

Synergetic role of strain relaxation and photoexcitation for enhanced nanoscale piezoelectricity in freestanding BaTiO₃ thin films

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Strain engineering has emerged as a strategic approach for modulating the piezoelectric and ferroelectric properties of thin films. We investigated local piezoelectric properties in clamped and freestanding epitaxial BaTiO₃ films via piezoresponse force microscopy. The freestanding membrane exhibits a $\sim 300\%$ increase in the effective piezoelectric coefficient compared to the clamped films, driven by increased nonlinearity. Quantitative analysis reveals about fourfold increase in the nonlinearity parameter, originating from enhanced domain wall motion enabled by strain relaxation after removal of substrate-induced clamping. Our molecular dynamics simulations further support about threefold increase in domain-wall velocity in the freestanding film. Additionally, under optical excitation, the membrane exhibits a photoinduced enhancement of the piezoelectric response arising from coupled photostriction effect and light-driven domain wall motion. Density functional theory calculations reveal $\sim 2\%$ decrease in the out-of-plane lattice parameter of the freestanding membrane under optical excitation, consistent with the observed photoinduced deformation. However, the corresponding change in the clamped film ceases to exist. These results identify substrate clamping as a critical limitation to piezoelectric performance and establish freestanding ferroelectric membranes as promising platforms for low-power electromechanical and optoelectronic devices.

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I. INTRODUCTION

Ferroelectric materials exhibit intriguing properties driven by strain, such as electromechanical response [1], electrocaloric effect [2], flexoelectric effect [3], photovoltaic effect [4], and photoelectrochemical performance [5]. These properties in ferroelectric thin films can be tuned by engineering lattice distortions through substrate-induced strain in epitaxial films or by applying *in situ* stress or external fields [6–8]. For example, Kelley *et al.* demonstrated thickness-dependent reduction in the effective piezoelectric coefficient ($d_{33\text{eff}}$) of BaTiO₃ (BTO) thin films, decreasing from ~ 20.5 pm/V for 80 nm to ~ 2 pm/V for 10 nm films. The reduction of the $d_{33\text{eff}}$ in BTO film is attributed to the enhancement of depolarization-field screening with strain,

where in-plane compressive strain varies from fully relaxed to 2.05% from 80 nm to 10 nm film [9]. Additionally, Shafir *et al.* observed that substrate-induced strain strongly correlates with the photovoltaic response in BTO thin films. Strain engineering modifies the crystal symmetry and electronic band structure, thereby enhancing carrier separation and current generation in the BTO films [10].

However, manipulating the strain states in epitaxial ferroelectric films poses a significant constraint due to the mechanical boundary conditions imposed by the substrate. The recent development of materials synthesis via substrate release or transfer on arbitrary substrates provides a versatile platform for exploring fascinating physical properties while maintaining the epitaxial nature of the films [11–13]. In this regard, freestanding membranes offer the ability to tune the strain through on-demand *in situ* strain engineering, demonstrating functionalities such as enhanced piezoelectricity, large uniaxial strain, and fast polarization rotation [11]. In addition, freestanding membranes have exhibited an optically tunable strain of 0.047%, further broadening their potential for integration into light-controlled electromechanical systems [14]. Recently, we also demonstrated the effect of strain relaxation on optical control polarization switching in a freestanding BTO membrane, opening up the possibility of

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optically controlled devices [15]. Overall, ferroelectric membranes experience a range of intriguing behaviors, including large uniaxial strain, dielectric tunability, polarization rotation, and polarization switching kinetics [15–18]. Therefore, this naturally leads to the question of what the main contributing factors are that drive the increase in electromechanical response and tunable ferroelectric properties in the membrane. Do these contributing factors respond to external stimuli, such as light, in a similar way to enable remote control operations? Study of such behavior can contribute substantially to the understanding of the interactions between piezoelectric properties, strain relaxation, substrate clamping, and external stimuli like light.

In this work, we compare the local piezoelectric responses using piezoresponse force microscopy (PFM) of 18 nm epitaxial BTO films grown on (001) Nb-doped SrTiO₃ (Nb:STO) substrates, referred to as clamped films, and freestanding membranes transferred onto indium tin oxide (ITO) substrates. Using contact-resonance PFM (CR-PFM), we demonstrate that the enhanced piezoelectricity in the freestanding membrane originates from an increase in non-linearity, which contributes to domain wall motion and plays a dominant role in increasing electromechanical behavior. Under light illumination, the piezoelectric response is enhanced through a combined contribution from intrinsic photoinduced deformation and extrinsic domain wall motion. The effect of strain relaxation on domain wall motion and photoinduced change in unit cell volume is further confirmed by molecular dynamics (MD) simulations and density functional theory (DFT) calculations, respectively. These findings establish the robustness of freestanding ferroelectric membranes and highlight their potential for remotely controlled photoactuation and optoelectronic device applications.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Synthesis of BTO film and transfer of membrane

BTO film was also grown on Nb-doped STO substrate to evaluate the influence of substrate-induced strain on the piezoelectric properties, known as clamped film, as schematically shown in Fig. 1(a). For freestanding membrane synthesis, BTO films were epitaxially grown on TiO₂-terminated (001) SrTiO₃ (STO) substrates with Sr₄Al₂O₇ (SAO) buffer layers using oxide molecular beam epitaxy at 850 °C and an oxygen pressure of 1×10^{-6} Torr. The conventional water-assisted delamination process was employed to remove the sacrificial layer, and subsequently, the freestanding BTO membrane was transferred onto an ITO substrate, as schematically shown in Fig. 1(a). Detailed procedures for the film transfer and XRD measurement details are provided elsewhere [15,17].

