Influence of Sub-nm Scale Dimensional Control on the Er\textsuperscript{3+} Luminescence Properties of Er-Doped Si/SiO\textsubscript{2} Superlattices

Ji Hong Jhe\textsuperscript{*} and Jung H. Shin

Department of Physics, Korea Advanced Institute of Science and Technology, Taejon 305-701

Yong Ho Ha and Dae Won Moon

Surface Analysis Group, Korea Research Institute of Standards and Science, Taejon 305-600

(Received 1 November 2000)

The Er\textsuperscript{3+} photoluminescent properties of Er-doped Si/SiO\textsubscript{2} superlattices in which the location of Er atoms and layer thickness were controlled with sub-nm precision are investigated. The superlattices were deposited either by ultra-high vacuum (UHV) ion beam sputter deposition method or electron-cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-PECVD) method with a subsequent anneal at 950°C. Er was doped only into the SiO\textsubscript{2} layers whose thickness was fixed. The Er-carrier interaction was controlled by either depositing nm-thin buffer layers of pure SiO\textsubscript{2} or by varying the thickness of the Si layers from 0.6 to 3.6 nm. The structure and the composition of the films were confirmed using transmission electron microscopy (TEM) and medium energy ion scattering spectroscopy (MEIS). We find that the Er\textsuperscript{3+} luminescence increases very strongly as the buffer layer thickness is increased, even though the excitation of Er\textsuperscript{3+} ions occurs through carriers generated in Si layers. Furthermore, Er\textsuperscript{3+} luminescence can be increased even further by decreasing the Si layer thickness down to the limit of one monolayer of Si. This demonstrates that with sub-nm scale dimensional control on the environment of Er atoms, we can achieve substantial enhancement in Er\textsuperscript{3+} luminescence.

I. INTRODUCTION

Er is a rare earth atom, which, in its trivalent state, has an intra-\textit{f} transition in from the first excited state to the ground state ($^4I_{13/2} \rightarrow ^4I_{15/2}$) that emits light near 1.54 \textmu m, which corresponds to the low loss window of the silica optical fibers. Furthermore, it has been shown that such intra-\textit{f} transition luminescence can be observed even when Er is doped into Si [1], and that excitation of Er\textsuperscript{3+} ions inside Si (or semiconductors in general) occurs via Auger-type excitation though electron-hole pairs [2], thus enabling electrical excitation of Er\textsuperscript{3+} ions. Therefore, Er doping of Si has been studied intensely in hopes of developing Si-based optoelectronics [3]. Already, light-emitting diodes based on Er-doped Si operating at room temperature have been demonstrated [4,5]. Despite the large advances, the luminescence efficiency is still too low to be practical. By now, it has been recognized that this is due to carrier-induced de-excitation of Er\textsuperscript{3+} ions, and that it is very difficult to circumvent as it is fundamental to luminescent mechanisms of Er\textsuperscript{3+} in Si [6,7].

Recently, however, it was demonstrated that by using Si nanoclusters such as silicon-rich silicon oxide (SRSO), which consists of Si nanoclusters embedded in SiO\textsubscript{2} matrix [8–10], the Er-carrier interaction can be controlled such that much of the problem facing Er doping of Si can be solved, and efficient Er\textsuperscript{3+} luminescence at room temperature can be obtained with possibility of population inversion of Er\textsuperscript{3+} [11]. However, with Si nanoclusters, the size and the number of the clusters and the location of Er atoms [10], which all play a significant role in determining the Er\textsuperscript{3+} luminescence, are difficult to control. Such problems, however, may be solved by using Si/SiO\textsubscript{2} superlattice [12,13] instead. By directly depositing Er-doped Si/SiO\textsubscript{2} superlattices, one can control not only the thickness of the Si and SiO\textsubscript{2} layers accurately, but also the location of Er atoms (in Si layers, in SiO\textsubscript{2} layers, or at the interface) as well. Recently, we have demonstrated improved Er\textsuperscript{3+} luminescence from such Er-doped Si/SiO\textsubscript{2} superlattices, and found that doping Er atoms only into the SiO\textsubscript{2} layers is actually beneficial for the Er\textsuperscript{3+} luminescence [14]. In this paper, we demonstrate that by either using nm thin buffer layer of pure SiO\textsubscript{2} layers between non-doped Si layers and Er-doped SiO\textsubscript{2} layers or by decreasing the Si layer thickness down to 1 monolayer, it is possible to increase the Er\textsuperscript{3+} lumines-
Influence of Sub-nm Scale Dimensional Control on the Er\textsuperscript{3+} Luminescence · · · · Ji Hong Jhe et al.

