Growth and characterization of $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ thin films deposited by pulsed excimer laser ablation

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Abstract

Thin films of $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ were deposited by pulsed excimer laser ablation technique on Pt substrates. The films were polycrystalline in nature. The room temperature dielectric constant was 450 at a frequency of 100 kHz. Studies indicated that deposition temperature and pressure both have an effect on the crystallinity of the films deposited. The films showed a slightly diffused phase transition in the range of 230–300 K. The ferroelectric nature of the film was confirmed by the polarization hysteresis curves. The saturation and remanent polarization were 13.4 and 5.9 $\mu\text{C}/\text{cm}^2$, respectively, with a coercive field of 45 kV/cm. The dispersion in both the real and the imaginary parts of the dielectric constant at low frequencies with increase in temperature was attributed to the space charge contribution to the complex dielectric constant. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

The continuing drive towards greater miniaturization of electronic components has led to the development of thin film materials for a wide variety of applications, and among these are the thin film ferroelectrics. Ferroelectric thin films have applications in dynamic random access memories (DRAM's), non-volatile RAM's, non-cooled IR detectors, piezoelectric actuators, microwave and electro-optic devices [1–5]. As the density of the dynamic random access memory increases beyond several megabits, more capacitance is required for reliability. Solid solutions of BaTiO_3 and BaZrO_3 have been established as one of the most important compositions for dielectrics. The high permittivity of the BaTiO_3 ceramic is increased more by the addition of zirconium. As the zirconium content increases, the phase transition temperature approaches each other, until, at a zirconium content of ~10% all the three transition points coalesce [6–8]. $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ could be a promising

material candidate for DRAM's due to its high dielectric constant in the paraelectric state. In this paper we report the growth and characterization of $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ thin films on platinum coated silicon substrates.

2. Experimental details

A dense ceramic target of $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ was prepared via the conventional ceramic processing route. The starting materials (BaCO_3 , TiO_2 and ZrO_2 all of purity 99.99%) were ball milled for 5 h in acetone and calcined at 1300 °C for 4 h. The calcined powder was then pressed into 18 mm targets. The target was sintered at 1360 °C for 5 h. A freshly polished surface was used each time for deposition. The target was mounted on a rotating carousel to ensure uniform ablation. Substrates were placed in parallel with the target at a distance of 3 cm. The depositions were carried out at substrate temperatures between 580 and 700 °C. During deposition highly pure oxygen was introduced into the chamber and the chamber pressure was maintained at 50 mTorr. The film thickness was measured using an optical spectrometer (Filmetrics F20) and thickness varied between 400 and 600 nm. Structural characterization of the thin films

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Fig. 1. (a) X-ray diffraction at different temperatures. (b) X-ray diffraction at different pressures.

was done by X-ray diffraction (XRD) to check for phase formation. Semi-quantitative analysis of the composition of the BZT thin films were done by energy dispersive X-ray analysis (EDAX). Gold dots of area 1.96×10^{-3} were deposited on the thin films by thermal evaporation. Dielectric studies were done using a Keithley 3330 LCZ meter with a small signal voltage of 10 mV over a temperature range of 200–450 K. The polarization hysteresis was confirmed by Radiant Technologies RT66A.

3. Results and discussion

The XRD patterns of the BZT thin films deposited in situ between 610 and 670 °C are shown in Fig. 1(a). All the films are polycrystalline in nature. It is seen that the crystallinity increased with increase of deposition temperature. The grain size was calculated from the Scherrer equation and found to be around 60 nm at 610 °C, neglecting stress effects. The grain size increased to around 130 nm when the temperature

Fig. 2. Polarization hysteresis at different voltages.

was increased to 670 °C. As observed from earlier reports [9] the variation can be attributed to the increase in mobility of the deposited species at higher substrate temperatures. In Fig. 1(b) the X-ray diffraction patterns of the films deposited at different oxygen pressures (50–100 mTorr) is shown. The temperature was kept constant at 670 °C. At low oxygen pressures, the films tend to show better crystallinity. With increase in oxygen pressure the intensity of the perovskite peaks decreases. It was seen that when the pressure was increased to 100 mTorr, the (100) and (200) peaks were almost absent and the intensity of (110) peak was reduced. With increase in pressure, the energy of the deposited species were reduced, hence affecting the crystallinity, which accounts for the decrease in peak intensities. The crystallite size was around 60 nm, calculated from the Scherrer equation.

The ferroelectric nature of the thin $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ films was confirmed from the polarization hysteresis measurements, done below its transition temperature, as shown in Fig. 2. The measured values of spontaneous and remanent polarization were 13.4 and $5.9 \mu\text{C}/\text{cm}^2$, respectively, with a coercive field of 45 kV/cm. The asymmetric behavior in the films can be induced by various factors, such as defect charges present in the ferroelectric material or due to different work functions of the top and the bottom electrodes [10].

The frequency dispersion of the real (ϵ'_r) and the imaginary (ϵ''_r) parts of the dielectric constant are shown in Fig. 3(a) and (b), respectively. A close inspection of Fig. 3(a) shows that the change in ϵ'_r with temperature for different frequencies is not similar. At lower frequencies (100 Hz) the value of ϵ'_r was found to rise sharply with increasing temperature, while the value for 100 kHz is found to decrease. Further, the onset of high dispersion becomes prominent after a certain temperature. This dependence of ϵ'_r on temperature at lower frequencies indicates the contribution of space charge to the complex dielectric constant. At higher frequencies, the gradual decrease of space charge effect was seen at all temperatures [11]. The influence of

Fig. 3. (a) Real part of dielectric constant versus frequency. (b) Imaginary part of dielectric constant versus frequency.

the space charge is also reflected in the imaginary part (Fig. 3(b)) of the dielectric constant ϵ'' , where we see similar frequency dispersion at higher temperature.

In Fig. 4, the dielectric constant–temperature (ϵ_r – T) curve is shown. In ceramics of composition $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, very high and broad maxima of the relative dielectric constant ϵ_r are found at the ferroelectric Curie point [6]. As in the case of pure BaTiO_3 , three ferroelectric phase transitions can also be observed for Zr concentrations $x < 0.1$: (1) rhombohedral–orthorhombic (2) orthorhombic–tetragonal (3) tetragonal–cubic. With increasing Zr content the three transition points and the three corresponding ϵ_r maxima move closer together and finally coalesce at $x \sim 0.1$ into a single broad maximum. In case of our $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ thin films, the phase transition was found to be diffused in nature, which could be attributed to the small grain size (60 nm) in the films. From the (ϵ_r – T) curve it is evident that the phase transition is between 230 and

Fig. 4. Dielectric constant versus temperature.

300 K. In case of ceramic $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ the phase transition is around 320–370 K [6]. Shift in T_c with reduction in grain size was well established in both bulk and thin films [12–14]. The present observation is consistent with those earlier reported.

4. Conclusions

The $\text{Ba}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ thin films deposited by pulsed excimer laser ablation technique are polycrystalline in nature. The ferroelectric nature of the film has been confirmed by the polarization hysteresis measured below its transition temperature. The measured values of saturation and remanent polarization were 13.4 and 5.9 $\mu\text{C}/\text{cm}^2$, respectively, with a coercive field of 45 kV/cm. The space charge contribution to the real and the imaginary parts were evident from the low frequency dispersion of ϵ'_r and ϵ''_r . The diffused nature of the phase transition was attributed to the small grain size.

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