B. PFM measurements

The PFM and CR-PFM measurements were performed using a Bruker Dimension Icon AFM and SCM-PIT-V2 (Pt/Ir-coated Si) cantilevers. Prior to the measurement, a standard calibration procedure was followed using a ferroelectric BTO crystal [19]. PFM measurements were performed with a 2 V ac bias. Switching spectroscopy measurements are performed in the off-field conditions. CR-PFM was measured

by keeping the force between the tip and the sample constant while varying the ac bias voltage. Conductive AFM (c-AFM) measurements were performed in contact mode for I-V characteristics under dark and illumination. The built-in current amplifier (sensitivity range 1 pA–100 nA) was calibrated prior to measurement using a 10 M Ω reference resistor, enabling quantitative current detection. Photoinduced PFM measurements on the freestanding membrane were performed under bottom illumination using a 365 nm LED light source with 1 W/cm² intensity (Thorlabs M365FP1) coupled to a multi-mode optical fiber. The photoinduced PFM measurements on the BTO/Nb:STO sample were carried out under top illumination using a 378 nm laser with 1 W/cm² intensity (Vortran Laser Technology). The area of the phase image under dark and illuminated conditions is extracted using ImageJ. The top and bottom illumination setups are shown in the Supplemental Material (Fig. S1) [20].

C. MD simulations

To estimate the velocities of the domain wall under various epitaxial (001) strains, we run coarse-grained molecular dynamics simulations using the open-source feram code [21] based on the effective Hamiltonian by Zhong *et al.* parametrized by DFT data [22–24]. We used systems of size $164 \times 164 \times 46$ f.u. under 3D periodic boundary conditions, and initialized them to contain two equi-volume tetragonal domains with polarization along the $\pm z$ directions. The systems are well equilibrated at 260 K using the Nosé-Poincaré thermostat with a time step of 1 fs [25]. As the domain wall movement is a kinetic process, three independent simulations are done for each strain value and an external electric field of 200 kV/cm. Strain range of -0.15% to $+0.1\%$ are sampled and the strain values are relative to 3.986 Å, which is the lattice constant for the metastable cubic phase at 0 K in our model. The lattice constant used to estimate the strain is 3.986 Å, while the unstrained case the lattice constant is 3.984 Å. Note that the influences of interfaces and surfaces, including depolarization, interface termination, and atomic relaxation, were neglected. The domain wall velocities are determined using the displacement of the domain wall center within 1 ~ 10 ps (The first 1 ps were excluded from the analysis, to exclude the nonequilibrium initial boost of the wall velocity under instantaneous field applications). The domain wall center is estimated by fitting the mean-polarization per x -layer $\langle P_z \rangle_x$ every 1 ps via $\langle P_z \rangle_x = P_0 \cdot \tanh(\frac{x-x_0}{d_{DW}}) + \varepsilon(x)$ [26]. Here, P_0 and d_{DW} saturation polarization and the width of the wall, respectively. The second term $\varepsilon(x)$ accounts for polarization response on the applied field within domains, including linear dielectric response and transient negative capacitance. We estimated intrinsic piezoelectric response by comparing equilibrium lattice constants of strained (1% compressive) and unstrained (freestanding) single domain tetragonal BTO (at 260 K) under an external electric field (100 kV/cm; below the coercive field of single domain BTO at 260 K) parallel and antiparallel of the tetragonal polarization direction. It is to be noted that the upper bound of the piezoelectric response for 180° multidomain state would be the difference in lattice constants of single domain structures with polarization parallel and antiparallel to the electric field, i.e., $(c_0^{E_{\text{parallel}}} - c_0^{E_{\text{antiparallel}}}) \text{ Å}$.

