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Violet/blue light-emitting cerium silicates

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We observed violet/blue light emitted from cerium silicates which may be useful for silicon-based optoelectronics. The cerium silicate was produced during a rapid thermal annealing at high temperature ($>1100\,^{\circ}C$) from the interface between silicon substrate and cerium oxide film. Detailed experiments including x-ray diffraction, high-resolution transmission electron microscope, and Auger depth profiling showed that the cerium silicate consists of $Ce_{4.667}(SiO_4)_3O$ and $Ce_2Si_2O_7$ phases. The photoluminescence of the cerium silicate is very strong at room temperature. Specifically, the 358 nm luminescence line is attributed to the $Ce_2Si_2O_7$ phase. © *1999 American Institute of Physics.* [S0003-6951(99)03342-2]

Rare-earth materials have drawn a great deal of attention due to their inherent thermal stability in optical transition. Owing to this advantage, many of them have been utilized in laser and optical fiber applications (e.g., Nd-YAG laser, Er-doped optical fiber and *a*-Si, etc). In particular, the cerium atom has been utilized as a luminescence center that dominates the electroluminescence of the phosphor layer in electroluminescent displays. Recently, interest in cerium dioxide (CeO_2) has increased substantially due to its chemical stability and close lattice match with silicon. Therefore, CeO_2 would be potentially important for applications such as silicon-on-insulator structures,[1] stable capacitor devices for large-scale integration,[2] and as stable buffer layers for high temperature superconducting materials on silicon.[3] More recently, blue luminescence with moderate intensity from cerium oxide on silicon was reported with the luminescence attributed to Ce_6O_{11}.[4] However, our observations showed a strong violet/blue luminescence from cerium oxide films on silicon having an entirely different origin from the aforementioned letter. Our experiments employ high-resolution transmission electron microscopy (HR-TEM), x-ray diffraction (XRD), and Auger electron spectroscopy measurements to reveal the origin of the luminescence. Using such assessment methods, we could confirm that the luminescence originates from an assembly of cerium silicate phases such as $Ce_{4.667}(SiO_4)_3O$ and $Ce_2Si_2O_7$. Furthermore, the spectral position and full width at half maximum value of the photoluminescence (PL) signal can be tuned using a weighting factor adjustment of individual phases.

Cerium oxide films were prepared on *p*-type silicon (100) at room temperature by radio-frequency sputtering in a reactive gas mixture of 80% argon and 20% oxygen by using a conventional 4-in.-diam Ce target (99.99% purity). The working gas pressure for all deposition processes was kept at 3.0×10^{-3} Torr. Some of cerium oxide film samples were annealed in the temperature range of $800-1100\,^{\circ}C$ in a nitrogen ambient for 5–10 min using rapid halogen lamp heating (RLH).

None of samples show luminescence by a He–Cd laser (50 mW) excitation at room temperature for annealing temperatures lower than $1100\,^{\circ}C$. By contrast, we observe very strong photoluminescence from the samples annealed at $1100\,^{\circ}C$. The result indicates an onset of structural change at $1100\,^{\circ}C$. The high intensity levels are, in fact, strong enough so that one can easily observe them in bright surrounding room conditions. As displayed in Fig. 1(a), the PL signal is centered at 388 nm having the spectral linewidth as narrow as 73 nm. A previous study[4] of thermally treated CeO_2 films has shown an emission at 400 nm. The emission was attributed to Ce_6O_{11} on the basis of the inherent thermal stability of Ce_6O_{11}. Although the spectral position and linewidth are similar in this letter, our emission is not due to Ce_6O_{11}. As shown in Fig. 1(b), the Auger depth profile shows the presence of a significant amount of Si in the film. The asymmetric profile of Si demonstrates that Si is diffused from Si substrate during the high temperature annealing. To clarify the role of Si in the film, several samples are prepared by intentional cosputtering of Si by employing small platelets along with the cerium target. As is the case of pure CeO_x films, no noticeable PL is observed when they are annealed at temperatures lower than $1100\,^{\circ}C$. However, after the annealing at temperatures of $1100\,^{\circ}C$ or higher, sharper PL centered at 358 nm with a shoulder at 388 nm is observed as displayed in Fig. 2(a). Figure 2(b) shows its Auger depth profile. The relatively uniform distribution of the Si profile

