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Boosting piezoelectricity under illumination via the bulk photovoltaic effect and the Schottky barrier effect in BiFeO<sub>3</sub>

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## Abstract

Piezoelectricity is a key functionality induced by conversion between mechanical and electrical energy. Enhancement of piezoelectricity in ferroelectrics often has been realized by complicated synthetical approaches to host unique structural boundaries, so-called morphotropic phase boundaries. While structural approaches have been well-known, enhancing piezoelectricity by external stimuli has yet to be clearly explored despite their advantages of offering not only simple and in-situ control without any prior processing requirement, but compatibility with other functionalities. Here, we show that light is a powerful control parameter to enhance the piezoelectric property of a BiFeO<sub>3</sub> single crystal. Our series of PFM and C-AFM based measurements under illumination reveal a locally enhanced effective piezoelectric coefficient,  $d_{zz}$ , eventually showing almost a seven-fold increase. We explain this phenomenon with theoretical models by introducing the two main underlying mechanisms attributed to the bulk photovoltaic effect and Schottky barrier effect, involving the role of open circuit voltage and photocharge carrier density. These results provide key insights to light-induced piezoelectricity enhancement, offering its potential for multifunctional optoelectronic devices.

BiFeO<sub>3</sub> (BFO) has remained arguably one of the most promising functional materials with several intriguing properties such as room temperature multiferroism,<sup>[1]</sup> magnetoelectric coupling,<sup>[2]</sup> domain wall conductance,<sup>[3]</sup> and metal-insulator transitions.<sup>[4]</sup> Ferroelectricity and piezoelectricity of bulk BFO are important functional properties for device implementation.

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BFO exhibits the largest switchable remnant polarization (e.g.  $100 \mu\text{Ccm}^{-2}$ )<sup>[5, 6]</sup>, but a relatively low piezoelectric coefficient,  $d_{33}$  of  $\sim 15\text{-}60 \text{ pm V}^{-1}$ . However, approaches by mixing with other materials,<sup>[7]</sup> doping,<sup>[8]</sup> and thin-film engineering<sup>[9]</sup> have been implemented to enhance piezoelectric properties of BFO. The key to these efforts is to structurally engineer the material for formation of the morphotropic phase boundary (MPB), consisting of two different phases with low energy barriers, like that of lead-based oxides.<sup>[10]</sup> Instead of the synthetical processes with complexity, alternative approaches by applying external stimuli can be rather simple and effective to enhance piezoelectricity and spontaneous polarization. Very recently, using localized fields within Schottky barriers in centrosymmetric materials has proven to locally break the symmetry, offering alternative tweaking parameters to generate interface piezoelectric and pyroelectricity effects.<sup>[11]</sup>

Here, we use light as the only control parameter to enhance piezoelectricity of a BFO single crystal. For this, a laser light source of 405 nm wavelength ( $h\nu = 3.06 \text{ eV}$ ) is used to excite free carriers in BFO, whose bandgap energy is 2.7 eV. We show a series of vertical (out-of-plane) piezoresponse force microscopy (PFM) amplitude scans and locally measured piezoelectric signals with increasing the laser-induced photon flux, revealing the overall impact of light on largely enhanced piezoelectricity. For insights to the underlying mechanisms, we employed spectroscopic measurements of current-voltage (I-V) curves and PFM amplitude hysteresis loops under illumination, showing the close link between light effects and enhanced piezoelectricity, primarily due to the bulk photovoltaic (BPV) effect and the Schottky barrier effect. These results provide fundamental insights to establish theoretical

models of light-induced piezoelectricity enhancement with its key underlying mechanisms for multifunctional optoelectronic devices.

