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Photoluminescence Properties of Europium and Cerium Co-Doped Tantalum-Oxide Thin Films Prepared Using Co-Sputtering Method

Kenta Miura*, Tetsuhito Suzuki, Osamu Hanaizumi

Graduate School of Science and Technology, Gunma University, Kiryu, Japan
Email: *mkenta@gunma-u.ac.jp

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Abstract

We fabricated europium and cerium co-doped tantalum (V) oxide (Ta_2O_5: Eu, Ce) thin films using our co-sputtering method for the first time, and evaluated photoluminescence (PL) properties of the films after annealing at 600˚C - 1100˚C for 20 min. Four remarkable PL peaks at wavelengths of 600, 620, 700, and 705 nm were observed from the film annealed at 900˚C. The intensities of the 700- and 705-nm peaks due to the $^5D_0 \rightarrow {}^7F_4$ transition of Eu^{3+} were much stronger than those of the 600-nm ($^5D_0 \rightarrow {}^7F_1$) and 620-nm ($^5D_0 \rightarrow {}^7F_2$) peaks of the film annealed at 900˚C. It seems that energy transfer from Ce^{3+} to Eu^{3+} occurs in the film, and much energy is selectively used for the $^5D_0 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_1$ transitions. Such a Ta_2O_5: Eu, Ce co-sputtered thin film seems to be used as a multi-functional coating film having both anti-reflection and down-conversion effects for realizing a high-efficiency silicon solar cell.

Keywords

Tantalum Oxide, Europium, Cerium, Co-Sputtering, Photoluminescence

1. Introduction

Tantalum (V) oxide (Ta_2O_5) is a high-refractive-index material used in passive optical elements such as Ta_2O_5/SiO_2 multilayered wavelength filters for dense wavelength-division multiplexing (DWDM). It has also been used as a high-index material of Ta_2O_5/SiO_2 multilayered photonic-crystal elements for the visible to near-infrared range fabricated using the “autocloning” method based on radio-frequency (RF) bias sputtering [1] [2],

*Corresponding author.

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and it can additionally be used as an anti-reflection coating material for silicon solar cells [3].

However, Ta_2O_5 has recently attracted much attention as an active optical material, since broad red photoluminescence (PL) spectra at wavelengths of 600 to 650 nm were observed from thermal-oxidized amorphous Ta_2O_5 thin films [4]. Many studies on rare-earth-doped Ta_2O_5 have also been conducted because Ta_2O_5 is a potential host material for new phosphors due to its lower phonon energy (100 - 450 cm^{-1}) than other popular oxide materials (e.g. silicon dioxide (SiO_2)) [5]. We have fabricated various rare-earth doped Ta_2O_5 thin films using simply co-sputtering of rare-earth oxide pellets and a Ta_2O_5 disc, and we obtained various PL properties from these rare-earth-doped Ta_2O_5 thin films [6]-[11]. We reported on red or orange PL from europium (Eu)-doped Ta_2O_5 (Ta_2O_5: Eu) thin films deposited using the same co-sputtering method [9]. In our recent study, we fabricated erbium (Er), Eu, and cerium (Ce) co-doped Ta_2O_5 (Ta_2O_5: Er, Eu, Ce) thin films using co-sputtering of Er_2O_3, Eu_2O_3, CeO_2 and Ta_2O_5, and observed yellow PL from a film annealed at 900˚C [10]. The yellow light emission seemed to be obtained from the result of enhancement of the 550-nm (green) PL peak due to Er^{3+} by Ce^{3+} doping [12]. We also prepared Er and Ce co-doped Ta_2O_5 (Ta_2O_5: Er, Ce) thin films using co-sputtering of Er_2O_3, CeO_2 and Ta_2O_5. An enhanced green PL peak that seems to be sensitized by Ce^{3+} was observed from a film annealed at 900˚C [11]. We can obtain Ce^{3+} from CeO_2 (cerium (IV) oxide) pellets because a small amount of Ce^{3+} exists at the surface of CeO_2 [13].

