Photoluminescence and Structural Analysis of Samarium Doped TiO$_2$ Thin Films and Their Applications to Visible LEDs

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Abstract

Samarium-doped anatase TiO$_2$ (A-TiO$_2$:Sm) and rutile (R-TiO$_2$:Sm) single phase thin films are fabricated by laser ablation and post-annealing at different temperatures. A-TiO$_2$:Sm samples exhibit intense PL emission, whilst R-TiO$_2$:Sm samples exhibit weak PL emission. The local crystal structure of Sm-dopants is investigated using X-ray absorption fine structure (XAFS) measurements. The thin films showing strong PL emission have lower crystal symmetry than the other samples, which show weak PL emission. We report the relationship between changing the symmetry of the local structure and activation of the luminescent center. The local structure of Sm$^{3+}$ thin films annealed at 600°C to 800°C, which possess an activated semi-stable Sm$^{3+}$ ions luminescent center, dramatically changes from having high symmetry to low symmetry. While the phase transitioned R-TiO$_2$:Sm and fabricated as R-TiO$_2$:Sm samples showed highly symmetric. Hence, the coordination around the doped-Sm$^{3+}$ ions is the key factor for exhibiting an intense PL emission. Therefore, activation of the luminescent center is strongly connected with the distorted local crystal symmetry, which is proposed as one of the factors defining the transfer probability. In this work, we discuss the connection between coordination around Sm$^{3+}$ ions and PL intensity, and optical and electrical properties of a n$^-$-ITO/TiO$_2$:Sm/p-NiO/p$^+$-Si hetero junction LED preparing with optimal fabricating condition.

Keywords

Rare-Earth, Semiconductor, Photoluminescence, XAFS, LEDs

1. Introduction

Rare earth element doped semiconductors and oxide materials have been studied...
for a long time as they have the potential for application in visible and infrared light emitting diodes and other optical devices [1]-[6]. Particularly, the combination of erbium (Er) and silicon (Si) is extensively studied because the Er-related 1.54 µm emission corresponds to a minimum loss window of the optical fibre, which makes it industrially profitable [7] [8] [9] [10]. The local structure of doped-Er³⁺ ions in oxide semiconductors is of particular interest. Er³⁺ is surrounded by oxygen (O) ligands, and the intensity of its luminescence is influenced by the symmetry of the surrounding O ligands [9] [10]. The chemical properties of both the doped rare earth and host materials can be considered to determine the atomic coordination of the doped rare earth element-O luminescent center. This fact indicates that analyzing the symmetry of rare earth-O would enable determination of the optimal conditions for the production of applicable materials with a luminescent center.

Selecting host semiconductors with a wide band gap is also known to be essential for effective excitation of the rare earth element. It was noted that certain semiconductors, including ZnO, GaN and TiO₂, would be good candidates as host materials for optical devices [1] [2] [3] [4] [11] [12] [13] [14]. Such semiconductors will enhance the rare earth ions-related emission as they possess a wide band gap [15] [16]. TiO₂ is attracting increasing attention as a host wide-gap semiconductor. It is an environmentally-friendly material, so can not only be used as a host for luminescence and applied to LEDs and other optoelectronic devices, but can also be applied to solar cells, photocatalysts and other energy-related products [17] [18] [19]. TiO₂ has three crystal phases: anatase (A-TiO₂, tetragonal, band gap: 3.2 eV), rutile (R-TiO₂, tetragonal, band gap: 3.0 eV) and brookite (orthorhombic) [19] [20]. Most of the applications select the crystal phase of A- or R-TiO₂ with suitable properties depending on the usage.

