**Excitation mechanism of visible, Tb$^{3+}$ photoluminescence from Tb-doped silicon oxynitride**

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The excitation mechanism of visible luminescence from Tb$^{3+}$-doped silicon oxynitride is investigated. Tb-doped silicon oxynitride films were deposited by inductive-coupled plasma-enhanced chemical vapor deposition of SiH$_4$, O$_2$, and N$_2$ with concurrent sputtering of Tb. Luminescences from both the host matrix and the Tb$^{3+}$ intra-4$f$ transition are observed, but no correlation is found between them as the composition and the annealing conditions were varied. Photoluminescence excitation spectroscopy shows a strong increase in the Tb$^{3+}$ luminescence intensity as the pump energy is increased above 3.5 eV while the host matrix luminescence decreases. Taken together, the results that there is little energy transfer between band-tail states of silicon oxynitride and Tb$^{3+}$, and that efficient excitation of Tb$^{3+}$ by carriers requires excitation of carriers into the extended states of oxynitride. © 2006 American Institute of Physics.

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There is a growing interest in doping complementary metal oxide semiconductor (CMOS) compatible dielectrics with rare earths to develop light emitters in the visible range that can be monolithically integrated with other photonic and electronic devices. So far, much of the research effort was focused on rare-earth doping of silica. Unfortunately, silica has an extremely large band gap (≈8 eV) that makes efficient injection of carrier difficult. Consequently, nearly all silica-based light-emitting diodes relied on impact excitation of rare-earth ions, and silicon nitrides have a band gap of only about 4 eV, allowing easier injection of current. Indeed, high efficiency, visible light-emitting diodes based on silicon nitride that operate under forward bias without hot-carrier injection have recently been demonstrated. An interesting alternative is rare-earth doping of silicon nitride. Nitrogen is very effective in optically activating rare-earth ions, and silicon nitrides have a band gap of only about 4 eV, allowing easier injection of current. Indeed, high efficiency, visible light-emitting diodes based on silicon nitride that operate under forward bias without hot-carrier injection have recently been demonstrated. However, previous investigations into rare-earth doping of silicon nitride have reported that carrier-mediated excitation of rare-earth ions is ineffective. On the other hand, the carrier-mediated excitation mechanism of rare-earth ions is very general, and should not depend on a particular combination of rare-earth/host materials suggesting that it should operate in silicon nitride as well.

In this letter, we report on Tb-doped oxynitride films grown by plasma-enhanced chemical vapor deposition (PECVD). Tb$^{3+}$ was chosen because it shows a strong, well-defined green luminescence due to the $^{5}D_{4} \rightarrow ^{7}F_{4}$ transition, and oxynitride was chosen to investigate the effect of oxygen on Tb$^{3+}$ luminescence from nitrides. We find that Tb$^{3+}$ ions can be excited via carrier recombination, but that excitation of carriers into the extended, above-band-gap states is necessary as the band-tail states are ineffective in transferring energy to Tb$^{3+}$ ions despite energy resonance.

Tb-doped 220±20 nm thick oxynitride films were grown using SiH$_4$, O$_2$, N$_2$, and Ar by inductive-coupled PECVD with concurrent sputtering of Tb in which a metal Tb target was placed inside the plasma and biased negatively, similar to the method reported in Ref. 14. The base and deposition pressures were $\sim 1 \times 10^{-6}$ and $\sim 4 \times 10^{-5}$ torr, respectively. The deposition temperature and rf power were 300 °C and 300 W, respectively. The film composition was varied by varying the gas flow rates. For comparison, a similar set of oxynitride films without Tb was also deposited. After deposition, the films were annealed for 30 min at temperatures ranging from 550 to 950 °C in flowing Ar environment. The Si and Tb contents were kept constant at 39±1 and 0.25±0.03 at. %, respectively, while the O/N ratio was varied between 0.14 and 0.44. In this letter, we will concentrate on three films with O/N ratios of 0.14, 0.37, and 0.44, henceforth referred to as low O, mid-O, and high O, respectively, as other films with intermediate O/N ratios had characteristics that were also intermediate of the three films (data not shown). Note that in all cases, we have no excess Si as the oxygen and nitrogen contents are higher than those necessary to form stoichiometric Si$_3$N$_4$ and SiO$_2$. Indeed, high resolution transmission electron microscopy showed that the films remain homogenous and amorphous even after high temperature anneals without any discernible Si nanoclusters or other crystalline phases (data not shown). Table I summarizes the compositions of the three films, as determined by Rutherford backscattering spectroscopy (RBS).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si (at. %)</th>
<th>N (at. %)</th>
<th>O (at. %)</th>
<th>Tb (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low O</td>
<td>38.1</td>
<td>54.1</td>
<td>7.5</td>
<td>0.28</td>
</tr>
<tr>
<td>Mid O</td>
<td>37.8</td>
<td>45.1</td>
<td>16.8</td>
<td>0.26</td>
</tr>
<tr>
<td>High O</td>
<td>38.0</td>
<td>43.2</td>
<td>18.6</td>
<td>0.22</td>
</tr>
</tbody>
</table>

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Photoluminescence (PL) measurements were performed at room temperature using the 325 nm line of a HeCd laser, a grating monochromator, and an InGaAs-Cs photomultiplier tube, and employing the standard lock-in technique. The nominal pump power was 45 mW, and the spectra were corrected for the system response. Photoluminescence excitation (PLE) spectroscopy was performed using Edinburgh FS920 spectrometer with a Xe light source.

