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Observation of Violet-Light Emission Band for Thulium-Doped Tantalum-Oxide Films Produced by Co-Sputtering

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Abstract

We prepared thulium-doped tantalum (V) oxide (Ta_2O_5:Tm) thin films using co-sputtering of two Tm_2O_3 pellets and a Ta_2O_5 disc, and we observed photoluminescence (PL) peaks not only around a wavelength of 800 nm due to the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} but also around a wavelength of 400 nm (violet) from the films after annealing for the first time. Comparatively narrow PL peaks around the wavelength of 400 nm were observed from the films annealed at 800˚C and 900˚C for 20 min. The peak intensity from the film annealed at 900˚C was approximately four-times stronger than that from the film annealed at 800˚C. The origin of the 400-nm peaks seems to be the same as our non-doped Ta_2O_5 thin films deposited using radio-frequency sputtering because we observe PL peaks around 400 - 430 nm from the Ta_2O_5 films. Such a Ta_2O_5:Tm 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, Thulium, Co-Sputtering, Violet-Light Emission Band

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. 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

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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].

In addition, many studies on rare-earth-doped Ta_2O_5 have been conducted because Ta_2O_5 is a potential host material for new phosphors or efficient down-conversion luminescent materials due to its lower phonon energy from 100 to 450 cm^{-1} than other popular oxides such as SiO_2 [6]. We have reported on various rare-earth (Er, Eu, Y, Yb, 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, Yb_2O_3, and CeO_2) pellets and a Ta_2O_5 disc, and we have observed various PL from our rare-earth-doped Ta_2O_5 thin films [7]-[17]. We also fabricated thulium-doped Ta_2O_5 (Ta_2O_5:Tm) thin films using co-sputtering of three Tm_2O_3 pellets and a Ta_2O_5 disc, and we obtained a remarkable PL peak around a wavelength of 800 nm due to the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} from a Ta_2O_5:Tm co-sputtered film after annealing at 900˚C for 20 min [17].

In this study, we prepared Ta_2O_5:Tm co-sputtered thin films using two Tm_2O_3 pellets, and we observed not only PL peaks around a wavelength of 800 nm but also violet PL peaks from the films after annealing for the first time.

2. Experimental

A Ta_2O_5:Tm thin film was deposited using a RF magnetron sputtering system (ULVAC, SH-350-SE). A schematic figure of the system was presented in our previous report [8]. A Ta_2O_5 disc (99.99% purity, diameter 100 mm) and two Tm_2O_3 pellets (99.9% purity, diameter 20 mm) were used as co-sputtering targets. The Tm_2O_3 pellets were placed on the Ta_2O_5 disc as shown in **Figure 1**. The flow rate of argon gas introduced into the vacuum chamber was 10 sccm, and the RF power supplied to the targets 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 600˚C, 700˚C, 800˚C, or 900˚C for 20 min using an electric furnace (Denken, KDF S-70). The annealing temperatures (600˚C - 900˚C) and the annealing time (20 min) are the same as those for our Ta_2O_5:Tm thin films reported in [17].

The PL spectra of the annealed 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 600˚C, 700˚C, 800˚C, or 900˚C for 20 min. The 800-nm-peaks due to the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} were observed from all the specimens though the similar peak was so far observed only from our Ta_2O_5:Tm co-sputtered film prepared using three Tm_2O_3 pellets and annealed at 900˚C [17]. The 800-nm-peak intensities from the specimens annealed at 600˚C and 900˚C were much stronger than the specimens annealed at 700˚C and 800˚C, and the maximum intensity was obtained from

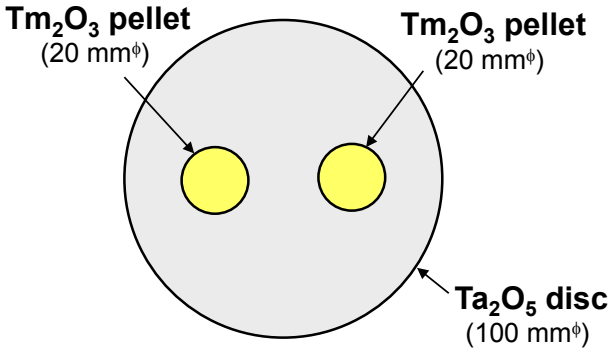

Figure 1. Schematic diagram of the sputtering target for co-sputtering of two Tm_2O_3 pellets and a Ta_2O_5 disc.

