

# Deposition of Europium Oxide on Si and its optical properties depending on thermal annealing conditions

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**Abstract** We investigate the influence of the ambient gas during thermal annealing on the photoluminescence (PL) properties of europium compound thin films on Si substrates. The films were deposited by radio-frequency magnetron sputtering and subsequently annealed in N<sub>2</sub> or O<sub>2</sub> ambient gas by rapid thermal annealing (RTA). The results of X-ray diffraction indicate that the resulting europium compound annealed in N<sub>2</sub> ambient have several silicate phases such as EuSiO<sub>3</sub> and Eu<sub>2</sub>SiO<sub>4</sub> compared to those annealed in O<sub>2</sub> ambient. The spectral results revealed that a broad luminescence associated with Eu<sup>2+</sup> ions, with a maximum intensity at 600 nm and a FWHM of 110 nm, was observed from the thin film annealed at 1000 °C in N<sub>2</sub> ambient. However, a series of narrow PL spectra from Eu<sup>3+</sup> ions were observed from the film annealed in O<sub>2</sub> ambient.

**Keywords** Europium silicate · RF-sputtering · Rapid thermal annealing · Photoluminescence

## 1 Introduction

Rare-earth silicate compounds have shown excellent luminescent properties [1, 2], and due to the thermal stability in optical transitions, they have been applied to lasers and optical fibers. In particular, europium-silicate compounds are materials that show intense and stable luminescence in the visible region. Several works have been done so far regarding the structure and the electrical/optical/magnetic properties of europium-silicate compounds [3–6]. Pure europium silicate is a kind of material known as a magnetic semiconductor. However, the growth of single-phased europium silicate crystals from EuO and SiO<sub>2</sub> generally requires temperatures as high as 1800 °C for Eu<sub>2</sub>SiO<sub>4</sub> [4] and 1400 °C for EuSiO<sub>4</sub> [5]. Due to difficulties in growing pure crystals, a few reports on the applications of europium silicates [6] have been made compared to other europium-doped materials in the visible region. Phosphor doped with Eu<sup>3+</sup> give rise to a strong red emission at approximately 610 nm, and they play an important role in emissive display technology such as plasma display panel (PDP) and field-emission display, and in the lighting industry such as fluorescent lamps [7–9]. In addition, Eu<sup>2+</sup> ions in the host lattice emit UV to red light under UV irradiation. Therefore, Eu<sup>2+</sup> is an attractive phosphor, especially in the blue region, for display technology [10–11].

In this work, we report on the formation and the optical characteristics of europium-compound thin films deposited by using an RF-sputtering method. The samples were annealed in N<sub>2</sub> or O<sub>2</sub> ambient gases by rapid thermal

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annealing (RTA) and were characterized by using X-ray diffraction (XRD) spectroscopy, Auger electron spectroscopy (AES), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The photoluminescence (PL) properties of the europium-compound thin films were investigated.

## 2 Experiments

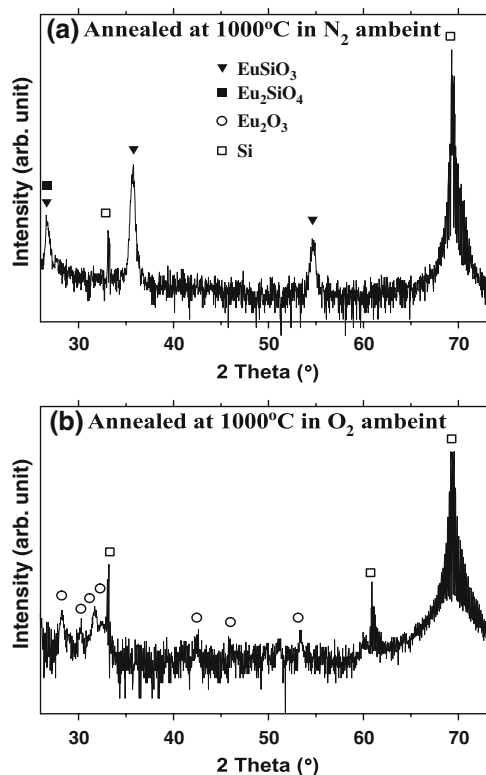
Europium-oxide thin films were prepared on *p*-type Si (100) substrates at room temperature by using an RF sputtering method in Ar gas with a  $\text{Eu}_2\text{O}_3$  (99.95%) target. During the sputtering process, the atmosphere gas pressure was kept at 4.4 mTorr, Ar flow rate was 50 sccm, and the RF power was 70 W. The deposited film thickness was about 0.17  $\mu\text{m}$ . The europium-oxide films were annealed in the temperature range of 1000 °C for 5 min in  $\text{N}_2$  or  $\text{O}_2$  ambient by using RTA.