Figure 1(a) shows the PL spectra of Tb-doped films after 650 °C anneal. We observe sharp peaks at 488, 544, and 590 nm due to the $^7D_4 \rightarrow ^7F_6$, $^7F_5$, and $^7F_4$ intra-4f transitions of Tb$^{3+}$, respectively, superimposed on background luminescence peak from the oxynitride host matrix centered around 550 nm. Such broad luminescence from oxynitride films has been observed before, and is ascribed to band-tail–band-tail transitions between localized states associated with Si–N bonds in the host matrix.\textsuperscript{15,16} Figure 1(b) shows the PL spectra after 950 °C anneal. We find that the Tb$^{3+}$ PL peaks have increased in intensity while the band tail PL is nearly completely quenched, leading to pure Tb$^{3+}$ PL. Furthermore, as the inset shows, the Tb$^{3+}$ luminescence decay after 950 °C is characterized by a single exponential decay with a lifetime of $\sim 750$ $\mu$s from all films. Such values are comparable to those from Tb-doped SiO$_2$,\textsuperscript{17} and indicate a high Tb$^{3+}$ luminescence efficiency.

Figures 2(a) and 2(b) show the PL spectra of Tb-free films after 650 and 950 °C anneals, respectively. The scales are the same as the ones used in Fig. 1 such that the intensities may be compared directly. We observe the same band tail luminescence centered around 550 nm from the films annealed at 600 °C, and a similar quenching of the band tail luminescence after 950 °C anneal.

The composition and anneal dependence of the Tb$^{3+}$ and band tail PL intensities are summarized in Fig. 3. We find that except for the low-O film, the Tb$^{3+}$ PL intensity generally increases with anneal temperature. In all cases, however, the Tb$^{3+}$ PL is reduced strongly as the temperature is raised to 1100 °C, coincident with the previous report on Tb-doped SiO$_2$. On the other hand, the band tail PL intensities are at their highest in the 500–700 °C anneal temperature range regardless of Tb doping or oxygen content, and decrease abruptly as the anneal temperature is increased further.

In case of other rare-earth-doped semiconductors transfer of energy from the host to rare-earth ions often result in strong suppression and/or modification of the host luminescence.\textsuperscript{18–22} In fact, such suppression is often taken to be an evidence for energy transfer from the host to the rare-earth ions. However, as Fig. 3 shows, Tb doping reduces the band tail PL intensities of oxynitride films by at most 50%, much less than what has been reported from other host materials.\textsuperscript{18,19,21} Furthermore, as Fig. 2 demonstrates, the quenching of band tail PL upon high temperature annealing is intrinsic to oxynitrides, and not related to Tb$^{3+}$ ions. As no
change in composition after high temperature anneals is detected by RBS (data not shown), we ascribe the band tail PL quenching to creation of silicon dangling bonds that act as PL quenching centers.15

Taken together, Figs. 1–3 seems to indicate that the energy transfer from the oxynitride matrix to Tb3+ ions is not effective. It should be noted, however, that the 325 nm pump beam does not coincide with any optical absorption band of Tb3+. Therefore, the fact that we observe Tb3+ PL at all indicates that some energy transfer must occur. In order to investigate the energy transfer mechanism in more detail, PLE spectroscopy was performed, the results of which are shown in Fig. 4. The PLE spectra of the band tail PL intensity monitored at 528 nm from Tb-doped and Tb-free films are again nearly identical. They both show an overall decrease in the PL intensity with increasing excitation energy except for a small peak centered near 3.9 eV, as had been reported before for silicon oxynitride films.15 The PLE spectra of Tb3+ PL intensity monitored at 544 nm is completely different. We find little Tb3+ PL intensity at low excitation energies, but as the excitation energy is increased to above 3.5 eV, the Tb3+ PL intensity increases strongly and continuously, providing a clear evidence for an efficient carrier-mediated excitation of Tb3+. Consequently, the Tb3+ peaks completely dominate the PL spectrum from all Tb-doped films when excited at energies in excess of 4 eV.

Such excitation-energy dependence of energy transfer from the host to Tb3+ ions is consistent with, and can be explained by, results of theoretical investigations into carrier-mediated excitation mechanism of rare-earth ions. They have shown that while almost any process in which carriers lose a sufficient amount of energy can excite rare-earth ions, recombination of carriers localized at a rare-earth-related state is the most effective excitation mechanism.11,12 The band tail states that are responsible for the oxynitride host luminescence, however, are caused by disorder and completely unrelated to Tb3+ ions. Thus, the lack of correlation between Tb3+ and host PL can be understood to simply reflect the predicted inefficiency of energy transfer to Tb3+ ions from recombination of carriers localized at a state unrelated to Tb3+. This also explains why previous investigators have failed to observe any energy transfer, as they used an Ar laser that can excite carriers only into such band tail states.9,10

The onset of efficient energy transfer at excitation energies exceeding 3.5 eV can be understood in the same way. We note that the threshold value of 3.5 eV agrees very well with the reported values of 3.5–4 eV for optical gap of comparable silicon nitride and oxynitride films,9,15,25 indicating that efficient energy transfer requires excitation of carriers across the optical gap into the extended states—carriers that can then be captured by Tb3+-related states. It interesting to note that previous investigation into Er-doped hydrogenated amorphous silicon film deposited by PECVD has come to the same conclusion,21 indicating that the necessity to excite carriers into extended states may apply to rare-earth ions doped into amorphous hosts in general. This also implies that in order for visible light-emitting diodes based on rare-earth-doped nitrides to operate under low forward bias, the contacts must be engineered to efficiently inject carriers directly into the extended states of the active layer.

In conclusion, we have investigated the excitation mechanism of Tb3+ in Tb-doped silicon oxynitride. We find that there is little transfer of energy to Tb3+ ions from recombination of carriers trapped in the localized, band tail states of oxynitrides. However, contrary to previous reports, efficient carrier-mediated excitation of Tb3+ ions is possible, provided that the excitation energy is high enough to excite carriers into the extended state of the oxynitride.

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