Structure and luminescence evolution of annealed Europium-doped silicon oxides films

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Abstract: Europium (Eu)-doped silicon oxide films with Eu concentrations from 2.1 to 4.7 at. % were deposited by electron beam evaporation. The Eu related luminescence from the films was found to be sensitive to the evolution of film microstructures at different annealing temperatures. Luminescence centers in the films changed from defects of silicon oxides to $4f^5d^4F^*(S_{22})$ transition of Eu$^{3+}$ after the films annealed in $N_2$ at temperature higher than 800 °C. The evolution of luminescence centers was attributed to the formation of europium silicate (EuSiO$_3$), which was confirmed by x-ray photoelectron spectroscopy, x-ray diffraction, time resolved photoluminescence, and transmission electron microscopy.

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References and links

1. Introduction

As a key component of future monolithic integrating photonic devices, efficient silicon-based light emitters have been attracting significant interest over the past several years [1–3]. Si-nanoclusters (Si-ncs), and rare earth (especially Er) doped silicon-based materials were two promising candidate materials that have enormous potential usefulness in areas of silicon-based light emitters, as well as solid state lighting (SSL) and displays [1,4–6]. Numerous papers concerned with their luminescent/electroluminescent process, including the fabrication of their electroluminescent devices, have been published [7–12]. However, little investigation was conducted into the luminescent properties of Si-based materials doped with rare earth elements other than Er. Recently, bright luminescence of Tb-, Ce-, and Eu-doped silicon oxide/nitride films was reported [8–10]. It was found that the luminescent properties of Ce- and Tb-doped silicon oxide/nitride films were determined by the composition and bonding structure of the host matrix. And it was worth noting that the luminescent properties of Ce-doped silicon oxide films were highly dependent on the film microstructures, which is determined by film composition and annealing conditions [9]. As for the Eu-doped silicon oxide films, few papers have been reported the detail luminescent properties of Europeum doped silicon oxide film, although an implantation, annealing, and electrical operation conditions sensitive multicolor electroluminescence from Eu-implanted SiO2 layers have been investigated [10–12].

In this work, we present the light emission properties of Eu-doped silicon-rich oxide (Eu:SiOx) films deposited by electron beam evaporation (EBE) and followed by annealing at different temperatures. It’s found that the luminescent centers shifted from radiative oxide defects to 4f5d-4f7 transition of Eu3+ when the films are annealed at a temperature higher than 800 °C. The evolution of luminescence centers was attributed to the formation of europium silicate (EuSiOx) in the films when the anneal temperature is higher than 800 °C.

2. Experiments

The mixture sources of highly purified SiO (99.99%) and Eu2O3 (99.99%) powders with Eu concentrations of 30, 40, 50, and 60 at. % were used to evaporate Eu:SiOx films on P-type (100) silicon substrates (1-30 Ω·cm) at 300 °C by EBE. The compositions of the as-deposited films were determined through an energy-dispersive X-ray spectrometer (EDS). The concentration of Eu in the Eu:SiOx films increased corresponding with its concentrations in the evaporated mixture sources as 2.3, 3.1, 3.9 and 4.7 at. %, respectively. After deposition, the films were annealed in the temperature range from 400 to 1100 °C under flowing N2 for 30 to 150 minutes. Photoluminescence (PL) spectra were recorded at room temperature by an Acton SpectraPro 2500i spectrometer using a photomultiplier tube, under the excitation of 325 nm He–Cd laser. The time resolved photoluminescence was detected by a multichannel photon counting system (Edinburg) excited by a pico-second laser of 405 nm. The composition of the samples was studied by X-Ray photoelectron spectroscopy (XPS), performed in a PHI Quantum 2000 Scanning ESCA Microprobe with a monochromatic x-ray source of Al Kα radiation to identify the chemical valence of Eu ions. To detect bulk information, the surface of samples was sputtered by Ar+ ions before every XPS measurement. The microstructures of the samples were examined by transmission electron microscopy (TEM) (JEM-200 CX, 160 kV) with an energy-dispersive X-ray spectrometer.
Furthermore, the Eu:SiO\textsubscript{x} films were characterized by x-ray diffraction (XRD) with graphite monochromatized Cu K\textalpha radiation (\( \gamma = 1.54178 \) Å) by a Rigaku D/max-rA X-ray diffractometer.

3. Results and discussion

![Graph showing luminescence data](image)

Fig. 1. Luminescence of the Eu:SiO\textsubscript{x} films with 3.9 at % Eu as a function of (a) the annealing temperature and (b) the annealing duration at 1100 °C. The inset of Fig. 1(a) shows the decay time of Eu-doped SRO films monitored at the emission peaks corresponding to the sample annealed at different temperatures.