The films were characterized by using XRD, AES, TEM and XPS. The XRD patterns were measured by using a Rigaku DMAX2500 X-ray diffractometer with  $\text{Cu K}\alpha$  (1.542 Å) radiation as the incident X-ray source to identify the formation of europium silicates based on the literature profiles of the Joint Committee on Powder Diffraction Standards (JCPDS). The sputtered films were depth profiled with AES (PHI-680 Auger Nanoprobe) in order to determine the compositional distribution as a function of depth in the film. The TEM studies were performed using JEOL JEM3010 electron microscope. The XPS measurements were carried out in a Perkin-Elmer Model PHI 5800 ESCA system with a monochromatic X-ray source of  $\text{Al K}\alpha$  (1,486.6 eV). The spectrometer was operated at a constant pass energy of 187.85 eV. An energy step of 0.125 eV was used to acquire the XPS spectra. The PL emission spectra of the samples were obtained using a 325 nm He-Cd laser at room temperature.

## 3 Results

Figure 1 shows the XRD patterns of the europium compound thin films, one of which was annealed in  $\text{N}_2$  ambient and the other was annealed in  $\text{O}_2$  ambient at 1000 °C for 5 min by using RTA. The XRD spectrum of the sample annealed at 1000 °C in  $\text{N}_2$  ambient shows that  $\text{EuSiO}_3$  and  $\text{Eu}_2\text{SiO}_4$  are formed. However, the XRD spectrum of the sample annealed in  $\text{O}_2$  ambient shows a diffraction peak only from the  $\text{Eu}_2\text{O}_3$  in the film as shown in Fig. 1(b). It is evident from these data that oxygen gas might restrain the formation of europium-silicate.

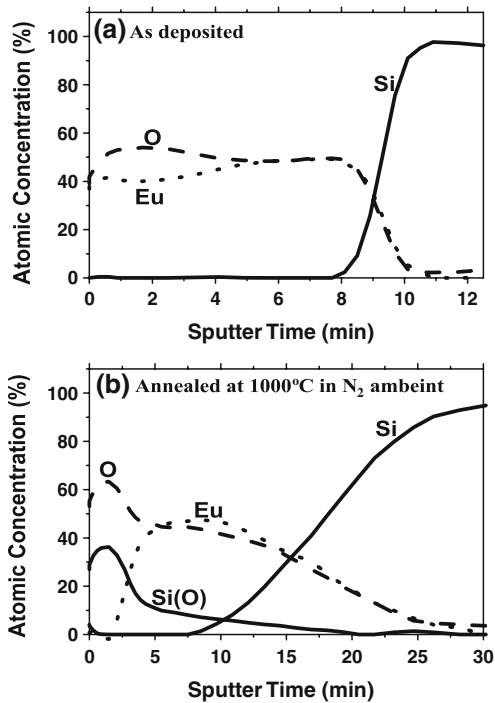
AES depth profiles obtained of europium compound thin films before and after thermal annealing in  $\text{N}_2$  ambient are



**Fig. 1** XRD patterns of the samples annealed at 1000 °C for 5 min in (a)  $\text{N}_2$  ambient and (b)  $\text{O}_2$  ambient

