Analysis of the Pockels effect in ferroelectric barium titanate thin films on Si(001)

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1. Abstract

High-quality epitaxial BaTiO₃ (BTO) on Si has emerged as a highly promising material for future electro-optic (EO) devices based on BTO's large effective Pockels coefficient. We report on the EO response of BTO films deposited on Si by molecular beam epitaxy (MBE), and characterize the structure of these films by reflection high-energy electron diffraction and x-ray diffraction. O₂ rapid thermal anneal at 600°C for 30 min ensures full oxidation of BTO for minimal leakage current with minimal change in crystalline structure.

2. Introduction

The large effective Pockels coefficient ($r_{\text{eff}}=148 \text{ pmV}^{-1}$) for high-quality epitaxial BTO films on Si distinguishes BTO as a highly promising material for integrated silicon nanophotonics [1,2]. Monolithic integration of BTO on Si is enabled by molecular beam epitaxy (MBE) through the use of buffer layers, including BaO [3], Ba_{0.7}Sr_{0.3}TiO₃ [4], and most commonly, SrTiO₃ (STO) [1,5,6].

Since the first successful integration of perovskite oxides on Si [7] and successive demonstration of ferroelectric functionality [6], electro-optic activity [1], and devices [2], it has become apparent that these interesting properties are strongly dependent on the crystalline structure of ferroelectric BTO. In order to achieve a strong electro-optic response, the film must have (1) the correct crystallographic orientation with respect to the applied electric field [8], and (2) low vacancy density to sustain a strong electric field [9].

In this work, we assess BTO films of thickness 40-130 nm in order to quantify the Pockels coefficient with respect to crystalline orientation. Highly insulating MBE-grown BTO films can be achieved through exposure to oxygen plasma during the deposition or post-deposition O₂ rapid thermal anneal (RTA). We also examine the role of oxygen vacancies and structural defects in films of intermediate thickness (80-90 nm).

3. Methods

Epitaxial BTO films of thickness 40-130 nm were deposited on highly insulating (>20,000 $\Omega\cdot\text{cm}$) 2"-diameter Si (001) wafers through use of a Sr Zintl template and 4-6 nm SrTiO₃ buffer layer [10], with the growth monitored by *in-situ* reflection high-energy electron diffraction (RHEED) (Fig. 1(a)-(c)).

We note that for the Ti-rich surface, an extra streak appears in the RHEED pattern along the {210} direction (Fig. 1(d)), indicating a doubling of the surface unit cell size. As shown in Fig. 1(e), this extra streak disappears during the background-subtracted line scan taken during one unit cell of BTO deposition (120 s), indicating stoichiometric BTO. For Ba-rich samples, BaO_x particles can nucleate at the surface of the as-grown film [11]. As indicated by AFM, soaking in water [12,13] at room temperature for 4 hours reduces the RMS roughness from 0.763 nm (Fig. 2(a)) to 0.359 nm (Fig. 2(b)).

The backside of the Si wafer was polished for optical transmission measurements. A 300 nm-thick tungsten layer was deposited by magnetron sputtering and subsequently dry-etched to define electrode pairs with a gap of $d=5 \mu\text{m}$.

The schematic of EO measurement in transmission geometry for is illustrated in Fig. 3(a). The in-plane field modulates the refractive index of BTO, $n(E) = n_0 - (1/2) n_0^3 E$, which, in turn, induces a rotation (δ) of the incident linearly polarized light. To detect δ , sinusoidal, alternating voltage ($E_{\text{AC}} = V_{\text{AC}}/d$) is applied to gain sensitivity using a lock-in amplifier. An additional DC voltage ($E_{\text{off}} = V_{\text{DC}}/d$) is also applied to align the ferroelectric domains.

4. Results and Discussion

Fig. 3(b) illustrates the EO response for films with varying crystalline orientation.

Since the magnitude of the response δ should scale with both the optical interaction length and the magnitude of the applied AC field, we compare the field- and thickness-normalized optical rotation $\delta' = \delta/(E_{\text{AC}} \cdot t)$, where t is the thickness of the BTO layer. The thickness of the STO and Si layers are not included, as no Pockels effect is expected for materials with inversion symmetry [14].

The strongest optical response δ' is observed when the BTO tetragonal axis is oriented in-plane ("a-axis", solid squares). The hysteresis of δ' vs DC offset electric field E_{off} is also characteristic of reorientation of multiple in-plane ferroelectric domains [1]. Alternatively, a vanishing EO response is measured when the BTO tetragonal axis is oriented out-of-plane ("c-axis", solid circles). Finally, a strong response is observed even for the "mixed" *a*- and *c*-axis film (open triangles), attributable to the fraction of *a*-axis domains.