In this study, we fabricated Eu and Ce co-doped Ta_2O_5 (Ta_2O_5: Eu, Ce) thin films using our co-sputtering method for the first time, and we evaluated PL properties of the films.

2. Experimental

Ta_2O_5: Eu, Ce thin films were deposited using our RF magnetron sputtering system (ULVAC, SH-350-SE). A schematic figure of the system was presented in our previous report [7]. A Ta_2O_5 sintered-compact disc (Furuuchi Chemical Corporation, 99.99% purity, diameter 100 mm) was used as a sputtering target in the system. We placed an Eu_2O_3 sintered-compact pellet (Furuuchi Chemical Corporation, 99.9% purity, diameter 20 mm) and two CeO_2 sintered-compact pellets (Furuuchi Chemical Corporation, 99.9% purity, diameter 20 mm) on the Ta_2O_5 disc as presented in **Figure 1**. They were co-sputtered by supplying RF power to the target. The flow rate of Ar gas introduced into the processing vacuum chamber was 15 sccm, and the pressure in the chamber during deposition was kept at ~5.4×10^{-4} Torr. The RF power supplied to the target was 200 W. Fused-silica plates (ATOCK Inc., 1 mm thick) were used as substrates, and they were not heated during sputtering. The thicknesses of the films were set to be ~1.5 μm by adjusting the sputtering times of the films.

We subsequently annealed the Ta_2O_5: Eu, Ce co-sputtered thin films in ambient air at 600˚C, 700˚C, 800˚C, 900˚C, 1000˚C, or 1100˚C for 20 min using an electric furnace (Denken, KDF S-70). We set the annealing time to 20 min because it was the proper condition for our Er-doped Ta_2O_5 (Ta_2O_5: Er) films to obtain strong PL intensities [6] [8]. The PL spectra of the films were measured using a dual-grating monochromator (Roper Scientific, SpectraPro 2150i) and a CCD detector (Roper Scientific, Pixis: 100B, electrically cooled to −80˚C). A He-Cd laser (Kimmon, IK3251R-F, wavelength λ = 325 nm) was used to excite the films. The Eu and Ce concentrations of the films after annealing were measured using an electron probe micro-analyzer (EPMA) (Shimadzu, EPMA-1610). The X-ray diffraction (XRD) patterns of the films were recorded using an X-ray diffractometer (RIGAKU, RINT2200VF+/PC system).

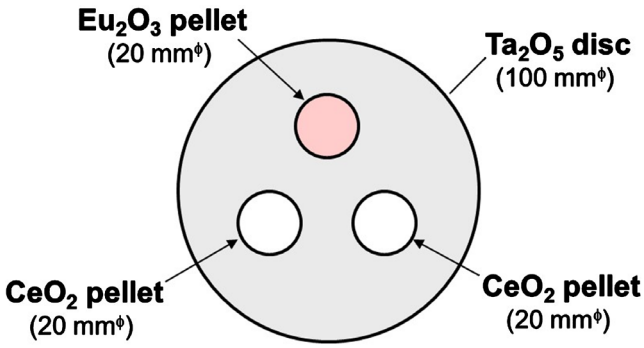

Figure 1. Schematic top view of the sputtering target for co-sputtering of an Eu_2O_3 pellet, two CeO_2 pellets, and a Ta_2O_5 disc.

3. Results and Discussion

Figure 2 presents PL spectra of Ta_2O_5: Eu, Ce films annealed at 600˚C, 700˚C, 800˚C, 900˚C, 1000˚C, or 1100˚C for 20 min. Four remarkable PL peaks at wavelengths of 600, 620, 700, and 705 nm were observed only from the film annealed at 900˚C. No PL peak was observed from the films annealed at 600˚C, 700˚C, 800˚C, 1000˚C, or 1100˚C. The peaks at the wavelengths of 600 and 620 nm seem to be the results of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+}, respectively [9], and the peaks at the wavelength of 700 and 705 nm seem to be due to the $^5D_0 \rightarrow {}^7F_4$ transition of Eu^{3+} [9]. We could not observe a remarkable peak around a wavelength of 650 nm due to the $^5D_0 \rightarrow {}^7F_3$ transition of Eu^{3+} that was observed in [9]. On the other hand, we found an additional 705-nm peak from the film annealed at 900˚C.

