Strong Blue-Green Luminescence of Silicon-Rich Silicon Oxide with Doping of C and Tb

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The effects of C doping and Tb co-doping on the enhancement of visible luminescence from silicon-rich silicon oxide (SRSO), which consists of Si nanoclusters embedded inside an SiO$_2$ matrix, are investigated. C-doped SRSO (SRSO : C) and Tb co-doped films were fabricated by an electron cyclotron resonance-plasma enhanced chemical vapor deposition method with concurrent sputtering of Tb target by 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 SRSO : C film with a nearly equal amount of C and excess Si, after an anneal at 950 $^\circ$C and furthermore tuned by controlling the C to excess Si ratio, the C content, and the anneal temperature. The film co-doped with Tb also shows strong Tb$^{3+}$ photoluminescence which is enhanced by the content of C. The 543 nm Tb$^{3+}$ lifetimes were in the range of 0.5 – 1.2 msec, comparable to those from Tb-doped silica. Based on the results, we conclude that exciton recombination in C-incorporated Si nanoclusters is responsible for visible luminescence of SRSO : C and can efficiently excite incorporated Tb$^{3+}$ ions.

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I. INTRODUCTION

Since strong visible luminescence was observed from porous Si at room-temperature [1], efficient light emission from Si rich Si oxide (SRSO), which consists of nanocluster Si (nc-Si) embedded in SiO$_2$ matrix, has gathered much interest in order to develop light emission from Si-based materials for highly compact and functional Si micro-photonic devices. Even though a lot of research into light-emitting devices based on nc-Si has been done, producing several fruitful results such as visible light emitting diodes (LEDs) [2] and the possibility of optical gain [3], some luminescence features of nc-Si act as obstacles for practical application. That is, nc-Si luminescence is mainly shown in the near-infrared range and luminescence even from single nc-Si is still too broad, $\sim$ 100 nm wide [4], to apply nc-Si to full-color display with high purity.

An interesting alternative to obtaining sharp luminescence is rare-earth (RE) doping [5–7]. In such a case, RE ions are excited via an energy transfer from the host matrix [8], and visible luminescence can be obtained if the bandgap of the host matrix is wide enough [9]. However, recent calculations suggest that the surface states play a critical role in determining the luminescence, and that while the bandgap 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 that by incorporation of suitable impurities other than oxygen, blue–green luminescence may be obtained from SRSO and such engineered SRSO is further utilized to be host matrix for RE ions to obtain sharp visible luminescence, 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 paper, we report on the enhancement of visible luminescence from SRSO by C doping and its utilization for the host matrix for sharp RE luminiscence by co-doping of Tb. We find that blue-white luminescence strong enough to be seen by the naked eye under daylight conditions can be obtained from an SRSO film after C doping and an anneal. We attribute the luminescence to exciton recombination in C-incorporated Si nanoclusters. By co-doping of Tb into C-doped SRSO film, we can observe strong and sharp green luminescence from SRSO film and find that Tb$^{3+}$ can be excited via an Auger-type interaction with nc-Si. The 543 nm Tb$^{3+}$ PL lifetimes were comparable to those from Tb-doped silica. The results indicate that C co-doping greatly increases the efficiency of such exciton-mediated excitation of Tb$^{3+}$. The implications of the results on developing Si-based luminescent material in the visible range are also discussed.

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II. EXPERIMENT

C-doped SRSO (SRSO : C) films were deposited on Si wafers by using a high-vacuum electron cyclotron resonance plasma enhanced chemical vapor deposition system. Ar, SiH₄, O₂, and CH₄ were used as source gases. By using similar deposition procedure, Tb doped SRSO : C films were also fabricated with concurrent sputtering of Tb target. The detailed deposition procedure can be found from Ref. [12–14]. The film thickness was ∼ 2 µm and 1.4 µm for SRSO : C and Tb-doped films, respectively. The compositions of the films were determined by Rutherford backscattering spectroscopy and wavelength dispersion X-ray spectroscopy, and the infrared absorption also was measured by Fourier Transform Infrared (FTIR) spectrometry. After deposition, the films were annealed in a flowing Ar environment at various temperatures. Finally, some films were further hydrogenated by a 1 hr anneal at 700 °C in flowing forming gas (10 % H₂ + 90 % N₂). Photoluminescence (PL) spectra were measured at room temperature by using the 325 nm line of a HeCd laser with nominal pump power of 50 mW. Either a charge coupled device or an InGaAs(Cs) photomultiplier tube and general lock-in technique was used for PL detection, and PL spectra were corrected for the system response. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the effect of C 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 shown in the inset.

We note that increasing the carbon content, C results in 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 O in the film bonds with Si to form SiO₂, then we can calculate Si_{Ex}, the excess Si that is not bonded with O. Comparing C with Si_{Ex}, we find that the appearance of strong blue-white PL in Fig. 1 coincides with the C/Si_{Ex} ratio approaching unity.