Sm³⁺ was chosen as the dopant in the semiconductor. Its optical and luminescent properties of Sm have been studied by using several techniques for preparations of samples, such as the atomic layer deposition, sol-gel method, doping on borate glasses, and laser ablation technique [21]-[26]. Each of the techniques has unique advantages. In this work, the samples were fabricated by using laser ablation, because the crystalline phase of the host material, TiO₂ need to be appropriately selected. Additionally, the local structure has been investigated [25] [26]. Addition of SmO₆ resulted in distortion of the host semiconductors of TiO₂ with C₄ᵥ symmetry and exhibited the most intense photoluminescence (PL) emission [26]. From the application as optical devices, these different crystalline structures may affect the rare earth-related PL emission; Sm³⁺ exhibits a sharp 1.2 µm emission, as it closely resembles Er. Based on these facts, we report the comparison of the local structures, especially estimation of symmetry by using XAFS measurement, and PL intensity of Sm-doped A- and R-TiO₂ with different annealing temperatures, and the coordination around Sm³⁺, while the Sm³⁺ ions luminescent center is activated. Also LED device has been fabricated based on the same sample of above. Electrical and optical properties are reported.
2. Experimental Procedure

The Sm-doped TiO₂ (TiO₂:Sm) thin films were deposited by laser ablation using a Q-switched yttrium aluminum garnet (YAG) laser (4ω₀ = 266 nm, 1 J/cm²). A TiO₂ ceramic target, including 1.0 wt% Sm₂O₃, was used as the deposition source. Laser ablation is a typical method for synthesizing a thin film with the same composition ratio as the target. The A-TiO₂ and R-TiO₂ thin films were deposited in a vacuum chamber with different atmospheres; A-TiO₂ with an O₂ pressure of 1 × 10⁻² Torr and R-TiO₂ without O₂ under a pressure of 1 × 10⁻⁷ Torr. As has been reported in our previous work, selecting an appropriate atmosphere enables the production of the suitable crystalline phase (A- or R-) of TiO₂ [24].

By ablation of the amorphous phase, TiO₂:Sm thin films of 300 nm thick were formed on Si (100) surfaces at room temperature. After the deposition, the samples were annealed at a temperature between 300°C to 1100°C, with temperature intervals of 100°C, for 2 min or 30 min in the O₂ atmosphere for optical activation of Sm³⁺ ions and formation of the nanometer-sized TiO₂ crystals. The crystal phase and grain sizes were estimated by X-ray diffraction (XRD). A He-Cd laser (λ = 325 nm) was used to excite the Sm³⁺ and to measure the PL spectra from the TiO₂:Sm thin films.

The X-ray absorption fine structure (XAFS) measurements using synchrotron radiation (SR) were performed at the High Energy Accelerator Research Organization on BL 27B Photon Factory in Tsukuba prefecture, Japan. A Si double crystal set was used to monochromatize the SR beam. A seven-element pure-Ge solid-state detector was used for counting the fluorescence X-rays proportional to the X-ray absorption of the TiO₂:Sm thin films. The X-ray incidence angle was fixed at 45°. The Athena and Artemis of Demeter, which are free programs for XAFS analysis created by Ravel B, were used for an ordinary process of XAFS analysis, that is, extracting the oscillations and fitting the Fourier spectra.

3. Result

3.1. Estimation of Crystal Phase and PL Properties of Sm-Doped Anatase and/or Rutile TiO₂

Figure 1 shows the XRD patterns of Sm-doped TiO₂ thin films annealed at different temperatures. The conditions for fabricating the samples were fixed for the experiments of A-TiO₂:Sm to keep the same preparation conditions. The atmosphere for the film deposition and an annealing time of 30 min for R-TiO₂:Sm are the only differences from the fabricating conditions for A-TiO₂:Sm. Selecting the appropriate atmosphere for ablation can enable the production of the suitable crystal phase (A- or R-) TiO₂:Sm, which we reported in a previous study [24]. The as-deposited thin film is yet to be used in any post-annealing processes. The strongest peak of A (101) at 2θ = 25.3° can be observed for the sample fabricated as anatase and post-annealed at 700°C in Figure 1(a). The crystal phase was indexed by the JCPDS card No. 21-1272 (25.323,
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Figure 1. XRD patterns of Sm-doped (a) A-TiO$_2$ and (b) R-TiO$_2$ thin films annealed at different temperatures.

