

Structural and luminescence properties of undoped and Eu-doped SiOC thin films

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2014 IOP Conf. Ser.: Mater. Sci. Eng. 56 012009

(<http://iopscience.iop.org/1757-899X/56/1/012009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 131.155.2.68

This content was downloaded on 10/07/2014 at 11:19

Please note that [terms and conditions apply](#).

Structural and luminescence properties of undoped and Eu-doped SiOC thin films

G Bellocchi^{1,2}, G Franzò¹, S Boninelli¹, M Miritello¹, T Cesca³, F Iacona¹
and F Priolo^{1,2}

¹ MATIS IMM CNR, via Santa Sofia 64, 95121 Catania, Italy.

² Dipartimento di Fisica e Astronomia, Università di Catania, via Santa Sofia 64, 95121 Catania, Italy.

³ Dipartimento di Fisica e Astronomia, Università di Padova, Via F. Marzolo 8, 35131 Padova, Italy

E-mail: gabriele.bellocchi@ct.infn.it

Abstract. We report on the investigation of the structural, chemical and optical properties of undoped and Eu-doped SiOC thin films synthesized by RF magnetron sputtering. Undoped SiOC exhibits an intense room temperature luminescence at ~ 500 nm, and an important contribution to this signal is due to the presence of Si-C bonds. Moreover, when inserted in a SiOC matrix, Eu ions have a higher solid solubility with respect to pure SiO₂; as a consequence, we observe a reduction of Eu clustering phenomena. Furthermore the reducing properties of SiOC, related to the presence of C, allow the prevalence of the Eu²⁺ emission over the Eu³⁺ one. Through the control of the annealing conditions it is possible to obtain an intense light emission at 440 nm. These properties propose SiOC as a novel and efficient Si-based host matrix for Eu and open the way to promising perspectives of Eu-based materials for photonic applications and LED fabrication.

1. Introduction

The realization of an efficient Si-based light source represents one of the most relevant issues for the scientific community currently working in the field of photonics. The main characteristics required for this source are high efficiency at room temperature, tunability in a wide wavelength range, easy integration in highly compact Si microphotonic devices. In this framework, a leading role is played by rare earth (RE) doped materials. RE doping of insulating or semiconducting host matrices has been recognized as a powerful method to provide intense luminescence signals spanning in a wide wavelength range, opening the way to several new applications for Si-based materials in the field of photonics [1]. Among the RE ions, a considerable attention has been devoted to Eu due to the coexistence of both divalent and trivalent oxidation states. Indeed Eu³⁺ and Eu²⁺ ions can act as efficient emitting centers in the visible region and their bright emission is widely employed in phosphors used in plasma display panels and in solid-state lighting [2]. Divalent Eu ions exhibit a very strong emission originating from dipole-allowed $4f^65d \rightarrow 4f^7$ transitions, favorite with respect to that of Eu³⁺ ions, whose intra 4f-shell transition, being electric dipole-forbidden, leads to a less intense luminescence [3]. On the other hand, applications of Eu in Si photonics require the availability of Eu-containing thin films compatible with CMOS technology. Several papers have studied the optical properties of Eu-doped SiO₂ films [4-7], but the low Eu solid solubility in silica (cluster formation occurs for Eu concentrations larger than 10^{18} cm⁻³ [8-10]) seems to seriously limit its perspectives in photonics.

A different approach to obtain efficient light emission from a Si-based material is represented by Si oxycarbide (SiOC), which has been extensively studied for its intense photoluminescence (PL) emission in the visible range [11-17]. Furthermore, it has been also evidenced that SiOC can be an interesting host material for RE ions, including Er [18] and Eu [10,19].



In this paper we will study the optical properties of SiOC and Eu-doped SiOC thin films synthesized by RF magnetron sputtering. It will be demonstrated that the temperature and the environment of the thermal annealing process following the deposition can improve the PL emission in the visible region from both materials. The mechanisms of the SiOC-Eu interaction, leading to a very bright visible emission assigned to Eu^{2+} ions, will be also elucidated. The relevance of the above data for the realization of an efficient Si-based light source, which can be of great interest for applications in photonics as well as in solid-state lighting, will be addressed.