Figure 2 (a) shows the 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 hundredfold decrease in the PL intensity as well as a strong redshift of the PL peak. Figure 2 (b) shows the effect of annealing temperature on visible PL of SRSO : C films with 39 at.% Si and C/Si_{Ex} ratio of ∼ 0.9. We observe blue-white luminescence from SRSO : C films after all anneals and the maximum PL intensity is obtained after a 950 °C anneal. For comparison, the PL spectrum of a C-free SRSO whose luminescence was optimized by an anneal at 1150 °C is also measured [12]. At its optimum of C-doped film, the integrated PL intensity from SRSO : C is stronger by a factor of three than that from C-free SRSO film. A further increase in the anneal temperature results in a 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 presented clearly indicate that C doping of SRSO is responsible for strong blue-white luminescence. However, the origin of such luminescence is not
clear. We measured the infrared absorption spectra of the SRSO : C films with 39 at.% Si and varying C [12]. We observe the presence of Si-C bonds, confirming incorporation of C into the film matrix, and cannot observe C=O and C=C bonds. Thus, 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 oxycarbide glasses. Detailed discussion can be found in Ref. [12]. The overall trend suggests that the results can be explained consistently by describing SRSO : C films as SiO$_2$-like matrix embedded with Si nanoclusters which incorporate a high concentration of C, and assigning the luminescence as due to excitons quantum-confined in such nanoclusters : the effect of hydrogenation and the variation of the PL intensity and peak position with composition and anneal temperature are very similar to those observed from C-free Si nanoclusters in SRSO. Therefore, the decrease of the PL intensity and the redshift of the PL peak with increasing C and $S_{EX}$ observed in Fig. 2 can be ascribed to the increasing size of the nanoclusters. Similarly, the redshift of the PL peak with increasing anneal temperature can also be explained by growth of the nanoclusters in size.

Figure 3 shows the effect of C co-doping on the PL spectra of Tb-doped SRSO whose Si content was fixed at 35 at.%. We observe a broad luminescence in the range of 400 – 700 nm, due to the SRSO : C matrix. Superimposed on the intrinsic SRSO : C luminescence are Tb$^{3+}$ luminescence peaks at 543 nm. Other intra-4f transitions such as the $^5D_4 \rightarrow ^7F_6$ and $^7F_4$ intra-4f transitions with peaks at 487 and 588 nm are possible, but are difficult to discern due to interference by internal reflection. Both the SRSO : C and Tb$^{3+}$ luminescence increase as the C content increases. The dependence of the Tb$^{3+}$ and the intrinsic SRSO : C PL intensity is summarized in the inset.

We find that they are well correlated. The maximum intensity of both the Tb$^{3+}$ and the SRSO : C PL is obtained at a C content of 4.5 at.%, at which the Tb$^{3+}$ PL is nearly 30 times stronger than that from the film with no C.

Figure 4 shows PL spectra of films with Si content of 35 at.%, C content of 10 at.%, and Tb content of 0.1 and 0.4 at.%. We find that increasing the Tb content increases the green, 543 nm Tb$^{3+}$ PL intensity while at the same time suppressing the intrinsic SRSO : C luminescence. The inset shows camera images of the films taken under ambient conditions. The film with 0.1 at.% Tb$^{3+}$ luminesces bluish white due to the strong intrinsic SRSO : C luminescence. The film with 0.4 at.% Tb, on the other hand, luminesces green due to the relative increase in the Tb$^{3+}$ PL intensity.

Figure 5 shows the time-resolved decay traces of the 543 nm Tb$^{3+}$ luminescence. Since the Tb$^{3+}$ luminescence is superimposed on the SRSO : C host luminescence that has a very fast luminescence lifetime limited by the system response (10 µsec), the Tb$^{3+}$ PL decay traces were isolated by deleting the fast initial decay that appears after the pump beam is turned off. We find that the Tb$^{3+}$ lifetime from C-free SRSO is 1.2 msec. The Tb$^{3+}$ PL lifetime decreases with increasing C content, reaching a value of 0.5 msec at a C content of 11 at.%. Such values for Tb$^{3+}$ PL lifetimes, and the luminescence characteristics overall, are similar to those of Tb doped SiO$_2$ [15], except for the fact that we observe luminescence even though the excitation beam of 325 nm is not absorbed by Tb$^{3+}$ ions. However, such non-resonant excitation of RE ions in SRSO, and the suppression of the intrinsic SRSO luminescence by RE co-doping as shown in Fig. 4, are well-documented for RE ions luminescent in the IR range [16–18], and explained by Auger-type
excitation of RE ions by non-radiative decay of excitons [16]. In the following, we will discuss the extendability of such excitation model to the visible Tb$^{3+}$ luminescence, and the role of C in enhancing it.

In fact, the SRSO luminescence is limited to the IR range even when nm-sized nc-Si formed by using a very low excess Si content [19], while 2.5-3.5 eV is required for excitation of Tb$^{3+}$. However, recent results indicate that the IR luminescence from SRSO is due to oxygen-related surface states, and that the actual bandgap of nm-sized nc-Si may be as large as 4 eV [10, 11], sufficient to excite Tb$^{3+}$. Furthermore, the fact that the Tb$^{3+}$ PL lifetime from Tb-doped SRSO is comparable to that from Tb-doped SiO$_2$ suggests that the Tb$^{3+}$ luminescence efficiency in SRSO is quite high.

The above results suggest that by C and Tb incorporation, sharp blue-green 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 up various applications of SRSO to Si-based photonics. Finally, note that Fig. 4 indicates that the overall luminescence spectra can be tailored by controlling the C and Tb$^{3+}$ concentrations. This suggests the feasibility that other RE ions, such as Er, Tm and Eu, may also be used as visible optical dopant for SRSO : C, as has been demonstrated for GaN [9], and that by combining them, light emitters for the whole visible range may be integrated on a single Si substrate [20].

IV. CONCLUSION

In conclusion, we have demonstrated intense blue-white luminescence from SRSO : C and the effect of C on Tb$^{3+}$ luminescence from Tb-doped SRSO : C films. C is essential for such blue-white luminescence. At its optimum, the luminescence intensity from such SRSO : C film is more intense than that from a C-free SRSO by factor of three. We attribute the luminescence to exciton recombination in C-incorporated Si nanoclusters. We also find that by using such blue luminescence from SRSO : C, Tb$^{3+}$ ions can be efficiently Auger-excited by interaction with nc-Si. The results support the idea that by incorporation of suitable impurities such as C and Tb, sharp and strong visible luminescence can be produced from nc-Si.

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REFERENCES