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Photoluminescence Properties of Thulium and Cerium Co-Doped Tantalum-Oxide Films Prepared by Radio-Frequency Co-Sputtering

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Abstract

We prepared thulium and cerium co-doped tantalum-oxide (Ta_2O_5:Tm, Ce) thin films by radio-frequency co-sputtering of Tm_2O_3 and CeO_2 pellets on a Ta_2O_5 disc for the first time, and photoluminescence (PL) properties of the films annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min were evaluated. PL peaks around a wavelength of 800 nm due to Tm^{3+} were observed for films annealed at 900˚C or 1000˚C. The peak intensities of films prepared using one Tm_2O_3 pellet and one CeO_2 pellet were much stronger than those of films prepared using one Tm_2O_3 pellet and two CeO_2 pellets or films prepared using two Tm_2O_3 pellets and one CeO_2 pellet. To obtain the strongest PL intensity from the film, the proper Tm concentration was estimated to be around 1.0 mol%, and the proper Ce concentration was estimated to be around 1.3 mol%. Such Ta_2O_5:Tm, Ce co-sputtered thin films can be used as high-refractive-index materials of autocloned photonic crystals that can be applied to novel light-emitting devices, and they will also be used as anti-reflection and down-conversion layers for realizing high-efficiency silicon solar cells.

Keywords

Tantalum Oxide, Thulium, 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-

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infrared range fabricated using the "autocloning" method based on radio-frequency (RF) bias sputtering [1]-[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 are observed from thermal-oxidized amorphous Ta_2O_5 thin films [4]. We demonstrated blue PL from Ta_2O_5 thin films deposited by RF magnetron sputtering [5]. Furthermore, many studies on rare-earth-doped Ta_2O_5 have been conducted because Ta_2O_5 is a potential host material for new phosphors due to its low phonon energy (100 to 450 cm^{-1}) compared with that of other oxide materials (e.g., SiO_2) [6]. We have reported on various rare-earth (Er, Eu, Y, and Ce) doping into Ta_2O_5 thin films using simply co-sputtering of rare-earth oxide (Er_2O_3, Eu_2O_3, Y_2O_3, and CeO_2) pellets and a Ta_2O_5 disc [7]-[11]. Such light-emitting Ta_2O_5-based sputtered films can be used as high-refractive-index materials of autocloned photonic crystals that can be applied to novel light-emission devices [1], and they will also be used as anti-reflection [12] and down-conversion [13] [14] layers for realizing high-efficiency silicon solar cells.

Recently, we have also reported on the preparation of thulium-doped Ta_2O_5 (Ta_2O_5:Tm) thin films using the same co-sputtering method and their PL properties having sharp peaks around a wavelength of 800 nm due to Tm^{3+} [15]. In addition, the sensitization of PL from rare-earth ions by Ce^{3+} is well known [16]. We can obtain Ce^{3+} ions by sputtering of CeO_2 because a small amount of Ce^{3+} exists at the surface of CeO_2 [17]. It is therefore expected that strong PL will be obtained from Tm and Ce co-doped Ta_2O_5 (Ta_2O_5:Tm, Ce) thin film deposited by co-sputtering of Tm_2O_3 and CeO_2 pellets on a Ta_2O_5 disc. In this study, we prepared Ta_2O_5:Tm, Ce co-sputtered thin films using RF magnetron sputtering for the first time, and the PL and X-ray diffraction (XRD) properties of the films after annealing at 700˚C, 800˚C, 900˚C, or 1000˚C were evaluated.

2. Experimental

Ta_2O_5:Tm, Ce thin films were deposited using a RF magnetron sputtering system (ULVAC, SH-350-SE). A Ta_2O_5 disc (Furuuchi Chemical Corporation, 99.99% purity, 100 mm diameter) was used as the sputtering target. We placed one or two Tm_2O_3 and CeO_2 pellets (Furuuchi Chemical Corporation, 99.9% purity, 20 mm diameter) on the Ta_2O_5 disc. The Ta_2O_5 disc and the Tm_2O_3 and CeO_2 pellets were co-sputtered by supplying RF power to the target. The flow rate of Ar gas introduced into the vacuum chamber was 15 sccm, and the RF power supplied to the target was 300 W. Commercial fused-silica plates (ATOCK Inc., 1 mm thick) were used as substrates, and they were not heated during sputtering.

