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# Structural and electrical characterization of $Bi_2VO_{5.5}$ / $Bi_4Ti_3O_{12}$ bilayer thin films deposited by pulsed laser ablation technique

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## ABSTRACT

**The pulsed laser ablation technique has been employed to fabricate bilayer thin films consisting of layered structure ferroelectric bismuth vanadate ($Bi_2VO_{5.5}$) and bismuth titanate ($Bi_4Ti_3O_{12}$) on platinized silicon substrate. The phase formation of these films was confirmed by X-ray diffraction (XRD) studies and the crystallites in these bilayers were randomly oriented as indicated by diffraction pattern consisting of the peaks corresponding to both the materials. The homogeneous distribution of grains (~300 nm) in these films was confirmed by atomic force microscopy. The cross-sectional scanning electron microscopy indicated the thickness of these films to be around 350 nm. The film exhibited P-E hysteresis loops with $P_r$ ~ 11 μC/cm$^2$ and $E_c$ ~ 115 kV/cm at room temperature. The dielectric constant of the bilayer was ~ 225 at 100 kHz which was higher than that of homogeneous $Bi_2VO_{5.5}$ film.**

**Keywords:** Thin Films; Ferroelectric; Dielectric; Laser ablation

## 1. INTRODUCTION

Fabrication and stabilization of materials that do not occur naturally has been the subject of great interest of current materials research [1]. Recently the investigations of ferroelectric multilayer and superlattices have received considerable attention due to the fact that these kinds of engineered materials have been identified as possessing functional properties in a sense superior to their single phase constituent films [2-4]. The control of properties could be achieved by tailoring the lattices [5], e.g. by lattice mismatch induced strain at the interface-strain engineering, polarization mismatch enhancing polarization, chemical heterogeneity, which in turn may enhance the physical properties or in many cases may give rise to new properties which were not exhibited by the starting materials. The Aurivillius family of layered bismuth oxides is a class of ferroelectrics whose properties have been widely studied [6]. More recently, there is a renewed interest because of the discovery of fatigue-free behavior in thin films for nonvolatile memory applications [7]. More importantly, Bismuth Titanate [$Bi_4Ti_3O_{12}$ (BTO)], which is an n = 3 member of this family has been reported to be a very good ferroelectric and electro-optic with small amount of the substitution of impurities, such as La, Sm and Nd for Bi and V, W and Nb for Ti in the pseudoperovskite $(Bi_2Ti_3O_{10})^{2-}$ layers of BTO to improve the remnant polarization and fatigue endurance. [8-11]. Bismuth Vanadate [$Bi_2VO_{5.5}$ (BVO)] is a vanadium analog of the n = 1 member of the Aurivillius family which has a Curie temperature of 720 K [12-14]. It has been reported in the literature that the composite of BVO and BTO solid solution possesses better physical properties and low leakage current than that of BVO [15]. The single phase BVO thin films have been prepared on platinum coated Si substrates and studied their ferroelectric and dielectric properties [16]. It has been found that these films possess non-negligible ionic conductivity attributed to the presence of oxide ion vacancies in the perovskite layer. Also the contribution of oxygen ion vacancies to the ferroelectric properties was quite high as established through fatigue characteristics.

In this article we report the structural and electrical properties of bilayer stacking of $Bi_2VO_{5.5}$ (BVO) and $Bi_4Ti_3O_{12}$ (BTO). We have fabricated bilayer thin films consisting of alternating BVO and BTO layers henceforth mentioned as BVBT. The presence of a BTO layer along with the BVO layer effectively suppressed the high electrical conductivity of BVO which is commonly observed in the laser ablated BVO thin films deposited on Pt / $TiO_2$ / $SiO_2$ / Si substrates. The BVBT bilayer thin films showed a fair increase in remnant polarization ($P_r$), and more interestingly a significant reduction in coercive field ($E_c$), as compared to the homogeneous BVO films

 

of the same thickness. The details pertaining to the structural, dielectric and ferroelectric properties of BV BT bilayers fabricated on platinized silicon in metal insulator metal (MIM) configuration are illustrated in the following sections.

