Photoluminescence from Er-doped Si-in-SiN<sub>x</sub> thin films

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Abstract

Photoluminescence from Er<sup>3+</sup>-implanted Si-in-SiN<sub>x</sub> films emitting efficiently visible light were investigated. A Stark structure in the Er<sup>3+</sup> photoluminescence spectrum was observed at room temperature, which reveals more than one site symmetry for the Er<sup>3+</sup>-centers in the Si-in-SiN<sub>x</sub> matrix. The correlation between the visible photoluminescence from the silicon nanoparticles and the 1.54 µm emission from the Er<sup>3+</sup>-centers was discussed.

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1. Introduction

Photoluminescence (PL) from rare-earth (RE) ions doped silicon-based materials [1–4] including from various silicon nanoparticles (Si–NP), have attracted much attention owing to their promising applications in opto-electronic and photonic devices. One of these examples is amorphous Si-in-SiN<sub>x</sub> thin film containing dense Si–NP of variable size [5–7] and Si rich SiO<sub>2</sub> (SRSO) is probably the most extensively exploration [8–10]. However, because of the large band gap of SRSO, carrier injection for obtaining electroluminescence in rare-earth doped SRSO devices remains a problem to be solved [11]. Si-in-SiN<sub>x</sub> has a relatively narrower band gap than that of SRSO, which might facilitate the carrier injection into the electroluminescent devices based on this material. Furthermore, a much larger density for Si–NP within SiN<sub>x</sub> can be achieved than that in SRSO, resulting in a more efficient light emission [5]. Since Si–NP play an important role in determining the PL behavior of Er<sup>3+</sup> in SRSO:Er films, their presence in the Er<sup>3+</sup>-doped Si-in-SiN<sub>x</sub> (Si-in-SiN<sub>x</sub>:Er) system is believed to be also effective in enhancing the PL intensity from Er<sup>3+</sup>-centers. In this work, we studied the property of PL from the Si-in-SiN<sub>x</sub>:Er films deposited on silicon wafers by plasma-enhanced chemical vapor deposition (PECVD). The Stark splitting of the emission from Er<sup>3+</sup>-centers, and the correlation between the PL from Si–NP and that from Er<sup>3+</sup>-centers were of main interest.

2. Experimental

Nanostructured Si-in-SiN<sub>x</sub> films of about 1 µm thick were grown on Si (100) substrates by PECVD with the gas mixture of SiH<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub> as precursor (as shown in Table 1). The substrate temperature was maintained below 50 °C during the deposition process. Chemical composition of the films can be adjusted by tuning flow rate ratio of [SiH<sub>4</sub>]/[N<sub>2</sub>] (R), and was then determined by energy-dispersive X-ray (EDX) analysis (SERION, FEI) in conjunction with X-ray photoelectron spectroscopy (XPS) (ESCA-Lab, VG) using Al K<sub>α</sub> line for excitation.

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The films were then implanted with Er\(^{3+}\)-ions at energy of 400 keV to a dose of \(3 \times 10^{14} \text{ cm}^{-2}\) and \(3 \times 10^{15} \text{ cm}^{-2}\), and subsequently annealed under Ar + H\(_2\) (95:5) ambient at different temperatures ranging from 400°C to 1000°C for two minutes. The samples were then divided into four groups and labeled according to flow rate ratio \(R\) as shown in Table 1. PL from Er\(^{3+}\)-centers was studied using a 514.5 nm exciting line from an Ar+-laser and detected by an InGaAs detector, while that for the Si–NP was investigated with the 306 nm line from a Xe-lamp and detected by a photoelectric electron-multiplier tube. All measurements were performed at room temperature.