2. Experimental

SiOC and Eu-doped SiOC thin films, ~ 190 nm thick, have been synthesized by using an UHV RF magnetron sputtering system. The chamber base pressure was $\sim 1 \times 10^{-9}$ mbar. The deposition has been obtained by co-sputtering of 4" diameter, water-cooled SiO_2 and SiC targets (in the case of SiOC samples), and SiO_2 , SiC and Eu_2O_3 targets (in the case of Eu-doped SiOC samples). C concentration has been fixed at 5 at.% in both doped and undoped SiOC films, while Eu concentration was $1.5 \times 10^{20} \text{ cm}^{-3}$. The films were deposited on Si substrates kept at 400°C in a 5×10^{-3} mbar Ar atmosphere. After deposition the films were thermally treated at temperatures ranging from 750 to 1000°C for 1 h in N_2 atmosphere.

Transmission electron microscopy (TEM) analysis in bright field (BF) mode, performed by a 200 kV Jeol 2010 microscope, was used to investigate the film structure. The atomic composition of the films was studied by Rutherford backscattering spectrometry (RBS), using a 2 MeV He^+ beam in random configuration, with a detector placed at 165° with respect to the incident beam.

PL measurements were performed by pumping with the 325 nm line of a He-Cd laser. The pump power was about 3 mW and the laser beam was chopped through an acousto-optic modulator at a frequency of 55 Hz. The PL signal was analyzed by a single grating monochromator and detected with a photomultiplier. Spectra were recorded with a lock-in amplifier using the acousto-optic modulator frequency as a reference. Photoluminescence excitation (PLE) measurements in the 250-475 nm range were performed by using a FluoroMax spectrofluorometer by Horiba. All the spectra have been measured at room temperature and corrected for the system spectral response.

3. Results and discussion

The room temperature PL spectra of as-deposited and thermally annealed SiOC films are reported in figure 1.

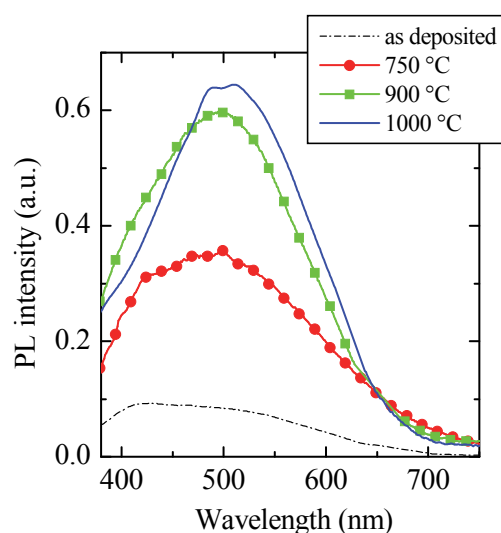


Figure 1. Room temperature PL spectra of SiOC films as deposited and annealed in N_2 ambient in the temperature range $750 - 1000^\circ\text{C}$.

These measurements show that SiOC films are efficient light emitters at room temperature in the visible region. It is evident that the temperature of the thermal treatment strongly influence the PL properties. Spectra of samples annealed at high temperatures are generally red-shifted and sharper with respect to those of the as-deposited or low temperatures annealed samples. More in detail, the spectrum of the as-deposited sample appears quite broad, suggesting the presence of multiple luminescent centers. After the annealing process, by increasing the temperature, a component at 510 nm becomes predominant, although it is still visible a shoulder at around 400 nm. Since in annealed samples a partial ordering of the film structure occurs (leading to the formation of optically active Si-C bonds and to the quenching of defects), the evidence that the system becomes more optically efficient at higher temperatures suggests that the PL at 510 nm can be assigned to Si-C bonds, while the PL at 400 nm is due to defect centers.

As previously reported [10,19-21], SiOC can be also a very suitable host matrix for optically active rare earth ions. In particular, Eu precipitation, which strongly limits the optical activity of Eu ions embedded in the more conventional SiO₂ matrix, can be reduced when incorporated in SiOC.

Figure 2 reports the BF XTEM images relative to Eu-doped SiOC films annealed at 900 °C (a) and 1000 °C (b) in N₂ ambient. The Eu concentration is $1.5 \times 10^{20} \text{ cm}^{-3}$ for both samples. From the analysis of the figure it is evident that when SiC is added to the SiO₂ matrix, in spite of the fact that the Eu concentration is about 2 orders of magnitude higher than the threshold for Eu precipitation in pure SiO₂, Eu precipitates are detected only at the sample surface.