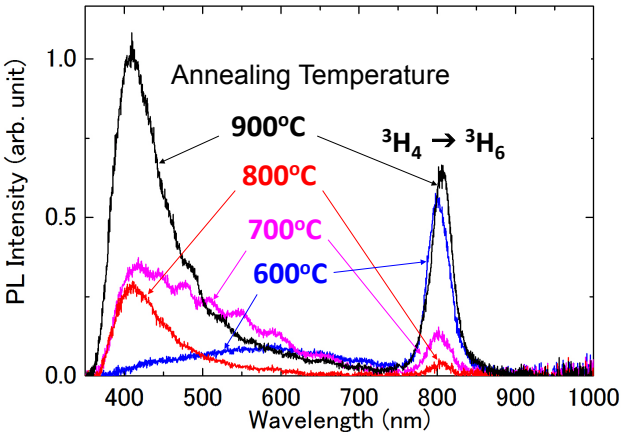

Figure 2. PL spectra of Ta_2O_5:Tm co-sputtered thin films annealed at 600˚C, 700˚C, 800˚C, or 900˚C for 20 min.

the specimen annealed at 900˚C. Broad PL spectra ranging from 400 to 750 nm were also observed from the specimens annealed at lower temperatures of 600˚C and 700˚C. The broad spectra seem to originate from the $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} [18] and/or oxygen-vacancy trap levels of Ta_2O_5 reported in [19].

On the other hand, comparatively narrow PL peaks around a wavelength of 400 nm (violet) were observed from the specimens annealed at higher temperatures of 800˚C and 900˚C. We thus observed violet-light emission bands from our Ta_2O_5:Tm co-sputtered thin films for the first time. The peak intensity from the specimen annealed at 900˚C was approximately four-times stronger than that from the specimen annealed at 800˚C. The origin of the 400-nm peaks seems to be the same as our non-doped Ta_2O_5 thin films deposited using RF sputtering because we observed PL peaks around wavelengths of 400 - 430 nm from Ta_2O_5 films annealed at 500˚C or 600˚C [5].

We previously reported that the δ-Ta_2O_5 (hexagonal) phase in a Ta_2O_5:Tm thin film is very important for obtaining a strong PL peak at the wavelength of 800 nm from the film [17]. Therefore, the crystallizabilities of our Ta_2O_5:Tm thin films seem to be very important to obtain such violet PL peaks. We will conduct X-ray diffraction (XRD) measurements of the films in order to determine the relationship between the violet PL intensity and the crystallizability, and we will try to make the origin of the violet PL clear.

Such a Ta_2O_5:Tm co-sputtered thin film seems to be used as a multi-functional coating film having both anti-reflection [3] and down-conversion [20]-[22] effects for realizing a high-efficiency silicon solar cell.

4. Summary

We prepared Ta_2O_5:Tm thin films using co-sputtering of two Tm_2O_3 pellets and a Ta_2O_5 disc, and we observed not only PL peaks around a wavelength of 800 nm due to the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} but also violet PL peaks from the films after annealing for the first time. Comparatively narrow PL peaks around a wavelength of 400 nm were observed from the films annealed at 800˚C and 900˚C for 20 min. The peak intensity from the film annealed at 900˚C was approximately four-times stronger than that from the film annealed at 800˚C. The origin of the 400-nm peaks seems to be the same as our non-doped Ta_2O_5 thin films deposited using RF sputtering because we observe PL peaks around wavelengths of 400 - 430 nm from the Ta_2O_5 films. We will conduct XRD measurements of the Ta_2O_5:Tm thin films in order to determine the relationship between the violet PL intensities and the crystallizabilities of the films, and we will try to make the origin of the violet PL clear. Such Ta_2O_5:Tm 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.

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