Ferroelectric domain patterns of a BFO crystal were initially examined by vertical PFM scans at room temperature in the dark and under illumination with increasing laser power intensities. The crystal, similar to our previously investigated crystals,<sup>[12]</sup> (see the Supporting Information for details of our sample preparations) was polished to a thin platelet of  $\sim 0.5$  mm, possessing a flat surface with a rms roughness of  $\sim 1$  nm for PFM measurements. A series of vertical PFM amplitude scans using an ac excitation voltage,  $V_{ac}$  of 2 V under illumination is shown in **Figure 1** for an overview of spatially resolved piezoelectricity. For this, we used the laser power up to  $\sim 30$  mW, corresponding to the photon flux of  $9.8 \times 10^{18}$   $\text{cm}^{-2}\text{s}^{-1}$  (see the Supporting Information for details of the conversion between the laser power and photon flux). In Figure 1a, the vertical PFM amplitude (top) and phase (bottom) scan images in the dark show pristine ferroelectric domain structures, consisting of up (dark) and down (bright) domains, implying possible polarization variants along the (111) directions of the rhombohedral symmetry as usual for a BFO single crystal. These represent the typical domain pattern previously analyzed in detail.<sup>[12]</sup> Upon light exposure with increasing the photon flux, the series of vertical PFM amplitude scans shows evolution of increasing piezoresponse signals, appearing brighter all over the scan area. The pristine up domains appear much brighter than the rest, indicating the largest piezoresponse signals. For more detailed analysis, cross-section profiles of the surface displacement converted from the piezoresponse signals (see Supporting Information for details of the conversion) along the white lines are shown in Figure 1f. Initially, the black profile of the pristine scan (a) shows

six dips of minimum piezoresponse signals at domain walls, while both up and down domains show almost comparable piezoreponse signals. The red profile of the scan (b) reveals light-induced enhancement of piezoresponse signals at the up domains, implying its polarization-orientation dependence, while the down domains and domain walls have similar values as the pristine state. The blue profile of the scan (c) shows an upward shift, indicating enhancement of piezoresponse signals across the whole domains and domain walls. It is interesting to note domain wall regions show such enhancement, compared to their pristine values in the dark. The green and purple profiles of the scan (d) and (e) reveal their further upward shift, indicating proportional increases of piezoresponse signals with the increased photon flux. Figure 1g shows quantitative comparison of evolving local piezoreponse signals at up, down domains, and domain walls, revealing their continuously increasing trends as a function the photon flux. Importantly, this shows a characteristic trend such that initially the piezoresponse signal of domain walls is the lowest but increases largely to be comparable with that of down domains with increasing the photon flux, and consequently even surpasses that of non-illuminated domains.