37.839, 48.071, 53.948), and its grain size was 25.8 nm. The as-deposited TiO$_2$:Sm thin films were in the amorphous phase. The series of samples which were fabricated as A-TiO$_2$:Sm and post-annealed at temperatures from 700°C to 1000°C showed the anatase phase, as was expected. A-TiO$_2$:Sm was changed to
R-TiO$_2$:Sm with an annealing temperature of 1100°C. Details have been reported in our previous work [25]. Additionally, Figure 1(b) shows that the peak at 2$\theta$ = 27.5$^\circ$ can be identified as rutile phase based on the JCPDS card No. 21-1276 (27.446). The sample was fabricated as R-TiO$_2$:Sm, as was expected. And its grain size was 1.5 nm which was very smaller than the sample fabricated as anatase crystalline phase.

Figure 2(a) shows the comparison of the PL spectra between A- and R-TiO$_2$:Sm thin films annealed at 600°C. The annealing time of each sample was

![Image](image_url)

Figure 2. (a) shows PL spectra of A- and R-TiO$_2$:Sm thin films at room temperature; (b) is the PL intensity ratio at 613 nm of A-TiO$_2$:Sm annealed at different temperatures.
2 min for A-TiO$_2$ and 30 min for R-TiO$_2$. The PL intensity of the R-TiO$_2$:Sm is 40 timed the actual intensity. The PL emissions corresponding to $^4$G$_{5/2} \rightarrow ^4$H$_J$ ($J = 5/2, 7/2, 9/2$ and $11/2$) intra-4f transitions in Sm$^{3+}$ ions can be observed. The different PL intensities indicate the difference of the transition probability, and the different fine structure of the PL spectra suggests the difference of coordination around the Sm$^{3+}$ ions, which is the luminescent center. Additionally, this result indicates that R-TiO$_2$:Sm is not suitable for application to optical devices compared with A-TiO$_2$:Sm, even if it is prepared under the optimal conditions for activation of the luminescent center. In our previous work, the crystal symmetry of Sm$^{3+}$ ions has been shown to be strongly connected with the luminescent center and the efficiency of luminescence [25]. These facts indicate that there must be a difference of the local structure between samples that show strong PL spectra and weak PL spectra. Figure 2(b) shows the PL emission intensity ratio at 613 nm of A-TiO$_2$:Sm annealed at different temperatures. PL intensity becomes stronger with an increasing annealing temperature. Jing et al reported that PL from Sm$^{3+}$ was activated from 400°C [24]. With a further increase of the temperature, the PL intensity became weaker after reaching 700°C. This result suggests that Sm$^{3+}$ with a crystal field allowing intra-4f transitions is formed in the crystal matrix by the annealing. Hence, the fabricated samples annealed at an appropriate temperature results in a window for making the luminescence center. As reported in our previous work, at an annealing temperature of 1100°C, anatase phase A-TiO$_2$:Sm transitioned to rutile phase R-TiO$_2$:Sm. Both the phase transitioned R-TiO$_2$:Sm and deposited R-TiO$_2$:Sm exhibited weak PL spectra.

3.2. Investigation of the Details of Electronic Levels by XAFS Experiment and Preparations for EXAFS Analysis

Figure 3 shows the XAFS spectra at the Sm L$_{III}$-edge (6720 eV) of A-TiO$_2$ obtained at temperatures between 400°C to 1100°C as well as the as-deposited sample. The series of samples are the same as that in Figure 1(a). The spectra of R-TiO$_2$:Sm obtained at annealing temperatures of 650°C and 400°C and the as-deposited sample are shown in Figure 4. The lowest spectrum is that from the Sm$_2$O$_3$ powder of the standard sample. An analysis of the X-ray absorption near edge structure (XANES) provides information on the electronic property. The most intense peak, called the “white-line”, is intrinsic to the Sm oxides: SmO$_x$ (generally $x > 6$). The drawn dotted line at the white-line shows the excitation energy of Sm$^{3+}$. The peak absorption of every spectrum appeared at the same peak from the Sm$_2$O$_3$ powder, which suggests that the Sm$^{3+}$ state was mainly formed in SmO$_x$ without any out diffusions. The full width at half maximum (FWHM) of the white-line for A-TiO$_2$ can be estimated as (b) 7.2 eV, (c) 9.5 eV, (d) 9.3 eV, (e) 10.4 eV, (f) 9.0 eV, (g) 9.0 eV and (h) 6.6 eV. The FWHM of the Sm$_2$O$_3$ powder has not been estimated because the XAFS spectra are incomparable owing to the difference in purity of the standard sample and our impurity samples; the absorption element, Sm was only doped at 1 wt%: $7.38 \times 10^{19}$/cm$^3$. 