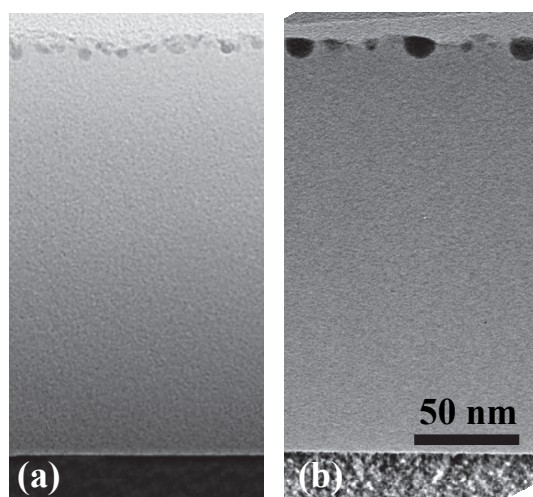


Figure 2. BF XTEM images relative to Eu-doped SiOC layers annealed at 900 °C (a) and 1000 °C (b) in N₂ ambient. The Eu concentration is $1.5 \times 10^{20} \text{ cm}^{-3}$ in both samples.

In order to understand why Eu precipitates are formed at the sample surface, we have performed RBS measurements to follow the evolution of the Eu profile with the annealing temperature. In figure 3, the comparison between the Eu concentration profiles relative to an as-deposited Eu-doped SiOC film (black line) and those corresponding to thermally annealed samples (900 °C, red line); 1000 °C, blue line) are shown. The data show an uniform Eu concentration in as-deposited film, while after annealing Eu surface segregation occurs and becomes more evident with increasing temperature. The surface Eu concentration peaks account for about 10% (at 900 °C) and 65% (at 1000 °C) of the total Eu concentration. In spite of the segregation process, a high Eu content ($\sim 1.5 \times 10^{20} / \text{cm}^3$ at 900 °C and $5.5 \times 10^{19} / \text{cm}^3$ at 1000 °C), well above Eu solid solubility in pure SiO₂, remains dissolved in the SiOC matrix, from 50 nm below the surface, without precipitating.

Furthermore, SiOC is also able to induce the $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction, providing a simple method to obtain high concentrations of the most optically efficient Eu species (Eu^{2+}). Figure 4 reports the room temperature PL spectra of undoped and Eu-doped SiOC samples, treated at 1000 °C in N₂. The Eu-

doped SiOC (blue line) exhibits a very intense PL band, centered at about 440 nm, due to the $4f^65d \rightarrow 4f^7$ transitions of Eu^{2+} ions, massively formed owing to a reduction reaction involving the C atoms of the SiOC matrix [12]. No sharp lines associated to Eu^{3+} PL emission are detected. The PL signal at 440 nm is 10 times higher than that measured in the undoped SiOC film (red line).

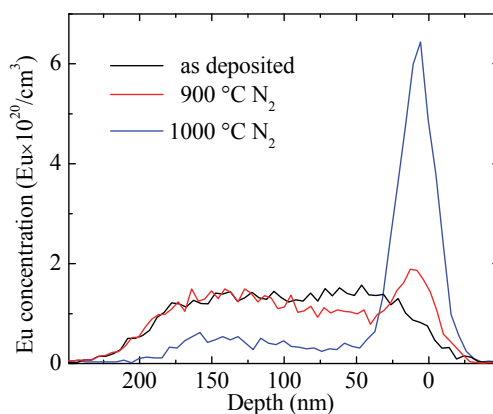


Figure 3. Eu concentration profiles, measured by RBS, relative to Eu-doped SiOC films as-deposited (black) and annealed in N_2 ambient at 900 (red) and 1000 °C (blue).

The integrated PL intensity measured in both undoped and Eu-doped SiOC as a function of the annealing temperature (not shown) shows a similar trend, probably due to the fact that Eu^{2+} ions are formed owing to a redox reaction involving Eu^{3+} ions and Si-C bonds (which give the main contribution to the PL signal of undoped SiOC films annealed at high temperature in N_2). Indeed, by increasing the annealing temperature, the concentration of Si-C bonds increases and, as a consequence, the number of emitting Eu^{2+} ions, formed through the redox reaction, becomes higher.