No appreciable PL of Eu\textsuperscript{3+} ions characterized by sharp lines at about 611 nm was observed from Eu:SiO\textsubscript{x} films even after annealing. On the contrary, a broad 400-800 nm emission band from films observed from the as deposited and annealed films. Figure 1 shows the PL of Eu:SiO\textsubscript{x} films with 3.9 at % Eu as a function of the annealing temperature (a) and the annealing duration at 1100 °C (b). The broad 400-800 nm emission band from the films could be attributed to the radiative oxide defects of films since the luminescence from \( ^5\text{D}_0-^7\text{F}_2 \) transitions of Eu\textsuperscript{3+} ions is usually at about 611 nm with sharp lines. However, the evolution of the PL intensity as indicated in Fig. 1(a) was not corresponding to the normal luminescent phenomena of radiative oxide defects, which tend to be eliminated at high temperature anneal in inert ambient due to the formation of nanocrystal silicon as reported in Ref \[4,13\]. In this study, the integrated PL intensity of the samples decreases with annealing temperatures from 400 °C to 800 °C, and then increases greatly at higher temperatures. Moreover, the PL intensity of the samples annealed at temperature higher than 800 °C can be further enhanced by increasing the annealing duration as shown in Fig. 1(b). It can be seen that the PL intensity of the film reaches its highest value after annealing for 90 minutes at 1100 °C. And the PL intensity maintained the same value with increasing annealing time up to 150 minutes (not shown here). Moreover, the decay time of the luminescence from films also evolved as a function of the annealing temperature as shown in the inset of Fig. 1(a), which was monitored at the emission peaks. The decay time of the 1100 °C annealed sample was about 0.8 μs, while that of the as-deposited sample was only 1.1 ns. In fact, the same nanosecond (ns) decay time level was observed in the time resolved photoluminescence measurement for all the Eu-doped samples annealed below 800 °C, while it would be the μs level for the samples after annealing at temperature higher than 800 °C. Therefore, it is considered that the luminescence centers for the Eu-doped films should be changed at higher temperature annealing, resulting in the variety of decay time of emission peaks. The nanosecond decay time obtained from the as-deposited and below 800 °C temperature annealed samples suggests that the luminescence of the as-deposited and below 800 °C temperature annealed samples was originated from radiative oxide defects in the films. And their intensity decreased with the increase of annealing temperatures, agreeing with the previously reported tendency \[4,13\]. However, the microsecond decay time of emission peaks obtained from the films after annealed at temperatures higher than 800 °C suggests their luminescence originated from the transition of energy level of Eu ions. Since the \( ^5\text{D}_0-^7\text{F}_2 \) transitions of Eu\textsuperscript{3+} ions characterized by sharp lines
was not observed in the PL spectra in Fig. 1, it is considered that the luminescence was attributed to the transition of 4f^65d-4f^7(^8S_7/2) of Eu^{2+} characterized by a broad band [14], which was verified by the XPS and XRD and TEM measurements.

![Graph showing XPS spectra of Eu 3d energy level](image)

**Fig. 2.** XPS spectra of the Eu 3d energy level of the Eu-doped SRO samples before and after annealing at 1100 °C for 2 h.

The bonding energy of Si 2p, O 1s, Eu 3d, and Eu 4d core levels of the as-deposited and annealed samples was measured by XPS, respectively. Figure 2 shows the XPS spectra of Eu 3d electrons in the as-deposited and 1100 °C annealed Eu:SiOx films, where two sets of structures corresponding to two different valence states (+2 and +3) of Eu ions can be observed. Each set exhibits simple spin-orbit doublet peaks, which split off 30 eV from each other. The peaks located at 1124 eV, 1133 eV, 1154 eV and 1163 eV can be assigned to Eu^{2+}(5/2), Eu^{3+}(5/2), Eu^{2+}(3/2) and Eu^{3+}(3/2), respectively [14,15]. It can be seen that the Eu atoms existed almost as divalent state in the as-deposited film, which indicates a reduction process took place during the film deposition because Eu ions are trivalent in Eu_2O_3 powder sources. After 1100 °C annealing, the intensity of XPS signal from Eu^{2+} decreases while that of Eu^{3+} increases a litter. It seems that the part of Eu^{2+} transfers to Eu^{3+} during annealing. However, due to the parity-forbidden f-f transitions, the weak absorption bands of Eu^{3+} resulted in the invalid excitation of ^5D_0-^7F_2 transitions by near-ultraviolet region light [16]. Moreover, the luminescence from ^5D_0-^7F_2 transitions of Eu^{3+} ions was never observed in our samples before and after annealing in N_2. Therefore, it is suggested that the Eu^{2+} ions but not the Eu^{3+} ions were responsible for the broad emission band of the samples annealed at temperatures higher than 800 °C. It is generally understood that the 5d electrons of REs strongly interact with the host crystal field. Therefore, the luminescence and peak position of Eu^{3+} varies more strongly with the host material [17,18]. This is also responsible for the luminescent properties of Eu:SiOx films in our studies.