In this study, we deposited three samples (A, B, and C) (**Table 1**). We changed the Tm or Ce concentrations of the Ta_2O_5:Tm, Ce films by changing the numbers of Tm_2O_3 or CeO_2 pellets placed on the Ta_2O_5 disc [8]. We prepared four specimens from one as-deposited sample by cutting it using a diamond-wire saw, and we subsequently annealed the specimens in ambient air at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min using an electric furnace (Denken, KDF S-70).

The PL spectra of the Ta_2O_5:Tm, Ce 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. XRD patterns of the films were recorded using an X-ray diffractometer (RIGAKU, RINT2200VF+/PC system). Tm and Ce concentrations of the films after annealing were measured using an electron probe micro-analyzer (EPMA) (Shimadzu, EPMA-1610).

3. Results and Discussion

Figure 1 presents PL spectra of specimens prepared from a Ta_2O_5:Tm, Ce film deposited using one Tm_2O_3 pellet and two CeO_2 pellets (sample A) and annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min. PL peaks around a wavelength of 800 nm were observed for specimens annealed at 900˚C or 1000˚C. The 800-nm peak

Table 1. Three samples prepared in this study.

Sample	Number of Tm_2O_3 pellets	Number of CeO_2 pellets
A	1	2
B	1	1
C	2	1

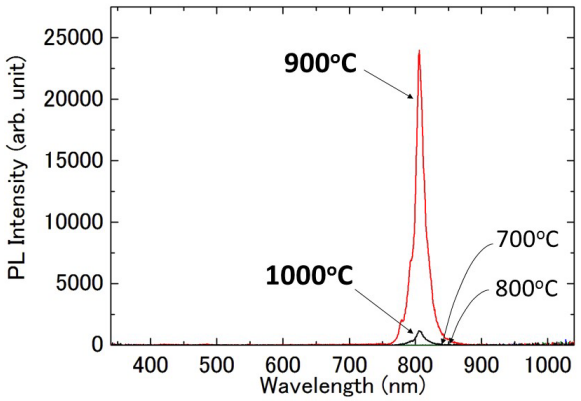

Figure 1. PL spectra of specimens prepared from a Ta_2O_5:Tm, Ce film deposited using one Tm_2O_3 pellet and two CeO_2 pellets (sample A) and annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min.

seems to be the result of the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} [15]. No PL peak was observed for specimens annealed at 700˚C or 800˚C. **Figure 2** presents PL spectra of specimens prepared from a Ta_2O_5:Tm, Ce film deposited using one Tm_2O_3 pellet and one CeO_2 pellet (sample B) and annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min. Much stronger PL peaks at almost the same wavelength of 800 nm were observed for specimens annealed at 900˚C or 1000˚C than for those prepared from sample A and annealed at the same temperature. The PL peak intensity of the specimen annealed at 900˚C was 3.3 times stronger, and that of the specimen annealed at 1000˚C was 14.4 times stronger than that of the specimen prepared from the sample A and annealed at the same temperature. **Figure 3** presents PL spectra of specimens prepared from a Ta_2O_5:Tm, Ce film deposited using two Tm_2O_3 pellets and one CeO_2 pellet (sample C) and annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min. PL peaks of specimens annealed at 900˚C or 1000˚C were similar to those of samples A and B, but much weaker than those of sample B.

Figure 4 plots normalized PL peak intensities of the specimens annealed at 900˚C or 1000˚C and prepared from samples A, B, and C. In our experiments, sample B exhibited the strongest PL intensity. The Tm concentration of film prepared from sample B and annealed at 900˚C was measured to be ~1.0 mol%, and the Ce concentration was measured to be ~1.3 mol%. These concentrations were thus estimated to be the proper Tm and Ce concentrations of such a Ta_2O_5:Tm, Ce film to obtain strong PL intensity.