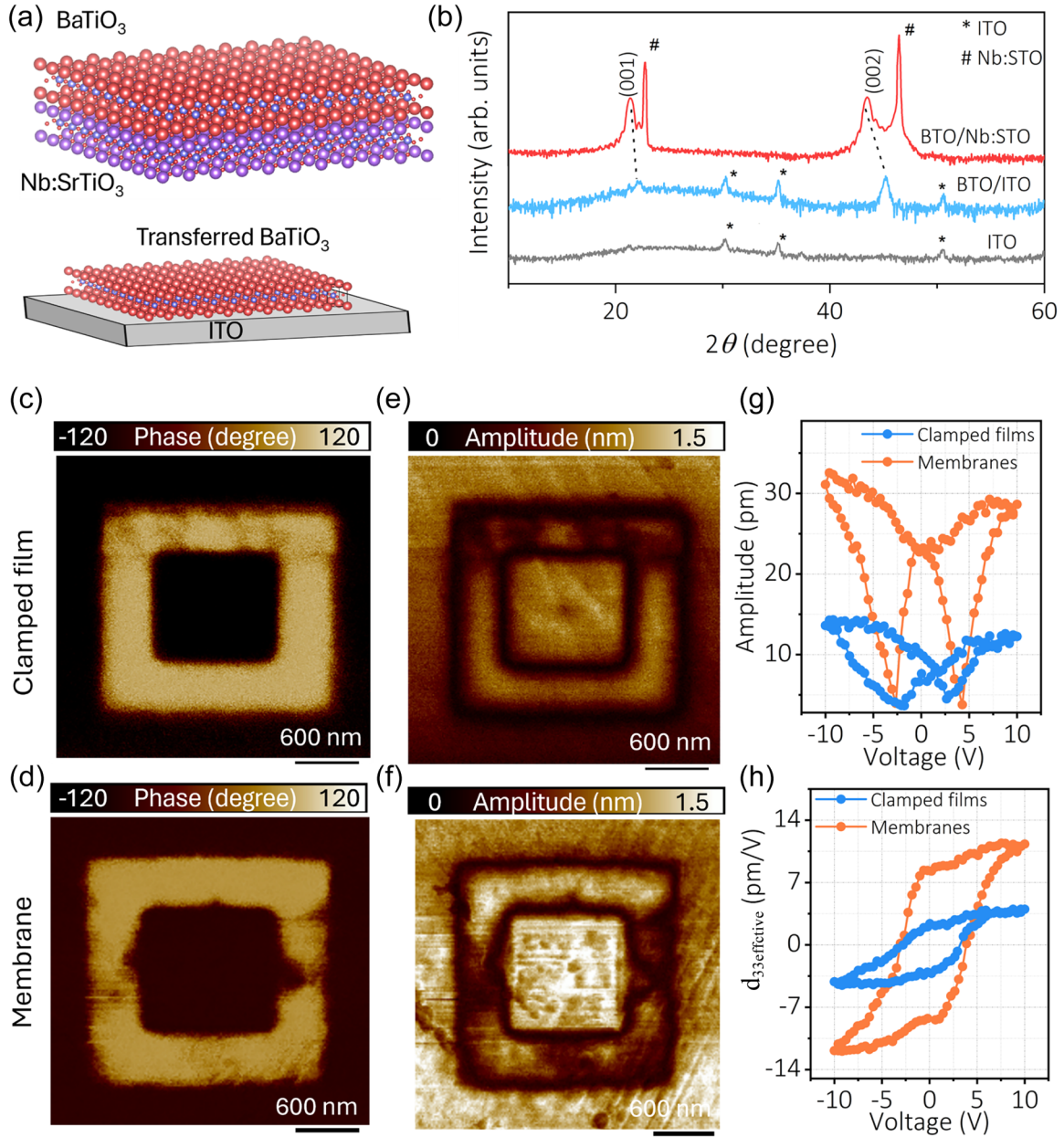


FIG. 1. (a) Schematic representation of BTO grown on Nb:STO substrate and membrane transferred to ITO after the sacrificial layer removal. (b) XRD pattern showing strain relaxation in the freestanding film compared to the clamped film. PFM phase and amplitude response of (c), (e) clamped (d), (f) freestanding BTO thin films. (g) Amplitude and (h) $d_{33\text{eff}}$ loop of freestanding membrane and clamped BTO films.

D. DFT calculations

DFT simulations of bulk tetragonal BTO were carried out using the *ab initio* package ABINIT with Wu-Cohen exchange–correlation functionals and Fermi-Dirac smearing of 0.1 eV [27,28]. A plane-wave energy cutoff of 952 eV and an $8 \times 8 \times 8$ k -point mesh were used, with convergence thresholds of 5×10^{-7} eV/Å for self-consistency and 2.5×10^{-5} eV/Å for ionic forces, ensuring high numerical accuracy for structure stabilization. Above-bandgap optical excitation was modeled by promoting 0–0.1 e/f.u. to the conduction band, following established approaches to simulate photoexcited carrier populations [29].

E. COMSOL simulation

To quantify the contribution of light-induced heating in our films, we simulated temperature distributions using the heat transfer module in COMSOL MULTIPHYSICS. Heat transfer in solids is described by $\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot q = Q$ with the heat flux defined as, $q = -k \nabla T$. Here, ρ is the material density, C_p the heat capacity, T temperature, Q as absorbed power density from the incident radiation (assuming full absorption), and k as thermal conductivity. For radiation, we considered the ambient surroundings as a boundary using a boundary condition based on the Stefan-Boltzmann law.

