

Microarticle

Fabrication and evaluation of green-light emitting Ta₂O₅:Er, Ce co-sputtered thin films

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ABSTRACT

Erbium and cerium co-doped tantalum-oxide (Ta₂O₅:Er, Ce) thin films were fabricated using radio-frequency co-sputtering of Ta₂O₅, Er₂O₃, and CeO₂ for the first time. Enhanced green-light emission due to Er³⁺ that seems to be sensitized by Ce³⁺ was observed from the film annealed at 900 °C for 20 min. From XRD measurements of the films, the β-Ta₂O₅ (orthorhombic), δ-Ta₂O₅ (hexagonal), and (201) Ta₂O₅ phases seem to be very important for obtaining green PL from them. Such Ta₂O₅:Er, Ce co-sputtered films can be used as high-refractive-index materials of autocloned photonic crystals that can be applied to novel green-light-emitting devices, and they will also be used as multi-functional coating films that can work both as anti-reflection and down-conversion films for realizing high-efficiency silicon solar cells.

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1. Introduction

Tantalum (V) oxide (Ta₂O₅) is a high-refractive-index material used in passive optical elements such as Ta₂O₅/SiO₂ multilayered wavelength filters for dense wavelength-division multiplexing (DWDM). It has also been used as a high-index material of Ta₂O₅/SiO₂ multilayered photonic-crystal elements for the visible to near-infrared range fabricated using the autocloning method based on radio-frequency (RF) bias sputtering [1–3], and it can additionally be used as an anti-reflection coating material for silicon solar cells [4].

On the other hand, many studies on rare-earth-doped Ta₂O₅ have been conducted because Ta₂O₅ is a potential host material for new phosphors due to its low phonon energy (100–450 cm⁻¹) compared with other oxide materials such as SiO₂ [5]. We have reported on various rare-earth (Er, Eu, Tm, Y, and Ce) doping into Ta₂O₅ thin films using simply co-sputtering of rare-earth-oxide (Er₂O₃, Eu₂O₃, Tm₂O₃, Y₂O₃, and CeO₂) pellets and a Ta₂O₅ disc [6–11]. Moreover, in our recent study, we fabricated Er, Eu, and Ce co-doped Ta₂O₅ (Ta₂O₅:Er, Eu, Ce) thin films using the same co-sputtering method, and observed yellow PL from the films [11]. The yellow light emission seemed to be obtained from the result of enhancement of the 550-nm (green) PL peak due to Er³⁺ by Ce doping [12]. Such Ta₂O₅-based sputtered films can be used as high-refractive-index and light-emitting materials of autocloned photonic crystals that can be applied to novel light-emission

devices [1], and they will also be used as down-conversion layers for realizing high-efficiency silicon solar cells [13,14].

In this study, we prepared Er and Ce co-doped Ta₂O₅ (Ta₂O₅:Er, Ce) thin films using RF magnetron co-sputtering of Ta₂O₅, Er₂O₃, and CeO₂, and observed an enhanced green PL peak due to Er³⁺ that seems to be sensitized by Ce ions from the films.

2. Fabrication

Ta₂O₅:Er, Ce thin films were deposited using an RF magnetron sputtering system (ULVAC, SH-350-SE). A Ta₂O₅ disc (99.99% purity, diameter 100 mm) was used as the sputtering target. We placed one CeO₂ and two Er₂O₃ pellets (99.9% purity, diameter 20 mm) on the Ta₂O₅ disc. They 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 200 W. Fused-silica plates (1 mm thick) were used as substrates, and they were not heated during sputtering. We subsequently annealed the films in ambient air at 600, 700, 800, or 900 °C for 20 min using an electric furnace (Denken, KDF S-70).

3. Evaluation

The PL spectra of the Ta₂O₅:Er, Ce co-sputtered films were measured using a dual-grating monochromator and a CCD detector (electrically cooled to -80 °C). An He-Cd laser (wavelength λ = 325 nm) was used to excite the films. The X-ray diffraction (XRD) patterns of the films were recorded using an X-ray diffractometer, and the Er and Ce concentrations of the films were

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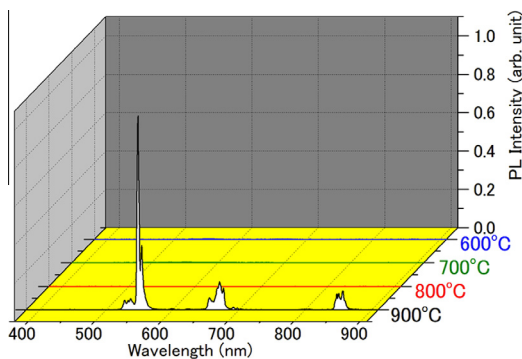


Fig. 1. PL spectra of Ta₂O₅:Er, Ce co-sputtered films annealed at 600, 700, 800, or 900 °C for 20 min.

