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Structural, morphology and electrical studies on ferroelectric bismuth titanate thin films prepared by sol–gel technique

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Abstract

Crystal structure, surface morphology, compositional homogeneity and electrical properties of layered perovskite bismuth titanate (BTO) thin films have been investigated. BTO thin films were deposited on silicon and platinum-coated silicon substrates by spin coating. X-ray diffraction analysis confirms that the crystallinity of the films increases with increasing annealing temperature and the optimum temperature is found to be 600°C. Morphology studies by AFM showed that the surface of the films were smooth, dense and crack free. Composition analysis on the surface and in-depth confirms the stoichiometry of the films. C–V measurements show a counter-clockwise dielectric hysteresis, indicating that the ferroelectric property sufficiently controls the silicon potential with a memory width of 2 V. The leakage current density of the films is measured to be 2×10^{-7} A/cm^2 from I–V characteristics at an applied voltage of 1 V.

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1. Introduction

Ferroelectric thin films have been extensively investigated due to their potential application for non-volatile memories and multi-functional devices used in microelectronics and opto-electronics. As a typical bismuth layer structured ferroelectric material, bismuth titanate, $Bi_4Ti_3O_{12}$ (BTO) has become a key candidate for memory storage capacitor, optical display and electro-optical devices owing to their promising ferroelectric and electro-optic properties [1–3]. Metal-ferroelectric-insulator-semiconductor (MFIS) hetero-structure with BTO as a gate electrode material for ferroelectric field effect transistor (FE–FET) in a non-destructive readout (NDRO) mode has been demonstrated [4–5]. Among the various techniques available for the fabrication of BTO thin films, sol–gel technique, which involves the use of liquid solution mixtures for achieving homogeneity at a molecular level within a short time, has been widely used [6–8]. The problems of chemical stability of the solution and reaction of bismuth nitrate with H_2O to yield a white precipitate of $BiONO_3$ have been overcome by the addition of ethanolamine [9]. The effect ethanolamine on the pH of the solution, growth behaviour and degree of orientation of the films has been reported. However, the structural and ferroelectric properties have not been studied in

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detail. This paper reports the structural, morphological and electrical properties of the BTO thin films prepared by sol–gel technique using ethanolamine as a stabilizing agent.

2. Experiment

The BTO precursor solution was prepared by mixing bismuth nitrate and titanium (iv) butoxide in glacial acetic acid. Initially, bismuth nitrate was dissolved in acetic acid in a reflux condenser heated at a temperature of 80°C. When the solution became transparent, titanium(iv)butoxide was mixed in a proper molar ratio with constant stirring at room temperature to form a yellow-gold, transparent solution. Ethanolamine was added as stabilizing agent and the precursor solution remained stable against precipitation over a longer period. In the present study, (1 0 0) oriented Si and Pt/Si substrates were used for the deposition of BTO thin films. The substrates were ultrasonically cleaned in acetone, then methanol, and then rinsed in de-ionized water, followed by a drying process. A platinum layer of thickness 500 Å was deposited by ultra-high vacuum electron beam evaporation technique at room temperature to act as the bottom electrode for electrical characterization. The precursor solution was spin-coated on the substrates at 2300 rpm for 60 s. After the coating process, films were kept in a preheated furnace at 300°C for 10 min to remove the volatile components. As-deposited amorphous films were subsequently annealed at different temperatures from 350°C to 600°C in order to convert them into crystalline films. The phase purity was confirmed by powder X-ray diffraction analysis using Cu K_α radiation ($\lambda = 1.5418$ Å). Surface morphology and microstructure of the films were studied by using a atomic force microscope (nanoscope II). Chemical composition on the surface and in-depth of the films was measured by field emission type auger electron spectroscopy (AES, PHI 670 nanoprobe). The dielectric property was studied in a M–I–M and M–F–I–S configuration using an impedance analyser.

