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Fabrication and characterization of epitaxial $BaTiO_3$ thin film employing platinum (111) template

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ABSTRACT

Epitaxial Barium Titanate ($BaTiO_3$) thin films were fabricated on Platinised (Pt 111) Si/SiO_2 wafer by spin coating of metalloorganic sol gel solution. A preferred directional growth was obtained for BT ($BaTiO_3$) thin film by employing Platinum (111) coating as a template. BT film was heat-treated at 700°C for 1 hour using the direct insertion method. The film was epitaxially grown with (111) and (211) being parallel to the Pt(111). The epitaxial growth of the thin film along (111) orientation was confirmed by XRD, AFM and SEM. The cross sectional view of SEM image showed that most nuclei were formed at the interface between the film and the substrate. BT thin film was characterized for its ferroelectric, dielectric and piezoelectric properties. Ferroelectric hysteresis measurement yielded high spontaneous polarization value ($12.3\mu C/cm^2$) comparatively at low electric field (150kV/cm). Substantial increase in piezoelectric d_{33} was explained in the light of domain wall engineering. Copyright © 2013 VBRI press.

Keywords: $BaTiO_3$; thin film; AFM; ferroelectricity.

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Introduction

Perovskite-type barium titanate (BT) has been of great interest because of their proven superior electrical and optical properties. Many researchers have been attracted by its versatile crystal structures [**1, 2**]. BT is known as one of the best ferroelectric (FE) materials among the lead free community. FE thin films offer advantages over bulk for a number of applications, including nonvolatile memories, dynamic random access memories, electro-optic switches, pyroelectric detectors, optical modulators etc. BT thin films have been prepared by methods such as hydrothermal **[3]**, pulsed laser deposition **[4]**, metalorganic chemical vapour deposition **[5]**, sputtering **[6]**, excimer laser ablation **[7]**, molecular beam epitaxy **[8]** evaporation **[9]**, electrochemical **[10]** and sol–gel **[11]**. Among these methods, sol–gel processing has various advantages over other deposition techniques in terms of good homogeneity, stoichiometric control, high purity, low processing temperature, ability to produce uniform thickness with good conformal coverage, large area applications and compatibility with the already existing semiconductor technology.

Epitaxial thin films have attracted the attention because of their superior properties over polycrystalline thin films and are recognised for many technological applications. They are free from crystallographic defects like high angle grain boundaries and having extended life than

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polycrystalline films. In this epitaxial process a specific crystallographic orientation is build up in the film as per the orientation of substrate as growth commences that induces anisotropy in the material. By this directional growth anisotropy like a single crystal can be induced to the material with a mechanical strength of polycrystalline material. Because of these advantages epitaxial thin films has been found to be extremely beneficial in many Si-based device applications which incorporate semiconductors, superconductors, ferroelectrics or magnetic materials. Combine advantages of sol-gel method and epitaxial growth enormously increases the potential of the material in the field of applied research with added advantage of cost effective route of preparation.

The main objective of the present study is to prepare BT thin film for achieving enhanced piezoelectric properties through directional growth (epitaxy) which is most commonly known as domain wall engineering. The second goal is to induce the anisotropy in the film which is very unusual for a polycrystalline film. Till date the enhanced piezoelectricity is reported for a single crystal BT along the preferential domain orientation. In this paper we report enhanced piezoelectricity in BT thin film prepared by sol-gel method with engineered domain configuration (111). Results on microstructural characterisation and ferroelectric property are also reported here in evidence of the formation of BT (111).

Experimental

Materials

The starting materials used for the preparation of $BaTiO_3$ thin film was barium acetate (99%, Loba Chemie, India), titanium IV isopropoxide (97%, Alfa Aesar, Ward hill, MA 01835), glacial acetic acid (100% GR, Merck, India) as solvent and ethylene glycol (99%, Merck, India) as stabilizing agent.

