Formation of Yttrium Oxide Composite Films by Electrodeposition in Organic Solutions

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有機溶媒からの電析によるイットリウム複合酸化物の作製

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Introduction

Many of rare earth compounds are known as advanced materials for optical, magnetic, electric and electronic uses. For example, yttrium oxide films, excellent substrates for fluorescent materials, are now produced by dry processes, vapor deposition, sputtering, etc. If we can apply electrochemical methods to the preparation of such thin films, it would be very advantageous from the view point of the cost and productivity. However, it is difficult to obtain rare earth metals by electrodeposition due to their negative reduction potentials. In order to prevent the cathodic hydrogen evolution, non-aqueous solvents have been used for the electrolyte solutions. Several workers have reported the electrodeposition of rare earth compounds using organic solutions^{1)~4)}. We have also investigated the cathodic electrodeposition of rare earth films from organic baths^{5), 6)}. We obtained the films of yttrium oxide and yttrium-europium oxide from organic electrolytes containing small amounts of water⁷⁾.

In the present work, the formation of lanthanide-containing yttrium oxide has been investigated in dimethylformamide (DMF)-based solutions, and then the composition and the fluorescent properties of the deposited films were briefly examined.

Experimental

The electrolytic cell was a glass beaker with a copper plate cathode, two parallel glassy carbon

plate anodes and a saturated calomel electrode (SCE) as the reference electrode. The solvent DMF was distilled at reduced pressure under an Ar atmosphere before use. Anhydrous YCl_3 (Soekawa Chem. Co. Ltd.), $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (High Purity Chem. Co. Ltd.) and AlCl_3 (Soekawa Chem. Co. Ltd.) were used as the electrolytic salts. The water content in the electrolytic cell was determined by Karl Fischer titration. The electrodeposition was performed using a constant-d. c. power supply (Nichia Keiki HP-5-1B). The morphology of the deposited films was observed by scanning electron microscopy (SEM). Electron probe microanalysis (EPMA) was also used to analyse the plated films. Photoluminescence spectroscopy was performed under the atmospheric conditions.

Results and Discussion

To investigate the electrodeposition process of the rare earth composite films, we have first carried out cyclic voltammetry (CV) in DMF containing rare earth ions. Fundamental behavior of Y^{3+} in DMF was described in a previous paper⁷⁾. In the solution containing Tb^{3+} , the first potential sweep clearly indicated a cathodic current peak at about -2.5V (vs. SCE), suggesting the formation of terbium as shown eq. (1).

Also, the current shoulder observed at about -1.0V (vs. SCE) shows the possibility of Tb_2O_3 formation (eq. (2)).

These results revealed that the electro-co-deposition of yttrium and terbium would be performed from DMF solutions containing Y^{3+} and Tb^{3+} with small amounts of water. In fact, we obtained thin films with white color and uniform surfaces by the constant-current electrodeposition. From the SEM observation, however, the depo-

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Fig. 1 EPMA spectra for films on Cu substrate by direct current deposition.

Bath : (a) $0.1 \text{ mol dm}^{-3} \text{ YCl}_3 + 0.01 \text{ mol dm}^{-3} \text{ TbCl}_3 \cdot 6 \text{ H}_2\text{O}/\text{DMF}$,

(b) $0.1 \text{ mol dm}^{-3} \text{ YCl}_3 + 0.01 \text{ mol dm}^{-3} \text{ TbCl}_3 \cdot 6 \text{ H}_2\text{O} + 0.05 \text{ mol dm}^{-3} \text{ AlCl}_3/\text{DMF}$

Current density : 1 A m^{-2}

Electricity passed : $5.0 \times 10^4 \text{ C m}^{-2}$

sited film had many micro-cracks. **Figure 1(a)** shows the EPMA spectrum of the film deposited from DMF containing Y^{3+} and Tb^{3+} . In addition to the spectra for the copper substrate, X-ray peaks based on yttrium and terbium were observed. We also examined the electro-co-deposition of Y-Tb-Al oxide system, relating to $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Tb}$ with green color luminescence, from DMF containing YCl_3 , TbCl_3 and AlCl_3 . **Figure 1(b)** shows the EPMA spectrum of the resulting film. The peaks of yttrium (L_α), terbium (L_α , L_β) and aluminum (K_α) shows that the film obtained by the electrodeposition consisted of yttrium, terbium and aluminum. The fluorescence spectra of the films are shown in **Fig. 2**. Typical luminescence for $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Tb}$ was observed at 490.5nm. This is attributed to the $^5\text{D}_4 \rightarrow ^7\text{F}_6$ transition. Also the luminescence at the range from 542.5 to 621.0 seems to correspond to the transition of $^5\text{D}_4 \rightarrow ^7\text{F}_6$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3^{8)}$. These suggest that the films obtained by the electrodeposition are candidates for luminescent material.

Conclusion

We obtained films consisting of yttrium, alumi-

Fig. 2 Fluorescence spectra (a) for a deposited film on Cu substrate by direct current deposition, and (b) for Cu substrate.

Bath : $0.1 \text{ mol dm}^{-3} \text{ YCl}_3 + 0.01 \text{ mol dm}^{-3} \text{ TbCl}_3 \cdot 6 \text{ H}_2\text{O} + 0.05 \text{ mol dm}^{-3} \text{ AlCl}_3/\text{DMF}$

Current density : 1 A m^{-2}

Electricity passed : $5.0 \times 10^4 \text{ C m}^{-2}$

num, terbium and/or their oxides by electro-co-deposition in DMF containing YCl_3 , TbCl_3 , AlCl_3 and small amounts of water. The films have potential of the terbium luminescent materials.

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