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REPORT



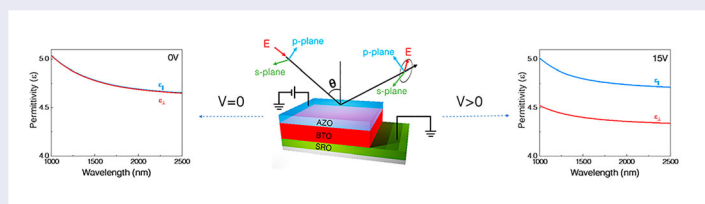
Dynamic tuning of dielectric permittivity in BaTiO₃ via electrical biasing

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ABSTRACT

Dynamic tuning of optical properties is technologically important for the development of future integrated electronic and photonic devices. Here, we demonstrate the electrically tunable permittivity in optical frequency in epitaxial BaTiO₃ (BTO) thin films using spectroscopic ellipsometer measurements under DC bias condition. The lattice tetragonal distortion and domain switching of biased BTO is evident based on the increased anisotropy in permittivity in-plane and out-of-plane. Specifically, out-of-plane permittivity, arising from the *c*-domains, shows a continuous decrease with the applied voltage, relative to the in-plane permittivity, arising from the *a*-domains. The dielectric constant can also be reversibly adjusted through electric-reset cycles.



IMPACT STATEMENT

The current study demonstrates the real-time electrically tunable dielectric permittivity in BaTiO₃, probed using spectroscopic ellipsometer at optical frequencies, towards future tunable waveguides, optical components and devices.

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KEYWORDS

Biased ellipsometer; tunable permittivity; barium titanate; ferroelectric; epitaxial thin films

Introduction

Non-linear dielectric materials are important for photonic device applications such as low-loss waveguides, wavelength conversion and electro-optic modulators [1,2]. Among them, optical waveguides are a key component in integrated optical circuits with potential use in all-optical signal processing and optical computing [3,4]. Specifically, waveguide materials, such as LiNbO₃ and BaTiO₃ [5,6] possessing a non-zero second-order nonlinear optical susceptibility owing to their non-centrosymmetric crystal structure, are important for nonlinear photon generation and manipulation (e.g. second harmonic generation (SHG) and spontaneous parametric down-conversion (SPDC)). Therefore, tunability in their dielectric properties is technologically important owing to their application in nanoscale integrated optical circuits. Such tunable optical properties have been

achieved via several methods such as doping and stoichiometry tuning [7–10]. However, integrated on-chip optical devices require real-time tunability using external stimuli such as electric field, magnetic field, laser excitation and temperature gradient. For example, optical transmission of thin Ag films has been tuned by applying a magnetic field; pump–probe ellipsometry has been used to study ultrafast phenomena; and, tunable reflectance has been achieved using thermal gradient [11–13]. Therefore, real-time tunability and detection of optical properties are very much needed for the development of integrated photonic devices.

On the other hand, such non-centrosymmetric crystal structures also enable ferroelectric properties. Ferroelectric materials have potential applications in electrically tunable dielectric applications due to the variation of their dielectric constant via applying DC bias [14].

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Recently, optical detection of ferroic switching properties has received wide interest particularly due to their switchable characteristics in response to an external stimulus such as electrical field, stress or light [15–18]. For example, the movement of ferroelectric domain walls has been realized using a low-power coherent light source [18,19]. Current measurement methods of electrically tunable dielectric properties are mainly done using impedance analyzer (preferred at low frequencies, < 100 MHz) or waveguide method (preferred at higher frequencies, GHz) [20]. However, both these techniques suffer from high losses at higher frequencies and are time-consuming to measure over the entire frequency range, thereby, enabling the measurements at the steady state of the sample. Therefore, new techniques are needed for the real-time dynamic measurement of electrically tunable dielectric constant in the THz frequency range. Spectroscopic ellipsometry could be an ideal technique for real-time dynamic measurement of optical tuning under DC bias in ferroelectric materials at optical frequencies (>100 THz).