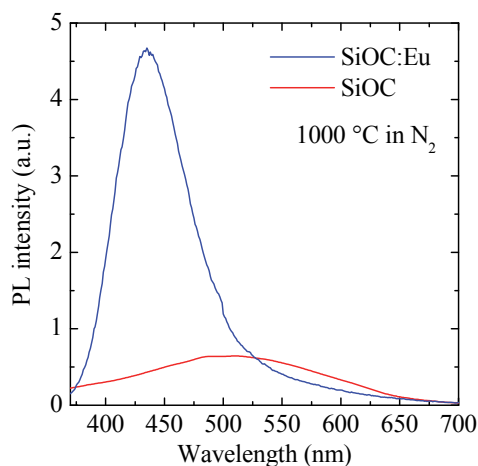


Figure 4. Room temperature PL spectra for Eu-doped SiOC (blue line), and undoped SiOC (red line) films, annealed at 1000 °C in N_2 . Eu concentration of the doped film is $1.5 \times 10^{20} \text{ cm}^{-3}$.

Figure 5 reports the room temperature PLE spectra of undoped and Eu-doped SiOC with an Eu concentration of $1.5 \times 10^{20} \text{ cm}^{-3}$, obtained by integrating the PL spectra measured by exciting in the 260-370 nm wavelength range. PLE curve of Eu-doped SiOC (blue line and triangles) exhibits a maximum at 250 nm followed by a monotonic decrease for longer excitation wavelengths. PLE spectrum of undoped SiOC (red line and circles) shows a maximum at 260 nm and monotonically decreases by increasing the excitation wavelength with a trend similar to that of Eu-doped SiOC. From

the comparison with the PLE spectrum of an Eu^{2+} silicate (green line and squares) [22], reported in the same figure, it is evident that the PL efficiency of Eu-doped SiOC is strongly enhanced for wavelengths ≤ 300 nm; indeed the Eu^{2+} silicate exhibits a maximum at about 350 nm and it is remarkably less efficient for shorter excitation wavelengths, in agreement with literature data concerning very different Eu^{2+} -containing systems [23-25].

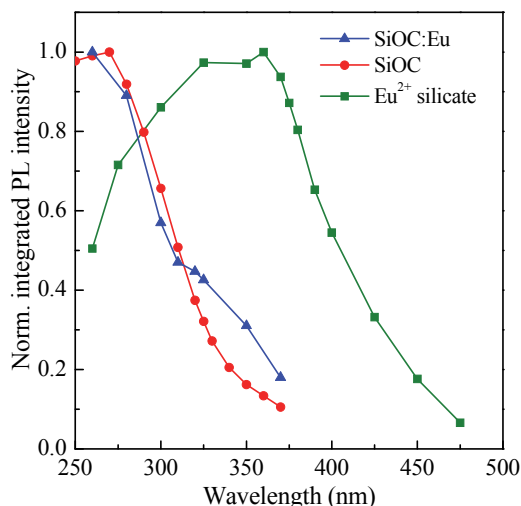


Figure 5. Comparison of the room temperature PLE spectra of undoped and Eu-doped SiOC films and of an Eu^{2+} silicate. The spectra are normalized to their maximum value.

It is possible to conclude that the SiOC matrix has an active role in the optical properties of Eu-doped SiOC. We can reasonably exclude that this role consists in the presence of a SiOC emission, since the spectral shape shown in figure 4 for an excitation wavelength of 325 nm does not appreciably change by changing the excitation wavelength, even by using the wavelengths which maximize a possible SiOC emission. We could therefore suppose the existence of an energy transfer mechanism, in which the very efficient absorption properties of SiOC in the short wavelength region are exploited to transfer the excitation energy to the Eu^{2+} ions, by enhancing their PL efficiency under excitation at short wavelength.

4. Conclusions

The intense visible emission of SiOC layers has been studied and its dependence on the parameters of the thermal annealing process elucidated. In particular, the presence of different emitting centers, and in particular one related to the presence of Si-C bonds, have been identified.

Although the emission of SiOC is bright enough to be considered potentially interesting for applications in photonics (as the active medium in Si-based light emitting devices) or in lighting technology, this material has been found to be even more promising as a host matrix for optically active Eu ions. Indeed a SiOC matrix is able to efficiently promote the $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction. Furthermore, TEM and RBS data have demonstrated that Eu ions in SiOC are characterized by an enhanced solubility; this peculiarity leads to a strongly reduced Eu precipitation, and, as a consequence, to a very intense and stable light emission at about 440 nm from Eu^{2+} ions, 10 times higher with respect to undoped SiOC. We have also found evidences of the occurrence of an energy transfer mechanism between the matrix and the Eu^{2+} ions which, by increasing the efficiency of photon absorption for excitation wavelengths shorter than 300 nm, further contributes to increase the optical efficiency of Eu-doped SiOC layers. These properties open the way to new promising perspectives for the application of Eu-doped materials in photonics and LED fabrication.