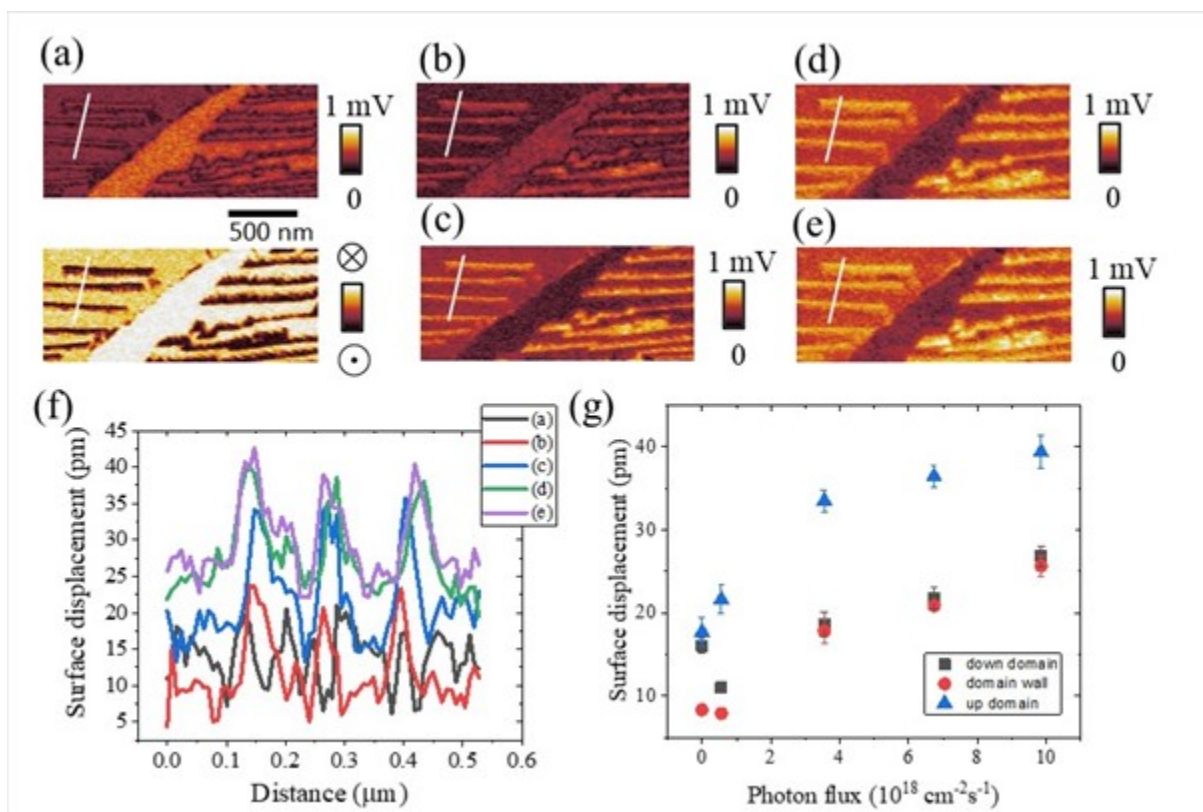
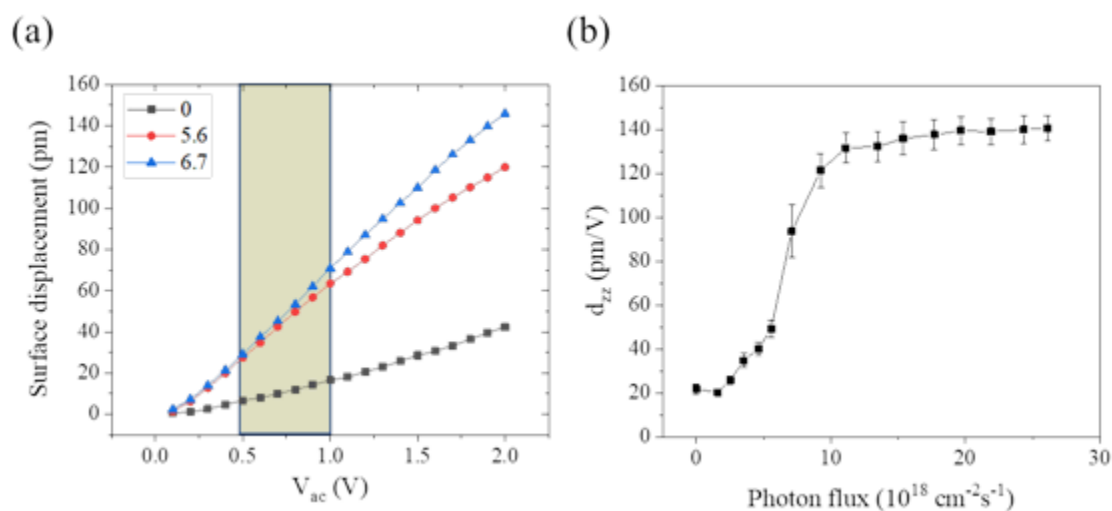


Figure 1. Spatially resolved light-induced enhancement of piezoelectricity by PFM scans. Pristine vertical PFM amplitude (top) and phase (bottom) scan images are shown in (a). A series of vertical PFM amplitude scans with the photon flux of (b) 0.6, (c) 3.5, (d) 6.7, and (e) 9.8 in the unit of  $10^{18} \text{ cm}^{-2}\text{s}^{-1}$ . (f) Cross-section profiles of the surface displacement (converted from PFM amplitude signals) along the white dotted line. (g) Evolution of the surface displacement at up, down domains, and domain walls. All these PFM scans were measured using an  $V_{ac}$  of 2 V.

