The formation of light emitting cerium silicates in cerium-doped silicon oxides

Jing Li, Othman Zalloum, Tyler Roschuk, Chenglin Heng, Jacek Wojcik, and Peter Mascher[a)]

Department of Engineering Physics and Centre for Emerging Device Technologies, McMaster University, Hamilton, Ontario L8S 4K1, Canada

(Received 11 August 2008; accepted 15 December 2008; published online 9 January 2009)

Cerium-doped silicon oxides with cerium concentrations of up to 0.9 at. % were deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition. Bright cerium related photoluminescence, easily seen even under room lighting conditions, was observed from the films and found to be sensitive to film composition and annealing temperature. The film containing 0.9 at. % Ce subjected to anneal in N_2 at 1200 °C for 3 h showed the most intense cerium-related emission, easily visible under bright room lighting conditions. This is attributed to the formation of cerium silicate [$Ce_2Si_2O_7$ or $Ce_{4.667}(SiO_4)_3O$], the presence of which was confirmed by high resolution transmission electron microscopy. © *2009 American Institute of Physics*.
[DOI: 10.1063/1.3067871]

Cerium (Ce)-doped silicon materials are attracting increasing interest due to their potential usefulness in silicon-based light emitting devices for integrated optoelectronics.[1–4] The conventional synthesis method of these luminescent materials is the sol-gel method. This method suffers, however, from several drawbacks, such as porous final products and luminescence quenching effects for Ce concentrations over 0.5 mol %.[5–8] Most importantly, the technique is incompatible with standard Si processing technology. Recently, it has been shown that through the synthesis of rare-earth (RE) silicate, more intense RE emission can be obtained. It was suggested that as a major component of the silicate, the RE concentration can be several orders of magnitude higher than as a dopant, giving rise to a larger number of luminescence centers.[9–12] However, there are very few reports on Ce silicates, and most of them employed high temperature diffusion at the interface of a two-layer structure, such as cerium oxide-silicon oxide (CeO_2-SiO_2) or cerium oxide-silicon (CeO_2-Si). One consequence of this method is that the Ce emission can only be obtained for very high annealing temperatures >1000 °C since Ce ions exist as a component of CeO_2 for lower annealing temperatures, which is optically inactive.

In this work, we report the results of studies of Ce-doped silicon oxide ($Ce:SiO_x$) films deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD), which is compatible with standard Si processing technology. A light emitting Ce silicate phase was formed in the films after anneal at 1200 °C, while Ce-related photoluminescence (PL) was also observed for annealing temperatures from 700 to 1100 °C.

$Ce:SiO_x$ films were prepared on *n*-type (100) silicon wafers using an ECR-PECVD system adapted for the *in situ* incorporation of Ce, using Ar and O_2 as plasma gases, SiH_4 as the Si source, and $Ce(tmhd)_4$ or tetrakis (2,2,6,6-teramethyl-3,5-heptanedionato)Ce(IV) as the Ce source. The details of the deposition system have been described elsewhere.[12,13] The thicknesses of the films were determined by *ex situ* ellipsometry and varied from 80 to 110 nm. The compositions of the as-deposited films were determined through Rutherford backscattering spectrometry (RBS) using a 1.0 MeV He^+ beam. A representative RBS spectrum for a sample containing 32 at. % Si and 0.9 at. % Ce is given in Fig. 1. For the samples in this study, the Si content is about 32 at. % and the Ce content ranges from 0.01 to 0.9 at. %. After deposition, the films were annealed in the temperature range from 700 to 1200 °C under flowing N_2 for 1 or 3 h. PL measurements were conducted at room temperature using a 325 nm He–Cd laser. A full description of the charge coupled device-based PL system and the data correction methodology is given elsewhere.[14] The integrated PL intensities of the films were normalized to a film thickness of 100 nm, assuming that the PL intensity scales linearly with thickness. Emission power intensity was measured by using a universal fiber detector and an optical power meter. Film microstructure was studied using a JEOL 2010F field emission gun transmission electron microscope (TEM) operating at 200 keV.

No appreciable PL was observed from the as-deposited samples since in the precursor phase Ce exists as tetravalent ions, which are optically inactive due to the lack of available

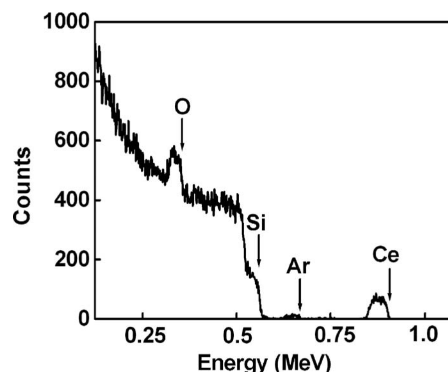

FIG. 1. A representative RBS spectrum for a sample containing 32 at. % Si and 0.9 at. % Ce. The surface energies of Ce, Ar, Si, and O are indicated by arrows.