Figure 5 presents XRD patterns of the specimens prepared from sample B and annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min. The specimens annealed at 900˚C or 1000˚C had almost the same major diffraction peaks corresponding to the (001); δ-Ta_2O_5 (orthorhombic), (200); δ-Ta_2O_5 (hexagonal); and (201) phases as our rare-earth doped Ta_2O_5 sputtered thin films [18]. The three phases seem to be very important for obtaining strong PL peaks from the present Ta_2O_5:Tm, Ce films, in addition to optimizing the Tm and Ce concentrations.

4. Summary

We prepared Ta_2O_5:Tm, Ce thin films using simply co-sputtering of one or two Tm_2O_3 and CeO_2 pellets on a Ta_2O_5 disc for the first time, and PL properties of the films annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min were evaluated. PL peaks around a wavelength of 800 nm due to Tm^{3+} were observed for films annealed at 900˚C or 1000˚C. The peak intensities of films prepared using one Tm_2O_3 pellet and one CeO_2 pellet were much stronger than those of films prepared using one Tm_2O_3 pellet and two CeO_2 pellets, or films prepared using two Tm_2O_3 pellets and one CeO_2 pellet. The proper Tm concentration to obtain strong PL intensity was estimated to be ~1.0 mol%, and proper Ce concentration was estimated to be ~1.3 mol%. Based on XRD measurements, the (001); δ-Ta_2O_5 (orthorhombic), (200); δ-Ta_2O_5 (hexagonal); and (201) phases of the Ta_2O_5:Tm, Ce films seem to be very important for obtaining a strong PL peak. Such light-emitting Ta_2O_5-based sputtered films can be used as high-refractive-index materials of autocloned photonic crystals that can be applied to novel light-emission devices, and they will also be used as anti-reflection and down-conversion layers for realizing high-efficiency silicon solar cells.

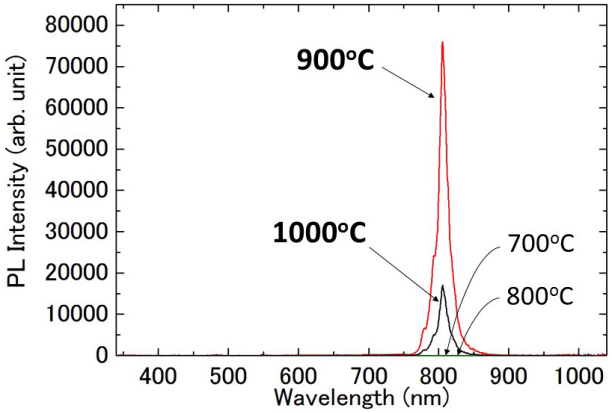

Figure 2. PL spectra of specimens prepared from a Ta_2O_5:Tm, Ce film deposited using one Tm_2O_3 pellet and one CeO_2 pellet (sample B) and annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min.

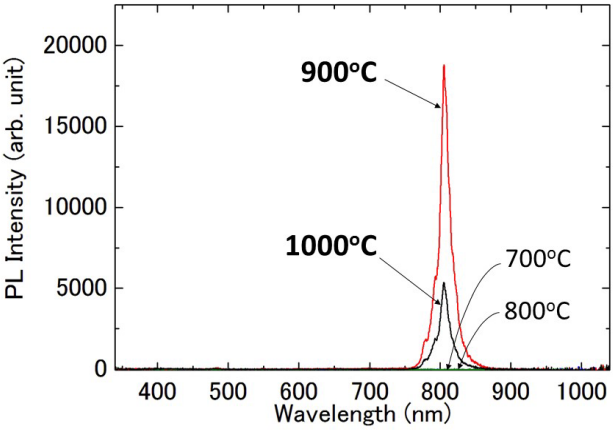

Figure 3. PL spectra of specimens prepared from a Ta_2O_5:Tm, Ce film deposited using two Tm_2O_3 pellets and one CeO_2 pellet (sample C) and annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min.