III. RESULTS AND DISCUSSIONS

The strain relaxation due to the removal of substrate-induced clamping in the freestanding membrane is analyzed through the peak shift of the XRD pattern [Fig. 1(b)], as described in our previous publication [15]. The lattice parameters of the clamped film are extracted from reciprocal space mapping (RSM) around the (103) reflection, providing $a = 3.904 \text{ \AA}$ and $c = 4.160 \text{ \AA}$ (Fig. S2a in the Supplemental Material) [20]. The RSM around (103) for the freestanding membrane shows a very weak response. The RSM around (002) is shown in Fig. S2b in the Supplemental Material [20]. For the freestanding film, the out-of-plane and in-plane lattice parameters were determined from the 2θ - ω scans around (002) and (011) peaks shown in the Supplemental Material (Figs. S2c and S2d) [20], extracting $a = 3.992 \text{ \AA}$ and $c = 4.014 \text{ \AA}$. It is observed that the c/a ratio decreases from 1.065 for the clamped film to 1.005 for the freestanding film, reflecting significant strain relaxation upon release from the substrate. Also, our clamped film exhibits a 2.2% compressive strain, while the freestanding film is fully relaxed. We use PFM measurements to probe the initial ferroelectric state and switching behaviors of clamped [Figs. 1(c) and 1(e)] and freestanding BTO [Figs. 1(d) and 1(f)] films. Applying bias voltages of -10 V and $+10 \text{ V}$ to the PFM tip produced a box-in-box switching pattern, where the bright and dark contrasts correspond to upward and downward polarization orientations, respectively. The dark contrast is observed in the unpoled regions of the clamped and freestanding membranes, indicating that both materials are self-polarized with polarization pointing downward [19,30]. The comparison between the out-of-plane butterfly shaped amplitude loop of the clamped and freestanding membrane is shown in Fig. 1(g). The significantly enhanced amplitude response in the freestanding membrane is explained by the fact that the clamped film is rigidly attached to the substrate, whereas freestanding membranes have a vertical degree of freedom for motion [31]. Therefore, it favors the vertical deflection of the materials. This behavior is also reflected in the $d_{33\text{eff}}$ loops of the clamped film and freestanding membrane [Fig. 1(f)], showing $\sim 300\%$ increase of remanent $d_{33\text{eff}}$ ($d_{33\text{eff}}^R$) in the freestanding film. We also ruled out the contribution of electric field-induced buckling to the observed $d_{33\text{eff}}$ response by comparing the surface topography before and after the application of an electric field through the PFM tip, as shown in the Supplemental Material (Fig. S3) [20]. The nearly identical surface profiles under both conditions indicate that electric field-induced buckling does not significantly contribute to the measured piezoelectric response. In order to validate the increase in the piezoelectric response, we have extracted the intrinsic piezoelectric value for the clamped (1% compressive strain) and freestanding BTO from our simulation results. It is estimated that the upper bound of piezoelectric response for the clamped and freestanding film is 0.004 and $0.019 \text{ \AA}$, corresponding to $\sim 375\%$ increase in intrinsic piezoelectric response for the freestanding film. Therefore, it is important to note that freestanding membranes undergo larger deflections under an applied electric field, enabling greater lattice distortion due to vertical degrees of freedom. In contrast, substrate-induced clamping in the BTO/Nb:STO

films restricts this motion, resulting in poor piezoelectric response.

In general, piezoelectric response comprises both intrinsic and extrinsic contributions [32,33]. The intrinsic component arises from lattice deformation, whereas the extrinsic component originates from domain wall and interphase boundary motion. The extrinsic contributions can be quantitatively measured through macroscopic piezoelectric hysteresis measurements or by nonlinearity measurements via PFM [34–36]. To understand nonlinear behavior, we used the CR-PFM technique to measure the local amplitude response for clamped films and freestanding membranes in the Rayleigh region by applying 0–50% of the coercive voltage at the contact resonance frequency. To avoid nonlinearities in the amplitude signal caused by cantilever nonlinearities, the CR-PFM measurement is performed at a constant applied force during the hold period on the sample [37,38]. The deflection error as a function of time during the CR-PFM measurements is shown in the Supplemental Material (Fig. S4a) [20], with the hold period indicated by the dotted line. In CR-PFM, pixel-by-pixel amplitude signals are acquired across the scanned area at the contact resonance frequency to construct a full amplitude map. The frequency-dependent amplitude response for a representative pixel is shown in the Supplemental Material (Fig. S4b) [20]. Amplitude maps collected under varying ac bias voltages for both systems are presented in Fig. 2. Pixel-by-pixel topography maps for the respective areas are provided in Fig. S5 [20]. The amplitude distributions for the respective system are plotted for the applied bias condition (Figs. S6 and S7) [20], and the extracted mean amplitude value is plotted as a function of the applied bias in Fig. 2(c). Consequently, the amplitude response is fitted with the polynomial function $A_{\text{Max}} = \alpha + \beta V_{\text{ac}} + \gamma V_{\text{ac}}^2$ to understand their nonlinear properties, where A_{Max} is the detected amplitude response and V_{ac} is the excitation ac voltage, β is a linear electromechanical coefficient, and γ is a higher-order coefficient representing nonlinearities [33]. The extracted values of α , β , and γ for clamped and freestanding films are $-3.22 \times 10^{-12} \text{ m}$, $2.28 \times 10^{-11} \text{ m/V}$, and $-8.17 \times 10^{-13} \text{ m/V}^2$ and $-7.87 \times 10^{-12} \text{ m}$, $5.17 \times 10^{-11} \text{ m/V}$, and $-8.38 \times 10^{-12} \text{ m/V}^2$, respectively. Figure 2(c) depicts that the freestanding film exhibits higher nonlinearity compared to the clamped film. The normalized nonlinear factor, represented by the γ/β ratio, is nearly fourfold higher in the freestanding film. In most cases, the nonlinearities in ferroelectrics arise predominantly from the motion of domain walls or phase boundaries, and variations in the nonlinearity influence the piezoelectric effect in the materials [39]. For instance, decreased piezoelectric response has been correlated with the decrease in nonlinear response at the grain boundary, resulting from a change in domain wall configurations that act as a strong pinning source for domain wall motion [40]. It is to be noted that the nonlinearity in freestanding and clamped films mainly arises from the motion of 180° domain walls. The motion of these domain walls is directed perpendicular to the applied electric field across the film plane. In our case, substrate clamping pins the domain wall motion via mechanical boundary conditions in the clamped film, resulting in a lower piezoelectric effect than in the freestanding BTO membrane. In contrast, enabling vertical degree of freedom in freestand-