## 2. EXPERIMENTAL

The bilayer structures consisting of BVO and BTO were fabricated by a multitarget-pulsed laser deposition (PLD) technique on platinized silicon substrate in the configuration Au / BVO / BTO / Pt (111) / $TiO_2$ / $SiO_2$ / Si (100). A 248 nm excimer laser (Lambda Physik Compex 201) operated at 5 Hz was alternately focused onto the well-sintered freshly polished BVO and BTO rotating targets with an energy density of 2 $Jcm^{-2}$ at an angle of 45˚ by a UV lens. The substrates were placed parallel to the target at a distance of 3.5 cm and heated to 650℃ by a resistance heater. The chamber was first pumped down to $1 \times 10^{-6}$ m bar, and then high purity oxygen was introduced using a mass flow controller to get oxygen partial pressure of 100 m Torr. After deposition of both the layers, the samples were cooled down to room temperature under an oxygen pressure of 1 mbar to minimize the oxygen ion vacancies. In these cases, the bilayer thin films were prepared with BTO as the first layer and BVO as the final layer with equal layer thickness.

The X-ray diffraction (XRD) studies were carried out to characterize the phase and crystallographic structure of the bilayer films using Cu $K_\alpha$ ~ 1.541 Å radiation (Scintag XR 2000 Diffractometer). Scanning electron microscope (SEM) (Sirion 200) and atomic force microscope (AFM) (Veeco CP II) were employed to monitor the microstructure of the films.

For electrical measurements, gold dots of $1.96 \times 10^{-3}$ $cm^2$ area were deposited on the top surface of the films through a shadow mask using thermal evaporation technique. The electrode dots were annealed at 250℃ for 30 min. The Pt surface was used as the bottom electrode for capacitance measurements. The dielectric constant and C-V measurements were performed at a signal strength of 0.5 V using impedance analyzer (HP4294A). The polarization-electric field (P-E) hysteresis was recorded using a Precision Workstation (Radiant Technologies, Inc.) ferroelectric test system in virtual ground mode.

## 3. RESULTS AND DISCUSSIONS

Bilayered thin films of BVO and BTO were fabricated on platinized silicon substrates by pulsed laser ablation using the optimized deposition conditions for BVO and BTO layers. A schematic diagram of the bilayer thin film grown in this work is shown in **Figure 1**. Equal thickness (~ 175 nm) of the individual layers was maintained in bilayer films. The BTO layer was grown first on platinized silicon substrate and then immediately followed by the growth of BVO layer without any delay in order to maintain the sharp interface between the two layers. The sequence of the layers was also reversed, but not much difference in terms of physical properties was observed, hence the one bilayer structure *i.e.* BVBT bilayer is discussed as a symbolic representative one.