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Figure 3. XAFS spectra at the Sm L_{III}-edge of A-TiO_{2}:Sm thin films obtained at different annealing temperatures. The lowest spectrum is that from the Sm_{2}O_{3} powder of the standard sample.

Figure 4. XAFS spectra at the Sm L_{III}-edge of R-TiO_{2}:Sm thin films obtained at different annealing temperatures. The lowest spectrum is that from the Sm_{2}O_{3} powder of the standard sample.
The wider FWHM of (c) to (g) in Figure 3 indicates a broadening of the 5d density of states (DOS) in A-TiO$_2$:Sm because of the excitation from an Sm 2p inner shell to 5d unoccupied states. However, for the sample that phase transitioned to R-TiO$_2$:Sm, the as-deposited sample, and the samples in Figure 4, R-TiO$_2$:Sm is sharper than the other A-TiO$_2$:Sm samples, which suggests condensed Sm 5d DOS. Additionally, there are tails on the lower energy side of the white-lines of spectra (c) to (g) in Figure 3, suggesting a lower ion charge number, Sm$^{Z+}$ ($Z < 3$) [9] [27]. However, this lower oxidation number can be considered to not be too low so as to affect the luminescence. Figure 2 has already showed that the thin films annealed at 700°C, which is curve (e) in Figure 3, exhibit the most intense photoluminescence in this study. These characteristics result from the existence of various bond lengths of Sm-O in A-TiO$_2$; Ishii et al reported that various orbital hybridizations of rare earth elements with O broaden the rare earth 5d DOS and partially yield its ion charges [9]. Curves of (b) and (h) in Figure 3 and Figure 4 suggest that these samples can be considered to have the same bonding lengths, more stability and higher symmetry than A-TiO$_2$:Sm.

Figure 5 shows the $k^2$-weighted extended X-ray absorption fine structure (EXAFS), that is, the $\chi(k)$ oscillations of Sm in TiO$_2$:Sm. The photoelectron vector, $k$, is defined as $k = (8\pi m (E - E_0)/h^2)^{1/2}$, where $m$ is the electron mass, $E$ is the photon energy, $E_0$ is the energy threshold of the absorption edge and $h$ is the Planck constant. A greater weighting $k^n$ results in emphasizing the higher oscillations. The equation for EXAFS oscillation is:

$$\chi(k) = S_0^2 \sum_j N_j \frac{R_j}{k} F_j(k) \exp \left( -2\sigma_j k^2 - \frac{2R_j}{\lambda_j(k)} \right) \sin \left( 2kR_j + \phi(k) \right)$$  \hspace{1cm} (1)

