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Preparation of Compositionally Gradient Ba-Sr-Al-O Thin Film by Ion-Beam Evaporation

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A compositionally gradient Ba-Sr-Al-O thin film was successfully prepared by ion-beam evaporation. Composition analysis showed that Ba and Sr contents were gradually changed on the substrate. The compositionally gradient area was 60 mm, and the atomic ratio of Ba and Sr was 0.13:0.87 to 1.00:0.00. From X-ray diffraction pattern for the thin film, solubilities of Sr in $BaAl_2O_4$ and Ba in $SrAl_2O_4$ phases at 900°C was close to the compositions of $(Ba_{0.32\text{-}0.50}Sr_{0.68\text{-}0.50})Al_2O_4$ and $(Ba_{0.15\text{-}0.19}Sr_{0.85\text{-}0.81})Al_2O_4$, respectively.

Key words: $SrAl_2O_4$, $BaAl_2O_4$, $(Ba,Sr)Al_2O_4$, compositionally gradient thin film, ion-beam evaporation

1. INTRODUCTION

$SrAl_2O_4$:Eu has been known to exhibit high brightness phosphorescence without radioactive isotopes [1]. Additionally $BaAl_2O_4$:Eu has also been known as a phosphor material [2]. The unit cells of $SrAl_2O_4$ and $BaAl_2O_4$ structures are monoclinic and hexagonal, respectively. Recently, $(Ba,Sr)Al_2O_4$:Eu which is the mixture of these materials was developed [3]. Ito *et al.*[4] and Sakaihara *et al.*[3] reported synthesis of samples in the $(Ba,Sr)Al_2O_4$ system at 900°C, 1100°C, 1300°C, 1350°C and 1600°C. Although it is required to obtain the phase diagram for the $(Ba,Sr)Al_2O_4$ system, the phase diagram proposed by the above authors were different. The former claimed complete series of solid solutions, while the latter insisted the presence of a two-phase region. For determining the phase diagram, many samples with various compositions have to be synthesized. However, in this process, much time and efforts are spent to obtain the samples.

Quick material synthesis methods as combinatorial chemistry have been developed [5]. In these methods using a sputtering or a pulsed laser deposition, a thin film which has various compositions, i.e., a compositionally gradient thin film, is produced on a substrate by controlling masks. The phase diagram is determined by characterizing this thin film. By using these methods, much time and effort are able to be saved for the development of novel materials. However, in order to prepare compositionally gradient thin films by those methods, the number of atoms from the sources must be varied at each position on the substrate. For this purpose, masks, which were placed between the sources and the substrate, have to be controlled precisely.

On the other hand, preparation of compositionally gradient thin film by ion-beam evaporation (IBE) [6] method was reported [7,8]. An intense pulsed ion beam was irradiated on a segmented target consisting of different materials. High temperature and high density plasma were formed from the segmented target and deposited on a substrate. By using this method, compositionally gradient thin films were prepared without mask control. It is thought that the phase diagram is easily determined by analyzing the thin film.

The purpose of this study is to prepare a compositionally gradient Ba-Sr-Al-O thin film and to determine the phase diagram of the $BaAl_2O_4$-$SrAl_2O_4$ system.

2. EXPERIMENTAL APPARATUS AND METHOD

Figure 1 shows a schematic illustration of the experimental setup on the IBE system. An intense pulsed ion beam was extracted from a magnetically

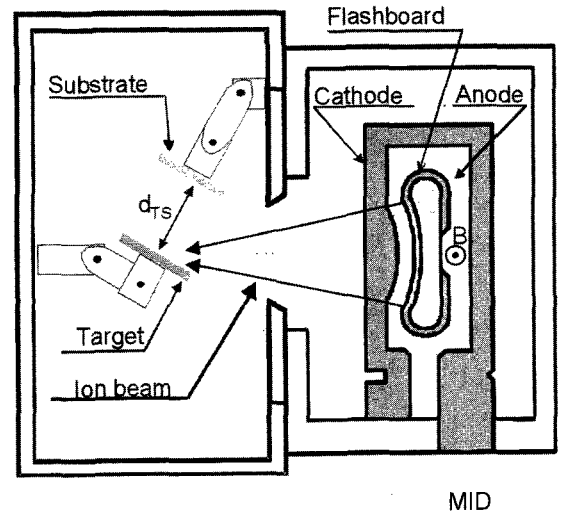

Fig. 1. Cross-sectional view of experimental setup of IBE method.

insulated diode (MID), which was connected to a pulse power generator "ETIGO-II". A polyethylene flashboard was attached to an anode as an ion source. A voltage of 1 MV (peak) was applied between a cathode and the anode with a pulse width of ~50 ns. To prevent a current of electrons between the anode and cathode, the transverse magnetic field of approximately 1 T was generated by the cathode as a theta-pinch coil.