3. Results and discussion

3.1. Crystallization and microstructure of BTO thin films

The sol–gel processing involves deposition of amorphous layer at the initial stage, followed by a crystallisation step during the heat treatment. Powder X-ray diffraction pattern of BTO films heat-treated at 350°C confirmed the amorphous nature. This amorphous behavior remains unaltered up to an annealing temperature of 400°C. The crystalline nature starts at an annealing temperature of above 400°C. The nuclei can form at the interface between the film and substrate, at the film surface, and/or at the surface of the impurity particles [10]. The nucleation is followed by the growth of discrete crystal grains dispersed on the substrate surface. A very specific growth stage in the structural evolution of thin films is the coalescence of grains. Coalescence takes place when the growing adjacent grains approach and touch each other. During the annealing process, the isolated grains interact by interfusing their structures to form a homogeneous crystalline phase. With further increase in the annealing temperature, the diffraction peaks became increasingly sharp, intense with a decrease in full width at half maximum (FWHM) as shown in Fig. 1, indicating the enhanced crystallinity of the films. The XRD pattern reveals that the films were polycrystalline with no evidence of secondary phases. The structure was found to be orthorhombic with lattice constants $a = 5.40$ Å, $b = 5.42$ Å and $c = 32.69$ Å, respectively. A typical AFM micrograph of the BTO film annealed at 600°C shown in Fig. 2 reveals that the surface appears to be dense, smooth and free from cracks. The grains are evenly distributed with an average grain size of 150 nm, which is comparable with recent report on BTO films obtained from oxide precursors [11] and higher than the films prepared by metallorganic solution deposition technique [12].

In-depth chemical composition of the film was analysed by Auger electron spectroscopy with Ar ion beam of 2 kV as the sputtering beam. Fig. 3 shows the depth profiles of the elements of the BTO film annealed at 600°C for 1 h. From the

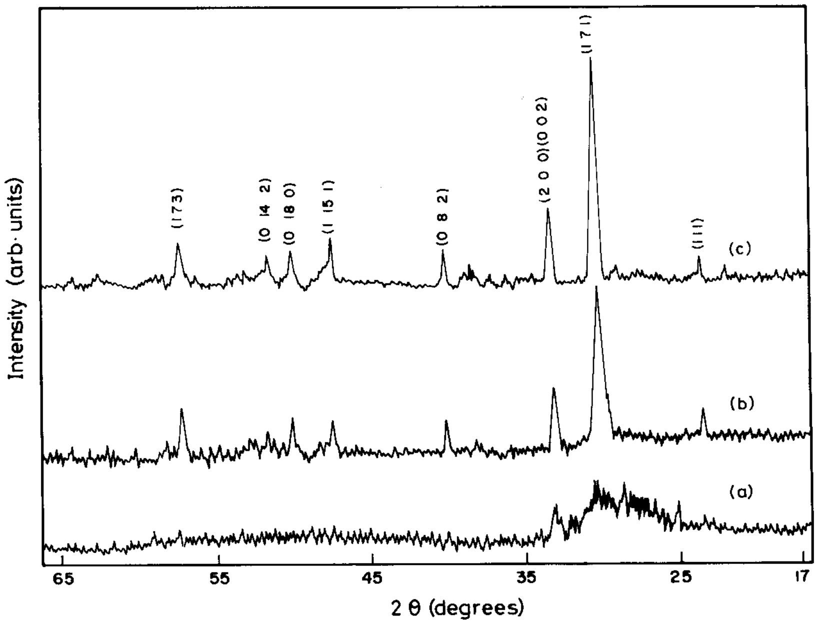

Fig. 1. Powder XRD patterns of BTO thin films annealed at different temperatures for 1 h: (a) 350°C (b) 450°C and (c) 600°C.