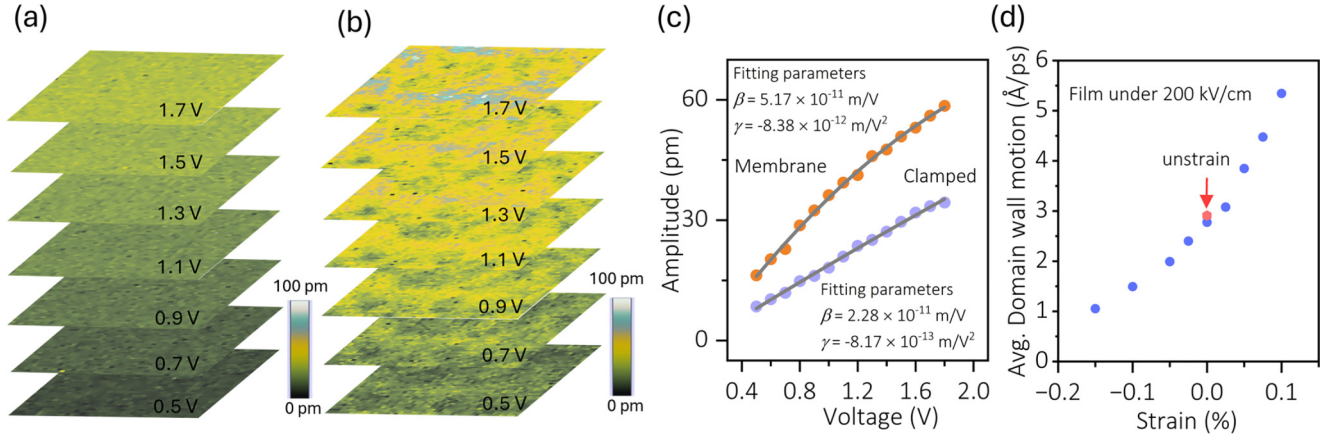


FIG. 2. CR-PFM amplitude response obtained by varying applied ac bias for (a) clamped BTO and (b) freestanding films. (c) Average amplitude response with respect to bias voltage for clamped BTO and freestanding membrane. (d) Domain wall velocity with respect to the strain of the materials is calculated under an applied field of 200 kV/cm.

ing films favors the domain wall motion, contributing to the higher piezoelectric effect. To quantify the exact difference in domain wall motion between the clamped and freestanding films, we performed MD simulations. We determined that the domain wall velocity of the freestanding film at 200 kV/cm is 2.91 Å/ps [Fig. 2(d)], which is nearly three times faster compared to the clamped film with 0.15% compressively strained (1.08 Å/ps), which contributes to the increase in nonlinear response in the membrane.

To further understand how illumination influences the piezoelectric response, PFM amplitude and phase hysteresis loops are obtained in the freestanding membrane using switching spectroscopy PFM under dark and illuminated conditions (Fig. 3). PFM amplitude and phase loops are collected at 25 different points under both dark [Fig. 3(a)] and illumi-

nated [Fig. 3(b)] conditions. The corresponding $d_{33\text{eff}}$ loops obtained from the PFM measurement are plotted for each case in Fig. 3(c) [15]. Under illumination, the $d_{33\text{eff}}^R$ value ($= \frac{d_{33}^{R+} - d_{33}^{R-}}{2}$) increases notably compared to that measured in the dark, where d_{33}^{R+} and d_{33}^{R-} denote effective remanent d_{33} value measured in the positive and negative y axis, respectively. For direct comparison, the $d_{33\text{eff}}^R$ values under dark and illuminated conditions are plotted in Fig. 3(d). However, the clamped film shows negligible variation in $d_{33\text{eff}}$ loops between dark and illuminated conditions, confirming the absence of a measurable photoinduced piezoelectric effect, as shown in the Supplemental Material (Fig. S8) [20]. The observed increase of the remanent piezoelectric response for the freestanding membrane under illumination could result from four reasons: localized heating, optically induced charge migration due to