For detailed quantitative characterization of piezoelectricity under illumination, we performed local spectroscopy measurements of vertical PFM amplitude signals on pristine downward ferroelectric domains by sweeping a laser power up to  $\sim 78 \text{ mW}$ , corresponding to

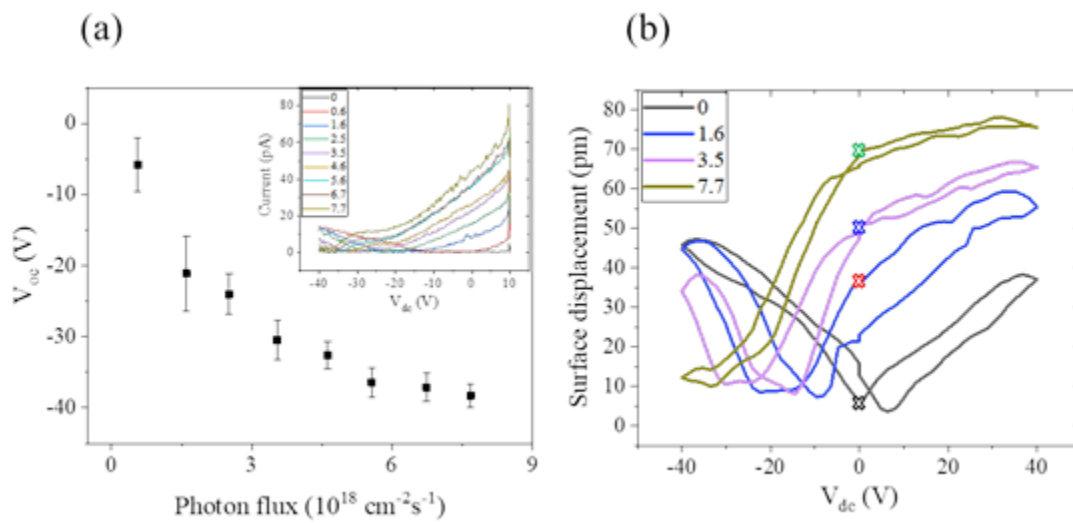
the photon flux of  $2.6 \times 10^{19} \text{ cm}^{-2}\text{s}^{-1}$ . **Figure 2a** shows the surface displacement versus  $V_{ac}$  curves obtained by sweeping up to 2 V. The slopes of these curves consisting of several data points in the yellow region indicate representative effective piezoelectric coefficients,  $d_{zz}$  (pm/V). Under illumination, these are clearly found to increase largely with increasing the photon flux, showing light-induced piezoelectricity enhancement. Figure 2b shows more detailed evolution of such light-induced enhancement of piezoelectricity with 15 representative  $d_{zz}$  values along with a large range of the increasing photon flux. It is also noticeable that the evolution of  $d_{zz}$  shows a characteristic trend such that initially it increases gradually and then sharply ( $5.6 \times 10^{18} \text{ cm}^{-2}\text{s}^{-1}$ ), eventually resulting in saturation. This quantifies enhancement of the  $d_{zz}$  from  $21 \pm 2.4 \text{ pm/V}$  (no illumination) to  $141 \pm 5.7 \text{ pm/V}$  ( $2.6 \times 10^{19} \text{ cm}^{-2}\text{s}^{-1}$ ), which is roughly a seven-fold increase. Furthermore, we note that the enhanced PFM signal returns to its pristine value by removing the light. Therefore, our results quantitatively prove that light plays a critical role in enhancement of piezoelectricity as a robust external and in-situ control parameter. The underlying mechanisms behind enhanced piezoelectricity may be related to generation of photoinduced charge carriers and their associated internal electric fields due to the bulk photovoltaic effect, as will be discussed in the following sections.



