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Preparation of Bismuth Titanate Films by Electron Cyclotron Resonance Plasma Sputtering-Chemical Vapor Deposition

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Abstract. Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$:BIT) thin films were prepared on the Pt coated $\text{MgO}(100)$ substrate by electron cyclotron resonance plasma sputtering-chemical vapor deposition (ECR plasma sputtering-CVD). Bi_2O_3 was used as a sputtering target and tetra-isopropoxy-titanium [$\text{Ti}(\text{i-C}_3\text{H}_7\text{O})_4$] as a CVD source. The composition of films was controlled by changing RF power (P_{RF}) of Bi_2O_3 target and Ti source temperature (T_{Ti}). The stoichiometric BIT film was prepared under the condition of $P_{\text{RF}}=500\text{W}$, $T_{\text{Ti}}=63^\circ\text{C}$, deposition temperature of 650°C and deposition rate of 14 nm/min . Epitaxial relationships between the BIT film and the substrate were determined $\text{MgO}(100)//\text{Pt}(100)//\text{BIT}(001)$ and $\text{MgO}\langle 100 \rangle // \text{Pt}\langle 100 \rangle // \text{BIT}\langle 110 \rangle$. The remanent polarization and coercive field measured by a Sawyer and Tower bridge circuit at 50 Hz were $1.12\text{ }\mu\text{C/cm}^2$ and 46 kV/cm , respectively.

1. INTRODUCTION

Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), which consists of Bi-O layers and pseudo-perovskite Bi-Ti-O layers, is a ferroelectric material with a curie-point (T_c) of 675°C . BIT is expected to be a useful material for ferroelectric memories and piezoelectrical devices because of novel electrical and optical properties. For these device applications, it is necessary to prepare an epitaxial film of BIT.

In the past reports, the BIT films were prepared by physical vapor deposition (PVD) methods, i.e. rf sputtering [1, 2], ECR plasma sputtering [3] and pulse laser deposition [4]. In resent, we succeeded in preparing a BIT film which have a high quality of crystallinity and fully developed crystallographic orientation at low substrate temperatures by using an ECR plasma sputtering method [5]. However, it was difficult to control precisely the composition of film to obtain sufficient properties.

Chemical vapor deposition (CVD) methods were also applied to prepare the BIT film [6-10]. In general, the CVD methods are known to be superior to controlling of the film composition. However, the lowest deposition temperature to obtain the BIT film is around 580°C and the films prepared exhibit low crystallinity.

In order to prepare the BIT films with well-controlled composition and crystallinity at low temperatures, we have adopted a new method by the combination of ECR plasma sputtering and CVD (ECR plasma sputtering-CVD). In the present paper, we report a newly developed equip-

ment, preparation conditions of the BIT film by this method and their crystallographic orientation and ferroelectric properties.

2. EXPERIMENT

Figure 1 shows the schematic diagram of the ECR plasma sputtering CVD apparatus used.

Figure 1: Schematic diagram of the ECR plasma Sputtering CVD apparatus.

Ti source was introduced from $\text{Ti}(\text{i-C}_3\text{H}_7\text{O})_4$ which was placed in a stainless steel bubbler heated in an oil bath. The Ti source was carried into a reactor by Ar gas.

The target of sputtering was a sintered Bi_2O_3 ceramic with a ring shape of 100 mm I.D., 110 mm O.D. and 50 mm height. The target was set at the plasma extraction port and RF power of 13.56 MHz was supplied to the target. A microwave (2.45 GHz, 500 W) was introduced into the ion chamber through a rectangular wave guide. A magnetic field (875 Gauss) was applied to the ion chamber to satisfy the ECR condition. A mirror-type magnetic field (450 Gauss at the substrate stage) was applied in order to raise a plasma density, which results in an increase of the deposition rates of films.