[a)]Electronic mail: mascher@mcmaster.ca.

 © 2009 American Institute of Physics

Downloaded 09 Jan 2009 to 160.36.192.110. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

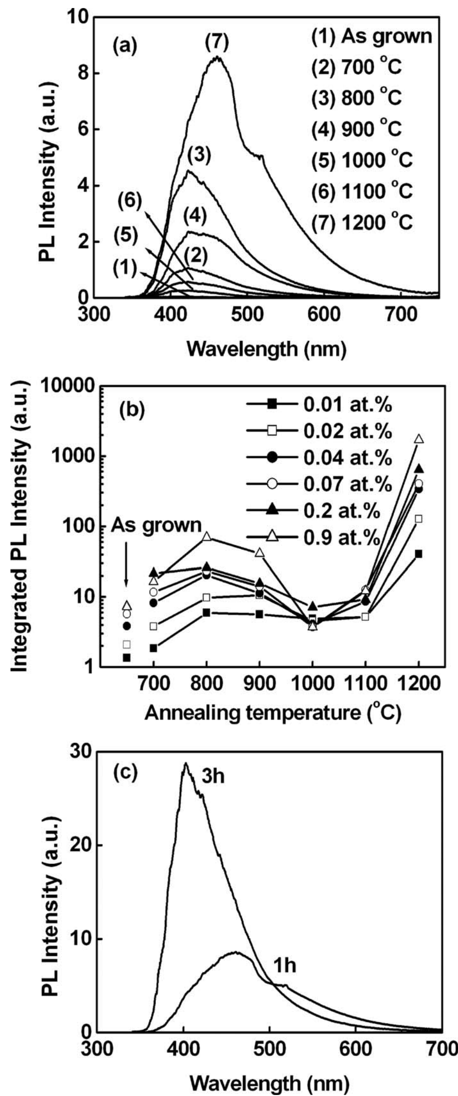

FIG. 2. (a) PL spectra from a sample containing 32 at. % Si and 0.9 at. % Ce as-grown and after 1 h N_2 anneal at various temperatures. (b) The integrated PL intensity in the range of 350–700 nm as a function of annealing temperature for samples containing 32 at. % Si and 0.01–0.9 at. % Ce. The data of the as-grown samples are also given. (c) The PL spectra of the sample containing 0.9 at. % Ce under N_2 anneal at 1200 °C for 1 and 3 h, respectively.

$4f$ electrons. Figure 2(a) shows the broad 350–700 nm emission from an annealed sample containing 32 at. % Si and 0.9 at. % Ce. According to the emission wavelength, both Ce^{3+} ions and radiative oxide defects could be responsible for the broad emission band.[15,16] However, radiative oxide defects tend to be eliminated during anneal in inert ambient, so the related PL intensity should decrease dramatically, while in this study, the PL intensity is enhanced significantly after anneal. In addition, the PL intensity was found to be strongly correlated with Ce concentrations. Therefore, Ce^{3+} ions appear as the major contributor. The observed broad emission band was attributed to be the superposition of two emission peaks that correspond to the $5d$-$4f$ transitions of Ce^{3+} from the energy state $^2D_{3/2}$, to the lower energy states $^2F_{7/2}$ and $^2F_{5/2}$, respectively.[17–20]

As is shown in Fig. 2(b), regardless of the different Ce concentrations of different samples, the integrated PL intensity in the range from 350 to 700 nm increases with annealing temperature up to 800 °C, reaching its second highest value, then decreases at higher annealing temperatures until 1100 °C, followed by a significant enhancement at 1200 °C, reaching the highest value. The PL intensity of the film containing 0.9 at. % Ce can be further enhanced by about three times by increasing the annealing duration to 3 h [Fig. 2(c)]. The emission from this sample was so intense that it can be easily observed under very bright room lighting conditions. By referencing its PL spectrum to a calibrated black body emitter, the collected PL power density was determined as 1.37 W/cm^2. Considering the small thickness of the sample (80 nm) and the low input power (15 mW), this emission intensity is quite impressive.

It is generally understood that annealing under an inert or reducing ambient may help to remove oxide defects and facilitate the conversion from optically inactive Ce^{4+} to Ce^{3+}.[8] This is responsible for the enhancement of the Ce emission at 700 and 800 °C. The quenching of the emission in the range from 800 to 1000 °C can be explained by the precipitation of Ce ions, with the sample having a higher Ce concentration showing a steeper decrease with increasing annealing temperature. It appears that Ce ions exist as dispersed dopants for annealing temperatures below 1100 °C and have a low concentration limit in silicon oxide. The significant enhancement of the Ce emission after annealing at 1200 °C can be explained by the gradual formation of cerium silicate in the film, which was verified by high resolution TEM (HR-TEM).