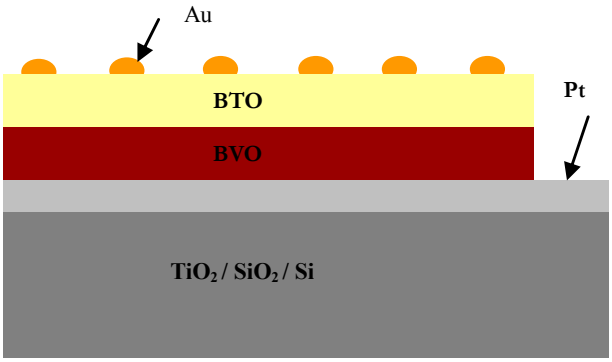


**Figure 1.** Schematic diagram of a BVBT bilayer thin film.

**Figure 2(a)** shows the representative XRD pattern of BVBT bilayer film deposited by PLD. The XRD diffraction peaks corresponding to both the BVO and BTO phases were observed and these were indexed on the basis of orthorhombic structure of BVO [JCPDS 42-0135] and BTO [JCPDS 72-1019]. It is observed that the film is polycrystalline in nature and main diffraction peaks of both BVO (113) and BTO (117) appear with higher intensities along with the other low intensity peaks. Also, the (002) reflection of BVO along with (004) of BTO appear so close that they overlap giving only one visible peak. The bilayer film possessed an interface between the two individual layers and this interface does influence the physical properties due to the lattice strain at the interface. **Figure 2(b)** shows the (002) diffraction peak corresponding to BVO of the bilayer thin film. The c-axis lattice parameter calculated for BVO from the (002) peak was found to increase from 15.42 Å for BVO layer [17] to 15.50 Å in BVBT bilayer. This increase in out-of-plane lattice parameter might be due to the in plane compressive stress on BVO in BVBT bilayer in the present case in order to keep the cell volume unchanged. Therefore, it is required to grow these films epitaxially and measure the in-plane lattice parameters along with the residual stress in these bilayer films in order to achieve the lattice driven effects in these films.

The surface morphology of the BVBT BL thin film was investigated by contact mode atomic force microscope (AFM). **Figure 3** shows the surface morphology of BVBT bilayer thin film over a 5 μm x 5 μm scan area as two-dimensional (a) and three-dimensional (b) mi-

 

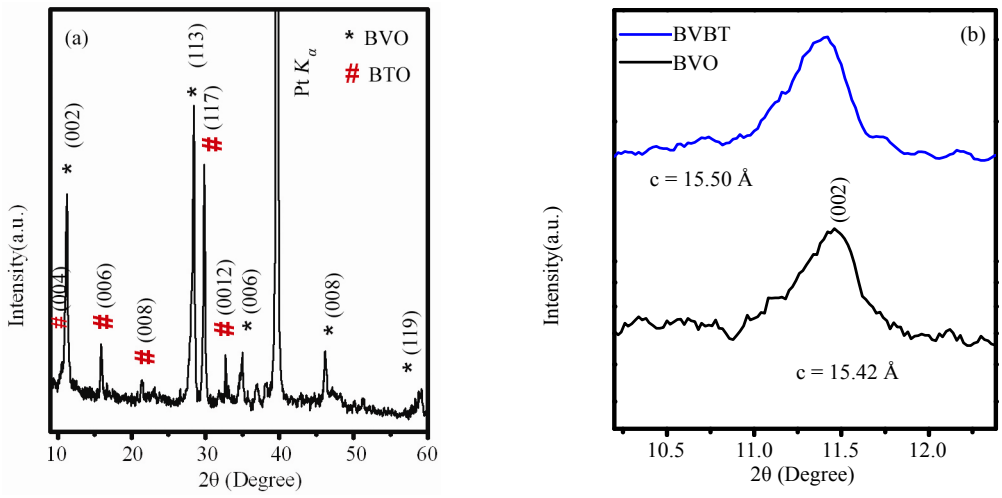


**Figure 2. (a)** X-ray diffraction pattern of BVBT bilayer thin film. **(b)** Comparison of BVO and BVBT bilayer diffraction pattern along (002) plane of BVO.