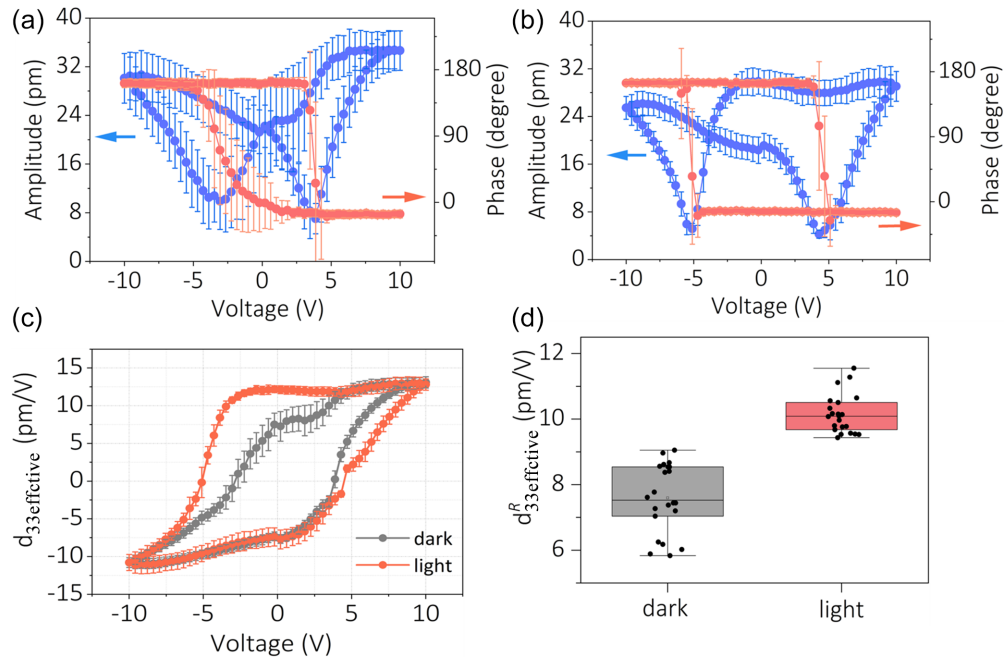


FIG. 3. Amplitude and phase hysteresis loop of a freestanding membrane under (a) dark and (b) 365 nm illumination with 1 W/cm² intensity. (c) $d_{33\text{eff}}$ loop and (d) estimated $d_{33\text{eff}}^R$ under both dark and illuminated conditions for the freestanding membrane.

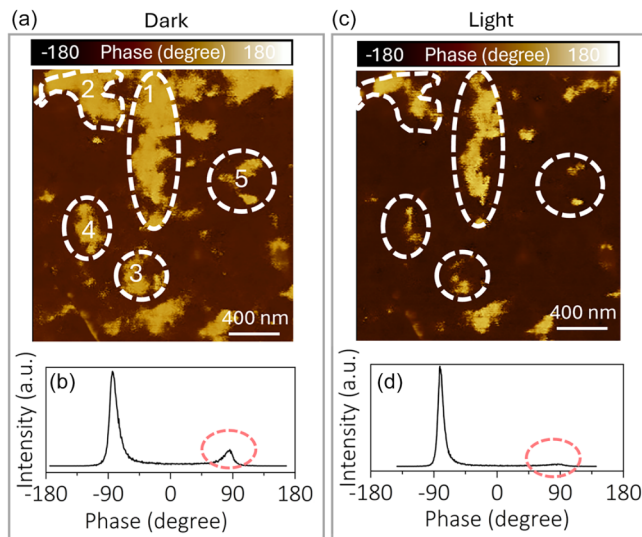


FIG. 4. PFM phase response and the phase distribution of the freestanding membrane under (a), (b) dark and (c), (d) illumination.

increased photoconductivity, photostimulated domain switching, and photoinduced lattice distortion [14,41]. In our case, we eliminated the local optical heating using COMSOL simulation [42,43]. It is observed that under illumination with an intensity of 1 W/cm^2 , the material changes its temperature by $\sim 3 \text{ K}$ (Fig. S9) [20], which is not sufficient to cause the $d_{33\text{eff}}^R$ value to enhance by $\sim 40\%$. The increase in photoconductivity in the freestanding membrane is evaluated by measuring the current-voltage characteristic under dark and illuminated conditions using a conducting AFM tip, as shown in the Supplemental Material (Fig. S10) [20]. It is observed that the photocurrent response is significantly increased at -2 V , indicating optically induced charge carrier generation due to photoconductivity in the freestanding membrane [14].

