

Bi₁₂SiO₂₀ Electro-Optic Thin Films Deposited on Sapphire by ECR Plasma Sputtering

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Bi₁₂SiO₂₀ thin films have been prepared on (0001) sapphire substrates by electron cyclotron resonance plasma sputtering with Bi and Si multi targets system. The epitaxial thin films of γ -phase Bi₁₂SiO₂₀ have been obtained at the substrate temperature of 600°C during the sputtering process. Excellent quadratic electro-optic effects for these thin films are successfully observed for the first time to our knowledge. The details of the preparation, structure and electro-optic properties of the Bi₁₂SiO₂₀ thin films are described in this paper.

1. INTRODUCTION

A Bismuth-Silicon-oxide (Bi₁₂SiO₂₀ or BSO) is an attractive material, since it exhibits large electro-optic effects and high photoconductivity. Especially the thin films of BSO are strongly expected to fabricate new integrated optical devices such as spatial light modulators⁽¹⁾⁽²⁾, hologram recording devices⁽³⁾, phase conjugation⁽⁴⁾, and two-wave mixing⁽⁵⁾. However, most of these devices were made of BSO single crystals prepared by Czochralski method⁽⁶⁾. But it is difficult to polish BSO plate to several tens of μm in thickness. Therefore, it is desirable to prepare BSO thin films on a transparent substrate. Several researchers have attempted metalorganic chemical vapor deposition (MOCVD) method which can grow very thin BSO single crystal films on BSO substrates⁽⁷⁾. However it is not easy to obtain a large scale BSO substrate with a uniform quality and a low price. So the preparation of BSO thin films on any other substrates is extremely interesting for the wide industrial applications. Few research on BSO electro-optic thin films deposited on heterogeneous substrates has been reported.

In this work, the BSO electro-optic thin films have been successfully prepared on (0001) sapphire substrates by electron cyclotron resonance (ECR) plasma sputtering method with Bi and Si multi targets system.

2. EXPERIMENTAL

A ECR plasma sputtering apparatus with Bi and Si multi target system has been

developed for the preparation of the thin films with multi component materials⁽⁸⁾. Figure 1 shows a schematic diagram of this apparatus. In this system, Bi and Si metal plates were placed alternately at the place outside the aperture which introduced plasma into the deposition chamber. The applied DC voltage of each target is individually controllable, so that the stoichiometric BSO thin films can be obtained easily. A mirror-polished single crystal sapphire with (0001) orientation was used as a substrate for epitaxial growth of the BSO thin films. Table I shows the sputtering conditions for the film preparation.

Crystalline structures of the films were determined by X-ray diffraction method, reflection high-energy electron diffraction (RHEED), and a scanning electron microscope.

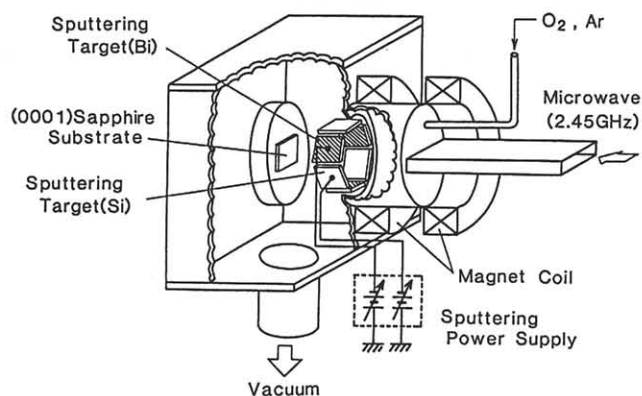


Fig.1 Schematic diagram of the ECR plasma sputtering apparatus.

TABLE I. Sputtering conditions for the film preparation

Sputtering gas	Ar(50%) + O ₂ (50%)
Gas pressure	1.0Pa
Background pressure	2.0×10^{-4} Pa
Microwave Power	200W(2.45GHz)
Target DC bias voltage	-100~-400V
Total target area	60cm ² (for Bi, Si)
Target-substrate spacing	4~8cm
Substrate temperature	R.T.~600°C
Deposition rate	10~60 Å/min.
Film thickness	0.3~3.0 μm

Compositions of the films were determined by electron-probe X-ray microanalysis (EPMA).

Electro-optic effects of the BSO thin films were measured with the He-Ne laser light transmission perpendicularly through the film. The relative shift of the phase retardation was measured by the system shown in Fig.2⁽⁹⁾. A electric field was applied up to 3.0×10^3 V/mm across 1.0mm Au electrode separation. He-Ne laser light polarizing at 45° with respect to the direction of the applied electric field passed through the BSO thin film. The light was linearly polarized again by using a $\lambda/4$ plate. The difference of two components, which were divided through Wollaston prism, were detected to measure the polarization angle shift. The phase retardation shift $\Delta\delta$ was obtained by doubling this angle shift. The birefringence shift $\Delta(\Delta n)$ is defined as $\Delta(\Delta n) = \lambda_0 \Delta\delta / 2\pi d$, where λ_0 is the wavelength of the laser light (6328 Å) and d is the thickness of the film.