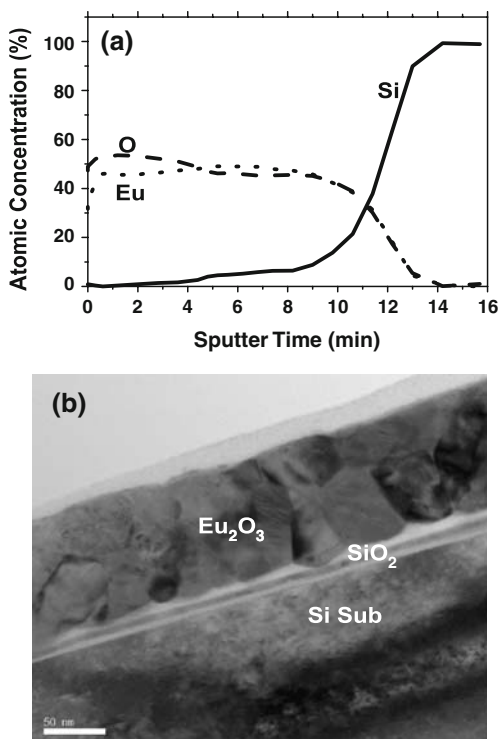
shown in Fig. 2. Compositional distribution of Eu and O of as-deposited thin film is shown in Fig. 2(a). After thermal annealing at 1000 °C in nitrogen ambient, depth profiles of the thin film are changed as shown in Fig. 2(b). The variations of the atomic concentrations show that some Si atoms are diffused into the deposited thin film out of the substrate while Eu and O are diffused into the substrate, leading to a composite film of Eu, O and Si. This indicates that the thin film forms europium-silicates after thermal annealing, which coincides with the XRD results. However, Fig. 3(a) shows different compositional profiles of the thin film after thermal annealing at 1000 °C in oxygen ambient. The thin film is composed of Eu and O. We confirm from the Auger spectrum that europium-silicates are rarely formed in the film during the annealing in  $\text{O}_2$  ambient. It is thought to be due to the  $\text{SiO}_2$  film formed by intermixing of Si coming from the substrate and oxygen coming from the thin film, preventing the intermixing of Si and Eu atoms. It was also verified by transmission electron microscopy. Figure 3(b) shows a cross-sectional TEM image of the interface between the europium oxide layer and silicon substrate in the sample which was annealed in  $\text{O}_2$  ambient. It is seen that the silicon oxide layer at the interface is formed.

The samples have been studied by the XPS to investigate the chemical binding states of the constituent atoms in the thin films. The peaks monitored in these spectra correspond



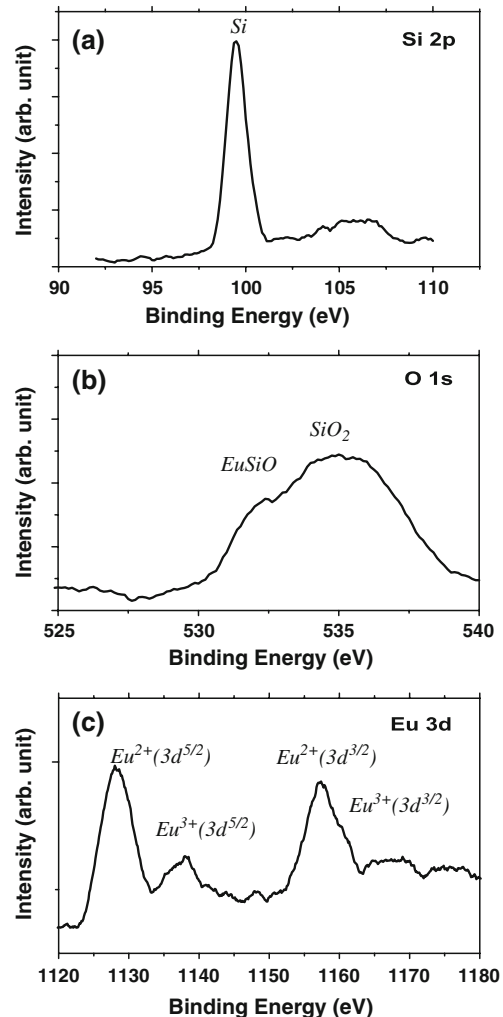
**Fig. 2** Auger depth profiles for (a) the “as deposited” sample, and (b) the sample annealed at 1000 °C for 5 min in N<sub>2</sub> ambient

to Si 2p, O 1s, and Eu 3d core levels. The XPS spectra of the sample annealed in nitrogen ambient are shown in Fig. 4. In the Si 2p spectrum [Fig. 4(a)] the spectral peak located at a binding energy of 99.6 eV is attributed to the



**Fig. 3** (a) Auger depth profile and (b) cross-sectional TEM image for the sample annealed at 1000 °C for 5 min in O<sub>2</sub> ambient