We also identify post-deposition O₂ rapid thermal anneal (RTA) as a route to increase the

fraction of *a*-axis BTO. Fig. 4 illustrates the structural changes of an as-grown *c*-axis film after successive rounds of RTA (500-850°C, 50°C increments, 30 min each). A reduced FWHM of the (002) BTO Bragg peak rocking curve indicates improved crystallinity. Between the 700°C and 850°C annealing steps, the out-of-plane lattice constant decreases from 4.03 Å to 3.99 Å, indicating a transition from *c*- to *a*-axis orientation.

An additional role of O₂ RTA is the healing of oxygen vacancies, electrically active defects which can impede build-up of a strong electric field. To illustrate, we compare (Fig. 5) two 90 nm BTO/STO/Si samples, one deposited in molecular oxygen and the other under oxygen plasma-assisted conditions. The sample as-grown in molecular O₂ exhibited a high leakage (Fig. 5, grey squares). While air anneal up to 300°C and RTA at 400°C resulted in minimal change, RTA at 600°C for 30 min reduced leakage current by 4 orders of magnitude, ensuring a strong electric field and enabling EO measurement (Fig. 5, black squares). A similarly low leakage current is measured for two as-grown oxygen plasma-assisted samples, one with Ti evaporated from a Knudsen cell (K-cell) at a rate of 4 Å/min (Fig. 5, red circles) while the other used an electron-beam evaporated (e-beam) Ti source at a rate of 12 Å/min (Fig. 5, blue triangles).

From EO measurements of the three highly insulating samples, we calculate an effective Pockels coefficient, $r_{\text{eff}} = (2\delta_{\text{max}})\lambda/(\pi n^3 t E_{\text{AC}})$, where δ_{max} is the maximum induced rotation angle in radians, $\lambda = 1550$ nm is the wavelength of incident light, $n = 2.26$ is the refractive index of the film as determined by spectroscopic ellipsometry, t the total thickness of the BTO layer [15]. Results are summarized in Table 1 for comparison with previous works, for example ~2 pm/V for strained Si, ~30 pm/V for LiNbO₃ on Si, and 148 pm/V for BTO/Si [1,16,17]. By comparing the effective Pockels coefficient for the mixed films, we see that the strongest response is observed for the e-beam Ti sample. XRD of this sample indicates a large fraction of in-plane oriented BTO as compared to the two K-cell Ti samples (Fig. 5(b)).

5. Conclusion

In conclusion, for epitaxial BTO/Si, we measure an increasing EO response for films with increasing *a*-axis fraction and low leakage current. We further identify post-deposition O₂ RTA as beneficial to achieve (1) in-plane tetragonal axis orientation and (2) full oxidation of BTO. Future work should focus on numerical simulations (based on the Pockels tensor, domain structure, field orientation, and angle of incidence) for modeling the response of *c*-axis domains. Such analysis might allow more

accurate modeling of the electro-optic response of *c*- and *a*-axis domains in films with mixed domains to extract the full Pockels tensor of these films.

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Fig. 1: RHEED patterns for (a) SrZintl template on Si along Si {110}, (b) 6 nm STO along STO {110}, and (c) 90 nm BTO along {110}. (d) The BTO <210> surface unit cell was monitored during growth. An extra streak appears in the RHEED pattern for the Ti-rich surface, indicating a doubling of the surface unit cell size. (e) In a line scan taken during one unit cell of BTO deposition (120 s), the extra streak disappears for stoichiometric BTO.

Fig. 2: Atomic force microscopy (AFM) of the as-grown sample (a) reveals many small particles (presumably BaOx) on the surface. After soaking in water for 4 hours (b), few particles remain.

Fig. 3: (a) Electro-optical characterization quantifies rotation (δ) of the polarization (ϑ_p) of a laser beam transmitted through pairs of lithographically defined electrodes. (b) Thickness-normalized electro-optic response $\delta' = \delta / (E_{AC} \cdot t)$, as a function of offset (DC) field for a-axis, mixed, and c-axis films.

Fig. 4: (a) Symmetric 2θ - ω scan of a 40-nm BTO film as a sample undergoes a series of 30 min RTA in O₂ at incremental temperatures (500-850°C). (b) Corresponding rocking curves about the (002) BTO Bragg peak. (c) Corresponding FWHM and out-of-plane lattice constants over the annealing series

Fig. 5: (a) Leakage current and (b) symmetric 2θ - ω scan for a series of films with varied growth conditions.

Sample	Oxygen source	Ti source	Thickness (nm)	Leakage current (A)	r_{eff} (pm/V)	FWHM (°)	a_{BTO} (Å)
A	Molecular	K-cell	90	10^{-3}	N/A	0.75 ± 0.07	4.023 ± 0.008
A'	Anneal	K-cell	90	10^{-7}	46	0.79 ± 0.11	4.031 ± 0.009
B	Plasma	K-cell	90	10^{-7}	39	0.40 ± 0.05	4.028 ± 0.004
C	Plasma	E-gun	80	10^{-7}	50	N/A	3.978 ± 0.009

Table 1: Pockels coefficients for samples grown under various growth conditions.