL at 1.54 μm.

Figure 3(b) shows the Er PL spectra for the film after the above annealing treatments. It should be noted that almost no Er PL was observed from the as-prepared film. After annealing at 540 °C, Er PL is evident in the spectrum although it is rather weak. By increasing the temperature to 625 °C, the PL intensity increases drastically and becomes the strongest. As the temperature increases further to 712 °C, the Er PL intensity begins to decrease. The intensity decreases to a large extent after 750 °C annealing and becomes very weak as the temperature increases further to 900 °C. Note that the full widths at half maximum (FWHM) of each spectrum are also different. The width is 64 nm in the case of the 540 °C anneal, then it decreases rapidly to 43 nm after the 625 °C anneal. With increasing the annealing temperature from 712 to 900 °C, the width increases monotonically from 47 to 85 nm. We suggest that the variations in intensity and FWHM are related to the size and density of the precipitated Ge-ncls at each annealing temperature.

We have reported that under the excitation of a 488 nm laser line, the Er PL intensity of an (Er, Ge) co-doped film is much stronger and has a wider FWHM than those in the spectrum of pure Er-doped SiO_2 films (9). This means that the existence of Ge-ncls has increased both the intensity and the width of Er PL spectrum. However, the direct correlation between the conditions (size and density) of Ge-ncls and the variation of the Er PL spectrum (intensity and FWHM) is complicated. We believe that in our films, Ge-ncls with a large average size and/or lower density will result in lower excitation efficiency of Er^{3+} ions, which leads to the relatively weak Er PL intensity and the wider calculated FWHM of the spectrum.

Figures 4(a) and 4(b) show the PL spectra of film B, which has similar Ge concentration but twice the Er concentration than film A. Figure 4(a) shows the PL spectra from the Ge+SiO_2 matrix of film B. The PL from the as-prepared sample is very weak. After the 500 °C anneal, we observe emission from the film, the resulting spectra are similar in shape to those of film A, but the near-infrared emissions are weaker. As the annealing temperature increases from 600 to 700 °C, the PL intensity increases by 50% while the interference peak positions remain the same. The intensity increases significantly after the 800 °C anneal. As the temperature increases further to 850 °C, the PL intensity of the spectrum turn out to be the highest with peak positions very close to the case of the 500 °C annealing. The PL intensity starts to decrease after the 900 °C annealing. The small deviations of the peak positions relative to the 500 °C annealing should be due to the slight changes in the interference effects on reflectivity caused by the small variations in the film thickness and refractive index with higher annealing temperatures.

Figure 4(b) shows the corresponding Er PL spectra for film B for the same annealing temperatures. Again, the Er PL signal in the as prepared sample is very weak.(not shown) After the 500 °C annealing, there is weak Er PL observed from the film, and the intensity increases after the 700 °C anneal. With increasing the temperature to 800 °C, the Er PL intensity is about 6 times stronger than that in the case of the 700 °C anneal. However, as the temperature increases further to 850 °C, the Er PL intensity decreases rapidly, and is only 6% of the maximum value after the 900 °C anneal. Note that in the case of the 500 °C anneal, the FWHM of the spectrum is 38 nm. With increasing the temperature to 700 °C, the width increases slightly to 39 nm, and to 46 nm after the 800 °C anneal. Increasing the temperature further to 850 and then to 900 °C, the width increases slightly

to 47 and 48 nm, respectively. The small increases in the FWHM mean that the parameters of Ge-ncls changed only slightly, while the significant change in the Er PL intensity should correspond to an enhanced excitation of Er ions.