In this work, epitaxial ferroelectric BaTiO₃ (BTO) thin film, deposited using pulsed laser deposition (PLD), is chosen to demonstrate the real-time tuning of dielectric characteristic under DC bias. BTO is a typical perovskite ferroelectric material which possesses non-linear optical properties due to its non-centrosymmetric crystal structure. It presents a cubic perovskite structure above the Curie temperature T_c and transforms to a tetragonal ferroelectric phase below T_c . It is widely used as thin-film capacitors, dynamic random-access memories, chemical sensors, optical modulators and microwave devices owing to its high permittivity, dielectric constant and spontaneous polarization at room temperature [21]. To demonstrate its tunable dielectric properties, out-of-plane DC bias is applied to BTO, and its dielectric response is measured using spectroscopic ellipsometer.

Materials and methods

Thin-film growth

The SrRuO₃(SRO)/BTO/Al-doped ZnO (AZO) multilayer stack was deposited using a PLD system, with a KrF excimer laser (Lambda Physik Compex Pro 205, $\lambda = 248$ nm), on single-crystal SrTiO₃ (STO) (001) substrate. The conventional solid-state sintering process was employed to make the SRO, BTO and AZO targets. The oxygen partial pressure was maintained at 200, 40 and 7 mTorr for depositing the SRO, BTO and AZO films, respectively. The growth temperature for the SRO and BTO layers was 700°C while the AZO layer was deposited at 420°C.

Microstructure characterization

The microstructural characterization of the films was done using X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM). XRD θ - 2θ scans were captured using a Panalytical X'Pert X-ray diffractometer while STEM micrographs were acquired using FEI Talos-200X microscope operated at 200kV. STEM was further used to conduct energy dispersive X-ray spectroscopy (EDS) for chemical mapping.

Optical characterization

The permittivity of BTO was calculated using spectroscopic ellipsometry (JA Woollam RC2). A fixed incident angle of 75° was used and the bias was applied using the top (AZO) and bottom (SRO) electrodes. The measured ellipsometer parameters ψ and Δ are related by the equation: $r_p/r_s = \tan(\psi)e^{i\Delta}$ (where r_s and r_p are the reflection coefficient for the s-polarization and p-polarization light, respectively) were fitted using physically consistent models (mentioned in the text) using the CompleteEASE software. The thickness of the three layers was calculated from the STEM images and input in the model.

Results and discussion

Figure 1 shows the multilayer stack of SRO, BTO and AZO film on STO substrate that was used for the measurement. Both SRO and AZO act as the bottom and top electrodes respectively. The electric bias is applied to this stack and the elliptically polarized light is measured using the ellipsometer *in-situ*. The transparent nature of AZO allows us to probe the bias effect on BTO. Being a non-linear optical material, BTO shows ferroelectricity on applying bias. BTO undergoes tetragonal distortion on applying bias, thus causing an increase in polarization as shown in Figure 1. Such tetragonal distortion increases the anisotropy and allows the measurement of in-plane and out-of-plane dielectric permittivity using ellipsometry measurement.

Figure 2 presents the cross-sectional STEM images taken under a high-angle annular dark field (HAADF) mode. The EDS mapping, shown in Figure 2(b), confirms the clear and sharp interfaces between the layers. The use of SRO as a bottom electrode facilitates the epitaxial growth of BTO as confirmed by the XRD spectra in Figure S1 (Supporting Information). Epitaxial BTO film of ~ 72 nm is deposited to overcome its critical thickness and to obtain both *a*-domains and *c*-domains with their polar axis lying in-plane and out-of-plane respectively [22]. Figure 2(c and d) shows the high-resolution