Synthesis and characterization

As per the stoichiometry Barium acetate was dissolved into glacial acetic acid (CH_3COOH) to prepare 0.7M solution with constant stirring at 70°C. Titanium IV isopropoxide was then added to the Barium precursor solution followed by the addition of ethylene glycol. Then poly vinyl pyrrolidone (with average molecular weight ~ 40000g/mol, Loba Chemie, India) was added to the solution. The solution was filtered and finally heated to promote the condensation reaction between acetic acid and ethylene glycol. BT thin films were then fabricated by spin coating by taking the solution in the increment of 0.05 mole fractions. The films were spun at 8000rpm for 50s on $Si/SiO_2/Pt$ substrates and immediately placed on a hot plate at 250°C for drying. The films were later pyrolysed at 450°C and then heated at 700°C for 1 hour. This process was repeated to achieve the desired film thickness of approximately 800nm to 1 µm. Prior to coating platinum (Pt) template was grown on Si/SiO_2 substrate along (111) direction. It was deliberately fabricated to grow BT in rhombohedral phase at room temperature which is not been reported for pure BT **[12]**. X-ray diffraction profile was taken to confirm the presence of predominant rhombohedral structure of the BT film. The surface profile was checked by AFM (atomic force micrograph). For the measurement of electrical property a portion of the bottom electrode was exposed using a chemical etch. Ag/Al top electrode was sputtered onto the surface of the film by lift off. The dielectric, ferroelectric and piezoelectric properties were measured by aixACCT thin film analyzer at different frequencies and bias voltages.

Result and discussion

XRD analysis

Fig. 1 shows the X-ray diffractogram of BT thin film coated over $Si/SiO_2/Pt$ and annealed at 700°C for 1hr. The predominant peak as seen in XRD pattern is grown preferentially along (111) direction with smaller peaks in (011), (211) and (220) directions. These peaks are considered as characteristic peaks of a pervoskite system. The acid catalyst addition in the preparation makes it easier to achieve perovskite phase at low temperature. The lattice constant of BT in rhombohedral phase was estimated to be 4.0Å and 3.94 Å for platinum which matches very well **[13, 14]**. The concept of matching of lattice parameters between the film and the substrate is an important aspect of epitaxy. In heteroepitaxy there is generally a lattice parameter mismatch between the film and the substrate due to use of dissimilar material and thus the interface gets strained (or relaxed depending upon the magnitude of the difference). But in this case there will be minimum interface strain which will increase the life of the material. Due to internal/induced strain the thin film materials exhibit inferior properties compared to bulk samples. Here improved properties of BT thin film is expected due to lattice matching and strain free structure.

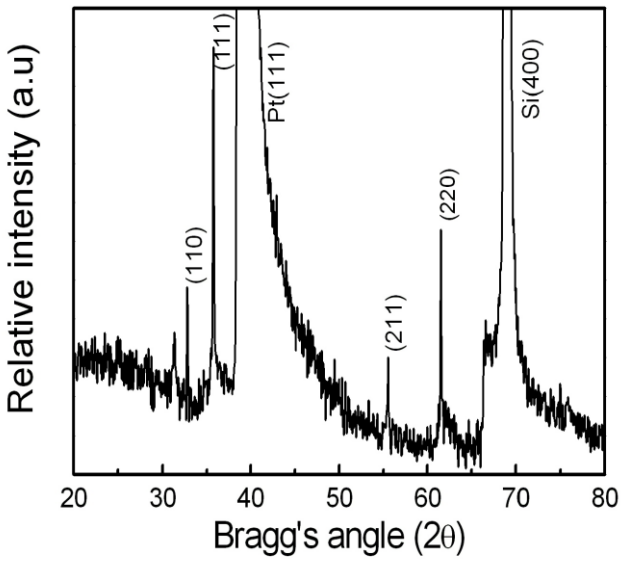

Fig. 1. XRD pattern of BT thin film coated over $Si/SiO_2/Pt$ (111) substrate

AFM study

Fig. 2 shows AFM micrograph of crystalline BT thin film grown on $Si/SiO_2/Pt$ (111) substrate. The preferred alignment (111) of the BT film reflects on its texture which is very uniform and highly oriented. Strongly orientated platinum along (111) helped in growing BT grains