The Eu and Ce concentrations of the film annealed at 800˚C were measured to be around 1.5 and 2.8 mol%, respectively. The concentrations may be almost the same as those of the films annealed at the other temperatures.

Figure 3 presents XRD patterns of the films annealed at 600˚C, 700˚C, or 800˚C (**Figure 3(a)**) and those of the films annealed at 900˚C, 1000˚C, or 1100˚C (**Figure 3(b)**). The films annealed at 600˚C, 700˚C, and 800˚C seemed to be almost amorphous phases because no significant diffraction peak was observed from them as seen in **Figure 3(a)**. On the other hand, three major peaks corresponding to the (0 0 1); β-Ta_2O_5 (orthorhombic), (2 0 0); δ-Ta_2O_5 (hexagonal), and (2 0 1) Ta_2O_5 phases were observed from the films annealed at 900˚C [7]. These crystalline phases of Ta_2O_5 seem to be very important for obtaining significant PL peaks from our Ta_2O_5: Eu, Ce films annealed at 900˚C. Furthermore, other diffraction peaks due to $CeTa_7O_{19}$ and $EuTa_7O_{19}$ crystals were observed from the films annealed at 1000˚C and 1100˚C. In particular, four peaks corresponding to the hexagonal $CeTa_7O_{19}$ phases ((1 0 0), (0 0 6), (1 1 1), and (1 1 5)) were remarkably observed as presented in **Figure 3(b)**. Therefore, it seems that the hexagonal $CeTa_7O_{19}$ phases should be avoided in order to obtain PL from our Ta_2O_5: Eu, Ce films.

Figure 4 illustrates energy level diagrams of Eu^{3+} and Ce^{3+} [14] [15]. As presented in **Figure 4**, electrons are excited to the $^2D_{5/2}$ state by the He-Cd laser irradiation (λ = 325 nm), and they relax to the $^2D_{3/2}$ state of Ce^{3+}. Subsequently, energy transfer from the $^2D_{3/2}$ state of Ce^{3+} to the $^5D_1$ state of Eu^{3+} occurs, and the electrons relax