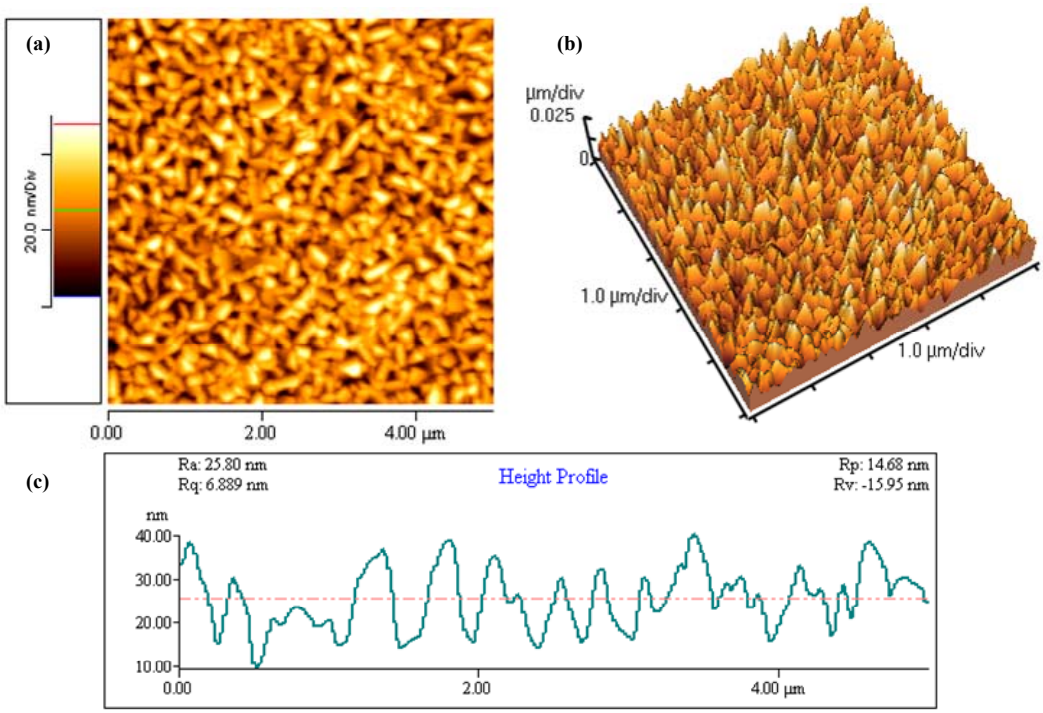


**Figure 3. (a)** AFM micrograph showing surface topography, **(b)** 3D image of BVBT bilayer thin film and **(c)** line profile.

crographs with the roughness profile mapped using line scan depicted in (c) The BVBT bilayer films exhibited dense surface morphology consisting of distinct grains. Further the homogeneous distribution of grains was observed with an average grain size of 0.3 µm. The root mean square of the surface roughness ($R_a$) was around 7 nm as observed from the roughness profile. It indicated a good quality of the deposited bilayer films.

The cross sectional microstructure of BVBT bilayer was studied by SEM and is depicted in **Figure 4** which indicated dense bilayer growth with sharp interface with Pt. A columnar like structure was observed for this sample and the thickness of the sample bilayer film was around 300 nm. It is noteworthy here that we could not distinguish between the top BVO and bottom BTO layer in this bilayer structure. This might be due to the very little difference in the atoms constituting the BVO and BTO layers which scatter the electrons almost with the

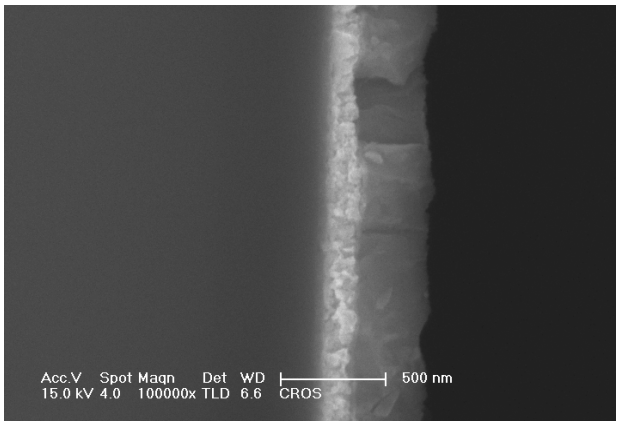


**Figure 4.** Cross sectional scanning electron micrograph of a representative BVBT bilayer film.

same intensity during and as a result the contrast between the two layers is poor.