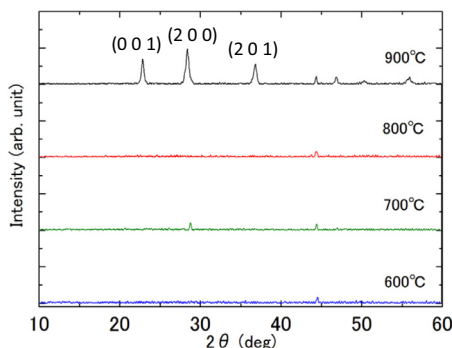


Fig. 2. XRD patterns observed from Ta₂O₅:Er, Ce co-sputtered films annealed at 600, 700, 800, or 900 °C for 20 min.

measured after annealing using an electron probe micro-analyzer (EPMA).

Fig. 1 presents the PL spectra of Ta₂O₅:Er, Ce films annealed at 600, 700, 800, or 900 °C for 20 min. We observed typical PL peaks around wavelengths of 550 and 670 nm from the film annealed at 900 °C. The 550-nm peak seems to be the result of the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition of Er³⁺, and the 670-nm peak seems to be the result of the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition of Er³⁺ [6]. The Er and Ce concentrations of the film were measured to be ~1.6 and 3.4 mol%, respectively. No PL peak was observed from the films annealed at 600, 700, or 800 °C.

Fig. 2 presents XRD patterns of the films annealed at 600, 700, 800, or 900 °C for 20 min. The film annealed at 900 °C exhibited three major diffraction peaks corresponding to the (001); β-Ta₂O₅ (orthorhombic), (200); δ-Ta₂O₅ (hexagonal), and (201) Ta₂O₅ phases [15]. On the other hand, the films annealed at 600, 700, and 800 °C seemed to be almost amorphous phases because no significant diffraction peak was observed from them. As the results shown in **Fig. 1**, we observed PL peaks only from the film annealed at 900 °C. Therefore, the above-mentioned three crystalline phases of Ta₂O₅ seem to be very important for obtaining green PL from our Ta₂O₅:Er, Ce co-sputtered films.

Fig. 3 presents PL spectra of our Ta₂O₅:Er, Ce and Ta₂O₅:Er (without Ce) co-sputtered films annealed at 900 °C for 20 min. We observed a significant enhancement of the PL intensity by Ce doping. The mechanism of the enhancement seems to be the energy transfer from Ce³⁺ to Er³⁺ reported by Du et al. [12]. It seems that Ce³⁺ (not Ce⁴⁺) ions can be exist in the films prepared using CeO₂ (cerium (IV) oxide) pellets because a small amount of Ce³⁺ exists at the surface of CeO₂ [16].

As well known, the light emission from Ce³⁺ is due to the transitions from 5d to 4f states, and the emission band of Ce³⁺ is usually broad covering wavelengths from 350 to 600 nm [17,18]. In addition, an excitation spectrum of Er³⁺ around the emission

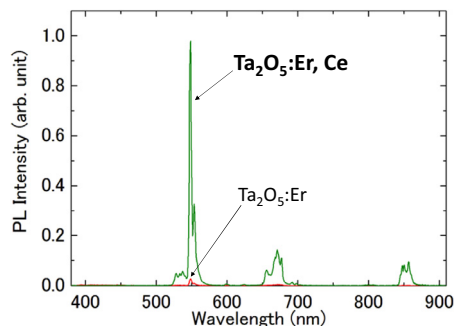


Fig. 3. PL spectra of Ta₂O₅:Er, Ce and Ta₂O₅:Er co-sputtered films annealed at 900 °C for 20 min.

wavelength of 550 nm seems to range from 350 to 500 nm [12]. The excitation-spectrum range overlaps with the emission-band range of Ce³⁺. Therefore, Ce³⁺ ions in our Ta₂O₅:Er, Ce co-sputtered films seem to act as efficient sensitizers for the green-light emission from Er³⁺ [12].

4. Summary

Ta₂O₅:Er, Ce thin films were fabricated using RF co-sputtering of Ta₂O₅, Er₂O₃, and CeO₂ for the first time. Enhanced green-light emission due to Er³⁺ that seems to be sensitized by Ce³⁺ was observed from the film annealed at 900 °C for 20 min. From XRD measurements of the films, the β-Ta₂O₅ (orthorhombic), δ-Ta₂O₅ (hexagonal), and (201) Ta₂O₅ phases seem to be very important for obtaining green PL from them. Such Ta₂O₅:Er, Ce co-sputtered films can be used as high-refractive-index materials of autocloned (multilayered) photonic crystals that can be applied to novel green-light-emitting devices, and they will also be used as multi-functional coating films that can work both as anti-reflection and down-conversion films for realizing high-efficiency silicon solar cells.

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