**II. EXPERIMENT**

The superlattices were deposited either by UHV-ion beam sputter deposition or electron-cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-PECVD) of SiH\textsubscript{4} and O\textsubscript{2} with concurrent sputtering of Er. In the case of ECR-PECVD deposited superlattices, the base pressure, the microwave power, and the substrate temperature were $1 \times 10^{-6}$ Torr, 400 W, and 450 °C, respectively. Under such condition, the deposition rates are expected to be $\sim 0.1$ nm/sec. The deposition times of both Si layers and the Er-doped SiO\textsubscript{2} layers were fixed at 20 sec. The deposition times of the pure SiO\textsubscript{2} buffer layers ranged from 0 to 15 sec. The total period of layers was fixed at 30 for all samples. UHV-ion beam sputter deposited superlattices were deposited at room temperature. The thickness of the Er-doped SiO\textsubscript{2} layers was fixed at 9.6 nm. They were deposited by sputtering Er and Si in oxygen atmosphere with 1 keV Ar\textsuperscript{+} beam. The Si layers were deposited by sputtering Si with 500 eV Ar\textsuperscript{+} beam. The deposition pressures of the Si layer and Er-doped SiO\textsubscript{2} layers were $8 \times 10^{-5}$ Torr and $1 \times 10^{-4}$ Torr, respectively. Under such conditions, the growth rate of both Si layers and the Er-doped SiO\textsubscript{2} layers was $\sim 0.014$ nm/sec. No buffer layers were deposited, but the nominal thickness of the Si layers was varied from 0.6 nm to 3.6 nm, which correspond to 0.5 ML and 16.3 ML Si interlayers, respectively. After deposition, the films were rapid thermal annealed in a sequence of 20 min at 600 °C and 5 min at 950 °C and 5 min at 600 °C in a flowing Ar atmosphere to avoid cracking and spalling of the films. Deposited films were analyzed using transmission electron microscopy (TEM), medium energy ion scattering spectroscopy (MEIS), and Rutherford backscattering spectroscopy (RBS). MEIS spectra were taken using 101.2 keV H\textsuperscript{+} beam was aligned to the [001] direction in the (001) plane, and the protons scattered from Si atoms along 16.3° off from surface were analysed. RBS spectra were taken using 2 MeV He\textsuperscript{++} ions incident 7° off the sample normal. The Er\textsuperscript{3+} luminescence spectra were measured using an Ar laser, a grating monochromator, a thermoelectrically cooled InGaAs detector, and the standard lock-in technique. The nominal laser power was 200 mW. A 477 nm line of Ar laser was used to ensure that Er\textsuperscript{3+} ions are excited only via carriers and to avoid any direct optical excitation. Low temperature PL spectra were measured using a closed-cycle helium cryostat.

**III. RESULTS**

Figure 1 shows the bright-field cross-section TEM images of ECR-PECVD deposited superlattice films and the schematic depictions of their composition. The Si layers are polycrystalline, and some grains can be observed. The Si and SiO\textsubscript{2} layer thicknesses are 4 nm and 3 nm, respectively, for the film with no buffer layers, and 5 and 6 nm, respectively, for the film with 10 sec buffer layers. Thus, we estimate a buffer layer thickness of $\sim 1.5$ nm for this particular film, in agreement with the expected deposition rates.

Figure 2 shows the MEIS spectra of the buffered Er-doped Si/SiO\textsubscript{2} superlattice film with 10 sec buffer layer before and after annealing. The Er peak is shown en-
Fig. 3. Bright field cross-section transmission electron microscope (TEM) image of the UHV-ion beam sputter deposited superlattice film. The Si layers of a film are amorphous. On the right is the schematic drawing showing the composition of the layers.

Fig. 4. Medium energy ion scattering (MEIS) spectra and fitted data for the UHV-ion beam sputter deposited superlattice film whose nominal Si layers thickness are 0.8 nm. The symbols and lines are data points and results of fit, respectively.

The width of the Er peak is 2.8 nm, in excellent agreement with the TEM result in Fig. 1. Moreover, the Er peak hardly changes following the anneal sequence, indicating that the diffusion of the doped Er atoms during the anneal sequence is negligible, and confirming that we indeed have pure SiO$_2$ buffer layers separating the Si layers and the Er-doped SiO$_2$ layers.

Figure 3 shows the bright-field cross-section TEM image of a UHV-ion beam sputter deposited superlattice film after annealing. The Si and SiO$_2$ layer thicknesses were 1.8 and 9.6 nm, respectively. The Si layers, however, are amorphous unlike the ECR-PECVD deposited films. This is in agreement with results of other researchers who have shown that very thin Si layers are very resistant to crystallization [15,16]. Other UHV-ion beam sputter deposited films were confirmed by TEM to be amorphous (not shown).

Figure 4 shows the MEIS spectra of the UHV-ion beam sputter deposited film with nominal thickness of 0.8 nm. The symbols are data points, and the lines are results of fit. Best results of fit were obtained by assuming no oxygen and $8 \times 10^{14}$ ($\sim$1.4 ML) Si atoms, indicating that we have continuous layer of pure Si even for such thin films. The large difference between the amount of Si in the Si layers and the amount of deposited Si is due to the transition layers between the Si layers and Er-doped SiO$_2$ layers which were formed during depositing the Si and Er-doped SiO$_2$ layers and annealing processes. Finally, the Er concentration of the ECR-PECVD deposited films and UHV-ion beam sputter deposited films were deduced using RBS to be $\sim$0.1 and $\sim$0.5 at.%, respectively (not shown).