**Figure 2.** Quantitative analysis of piezoelectricity under illumination. (a) Surface displacement versus  $V_{ac}$  curves, wherein the inset shows the photon flux in the unit of  $10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ . Slopes of these curves measured in yellow region indicate the effective piezoelectric constants,  $d_{zz}$ . (b) Evolution of the 15 representative  $d_{zz}$  values with increasing the photon flux.

To unveil origins of light-induced piezoelectricity enhancement associated with its internal electric field, we performed a series of local I-V curve and PFM amplitude hysteresis loop measurements under illumination to investigate their correlation. **Figure 3a** shows the open circuit voltages ( $V_{oc}$ ) obtained from local photo I-V curves (inset) under illumination with increasing the photon flux up to  $\sim 8 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ . The BPV effect is seen with an increase of short circuit current ( $I_{sc}$ ) and  $V_{oc}$  along with the increased photon flux. Importantly, this reveals evolution of increasing  $V_{oc}$  as a function of the photon flux, implying stronger internal electric fields are generated by photoinduced charge carriers. Then, we also measured a series of PFM hysteresis loops at an  $V_{ac}$  of 1 V by sweeping a  $V_{dc}$  up to  $\pm 40$  V with increasing the

photon flux, from which after conversion, the surface displacement (pm) over the applied  $V_{ac}$  (V), is shown in Figure 3b. The surface displacement is also equivalent of the  $d_{zz}$  (see the Supporting Information for the detailed explanation). Initially, the hysteresis loop without illumination exhibits a butterfly shape of ferroelectrics with bias-dependent switching of polarization along both positive and negative bias directions. In addition, the hysteresis loop seems to show rather an increasing slope without reaching a plateau at the maximum bias sweep of  $\pm 40$  V, indicating ferroelectric polarization is not fully switched across the whole bulk material.<sup>[13, 14]</sup> Such behavior is seen due to firstly the linear relationship between the surface displacement and the  $V_{ac}$ , and secondly the non-uniform field distribution generated within the bulk by the point contact at the tip-sample surface, resulting in a continuously increase of the switched volume and the surface displacement. Under illumination with increasing the photon flux, the hysteresis loops shift towards the negative bias, resulting in asymmetric behavior with the right part of the loop stretched towards the positive bias direction. This indicates that light has an effect of applying a positive  $V_{dc}$ , simulating the effect of  $V_{oc}$ , eventually resulting in a larger  $d_{zz}$  at zero bias, as shown by the cross markers for each hysteresis loop with its corresponding photon flux.



**Figure 3.** Correlation between the bulk photovoltaic effect and light-induced piezoelectricity enhancement. (a) The  $V_{oc}$  from the photo I-V curves (inset) under illumination with increasing the photon flux. (b) The surface displacement from PFM amplitude hysteresis loops measured at an  $V_{ac}$  of 1 V by sweeping a  $V_{dc}$  up to  $\pm 40$  V. The surface displacement in (b) also represents the  $d_{zz}$  (pm/V). The cross markers show the  $d_{zz}$  values at zero bias, corresponding to the photon flux. The insets in inner part of (a) and (b) indicate the photon flux in the unit of  $10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ .

For deeper insights, we analyzed light-induced piezoelectricity enhancement in terms of the BPV effect. According to the review paper by Vasudevan et al.,<sup>[15]</sup> based on Hong et al.,<sup>[16]</sup> the surface displacement measured by PFM has two components, the first given by the true piezoelectric displacement, and the second given by the electrostatic interaction between the

$$D = D_{piezo} + D_{electrostatic} \quad (1)$$

cantilever and sample surface, as the following:

Which is:

$$D = d_{zz}V_{ac} + \frac{C'}{k^*}(V_{dc} - V_{sp})V_{ac} \quad (2)$$

Where  $C' = \frac{dC}{dz}$  is the derivative of the tip capacitance in the z-direction,  $k^*$  is the effective contact elastic stiffness, and  $V_{sp}$  is the surface potential.

