Enhancement of the green, visible Tb$^{3+}$ luminescence from Tb-doped silicon-rich silicon oxide by C co-doping

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(Received 27 October 2003; accepted 12 April 2004; published online 12 May 2004)

The effect of C co-doping on the Tb$^{3+}$ luminescence from Tb-doped silicon-rich silicon oxide (SRSO) films is investigated. Tb-doped SRSO films co-doped with C (SRSO:C) were deposited by electron cyclotron resonance plasma-enhanced chemical vapor deposition. The Tb$^{3+}$ photoluminescence intensity is enhanced by the presence of nanocluster Si (nc-Si), and C co-doping further increases the Tb$^{3+}$ photoluminescence intensity by more than an order of magnitude. The maximum enhancement is observed at the C content of ~5 at. %, at which the Tb$^{3+}$ luminescence is bright enough to be observed by the naked eye under ambient conditions. The 543 nm Tb$^{3+}$ lifetimes were in the range of 0.5–1.2 ms, comparable to those from Tb-doped silica. Based on the results, we conclude that nanometer-sized nc-Si can excite Tb$^{3+}$ ions via an Auger-type energy transfer, and that C co-doping greatly increases the efficiency of such exciton-mediated excitation of Tb$^{3+}$.

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Ever since the report on the visible photoluminescence (PL) from porous Si,$^1$ the luminescence from nanocluster Si (nc-Si) has been the subject of prolonged and intense investigations.$^2$ In particular, silicon-rich silicon oxide (SRSO), which consists of nc-Si embedded inside an SiO$_2$ matrix, has attracted particular attention due to its robustness and compatibility with Si processing technologies.$^3$ By now, light emitting diodes$^4$ and the possibility of optical gain$^5$ using SRSO have been reported. However, the SRSO luminescence is centered in the near IR range even with nanometer-sized nc-Si, and obtaining visible luminescence from nc-Si has proved to be difficult.$^6$ Furthermore, the luminescence peak was reported to be very broad even with a single nc-Si.$^7$

An interesting alternative to obtaining sharp luminescence is rare-earth (RE) doping. 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 band gap of the host matrix is wide enough.$^9$ Yet due to the above-discussed limitations, only IR RE luminescence has been demonstrated from RE-doped SRSO$^{10}$ even though obtaining visible luminescence from silicon-based material such as SRSO remains an important technological challenge. Recently, we reported that SRSO co-doped with carbon (SRSO:C) displays strong blue-white PL.$^{11}$ In this letter, we report on the effect of C co-doping on the Tb$^{3+}$ PL from Tb-doped SRSO. Tb$^{3+}$ was chosen because it has a strong luminescence peak near 543 nm, very close to the primary color standard for green adopted by the U.S. Federal Communications Commission. We find that Tb$^{3+}$ can be excited via an Auger-type interaction with nc-Si, and that C co-doping greatly enhances the Tb$^{3+}$ PL intensity such that the Tb$^{3+}$ luminescence can be seen by the naked eye under ambient conditions. The 543 nm Tb$^{3+}$ PL lifetimes were in the range of 0.5–1.2 ms, comparable to those from Tb-doped silica. The results support recent reports that the band gap of nanometer-sized nc-Si in SRSO is much wider than indicated by its luminescence,$^{12,13}$ and indicates 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.

Tb-doped SRSO:C films were deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition of SiH$_4$, CH$_4$, and O$_2$ with concurrent sputtering of Tb. The detailed procedure of film fabrication can be found in Refs. 11 and 14. After deposition, the films were annealed at 950 °C for 5 min under Ar environment in order to precipitate nc-Si, and hydrogenated by anneal at 700 °C for 1 h flowing forming gas (10% H$_2$ + 90% N$_2$). The composition of the films was determined by Rutherford backscattering spectroscopy and wavelength dispersion x-ray spectroscopy. The Si and C contents were in the range of 34–41 at. % and 0–10.4 at. %, respectively, but the film thickness and the Tb content was fixed at 1.4–10.4 at. %, respectively, and the Si content was increased to below 34 at. %. The dependence of the Tb$^{3+}$ PL intensity on the Si content is summarized in the inset.

Figure 1 shows PL spectra of Tb-doped, carbon-free SRSO films. We observe a weak background luminescence, most likely due to oxide defects, whose intensity oscillates due to multiple reflections. However, within a narrow range of Si content between 35 and 37 at. %, a PL peak at 543 nm due to $^5D_4 \rightarrow ^7F_5$ transition of Tb$^{3+}$ is clearly observable. However, no Tb$^{3+}$ PL can be observed when the Si content is decreased to below 34 at. %. The dependence of the Tb$^{3+}$ PL intensity on the Si content is summarized in the inset.