In the present study we have further focused on the ferroelectric (FE) properties of these BVBT bilayer thin films deposited on platinized silicon substrate. Polarization measurements were carried out using a Precision Workstation operating in the virtual ground mode as explained earlier. A simple triangular pulse of voltage is applied across the electrodes of the sample which was fabricated in Metal-Insulator-Metal (MIM) configuration and the polarization response of the sample is observed under an integrator circuit. **Figure 5(a)** shows a typical P-E loop obtained for a BVBT bilayer thin film at room temperature. At the applied voltage of 12 V, the measured values of remnant polarization ($P_r$) and coercive field ($E_c$) for ~ 350 nm thick BVBT bilayer film were around 11 μC/cm$^2$ and 115 kV/cm, respectively. The non zero switchable polarization observed at zero applied field is a general characteristic of a FE material [18-19]. It showed two key characteristics of a ferroelectric which are, polarization is reversible by an application of an electric field and polarization remains at a finite value even after the removal of the electric field [20]. The value of remnant polarization observed for these bilayer films is higher than that of the homogeneous BVO thin films of similar thickness [16]. Further the asymmetric nature of the P-E loops with respect to electric field axis indicates interface dominated behavior.

The capacitance voltage (C-V) characteristics of a BVBT bilayer thin film measured at 100 kHz as probing frequency is shown **Figure 5(b)**. The C-V measurements were carried out by applying a small ac signal of 0.5 V amplitude, with a varying dc electric field. The dc voltage was swept from negative bias (–8 V) to positive (8 V) in steps of 0.1 V with a sweep rate of 0.1 V/s and back again. The butterfly shape of the curve confirmed the ferroelectric nature of the BVBT BL film and the capacitance shows strong voltage dependence. The two maxima of the loop correspond to the domain switching voltage in forward and reverse directions where the polarization reversal takes place. The asymmetry that is observed in C-V curve suggests that the electrodes are asymmetric and the film contains mobile ions or charges accumulated at the interface between the film and the electrode. In addition there is a difference between the capacitance values of the two peaks, which may be due to some defect energy levels in the film.

The dielectric dispersion studies were carried out on BVBT bilayer thin film at room temperature in the frequency range of 1 kHz to 1 MHz. **Figure 6** shows the variation of dielectric constant ($\varepsilon_r'$) and the dissipation factor (D) as a function of frequency measured at room temperature. The dielectric constant as well as dissipation factor was found to decrease abruptly in the low frequency region. The variation in dielectric constant is not significant at higher frequencies. Similar trend has been observed at lower frequencies for BVO films grown on platinized silicon substrate [16]. The small

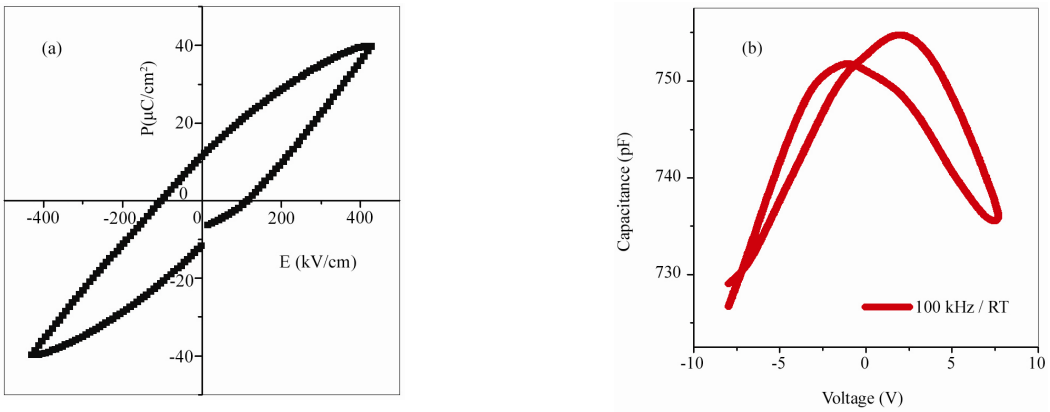


**Figure 5. (a)** The P-E hysteresis loop and **(b)** Capacitance- Voltage characteristics of a BVBT BL thin film measured at room temperature.