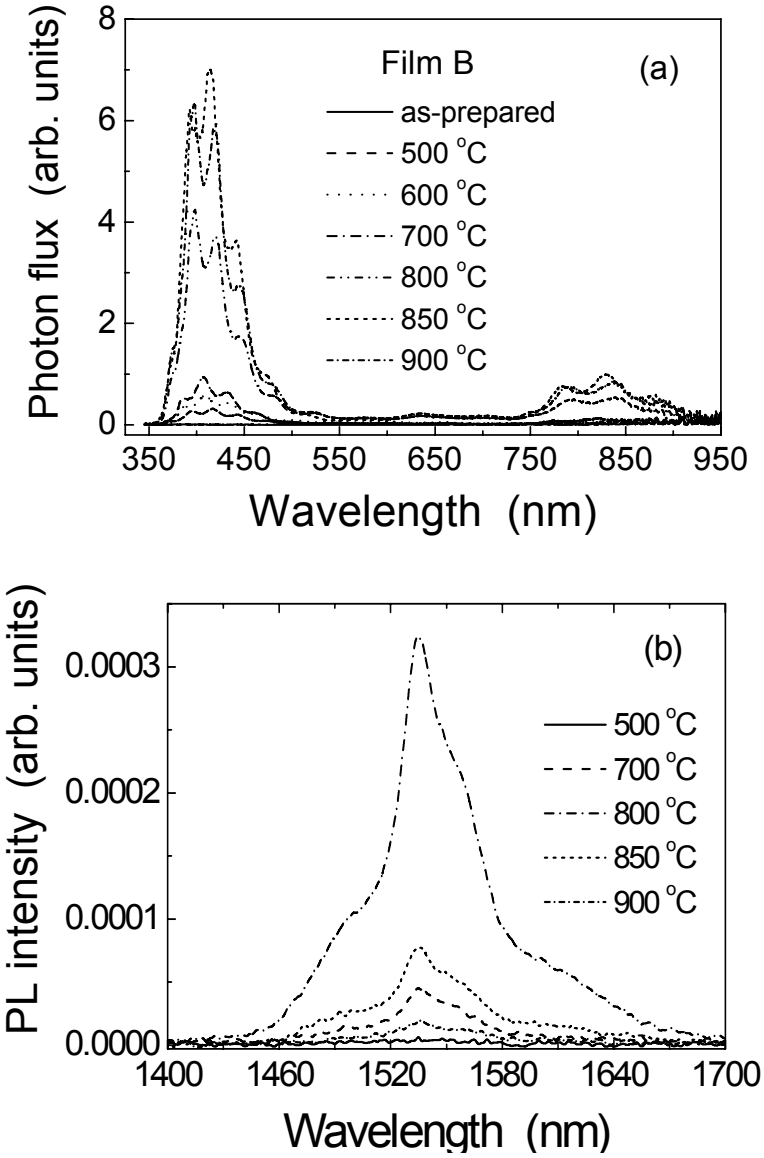

Figure 4. The PL spectra of film B after annealing in N_2 for 30 minutes at 500, 700, 800, 850 and 900 °C, respectively: (a) from the Ge+SiO_2 matrix of the film, and (b) the Er PL at 1.54 μm.

The precipitation of Ge clusters in both (Er, Ge) co-doped films (A and B) have been investigated by using TEM. Figures 5(a) and 5(b) show the TEM images for film A after annealing in N_2 for 30 minutes at 625 and 850 °C, respectively. After the 625 °C annealing, a great number of Ge (or Ge-rich) clusters precipitated in the film. The average size of the clusters is 4-5 nm. The selected area diffraction of the film is a halo which indicates that the film is in an amorphous state (not shown). However, after the 850 °C annealing (Fig. 5(b)), the average size of the clusters has increased to about 11 nm. In the inset of Fig. 5(b), the selected area diffraction shows small dots superimposed on

the halo which indicates that Ge nanocrystals have precipitated in the film after the 850 °C anneal.

