Effect of doping concentration on Nd-related photoluminescence in TiO$_2$ with Al co-doping

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Abstract. Nd doped, Nd-Al co-doped anatase phase TiO$_2$ thin films were fabricated on silicon substrates by laser ablation and post annealing. The result of measuring PL spectra showed intense emissions from a luminescent centre of Nd$^{3+}$ ions in these thin films. The luminescence of Nd-Al co-doped samples were stronger and broader than only Nd doped samples. Doping concentration of Nd determined suitable co-doping concentration of Al and post annealing temperature. Also there is the difference of shape of the PL spectra which indicates that the difference of local fine structure around Nd. Based on these facts, XAFS spectra was measured and suggested that the coordination around Nd was changed by this Al-co-doping.

1. Introduction

Rare earth element doped semiconductors and oxide materials have been studied for long years because of their possibilities of being applicable materials for visible and infrared light emitting diodes and other optoelectronic devices[1-4]. Trivalent neodymium (Nd$^{3+}$) exhibits sharp luminescence in the infrared and near-infrared wavelength regions. Titanium dioxide (TiO$_2$) has been received attention as an optimal candidate for host materials to activate doped rare earth ions, because of its large band gap energy works as a window[5, 6]. One of keys of enhancing PL emission, which is distorted coordinations around rare earth dopant, was reported in our previous work[7, 8]. Distortion has been caused by growing annealing temperature, and the luminescent centre was optimally activated without co-doping. On this paper, enhancing PL emission with co-doping is focused. On our previous work[9], Nd-doped anatase phase TiO$_2$ (A-TiO$_2$:Nd) has been confirmed emitting intense luminescence and these emissions were enhanced with co-doping aluminium (Al). Other effects of sensitisation are improving the Nd$^{3+}$-emission lifetime and broadening shapes of PL spectra. These facts suggest that different concentration of dopants would change the bond length or coordination around Nd, and that enhance Nd$^{3+}$-related emissions. In this paper, we report PL and XAFS analysis for different concentrations of Nd and Al in TiO$_2$.

2. Experimental procedure

The Nd doped and Nd-Al co-doped TiO$_2$ (TiO$_2$:Nd, TiO$_2$:Nd-Al) thin films were deposited by laser ablation using a YAG laser ($4_\omega = 266$ nm, 1 J/cm$^2$). A TiO$_2$ ceramic target, including 0.2 or 1.0 wt% Nd$_2$O$_3$ and 0.0 or 0.5 wt% Al$_2$O$_3$, was used as the deposition source. A-TiO$_2$...
thin films were fabricated in a vacuum chamber with an $O_2$ pressure of $1.5 \times 10^{-2}$ Torr. As has been reported in our previous work, selecting an appropriate atmosphere enables the production of the suitable crystalline phase A-TiO$_2$[10]. A-TiO$_2$:Nd/ Nd-Al thin films of 300 nm thick were formed on the Si (100) surfaces at room temperature. After the deposition, the samples were annealed at a temperature of 700 °C for Nd (0.2 wt%)-Al (0.0 or 0.5 wt%) and of 500 °C for Nd (1.0 wt%)-Al (0.0 or 0.5 wt%), for 3 min in the $O_2$ atmosphere for optical activation of Nd$^{3+}$ ions and formation of the nanometer-sized TiO$_2$ crystals. The annealing temperatures were settled as the optimal conditions to enhance PL emissions at intra-shell $4F_{3/2} \rightarrow 4I_{11/2}$ transitions in Nd$^{3+}$ ions (1080-1096 nm) with Al co-doping. Based on these recognitions, selected annealing temperature of Nd (0.2 wt%) and Nd (1.0 wt%) was different. Besides these samples, the samples for XAFS measurements were prepared, because Nd (0.2 wt%) is too dilute to measure XAFS spectra. Deposition time of Nd (0.2 wt%) samples were 3 times longer than the other samples. All samples were prepared with an $O_2$ pressure of $2.0 \times 10^{-2}$ Torr, and post annealed at 700 °C for 3 min. The A-TiO$_2$:Nd/ Nd-Al thin films of approximately 900 nm thick were formed. Other conditions of these samples are the same with the measuring PL samples.

A He-Cd laser ($\lambda = 325$ nm) was used to excite the Nd$^{3+}$ and to measure PL spectra from the TiO$_2$:Nd thin films. The X-ray absorption fine structure (XAFS) measurements using synchrotron radiation (SR) were performed at the High Energy Accelerator Research Organization BL 27B Photon Factory in Tsukuba prefecture, Japan. A Si double crystal set was used to monochromatise 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 TiO$_2$:Nd thin films. The X-ray incidence angle was fixed at 45°. The Athena of Demeter, which is a free programme for XAFS analysis created by Ravel B, was used for an ordinary process of XAFS analysis, that is, extracting the oscillations and fitting the Fourier spectra[11, 12].