In the first approximation without application of an external  $V_{dc}$  under illumination, the BPV effect will modify the  $V_{sp}$  into a value related to an  $V_{oc}$ . Under the assumption that the  $V_{sp}$  and  $V_{oc}$  are identical, then the total displacement would be rearranged as:

Which yields an effective piezoelectric coefficient under illumination as:

$$D = d_{zz}^{pl} \left( d_{zz} + \frac{C'}{k^*} \frac{C'}{k^*} V_{oc} \right) V_{ac} \quad (4)$$

According to Sturman and Fridkin,<sup>[17]</sup> the  $V_{oc}$  is given by:

$$V_{oc} = -\frac{J}{(\sigma_d + \sigma_{ph})}l \quad (5)$$

Where  $J$  is the BPV current,  $\sigma_d$  and  $\sigma_{ph}$  are the dark- and photo-conductivity respectively, and  $l$  is the effective device length. The photocurrent  $J_i$  along the  $i$ -th direction in the crystal is given by:

$$J_i = I_0 \beta_{ijk} e_i e_j^* \quad (6)$$

Where  $I_0$  is the incident light intensity,  $\beta_{ijk}$  is the BPV tensor, while  $e_i$  and  $e_j^*$  are the projections of the light-induced electric field along and perpendicular to the  $i$ -th direction of the current  $J_i$ . This relationship can be further simplified by adopting a one-dimensional form. Considering the BPV current along the direction pointing normal to the sample surface (along the top AFM tip), and the light polarization is perfectly aligned with the current direction, then using an effective Glass coefficient  $G_{zz} = \frac{1}{\alpha} \beta_{zzz}$ , the photocurrent is:

$$J_z = \alpha I_0 G_{zz} \quad (7)$$

Where  $\alpha$  is the absorption coefficient. Then, the open circuit voltage will be:

$$V_{oc} = -\frac{\alpha G_{zz} l}{(\sigma_d + \sigma_{ph})} I_0 \quad (8)$$

And the effective piezoelectric coefficient under illumination is:

$$d_{zz}^{ph} = d_{zz} + \frac{C'}{k^*} \frac{\alpha l}{(\sigma_d + \sigma_{ph})} G_{zz} I_0 \quad (9)$$

Since the piezoelectric tensor and the BPV effect tensor (as well as the Glass coefficient tensors) share the same symmetry, the additional factor to the piezoelectric coefficient has same components as the effective piezoelectric coefficient  $d_{zz}$ .

It is obvious to see that illumination will induce enhancement of the piezoelectricity only in one polarity of the photocurrent, which is found to be positive, generating a negative  $V_{oc}$ . Given a larger  $V_{oc}$  with increasing the photon flux, the effective piezoelectric coefficient under illumination,  $d_{zz}^{ph}$  also increases, as explained by the equation (4). Therefore, the effect of  $V_{oc}$  is one of the key factors for enhanced piezoelectricity. However, this effect would be minimal for systems in which the product  $\alpha l$  is small, because it is related to the absorption coefficient and the effective length of the material, as inferred from the equations (5-9). Thus, both large absorption coefficient and effective length of the device are required. This implies that for the most common thin film geometry when a tip scans on top of a film with a bottom electrode, light would have only a marginal effect, because the effective length here would be the film thickness, which is usually only in the range of tens to hundreds of nanometers. Moreover, it is important to consider high dark- and photo-conductivity are reducing factors for light-induced piezoelectricity enhancement.

