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HTML ABSTRACT + LINKS

Formation and oxidation of Si nanoclusters in Er-doped Si-rich SiO_x

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The mechanisms for the formation and oxidation of Si nanoclusters (Si-ncls) are elucidated by means of the study of their effects on the photoluminescence of Er in Er-doped Si-rich SiO_x ($x < 2$) films. We find that the light emission of Er is the most intense in films with a Si concentration of ~40% after annealing at 875 °C in an argon ambient, which yields an optimum Si-ncl size. The nucleation rate of Si-ncls increases with temperature, however, they stabilize around a critical size which increases with annealing temperature. We determine that the activation energy for the formation of Si-ncls is 1.4±0.5 eV. During annealing in an oxygen ambient Si-ncls are oxidized. The resultant oxide reduces the efficiency of energy transfer from them to Er ions and thus the light emission of Er. The activation energy for the oxidation is 1.06±0.03 eV. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1894600]

The development of efficient Si-based light-emitting devices operating at room temperature is the subject of intense research activity.[1,2] Significantly, it has been demonstrated that Er-doped Si-rich SiO_x ($x<2$) (SRSO) can be processed to generate Si nanoclusters (Si-ncls), which greatly enhance the light emission of Er around the wavelength of 1.53 μm.[3–5] It is also well known that such Si-ncls are efficiently pumped through direct optical absorption, which can be followed by energy transfer from the resultant excitons in the Si-ncls to Er ions that subsequently radiatively decay. The efficiency η_t of the energy transfer decreases with the distance d between the Si-ncls and Er ions.[6,7] Because of the negligible diffusion of Er during device fabrication with temperatures <1050 °C,[8] d is predominantly determined by the size of the Si-ncls, which randomly form throughout the doped layer. An increase of Si-ncl size reduces the average value of d, leading to the increase of η_t. Further, large Si-ncls support excitons with an energy close to that corresponding to a maximum for absorption by the Er ions.[9] The formation of a high concentration of large Si-ncls would appear, therefore, to be beneficial for maximizing η_t.

It has been demonstrated that the concentration of excited Er ions is proportional to that of Si-ncls in Er-doped SRSO (Ref. 10) giving $I \propto \eta_t C$, where I and C are the intensity of light emission of Er and the concentration of Si-ncls, respectively. For a fixed concentration of Si in a SRSO film, C decreases as the size of Si-ncls increases. Therefore, the change of Si-ncl size has a contradictory effect on the intensity of light emission of Er. This justifies the search for an optimum value of Si-ncl size for a specific value of Si concentration. It has been shown previously that Si-ncl size is mainly determined by the annealing temperature and time. Although optimum annealing conditions have been described for specific sample sets,[11–13] a comprehensive study of the annealing, leading to the elucidation of the underlying formation mechanism of Si-ncls in Er-doped SRSO, has not been reported. The annealing ambient may also impact Si-ncl size, especially when active elements such as oxygen are incorporated. In this letter, we present a study of the formation and oxidation of Si-ncls by annealing Er-doped SRSO films at 800–950 °C for up to 7 h in argon or oxygen ambients. We show that the formation of Si-ncls can be consistently described using classical nucleation theory. Oxidation reduces the effective Si-ncl size, leading to a decrease in the intensity of light emission of Er.

Two Er-doped SRSO films (A and B) were grown on Si substrates by electron cyclotron resonance plasma-enhanced chemical-vapor deposition (ECR-PECVD), in which an organic Er source was employed to achieve high-concentration doping of Er. The deposition system has been described elsewhere.[14] The atomic concentrations of Si and Er [previously determined using Rutherford backscattering spectroscopy (RBS)] in film A were ~40% and 1.8%, respectively, and in film B were ~40% and 2.4%, respectively. Film A was 440 nm thick and film B was 250 nm thick. Both films were divided into smaller samples and annealed at 800–950 °C for up to 7 h in a furnace with flowing argon or oxygen gas. Their photoluminescence (PL) at a wavelength of ~1.53 μm was measured at room temperature after each annealing step. The PL setup is comprised of a Cd–He laser operating at a wavelength of 325 nm, a grating monochromator, a lock-in amplifier with a chopper, and an InGaAs detector. The effective power density of the laser beam on the surface of the films was ~0.26 W/cm^2. A 3-mm-wide slit for the monochromator was used.

