Effective thickness and dielectric constant of interfacial layers of Pt/Bi_{3.15}Nd_{0.85}Ti_{3}O_{12}/SrRuO_{3} capacitors

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Epitaxial c-axis-oriented Bi_{3.15}Nd_{0.85}Ti_{3}O_{12} (BNT) thin films with thickness ranging from 150 to 350 nm were deposited on conductive SrRuO_{3} (SRO) on (001) SrTiO_{3} substrates by pulsed laser deposition. The top Pt electrode was deposited by sputtering to construct a capacitor Pt/BNT/SRO. The authors have evaluated the effective thickness (\( t_{e} \)) and dielectric constant (\( e_{i} \)) of interfacial layers at the Pt/BNT and BNT/SRO interfaces based on the optical refractive index of the BNT layer and the capacitance frequency as well as the current-voltage characteristics of the capacitors. Using a series capacitor model, they have found that the dielectric constant of bulk BNT and the \( t_{e}/e_{i} \) ratio are 586 and 1.46 nm, respectively. Knowing the optical dielectric constant (\( e_{opt} \)) and the product of \( e_{opt}t \) of BNT thin films, the authors have estimated that the effective thickness and dielectric constant of the interfacial layers are 20.1 nm and 13.7, respectively. © 2007 American Institute of Physics. [DOI: 10.1063/1.2746953]

Due to fatigue-free and fast switching speed characteristics, bismuth-layered perovskite ferroelectrics have been favorably considered as the materials for nonvolatile ferroelectric random access memory (NVFRAM) devices. 1 A recent study found that highly c-axis-oriented Bi_{15}Nd_{0.85}Ti_{3}O_{12} (BNT) thin films on Pt/TiO_{2}/SiO_{2}/Si substrates exhibit switchable remanent polarization 2P_{r} of over 100 \( \mu \)C/cm^{2} and imprint-free behavior. 2 These results clearly show that ferroelectric Bi_{4−x}Nd_{x}Ti_{3}O_{12} is a very promising candidate for NVFRAM devices. Following the report from Chon et al., 2,3 the electrical properties of Bi_{4−x}Nd_{x}Ti_{3}O_{12} thin films on different bottom electrodes and substrates have been investigated by Xi et al. 3,4 On the other hand, a distinctive feature of ferroelectric thin films is their thickness dependent dielectric properties. A number of experimental results have shown that the dielectric constant decreases with a decrease in film thickness. 5-7 The collapse of bulk dielectric behavior is usually explained by assuming the existence of “dead” or interfacial layers with a severely depressed dielectric constant at the electrode/film interfaces. Similar to other ferroelectric films, thickness dependent dielectric properties in Bi_{4−x}Nd_{x}Ti_{3}O_{12} thin films has been reported. 8-10 Gao and Wang investigated the thickness dependence of dielectric properties in rf sputter deposited Bi_{15}Nd_{0.85}Ti_{3}O_{12} thin films. 10 Their experimental results revealed the existence of an interfacial layer at the Pt/Bi_{15}Nd_{0.85}Ti_{3}O_{12} interface. Because the dielectric constant was independent of the film thickness, Watanabe et al. demonstrated that there was no interfacial layer between the electrode and epitaxial Bi_{4}Ti_{3}O_{12} thin films prepared by metal-organic chemical vapor deposition. 8 However, there is no report about the effective thickness and dielectric constant of interfacial layers between the electrode and the epitaxial Bi_{15}Nd_{0.85}Ti_{3}O_{12} thin films prepared by pulsed laser deposition (PLD). In this letter, we report on our analytical approach to evaluate the effective thickness and dielectric constant of such interfacial layers through the measurement of the optical refractive index of Bi_{15}Nd_{0.85}Ti_{3}O_{12} (BNT) films and the capacitance-frequency (C-f) and current-voltage (I-V) characteristics of Pt/BNT/SrRuO_{3} capacitors.

It is well known that the polarization vector in BNT thin films is close to the c axis of the BNT unit cell because of its structural distortion. 2 To evaluate the physical properties of the interfacial layer between the electrode and BNT film, we fabricated vertical capacitors having a Pt/BNT/SrRuO_{3} configuration, where epitaxial c-axis-oriented BNT films were grown on (001) SrRuO_{3} (SRO) on (001) SrTiO_{3} (STO) substrates. It should be pointed out that in the present work we considered two interfaces: Pt/BNT and BNT/SRO, hence, two interfacial layers. We have treated these two interfacial layers as an effective interfacial layer and use an effective thickness and dielectric constant in our analytical model.