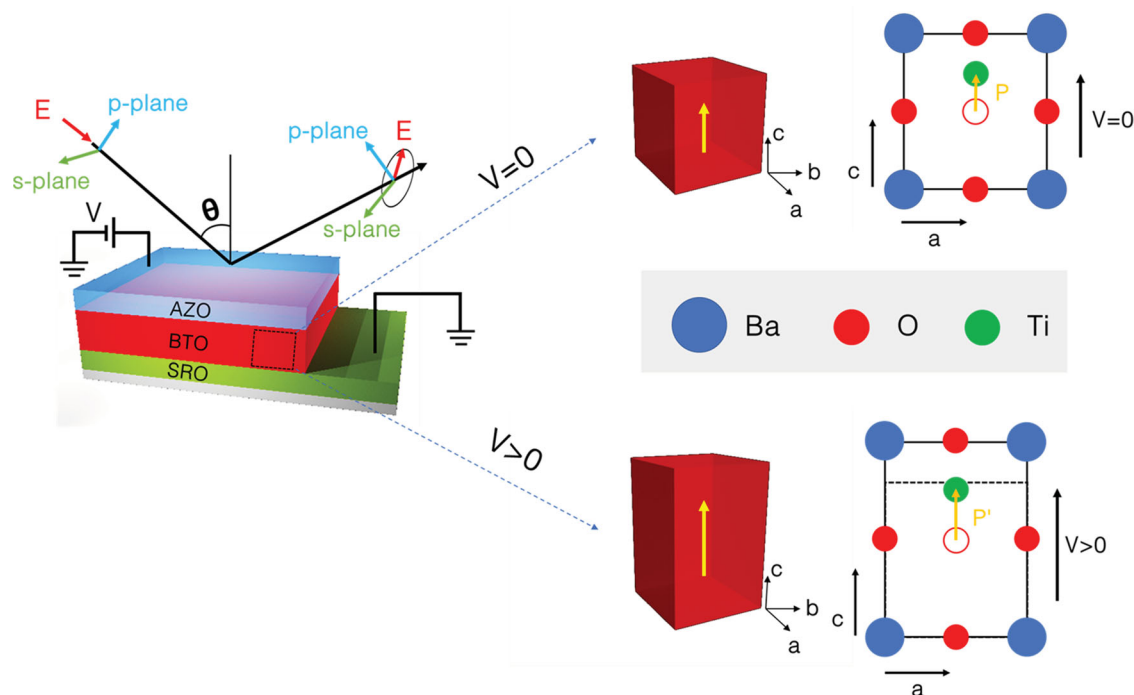


Figure 1. Schematic of the measurement setup. The SRO/BTO/AZO multilayer stack is deposited on single-crystal STO(001) with the bias applied on the top and bottom electrodes, respectively. The permittivity change due to the applied bias is calculated using ellipsometer. Without bias, BTO remains as a pseudocubic perovskite structure with a polarization P . On applying bias, BTO undergoes tetragonal distortion and its polarization increases to P' .

STEM image of the AZO layer and AZO-BTO interface, respectively. Clearly, the interfaces are nearly perfect with no obvious inter-diffusion. BTO grows along $[001]$ direction with an out-of-plane lattice parameter of ~ 4.1 Å, which is well consistent with the XRD results.

The non-linear electronic response of BTO is confirmed using piezoresponse force microscopy (PFM). The phase and amplitude maps confirm the switchable and ferroelectric nature of the BTO. The ellipsometry measurements were performed on this multilayer stack at an angle of 75° along with the voltage bias as shown in Figure S2 (Supporting Information). Separate ellipsometer measurements were performed on SRO and AZO films deposited on STO to estimate their permittivity for modeling the multilayer stack. A Drude–Lorentz model was used for modelling SRO permittivity while a combination of Drude, Tauc–Lorentz and Gaussian model was used to model the permittivity of AZO to enforce the Kramers–Kronig consistency. These fitted models were used to model the SRO and AZO layers in the multilayer stack and their permittivity was assumed to be constant with the applied voltage. The BTO permittivity was modeled using the anisotropic Tauc–Lorentz model. The thickness of all the three layers was measured using STEM images and input in the model. Figure 3(b and c) shows the ellipsometer parameter ψ and Δ with and without applied bias, which was fitted using this model to

calculate the dielectric permittivity plotted in Figure 3(d and e). Interestingly, BTO shows an increased anisotropy in the biased state with both the in-plane ($\epsilon'_{\parallel}$) and out-of-plane ($\epsilon'_{\perp}$) permittivity decreasing with an increased bias.