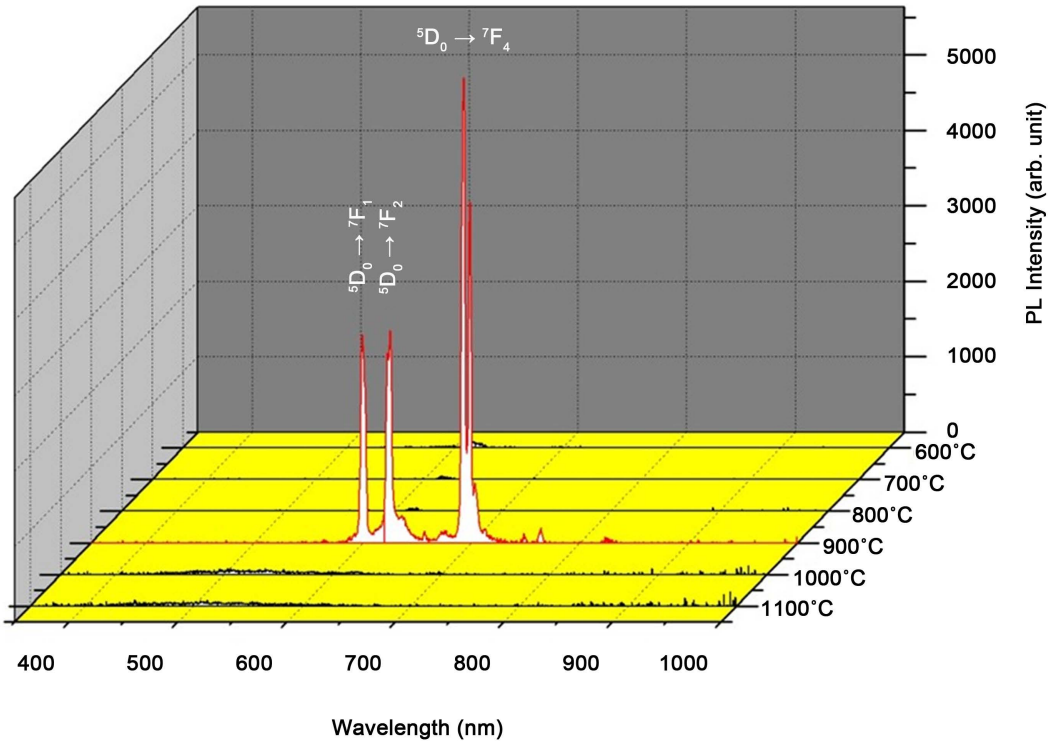

Figure 2. PL spectra of Ta_2O_5: Eu, Ce co-sputtered thin films annealed at 600˚C, 700˚C, 800˚C, 900˚C, 1000˚C, or 1100˚C.

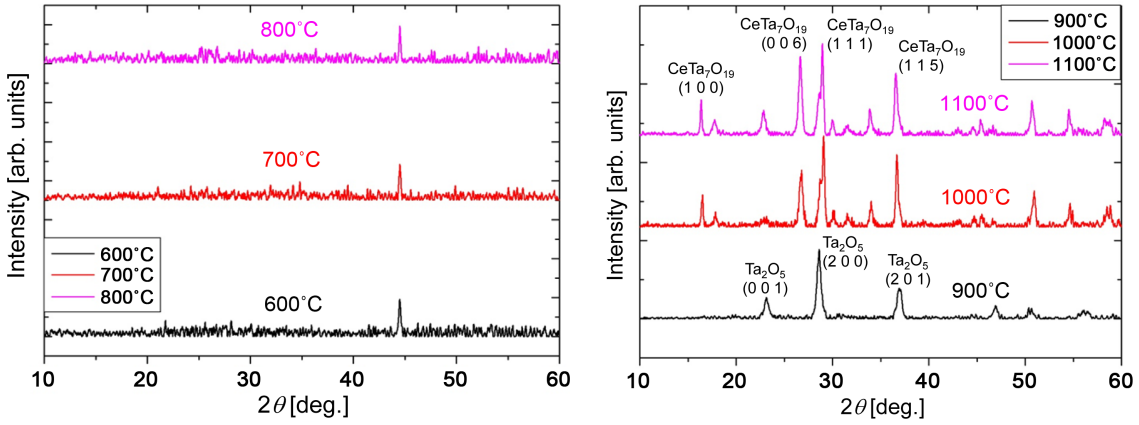

Figure 3. XRD patterns of Ta_2O_5: Eu, Ce films annealed at (a) 600˚C, 700˚C, or 800˚C and (b) 900˚C, 1000˚C, or 1100˚C.

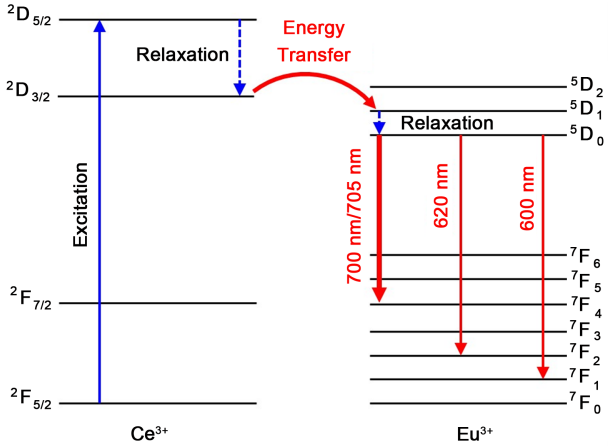

Figure 4. Energy level diagrams of Eu^{3+} and Ce^{3+}.