The PL spectra from the films are representatively illustrated in Fig. 1 by those for film A annealed in an argon ambient at 800 °C for 10 min, 30 min, and 3 h. The wavelength range of 1400–1700 nm for this measurement contains the dominant luminescence intensity observed for all samples in this study. No significant luminescence intensity was observed for wavelengths from 600 to 1000 nm (the

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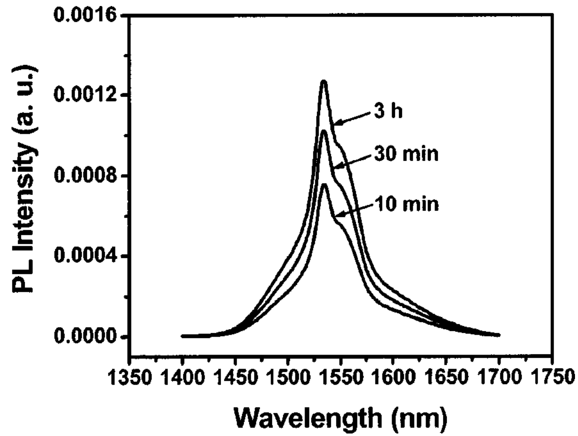

FIG. 1. The PL spectra of Er-doped Si-rich SiO_x ($x<2$) film *A* for wavelengths around 1.53 μm annealed in an argon ambient at 800 °C for 10 min, 30 min, and 3 h.

usual response for Si-ncls), suggesting that all of the Si-ncls in these samples are coupled with Er ions.

The integrated PL intensity for the peak at ~1.53 μm from films *A* and *B* annealed at 800–950 °C for up to 6 h in an argon ambient is shown in Figs. 2(a) and 2(b), respectively. For this range of annealing time, it is clear that following a rapid increase in PL intensity, the signal reaches a maximum value which is dependent on the annealing temperature. Further annealing after this maximum has been achieved has little effect on the integrated intensity. In terms of classical nucleation theory[15,16] it is expected that following initial nucleation of the Si-ncls, there is little subsequent growth in Si-ncl size, mainly as a consequence of the annealing temperatures being much lower than the melting point of Si. Here then, we can treat the films as containing Si nuclei (Si-ncls) of a certain critical size r^*. The resultant static values for r^* and Si-ncl concentration lead to the stabilized PL intensity of Er observed for long annealing times (i.e., > a few thousand seconds).

It is known that r^* is a function of nucleation temperature T: $r^*=A_c/(T_m-T)$, where A_c is a constant determined by the molar enthalpy of nucleation at the melting point T_m, the interfacial energy per unit area, and the volume of a Si atom. With an increase in annealing temperature the size of the Si-ncls increases, creating a simultaneous decrease in both *d* and *C*. Owing to their contradictory effects on the intensity of light emission of Er, an optimum processing temperature exists at 875 °C, characteristic of an optimum Si-ncl size. The same Si-ncl concentration exists in both films *A* and *B* after the same annealing process because of their similar Si concentration and temperature-determined Si-ncl size, and therefore, the same PL intensity might be expected from both films if they had the same thickness. Allowing for the thickness difference (440 nm for film *A* versus 250 nm for film *B*), the PL intensity of film *A* might be expected to be no more than two times larger than that of film *B*. In fact, the ratio is ~8 [Figs. 2(a) and 2(b)]. It has been reported previously that deexcitation processes such as cooperative upconversion and energy migration occur between Er ions when they are very close.[17] We believe that such deexcitation processes occur in film *B* because of the increased concen-