Thus, EXAFS oscillation is a sum of exponentially damped sine waves. $S_0^2$ is a loss term which accounts for multi-electron excitations and inelastic scattering, $N_j$ is the number of atoms in each shell, $R_j$ is the distance between absorbing and scattering atoms, $F_j(k)$ is the magnitude of the complex function describing the scattering, $\sigma_j$ is a Debye-Waller factor between the absorber and a scattering atom, $\lambda_j$ is the mean free path of the electron, $\phi(k)$ is the phase shift and the index $j$ references a shell of the element. $N_j$ and $R_j$ are already known if it is a standard sample, $F_j(k)$ and $\phi(k)$ can be obtained by calculation using the FEFF program [28] [29]. The reliability of XAFS analysis is one of the big issues for all studies which use XAFS measurement. Binsted et al reported EXAFS data analysis with curved wave theory [30]. This equation and parameters will be used for the fitting of the samples. The EXAFS oscillations are obtained from the background removed XAFS spectra with proper $k^n$ weighting ($n = 1, 2, 3$). We chose $k^2$ because the higher range of oscillations (after 8.0 Å$^{-1}$) were noisy. The window function was performed in the range of 2.0 - 8.0 Å$^{-1}$, $dk = 0.5$. The chosen ranges in the XAFS analysis used in this study are all the same to facilitate comparison. There are no significant differences of the different annealing temperatures or the different crystal phases. More detailed estimations of the local
Figure 5. \(k^2\)-weighted EXAFS oscillations (solid line) and window functions (dashed line) of A-TiO\(_2\):Sm (a) and R-TiO\(_2\):Sm (b) thin films.
structure are expected from the Fourier transformed spectra. The EXAFS analysis was performed to clarify the details of the local structure of the absorption element, such as the atomic distance of the nearest-neighbors to the Sm. **Figure 6** shows the radial structural function (RSF) around Sm obtained by the Fourier transform (FT) of $k^2$-weighted XAFS spectra and the $k^2 \chi$ of (a) A- and (b) R-TiO$_2$:Sm. The first nearest-neighbor (NN) atom from Sm was observed at approximately 1.5 - 2.0 Å for all samples in **Figure 6(a)**. This value is

![Figure 6](image-url)
shorter than the actual distance, because the result does not account for the phase shift of the photoelectrons by scattering of atoms in the FT. The actual distance can be obtained by the fitting result that will be discussed later. There were peaks located at an average distance of less than 1.1 Å owing to the low frequency waves in the background. This range was not taken into consideration owing to this reason. As shown in Figure 6, these small radii can be considered when the first NN atoms from Sm is O. The samples which exhibit the most far distance are the as-deposited and 1100°C samples, and exhibit a shorter distance with an increasing annealing temperature, as shown in Figure 6(a). The sample annealed at 700°C has the shortest distance, and the samples annealed at higher temperature than 700°C exhibit a longer distance. The peak of the as-deposited and 1100°C samples appeared near the peak of the Sm₂O₃ powder, suggesting the distance of these samples is closer to the Sm-O bond length in Sm₂O₃ rather than the Ti-O bond length in TiO₂. The ion radii of Ti⁴⁺ is smaller than that of Sm³⁺, so the Ti-O bond length is shorter than the Sm-O bond length in Sm₂O₃, from the FEFF calculation. Hence, we can predict that the bond length of the other samples is closer to the Ti-O bond length rather than that of Sm-O. These tendencies are also observed in other properties. The RSF of R-TiO₂:Sm shows a similar tendency as that of A-TiO₂:Sm. The samples annealed at higher temperature exhibit a shorter bond length. The back FT was performed in the range of 2.0 - 2.9, with \( dr = 1.0 \) for the fitting process.

3.3. Analysis and Mechanism of the Activation of the Luminescent Center

We used the model of crystallographically valid TiO₂:Sm or Nd, and calculated the path of TiO₂ which replaced Ti with doped rare earth element in our previous work [25] [31] because we already know the first NN of Sm is O, and doped Sm replaces at the Ti site; that is, a rare earth-O complex forms at the lattice site of II-IV semiconductors, as was reported in the case of Er-doped TiO₂ [9]. This hypothesis is reliable, because of the similarity of the chemical properties of the rare earth elements. In this paper, we used only one path of Sm₂O₃, which was calculated by FEFF. This is a reasonable fitting process, because our only interest currently is relative to Sm-O. Firstly, the Sm₂O₃ powder was fitted as the standard sample. Then, the fabricated samples were fitted by using the parameter of \( S_0^2 \) obtained from the fitting of the powder [27]. As shown in Equation (1), \( S_0^2 \) is a loss term. There is a parameter in the fitting process termed “amp (amplitude)”. This amp is defined as \( amp = S_0^2 \times N_j \). \( N_j \) is determined from the standard sample. Fitting the standard sample means obtaining \( S_0^2 \), which can be used for fitting other samples because both the standard sample and the fabricated samples are relative to Sm-O. It was hypothesized that there are two patterns of the local structure of Sm: the Sm-O₆ complex with the same distance, and the Sm-O₂ and Sm-O₄ complex bonding Sm with two different distances. Even if the peak was fitted as having the same distance, this does not
mean all of the Sm-O₆ complex actually binds with the same distance, although a benefit of this fitting process is the ease of determining the symmetry.