The application of the high-voltage pulse produced the pulsed ion beam. The ion beam was geometrically focused on sintered $SrAl_2O_4$ and $BaAl_2O_4$ targets. The $SrAl_2O_4$ and $BaAl_2O_4$ targets were prepared from $SrCO_3$, $BaCO_3$ and Al_2O_3. The $SrAl_2O_4$ and the $BaAl_2O_4$ targets were synthesized at 1450 °C for 120 h in air and at 1300 °C for 24 h in air, respectively. Positions of these targets and substrate are shown Fig. 2. The targets were placed in the chamber at an angle of 30°, and a SiO_2 substrate with size of 90 mm × 15 mm × 1 mm was set parallel to the targets. The position on the substrate which face boundary of the targets was defined as r=0 mm. The $BaAl_2O_4$ side was defined as +r, while the $SrAl_2O_4$ side was defined as – r.

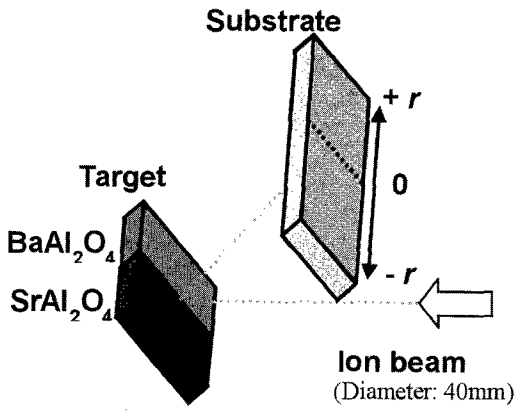

Fig. 2. Arrangement of targets and substrate for the preparation of compositionally gradient Ba-Sr-Al-O thin film.

Prior to the deposition, a substrate was kept at room temperature and in a vacuum of 2×10^{-4} Torr. The energy density applied by the ion beam to the target was 20 J/cm^2. The distance between the target and substrate (d_{TS}) was 80 mm. The ion beam was irradiated on targets for 20 times.

The produced thin film was amorphous and was annealed at 900 °C for 1 h in air.

Composition of the $(Ba_{1-x}Sr_x)Al_2O_4$ thin film was measured by an energy dispersive X-ray analyzer (EDX) equipped on a scanning electron microscope (SEM) operated at acceleration voltage of 10 kV. Standard samples of $BaAl_2O_4$ and $SrAl_2O_4$ were used for determining Cliff- Lorimer factors. Phases in the thin film were identified by an X-ray diffractometer (XRD) (Cu$K\alpha$ radiation) operated at 50 kV and 300 mA.

3. RESULTS AND DISCUSSION

A thin film was deposited on the SiO_2 substrate after 20 pulsed ion beam irradiations on the target and the composition was measured by EDX. In the EDX spectra, no peaks for Si from the substrate were detected so that the thin film was thicker than the penetration depth of the incident electrons with energy of 10 keV. Figure 3 shows composition distribution of the prepared thin film determined by EDX. The thin film at r=+45 mm consisted of Ba-Al-O and did not contain Sr. Compositions of the thin film at r=+30 mm and r=+15 mm were similar to that at r=+45 mm. At r=0 mm, x was measured to be 0.12. Moreover, with the decrease in r at -15, -30 and –45 mm, x was increased from 0.47, 0.78 to 0.87, respectively. From these results, the Sr and Ba contents were gradually changed on the substrate. The compositionally gradient area, which was defined to be the width between x=0 and 0.87, in the thin film was approximately 60 mm.

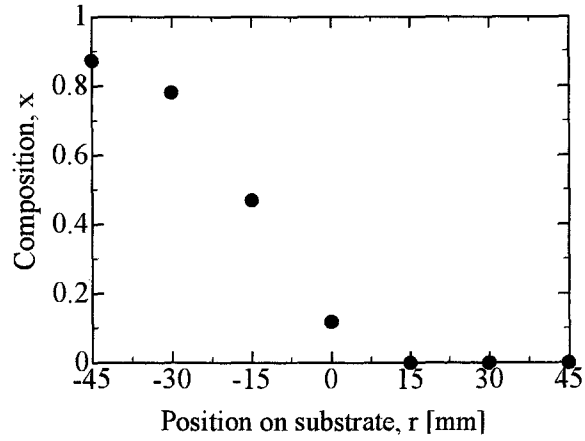

Fig. 3. Composition distribution of compositionally gradient Ba-Sr-Al-O thin film.