to the $^5D_0$ state of Eu^{3+}. Finally, the transitions of $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$ occur, and light emission at wavelengths of 600, 620, 700, and 705 nm can be observed. In our previous study, the 620-nm peaks observed from our Ta_2O_5: Eu co-sputtered thin films were much stronger than the other peaks around the wavelengths of 600 and 700 nm [9]. However, as seen in **Figure 2**, the intensities of the 600-nm ($^5D_0 \rightarrow {}^7F_1$) and 620-nm ($^5D_0 \rightarrow {}^7F_2$) peaks were almost the same, and the intensity of the 700- and 705-nm ($^5D_0 \rightarrow {}^7F_4$) was much stronger than that of the 620-nm peak of the Ta_2O_5: Eu, Ce co-sputtered thin film annealed at 900˚C. It seems that energy transfer from Ce^{3+} to Eu^{3+} occurs in the film, and much energy is selectively used for the $^5D_0 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_1$ transitions.

Such Ta_2O_5-based thin films seem to be used as high-refractive-index and light-emitting materials of "autocloning" photonic crystals that can be applied to novel light-emission devices [1], and they also seem to be used as multi-functional coating films having both anti-reflection [3] and down-conversion [16]-[18] effects for realizing high-efficiency silicon solar cells.

4. Conclusion

We fabricated Ta_2O_5: Eu, Ce thin films using our co-sputtering method for the first time, and evaluated the PL properties of the films after annealing at 600˚C - 1100˚C for 20 min. Four remarkable PL peaks at wavelengths of 600, 620, 700, and 705 nm were observed from the film annealed at 900˚C. The intensities of the 700- and 705-nm peaks due to the $^5D_0 \rightarrow {}^7F_4$ transition of Eu^{3+} were much stronger than those of the 600-nm ($^5D_0 \rightarrow {}^7F_1$) and 620-nm ($^5D_0 \rightarrow {}^7F_2$) peaks of the film annealed at 900˚C. It seems that energy transfer from Ce^{3+} to Eu^{3+} occurs in the film, and much energy is selectively used for the $^5D_0 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_1$ transitions.

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References

[1] Hanaizumi, O., Miura, K., Saito, M., Sato, T., Kawakami, S., Kuramochi, E. and Oku, S. (2000) Frontiers Related with Automatic Shaping of Photonic Crystals. *IEICE Transactions on Electronics*, **E83-C**, 912-919.

[2] Sato, T., Miura, K., Ishino, N., Ohtera, Y., Tamamura, T. and Kawakami, S. (2002) Photonic Crystals for the Visible Range Fabricated by Autocloning Technique and Their Application. *Optical and Quantum Electronics*, **34**, 63-70. http://dx.doi.org/10.1023/A:1013382711983

[3] Cid, M., Stem, N., Brunetti, C., Beloto, A.F. and Ramos, C.A.S. (1998) Improvements in Anti-Reflection Coatings for High-Efficiency Silicon Solar Cells. *Surface and Coatings Technology*, **106**, 117-120. http://dx.doi.org/10.1016/S0257-8972(98)00499-X

[4] Zhu, M., Zhang, Z. and Miao, W. (2006) Intense Photoluminescence from Amorphous Tantalum Oxide Films. *Applied Physics Letters*, **89**, Article ID: 021915. http://dx.doi.org/10.1063/1.2219991

[5] Sanada, T., Wakai, Y., Nakashita, H., Matsumoto, T., Yogi, C., Ikeda, S., Wada, N. and Kojima, K. (2010) Preparation of Eu^{3+}-Doped Ta_2O_5 Phosphor Particles by Sol-Gel Method. *Optical Materials*, **33**, 164-169. http://dx.doi.org/10.1016/j.optmat.2010.08.018

[6] Singh, M.K., Fusegi, G., Kano, K., Bange, J.P., Miura, K. and Hanaizumi, O. (2009) Intense Photoluminescence from Erbium-Doped Tantalum Oxide Thin Films Deposited by Sputtering. *IEICE Electronics Express*, **6**, 1676-1682. http://dx.doi.org/10.1587/elex.6.1676