Table 1 and Table 2 show the bond lengths of the fitting result of A- and R-TiO₂:Sm with different annealing temperatures. The as-deposited sample in Table 1, 400°C, 900°C and 1100°C were fitted using the Sm-O₆ complex with the same distance. As mentioned above, this does not mean all 6 bond lengths were exactly the same distance, but rather enabled easy determination of a change of symmetry state. For relatively highly symmetrical samples, where the distance between the first NN and the second NN is within the fitting error, it is suitable to fit using only one distance. At each temperature, the first NN were 2.41 Å, 2.29 Å, 2.34 Å and 2.41 Å, for as-deposited, 400°C, 900°C and 1100°C samples, respectively, as shown in Table 1. The samples annealed at temperatures of 600°C, 700°C and 800°C were suitable for fitting the Sm-O₆ complex using two distances. For each temperature, the first NN were 2.19 Å, 2.16 Å and 2.37 Å and the second NN were 2.43 Å, 2.63 Å and 2.66 Å, respectively. The distance between the first NN and the second NN were 0.24 Å, 0.47 Å and 0.29 Å. The fitting error of all the fitting results of the first NN was approximately ±0.02 to ±0.04 Å. The fitting error of all results of the second NN was approximately ±0.05 to ±0.07 Å. The difference between the distance of the standard value and experimental value should be considered. Even if the standard sample is measured, there is always an error between the standard value and experimental value. The fitting result of the Sm₂O₃ powder, the standard sample, can be used to estimate this error. The standard value of Sm₂O₃ is 2.29 Å and the fitting result

Table 1. The bond length from the fitting result of A-TiO₂:Sm annealed at different temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Fitting result</th>
<th>Distance between 1 and 2</th>
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<tbody>
<tr>
<td></td>
<td>1. The first NN</td>
<td>2. The second NN</td>
</tr>
<tr>
<td>As-depo</td>
<td>2.41 Å</td>
<td>-</td>
</tr>
<tr>
<td>400°C</td>
<td>2.29 Å</td>
<td>-</td>
</tr>
<tr>
<td>600°C</td>
<td>2.19 Å</td>
<td>2.43 Å</td>
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<tr>
<td>700°C</td>
<td>2.16 Å</td>
<td>2.63 Å</td>
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<tr>
<td>800°C</td>
<td>2.37 Å</td>
<td>2.66 Å</td>
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<tr>
<td>900°C</td>
<td>2.34 Å</td>
<td>-</td>
</tr>
<tr>
<td>1100°C</td>
<td>2.41 Å</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. The bond length from the fitting result of R-TiO₂:Sm as-deposited and annealed at different temperatures.