References

- [1] Franzò G, Vinciguerra V and Priolo F 1999 *Appl. Phys. A: Mater. Sci. Process.* **69** 3-12
- [2] Ye X, Zhuang W, Hu Y, He T, Huang X, Liao C, Zhong S, Xu Z, Nie H and Deng G 2009 *J. Appl. Phys.* **105** 064302
- [3] Blasse G and Grabmaier B C 1994 *Luminescent Materials* (Berlin: Springer Verlag)
- [4] Li D, Zhang X, Jin L, and Yang D 2010 *Opt. Express* **18** 27191-27196
- [5] Rebohle L, Lehmann J, Prucnal S, Kanjilal A, Nazarov A, Tyagulskii I, Skorupa W, and Helm M 2008 *Appl. Phys. Lett.* **93** 071908
- [6] Rebohle L, Lehmann J, Prucnal S, Nazarov A, Tyagulskii I, Tyagulskii S, Kanjilal A, Voelskow M, Grambole D, Skorupa W and Helm M 2009 *J. Appl. Phys.* **106** 123103
- [7] Prucnal S, Sun J M, Skorupa W and Helm M 2007 *Appl. Phys. Lett.* **90** 181121
- [8] Afify N D and Mountjoy G 2009 *Phys. Rev. B* **79** 024202
- [9] Laegsgaard J 2002 *Phys. Rev. B* **65** 174114
- [10] Boninelli S, Bellocchi G, Franzò G, Miritello M and Iacona F 2013 *J. Appl. Phys.* **113** 143503
- [11] Seo S-Y, Cho K-S and Shin J H 2004 *Appl. Phys. Lett.* **84** 717-719
- [12] Gallis S, Nikas V, Suhag H, Huang M and Kaloyeros A E 2010 *Appl. Phys. Lett.* **97** 081905
- [13] Guo Y P, Zheng J C, Wee A T S, Huan C H A, Li K, Pan J S, Feng Z C and Chua S 2001 *J. Chem. Phys. Lett.* **339** 319-322
- [14] Perez-Rodriguez A, Gonzalez-Varona O, Garrido B, Pellegrino P, Morante J R, Bonafos C, Carrada M and Claverie A 2003 *J. Appl. Phys.* **94** 254-262
- [15] Ishikawa Y, Vasin A V, Salonen J, Muto S, Lysenko V S, Nazarov A N, Shibata N and Lehto V-P 2008 *J. Appl. Phys.* **104** 083522
- [16] Ding Y and Shirai H 2009 *J. Appl. Phys.* **105** 043515
- [17] Vasin A V, Ishikawa Y, Shibata N, Salonen J, and Lehto V-P 2007 *Jpn. J. Appl. Phys.* **46** L465-L467
- [18] Gallis S, Huang M and Kaloyeros A E 2007 *Appl. Phys. Lett.* **90** 161914
- [19] Zhang Y, Quaranta A and Soraru G D 2004 *Opt. Mater.* **24** 601-605
- [20] Gallis S, Huang M, Efstathiadis H, Eisenbraun E, Kaloyeros A E, Nyein E E and Hommerich U 2005 *Appl. Phys. Lett.* **87** 091901
- [21] Seo S-Y and Shin J H 2004 *Appl. Phys. Lett.* **84** 4379
- [22] Bellocchi G, Franzò G, Iacona F, Boninelli S, Miritello M, Cesca T and Priolo F 2012 *Opt. Express* **20** 5501-5507
- [23] Zhang Q, Liu X, Qiao Y, Qian B, Dong G, Ruan J, Zhou Q, Qiu J and Chen D 2010 *Opt. Mater.* **32** 427-431
- [24] Kishimoto Y, Zhang X, Hayakawa T and Nogami M 2009 *J. Lumin.* **129** 1055-1059
- [25] Qiao Y, Chen D, Ren J, Wu B, Qiu J, and Akai T 2008 *J. Appl. Phys.* **103** 023108