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Ferroelectric bismuth titanate thin films were successfully deposited on Si, sapphire disks, and Pt/Ti/SiO2/Si substrates by hot wall metalorganic chemical vapor deposition. Triphenyl bismuth \([\text{Bi}(\text{C}_6\text{H}_5\text{s})_3]\) and titanium ethoxide \([\text{Ti}(\text{C}_2\text{H}_4\text{O})_4]\) were used as the precursors. The deposition rates were in the range of 3.9–12.5 nm/min. The Bi/Ti ratio was easily controlled by precursor temperature, carrier gas flow rate, and deposition temperature. As-deposited films were pure Bi,Ti,O12 phase. The films were specular and showed uniform and fine grain size. Optical constants as a function of wavelength were calculated from the film transmission characteristics in the ultraviolet-visible-near infrared (UV-VIS-NIR) region. The 550 °C annealed film showed a spontaneous polarization of 26.5 μC/cm² and a coercive field of 244.3 kV/cm.

I. INTRODUCTION

Bismuth titanate \((\text{Bi}_4\text{Ti}_3\text{O}_{12})\) is one of the few important ferroelectric materials. This compound has a high Curie temperature of 675 °C. In a single crystal, there are two polarization axes: the major one, with \(P_z = 50 \mu\text{C/cm}^2\), along the \(a\) axis of the (pseudo-)orthorhombic structure, while the minor polarization axis, with \(P_x = 4 \mu\text{C/cm}^2\), along the \(c\) axis. The coercive fields are 50 and 3–5 kV/cm for the \(a\) and \(c\) axes, respectively.\(^1\) \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) also has a unique rotation of the optical indicatrix upon polarization switching.\(^2\) These interesting properties have enabled a variety of applications. A ferroelectric field-effect memory device using \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) thin film has been reported.\(^3\) It has been also considered as an alternate ferroelectric material for ferroelectric random access memories (FRAMs) and dynamic random access memories (DRAMs). \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) thin films formed on a superconducting \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}\) bottom electrode showed promising ferroelectric properties, as well as good radiation hardness, excellent aging characteristics, and the potential for integration into semiconductor device processing technology.\(^4\) In addition, modulator and display applications of \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) have also been evaluated.\(^2\)

\(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) thin films have been prepared by rf sputtering,\(^5\) pulsed laser ablation,\(^6\) sol-gel processing,\(^7\) and metalorganic chemical vapor deposition (MOCVD).\(^8\) Among these techniques, MOCVD allows high deposition rate, excellent step coverage, and easy composition control, which are compatible with large scale processing. Miyajima et al. reported MOCVD \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) thin films on a heated substrate at 750 °C by a cold wall type reactor.\(^8\) To allow large scale processing and mass production, a low processing temperature and a hot wall type reactor are desirable. In this article, we report on the structure and composition of the hot wall MOCVD \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) thin films using \(\text{Bi}(\text{C}_6\text{H}_5\text{s})_3\) and \(\text{Ti}(\text{C}_2\text{H}_4\text{O})_4\) as precursors, as well as their optical and ferroelectric properties.

II. EXPERIMENTAL PROCEDURE

\(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) thin films were deposited in a MOCVD apparatus that is shown in Fig. 1. \(\text{Bi}(\text{C}_6\text{H}_5\text{s})_3\) and \(\text{Ti}(\text{C}_2\text{H}_4\text{O})_4\) were used as the precursors. The precursors were kept at desired temperatures within 1 °C accuracy and carried by nitrogen gas into the reactor during deposition. Pure oxygen was used as a dilute gas. Depositions were carried out at reduced pressures (6 Torr). Substrate temperatures were varied from 450 to 500 °C. The typical deposition conditions are listed in Table I.

The identification of \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) phases were carried out by x-ray diffractometer with CuKα radiation. The composition of the films was investigated using energy dispersive spectroscopy (EDS). Scanning electron microscopy (SEM) was used to study the surface morphology of the films. Film thicknesses, refractive indices \((n)\), and extinction coefficients \((k)\) were obtained from ultraviolet-visible-near infrared (UV-VIS-NIR) transmission measurements.
TABLE I. Typical deposition conditions for MOCVD Bi$_4$Ti$_3$O$_{12}$ thin films.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Bi(C$_2$H$_5$)$_3$ + Ti(C$_2$H$_5$O)$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursors temp. (°C)</td>
<td>165–170 75–127</td>
</tr>
<tr>
<td>Carrier gas (sccm, N$_2$)</td>
<td>30–50 0–8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Sapphire, Pt/Ti/SiO$_2$/Si, Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temp. (°C)</td>
<td>450–500</td>
</tr>
<tr>
<td>Dilute gas (sccm, O$_2$ &amp; N$_2$)</td>
<td>650</td>
</tr>
<tr>
<td>Total pressure (Torr)</td>
<td>6</td>
</tr>
</tbody>
</table>

For the ferroelectric property measurement, Bi$_4$Ti$_3$O$_{12}$ film was deposited on a Pt/Ti/SiO$_2$/Si substrate and contacted with $2.14 \times 10^{-4}$ cm$^2$ palladium as top electrodes. A Sawyer–Tower circuit at 60 Hz was used to measure the ferroelectric properties.