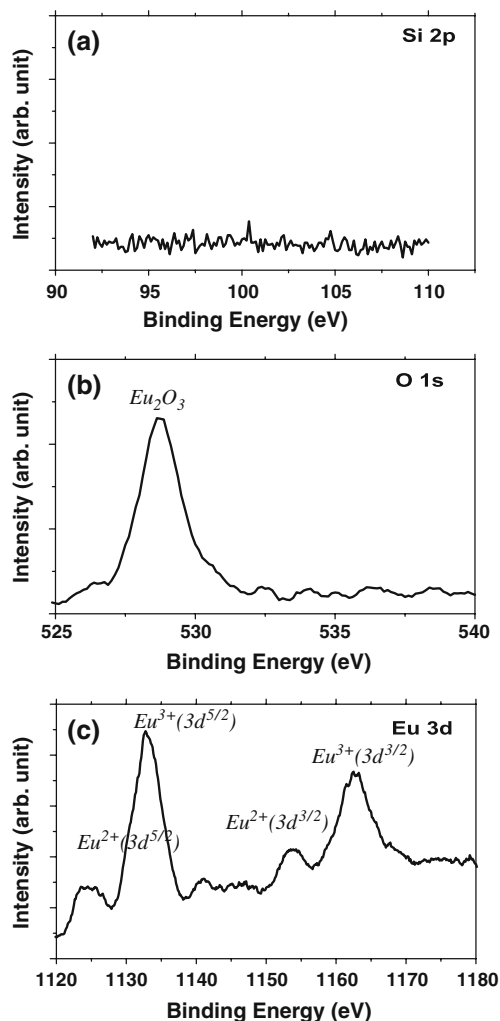
Si. In the O 1s spectrum [Fig. 4(b)] the spectral peak at the binding energy of 531.8 eV is considered to originate from silicate compounds. The main peak at 533.0 eV is due to the contribution of silicon oxide. In the Eu 3d (5/2) spectrum [Fig. 4(c)], both for Eu<sup>2+</sup> and Eu<sup>3+</sup> systems the 3d (5/2) line is split into two compounds (the main peak at a binding energy of 1,128.3 eV corresponds to the divalent europium ions; while the binding energy peak at about 1,137.0 eV originates from the trivalent europium ions together with the contribution of the shake-up of divalent europium ions). The shape and widths of the two components are different, which can be expected due to multiplet splitting for two different final-state 4f configurations. In a similar manner, the strong peak at the binding energy of 1,156.7 eV in the Eu 3d (3/2) spectrum corresponds to the divalent europium ions. No trivalent europium state was observed in the XPS spectra of the sample. The spectrum of the Eu 3d (5/2) core level is similar to the spectrum of typical



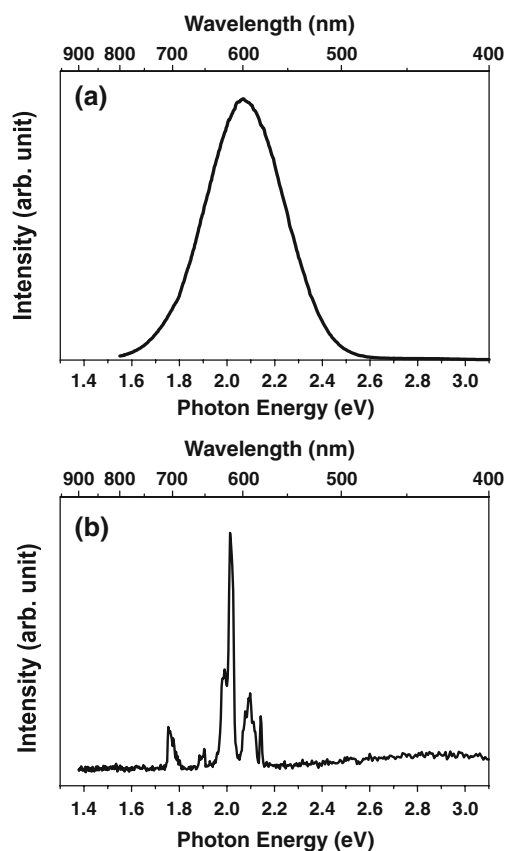
**Fig. 4** XPS spectra of (a) Si 2p, (b) O 1s, and (c) Eu 3d for the samples annealed at 1000 °C for 5 min in N<sub>2</sub> ambient

divalent (Eu metal) europium compounds [12]. Since the shape and the binding energy position of the Eu 3d (5/2) peak agree with those of Eu metal, we can conclude that the Eu ion exists in the divalent state in this film.