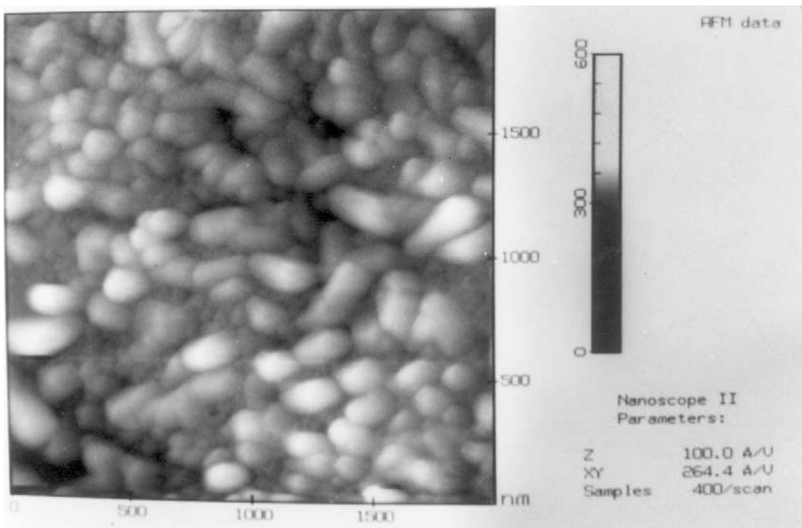

Fig. 2. AFM micrograph of BTO thin film showing uniform grain distribution.

depth profile, it appears that the film is composed of three regions: surface, bulk film, and the interface. Although a carbon peak was detected on the surface of the film, as soon as the first monolayer is removed by Ar ion bombardment, the carbon peak intensity decreased to the level of not being distinguishable from the noise. The film thickness was approximately 400 nm. From the

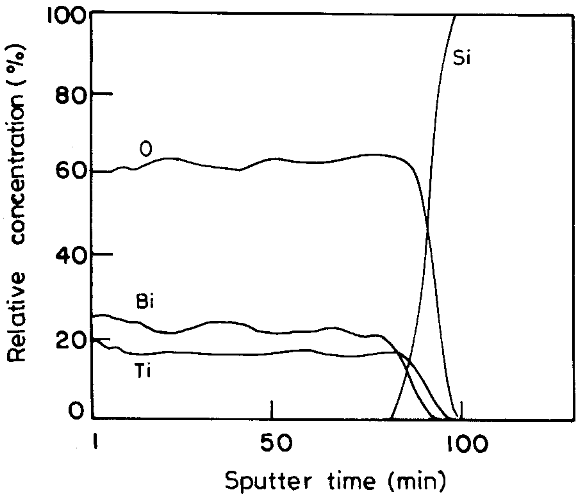

Fig. 3. AES depth profiles of the elements of BTO films annealed at 600°C.

profiles, it is apparent that each element is uniformly distributed in the film, indicating the compositional uniformity.

3.2. Dielectric and ferroelectric properties

The dielectric measurements were carried out on the films fabricated on platinum coated silicon substrates with a metal-insulator-metal (M–I–M) configuration [13]. Fig. 4 shows the dielectric constant and dissipation factor measured at room temperature as a function of frequency in the range 1 kHz–1 MHz. The dielectric properties in different regions of the films vary within 2–3%, confirming the compositional homogeneity and thickness uniformity of the film. The dielectric constant and the dissipation factor at 1 kHz are measured to be 132 and 0.018. The dielectric constant slightly decreased with increasing frequency. Fig. 5 shows a typical capacitance–voltage (C–V) characteristics measured at 1 MHz for a Pt/BTO/SiO_2/Si structure with a film thickness of 400 nm.The C–V characteristics exhibit clear regions of accumulation, depletion and inversion. The counter clockwise C–V hysteresis indicated by the arrows shows that the capacitance changes from the accumulation to inversion states and the memory window of the loop is 2 V. The current-voltage (I–V) characteristics of BTO film in M–I–