Figure 2 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 is 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 3 shows PL spectra of films with Si content of 35 at. %, C content of 10 at. %, and with 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 the 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 4 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 $\mu$s), 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 carbon-free SRSO is 1.2 ms. The Tb$^{3+}$ PL lifetime decreases with increasing C content, reaching a value of 0.5 ms at a C content of 11 at. %.

Such values for Tb$^{3+}$ PL lifetimes, and the luminescence characteristics overall, are similar to that of Tb-doped SiO$_2$, 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 nonresonant excitation of RE ions in SRSO, and the suppression of the intrinsic SRSO luminescence by RE co-doping as shown in Fig. 3, are well-documented for RE ions luminescent in the IR range, and explained by Auger-type excitation of RE ions by non-radiative decay of excitons. In the following, we will discuss the extendability of such excitation model to the visible Tb$^{3+}$ luminescence, and the role of carbon in enhancing it.

Extending the exciton-mediated excitation model to Tb-doped SRSO may seem problematic, since the SRSO luminescence is limited to the IR range even when nanometer-sized nc-Si formed by using a very low excess Si content, 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 band gap of nanometer-sized nc-Si may be as large as 4 eV,\textsuperscript{12,13} sufficient to excite Tb\textsuperscript{3+}. The composition dependence of Tb\textsuperscript{3+} luminescence shown in Fig. 1 supports such results, since it indicates that small enough nc-Si has wide enough band gap to be able to excite Tb\textsuperscript{3+} even though it luminesces in the IR range. We note that excitons trapped at oxide defects may also be able to excite Tb\textsuperscript{3+} ions. However, the fact that we do not observe Tb\textsuperscript{3+} PL from the SRSO film with Si content of 34.2 at.% even though it, too, displays defect luminescence suggests that such defect-mediated excitation mechanism is not very efficient.

Furthermore, the fact that the Tb\textsuperscript{3+} PL lifetime from Tb-doped SRSO is comparable to that from Tb-doped SiO\textsubscript{2} suggests that the Tb\textsuperscript{3+} luminescence efficiency in SRSO is quite high. Yet the Tb\textsuperscript{3+} PL intensity from C-free SRSO is quite low, indicating that the efficiency of such nc-Si mediated excitation of Tb\textsuperscript{3+} ions in C-free SRSO is very low. We attribute such low excitation efficiency to the wide distribution of the nc-Si size and the competitive formation of oxygen-related, low-energy excitons.

Thus, in order to increase the Tb\textsuperscript{3+} luminescence, it is necessary to promote formation of high-energy excitons that can excite Tb\textsuperscript{3+}. And such is precisely the role of carbon, as the increase in the visible luminescence by C co-doping and the close correlation between the increase in the SRSO:C and Tb\textsuperscript{3+} luminescence demonstrate. Furthermore, the fact that the reduction in the Tb\textsuperscript{3+} PL lifetime due to C co-doping is less than 20% indicates that C co-doping enhances the Tb\textsuperscript{3+} excitation without significantly reducing the Tb\textsuperscript{3+} luminescence efficiency. The exact reason for such enhancement is not yet clear. It is possible that the C increases the formation of very small nc-Si by acting as nucleation sites. We note, however, that without C co-doping, there still remains the problem of competitive formation of oxygen-related low-energy excitons. Thus, C co-doping most likely increases the effective coupling coefficient between high-energy excitons and Tb\textsuperscript{3+} ions as well. Further investigations on this subject are currently under way.

Finally, note that Fig. 3 indicates that the overall luminescence spectra can be tailored by controlling the C and Tb\textsuperscript{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,\textsuperscript{8} and that by combining them, light emitters for the whole visible range may be integrated on a single Si substrate.\textsuperscript{18}

In conclusion, we have investigated the effect of C co-doping on Tb\textsuperscript{3+} luminescence from Tb-doped SRSO. We find that Tb\textsuperscript{3+} can be excited via an Auger-type interaction with nc-Si, and that C co-doping greatly enhances the Tb\textsuperscript{3+} PL intensity such that the Tb\textsuperscript{3+} luminescence can be seen by the naked eye under ambient conditions. The results support recent reports that the band gap of nanometer-sized nc-Si in SRSO is much wider than indicated by its luminescence,\textsuperscript{12,13} and indicates that C co-doping greatly increases the efficiency of such exciton-mediated excitation of Tb\textsuperscript{3+}.

This work is supported by National Research Laboratory Project of MOST in Korea.