[7] Bange, J.P., Singh, M.K., Kano, K., Miura, K. and Hanaizumi, O. (2011) Structural Analysis of RF Sputtered Er Doped Ta_2O_5 Films. *Key Engineering Materials*, **459**, 32-37. http://dx.doi.org/10.4028/www.scientific.net/KEM.459.32

[8] Singh, M.K., Miura, K., Fusegi, G., Kano, K. and Hanaizumi, O. (2013) Visible-Light Emission Properties of Erbium-Doped Tantalum-Oxide Films Produced by Co-Sputtering. *Key Engineering Materials*, **534**, 154-157. http://dx.doi.org/10.4028/www.scientific.net/KEM.534.154

[9] Miura, K., Arai, Y., Osawa, T. and Hanaizumi, O. (2012) Light-Emission Properties of Europium-Doped Tantalum-Oxide Thin Films Deposited by Radio-Frequency Magnetron Sputtering. *Journal of Light & Visual Environment*, **36**, 64-67. http://dx.doi.org/10.2150/jlve.36.64

[10] Miura, K., Osawa, T., Suzuki, T., Yokota, Y. and Hanaizumi, O. (2015) Yellow Light Emission from Ta_2O_5:Er, Eu, Ce Thin Films Deposited Using a Simple Co-Sputtering Method. *Results in Physics*, **5**, 26-27. http://dx.doi.org/10.1016/j.rinp.2014.11.003

[11] Miura, K., Osawa, T., Suzuki, T., Yokota, Y. and Hanaizumi, O. (2015) Fabrication and Evaluation of Green-Light Emitting Ta_2O_5:Er, Ce Co-Sputtered Thin Films. *Results in Physics*, **5**, 78-79. http://dx.doi.org/10.1016/j.rinp.2015.02.002

[12] Du, Q., Zhou, G., Zhou, J., Zhou, H. and Zhan, J. (2012) Enhanced Photoluminescence of $CaZrO_3$:Er^{3+} by Efficient Energy Transfer from Ce^{3+}. *Materials Research Bulletin*, **47**, 3774-3779. http://dx.doi.org/10.1016/j.materresbull.2012.06.022

[13] Roh, J., Hwang, S.H. and Jang, J. (2014) Dual-Functional CeO_2:Eu^{3+} Nanocrystals for Performance-Enhanced Dye-Sensitized Solar Cells. *ACS Applied Materials Interfaces*, **6**, 19825-19832. http://dx.doi.org/10.1021/am505194k

[14] Kim, G.C., Mho, S.I. and Park, H.L. (1995) Observation of Energy Transfer between Ce^{3+} and Eu^{3+} in $YAlO_3$:Ce,Eu. *Journal of Materials Science Letters*. **14**, 805-806. http://dx.doi.org/10.1007/BF00278135

[15] Wang, Y.F., Wang, S., Wu, Z.L., Li, W.R. and Ruan, Y.F. (2013) Photoluminescence Properties of Ce and Eu Co-Doped YVO_4 Crystals. *Journal of Alloys and Compounds*, **551**, 262-266. http://dx.doi.org/10.1016/j.jallcom.2012.10.042

[16] Rodriguez, V.D., Tikhomirov, V.K., Mendez-Ramos, J., Yanes, A.C. and Moshchalkov, V.V. (2010) Towards Broad Range and Highly Efficient Down-Conversion of Solar Spectrum by Er^{3+}-Yb^{3+} Co-Doped Nano-Structured Glass-Ceramics. *Solar Energy Materials and Solar Cells*, **94**, 1612-1617. http://dx.doi.org/10.1016/j.solmat.2010.04.081

[17] Aarts, L., van der Ende, B.M. and Meijerink, A. (2009) Downconversion for Solar Cells in $NaYF_4$:Er, Yb. *Journal of Applied Physics*, **106**, Article ID: 023522. http://dx.doi.org/10.1063/1.3177257

[18] Ueda, J. and Tanabe, S. (2011) Broadband near Ultra Violet Sensitization of 1 μm Luminescence in Yb^{3+}-Doped CeO_2 Crystal. *Journal of Applied Physics*, **110**, Article ID: 073104. http://dx.doi.org/10.1063/1.3642984