The XPS spectra of Si 2p, O 1s and Eu 3d core levels of the sample annealed in oxygen ambient are shown in Fig. 5. However, Si 2p peak is not detected because of its low concentration in the film. In the XPS spectrum of O 1s [Fig. 5(b)] the spectral peak is the contribution from europium oxides at the binding energy of 528.6 eV. No europium silicate peak in Fig. 5(b) exists compared to that of the sample annealed in N<sub>2</sub> ambient [Fig. 4(b)]. In the spectrum of Eu 3d [5/2; Fig. 5(b)] the spectral peak at a binding energy of 1,124.0 eV corresponds to the divalent europium ions, while the binding energy peak at about 1,132.8 eV originates from the trivalent europium ions together with the contribution of the shake-up of divalent europium ions. Obviously, the spectral shapes of the sample



**Fig. 5** XPS spectra of (a) Si 2p, (b) O 1s, and (c) Eu 3d for the samples annealed at 1000 °C for 5 min in O<sub>2</sub> ambient



**Fig. 6** Photoluminescence emission spectra with an excitation wavelength of 325 nm (He-Cd laser) from the samples annealed at 1000 °C for 5 min in (a) N<sub>2</sub> ambient (b) O<sub>2</sub> ambient

annealed in O<sub>2</sub> ambient are different from those of the sample annealed in N<sub>2</sub> ambient. Much strong spectral peak of trivalent europium state was observed in the XPS spectra of the sample annealed in O<sub>2</sub> ambient than that of the sample annealed in N<sub>2</sub> ambient. The spectrum of the Eu 3d (5/2) core level is along with the spectrum of typical trivalent (Eu<sub>2</sub>O<sub>3</sub>) europium compounds [12]. It shows that the shape and the binding energy position of the Eu 3d (5/2) peak agree with those of Eu<sub>2</sub>O<sub>3</sub>.

Figure 6 shows the emission spectra from the europium-compound thin films annealed at different temperature in nitrogen or oxygen ambient. Figure 6(a) shows the broadband PL spectra from the thin films, with the maximum intensity at 600 nm and a full width at maximum of 110 nm, annealed at 1000 °C in nitrogen ambient. This broad spectrum is thought to originate from the 4f<sup>6</sup>5d–4f<sup>7</sup> transition of divalent europium ions Eu<sup>2+</sup> at different sites. The intense and broad luminescent properties of the europium-silicate thin films are expected to have wide applications in areas of passive optical components, like thin film phosphors, and active components, like electroluminescence devices. By contrast, in Fig. 6(b), a series of narrow PL spectra are observed from the film annealed in

O<sub>2</sub> ambient, which is thought to originate from the 5D<sup>J</sup>–7F<sup>J</sup> transition energy of Eu<sup>3+</sup> ions in solid matrices.

#### 4 Conclusion

Europium-compound thin films on silicon substrates were fabricated by radio-frequency magnetron sputtering and subsequent annealing. We investigated the influence of the ambient gas during thermal annealing on the PL properties and studied the films by XRD, AES, TEM and XPS. The results of X-ray diffraction indicated that the resulting europium compound annealed in N<sub>2</sub> ambient have several silicate phases such as EuSiO<sub>3</sub> and Eu<sub>2</sub>SiO<sub>4</sub> compared to those annealed in O<sub>2</sub> ambient. The spectral results revealed that a broad luminescence associated with Eu<sup>2+</sup> ions, with a maximum intensity at 600 nm and a FWHM of 110 nm, was observed from the thin film annealed at 1000 °C in N<sub>2</sub> ambient. However, a series of narrow PL spectra from Eu<sup>3+</sup> ions were observed from the film annealed in O<sub>2</sub> ambient due to the SiO<sub>2</sub> diffusion barrier produced between Eu<sub>2</sub>O<sub>3</sub> and Si substrates.

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