

Influence of Preparation Ambient on Luminescent and Electrical Properties of TiO₂:Sm Thin Films

S. Kaku¹, K. Miyano¹, X. Zhao^{1,2} and M. Murayama^{1,3}

¹Tokyo Univ. of Sci., Kagurazaka, Tokyo, 162-8601, Japan

²Henan University of Technology, Henan, 450001, China

³Toyo Univ. Research Institute of Industrial Technology, Kawagoe, Saitama, 350-8585, Japan

mariko.murayama@rs.tus.ac.jp

Rare earth (RE) doped TiO₂ (TiO₂:RE) shows sharp and strong emission, which makes it a promising candidate for applications in optoelectronic devices. Generally, oxygen-deficient oxide semiconductors such as TiO₂ behave as n-type, which generate free electrons. [1] It suggests that an increase in oxygen vacancies could enhance carrier concentration and reduce resistivity. On the other hand, oxygen also plays an important role in the luminescent properties of RE-doped oxide semiconductors. A 6-fold oxygen surrounds the RE ions critically influencing their luminescent properties. For instance, Samarium (Sm)-doped TiO₂ showed a significant improvement in its luminescent intensity, when the local fine structure around Sm³⁺ was distorted. [2] Therefore, this study reveals how the fabrication and annealing atmospheres (N₂+H₂ and O₂) influence the coordination and structure around Sm³⁺ and their effect on the luminescent properties of TiO₂:Sm thin films. Furthermore, the electrical properties including carrier concentration determined by capacitance-voltage (CV) measurements are discussed.

TiO₂:Sm thin films were deposited on SrTiO₃:Nb (100) substrates using pulsed laser deposition (PLD). A ceramic target consisting of TiO₂ and Sm₂O₃ (1 wt%) was laser ablated by the third harmonic generation (355 nm) of a Q-switched yttrium aluminum garnet (YAG) laser. A chamber was controlled under the pressure of 1.0×10⁻² Torr in atmospheres of O₂ and H₂+N₂ forming gas (H₂:N₂=5:95%). The films were annealed at 700°C for 10 minutes in either an O₂ atmosphere or a H₂+N₂ forming gas atmosphere. RuO₂ was deposited on the TiO₂:Sm thin films to make Schottky contacts for CV and current-voltage (IV) measurements.

Figure 1 shows photoluminescence (PL) spectra of TiO₂:Sm thin films with different fabricating and annealing atmospheres. Samples prepared in an O₂ atmosphere for both the deposition and annealing phases (denoted as OO) exhibited the strongest PL intensity. In contrast, samples deposited in a H₂ atmosphere and annealed in an O₂ (HO), as well as those deposited in an O₂ and annealed in a H₂ (OH), exhibited significantly weaker than OO PL intensity. The luminescence intensity of HO was about one-eighth and OH about one-fifteenth of that observed for OO. Samples processed in a H₂ atmosphere for both deposition and annealing (HH) did not exhibit any luminescence. However, IV and CV measurements revealed that the HH sample marked the highest conductivity with carrier concentrations exceeding 10¹⁹/cm³. This is markedly higher than that for OO, OH, and HO, hovering around 10¹⁷/cm³. Further details including the local fine structure around Sm³⁺ in TiO₂ matrix characterized by X-ray absorption fine structure (XAFS) analysis, evaluations of crystallinity via X-ray diffraction (XRD), and detailed outcomes of both CV and I-V measurements and its effect on luminescent and electrical properties will be discussed.

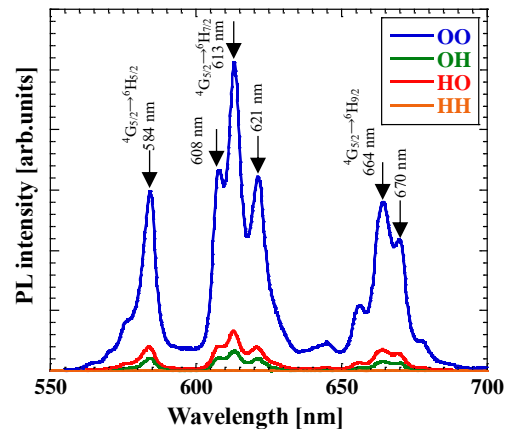


Fig.1. PL spectra of TiO₂:Sm with different fabricating/annealing atmospheres.

References

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- [2] M. Murayama, "Optical, electrical and local fine structural characterization of Rare-Earth doped TiO₂ thin films for application as luminescent phosphors in LEDs," PhD Thesis, Tokyo University of Science, (2021).