The bilayers of BNT/SRO were deposited \textit{in situ} on (001) STO substrates by PLD using a XeCl excimer laser (\( \lambda = 308 \) nm). The processing parameters for both SRO and BNT were initially optimized in order to get the best structural and electrical properties. In brief, a substrate temperature of 775 °C and an oxygen pressure of 200 mTorr were used for the deposition of SRO electrodes. A substrate temperature of 765 °C and an oxygen pressure of 200 mTorr were used for the deposition of BNT films. Following deposition, the films were cooled down to room temperature in an oxygen pressure of 300 Torr without any further thermal treatment. It should be noted that the deposition of BNT was done right after the deposition of SRO electrode without breaking the vacuum. The thickness of the SRO layer was...
100 nm and the thickness of the BNT layer varied from 150 to 350 nm. The top Pt electrode, with an area of $4 \times 10^{-6} \text{ cm}^2$ and a thickness of $\sim 300$ nm, was deposited by sputtering. The capacitance-frequency ($C$-$f$) and dielectric loss-frequency characteristics were measured using an HP4194A impedance analyzer. The current-voltage ($I$-$V$) characteristics were measured using a Keithley 487 picoammeter/voltage source with a delay time of 3 s. To evaluate the optical refractive index, spectroscopic ellipsometry (SE) measurements (variable angle spectroscopic ellipsometry, J.A.Woollam Co., Inc.) were carried out on BNT films deposited on STO substrates at incident angles of 60°, 65°, and 70°. All the optical measurements were performed in air.

Figure 1 shows a typical x-ray diffraction (XRD) $\theta$-$2\theta$ scan from a BNT thin film deposited on a SRO/STO substrate. As can be seen from this figure, the BNT film is preferentially oriented along the $c$ axis (perpendicular to the substrate surface) since it shows only (00$l$) diffraction peaks. The inset of Fig. 1 shows the rocking curve of the BNT (0014) reflection. The full width at half maximum (FWHM) is 0.35°. All these results indicated that the BNT film is well crystallized with no impurities from any other phase. The epitaxial nature of the BNT/SRO/STO heterostructure is confirmed by XRD phi scans (not shown) by the in-plane alignment of both the BNT and SRO with respect to the major axes of the STO substrate. The out-of-plane and in-plane orientational relationships are (001)$_{\text{BNT}}$||(001)$_{\text{SRO}}$||(001)$_{\text{STO}}$ and [100]$_{\text{BNT}}$|[110]$_{\text{SRO}}$|[110]$_{\text{STO}}$.

Typically, the thickness dependence of the dielectric constant in ferroelectric thin films was investigated based on the series capacitor model, which consists of the bulk ferroelectric layer and two interfacial layers at the top and bottom electrode interfaces.\(^{11-13}\) As discussed earlier, we model the interfacial layers at the Pt/BNT and BNT/SRO interfaces by an effective thickness and dielectric constant. Thus, the capacitance for such a series capacitor can be expressed as

$$\frac{1}{C} = \frac{1}{C_b} + \frac{1}{C_i},$$

where subscripts $b$ and $i$ refer to the bulk layer and the effective interfacial layer, respectively. $C$ is the capacitance of the whole capacitor with architecture of Pt/BNT/SRO. According to the phenomenological thermodynamic approach,\(^{7,14}\) the interfacial layer thickness and dielectric constant can be considered to be independent of the total film thickness. Then we can get the dielectric constant of the BNT thin film

$$\frac{t}{\varepsilon} = \frac{t - t_i}{\varepsilon_b} + \frac{t_i}{\varepsilon_i} = \frac{t}{\varepsilon_b} + t_i \left( \frac{1}{\varepsilon_i} - \frac{1}{\varepsilon_b} \right).$$

where $t$ is the total thickness of the BNT film, $\varepsilon$ is the dielectric constant of the BNT film, $\varepsilon_b$ is the dielectric constant of the bulk layer, $t_i$ is the effective thickness of the interfacial layers, and $\varepsilon_i$ is the effective dielectric constant of the interfacial layers. The dielectric constant of BNT thin films with different thicknesses as a function of frequency is plotted in Fig. 2. The dielectric loss as a function of frequency of BNT thin films with different thicknesses was also measured (not shown). The $\varepsilon$ decreases with decreasing BNT thickness. The dielectric loss decreases from 0.065 to 0.046 with the increase of thickness from 150 to 350 nm at a frequency of 1 MHz, which is in agreement with the results reported by Gao and Wang.\(^{10}\) Experimentally, the dielectric constant of ferroelectric films satisfies the condition of $\varepsilon_b \gg \varepsilon_i$.\(^{12,15}\) Equation (2) can be simplified to $\frac{t}{\varepsilon} = \frac{t}{\varepsilon_b} + \frac{t_i}{\varepsilon_i}$. Therefore, a linear relationship is expected between the $t/\varepsilon$ and the $t$ with a slope of $1/\varepsilon_b$ and a vertical-axis interception of $t_i/\varepsilon_i$. As shown in Fig. 3, the experimental results can be fitted by a perfect linear relationship between the $t/\varepsilon$ and the $t$. From such a plot, we have found that $t_i/\varepsilon_i = 1.46$ nm and $\varepsilon_i = 586$. The dielectric constant of the bulk layer is comparable to or slightly larger than the results reported by others.\(^{4,10}\) It should be noted that another possible origin of the thickness dependent of electrical properties in ferroelectric films is the change of grain size with film thickness.\(^{6}\) In our BNT/SRO/STO heterostructures, the grain size of the BNT layer measured by XRD (using the Scherrer formula) remained almost the same with a value of 38 nm for different film thicknesses. Therefore, this effect is negligible in the current study.