 

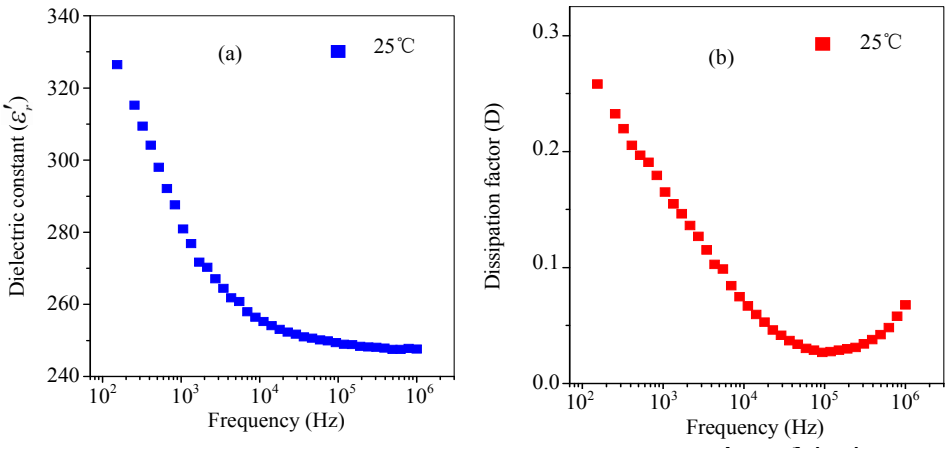


**Figure 6. (a)** Variation of dielectric constant and **(b)** dissipation factor of a BVBT BL thin film as a function of frequency.

dispersion observed at higher frequency has its contribution from the response of the grains, while at lower frequencies grain boundaries, free charges etc. would contribute significantly. However the dielectric loss for BVBT bilayer thin film shows an increasing trend subsequent to 100 kHz. The dissipation factor has the minimum value (~ 0.03) around 100 kHz, where the dielectric constant is ~ 252.

The comparison of the observed dielectric constant of BVBT bilayer with that of the single layer BVO and BTO films is shown in **Figure 7**. The dielectric constant of BVBT bilayer film shows less dispersion as compared to that of homogeneous BVO film. This might be due to the reduced number of defect states in bilayer films due to the presence of BTO layer. Further the observed dielectric constant of bilayer film is higher(e.g. ~ 225 at 1 M Hz) than that of single layer BVO film.

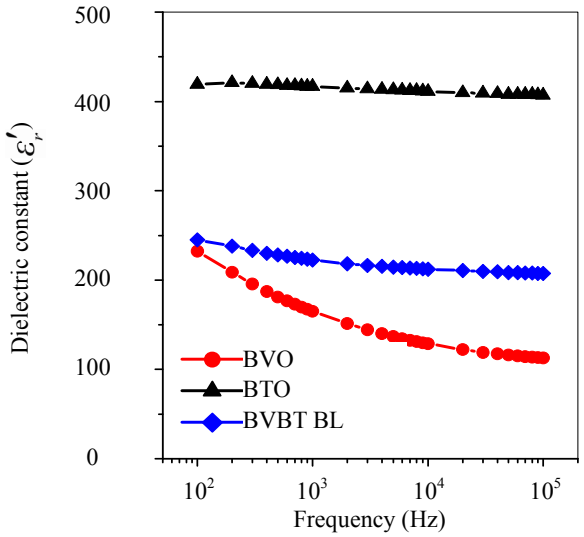


**Figure 7.** Comparison of dielectric constant of BTO, BTO and BVBT bilayer films.

## 4. CONCLUSIONS

Bilayer thin film structures consisting of ferroelectric Bismuth vanadate ($Bi_2VO_{5.5}$) and Bismuth titanate ($Bi_4Ti_3O_{12}$) individual layers were fabricated on platinized silicon substrate (Pt(111) / Ti / $SiO_2$ / Si) using pulsed laser ablation technique and investigated systematically their structural and electrical properties. The X-ray diffraction (XRD) studies indicated that bilayer is randomly oriented and the diffraction pattern consists of diffraction peaks from both starting materials. The Atomic force microscopy of the films indicates that there is a homogeneous distribution of grains in these films. The cross-sectional scanning electron microscopy established the dense nature of these films. The polarization hysteresis and C-V studies established the ferroelectric nature of these films. The observed dielectric constant of these bilayer films was higher than that of single layer BVO films.

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