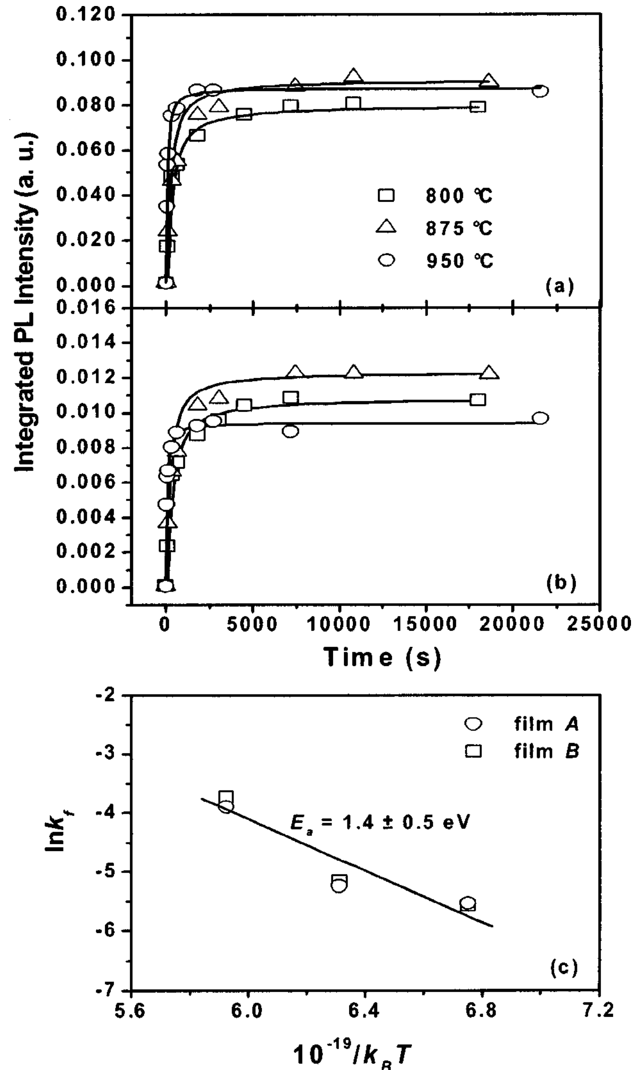

FIG. 2. The change in the intensity of PL at a wavelength of ~1.53 μm in (a) film *A* and (b) film *B* during annealing at 800–950 °C in an argon ambient. The solid lines indicate PL intensity from fitting, which gives (c) the formation rate of Si-ncls at each temperature. k_B is the Boltzmann constant. The derived activation energy E_a for the formation of Si-ncls is also shown.

tration of Er as compared to that of film *A*, which gives rise to the large ratio of PL intensity for the two films.

The time needed to reach the maximum PL intensity decreases with increasing temperature [Figs. 2(a) and 2(b)]. This is consistent with the increase in the formation rate of Si nuclei with temperature. We have fitted the data in Figs. 2(a) and 2(b) using $I=I_0+(I_{\max}-I_0)\exp(-1/k_f t)$, where I, I_0, and $I_{\max}$ are the PL intensity at time t, the PL intensity from the as-grown films, and the maximum PL intensity after long annealing times, respectively; and k_f is the formation rate of Si-ncls with the assumption that the PL intensity is proportional to the concentration of Si-ncls in both films *A* and *B* despite the deexcitation processes between Er ions in the latter. Figure 2(c) shows the change of k_f with temperature obtained from the data fitting. Using the Arrhenius equation we calculate the activation energy E_a for the formation of Si-ncls to be 1.4±0.5 eV. This result approximates the previously reported E_a of 1.9 eV for Si diffusion in SiO_x.[18] A