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>Fitting result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The first NN</td>
</tr>
<tr>
<td>As-depo</td>
<td>2.46 Å</td>
</tr>
<tr>
<td>400°C</td>
<td>2.35 Å</td>
</tr>
<tr>
<td>600°C</td>
<td>2.21 Å</td>
</tr>
</tbody>
</table>
was 2.52 Å. Hence, the error was approximately 10%. The standard value obtained from ATOMS showed that A-TiO₂ consisted of Ti-O₄ of 1.937 Å and Ti-O₂ of 1.966 Å. R-TiO₂ consisted of Ti-O₄ of 1.948 Å and Ti-O₂ of 1.980 Å. There was also a considerable error of 10% between the standard value and the investigated samples. These differences mainly arose from the XAFS measurements, which exhibited an off-shift from the literature data. There was also a difference in the ionic radii because Sm³⁺ replaced Ti⁴⁺. However, these errors do not negate the fitting results. For the A-TiO₂ samples annealed at 600°C to 800°C, the distances can be fitted as two lengths, such as Sm-O₄ and longer Sm-O₂, as shown in Table 1. This result indicates that the coordination around the Sm atom was more distorted than others, which can be fitted as Sm-O₆ with the same distance. The difference can be estimated within the fitting error or the standard value of the distance between Ti-O₄ and Ti-O₂, and this low symmetrical tendency was increased at an annealing temperature of 700°C, which was the sample with the most intense PL. This fact reveals the connection between the activation of the Sm luminescent center and the coordination around Sm³⁺ ions. In Table 2, the fitting results of the R-TiO₂ are shown and indicate the samples were all highly symmetrical. The analysis of the XANES showed the same result regarding the symmetry, suggesting our prediction was reasonable.

3.4. Discussion

Ishii et al reported the effect of oxidization on the optical and electrical properties. The optimal sample, which was A-TiO₂:Sm annealed at 700°C for 3 min, is the optimal conditions for exhibiting strong PL emission. On the other word, this sample was sufficiently oxidized to emit intense PL [14].

They also reported that Sm is known to easily form chemical bonds with oxygen and produces large Sm and oxygen complexes, such as SmOₓ (generally, x > 6). The SmOₓ-like complexes are considered to have a definite structure that is determined by the molecules surrounding A-TiO₂, and so a local distortion owing to the complexes produces a uniform trapping level. The optimally oxidized sample has larger A-TiO₂ grains. However, the insufficiently oxidized samples have indefinite coordination numbers, resulting in an optically unfavorable structure. These facts might aid in the energy transfer process of the doped Sm³⁺ ions, giving rise to the intense PL emission.

Figure 7 shows the grain sizes of A- and transition to rutile phase of R-TiO₂:Sm obtained with different annealing temperatures evaluated from XRD patterns [25]. They were estimated according to the Scherrer equation \( D = \frac{0.9 \lambda}{\beta \cos \theta} \), where \( \lambda \) is the X-ray wavelength (0.154 nm), \( \beta \) is the FWHM of the XRD, and \( \theta \) is the diffraction angle. The values of \( \beta \) and \( \theta \) were taken from A (101) and R (110) diffraction lines. The crystallite diameters of all A-TiO₂:Sm samples annealed at 700°C to 1000°C were estimated to be approximately 25.8 nm. There is also a probability that the high crystallinity would result in intense luminescence [24] [32]. For the discussion of this point of view on R-TiO₂, we prepared the
A-TiO$_2$:Sm thin films annealed at 1100°C, which showed rutile phase of R-TiO$_2$:Sm in the XRD patterns. This sample can be expected to exhibit higher crystallinity than A-TiO$_2$:Sm, and the evaluation of its crystallite diameter was 26.3 nm. As a reference, the trapping center of the optically optimal sample is optimally oxidized with larger A-TiO$_2$ grains, and locally distorted to produce a uniform trapping level [14]. This result and facts indicate the reason that R-TiO$_2$:Sm shows a weaker PL spectra than A-TiO$_2$:Sm is not due to the grain sizes being so small that the thin films show weak luminescence, but rather the difference of the crystal symmetry. This indicates that the crystallinity is not the most important factor to achieve an intense PL emission, but rather the atomic coordination around Sm$^{3+}$.

Hence, the transition probability enables determination of the conditions of materials with an optimal luminous efficiency for application. We have not reached that point in theory, but the symmetry around the doped rare earth element can be shown to be key for obtaining intense luminescence. Further research is required to understand these processes in greater detail.