III. RESULTS AND DISCUSSION

For the conditions described in Table I, film growth rates were typically in the range of 3.9–12.5 nm/min. In the range of experimental parameters investigated, source temperature, substrate temperature, and carrier gas flow rate were found to have significant effect on the film composition. Figure 2 shows the variation of the composition with the source temperature of Ti(C$_2$H$_5$O)$_4$ and carrier gas flow rate of Bi(C$_2$H$_5$)$_3$, at fixed source temperature of Bi(C$_6$H$_5$)$_3$ and no carrier gas for Ti(C$_2$H$_5$O)$_4$. The Bi/Ti ratio increased with the increasing carrier gas flow rate and the decreasing source temperature. The variation of Bi/Ti ratio with substrate temperature was also studied. It was found that Bi/Ti ratio dropped considerably at a substrate temperature of 450 °C, as shown in Fig. 3. In this study, the stoichiometry of the films were mainly controlled by varying the individual precursor temperature and the carrier gas flow rate, and the desired Bi/Ti ratio was achieved by optimizing the processing parameters.

Both as-deposited and annealed MOCVD Bi$_4$Ti$_3$O$_{12}$ films were specular, crack-free, uniform, adhered well on Si, sapphire, and Pt/Ti/SiO$_2$/Si substrates, and were highly transparent on sapphire substrate. The surface morphologies of the annealed films were investigated by SEM, and were shown in Fig. 4. The SEM micrographs showed that the films were dense and smooth on all substrates. The grains were very fine and uniformly distributed. The average grain size was estimated to be around 0.1 μm.

The stoichiometric MOCVD Bi$_4$Ti$_3$O$_{12}$ thin film prepared on Si substrate was used for structure study. Figure 5 displays the x-ray diffraction (XRD) patterns for the Bi$_4$Ti$_3$O$_{12}$ film at different post-deposition annealing temperatures. Bi$_4$Ti$_3$O$_{12}$ phase was observed in the as-deposited thin film. Crystallinity was improved as the annealing temperature was increased. The XRD patterns also

FIG. 2. Variation of thin film composition with source temperature and carrier gas flow rate.

FIG. 3. Variation of thin film composition with substrate temperature.

FIG. 4. SEM micrographs of MOCVD Bi$_4$Ti$_3$O$_{12}$ thin film annealed at 550 °C: (a) on Si, (b) on Pt/Ti/SiO$_2$/Si, (c) on sapphire substrates.
FIG. 5. X-ray diffraction patterns of the Bi$_4$Ti$_3$O$_{12}$ film at different post-deposition annealing temperature.

revealed that good crystalline films were obtained with no secondary phases and no preferred orientation, even at annealing temperatures as low as 550 °C.

The Auger electron spectroscopy (AES) depth profile of the annealed MOCVD Bi$_4$Ti$_3$O$_{12}$ film on Pt/Ti/SiO$_2$/Si is shown in Fig. 6. The composition of the film was uniform except the Bi content decreased and the Ti content increased at the film/substrate interface.

Figure 7 shows the typical D-E hysteresis loop of the MOCVD Bi$_4$Ti$_3$O$_{12}$ film on Pt/Ti/SiO$_2$/Si substrate. The film was annealed at 550 °C for one hour to obtain good crystallinity. The Bi/Ti ratio of the film was 57/43 by EDS measurement. The spontaneous polarization $P_s$, remnant polarization $P_r$, and coercive field $E_c$ had values of 26.5 $\mu$C/cm$^2$ and 19.6 $\mu$C/cm$^2$, 244.3 kV/cm, respectively.

The UV-VIS-NIR transmission and reflectance spectra of the MOCVD Bi$_4$Ti$_3$O$_{12}$ film on the sapphire substrate is shown in Fig. 8. The transmission spectrum illustrates that the transmittance drops to 0% (the absorption edge) at $\lambda = 338$ nm and has a value of 64% at $\lambda = 2000$ nm. An envelope method was used to calculate the film thickness as well as the refractive index, and extinction coefficient of the film as a function of wavelength. The film thickness calculated using this method is 752 nm. The $n$ and $k$ values were 2.507 and $2.88 \times 10^{-3}$, respectively, at $\lambda = 633$ nm. The high refractive index value, compared to the value of 2.33 from sol-gel films,$^7$ indicates the Bi$_4$Ti$_3$O$_{12}$ film is dense. The very low extinction coefficient illustrates the nature of the specular and highly transparent film. The $n$ and $k$ as a function of wavelength are shown in Fig. 9.

IV. SUMMARY

Crystalline Bi$_4$Ti$_3$O$_{12}$ thin films were successfully and reproducibly fabricated at low temperature (470 °C) on Si, sapphire, and Pt/Ti/SiO$_2$/Si substrates by an optimized MOCVD process. The Bi/Ti ratio of the films were con-
trolled by varying the MOCVD parameters, namely precursor temperature, carrier gas flow rate, and deposition temperature. The electron spectroscopy for chemical analysis (ESCA) spectrum showed no carbon contamination in the bulk of the film. A high refractive index (2.507) was obtained at $\lambda = 633$ nm in the 550 °C annealed film. Very fine grains were observed for the films on all three different substrates used. The $D-E$ hysteresis loop was observed with the ferroelectric properties of $P_r = 26.5 \ \mu C/cm^2$, $P_c = 19.6 \ \mu C/cm^2$, and $E_c = 244.3 \ \text{kV/cm}$.

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