If the light would change only the surface potential via  $V_{oc}$ , by applying its equivalent external  $V_{dc}$ , we shall entirely reproduce the effect, obtaining the same  $d_{zz}$ . **Figure 4a** shows comparison of the  $d_{zz}$  values measured only under illumination and application of a  $V_{dc}$ , that is the  $V_{oc}$  of the corresponding photon flux induced by illumination. Both cases show an increasing trend of  $d_{zz}$  along with increasing the photon flux. However, their differences are seen with larger  $d_{zz}$  values found under illumination, indicating an additional contribution to the more enhanced  $d_{zz}$  besides the simple  $V_{dc}$  effect, that is simulating the condition of  $V_{oc}$  due to the BPV. To explain this difference, we refer to the recently discovered effect, which is piezoelectricity generated at the metal-semiconductor (Schottky) contact due to local symmetry breaking.<sup>[11]</sup> Accordingly, the Schottky barrier-induced piezoelectric coefficient,  $d_{ijk}$  can be written as:

Where  $Q_{ijk3}$  is the electrostrictive coefficient,  $\chi_3$  is the dielectric susceptibility,  $q$  is the elemental charge,  $N_D$  is the doping density, and  $V_{bi}$  is the built-in voltage. Since the effective field at the metal

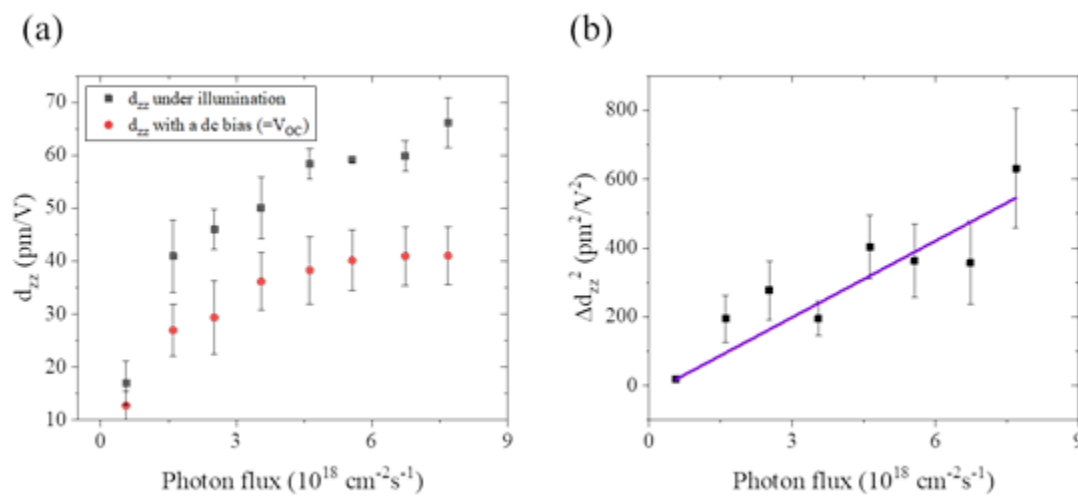
$$d_{ijk} = 2Q_{ijk3}\chi_3\sqrt{2qN_D\chi_3V_{bi}} \quad (10)$$

tip-interface is inhomogeneous and the crystal symmetry overlaps with the polar symmetry of the Schottky barrier, we can simplify the above equation, taking the effective values of the tensors:

$$d_{zz} = 2Q_{zz}\epsilon_z\sqrt{2qN_D\epsilon_zV_{bi}} \quad (11)$$

Where the dielectric susceptibility is approximated to be the normal component of the dielectric constant,  $\epsilon_z$ .