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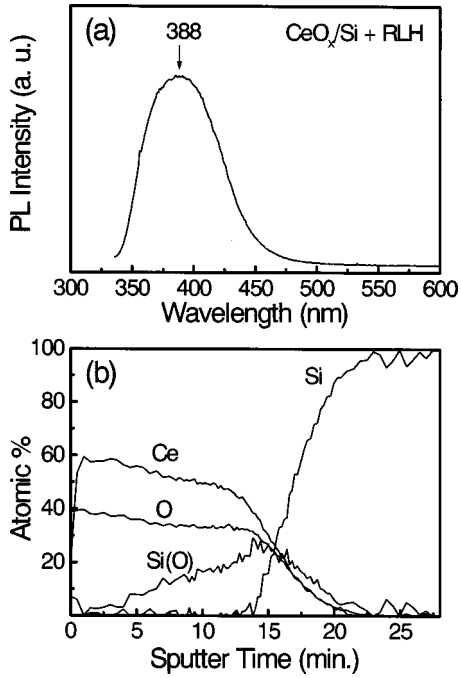

FIG. 1. PL spectrum (a) at room temperature and the Auger depth profile data (b) measured from the CeO_x/Si(100) sample after thermal treatment at 1100 °C.

indicates a successful incorporation of Si in the film during cosputtering. Figure 3 shows a HR-TEM image of the sample. Surprisingly, two crystalline phases with different lattice constants are clearly visible in the TEM images. In conjunction with XRD studies (not shown here), the stoichiometric compositions of individual phases are $Ce_2Si_2O_7$ and $Ce_{4.667}(SiO_4)_3O$, respectively. In the analysis, we assume that x-ray peaks are originated from the phases composed of Ce, Si, and O. In a separate TEM experiment, we observed

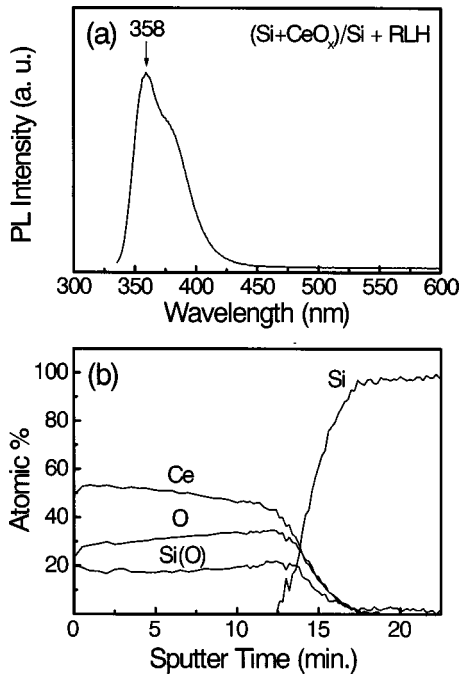

FIG. 2. PL spectrum (a) at room temperature and the Auger depth profile data (b) obtained from the $(Si+CeO_x)$/Si(100) sample after thermal treatment at 1100 °C.

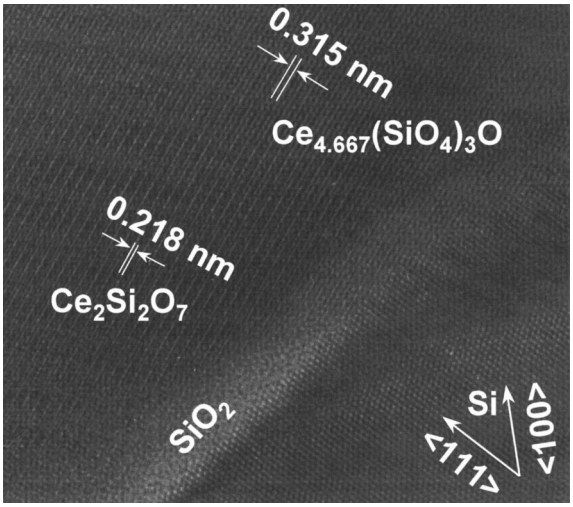

FIG. 3. HR-TEM image obtained from the $(Si+CeO_x)$/Si(100) sample after thermal treatment at 1100 °C.