The photoinduced domain evolution under dark and illuminated conditions is examined using PFM phase imaging [Figs. 4(a) and 4(c)], with the regions of change highlighted by white dotted boundaries. Under illumination, a clear phase reversal is observed, indicating a transition from upward (bright contrast) to downward (dark contrast) domain orientation. Upon illumination, the upward-oriented domain's areas of the numbered regions (1, 2, and 3) in the PFM phase image decrease from 0.155 ± 0.03 , 0.1003 ± 0.01 , and $0.0244 \pm 0.005 \mu\text{m}^2$ to 0.1018 ± 0.06 , 0.0516 ± 0.004 , and $0.0124 \pm 0.007 \mu\text{m}^2$, respectively. Additionally, the phase distribution plots [Figs. 4(b) and 4(d)] show a reduction in intensity counts in the upward-oriented domain ($+90^\circ$), as indicated by the red dotted circle. During the domain-reversal process, illumination enhances domain wall motion, enabling upward-oriented domains to switch into the downward state. Consequently, an increase in PFM amplitude under illumination reveals a corresponding enhancement in the piezoelectric response, as shown in the Supplemental Material (Fig. S11) [20]. This behavior is attributed to light-induced domain wall motion, leading to a photoenhanced piezoelectric effect [15,28,44]. Vats *et al.* reported that continuous illumination can act as a light-induced poling mechanism, which directly contributes to the enhancement of the piezoelectric response [45]. To

investigate this, we performed PFM amplitude measurements under dark conditions and repeated the measurements in the dark condition after 5 min of illumination, shown in the Supplemental Material (Fig. S12) [20]. The amplitude showed negligible variation, indicating that the enhanced piezoelectric response in our study is not due to a persistent light-induced poling effect.

To understand the photoinduced deformation in freestanding membranes, we measure CR-PFM under both dark and illuminated conditions. The pixel-by-pixel amplitude images acquired under dark and illumination conditions are shown in Supplemental Material (Figs. S13a and S13b) [20], along with the corresponding amplitude distributions, which are compared in Fig. S13c [20]. The increase in the mean value of amplitude under illumination illustrates a light-enhanced piezoelectric effect in the freestanding membrane. During the measurements, the contact resonance frequency was continuously monitored, and the corresponding pixel-by-pixel maps and distribution plots are presented in Figs. 5(a)–5(c). A clear change in the contrast of the resonant-frequency images is observed between dark and illuminated conditions [Figs. 5(a) and 5(b)], consistent with the distribution plot showing a 1 Hz downward shift in frequency relative to the resonance measured under dark conditions. It is worth noting that, as the resonance frequency of the system depends on both the geometrical characteristics of the tip and the tip-sample mechanical contact characteristics, the force between the tip and the sample is also kept constant. The deflection error as a function of time during the CR-PFM measurements is shown in the Supplemental Material (Fig. S14) [20], with the hold period indicated by the dotted line. Therefore, changes in resonant frequency indicate changes in the stiffness of the sample. The lower resonance frequency indicates a softer material. It is important to note that the resonance-frequency variability under applied ac bias is $< 0.1 \text{ Hz}$; therefore, the observed $\sim 1 \text{ Hz}$ shift under illumination is attributed to photoinduced variation in the material rather than instrumental artifacts. Under light illumination, deformation alters the stiffness due to the photostriction effect, resulting in reduced strain and, consequently, softening of the material. This behavior is further confirmed by the deflection error versus displacement analysis, as shown in the Supplemental Material (Fig. S15) [20], where the slope proportional to the Young's modulus of the materials decreases under illumination, evidencing an increase in material softness [31]. We also performed CR-PFM measurements on the clamped BTO film under both dark and illuminated conditions. No noticeable change in the contact resonance frequency was observed, indicating the absence of photoinduced deformation in the clamped BTO film, as shown in the Supplemental Material (Fig. S16) [20]. The DFT calculations further confirm the photoinduced deformation in the freestanding membrane. Figure 5(d) illustrates the evolution of lattice parameters under excitation, revealing a reduction of $\sim 2\%$ in c value for the freestanding membrane, which does not occur in the clamped film [Fig. 5(e)]. Overall, photoexcited carriers lower the ferroelectric instability, the tetragonal strain, and the energy barrier for domain wall motion. As a result, the material becomes more responsive to external electric fields, allowing for a change in volume of the unit