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epitaxially in the same direction. Surface profile study of the BT film shows crack free, smooth surface with homogenous microstructure. The highly oriented film will show lesser roughness value and it was found to be 5.31nm. The crack free film was obtained due to the relaxation in the internal strain caused during the thermal expansion coefficient of the film and the substrate. The stress on the coating was reduced by addition flexible polymer PVP at higher temperature. Even use of EG as stabilizing agent helps in getting crack free thin film by slowing down the polycondensation that takes place during thermal treatment of the thin film. This could also be correlated with the XRD results. Since the lattice parameters for the BT and Pt matches very well overall stain was less in the structure which might have helped to get crack free thin films. However, the AFM study gives an evidence of epitaxial growth of BT film which can be correlated with XRD results.

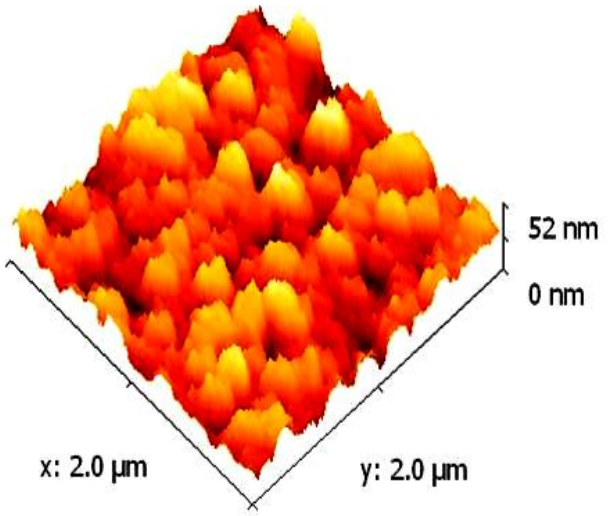

Fig. 2. AFM image of BT thin film fabricated on $Si/SiO_2/Pt$ (111) substrate

SEM analysis

Fig. 3 shows SEM image of the fracture surface of BT thin film fabricated on $Si/SiO_2/Pt$ (111) substrate. A very homogeneous, void free and uniform microstructure is observed throughout the surface area, which is a major advantage of the sol-gel processing. Use of acetic acid (CH_3COOH) for the dissolution of metallic salt produces a chelating ligand which generally reacts with alkoxide metal compounds and form very stable chelates which are not easily replaced by H_2O. It can control the hydrolysis and condensation reactions (uniform shrinkage during drying) resulting uniform microstructure and a high quality film. The cross sectional view of SEM image showed that most nuclei were formed at the interface between the film and the substrate which facilitated epitaxial growth.

Electrical characterization

BT thin film was characterized for its dielectric, ferroelectric and piezoelectric properties. Under this characterization the electrical properties measured were, P-E Hysteresis loop, Capacitance with Voltage (C-V) at constant frequency and piezoelectric d_{33} value. The results are discussed below.

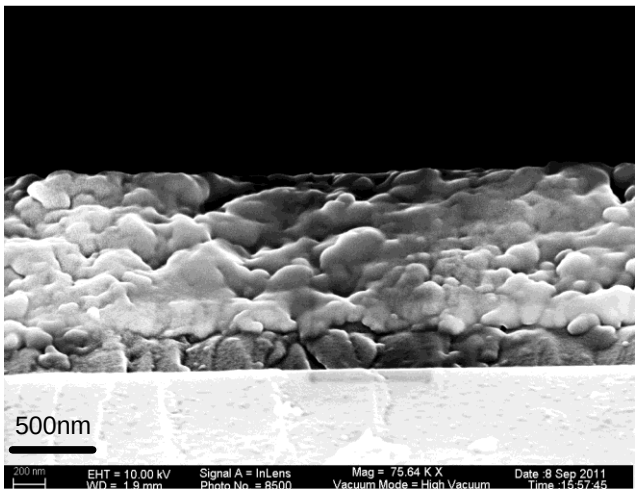

Fig. 3. Cross- sectional view of SEM image of BT thin film.