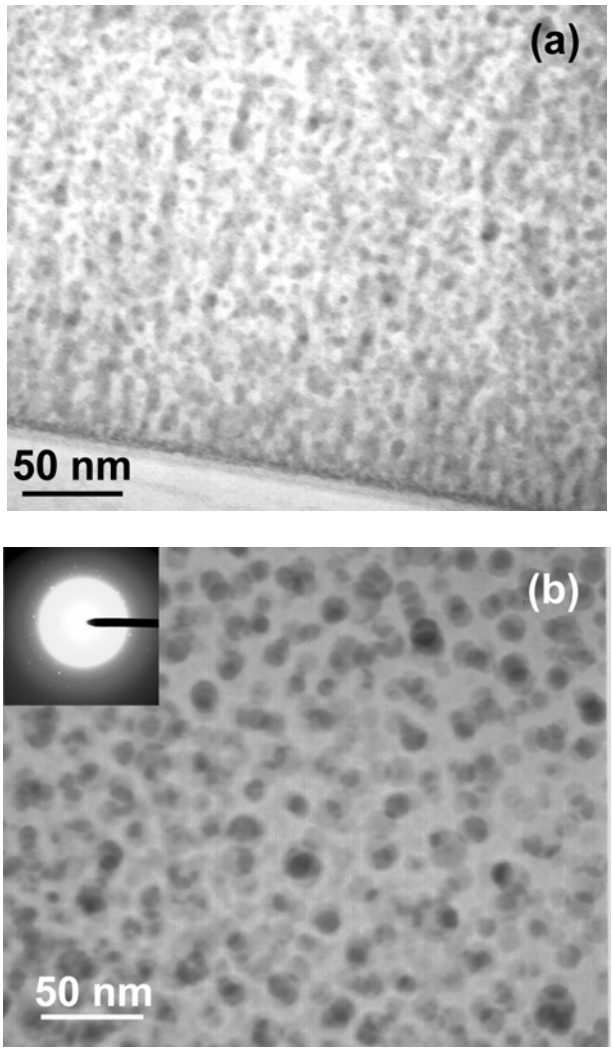

Figure 5. The TEM pictures for the film A which has been annealed in N_2 for 30 minutes at (a) 625 °C and (b) 850 °C, respectively. The inset in Fig. 5(b) shows small diffraction spots on the halo indicating the formed Ge-ncls are crystalline.

Figures 6 (a)-(c) show the TEM images for film B which has been annealed in N_2 for 30 minutes at 500, 800 and 900 °C, respectively. Similar to the case in Fig. 5(a), after 500 °C annealing, in Fig. 6(a), Ge (or Ge-rich)-ncls have formed in the film, but the shape of the clusters is not very spherical and the particles connect each other in some areas, which means that the phase separation of Ge from its oxide states has not been completed. The average size of the clusters is about 4 nm. The diffraction patterns are halo indicative of the amorphous states of the film.

Figure 6(b) shows the precipitated Ge-ncls with an average size of about 14.3 nm at the 800 °C anneal. This assertion is also evidenced from the selective area diffraction which shows small spots being present on the halo, indicating that Ge nanocrystals have formed in the film after the 800 °C anneal. Note that there is a layer of smaller Ge clusters lying close to the SiO_2/Si substrate interface. This is due to the out-diffusion of Ge

toward the interface (or surface) upon the annealing. After 900 °C annealing (Fig. 6(c)), the Ge nanocrystals become more distinctive in shape with an average size increase to 15.9 nm.

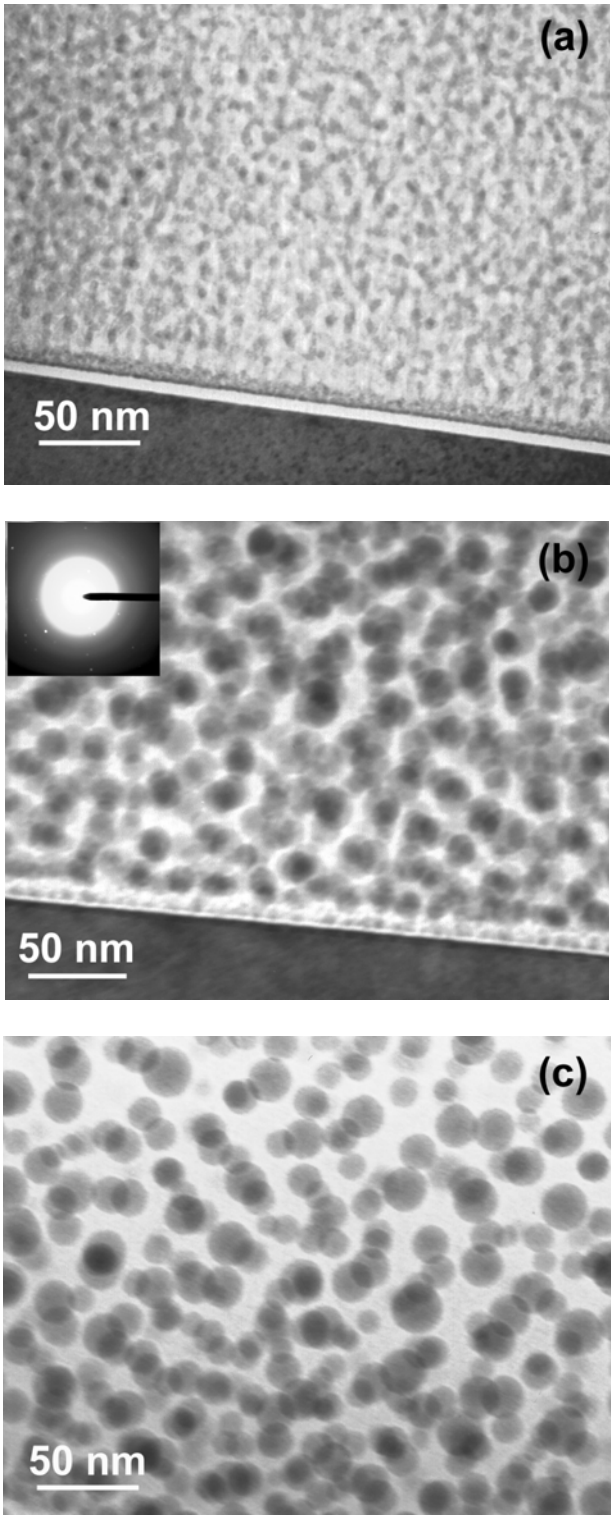

Figure 6. The TEM pictures for the film B after annealing in N_2 for 30 minutes at (a) 500, (b) 800 and (c) 900 °C, respectively. Small diffraction spots on the halo showing in the inset of Fig. 6(b) reveals that the Ge-ncls are crystalline.