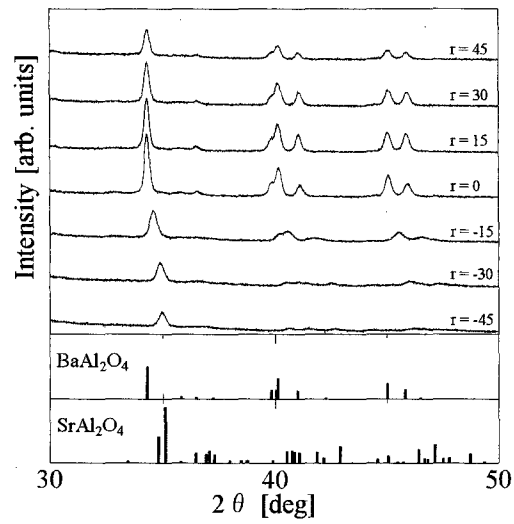

Fig. 4. XRD patterns of compositionally gradient Ba-Sr-Al-O thin film.

In Fig. 3, the composition of x=0.5 is located at r=-16

mm, where is apart from the center of the substrate and close to the $SrAl_2O_4$ target. From the results of thin film depositions using monolithic $BaAl_2O_4$ and $SrAl_2O_4$ targets with the same experimental conditions, 120 nm-thick $SrAl_2O_4$ thin films were obtained by each ion beam irradiation, while the thickness of $BaAl_2O_4$ thin films was 100 nm. Thus, it was concluded that the difference in the deposition rates caused the shift of the position with x=0.5 in Fig. 3.

Figure 4 shows XRD patterns of the thin film. In the XRD pattern of the thin film at r=+45 mm, all the peaks correspond to those of the $BaAl_2O_4$ phase. The peak shift was not observed. The XRD patterns for the thin film at r=+30 mm and r=+15 mm were similar to that at r=+45 mm. From these results, single-phase and crystalline $BaAl_2O_4$ thin film was prepared at r=+45 mm to r=+15 mm. In the XRD pattern of the thin film at r=0 mm, all peaks corresponded to those of $BaAl_2O_4$ phase, but slightly shifted to higher angles. In the XRD pattern of thin film at r=-15 mm, the peaks have shifted to higher angles.

XRD patterns, which have been obtained at a scanning speed of a half for Fig. 4, are shown in Fig. 5 (a). In the XRD patterns of the thin films at r=0 mm to r=-20 mm, all the peaks were gradually shifted to higher angles with the decrease in r. From this result and Fig. 3, it was found that the lattice constant was slightly decreased with the increase in x. It was explained that Ba in $BaAl_2O_4$ was partially replaced by Sr with small ionic radius.

From International Center for Diffraction Data (ICDD) shown at the bottom of Fig. 5 (a), strong 222 and 004 peaks are seen around 2θ=40 - 41° for $BaAl_2O_4$ phase, while a strong 400 and many weak peaks are located around 2θ=41 and 42° for $SrAl_2O_4$ phase, respectively. Thus, the peak height ratio of 2θ=40 - 41 and 41 - 42° was used for determining the phases. From Fig. 5 (a), it was thought that the thin film between r=0 mm and r=-20 mm have the almost similar peak height ratios and hexagonal structure based on that of $BaAl_2O_4$.

In the XRD pattern of the thin film at r=-25 mm, the peak height ratio of $BaAl_2O_4$ was decreased so that another phase was formed. It is considered that monoclinic structure based on $SrAl_2O_4$ and hexagonal structure based on $BaAl_2O_4$ coexisted in the thin film at r=-25 mm. From these results, the solubility of Sr in $BaAl_2O_4$ should be close to the composition between $(Ba_{0.50}Sr_{0.50})Al_2O_4$ and $(Ba_{0.32}Sr_{0.68})Al_2O_4$. This result was similar to the report of Sakaihara *et al.*[3] even though the synthesis temperature (1600 °C) is higher than that in the present research (900 °C).

Intensities of XRD patterns at r=-35 and -40 mm were enhanced and shown in Fig. 5 (b). In the XRD pattern of the thin film at r=-40 mm, the broad peaks of 40.5°, 41.5° and 42.5° were observed. Since relative intensities of these peaks were close to those of $SrAl_2O_4$ in ICDD, the peaks came from the $SrAl_2O_4$ phase. However, the peaks shifted to lower angles. It is considered that Sr in $SrAl_2O_4$ was replaced by Ba with large ionic radius. In the XRD pattern of the thin film at r=-35 mm, the broad peaks were not separated. It was thought that hexagonal phase were co-existed with monoclinic phase at r=-35mm. From these results, the solubility of Ba in $SrAl_2O_4$ should be close to the composition between $(Ba_{0.15}Sr_{0.85})Al_2O_4$ and $(Ba_{0.19}Sr_{0.81})Al_2O_4$.