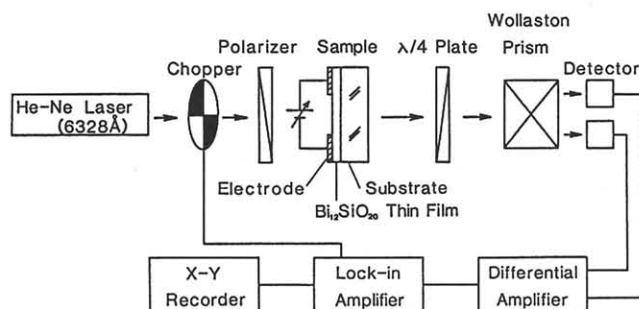


Fig.2 Schematic diagram of the optical system for the measurement of electro-optic effects.

3. RESULTS AND DISCUSSION

The film compositions were determined by EPMA. To get the BSO thin films close to stoichiometry ($\text{Si}/(\text{Si}+\text{Bi}) \sim 7.7\text{at.}\%$), we investigated the relationship between the film composition and the each target voltage beforehand. In this work, the composition range of $6.3\text{at.}\% < \text{Si}/(\text{Si}+\text{Bi}) < 7.7\text{at.}\%$ were obtained.

It was observed that the crystalline structure of the sputtered films was greatly influenced by the substrate temperature during the sputtering process. From the X-ray diffraction method, the crystalline structure of the BSO thin films, which were sputtered without any substrate heating, were completely amorphous, and these films were transformed into the γ -phase BSO⁽¹⁰⁾ by the heat treatment above 400°C. This phase is a body-centered cubic (bcc) and is found to be the impure phase of δ -phase BSO with a face-centered cubic (fcc)⁽¹¹⁾. This bcc phase is stable at any temperature below the melting point of 935°C. However, the fcc phase is considered to be a metastable state⁽¹²⁾. The films with heat treatment exhibited rough surface and were not transparent, which was probably due to the recrystallization of the films. So it was difficult to utilize these films for optical use. The films sputtered at the substrate temperature of 500°C is a polycrystalline of δ -phase BSO and has a highly (111) orientation.

Figure 3 shows typical scanning electron micrograph and RHEED pattern of the BSO thin film sputtered at the substrate temperature of 600°C. The RHEED pattern shown in Fig.3(a) is a spot pattern and indicates that the BSO thin film grow epitaxially on (0001) sapphire substrate. The scanning electron micrograph shows that there are some steps on the surface of the film as shown in Fig.3(b). The X-ray diffraction pattern shows that the BSO thin film sputtered at the substrate temperature of 600°C is a highly (310) oriented γ -phase BSO as shown in Fig.4. From the X-ray diffraction data of (310) peak, the lattice constant of the BSO thin film was 10.12 Å, which was very close to 10.18 Å for a γ -phase BSO single crystal.

The electro-optic effect of the BSO thin films on (0001) sapphire substrate were successfully observed for the first time to our knowledge. Figure 5 shows the effective birefringence shift of epitaxial BSO thin film as a function of the applied electric

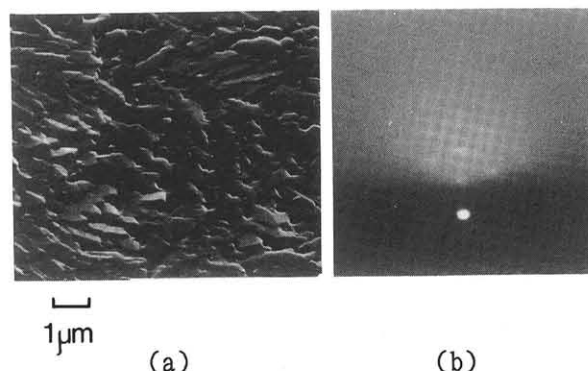


Fig.3 Typical scanning electron micrograph(a) and RHEED pattern(b) of the BSO thin film deposited at the substrate temperature of 600°C.

