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New Low Temperature Processing of MOCVD-$Bi_4Ti_3O_{12}$ Thin Films Using BiO_x Buffer Layer

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1.Introduction

Recently, $Bi_4Ti_3O_{12}$ (abbreviated as BIT) thin films have been widely investigated for nonvolatile ferroelectric memory (NVFRAMs) applications. Previously, we have proposed the low temperature growth technique of MO-CVD-BIT thin films with ultra-thin double buffer layer (5nm-BIT/5nm-TiO_2) and succeeded to obtain high quality and fatigue free BIT thin films at low substrate temperature of 400°C[1]. However, partially high temperature (550°C) process is necessary for this technique in order to make a single phase crystalline BIT buffer layer. In the practical device process, it is desired that the deposition temperature is lowered to avoid the inter-diffusion between BIT and the substrate materials. In this paper, we report a new low temperature MOCVD process using a BiO_x buffer layer. In this process, we could keep the substrate temperature at 400°C through the whole deposition process, and obtained 120nm-BIT thin films with good crystallinity and electrical properties; remanent polarization of Pr=8.2 $\mu C/cm^2$ and coercive field of Ec=90kV/cm.

2.Experimental

BIT films were deposited on a Pt-coated Si wafer substrate using the equipment and BIT film deposition conditions as shown in Fig.1 and Table I, respectively. The substrate temperature profile and deposition steps are shown in Fig.2, in which the substrate is kept at 400°C. In step 1, BiO_x buffer layer with 30nm thickness was deposited, and in step 2, BIT film with 90nm thickness was deposited. The crystallinity and electrical properties of the obtained films were examined after annealing at 400°C in air or N_2.

Table I Deposition conditions

Precursors	$Bi(o\text{-}C_7H_7)_3$	$Ti(i\text{-}OC_3H_7)_4$
Precursors temp.	160°C	50°C
Gas flow rate		
Ar carrier gas	200-350sccm	50sccm
O_2 gas	1000sccm	
Total gas flow rate	2500sccm	
Pressure	5Torr	
Substrate	$Pt/Ta/SiO_2/Si(100)$	

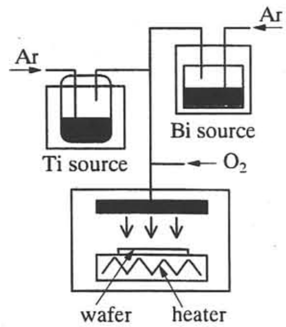

Fig.1 Schematic diagram of the apparatus for MOCVD-BIT.

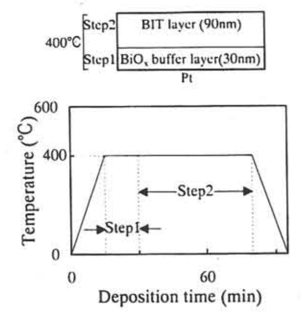

Fig.2 Temp. profile for BIT deposition and film struture.

3.Results and Discussion

3.1 The effects of BiO_x buffer layer

The Bi/Ti composition ratio of the deposited films with and without a BiO_x buffer layer, where Bi gas flow rate was varied keeping Ti gas flow rate as constant, are compared in Fig.3. The Bi/Ti ratio of films without a BiO_x buffer layer was saturated to about 0.35, but the ones with a buffer layer increased with Bi gas flow rate. The BiO_x buffer layers are very effective for controlling the film composition at low substrate temperature.

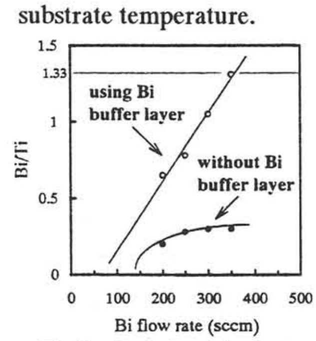

Fig.3 Relationships between Bi flow rate and Bi/Ti ratio.

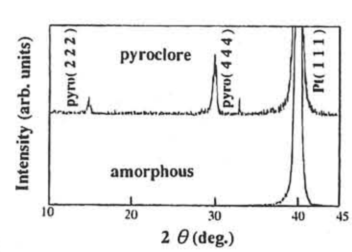

Fig.4 XRD patterns of BIT film without buffer layer

Furthermore, though XRD pattern of the film without BiO_x buffer layer was amorphous or pyroclore phase as shown in Fig.4, the film with BiO_x buffer layer was the single phase BIT polycrystalline film as shown in Fig.5, even if Bi content was poor (Bi/Ti=0.65). As for the BiO_x peak, it was found that it disappeared. In other words, Bi content in the BIT film is to be mainly Bi in the BiO_x buffer layer. It is thought that the BiO_x changed to BIT due to a solid phase reaction which finally disappeared.

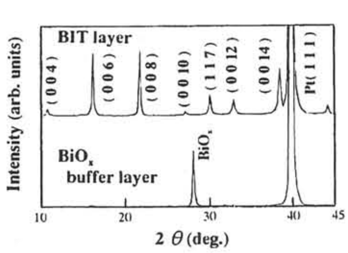

Fig.5 XRD patterns of BIT film with BiOx buffer layer

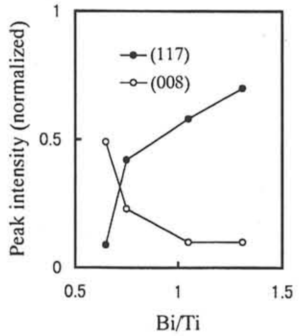

Fig.6 Comparison of (008) and (117) peak intensity.