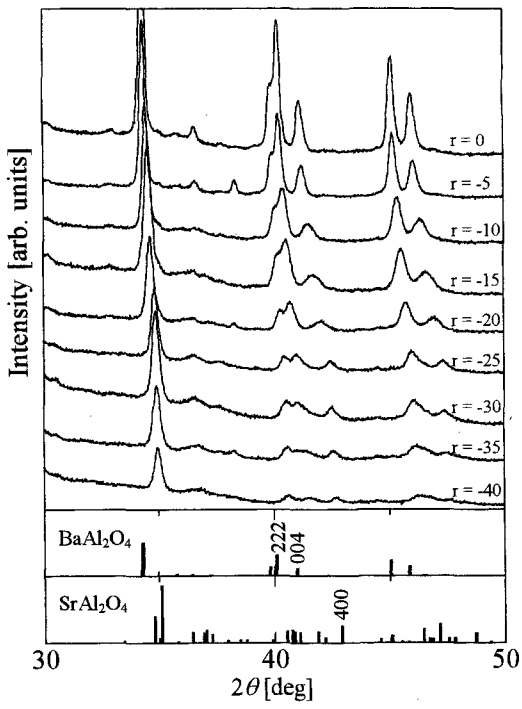

Fig. 5. (a) XRD patterns of compositionally gradient Ba-Sr-Al-O thin film measured at an interval of 5 mm.

4.CONCLUSIONS

A compositionally gradient Ba-Sr-Al-O thin film was successfully prepared on a SiO_2 substrate by IBE method. Compositionally gradient area in the thin film

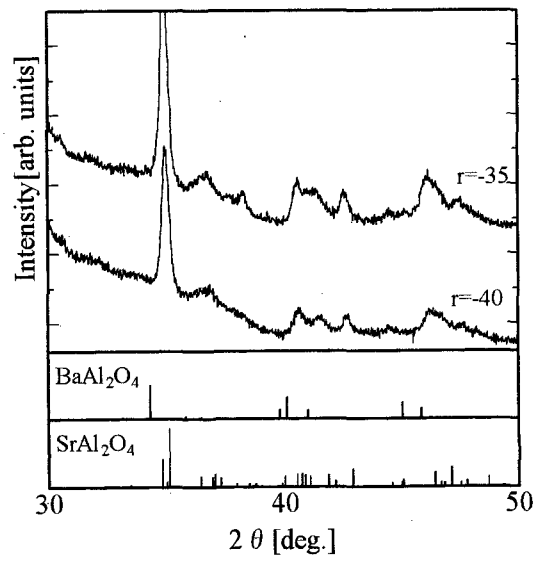

Fig. 5. (b) Close-up of XRD patterns at r=-35 mm and r=-40 mm

was approximately 60 mm. The solubilities of Ba in $SrAl_2O_4$ and Sr in $BaAl_2O_4$ at the temperature of 900 °C were in the vicinity of $(Ba_{0.15\text{-}0.19}Sr_{0.81\text{-}0.85})Al_2O_4$ and $(Ba_{0.32\text{-}0.5}Sr_{0.68\text{-}0.5})Al_2O_4$, respectively.

REFERENCES

[1] T. Matsuzawa, Y. Aoki, N. Takeuchi and Y. Murayama, *J. Electrochem. Soc,*. **143,** 2670-2673 (1996).
[2] F. C. Palilla, A. K. Levine and M. R. Tomkus, *J. Electrochem. Sci.*, **115,** 642-644 (1968).
[3] I. Sakaihara, K. Tanaka, T. Wakasugi, R. Ota, K. Fujita, K. Hirao and T. Ishihara, *Jpn. J. Appl. Phys.*, **41,** 1419-1423 (2002).
[4] S. Ito, S. Banno, K. Suzuki and M. Inagaki, *Yogyo Kyokai-shi*, **87**, 344-349 (1979) [in Japanese].
[5] H. Koinuma, *Solid State Ionics,* **108,** 1-4 (1998).
[6] K. Yatsui, *Laser and Particle Beams*, **3**, 119-155 (1989).
[7] H. Suematsu, T. Honzawa, M. Hirai, T. Suzuki, W. Jiang and K. Yatsui, *Trans. Mater. Res. Soc. Jpn.*, **28**, 425-428 (2003).
[8] T. Honzawa, M. Hirai, T. Suzuki, H. Suematsu, W. Jiang and K. Yatsui, *Trans. Mater. Res. Soc. Jpn.*, **29**, 651-654 (2004).

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