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Observation of Blue-Light Emission Band from Eu-Doped Ta_2O_5 Thin Films Prepared Using Co-Sputtering

Kenta Miura*, Yuki Arai, Osamu Hanaizumi

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

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Abstract

In this paper, we report on the first observation of blue-light emission bands from europium-doped tantalum pentoxide (Ta_2O_5:Eu) thin films prepared using a simple co-sputtering method. We prepared four specimens from one as-deposited sample, and we subsequently annealed them at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min. Four remarkable photoluminescence (PL) peaks at wavelengths of 600, 620, 650, and 700 nm due to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+} were observed from all the specimens, and blue PL peaks around a wavelength of 450 nm were also observed from the specimens annealed at 800˚C, 900˚C, and 1000˚C. The blue PL peaks seem to be originated from the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. Both Eu^{3+} and Eu^{2+} ions seem to exist in our Ta_2O_5:Eu co-sputtered thin films annealed at temperatures from 800˚C to 1000˚C. Such Ta_2O_5:Eu co-sputtered thin films seem to be used as multi-functional coating films having both anti-reflection and down-conversion effects for realizing high-efficiency silicon solar cells.

Keywords

Ta_2O_5, Eu, Co-Sputtering, Blue-Light Emission Band

1. Introduction

Tantalum pentoxide (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

*Corresponding author.

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range fabricated using the "autocloning" method based on radio-frequency (RF) bias sputtering [1] [2], 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 are observed from thermal-oxidized amorphous Ta_2O_5 thin films [4]. In our previous work, we demonstrated blue PL from Ta_2O_5 thin films deposited by RF magnetron sputtering [5].

Moreover, 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 lower phonon energy (100 - 450 cm^{-1}) than other popular oxide materials (e.g. SiO_2) [6]. We have so far fabricated various rare-earth (Er [7]-[11], Tm [12] [13], Y [14], Yb [10] [15], and Ce [9] [11] [13]) doped Ta_2O_5 thin films using simply co-sputtering of rare-earth oxide (Er_2O_3, Tm_2O_3, Y_2O_3, Yb_2O_3, and CeO_2) pellets and a Ta_2O_5 disc, and we have obtained various PL properties from the rare-earth-doped Ta_2O_5 thin films [7]-[15]. 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.

Furthermore, we also reported on red or orange PL from Eu-doped Ta_2O_5 (Ta_2O_5:Eu) thin films deposited using the same co-sputtering method [19]. In this paper, we report on the first observation of blue PL peaks from our Ta_2O_5:Eu co-sputtered thin films.

2. Experimental

A Ta_2O_5:Eu thin film was deposited using our simple co-sputtering method reported in [7]-[15] [19]. A Ta_2O_5 disc (99.99% purity, diameter 100 mm) and two Eu_2O_3 pellets (99.9% purity, diameter 20 mm) were used as a co-sputtering target as shown in **Figure 1**. We can prepare Ta_2O_5:Eu co-sputtered thin films with different Eu concentrations by changing the number of Eu_2O_3 pellets on the Ta_2O_5 disc [8], and we can obtain a Ta_2O_5:Eu film with an Eu concentration around 2.5 mol% by using two Eu_2O_3 pellets [20]. The film was deposited using a RF magnetron sputtering system (ULVAC, SH-350-SE). The flow rate of Ar gas introduced into the vacuum chamber was 10 sccm, and the RF power supplied to the target was 300 W. A fused-silica plate (1 mm thick) was used as a substrate, and it was not heated during co-sputtering. 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 from the specimens were measured using a dual-grating monochromator (Roper Scientific, SpectraPro 2150i) and a CCD detector (Roper Scientific, Pixis:100B, electrically cooled to −80˚C) under excitation with a He-Cd laser (Kimmon, IK3251R-F, wavelength λ = 325 nm).

3. Results and Discussion

Figure 2 presents PL spectra from the four specimens annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min.

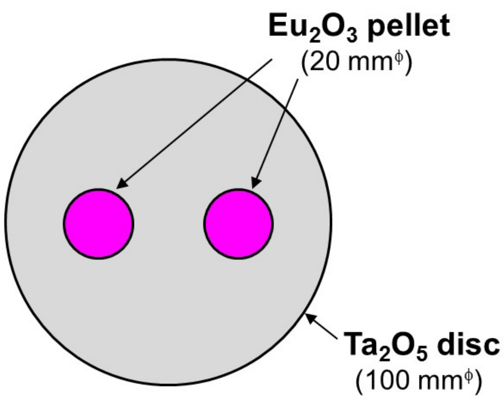

Figure 1. Schematic diagram of the sputtering target for co-sputtering of two Eu_2O_3 pellets and a Ta_2O_5 disc.