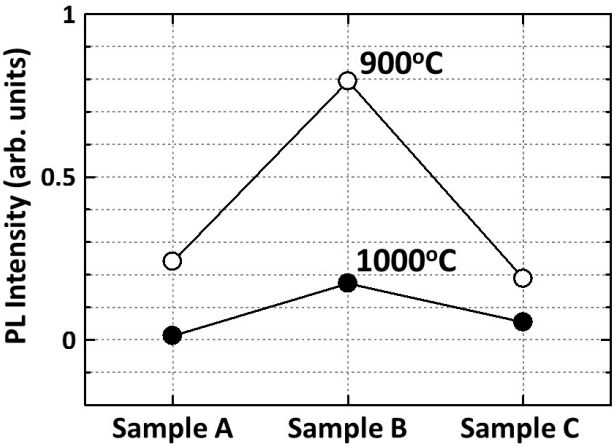

Figure 4. Normalized PL-peak intensities of the specimens annealed at 900˚C or 1000˚C and prepared from samples A, B, and C.

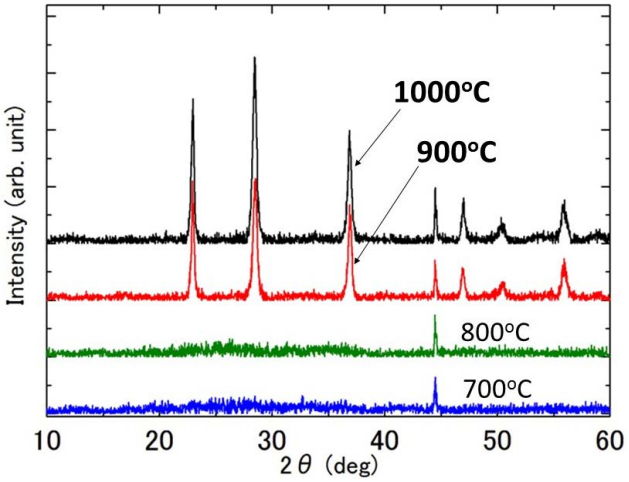

Figure 5. XRD patterns of the specimens prepared from the Ta_2O_5:Tm, Ce film deposited using one Tm_2O_3 and one CeO_2 pellets (sample B) and annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min.

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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] Miura, K., Ohtera, Y., Ohkubo, H., Akutsu, N. and Kawakami, S. (2003) Reduction of Propagation and Bending Losses of Hetero-Structured Photonic Crystal Waveguides by Use of a High-Δ Structure. *Optics Letters*, **28**, 734-736. http://dx.doi.org/10.1364/OL.28.000734

[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] Miura, K., Miyazaki, H. and Hanaizumi, O. (2008) Observation of Blue-Light Emission from Tantalum Oxide Films Deposited by Radio-Frequency Magnetron Sputtering. *IEICE Transactions on Electronics*, **E91-C**, 1669-1672. http://dx.doi.org/10.1093/ietele/e91-c.10.1669

[6] 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

[7] 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

[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., Yokota, Y. and Hanaizumi, O. (2014) Fabrication and Evaluation of Ta_2O_5:Y_2O_3 Co-Sputtered Thin Films. *Results in Physics*, **4**, 185-186. http://dx.doi.org/10.1016/j.rinp.2014.09.004

[11] 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

[12] 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

[13] 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

[14] 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

[15] Miura, K., Osawa, T., Yokota, Y., Suzuki, T. and Hanaizumi, O. (2014) Fabrication of Tm-Doped Ta_2O_5 Thin Films Using a Co-Sputtering Method. *Results in Physics*, **4**, 148-149. http://dx.doi.org/10.1016/j.rinp.2014.08.011

[16] 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

[17] 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

[18] 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