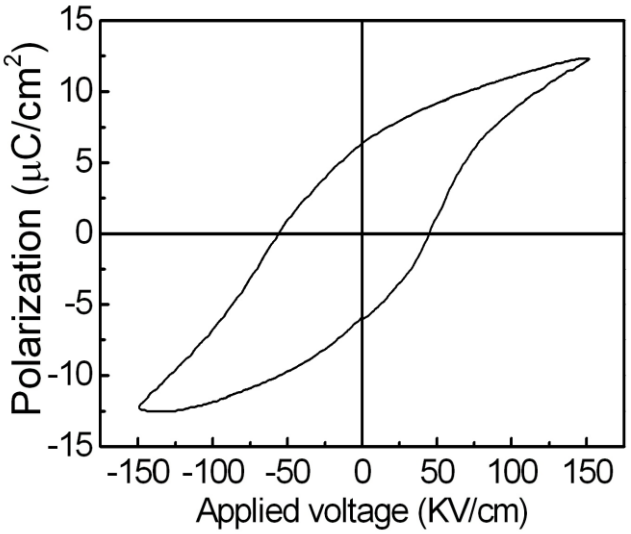

Fig. 4. P-E Hysteresis loop of BT thin film

P-E measurement

Fig. 4 shows the polarization behaviour of the BT thin film as a function of applied electric field at constant frequency of 100Hz. Presence of hysteresis loop is an identification test for a ferroelectric material. The spontaneous polarisation (P_{max}) of BT increases from 6.41µC/cm^2 to 12.3µC/cm^2 with the increase of electric field from 0 to 150 kV/cm. This increased polarisation in low frequency region (100Hz) can be attributed to the reconfiguration of lattice and surface adsorbed hydroxyl group that generated during acid hydrolysis. When an alternating electric field is applied at sufficiently low frequency the hydrogen and oxygen ions can exchange positions. This switchable dipole contributes to the net polarization (dipolar polarisability) and the spontaneous polarisation gets doubled when an electic field is applied. Bigger grain size also helps in improving polarisation. The slimmer hysteresis loop and low coercive field (50KV/cm) in the PE loop indicates the epitaxial growth and confirms the growth of BT film at the

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interface of Substrate. Presence of any other non ferroelectric intermediate layer would have increased the coercive field. This fact suggests that the absence of grain boundaries in the epitaxial film is beneficial for polarisation switching without any obstruction in the movement of ferroelectric domains.

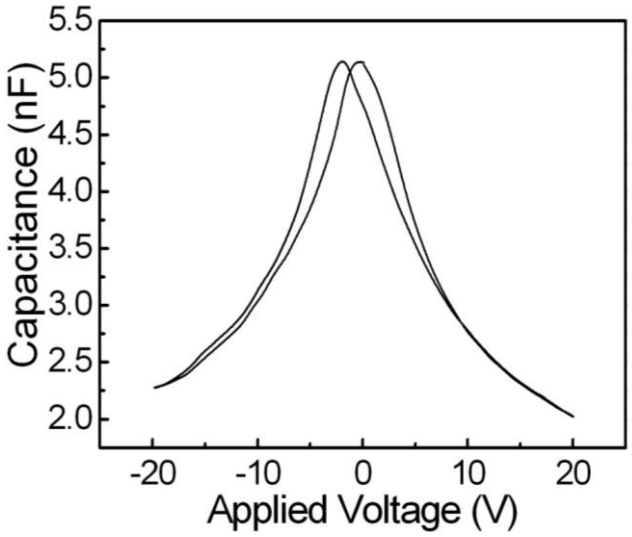

Fig. 5. Capacitance versus Voltage (C-V) characteristics of BT thin film.