### 3. Results and discussion

The Si 2p peak (labeled by “P”) at about 99.0 eV for samples C0 and D0 can be assigned to elemental silicon as shown in Fig. 1. The 99.0 eV Si 2p peak indicates the presence of silicon rich areas in the samples C0 and D0.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>(R) = [SiH(_4)]/[N(_2)]</th>
<th>(H_2/\text{scm})</th>
<th>(\gamma = [\text{Si}] / [\text{N}])</th>
<th>(\text{Er}^{3+}/\text{cm}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>6</td>
<td>10</td>
<td>0.87</td>
<td>0</td>
</tr>
<tr>
<td>A4</td>
<td>6</td>
<td>10</td>
<td>0.87</td>
<td>(3 \times 10^{14})</td>
</tr>
<tr>
<td>A5</td>
<td>6</td>
<td>10</td>
<td>0.87</td>
<td>(3 \times 10^{15})</td>
</tr>
<tr>
<td>B0</td>
<td>18</td>
<td>10</td>
<td>1.49</td>
<td>0</td>
</tr>
<tr>
<td>B4</td>
<td>18</td>
<td>10</td>
<td>1.49</td>
<td>(3 \times 10^{14})</td>
</tr>
<tr>
<td>B5</td>
<td>18</td>
<td>10</td>
<td>1.49</td>
<td>(3 \times 10^{15})</td>
</tr>
<tr>
<td>C0</td>
<td>36</td>
<td>10</td>
<td>2.06</td>
<td>0</td>
</tr>
<tr>
<td>C4</td>
<td>36</td>
<td>10</td>
<td>2.06</td>
<td>(3 \times 10^{14})</td>
</tr>
<tr>
<td>C5</td>
<td>36</td>
<td>10</td>
<td>2.06</td>
<td>(3 \times 10^{15})</td>
</tr>
<tr>
<td>D0</td>
<td>90</td>
<td>10</td>
<td>2.33</td>
<td>0</td>
</tr>
<tr>
<td>D4</td>
<td>90</td>
<td>10</td>
<td>2.33</td>
<td>(3 \times 10^{14})</td>
</tr>
<tr>
<td>D5</td>
<td>90</td>
<td>10</td>
<td>2.33</td>
<td>(3 \times 10^{15})</td>
</tr>
</tbody>
</table>

Note: If sample X-annealed at 600°C (annealing temperature), we label this sample X-600 (X-annealing temperature).

In sample B0-600, silicon particles also make their presence and emit light, though no well-resolved Si 2p line for elemental silicon is detectable. After being annealed at 600°C, the silicon clusters in A0-600, B0-600, C0-600 and D0-600 samples are generally amorphous and nanosized, as revealed by transmission electron micrographs (not shown here, refer to our previous report Ref. [5]). The inset of Fig. 1 shows the particle size of annealed samples.

After annealing treatments, strong visible PL can be observed in samples containing Si–NP. Fig. 2 displays the PL spectra measured for B0-600, C0-600 and D0-600, respectively. Obviously, in sample B0-600 having the smallest Si–NP, the PL is the most intense at the shortest wavelength. A detailed investigation of the PL properties from Si-in-Si\(_x\)N\(_y\) films prepared with the same procedure and their correlation between the features of Si–NP have been reported elsewhere [5]. It was concluded that the PL characteristic is in consistence with the result predicted by quantum confinement mechanism. By the previous results, the particle size of Si–NP in samples B0-600, C0-600 and D0-600 is estimated to be within about 2.5–4.0 nm.

From our results, we can see that the PL peak position depends on \(R\). With increasing \(R\), the PL peaks are red-shifted, indicating the particle size of Si–NP growing larger. Because of the Si–NP having broad size distribution, the wide PL spectral width of Si–NP was also observed. Note that the PL signal from the Si–NP was not detectable for our samples A0, A4, A5 series (annealed at temperature from 400°C to 1000°C). This is probably because the flow rate ratio \(R\) is too small, which results in inadequate Si content for forming enough Si–NP. Therefore, it is important to find a best \(R\) for intensive emission of Si–NP.