The unbiased BTO presents a mix of a and c -domains, thus yielding a nearly isotropic response with $\epsilon'_{\parallel}$ and $\epsilon'_{\perp}$ being almost equal. Applying a bias increases the tetragonal distortion by favoring the c -domain formation as seen by the decrease in $\epsilon'_{\perp}$. Under the 15 V-bias condition, $\epsilon'_{\parallel}$ and $\epsilon'_{\perp}$ can be effectively treated as ϵ_a and ϵ_c , respectively. As observed, ϵ_a ($\epsilon'_{\parallel}$) is greater than ϵ_c ($\epsilon'_{\perp}$) which is typically observed in BTO. This arises mainly due to the greater probability of the Ti ion in the oxygen octahedra to displace itself from its $[001]$ position towards the $[011]$ position [23]. Therefore, a small electric field can cause a large polarization in the a -direction as compared to the c -direction, thus leading to $\epsilon_a > \epsilon_c$, which is consistent with the above results. Additionally, separate temperature-dependent ellipsometer measurements were conducted to confirm that the anisotropic dielectric permittivity is caused by the DC voltage bias. The 15 V bias increased temperature to $\sim 50^\circ\text{C}$ as measured using a type-K thermocouple. Figure S3 (Supporting Information) shows the fitted permittivity of BTO at 50°C using an external heating stage. Clearly, the temperature increase plays a minor role in tuning the permittivity of

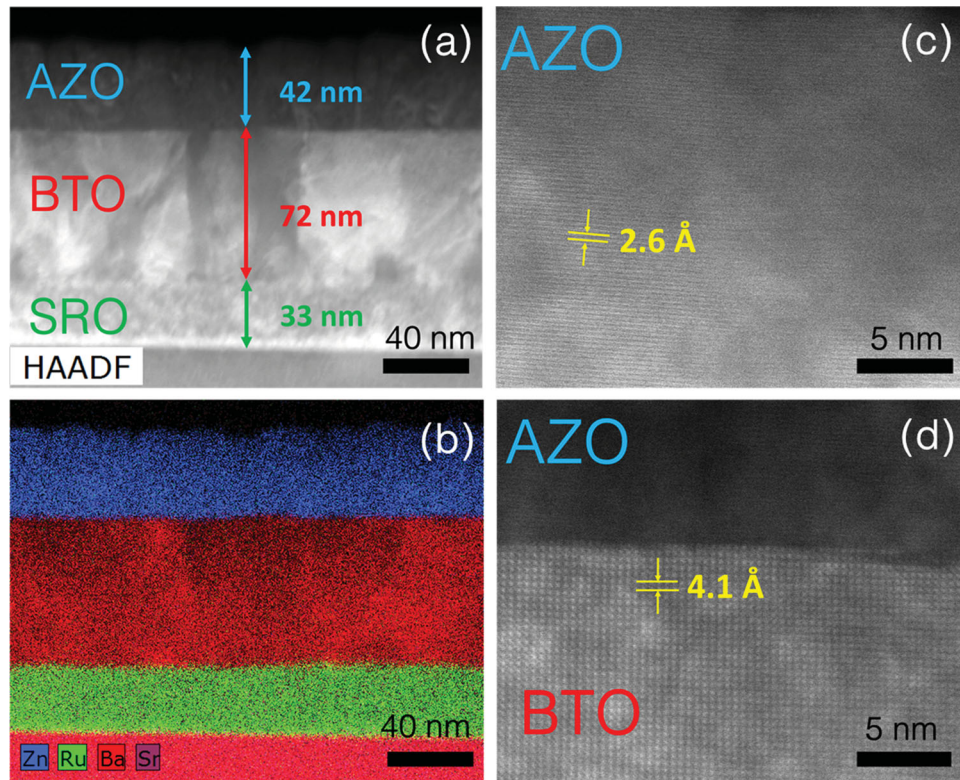


Figure 2. Microstructural characterization. (a) Cross-section STEM image showing the multilayer stack containing SRO, BTO and AZO and (b) the corresponding elemental EDS mapping. (c) High-resolution STEM image of the AZO thin film and (d) AZO-BTO interface showing the highly textured growth of the films.