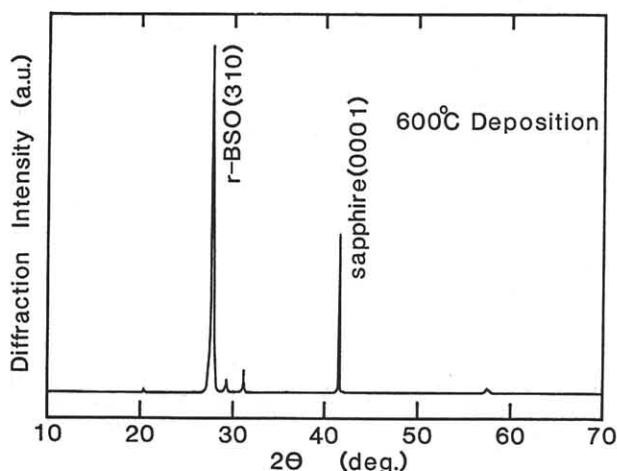


Fig.4 X-ray diffraction pattern of the BSO thin film on (0001) sapphire substrate. The sample is deposited at the substrate temperature of 600°C.

field. A thickness of the film was 520nm. This film shows nearly quadratic effect and do not show linear effect as same as the BSO single crystal. These quadratic dependence on applied field cannot be explained exactly, but it is probably due to the lack of uniformity of the films. Namely, there may be several domains of BSO single crystal, which have (310) orientation but are aligned in different direction laterally to the substrate, and the electro-optic effect of each domain may have diode-like characteristic due to the domain wall moving, the electron charge injection inhomogeneously, and strain in the films, etc. Then the sum total of the birefringence shift of these domains may show a quadratic characteristic. The effective electro-optic coefficient R was calculated to $1.0 \times 10^{-18} \text{m}^2/\text{V}^2$. The birefringence shift of epitaxial BSO thin film was nearly equal to

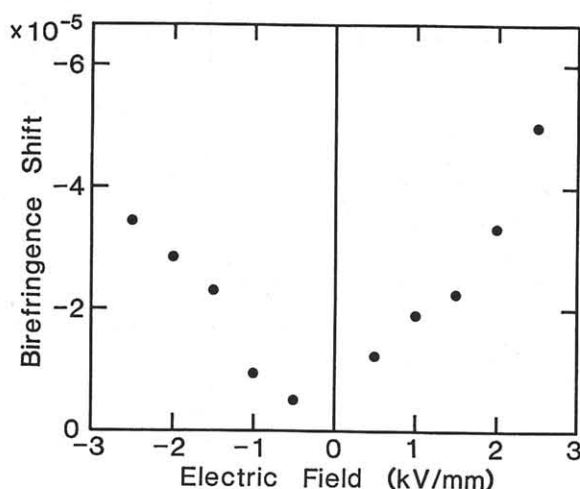


Fig.5 Effective birefringence shift as a function of the applied electric field for epitaxial BSO thin film.

the value of BSO single crystal plate.

IV. CONCLUSIONS

It has been attempted the growth of epitaxial $\text{Bi}_{12}\text{SiO}_{20}$ thin films on (0001) sapphire substrates by ECR plasma sputtering with Bi and Si multi targets system. The structure of the BSO thin films were strongly depended on the substrate temperature. At the substrate temperature of 500°C, the films were polycrystalline of δ -phase BSO and showed highly (111) orientation. At the substrate temperature of 600°C, the films grew epitaxially and showed highly (310) orientation. It was made clear that the epitaxial BSO thin films exhibited the excellent electro-optic effects as same as a single crystal BSO plate. This large electro-optic effects of the BSO thin films are the first experimental result to our knowledge.

The availability of the large electro-optic effects, high photoconductivity and high speed optical switching characteristics of this BSO thin films could greatly simplify the construction of optical processing systems such as neural networks, and result in compact modules that can be readily interconnected to perform more massive computation.

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REFERENCES

- (1) S. L. Hou and D. S. Oliver, *Appl. Phys. Lett.*, **18**, 325 (1971).
- (2) T. Minemoto, H. Yoshimura, Y. Suemoto and S. Fujita, *Japan. J. Appl. Phys.*, **18**, 1727 (1979).
- (3) J. P. Huignard and F. Micheron, *Appl. Phys. Lett.*, **29**, 591 (1976).
- (4) J. P. Huignard, J. P. Herriau, P. Aubourg and E. Spitz, *Opt. Lett.*, **4**, 21 (1979).
- (5) G. Hamel de Montchenault, B. Loiseaux, and J. P. Huignard, *Appl. Phys. Lett.*, **50**, 1794 (1987).
- (6) A. R. Tanguay, Jr., S. Mroczkowski, and R. C. Barker, *J. Cryst. Growth*, **42**, 431 (1977).
- (7) Y. Nagao and Y. Mimura, *IEEE J. Quantum Electron.*, **QE-23**, 2152 (1987).
- (8) K. Nomura and H. Ogawa, *J. Electrochem. Soc.* (to be published).
- (9) H. Adachi, T. Kawaguchi, K. Setsune, K. Ohji, and K. Wasa, *Appl. Phys. Lett.*, **42**, 867 (1983).
- (10) E. M. Levin and R. S. Roth, *J. Res. Natl. Bur. Std.*, **A68**, 197 (1964).
- (11) G. Gattow and H. Schroder, *Z. Anorg. Allgem. Chem.*, **318**, 176 (1962).
- (12) T. Mitsuyu, K. Wasa, and S. Hayakawa, *J. Electrochem. Soc.*, **123**, 94 (1976).