Figure 3 shows the XRD pattern of the Eu-doped SRO films annealed at (a) 400 °C and (b) 1100 °C for 0.5 h in N_2 atmosphere. The diffraction peaks at 52.8° for both the samples originated from the silicon substrates. The broad band in Fig. 3(a) indicates the film was amorphous even after 400 °C annealing. While EuSiO_3 phase was found in the film after 1100 °C annealing according to JCPDS (card number 35-0298), as shown in Fig. 3(b). In fact, we have conducted XRD measurements of all samples annealed at different temperatures, EuSiO_3 phase was found only in the samples at temperatures above 800 °C.
Fig. 3. XRD pattern of the Eu-doped SRO films annealed at (a) 400 °C and (b) 1100 °C for 0.5 h.

Fig. 4. TEM images and their SAED images of the films annealed at (a) 600 °C, (b) 800 °C, (c) 1000 °C, (d) 1100 °C for 0.5h.

The gradual formation of EuSiO$_3$ was confirmed by TEM and EDS measurement. Figure 4 shows the bright field TEM and selected area electron diffraction (SAED) images of the samples annealed at temperatures 600, 800, 1000 and 1100 °C. Figure 4(a) shows a dense film structure for the 600 °C annealed sample, and the SAED image indicates the film is amorphous. In fact, the as-deposited sample and the samples annealed below 600 °C present the same structure. It is clear from the TEM images in Figs. 4(b)-4(d) that nano-size clusters are formed when the samples are annealed at above 800 °C. From the aspect of thermodynamic, it is known that the formation enthalpy of EuO, Eu$_2$O$_3$ and SiO$_2$ at 300 °C is $-575.9$ KJ·mol$^{-1}$, $-1615.5$ KJ·mol$^{-1}$ ($-807.8$ KJ·mol$^{-1}$ per Eu atoms) [19] and $-895.6$ KJ·mol$^{-1}$ [20], respectively. Thus, it is understandable that SiO$_2$ formed firstly in the SRO films due to its lowest formation enthalpy. And EuO was formed simultaneously during the
oxidation-reduction process of SiO$_2$ formation. Indeed, there will be a competition for the combination of oxygen between Si and Eu atoms leading to a local excess of Si that in turn triggers the formation of radiative oxide defects. As efficient luminescent centers, radiative oxide defects emitted the blue range luminescence as shown in Fig. 1 for the as-deposited Eu-doped SiO$_x$ films. And due to these centers tended to be eliminated by high temperature anneal in inert ambient, the luminescence quenched gradually as the annealing temperatures increase from 400 °C to 800 °C. At same time, the Eu$^{2+}$ ions is considered to exist as dispersed dopants in the as-deposited and below 800 °C annealed SiO$_x$ films based the XRD and TEM measurements. Under this case, excited electrons in the energy level of Eu$^{2+}$ ions can nonradiatively relax into the ground state, since the high covalency of the Eu–O bond produces a large offset of the $5d$ configuration [21]. Thus, in the as-deposited or lower temperature annealed samples, the unfavorable transition of 4f$^6$5d-4f$^7(^8S_{7/2})$ of Eu$^{2+}$ ions could not contribute any light emitting although the concentration of Eu$^{2+}$ ions were higher.

However, when the annealing temperature above 800 °C, the transition 4f$^6$5d-4f$^7(^8S_{7/2})$ of Eu$^{2+}$ became favorable due to the EuSiO$_3$ phase. When the annealing temperature reached to 800 °C, a new phase of EuSiO$_3$ formed in the Eu-doped SiO$_x$ films undergoing a chemical reaction to form as followed to reduce the free energy of whole system:

$$\text{EuO}(s) + \text{SiO}_2(s) \rightarrow \text{EuSiO}_3(s)$$

With the increasing of annealing temperature from 800 °C to 1100 °C, more EuSiO$_3$ clusters formed and grew bigger as shown in Figs. 4(c) and 4(d). EDS analysis also convinced that the elemental ratio of O:Si:Eu in the as-deposited film was 66.4:29.7:3.9, while it was 55.9:21.7:22.4 in the clusters for the sample annealed at 1100 °C. The much higher concentration of Eu in the clusters indicates that Eu related clusters have been formed after annealing above 800 °C. In addition, the SAED images in Figs. 4(c) and 4(d) also exhibit several bright rings which further indicate the clusters are crystalline. Companying with the formation and growth of EuSiO$_3$ clusters, the luminescence from the transition of 4f$^6$5d-4f$^7(^8S_{7/2})$ energy level of Eu$^{2+}$ became more and more intense as shown in Fig. 1.

4. Conclusion

In Conclusion, the luminescence properties and microstructures of Eu-doped SiO$_x$ films have been investigated. The luminescence properties were closely related to the evolution of the film microstructures when the samples were annealed. TEM and XRD analyses show the EuSiO$_3$ formation when the annealing temperature was above 800 °C. Accompanying with the EuSiO$_3$ formation, the light emission mechanism shifted from SiO$_x$ host defects to Eu$^{2+}$ in EuSiO$_3$, where the transition between 4f$^5$5d-4f$^7(^8S_{7/2})$ energy level gives intense yellow luminescence.

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