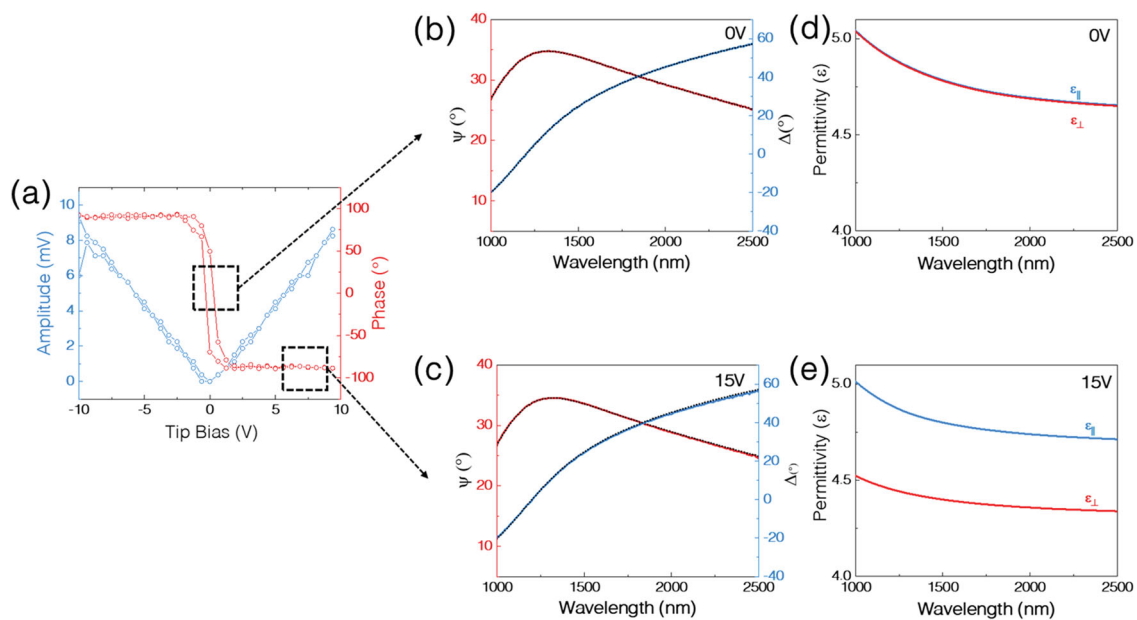


Figure 3. Tunable dielectric permittivity. (a) PFM phase and amplitude switching as a function of tip bias confirming the ferroelectric behavior of BTO. Experimental (solid) and fitted (dot) components of the ellipsometric parameter ψ for the (b) unbiased state, and (c) with 15 V applied bias. The corresponding in-plane ($\epsilon_{||}$) and out-of-plane ($\epsilon_{\perp}$) permittivity of BTO for the (d) unbiased state, and (e) with 15 V applied bias.