3. Results and discussion

![Figure 1: PL spectra of A-TiO$_2$:Nd$_2$O$_3$ (x wt%)-Al$_2$O$_3$ (y wt%): (a) x=0.2, y=0.0, (b) x=0.2, y=0.5, (c) x=1.0, y=0.0, (d) x=1.0, y=0.5.](image1)

![Figure 2: PL intensity ratio at $4F_{3/2} \rightarrow 4I_{11/2}$ transitions of A-TiO$_2$:Nd (0.2/ 1.0 wt%) with different Al co-doing concentrations.](image2)

Figure 1 shows PL spectra of A-TiO$_2$:Nd$_2$O$_3$ (0.2 wt%)-Al$_2$O$_3$ (0.0, 0.5 wt%) post annealed at 700 °C, with A-TiO$_2$:Nd$_2$O$_3$ (1.0 wt%)-Al$_2$O$_3$ (0.0, 0.5 wt%) post annealed at 500 °C. The PL emissions corresponding to $4F_{3/2} \rightarrow 4I_{J}$ ($J = 9/2, 11/2, 13/2$) intra-$4f$ transitions in Nd$^{3+}$ ions can be observed. Every sample showed strong luminescent emissions.
This result demonstrates that Nd$^{3+}$ with a crystal field allowing intra-4f transitions is formed in crystal matrix by annealing. These facts indicate that the fabricated samples annealed at an appropriate temperature and concentration of co-doping results in a window for making the luminescence centre. Increasing of concentration of Al co-dopant made stronger PL intensity, sifting from the peak of non co-doping samples, and changed the shape of PL spectra with remaining similar tendency of non co-doping samples. Different PL intensities suggest difference of the transition probability, and different fine structures of PL spectra suggest difference of coordination around the Nd$^{3+}$ ions, which is the luminescent centre.

Figure 2 shows PL intensity ratio at $^{4}F_{3/2} \rightarrow ^{4}I_{11/2}$ transition of A-TiO$_2$:Nd (0.2/ 1.0 wt%) with different Al co-doping concentrations. As shown in Fig. 1, the shape of spectra changed with co-doping Al (0.5 wt%). Because of this reason, the most intensive peak of the PL emission of these samples was not the same wavelength, but the same transitions. The samples co-doped with 1.0 wt% Al were also shown for comparison. The influence of Al co-doping on the Nd$^{3+}$ with different Nd concentrations will be discussed by analysing the local microstructure around the Nd$^{3+}$ ions.

The XAFS spectra at the Nd L$_{III}$-edge (6713 eV) of A-TiO$_2$:Nd with/ without co-doping Al are shown in Fig. 3. The lowest spectrum is from Nd$_2$O$_3$ powder of the standard sample. These series of samples are the same concentrations as showed in Fig. 1. The most intense peak means absorption of Nd dopant and Nd oxides. Every spectrum appeared at the same peak position as the Nd$_2$O$_3$ powder, which suggests the Nd$^{3+}$ state was mainly formed in Nd$_2$O$_3$ thin films without any out diffusions. The spectra obtaining from the samples of doping Nd (0.2 wt%) were very noisy because of dilute doping.

The inset of Figure 4 shows the $k^2$-weighted extended X-ray absorption fine structure (EXAFS), $\chi(k)$ oscillations of Nd in TiO$_2$:Nd/ Nd-Al. $k$ is the photoelectron vector. A bigger weighting $k^n$ means emphasising higher oscillation. $k^2$ were chosen because higher range of oscillations (after 9.3 Å) were noisy. The window function was performed in the range of 3.0-9.3 Å$^{-1}$, $dk = 0.5$. The chosen ranges in the XAFS analysis of this experiment are all the same because of comparison.

Figure 4 shows the radial structural function (RSF) around Nd obtained by the Fourier transform (FT) of $k^2$-weighted XAFS spectra in inset, $k^2\chi$ of A-TiO$_2$:Nd-Al samples shown in Fig. 3. The inset is $k^2$-weighted EXAFS oscillations (solid line) and window functions (dashed line) of A-TiO$_2$:Nd/ Nd-Al.
in our previous work[8]. On the other hand, the first NN of Nd in the samples with Al co-doping were broadened and splitted. This result indicates that local fine structure of Nd was changed by co-doping Al as suggestion from the result of PL measurement.

The optimal annealing temperature and concentration of co-doping was selected to prepare the most effective condition as sensitisier. In our previous work, enhancing PL emission, which is distorted coordinations around rare earth dopant, was reported[7, 8]. The distortion has been caused by growing annealing temperature without co-doping, and the luminescent centre was optimally activated. The way of approaching to enhance PL emission is different. One is optimally annealed samples without co-doped and the other is samples with co-doping. Both samples showed intense PL spectra. As shown in Fig. 4, changing local fine structure of Nd was confirmed. These results predicted that not the same way, but the same tendency, the coordinations around Nd ions were distorted both in concentration controlled and annealing temperature controlled samples. These XAFS spectra of samples have not been completely fitted because of noise. Hence this is still in hypothetical process, but further experiments have been already planned to gain the XAFS spectra to analyse the second NN.

4. Conclusion

Nd$^{3+}$ ions doped, Nd$^{3+}$-Al co-doped anatase (A-)TiO$_2$ thin films were deposited by laser ablation technique. The crystal phase was properly selected by under controlling of the O$_2$ pressure. After ablating, the samples were annealed. The samples were estimated by PL and XAFS. The samples of co-doping Al (0.5 wt%) of A-TiO$_2$:Nd exhibited stronger PL emission than non co-doping samples. This result suggests co-doped Al sensitises PL emission, and this effect appeared when the optimal concentration and annealing temperature were selected. The result of PL measurement revealed different fine structure of the PL spectra which suggests the difference of coordination around the Nd$^{3+}$ ions of the luminescent centre. Based on these results, XAFS spectra were measured. The result of the XAFS analysis revealed the local structures of A-TiO$_2$:Nd and A-TiO$_2$:Nd-Al. The coordination around Nd$^{3+}$ of non co-doped and co-doped samples was different. The first NN of Nd in co-doping samples was splitted and broadened. This result suggests the coordination around Nd$^{3+}$ was distorted as the without co-doping samples optimally annealed, and showed the intense PL emission.

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