Figure 3(a) shows a TEM image of a cross-sectional sample containing 32 at. % Si and 0.9 at. % Ce annealed in flowing N_2 at 1200 °C for 1 h. The image shows the distinct regions of the glue layer, film, and substrate, respectively. The worm shaped gray strips containing black particles were observed to be dispersed in the glue layer. X-ray energy dispersive spectroscopy (XEDS) spot analysis was conducted for four selected spots, and the presence of Ce was only detected from the dark particle (SP4) as shown in Fig. 3(b). Figures 3(d) and 3(e) show the XEDS line-scan analysis result for the film-substrate interface region, in which Ce was found to be accumulated within an 8 nm thick layer near the Si substrate.

The RBS spectrum from an as-deposited sample containing 32 at. % Si and 0.9 at. % Ce shows a relatively uniform distribution of Ce, indicating the successful incorporation of this high concentration of Ce throughout the film. However, high temperature annealing may provide enough energy for Ce ions to diffuse and accumulate near the interfaces, forming Ce abundant layers. The interface stresses between Ce abundant and deficient areas might cause the delamination. It is possible that the delaminated layers near the film surface were separated and pushed into the glue layer during the TEM sample preparation process, eventually forming the dispersed gray strips and dark particles in Fig. 3(a).

Figure 3(c) shows the magnified HR-TEM lattice image of SP4, in which the crystalline structure is clearly visible. The lattice spacing of the structure is 0.274 nm, in agreement with the reported value for $Ce_2Si_2O_7$ and $Ce_{4.667}(SiO_4)_3O$ and is considered as direct evidence for the formation of Ce silicate.[5] Since Ce is a major component of Ce silicate, a much higher concentration of effective luminescence centers leads to the significant enhancement of the PL intensities. This hypothesis is consistent with the trend observed in Fig. 2(b): the PL intensities at 1200 °C increase almost linearly

Downloaded 09 Jan 2009 to 160.36.192.110. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

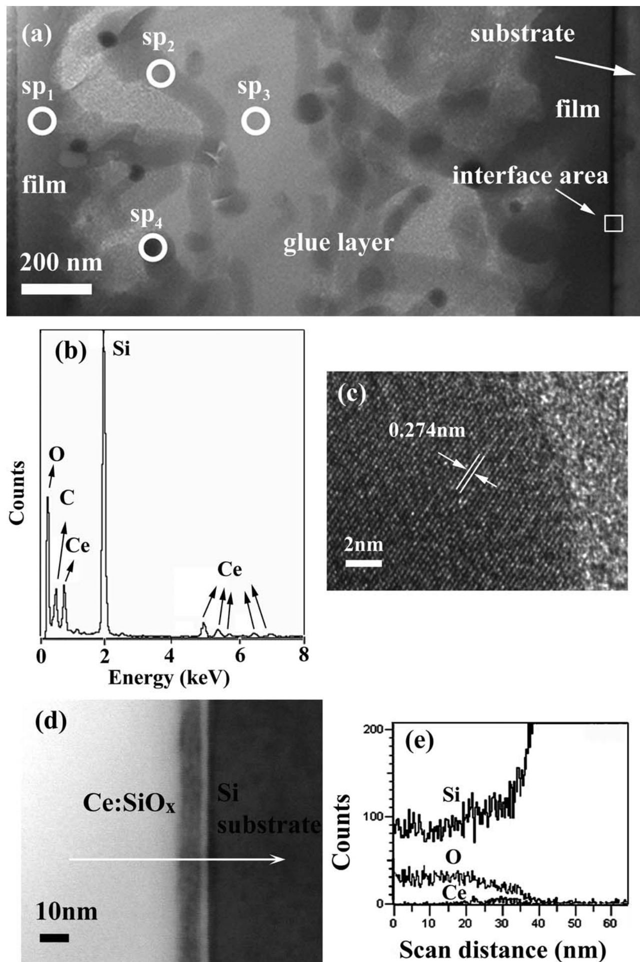

FIG. 3. (a) HR-TEM cross-sectional image of a sample containing 32 at. % Si and 0.9 at. % Ce after 1 h N_2 anneal at 1200 °C, which shows four selected spots for XEDS elemental spot analysis and one area for XEDS elemental line-scan analysis. (b) Elemental analysis result of SP4. (c) Magnified HR-TEM image for spot SP4 that shows the lattice profile. (d) Magnified HR-TEM image of the film-substrate interface area, in which the arrow indicates the line-scan direction and distance. (e) XEDS elemental line-scan analysis result.

with increasing Ce concentration. No significant quenching is observed in samples with Ce concentrations of up to 0.9 at. %.