Based on the above results, it is seen that under the non-resonant excitation, almost no direct excitation of Er^{3+} was observed; the pronounced Er PL in the (Er, Ge) co-doped SiO_2 films should be due to the incorporation of Ge. Also note that the Er PL intensity is very weak in the as-prepared films but varies a lot after the formation of Ge-ncls. Thus, we suggest that the excitation of Er^{3+} is mediated through the Ge-ncls that absorb photon energies and then transfer the energy to nearby Er ions. If a Föster energy transfer process is dominant (17, 18), then the prerequisite of the energy transfer is that the size of Ge-ncl should be small enough so that the energy "band gap" (the energy difference between the highest occupied energy level and the lowest unoccupied energy level for a nanocluster) is not less than ~ 0.8 eV, which corresponds to the Er ion transition ($^4I_{15/2} \rightarrow {}^4I_{13/2}$). For our films A and B, the 800-900 $^{\circ}$C anneal results in average size distributions in the range of 11-16 nm, with the "band gap" probably still comparable to or higher than 0.8 eV according to the calculation of Niquet *et al.* (19). Accordingly, the increase of the Er PL intensities should generally be due to the increased formation of Ge-ncls with higher annealing temperatures, while the decrease is likely related to the clusters decreasing in density with increasing size in a given concentrations of (Er, Ge) co-doped SiO_2 film.

The PL intensities normalized to corresponding film thickness from films A and B reveal that the PL intensity from the Ge+SiO_2 matrix of film B is twice as strong as that from film A, but the Er PL intensity of film B (which has a higher Er concentration than film A) has not noticeably improved. The increased PL intensity and the formation of Ge-related defects is likely related to the increased formation of Ge-ncls in the presence of high Er^{3+} concentrations that may act as nucleating centers upon annealing. Note that the Er PL intensities of film B are relatively weaker than those in film A. This can be attributed to concentration quenching (1). The enhanced Er PL intensity after the 800 $^{\circ}$C annealing could be related to Er^{3+} resonant excitation. That is, as the average size of Ge-ncls is 14.3 nm, the energy gap of Ge-ncls may have happened to align with that of Er^{3+} first excited level, which results in an improved pumping efficiency.

Kuritsyn *et al.* have suggested that in Er-doped SRSO systems, besides the energy transfer by Si-ncls, any defects due to excess Si can also act as sensitizers to the Er ions (20). In our (Er, Ge) co-doped system, the blue emission bands, which originate from the GeO color centers or Ge-related neutral vacancy defects have an intensity much stronger than that from the Ge-ncls. One may speculate that these defects will also transfer energy to the Er ions. According to the Föster energy transfer model, the nanoclusters and Er^{3+} are regarded as donors and acceptors, respectively. The distance between them (which indicates the interaction of their wave-functions) should be smaller than the radius of the Förster zone:

$$r_F = 0.1\frac{\lambda}{2\pi \cdot n} \qquad [1]$$

where λ is the wavelength of the donor luminescence (18). Under the 325 nm laser line excitation, the λ from the defects and Ge-ncls are around 0.4 and 0.8 μm, respectively. In the case of pure Ge-doped SiO_2 the refractive index n is ~ 1.5. Consequently, the values of r_F are estimated to be around 4.2 and 8.4 nm, respectively. As a result, whether the defect emission plays a role or not in the sensitization of Er ions depends on the distance

between the defects and the Er ions. If the defects are located at the surface of Ge-ncls, we suppose that defects may transfer their energy to nearby Er^{3+}.

Conclusions

In summary, we have studied the PL from two types of SiO_2 films co-doped with (Er, Ge) and excited by the non-resonant excitation of a 325 nm laser line. Strong blue emission bands at around 400 nm and in the near infrared at around 800 nm were observed. These are attributed to Ge-related defects and Ge-ncls, respectively. Strong Er^{3+} PL near 1.54 μm was also observed from the films. The results suggest that the excitation of the Er ions occurs through Ge-ncl-mediated energy transfer. However, we do not rule out defect-mediated excitation.

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