C-V measurement

The capacitance-voltage (C-V) characteristic of BT thin film at constant frequency (1000Hz) is shown in **Fig. 5**. The butterfly loop of *C–V* measurement was carried out in the forward and reverse bias conditions after holding the sample at −20 and +20 V. It shows a conventional butterfly loop during the sweep up and down processes where the curve is symmetrical on either side of zero bias voltage. It confirms the ferroelectricity in rhombohedral BT. The capacitance value decreases with the bias voltage as usually happens in capacitors. With the increase in bias voltage from 2 to 20 volts, the capacitance value decreases from 5.1 nF to 2.3 nF. An improved capacitance value of 5.1 nF is achieved at 2V that could be considered as the approximate coercive field of the corresponding hysteresis loop **[15]**. The capacitance value depends on quality of the film. If the material is free from porosity and having good surface profile, there will be less leakage in current density and material will behave as good capacitor. Presence of acetic acid, EG and PVP in sol gel precursor improves the inter-hydrogen bonding network between the metallorganic molecules (M-OH) that leads to a stronger gel. In addition it also allows fully hydrolysed monomers to condense thereby maximizing the number of M-O-M bridging bonds and thus creating a high connectivity polymeric structure resulting a high quality film free of cracks and pores.

Piezo measurement

A well established piezoelectric butterfly loop (stress-strain curve) for the BT film is shown in **Fig. 6**. The displacement increases with increase in bias voltage, reaches maximum and reverses with negative bias voltage. The piezoelectric d_{33} value obtained from this measurement is 5nm/V which is much higher than that of the reported results **[16, 17]**. Domain engineering is a very important technique for obtaining enhanced piezoelectricity. It is reported that with the engineered domain structure of (111) orientation piezoelectricity can be ten times enhanced than that of (001) **[18]**. This can be attributed with the domain size of the engineered domain configuration. It can be assumed that the domain size of this engineered material will be very small as it is seen from AFM and SEM that grain size lies in the range of 200nm. Generally when a fine domain configuration is induced it is expected to obtain greatly enhanced piezoelectric property.

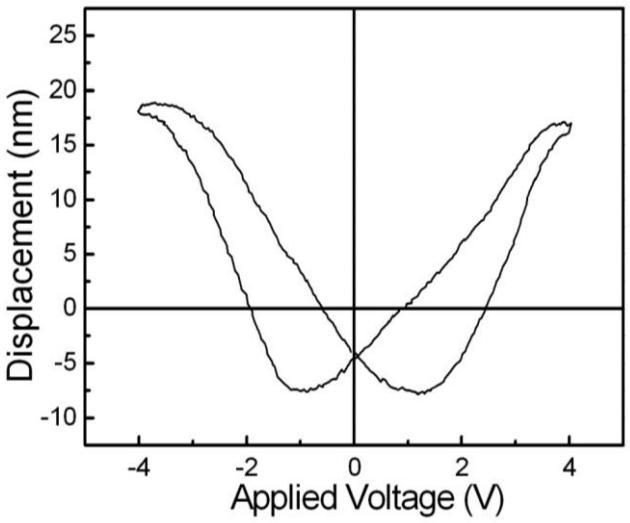

Fig. 6. Piezoelectric butterfly loop of BT thin film.

Conclusion

Crack free BT thin film was fabricated by spin coating of sol-gel solution on Platinised Si template (111). XRD analysis of the BT film gave an evidence of epitaxial growth along (111) and (211) crystal plane which is parallel to the Pt(111). The morphology and orientation of the grains as seen in AFM and SEM images is controlled by the chemistry of the preparation. Substantial enhancement in piezoelectric d_{33} value is achieved by domain wall engineering and submicron domain structure.

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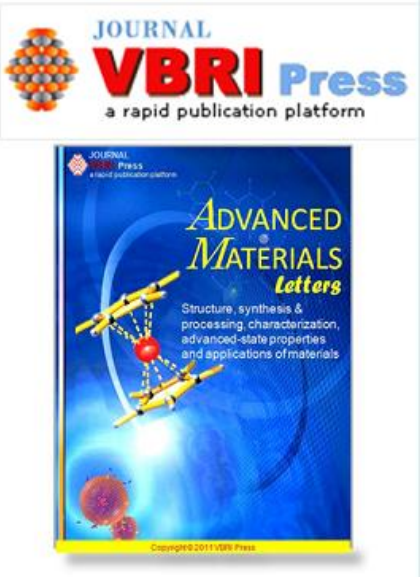

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