The substrate used was a $\text{MgO}(100)$ crystal (10 mm x 10 mm x 1.0 mm) coated with epitaxial $\text{Pt}(100)$ which is necessary to measure ferroelectric properties. The substrate was heated up to 650 °C using an infrared lamp. The substrate temperature was measured by a Pt-13%PtRh thermocouple. The apparatus was evacuated at 5.0×10^{-7} Torr by a turbo molecular pump and then Ar10%-90% O_2 mixture gas (30 cm^3/min) was introduced into the chamber. The gas pressure during deposition was 1.1×10^{-3} Torr and the deposition time was from 30 to 180 minutes. After deposition, the apparatus was cooled down to room temperature at the rate of about 100 °C/min. Deposition conditions are summarized in Table 1.

Table 1: Deposition conditions of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film by ECR plasma Sputtering CVD method.

Substrate	:	Pt (100) on Mg (100); Pt<100>/MgO<100>
Substrate temperature	:	650 °C
Oxidation gas flow rate (O_2)	:	25 cm^3/min
Gas pressure	:	1.1 $\times 10^{-3}$ Torr
Deposition time	:	30 -180 min
<u>CVD</u>		
Source	:	Ti (i- $\text{C}_3\text{H}_7\text{O}$) ₄
Ti bubbler temperature [T_{Ti}]	:	45 - 90 °C
Ribbon heater temperature	:	100 °C
Carrier gas flow rate (Ar) [F_{Ti}]	:	7 - 50 cm^3/min
Bubbler pressure	:	0.5 atm
<u>Sputtering</u>		
Target	:	Bi_2O_3
Sputtering gas flow rate (Ar)	:	5 cm^3/min
ECR coil current	:	21 A
Mirror coil current	:	12 A
Microwave power	:	500 W
Target RF power [P_{RF}]	:	200 - 700 W
Target-substrate distance	:	160 mm

The composition of films was analyzed by an inductively coupled plasma emission spectrochemical apparatus (Shimadzu: P-5200) and a X-ray fluorescence apparatus (Rigaku: system3270). The thickness of films was measured by a thickness tester (Talystep). The structure of films was characterized by X-ray diffraction analysis using $\text{CuK}\alpha$ radiation (XRD: Rigaku RAD-C system). Preferred orientation and epitaxial relationship were evaluated by the rocking curve of $\text{BiTi}(008)$ peak and the pole figure, respectively. Ferroelectric hysteresis was measured at 50 Hz using a Sawyer and Tower bridge circuit [11].

3. RESULTS AND DISCUSSION

Figure 2 shows the effect of Ti source temperature (T_{Ti})(a), deposition time (b) and carrier gas flow rate (F_{Ti})(c) on the thickness of TiO_2 films prepared by CVD process using the Ti source. The deposition rate of TiO_2 films is increased with increasing Ti source temperature, deposition time and carrier gas flow rate. These results indicate that the amount of Ti deposition in the films can be controlled by T_{Ti} and F_{Ti} as well as by deposition time.

Figure 2: Thickness of TiO_2 films versus (a) Ti bubbler temperature, (b) deposition time and (c) Ar flow rate.

Figure 3: RF power dependence of the film composition.

Figure 3 shows the dependence of the RF power of Bi target (P_{RF}) on the Bi:Ti ratio of film composition for $T_{Ti}=63^\circ\text{C}$, $\text{time}=60\text{ min}$ and $F_{Ti}=20\text{ cm}^3/\text{min}$. The Bi content of films is increased linearly with the target RF power. This means that the Bi:Ti ratio can be controlled by P_{RF} .