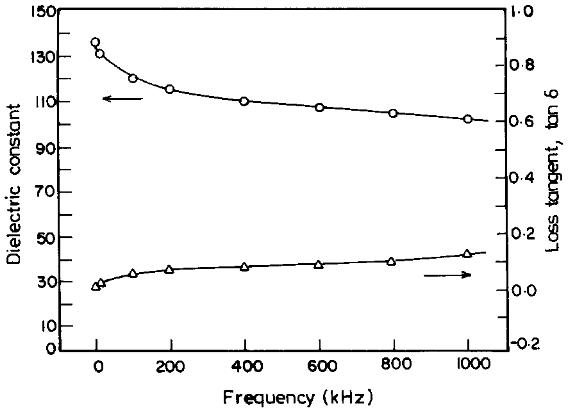

Fig. 4. Variation of dielectric constant and dissipation factor of BTO thin films with frequency.

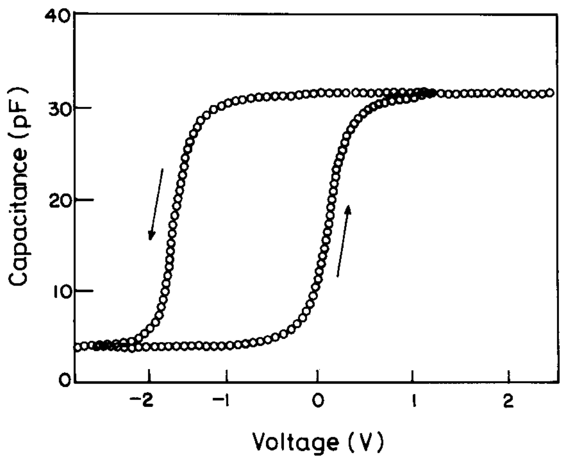

Fig. 5. C–V characteristics of Pt/BTO/SiO_2/Si structure with a film thickness of 400 nm.

M configuration annealed at 600°C is shown in Fig. 6. From the figure, it is observed that, BTO films possess good leakage current density characteristics suitable for device fabrication.

4. Conclusion

Perovskite bismuth titanate thin films prepared by sol–gel technique have been investigated for their structure, morphology, compositional homogeneity and electrical properties. The annealing

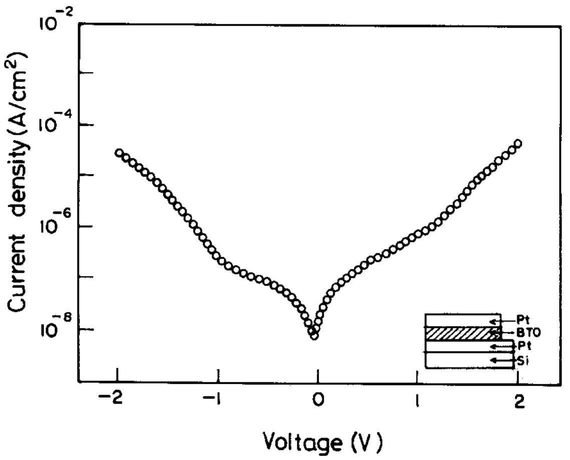

Fig. 6. Leakage current density characteristics of a BTO thin film. The inset shows the M–I–M configuration of the sample used for *I–V* measurements.

temperature of 600°C was found to be the optimum value to achieve maximum crystallinity without any secondary phases. Surface of the films were smooth, dense and crack free as confirmed by AFM studies. Chemical composition by AES study reveals the stoichiometric nature of the films. Dielectric constant and dissipation factor at 1 kHz at room temperature are measured to be 135 and 0.018 respectively. BTO films possess very low leakage current density of the order of $\sim 10^{-7}$ A/cm^2 at an applied voltage of 1 V. The counter-clockwise hysteresis infers that the ferroelectric behavior controls the silicon surface potential, which is considered to be a suitable choice for MFIS-FET type memory devices.

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