### 3.5. Fabrication of a n+-ITO/TiO$_2$:Sm/p-NiO/p+-Si Hetero Junction LED

The result and analysis of PL property and local fine structure revealed the optimal preparing condition, annealing temperature of 700°C, of A-TiO$_2$:Sm thin films for enhancing emission. LEDs were prepared under this condition on Si (100) surface. The structure of LED was shown in the inset of Figure 8. At first,
140-nm-thick p-NiO thin film was fabricated at the substrate temperature of 150°C. Then, TiO2:Sm thin film was formed as the same thickness of p-NiO on NiO surface at RT. Finally, 100-nm-thick transparent ITO layer was formed as a surface electrode. After deposition, the samples were annealed in an O2 ambient at 700°C for 3 minutes. Al was selected as a back electrode which was formed 100-nm-thick.

The inset of Figure 8 shows current-voltage characteristics of the same LED. Threshold was approximately 8 V. This slightly high threshold was due to high electrical resistivity of TiO2:Sm layer which increased after annealing process. Although, this LED works very well at RT. Also this result suggests that formation of the heterodiode was successfully formed. Figure 8 shows forward pulse bias dependence of EL intensities of the n'-ITO/i-TiO2:Sm/p-NiO/p'-Si LED measured. Pulsed bias was chosen because of preventing damages to the LED. The EL measurement was started with 12 V at RT. The EL intensity exponentially increased with increasing applied forward voltage. The applied bias voltage dependence was very similar with EL intensity of each peak. This result indicates that a single-typed Sm3+ luminescent center was formed. That is the same center which was focused at previous section of PL property and local structure. In addition, EL intensity is corresponding to current injection.
Figure 9 shows EL spectra of the n+-ITO/i-TiO2:Sm/p-NiO/p+-Si LED and PL/CL spectra of a TiO2:Sm layer such as previous section. A bare TiO2:Sm sample was excited by using He-Cd laser (325 nm) for measuring PL spectra and by using electron gun (4 KeV), 100 mA/cm² for measuring cathodoluminescence (CL) spectra. These three spectra showed similar shapes and their peak positions. It suggests that this EL emission is originated from the same luminescent center of PL and CL. Wider slit was used for detector for EL measurement, hence broadened EL spectra was observed. Moreover, the way of transferring energy to luminescent center of Sm³⁺ was the same. Again, this result indicates that this center is the same one which has been focused at other estimation.

4. Conclusion

Sm³⁺ ions doped anatase (A-) and rutile (R-) TiO₂ thin films were deposited by the laser ablation technique. The crystal phase was selected by controlling the O₂ pressure. After ablation, the samples were annealed at different temperatures, and analyzed by XRD, PL and XAFS. The samples annealed at 700°C of A-TiO₂ exhibited the strongest PL emission, and the samples annealed at 1100°C of A-TiO₂ and fabricated as R-TiO₂ crystal phase showed a weak PL emission. The result of the XAFS analysis revealed the local structures of A- and R-TiO₂. The coordination around Sm³⁺ was completely different. The coordination around Sm³⁺ of the samples showing weak PL emission was highly symmetric, and was
fitted as Sm bonded to six O atoms with the same distance. However, while the Sm$^{3+}$ luminescent center was being activated, the A-TiO$_2$ samples annealed at 600˚C to 800˚C, and the coordination around Sm$^{3+}$ was distorted. The distances can be fitted as two lengths, Sm-O$_4$ and longer Sm-O$_2$. There is the possibility that the higher crystallinity results in more intensive luminescence. A-TiO$_2$ annealed at 1100˚C, which phase transitioned to the R-TiO$_2$ sample exhibiting the highest crystallinity, showed that even if the crystallinity was high, the PL emission was not as strong as the A-TiO$_2$ samples. These facts indicate the strong connection between the activation of the luminescent center and the crystal distortion of the coordination around Sm. The transition possibility has not been determined yet, but fabricating samples with a low symmetry results in the sample having a semi-stable luminescent center which yields an intense PL emission. Based on these results, n'-ITO/i-TiO$_2$:Sm/p-NiO/p'-Si light emitting diode was fabricated with a threshold of approximately 8 V. Clear EL spectra from LED were observed by current injection at RT. Also, single-typed Sm$^{3+}$ luminescent center which was focused at PL property and local structure, was formed. A formation of the heterodiode was successfully formed.

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