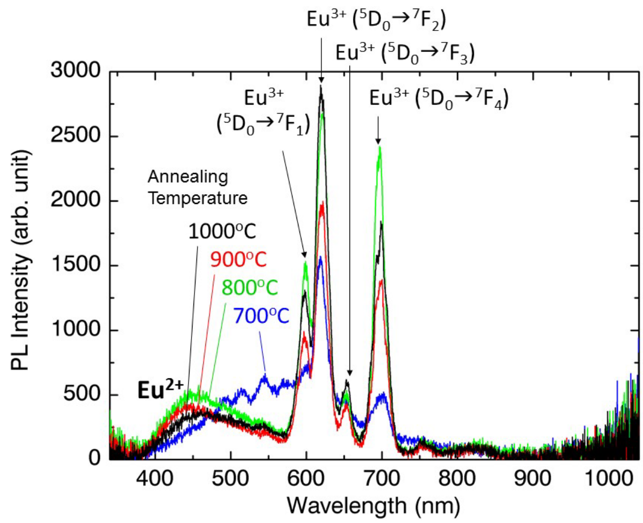

Figure 2. PL spectra of Ta_2O_5:Eu co-sputtered thin films annealed at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min.

Four remarkable PL peaks at wavelengths of 600, 620, 650, and 700 nm were observed from all the specimens prepared from our Ta_2O_5:Eu thin film. These four peaks seem to be the results of the $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions of Eu^{3+}, respectively [19]. A broad PL spectrum ranging from 400 to 900 nm was also observed from the specimen annealed at 700˚C. The broad spectrum seems to originate from oxygen vacancies in Ta_2O_5 reported in [4]. Additionally, blue PL bands around a wavelength of 450 nm were observed from the specimens annealed at 800˚C, 900˚C, and 1000˚C. The blue PL peaks seem to be originate from the $4f^65d^1 \rightarrow 4f^7$ ($^8S_{7/2}$) transition of Eu^{2+} [21]. This result suggests that both Eu^{3+} and Eu^{2+} ions exist in our Ta_2O_5:Eu co-sputtered thin films annealed at temperatures from 800˚C to 1000˚C.

As seen in **Figure 2**, the blue peak intensity was decreased with increasing the annealing temperature, and the maximum intensity was obtained from the specimen annealed at 800˚C. Therefore, the proper annealing temperature to obtain stronger blue peak intensities seems to be between 700˚C and 800˚C.

The relationship between the annealing temperatures and the crystallizabilities of Ta_2O_5 sputtered thin films doped with Er have been investigated in [22]. No X-ray diffraction (XRD) peak was observed from a film annealed at 700˚C, but three major XRD 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 films annealed from 800˚C to 1000˚C. The film annealed at 700˚C seemed to be amorphous phase, and the films annealed above 800˚C seemed to be polycrystalline phase. The crystallizabilities of our Ta_2O_5:Eu co-sputtered thin films similarly seem to be very important to obtain blue PL peaks.

We will try to optimize the annealing temperature by preparing and evaluating additional Ta_2O_5:Eu co-sputtered thin films annealed at the other temperatures from 700˚C to 800˚C, and we will also conduct XRD measurements of our Ta_2O_5:Eu co-sputtered thin films in order to make the origin of the blue PL peaks clear from the crystallizabilities of the films.

4. Summary

We reported on the first observation of blue-light emission bands from our Ta_2O_5:Eu co-sputtered thin films.

We prepared four specimens from one as-deposited sample, and we subsequently annealed them at 700˚C, 800˚C, 900˚C, or 1000˚C for 20 min. Four remarkable PL peaks at wavelengths of 600, 620, 650, and 700 nm due to the $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions of Eu^{3+} were observed from all the specimens. We also observed blue PL peaks around a wavelength of 450 nm from the specimens annealed at 800˚C, 900˚C, and 1000˚C. The blue peaks seem to be originated from the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. This suggests that both Eu^{3+} and Eu^{2+} ions exist in our Ta_2O_5:Eu co-sputtered thin films annealed at temperatures from 800˚C to 1000˚C.

We will try to optimize the annealing temperature by preparing and evaluating Ta_2O_5:Eu co-sputtered thin films annealed at the other temperatures from 700˚C to 800˚C because the proper annealing temperature to obtain stronger blue peak intensities seems to be in the temperature range. Such Ta_2O_5:Eu co-sputtered 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, and they also seem to be used as multi-functional coating films having both anti-reflection and down-conversion effects for realizing high-efficiency silicon solar cells.

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