The XRD peak intensities of prepared films with different Bi/Ti ratios are shown in Fig.6. The crystalline films changed from c-axis preferred orientation to (117) orientation as the Bi/Ti ratio increased.

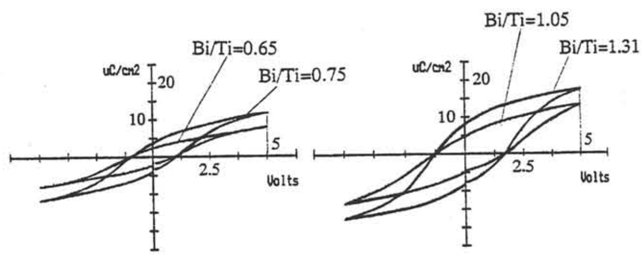

Fig.7 Relationships between Bi/Ti and hysteresys loops at 5V.

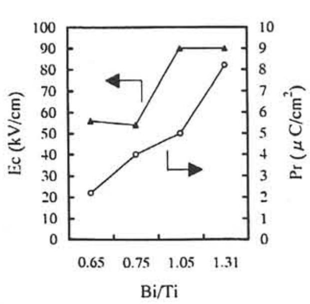

Fig.8 Rerationships between Bi/Ti and value of Pr and Ec.

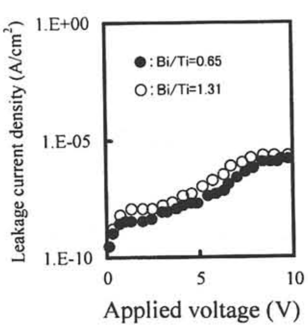

Fig.9 Leakage current characteristics at room temp.

The electrical properties of these different composition films were examined, but the ferroelectric hysteresis loop could not observed in spite of good crystallinities and surface morphology. However, after annealing for from 30min to 1hr at 400°C in air or N_2, good ferroelectric hysteresis loops were obtained for all films as shown in Fig.7. The remanent polarization Pr and coercive field Ec increased with the Bi/Ti ratio of film composition as shown in Fig.8. The Pr and Ec were 1.9μC/cm^2 and 55kV/cm for c-axis preferred orientation film with Bi/Ti=0.65, 8.2μC/cm^2 and 90kV/cm for (117) preferred orientation film with Bi/Ti=1.31 at 5V. Both BIT films showed the very low leakage current densities of the order of 10^{-8}A/cm^2 at 5V as shown in Fig.9. The above results show that this new BIT film deposition process and simple buffer structure are very advantageous for the low temperature film growth.

3.2 The effects of annealing process

In order to clarify the above annealing effects, the peak position shifts of (008) and (117) reflections of XRD patterns were measured. Figure 10 shows the peak positions measured from substrate Pt(111) peak after annealing for 1hr at 400°C. Each reflection was shifted to a higher angle corresponding to the bulk crystal, which suggested that strain relaxation of BIT thin films has occurred in the low temperature annealing process. Figure 11 shows the change of Pr and leakage current density I_L of BIT film (Bi/Ti=0.65) versus the time left in a desiccater after annealing. The Pr increased, about 40%, from 1.9μC/cm^2 to 2.5μC/cm^2 and the I_L decreased, about a one-digit, from 5×10^{-8}A/cm^2 to 3×10^{-9} A/cm^2 for 35 days after annealing. As for the above, it is thought that the annealing process removes the distortion right after deposition, and the remaining distortion is eased gradually.

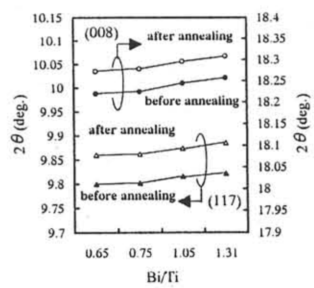

Fig.10 Change of BIT peak position after annealing.

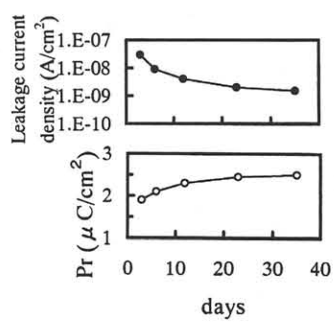

Fig.11 Change of Pr and I_L after annealing (at 5V).

4.Conclusions

We obtained single phase BIT crystalline film in a processing a substrate temperature of 400°C by using a BiO_x buffer layer. We postulate that BiO_x changed in the BIT film due to the solid phase reaction. When these BIT films were annealed at 400°C in air or N_2, good ferroelectrical property were obtained. Furthermore, when the Bi/Ti ratio of the BIT film became Bi rich, the Pr value increased and at the same time the (117) peak intensity increased. It is thought that the ferroelectric property was instigated and improved by annealing, with the effect of the removing the strain in the deposited BIT film.

Reference

1) T. Kijima, S. Satoh, H. Matsunaga and M. Koba: Jpn. J. Appl. Phys. **35** (1996) 1246.