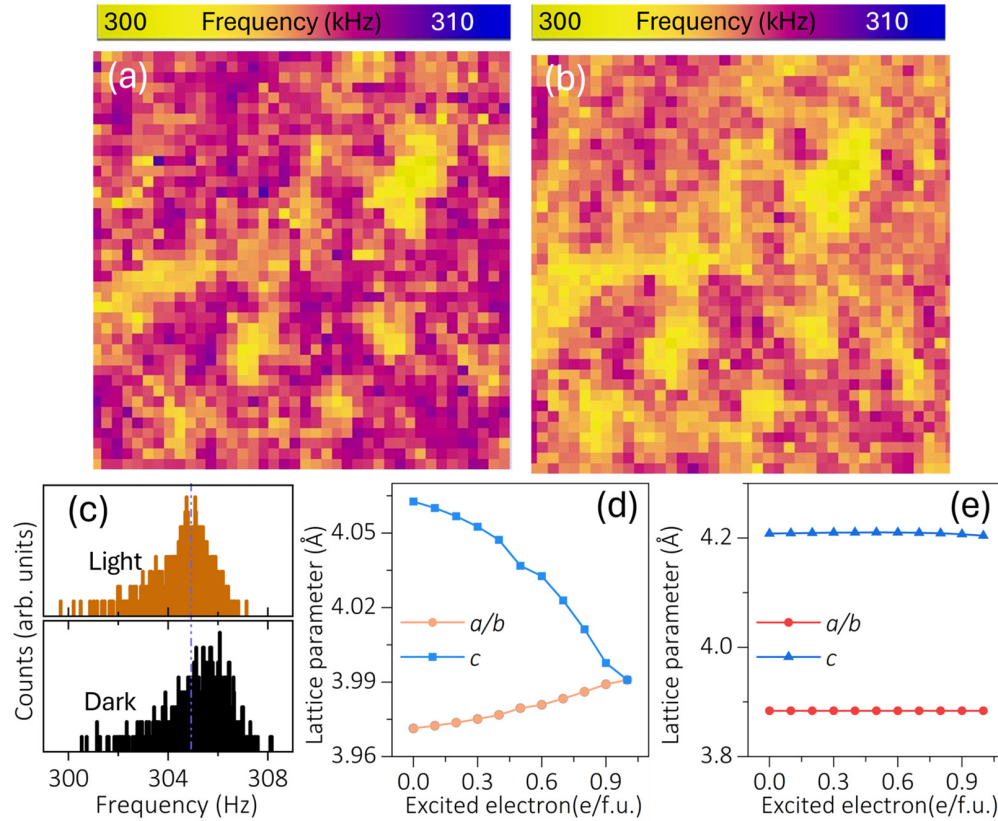


FIG. 5. CR-PFM frequency response of freestanding BTO film under (a) dark and (b) illumination. (c) Frequency distribution plots in the respective conditions. (d) The DFT calculations show the change of lattice parameters of the freestanding film under various electron excitation. (e) DFT calculation on the clamped film (2.2% compressive strain) demonstrates no noticeable change in lattice parameter under increased electron excitations.

cell and thereby enhancing the overall photoinduced piezoelectric effect. Therefore, in our BTO membrane, this light-enhanced piezoelectric effect originates from a synergistic combination of light-induced domain wall motion and photostriction effect.

IV. CONCLUSIONS AND OUTLOOKS

In summary, our results demonstrate that the freestanding membrane exhibits $\sim 300\%$ enhancement in the d_{33}^R compared to the clamped BTO film, primarily driven by an increase in domain wall-driven nonlinear electromechanical response. The nonlinearity (γ/β ratio) in the freestanding membrane is nearly four times larger than that of clamped BTO films, indicating a substantial increase in domain wall motion. This increase in domain wall motion results from the complete strain relaxation in the freestanding membrane, facilitated by the removal of substrate-induced mechanical clamping. MD simulations reveal 250% higher domain wall velocity in the freestanding film compared with the clamped film having 0.2% compressive strain. We also demonstrate that the freestanding membrane exhibits a photoinduced piezoelectric effect. The photoinduced enhancement in piezoelectric response is attributed to the combined effect of photoinduced domain wall motion and lattice deformation. The effect of local heating on the photoinduced piezoelectric properties is eliminated in our work, as the temperature

change is only 3 K under 1 W/cm^2 illumination. Additionally, our DFT results show that the lattice parameter c value reduces to $\sim 2\%$ under optical excitations. Overall, this work highlights the impact of strain relaxation and photoexcitation on the piezoelectric properties of ferroelectric materials. These observations suggest that the effects of mechanical clamping by the substrate are broadly applicable to epitaxial ferroelectric oxides, and understanding their properties in the membrane state facilitates the design of remote-controlled low-power nanoelectromechanical systems.

Importantly, the large strain gradients imposed by the PFM tip during nanoscale measurements can induce a flexoelectric response in both ferroelectric and paraelectric thin films. In particular, the mechanical compliance of freestanding membranes may contribute to flexoelectric-enhanced d_{33}^R , a contribution that cannot be excluded [46]. Furthermore, illumination may further enhance d_{33}^R through a flexophotovoltaic effect induced strain, thereby influencing the overall electromechanical response [47,48]. In this work, we primarily focused on the piezoelectric response arising from domain wall motion and lattice deformation, and the contribution of flexoelectricity was not explicitly considered. Nevertheless, quantitatively separating the piezoelectric and flexoelectric components of the electromechanical response could provide a more comprehensive understanding of the observed behavior and enable accurate quantification of the overall electromechanical response in freestanding membranes.

Separating such contributions would require dedicated experiments involving controlled strain gradients and carefully designed membrane geometries, which are beyond the scope of our present study. These studies could establish an additional route for tuning electromechanical properties through multiple external stimuli, representing a promising direction for low-power MEMS technology and optoelectronic devices.

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DATA AVAILABILITY

The data that support the findings of this study are available in the article and its Supplemental Material [20]. The data that support the findings of this article are openly available [49].

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