As Fig. 5 shows, such increase in the Er$^{3+}$ luminescence intensity is nearly completely suppressed when the deposition time of a buffer layer increases beyond 10 sec.

Figure 6 shows the room temperature Er$^{3+}$ luminescence intensities of the UHV-ion beam sputter deposited superlattice films. We find that as the Si layer thickness decreases from 3.6 to 0.6 nm, the luminescence intensity increases by over an order of magnitude, as shown more clearly in the inset. The temperature dependence of the Er$^{3+}$ luminescence intensities from UHV-ion beam sputter deposited superlattice films are shown in Fig. 7. We find virtually no difference between films with different Si layer thicknesses. In all case, the Er$^{3+}$ luminescence intensity is reduced by a factor of $\sim$2 as the temperature is raised from 25 K to room temperature.

IV. DISCUSSION

The effects shown in Figs 5 and 6 are surprising, as it is opposite of what one might expect at first. First, as the buffer layer thickness increases, there should less of an interaction between the carriers generated in the Si layers and the Er$^{3+}$ ions doped into the SiO$_2$ layers, leading to the reduction of the Er$^{3+}$ luminescence.

But as Fig. 5 shows, such increase in the Er$^{3+}$ luminescence intensity is accompanied by a decrease in the temperature quenching of the Er$^{3+}$ luminescence. As temperature quenching of Er$^{3+}$ luminescence in Si is known to be dominated by "back-transfer", in which excited Er$^{3+}$ ions decay non-radiatively by Auger-exciting a free electron in Si. This suggests that we can explain this result as follows.
In general, Eu³⁺ ions can be excited and de-excited by both free and trapped carriers. For excitation, the trapped carriers are far more efficient. The cross section for trapped-carrier mediated and free-carrier mediated excitation of Eu³⁺ in Si is $3 \times 10^{-15}$ cm² and $6 \times 10^{-17}$ cm², respectively [7]. On the other hand, free carriers are far more efficient for de-excitation of Eu³⁺ ions. The Auger-coefficient for trapped-carrier mediated and free-carrier mediated de-excitation of excited Eu³⁺ in Si is about $1 \times 10^{-15}$ cm³ s⁻¹ and $4 \times 10^{-13}$ cm³ s⁻¹, respectively [7]. A thin buffer layer of pure SiO₂ is very likely to screen effectively such interactions of Eu³⁺ 4f electrons with free carriers in the Si layers since the 4f electrons remain well-localized and atom-like even when doped into a host material [17]. On the other hand, if the buffer layer is thin enough, carriers photo-generated in Si layers can tunnel through the SiO₂ buffer layers to any trap sites in the Er-doped SiO₂ layers (e.g., Er-related defects). Therefore, we can expect that there exists a thickness window in which buffer layers will block the interaction of Eu³⁺ ion with the free carriers only. Given the above mentioned asymmetry between the excitation and de-excitation mechanisms, such buffer layers will then suppress carrier-mediated de-excitation of Eu³⁺ ions while still allowing carrier-mediated excitation of Eu³⁺ ions to proceed.

The increase in the Eu³⁺ luminescence by decreasing the Si layer thickness also presents an apparent paradox since decreasing the Si layer thickness should lead to decrease in the carrier generation rate, thus leading to decrease in the Eu³⁺ luminescence. In contrast to the effects of the buffer layer, however, such increase in the Eu³⁺ luminescence is not accompanied by a reduced thermal quenching of the Eu³⁺ luminescence. This indicates that carrier-mediated de-excitation mechanisms of Eu³⁺ ions are not affected by change in the Si layer thickness.

Such conclusion is consistent with the fact that in UHV-ion beam sputter deposited Si/SiO₂ superlattice films, the Si layers are amorphous. As the carrier localization distance in a-Si is expected to be only 0.6 - 1 nm [18-20], there will be very little quantum effect as the layer thickness is reduced. However, such a short localization length also means that only carriers generated very near the interface will be able to tunnel to the Er-containing oxide layers to excite Eu³⁺ ions. Furthermore, not only will the interior region of the Si layers not contribute to excitation, they will actively militate against efficient Eu³⁺ luminescence, since they will act as efficient recombination centers for carriers generated near the interface. Reducing the volume of the interior region of a-Si layers will then increase only the excitation of Eu³⁺ ions.
tion rate of Er\textsuperscript{3+} ions without affecting its non-radiative decay rates, leading to the effect observed above.

V. CONCLUSION

In conclusion, we have investigated the effect of sub-nm scale dimensional control on the Er\textsuperscript{3+} luminescence properties of Er-doped Si/SiO\textsubscript{2} superlattices. We find that by isolating Er atoms from direct interaction with carriers and decreasing thickness of the Si layers, orders of magnitude increase in the Er\textsuperscript{3+} luminescence can be achieved. The observed effects are ascribed to the results of altered Er-carrier interaction dynamics.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge Dr. J. H. Song for help with RBS analysis. This work was supported in part by Advanced Photonics Technology Project and University Research Program supported by Ministry of Information and Communications in South Korea.

REFERENCES