only $Ce_{4.667}(SiO_4)_3O$ phase for pure CeO_x film (i.e., not cosputtered) annealed at the temperature of 1100 °C. The observation lead us to conclusion that $Ce_2Si_2O_7$ phase should be responsible for 358 nm emission. Noticing the relative richness of oxygen in the $Ce_2Si_2O_7$ phase, a set of experiments was performed. In the experiment, CeO_x films were prepared on SiO_x/Si substrate and they are annealed at 1100 °C. It was expected that the SiO_x/Si substrate would provide an oxygen-rich environment during diffusion. The samples show bright violet luminescence like the other

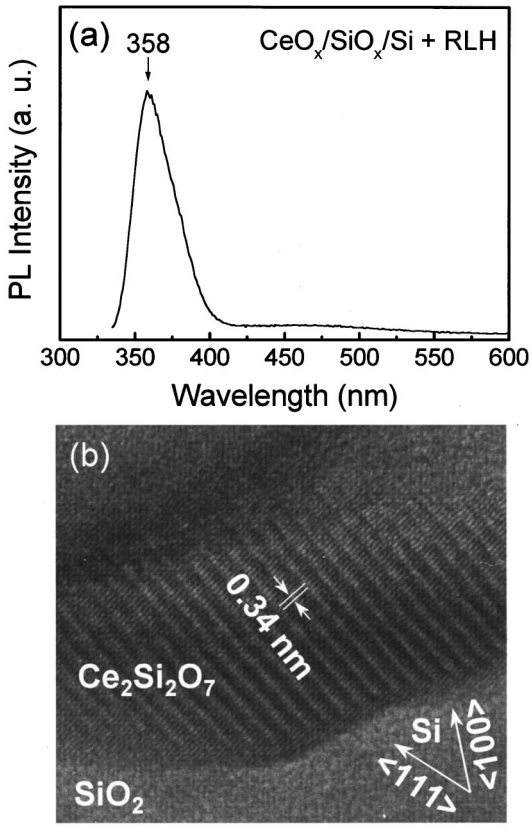

FIG. 4. PL spectrum (a) and cross-sectional HRTEM micrograph (b) obtained from the CeO_x/SiO_x/Si(100) sample after thermal treatment at 1100 °C. Analysis of the XRD (not shown here) and the HR-TEM show the formation of only one phase of the $Ce_2Si_2O_7$ oriented to the (002) plane.

samples. However, as shown in Fig. 4(a), the peak is centered at 358 nm without any shoulder and its spectral width ($\sim$32 nm) is the narrowest. As shown in Fig. 4(b), the HR-TEM image for the sample shows only one phase of $Ce_2Si_2O_7$ oriented to the (002) direction. Therefore, the 358 nm line appears to be originated in the $Ce_2Si_2O_7$ phase. However, diffusion on the atomic scale toward a formation of such a phase is not clear yet. Atomic configuration modeling of such phases remains for further study.

To conclude, we have observed cerium silicate phases ($Ce_2Si_2O_7$, $Ce_{4.667}(SiO_4)_3O$ phases) which emit intense violet light. The phases are generated during the high temperature annealing of CeO_x film on Si or SiO_x/Si substrates. The luminescence at 358 nm was attributed to the $Ce_2Si_2O_7$ phase, while the luminescence at 388 nm was due to the $Ce_{4.667}(SiO_4)_3O$ phase. These types of cerium silicates could be promising for future silicon-based optoelectronic applications.

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