Figure 4 shows X-ray diffraction patterns of the films having (a) an excess of Ti, (b) stoichiometric composition of Ti:Bi and (c) an excess of Bi compared with the BIT phase. The BIT phase is observed in these films. But the film with an excess of Ti contains $\text{Bi}_2\text{Ti}_2\text{O}_7$ phase as seen in Fig. 4 (a) and the film with an excess of Bi contains $\text{Bi}_{12}\text{TiO}_{20}$ as seen in Fig. 4 (c) as

Figure 4: X-ray diffraction patterns of BIT films deposited at (a) $P_{RF}=700\text{W}$, $T_{Ti}=63^\circ\text{C}$, (b) $P_{RF}=500\text{W}$, $T_{Ti}=63^\circ\text{C}$ and (c) $P_{RF}=500\text{W}$, $T_{Ti}=90^\circ\text{C}$.

second phases. In Fig. 4 (b), it is seen that the film with the stoichiometric composition consists of a BIT single phase and the (001) plane of BIT is oriented parallel to the substrate surface. The full width at half maximum (FWHM) of BIT(008) rocking curve was estimated to be about 0.4° . This value indicates that the film obtained has excellent crystallinity in comparison with the CVD film (about 2.2°) prepared at 650°C [12]. The deposition rate was about 14 nm/min.

Figure 5(a) indicates the pole figure taken from (110) reflection of the BIT film. In the figure, four poles observed at α angle of 45° and β angles of every 90° are a contour line indicating 50% of the maximum intensity. This means that epitaxial growth of the BIT film on MgO(100)//Pt(100) substrate takes place with a crystallographic relation as shown in fig. 5 (b)

Figure 5: (a) X-ray pole figure of the BIT film deposited on the MgO(100)//Pt(100) substrate and (b) the direction relationship between the MgO(100)//Pt(100) substrate and (001) oriented BIT film.

Figure 6: Atomic configuration on (a) Pt(100) and (b) BIT(001) planes.

and the relationship is expressed as $\text{MgO}(100)//\text{Pt}(100)//\text{BIT}(001)$ and $\text{MgO}\langle 100 \rangle//\text{Pt}\langle 100 \rangle//\text{BIT}\langle 110 \rangle$.

In Fig. 6, the atomic arrangements of $\text{BIT}(001)$ and $\text{Pt}(100)$ plane are illustrated. The distance between the atoms in $\langle 100 \rangle$ of Pt is $3.92 \text{ \AA}$, which is close to the distances ($3.83 \text{ \AA}$) between the oxygen atoms in $\langle 110 \rangle$ direction on $\text{BIT}(100)$. Such a small mismatch probably results in epitaxial growth of the BIT phase on the $\text{Pt}(100)$ surface.

Figure 7 shows a ferroelectric hysteresis loop of the BIT film prepared at $T_{\text{Ti}} = 63^\circ\text{C}$, $F_{\text{Ti}} = 20 \text{ cm}^3/\text{min}$, $P_{\text{RF}} = 500 \text{ W}$ and time = 180 min. The values of the residual polarization (P_r) and the coercive field (E_c) estimated from the loop are 46 kV/cm and $1.12 \text{ } \mu\text{C}/\text{cm}^2$, respectively. These values are superior to those of the BIT film prepared by CVD at 580°C [7].

Figure 7: D-E hysteresis loop of the BIT film prepared by the ECR plasma sputtering CVD method.

4. CONCLUSION

Thin films of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ were prepared by using an ECR plasma sputtering-CVD method, where $\text{MgO}(100)$ coated by $\text{Pt}(100)$ as substrate, Bi_2O_3 ceramic as sputtering target and tetra-isopropoxy-titanium $[\text{Ti}(\text{i-C}_3\text{H}_7\text{O})_4]$ as CVD source were employed.

The composition ratio of Bi and Ti in films was controlled by RF power of Bi_2O_3 target and bubbling temperature of Ti source. The film having stoichiometric composition exhibited the single phase. The BIT crystal showed epitaxial relationships against the substrate surface $\text{Pt}(100)$ as follows;

$\text{MgO}(100)//\text{Pt}(100)//\text{BIT}(001)$ and $\text{MgO}\langle 100 \rangle//\text{Pt}\langle 100 \rangle//\text{BIT}\langle 110 \rangle$.

The values of residual polarization and coercive field estimated from a ferroelectric hysteresis loop were 46 kV/cm and $1.12 \text{ } \mu\text{C}/\text{cm}^2$, respectively.

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