Considering that the BFO crystal is undoped or lightly doped with a doping density of  $N_D = 10^{17} \text{ cm}^{-3}$ ,<sup>[18]</sup> a computationally approximated value of an electrostrictive coefficient,  $Q = 0.032 \text{ m}^4 \text{ C}^{-2}$ ,<sup>[19]</sup> a relative dielectric constant,  $\epsilon_r \cong 50$ ,<sup>[20]</sup> and a built-in voltage,  $V_{bi} = 0.5 \text{ V}$ ,<sup>[21]</sup> the contribution to the  $d_{zz}$  of the Schottky surface piezoelectricity without illumination can be estimated to be about  $0.075 \text{ pm/V}$ . This is about three orders of magnitude lower than the effective piezoelectric coefficient of BFO. Under illumination with the photon flux of  $7.7 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ , assuming that the carriers are generated with a similar rate, we can estimate its resultant increase of the local effective doping density. According to the Beer-Lamber law,<sup>[22]</sup> light intensity decays as  $I(x) = I_0 \exp(-\alpha \cdot x)$ , where  $I_0$  is the incoming light intensity and  $\alpha$  is the absorption coefficient. Because the photon energy (3.06 eV) of the laser wavelength (405 nm) is above the band gap (2.7 eV) of BFO, the absorption should be very strong. Given the absorption coefficient of roughly  $4 \cdot 10^4 \text{ cm}^{-1}$ ,<sup>[23]</sup> the estimated penetration depth should be about  $1 \mu\text{m}$  at which almost 98 % of the incident light is absorbed. This is on the same order of magnitude as the space charge region of the Schottky diode, leading to a total carrier density of around  $7.7 \times 10^{22} \text{ cm}^{-3}$ . As a result, such an increase of carrier density would increase the  $d_{zz}$  due to the addition of the effective contribution of the Schottky junction by roughly  $66 \text{ pm/V}$ , which is slightly higher but on the same order of our experimentally observed  $d_{zz}$  value under illumination after subtracting the  $V_{dc}$  contribution. Further, the squared differences of  $d_{zz}$  ( $\Delta d_{zz}^2$ ) under illumination and application of the  $V_{dc}$  are found to linearly increase with the increased photon flux, proving the light-induced doping dependence of the Schottky barrier contribution to the  $d_{zz}$ , as shown in Figure 4b. Therefore, we can state that large light-induced enhancement of piezoelectricity has two main components: the first originating from the  $V_{oc}$ -induced change of the surface potential due to the BPV effect, and the second arising from the  $N_D$  due to the additional piezoelectric effect at the metal tip-BFO Schottky barrier.



**Figure 4.** Analysis of underlying mechanisms behind light-induced  $d_{zz}$  enhancement. (a) Comparison of  $d_{zz}$  measured only under illumination and application of a  $V_{dc}$  ( $=V_{oc}$  of the corresponding photon flux), and (b) their differences of  $d_{zz}$  squared ( $\Delta d_{zz}^2$ ), showing a linear relationship with the increased photon flux.

In summary, we show that light can be an effective pathway to induce significantly large enhancement of piezoelectricity in bulk BFO. Upon increasing the photon flux up to  $2.6 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$ , the  $d_{zz}$  is seen to show almost a seven-fold enhancement. Two key factors to such large enhancement are found to be the  $V_{oc}$  due to the BPV and the  $N_D$  due to the Schottky barrier effect under illumination, as proved by our local PFM, hysteresis, and photo I-V curve measurements. It will be of great interest to also investigate new possibilities for the presence of light- or doping-induced polar symmetry in centrosymmetric materials. Our results provide fundamental insights to establish a close link between light and piezoelectricity, offering its promising opportunities compatible with photovoltaics to design multifunctional optoelectronic devices.

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Piezoelectricity is a key functionality induced by conversion between mechanical and electrical energy. Enhancement of piezoelectricity is promising for device implementation. Here, we show light is a powerful control parameter to induce a seven-fold enhancement of piezoelectric coefficient in a single crystal of  $\text{BiFeO}_3$  due to the bulk photovoltaic and Schottky barrier effects, offering its potential for multifunctional optoelectronic devices.