Various crystal field Stark-splittings of Er\(^{3+}\) energy levels occur in different samples containing Er\(^{3+}\). These differences can be found in the Er emission PL spectra. Among the studies of the PL properties of Er\(^{3+}\) in Si based materials, the identifications of the microscopic structure of the optically active Er\(^{3+}\)-centers seems to be crucial for understanding and optimizing the Er\(^{3+}\) emission. During the past
decade, optically active Er$^{3+}$-centers in crystalline Si have been intensively studied [12–14]. The intra-4f transition close to 1.54 μm of Er$^{3+}$ implanted into Si shows rich fine structures due to the crystal field splitting of different defect types. However, the observation was usually made at low temperature, such as 10 K. But to our knowledge, no work has been conducted on PL properties for Si-in-SiN$_x$:Er films. The room temperature PL spectra of two samples (3 × 10$^{15}$, 400 keV, annealed at 600 °C) with different $R$ is shown in Fig. 3. Three strong peaks, P1 (1.528 μm), P2 (1.536 μm) and P3 (1.550 μm) are clearly observed. The most intense emission P2 peak located at 1.536 μm, showing the main emission coming from the $^4I_{13/2}$ to $^4I_{15/2}$ transition of Er$^{3+}$, is as commonly observed for Er$^{3+}$ in Si. The other two PL peaks, P1 and P3, in the vicinity of main emission PL peak P2, are related to Er$^{3+}$-centers from slightly different sites with lower site symmetry. However, the detailed assignment requires a full understanding of the symmetry of different Er$^{3+}$ sites, and therefore further works remain to be done. Fig. 4 presents the dependence of P1, P2 and P3 PL bands on various annealing temperatures for the samples C5 series. From Fig. 4, we can see that these PL bands first increase with increasing annealing temperature. After reaching maximum value at 600 °C, these bands then decrease with further increasing annealing temperature, nearly undetectable at 1000 °C because of the decomposition of the samples. These results imply that the annealing induces the formation of Si–NP when the annealing temperature is lower than 800 °C. The role of Si–NP looks like an efficient sensitizer for Er$^{3+}$ emission.

Fig. 5 shows a typical correlation of the 1.54 μm 4f shell Er transition PL peak measured at room temperature with the 570 nm PL band, which is due to the recombinations of confined excitons within the Si–NP for samples C0-600, C4-600 and C5-600. It can be seen clearly from Fig. 5 that with increasing Er$^{3+}$ doses, the 1.54 μm Er$^{3+}$ emission increases while the 570 nm band decreases, demonstrating a competitive relationship between the light emission from Er$^{3+}$ and from Si–NP in the erbium-doped Si-in-SiN$_x$ films. It infers that the excitation mechanism of Er$^{3+}$ emission in the erbium-doped Si-in-SiN$_x$ is due to the interaction between the Si–NP and the Er$^{3+}$ with energy preferentially transferred from the Si–NP de-excited nonradiatively to Er$^{3+}$. In this process, Si–NP look like as acting as the efficient sensitizers. It should note that this is an identical excitation mechanism which has been found in erbium-doped nanocluster-Si embedded in SiO$_2$ matrix by several research groups before [1–3].

We also studied the PL properties of Er-doped Si$_3$N$_4$ films. The Si$_3$N$_4$ films were prepared by MBE, and the Er$^{3+}$ ions were subsequently implanted. The conditions of implantation and annealing were the same as mentioned above. No detectable PL signal of Er$^{3+}$ at room temperature was observed. This result further demonstrates that the important role of the Si–NP for intensive emission of Er$^{3+}$.
In comparison with the emission mechanism in SRSO:Er, a clear picture emerges from the data we have just shown and it is schematically summarized in Fig. 6. In the absence of the Er, a well known signal at ~570 nm is observed coming from the Si–NP as a result of confined excitons recombination (Fig. 6 (a)). As soon as Er is introduced, when we pump Er-doped Si-in-SiN\textsubscript{x} with a laser beam, a new peak at around 1.54 μm, coming from the \textit{4}I\textsubscript{13/2} to \textit{4}I\textsubscript{15/2} intra 4f shell Er transition, appears. With increasing Er dose, this phenomenon becomes particularly evident with a quenching of the Si–NP luminescence corresponding to a simultaneous enhancement in the Er-related luminescence. This effect is a demonstration of an energy transfer from confined excitons recombination in Si–NP to the erbium ions (Fig. 6(b) and (c)). Processes (b) and (c) are in competition with one another. Si–NP act as a sensitizer for Er\textsuperscript{3+} emission in Er-doped Si-in-SiN\textsubscript{x}.

4. Conclusion

The PL properties of Si-in-SiN\textsubscript{x} and Si-in-SiN\textsubscript{x}:Er films were studied. We observed defined Stark structure with three peaks of PL spectrum of Er\textsuperscript{3+} in Si-in-SiN\textsubscript{x}:Er films at room temperature. The detailed assignment for these bands requires a further understanding of the different symmetries of various Er\textsuperscript{3+} sites. A competitive relation between the light emission from Er\textsuperscript{3+} and from Si–NP in Si-in-SiN\textsubscript{x}:Er is arising from the interaction between the Si–NP and Er\textsuperscript{3+} with energy preferentially transferred from the Si–NP de-excited nonradiatively to the Er\textsuperscript{3+} to excite it. In this process, Si–NP look like an efficient sensitizer.

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References