In conclusion, Ce-doped silicon oxide thin films with Ce concentrations of up to 0.9 at. % were successfully prepared. The PL properties of the films are highly dependent on the film microstructure, which is determined by film composition and annealing conditions. It was found that samples with high Ce concentrations emit the strongest UV/blue light after being annealed at 1200 °C for 3 h due to the formation of a cerium silicate at the substrate-film interface. In the near future, the electronic structure of the material will be studied by x-ray-excited optical luminescence and absorption spectroscopy to better understand the luminescence mechanism. The deposition and annealing conditions will be optimized to further enhance the Ce emission intensity.

The authors sincerely thank Dr. Carla Miner (Group IV Semiconductor Inc.) for providing unpublished luminescence intensity data, and acknowledge W. Lennard and J. Hendriks at the University of Western Ontario, and J. Garrett, G. Pearson, J. Huang, F. Pearson, and H. Zhang at McMaster University for their technical support. This work has been cofunded by the Ontario Photonics Consortium (OPC), the Ontario Centres of Excellence (OCE), the Centre for Photonics Fabrication Research (CPFR), and the Canadian Institute for Photonic Innovation (CIPI). Financial and technical support from Group IV Semiconductor Inc. (Kanata, Ontario), Johnsen-Ultravac (Burlington, Ontario), and the Canadian Centre for Electron Microscopy (CCEM) is gratefully acknowledged.

[1]A. J. Kenyon, Prog. Quantum Electron. **26**, 225 (2002).
[2]D. J. Lockwood, *Light Emission in Silicon: From Physics to Devices* (Academic, USA, 1998).
[3]G. T. Reed and A. P. Knights, *Silicon Photonics–An Introduction* (Wiley, USA, 2004).
[4]H. Rong, A. Liu, R. Jones, O. Cohen, D. Hak, R. Nicolaescu, A. Fang, and M. Paniccia, Nature (London) **433**, 292 (2005).
[5]Q. Guodong, W. Minquan, W. Mang, F. Xianping, and H. Zhanglian, J. Lumin. **75**, 63 (1997).
[6]Y. Zhou, Y. L. Lam, S. S. Wang, H. L. Liu, C. H. Kam, and Y. C. Chan, Appl. Phys. Lett. **71**, 587 (1997).
[7]R. Reisfeld H. Mintia, A. Patra, D. Ganguli, and M. Gaft, Spectrochim. Acta, Part A **54**, 43 (1998).
[8]G. Q. Xu, Z. X. Zheng, W. M. Tang, and Y. C. Wu, J. Lumin. **124**, 151 (2007).
[9]A. H. Morshed, M. E. Moussa, S. M. Bedair, R. Leonard, S. X. Liu, and N. E. Masry, Appl. Phys. Lett. **70**, 1647 (1997).
[10]W. C. Choi, H. N. Lee, E. K. Kim, C. Seoul, Y. Kim, C. Park, H. C. Kim, J. Y. Lee, and Y. Ku, Appl. Phys. Lett. **75**, 2389 (1999).
[11]M. Miritello, R. L. Savio, F. Iacona, G. Franzò, A. Irrera, A. M. Prio, C. Bongiorno, and F. Priolo, Adv. Mater. (Weinheim, Ger.) **19**, 1582 (2007).
[12]J. Li, O. H. Y. Zalloum, T. Roschuk, C. L. Heng, J. Wojcik, and P. Mascher, Adv. Opt. Technol. **2008**, 295601 (2008).
[13]T. Roschuk, J. Wojcik, X. Tan, J. A. Davies, and P. Mascher, J. Vac. Sci. Technol. A **22**, 883 (2004).
[14]O. H. Y. Zalloum, M. Flynn, T. Roschuk, J. Wojcik, E. Irving, and P. Mascher, Rev. Sci. Instrum. **77**, 023907 (2006).
[15]A. Paleari, N. Chiodini, D. Di Martino, and F. Meinardi, Phys. Rev. B **71**, 075101 (2005).
[16]H.-J. Fitting, A. N. Trukhin, T. Barfels, B. Schmidt, and A. V. Czarnowski, Radiat. Eff. Defects Solids **157**, 575 (2002).
[17]A. Paul, M. Mullholland, and M. S. Zaman, J. Mater. Sci. **11**, 2082 (1976).
[18]H. Bi, W. Cai, H. Shi, B. Yao, and L. Zhang, J. Phys. D **33**, 2369 (2000).
[19]G. E. Malashkevich, E. N. Poddenezhny, and I. M. Melnichenko, J. Non-Cryst. Solids **188**, 107 (1995).
[20]M. Yamaga, D. Lee, B. Henderson, T. P. J. Han, H. G. Gallgher, and T. Yosida, J. Phys.: Condens. Matter **10**, 3223 (1998).

Downloaded 09 Jan 2009 to 160.36.192.110. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp