Intense blue–white luminescence from carbon-doped silicon-rich silicon oxide

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The effect of carbon doping on the enhancement of visible luminescence from silicon-rich silicon oxide (SRSO), which consists of Si nanoclusters embedded inside a SiO_2 matrix, is investigated. C-doped SRSO films were fabricated by electron cyclotron resonance-plasma enhanced chemical vapor deposition method using SiH_4, O_2, and CH_4 source gases followed by a high-temperature anneal. Intense blue-white visible luminescence, visible to the naked eye under daylight conditions, was observed from the film with a nearly equal amount of C and excess Si ($\sim$16 at. %) after an anneal at 950 °C. Furthermore luminescence could be tuned from 1.8 to 2.5 eV by controlling the C to excess Si ratio, the C content, and the anneal temperature. Taken together with the infrared absorption spectra, these results indicate that the luminescence is attributed to exciton recombination in C-incorporated Si nanoclusters. © *2004 American Institute of Physics.*
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The observation of visible luminescence at room temperature from porous Si (Ref. 1) has spurred a tremendous amount of research into using nm-sized Si to develop a Si-based light source. One widely used method of fabricating nanocluster Si (nc-Si) is precipitating them out of SiO_x ($x < 2$) to produce a film with nc-Si embedded inside an SiO_2 matrix.[2] Such a film, often called silicon-rich silicon oxide (SRSO), has the advantage of producing dense, oxide-passivated, nc-Si in a robust film that is compatible with the standard Si processing technologies. By now, light-emitting diodes using SRSO have been demonstrated,[3] and the possibility of optical gain reported.[4]

However, it has been very difficult to obtain efficient visible luminescence, especially in the blue–green range. Some have reported visible luminescence from nc-Si containing films but these were attributed to defects, either in the SiO_2 matrix[5,6] or in nc-Si.[7] Indeed, the luminescence from SRSO films peaks in the near-infrared range even when the nc-Si size is controlled down to 2 nm.[8,9] In fact, recent calculations suggest that the surface states play a critical role in determining the luminescence, and that while the band gap of nc-Si can be increased to 3 eV or greater by the quantum confinement effect, the luminescence from oxide-passivated nc-Si is limited to the near-infrared range due to oxygen-related surface states.[10,11]

Such results suggest, however, that by a suitable impurity incorporation, visible luminescence may yet be obtained from SRSO, substantially increasing the possible impact of SRSO on a wide range of possible applications ranging from display to compact, efficient Si-based photonics. In this letter, we report on the enhancement of visible luminescence from SRSO by carbon doping. We find that blue–white luminescence, visible to the naked eye under daylight conditions, can be obtained from an SRSO film after an anneal at 950 °C when the carbon and excess Si concentrations are nearly equal. Based on the infrared absorption and the tun-

ability of luminescence by anneal temperature and excess Si content, we attribute the luminescence to exciton recombination in carbon-incorporated Si nanoclusters.

Carbon-doped SRSO (SRSO:C) films were deposited on Si wafers using a high-vacuum electron cyclotron resonance-plasma enhanced chemical vapor deposition system. The base pressure, the deposition pressure, the deposition temperature, and the microwave power were 5×10^{-7} Torr, 5×10^{-5} Torr, 450 °C, and 400 W, respectively. Ar, SiH_4, O_2, and CH_4 were used as source gases. The film thickness was $\sim$2 μm. The Si and carbon content was determined using Rutherford backscattering spectroscopy and wavelength dispersion x-ray spectroscopy, and the infrared absorption also measured by fourier transform infrared spectrometry. After deposition, the films were annealed in a flowing Ar (99.999% pure) environment at various temperatures. Finally, annealed films were hydrogenated for a 1 h anneal at 700 °C in flowing forming gas (10% H_2 + 90% N_2). Photoluminescence (PL) spectra were measured at room temperature using the 325 nm line of a HeCd laser as the pump source and a charge coupled device. The nominal pump power was 50 mW.

Figure 1 shows the infrared absorption spectra of the SRSO:C films with 39 at. % Si and varying C, the carbon
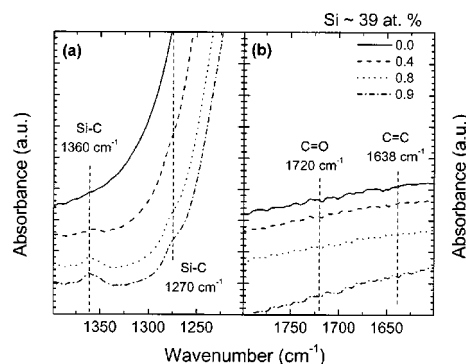

FIG. 1. Infrared absorption spectra for the films with Si content of $\sim$39 at. % and different C to Si content ratio at 1400–1200 cm^{-1} (a) and at 1800–1600 cm^{-1} (b).

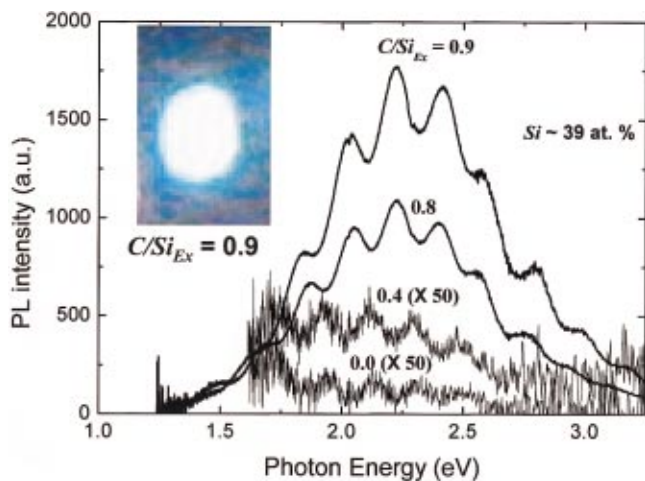[a] Electronic mail: seyoungseo@kaist.ac.kr

FIG. 2. (Color) PL spectra of SRSO:C film with Si content of 39 at. % and different C to excess Si content ratio. The inset is a camera image of visible luminescence of the film with C/Si_{Ex} of 0.9.
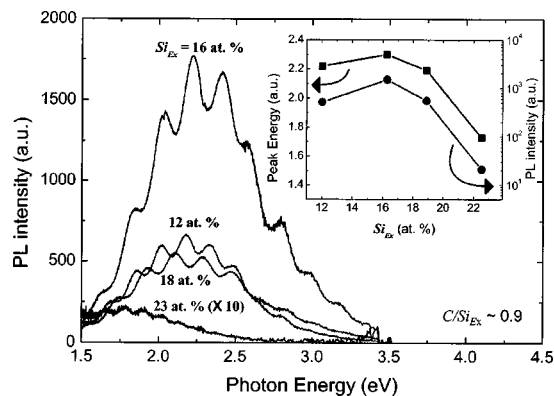

FIG. 3. PL spectra of SRSO:C film with C/Si_{Ex} content ratio of 0.9 and different excess Si content. The inset shows PL peak energy and integrated PL intensity as function of excess Si content.

concentration. All films underwent a 5 min anneal at 950 °C prior to measurements. We observe peaks at 1360 and 1270 cm^{-1}, indicating the presence of Si—C bonds and confirming incorporation of carbon into the film matrix. However, we do not observe any peaks in the 1720 and 1638 cm^{-1} corresponding to C=O and C=C bonds.

Figure 2 shows the effect of carbon incorporation on the PL spectra. All films had a Si content of 39 at. %, and were annealed for 5 min at 950 °C. The sigmoid oscillation in the PL intensity is an optical artifact due to multiple reflections. We observe very little PL without C. However, by increasing the C content to 16 at. %, the PL intensity can be increased nearly 500 fold. The resulting blue–white luminescence is strong enough to be seen easily with the naked eye under daylight conditions, as is shown in the inset of Fig. 2.