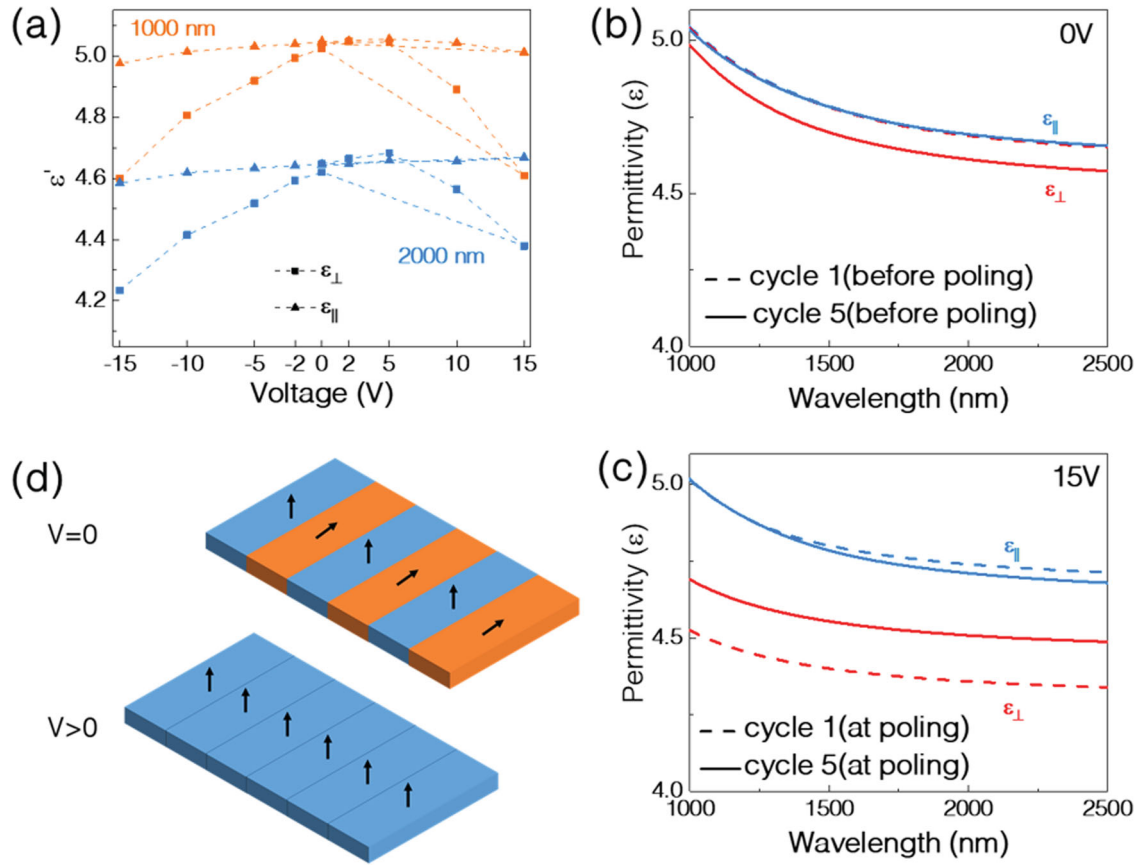


Figure 4. Cyclability. (a) In-plane and out-of-plane permittivity vs voltage curve of BTO at 1000 and 2000 nm. The anisotropic permittivity response of BTO at (b) 0 V (before poling) and (c) 15 V (at poling) after 5 cycles of measurement. (d) Schematic of *a* and *c* domains present in BTO at unbiased and biased state.

BTO while the applied bias has a major contribution in tuning the permittivity of BTO.

Figure 4(a) shows the DC bias dependent dielectric permittivity of BTO at optical frequencies. Overall, $\epsilon'_{\perp}$ decreases with an increase in voltage. The maxima observed in the ϵ - V plot is not symmetrical around 0 V which might be due to the domain pinning at the substrate interface. Such asymmetrical C - V plots have been reported in prior works and have been attributed to the formation of charged domain walls at the film-substrate interface [24,25]. The decrease in $\epsilon'_{\perp}$ is consistent with the fact that the BTO becomes less polarizable because of the saturation of the polarizable charge, resulting in the decrease of the dielectric constant for the increasing DC bias voltage. In addition, its permittivity decreases with increasing wavelength (shown for two different wavelengths: 1000 nm and 2000 nm) which is consistent with its normal dielectric dispersion characteristic. On the contrary, the presence of the other four O^{2-} ions in-plane with the Ti^{4+} ion tends to cancel the in-plane polarization change of each other due to the movement