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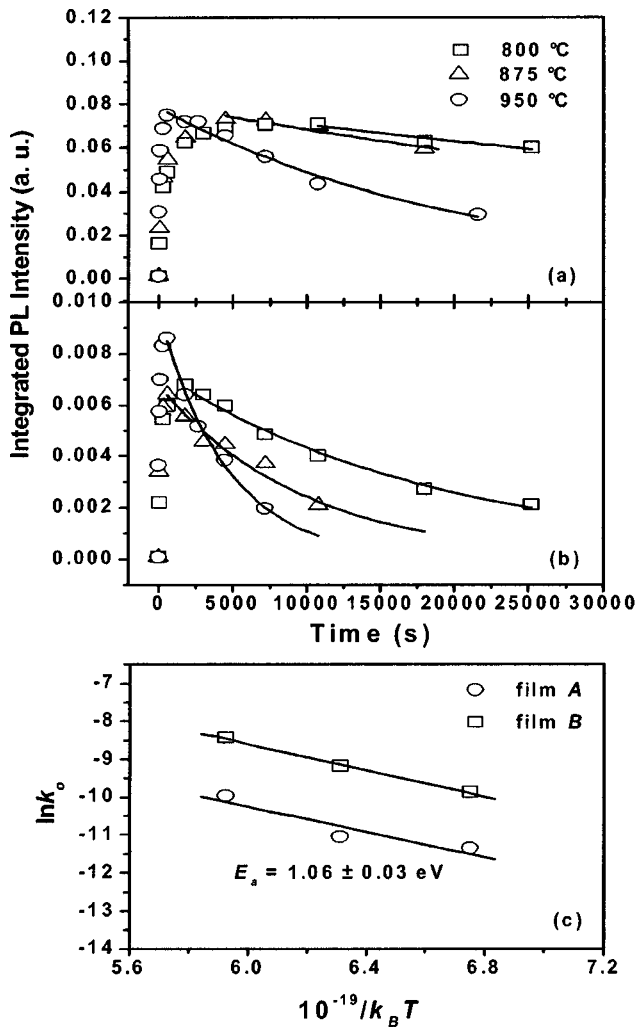

FIG. 3. The change in the intensity of PL at a wavelength of ~1.53 μm in (a) film *A* and (b) film *B* during annealing at 800–950 °C in an oxygen ambient. The solid lines indicate PL intensity from fitting, which gives (c) the oxidation rate of Si-ncls at each temperature. k_B is the Boltzmann constant. The derived activation energy E_a for the oxidation of Si-ncls is also shown.

similar E_a can also be derived from a recent work[19] by subtracting the Si–O bond energy (2.9 eV) from the E_a (4.74 eV) for Si diffusion in SiO_2. Therefore, we suggest that the formation of Si-ncls in these Er-doped SRSO films is controlled by Si diffusion, which does not require the breaking of Si–O bonds because of the already existent excess Si.

The formation of Si-ncls naturally introduces Si surfaces where thermal oxidation may easily take place. Figures 3(a) and 3(b) show the PL results for annealing at 800–950 °C for up to 7 h in an oxygen ambient. At the beginning of the annealing process, the formation of Si-ncls dominates, leading to the increase in PL intensity. However, the oxidation of the Si-ncls eventually dominates when oxygen has completely diffused into the film and reacted with the Si-ncl surface. This causes the effective Si-ncl size to decrease, resulting in a decrease in the intensity of light emission of Er as is observed for long annealing times. The values of maximum PL intensity after annealing in an oxygen ambient are smaller than those obtained in an argon ambient. This indicates that there are periods during which Si-ncl formation and oxidation occur simultaneously.

Assuming that the decrease of PL intensity is proportional to the volume of oxidized Si-ncls, we have fitted the decay of PL intensity in Figs. 3(a) and 3(b) with the expression $I=I_{\max}\exp(-k_o t)$, where I and $I_{\max}$ are the PL intensity at time t and the maximum PL intensity obtained in the films, respectively; and k_o is the oxidation rate of Si-ncls. The value of k_o at each temperature obtained from the fitting is illustrated in Fig. 3(c). In spite of the thickness-induced difference in k_o between films *A* and *B*, the same value of E_a of 1.06 ± 0.03 eV for the oxidation of Si-ncls is derived for both. Both theoretical and experimental works have shown that the E_a for O_2 diffusion in SiO_2 is 1.04–1.26 eV.[20,21] Therefore, our result suggests that the oxidation of Si-ncls is controlled by O_2 diffusion.

In summary, we find that the light emission of Er is the most intense in Er-doped SRSO with a Si concentration of ~40% after annealing at 875 °C in an argon ambient, which results in an optimum Si-ncl size. It is indicated that the formation of Si-ncls is controlled by Si diffusion, while their oxidation is controlled by O_2 diffusion. The oxidation reduces the energy transfer and thus the light emission of Er.

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