We note that increasing C results in a reduction in the overall O content in the film since the total Si content was kept at 39 at. %. Thus, if we assume that most of the O in the film bonds with Si to form SiO_2, then, we can calculate Si_{Ex}, the excess Si that is not bonded with O. The reason for such an assumption will be discussed later. Comparing C with Si_{Ex}, we find that the appearance of strong blue–white PL in Fig. 2 coincides with the C/Si_{Ex} ratio approaching unity. Attempts at achieving a higher C/Si_{Ex} ratio failed, however, as it remained near unity even when the CH_4 flow rate was increased even further (data not shown).

Figure 3 shows effect of increasing C and Si_{Ex} in SRSO:C films while keeping the C/Si_{Ex} ratio constant near unity. The strongest PL is observed at C and Si_{Ex} values of 16 at. %. Further increase in C and Si_{Ex} results in a one hundred-fold decrease in the PL intensity as well as a strong redshift of the PL peak from 2.3 to 1.7 eV. The results are summarized in the inset of Fig. 3.

Figure 4 shows PL spectra of SRSO:C films with 39 at. % Si and C/Si_{Ex} ratio of ~0.9 after anneals at different temperatures ranging from 700 to 1250 °C. For comparison, the PL spectrum of a C-free SRSO, whose luminescence was optimized by an anneal at 1150 °C is also shown. We observe a broad PL peak in the near-infrared region from the carbon-free sample, in agreement with previous reports.[8,12] On the other hand, we observe blue–white luminescence from SRSO:C films after all anneals. The maximum PL intensity

is obtained after a 950 °C anneal. At its optimum, the integrated PL intensity from SRSO:C is stronger by factor of 3 than that from carbon-free SRSO film. A further increase in the anneal temperature results in strong decrease of the PL intensity from SRSO:C films. However, the PL peak position shows a near monotonic redshift with the anneal temperature, decreasing from 2.46 eV to 2.25 eV. The results are again summarized in the inset.

The results presented clearly demonstrate that carbon doping of SRSO results in strong blue–white luminescence. What is not yet clear, however, is the origin of such luminescence. One possible origin is the defects. However, the high anneal temperatures required to obtain the optimum PL, the tunability of luminescence by controlling excess Si content and anneal temperature, and the fact that optimum luminescence is observed even after hydrogenation, are contrary to previously reported results on defect luminescence.[6,7,12] Thus, we consider it unlikely that defects, either in the oxide or the nc-Si, are the cause of the blue–white luminescence from SRSO:C films.

On the other hand, it is clear that the presence of C is essential to the blue–green luminescence. However, we do not believe that the PL is due to formation of oxicarbide glasses. While there have been some reports of blue luminescence from carbon-rich silica,[13] some of the results are at odds with such possibility. First, it has been reported that bulk silicon oxicarbides contain a large fraction of elemental carbon[14] that may lead to luminescence.[13] However, the lack of C=C and C=O bonds in Fig. 1 indicate that our films do
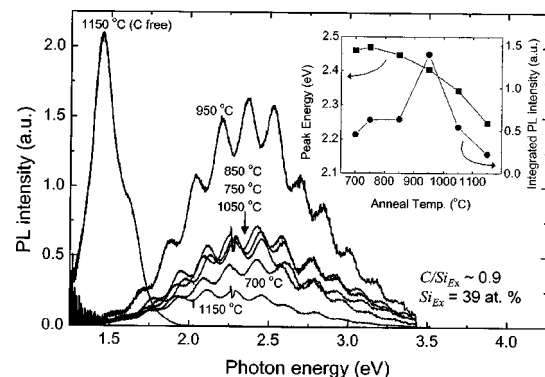

FIG. 4. PL spectra of SRSO:C films with Si content of 39 at. % and C/Si_{Ex} of 0.9, annealed at different temperatures. The inset shows PL peak energy and integrated PL intensity as functions of annealing temperature.

not contain such elemental carbon. Second, it has been reported that the cohesive energy of even pure silicon oxycarbides are always smaller than either SiC or SiO_2,[15] and that the formation of the oxycarbide phase is nearly completely suppressed during oxygen plasma oxidation of deposited SiC.[16] As the SRSO:C films were deposited using oxygen plasma and underwent high-temperature anneals, formation of the unstable oxycarbide phases would be less favorable. Finally, if the blue–white luminescence were due to the formation of oxycarbide phase, then increasing the carbon concentration should increase the oxycarbide phase, and lead to increase in the PL intensity. However, that is clearly not the case, as Fig. 3 shows. Similarly, it is also not clear why increasing the annealing temperature should lead to a systematic redshift of the luminescence peak.

Instead, the overall trend suggests that the results can be explained consistently by describing SRSO:C films as a SiO_2-like matrix embedded with Si nanoclusters which incorporate a high concentration of carbon, and assigning the luminescence due to excitons being quantum confined in such nanoclusters. First, such a phase separation would be consistent with the cohesive energies as discussed above. Second, the effect of hydrogenation is also consistent with nanocluster luminescence. Finally, the variation of the PL intensity and peak position with composition and anneal temperature are very similar to that observed from carbon-free Si nanoclusters in SRSO. Thus, the decrease of the PL intensity and the redshift of the PL peak with increasing C and Si_{Ex} observed in Fig. 3 can be ascribed to the increasing size of the nanoclusters. Similarly, the redshift of the PL peak with the increasing anneal temperature can also be explained by growing of the nanoclusters in size.

The exact nature of the nanocluster is not yet clear. The C/Si_{Ex} ratio of near unity suggests the formation of SiC. While the luminescence energy of 2.3 eV is much lower than the band gap of SiC, it has been reported that porous SiC luminesces in this energy range.[17] However, there have also been reports that carbon-implanted porous Si luminesces in this energy range without forming SiC.[18] We note that while the equilibrium solubility of carbon in bulk Si is less than $10^{-3}\%$, several theoretical and experimental results have shown that it can be higher by several orders of magnitude near the surface.[19,20] In the case of 2–3 nm-sized Si clusters, the formation of such carbon-rich surface layer is sufficient to reach C/Si_{Ex} of near unity due to the large surface/volume ratio. Thus, the possibility that the luminescence we observe is due to such a carbon-rich surface layer cannot be ruled out.

Specifically, note that the amount of redshift in PL peak energy of SRSO:C as function of Si_{Ex} is rather larger than that of C-free SRSO.[8] Such a difference can be attributed to larger energy of surface states of C-rich nc-Si compared to oxide capped. That is, while the band gap of nm-sized Si nanoclusters can be sufficiently high as 3 eV, the PL peak energy for C-free SRSO is limited to <2 eV by the small energy of the oxide capped surface.[10,11] On the other hand, the higher-energy states of the C-rich surface can more sensitively reflect the band gap energy of nc-Si. Therefore, due to such a reason, as Si_{Ex} increases, the band gap of nc-Si becomes insufficient to excite C-rich surface, and the overall PL intensity is dramatically quenched as shown in Fig. 3. In

the same manner, the anneal temperature dependence of the PL intensity shown in Fig. 4, can be also explained with the competition between the elimination of luminescence quenching centers, such as defects and the growth of nc-Si.

The above results suggest that by C incorporation blue–white luminescence, visible to the eyes, can be obtained from SRSO. The compatible fabrication procedure of SRSO:C films with Si process techniques, in addition to dense and robust formation of nc-Si in SRSO, opens various applications of SRSO to Si-based photonics. For example, such large energy of blue–white luminescence can be also used as host matrix for visible phosphors, which have hardly been demonstrated so far, and we are investigating such applicable possibilities.

In conclusion, we have demonstrated intense blue–white luminescence from SRSO:C. The presence of high concentration of carbon is essential for such blue–white luminescence, and the optimum luminescence is obtained when the fils has a nearly equal carbon and the excess Si concentration of about 16 at. %, and is annealed at 950 °C. At its optimum, the luminescence intensity from such SRSO:C film is more intense than that from a carbon-free SRSO by factor of 3. Based on the infrared absorption, the effect of hydrogenation on luminescence, and the tunability of luminescence by anneal temperature and excess Si content, we attribute the luminescence to exciton recombination in carbon-incorporated Si nanoclusters.

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