![FIG. 1. XRD θ-2θ scan of BNT thin film on SRO/STO substrate; the inset shows the rocking curve of BNT (0014) reflection with a FWHM of 0.35°.](image1)

![FIG. 2. (Color online) Dielectric constant of BNT thin films as a function of frequency with different thicknesses from 150 to 350 nm.](image2)

![FIG. 3. $t/\varepsilon$ as a function of BNT thickness $t$ from 150 to 350 nm. The calculated $t_i/\varepsilon_i$ and $\varepsilon_i$ are 1.46 and 586, respectively.](image3)
To get the value of $t_i$ and $\varepsilon_i$, we further measured the leakage current and the optical refractive index. The $I$-$V$ characteristics of the Pt/BNT/SRO capacitors were measured with various BNT film thicknesses ranging from 150 to 350 nm (not shown). In order to minimize the influence of the polarization of charge carriers on the leakage current of the capacitor, a relatively long delay time of 3 s was used, i.e., the current was measured by waiting for 3 s after each application of bias voltage. As commonly observed, the leakage current increases with increasing bias voltage. The Schottky equation originally derived from the metal/vacuum interface is widely used to analyze the leakage current of ferroelectric films. If most of the applied voltage drops are across the interfacial layers, the Schottky equation can be expressed as\cite{15,16,17}

$$J = A^* T^2 \exp \left[ \frac{-(\phi_0 - eV/4\pi\varepsilon_0\varepsilon_{opt}d_i)T}{kT} \right]$$

where $J$ is the leakage current density, $A^*$ is the effective Richardson constant, $T$ is the temperature, $\phi_0$ is the potential barrier height, $e$ is the elementary charge, $k$ is Boltzmann’s constant, $V$ is the applied voltage, $\varepsilon_0$ is the permittivity of free space, and $\varepsilon_{opt}$ is the optical dielectric constant of BNT film. From Eq. (3), a linear relationship between $\ln(J)$ and $V^{1/2}$ with a slope of $e\sqrt{4\pi\varepsilon_0\varepsilon_{opt}d_i/kT}$ should be obtained if the leakage current is governed by the Schottky equation. Figure 4 shows the $\ln(J)$ vs $V^{1/2}$ of the Pt/BNT/SRO capacitors with various BNT film thicknesses.\cite{18} The plots are straight lines at a bias voltage above 0.85 V for all the thicknesses. The slopes, being independent of the film thickness, can be used to calculate the product of $\varepsilon_{opt}d_i$ with a value of 134.6 nm.

The optical dielectric constant is commonly determined from an optical refractive index ($n$) with a relation of $\varepsilon_{opt} = n^2$.\cite{19,20,21} The refractive index $n$ of BNT thin film deposited on STO substrate was extracted from SE data through model based analysis. A value of 2.59 at a wavelength of 633 nm was measured and further used to calculate $\varepsilon_{opt}$. The optical dielectric constant of our BNT film is 6.71. Combining $t_i/\varepsilon_i = 1.46$ nm, $\varepsilon_{opt}d_i = 134.6$ nm, and $\varepsilon_{opt} = 6.71$, the $t_i$ and $\varepsilon_i$ were estimated to be 20.1 and 13.7, respectively. The origin of the interfacial layers has been a subject of debate for some time; the explanations include a depleted layer from the Schottky barriers at the interface and Thomas-Fermi screening from space charge. In our case, a possible origin of the interfacial layer at the Pt/BNT interface is that Bi violently reacts with Pt,\cite{22} which constitutes the main disadvantage of using a Pt electrode for Bi-based ferroelectric films. The interfacial layer at the BNT/SRO interface may come from the incomplete screening at the SRO electrode, even though there is good crystal structure and reasonable lattice match between BNT and SRO.\cite{23}

In conclusion, we have fabricated BNT films with different thicknesses ranging from 150 to 350 nm on SRO/STO substrates by PLD. Based on the dielectric constant, leakage current, and optical refractive index measurements, the dielectric properties of interfacial layers of Pt/BNT/SRO capacitors were estimated. The effective thickness and dielectric constant of the interfacial layers were estimated to be 20.1 and 13.7, respectively. On the other hand, the dielectric constant of the bulk BNT layer was 586.

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17. Here, the $I$-$V$ data were taken with Pt electrode negatively biased.