of the Ti^{4+} ion, and thus such canceling effects result in a less obvious change in the in-plane permittivity compared to the out-of-plane permittivity. Therefore, the increase in the anisotropy of dielectric permittivity at higher voltages is attributed to higher tetragonal distortion. To evaluate the reliability of the measurements, continuous electric-reset cycles were performed. Figure 4(b and c) compares the fitted permittivity after five cycles for the unbiased and biased state, respectively. The comparison between the permittivity of the films before poling and after the applied electric field removed is made in Figure 4(b), showing the permittivity of the thin films at 0 V, cycle 1 (before poling) and 0 V, cycle 5 (after repeating the cycle 5 times). The in-plane ($\epsilon'_{\parallel}$) and out-of-plane permittivities ($\epsilon'_{\perp}$) are very similar at cycle 1 while $\epsilon'_{\perp}$ shows a small decrease after the electric field removed after 5 cycles. This might be attributed to a relative increase in the number of *c* domains after poling since *c* domains have a lower permittivity than *a* domains. The dielectric permittivity for both 0 V and 15 V after five cycles shows a similar

trend, which demonstrate a reliable repeatability of the measurements.

Figure 4(d) illustrates the domain switching mechanism on applying bias. Initially, both a and c domains are present to reduce the overall lattice strain as previously reported [22]. Since all the measurements were done within optical frequency range, only electronic polarization contributes to the overall dielectric permittivity variation. $\epsilon_{\text{electronic}}$ being relatively small, the degree of anisotropy is also small in the unbiased state. Under the biased state, the majority of the domains become c oriented. A deep double-well potential ($\Delta E = 11.7$ meV) is present along the c -axis as compared to the very shallow double-well potential ($\Delta E = 0.8$ meV) present along the a -axis, therefore, making the shorter axis to be more polarizable [26]. This is due to the increased interaction of two out of the six O^{2-} ions (along the c -axis) with Ti^{4+} ions, thereby, reducing their electronic polarizabilities. Furthermore, the polarization saturation also decreases $\epsilon'_{\perp}$ with increasing DC bias. Therefore, $\epsilon'_{\perp}$ decreases with increasing DC bias voltage.

The tuning of optical permittivity via DC bias in ferroelectric BTO thin films demonstrated in this work presents great opportunities in several aspects. First, the study provides an early demonstration of dielectric tunability in ferroelectric materials at optical frequencies. Demonstrating the tunability at lower voltages by using thinner films and high- k materials could be useful in future device-related applications. Second, this real-time ellipsometry under DC bias technique can be used to probe the domain relaxation dynamics and optical monitoring of opto-electronic devices. Third, applying bias also dynamically tunes the permittivity and produces discrete values, that can be used in integrated opto-electronic logic devices. Besides, these dynamic discrete states can also be used in neuromorphic computing applications. Last, using picosecond time resolution ellipsometer [27] could lead to the detection of ultrafast phenomena, such as the negative capacitance in ferroelectric materials [28] and many others. One of the potential limitations of this study is the limited range of tunability achieved by electric field applied and measured by *in-situ* ellipsometer due to the relatively small electronic polarization in the optical frequency range. Therefore, BTO films with better ferroelectric properties or other stronger ferroelectric materials such as PZT or LiNbO_3 could show greater tunability under lower applied electrical field.

Conclusion

Optical-based detection of ferroelectric domain switching under DC bias has been demonstrated in ferroelectric

BTO films. Real-time ellipsometer measurements of BTO under biased condition reveal the tetragonal distortion confirmed by the increased anisotropy in the in-plane and out-of-plane permittivity. The stability and repeatability of this dynamic tuning is shown by the electric-reset cycles. These measurements allow the exploration of phase change properties in ferroelectric materials using light. Such real-time ellipsometer measurements allow the examination of novel physical phenomena in other materials including phase change materials and metal-oxide nanocomposites under optical frequency range.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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