

Long-time relaxation of photo-induced influence on BiFeO₃ thin films

Jun-xing Gu, Kui-juan Jin, Le Wang, Xu He, Hai-zhong Guo, Can Wang, Meng He, and Guo-zhen Yang

Citation: *Journal of Applied Physics* **118**, 204103 (2015); doi: 10.1063/1.4936306

View online: <http://dx.doi.org/10.1063/1.4936306>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/118/20?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Optimization of excess Bi doping to enhance ferroic orders of spin casted BiFeO₃ thin film](#)

J. Appl. Phys. **115**, 234105 (2014); 10.1063/1.4884680

[Multiferroic properties of Aurivillius phase Bi₆Fe_{2- \$x\$} Co _{\$x\$} Ti₃O₁₈ thin films prepared by a chemical solution deposition route](#)

Appl. Phys. Lett. **101**, 122402 (2012); 10.1063/1.4752748

[Strain effect on the surface potential and nanoscale switching characteristics of multiferroic BiFeO₃ thin films](#)

Appl. Phys. Lett. **100**, 132907 (2012); 10.1063/1.3698155

[Piezoresponse force microscopy and vibrating sample magnetometer study of single phased Mn induced multiferroic BiFeO₃ thin film](#)

J. Appl. Phys. **111**, 064110 (2012); 10.1063/1.3699021

[Role of Pb\(Zr_{0.52}Ti_{0.48}\)O₃ substitution in multiferroic properties of polycrystalline BiFeO₃ thin films](#)

J. Appl. Phys. **110**, 114116 (2011); 10.1063/1.3668123

A promotional banner for AIP Applied Physics Reviews. On the left is a small image of the journal cover for 'Applied Physics Reviews', which shows a diagram of a device structure. The main part of the banner has a blue background with a bright light source on the right. The text 'NEW Special Topic Sections' is written in large, white, sans-serif font. Below this, in a smaller white font, is 'NOW ONLINE' followed by 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends'. In the bottom right corner, the AIP logo is shown next to the text 'Applied Physics Reviews'.

Long-time relaxation of photo-induced influence on BiFeO₃ thin films

Jun-xing Gu,¹ Kui-juan Jin,^{1,2,a)} Le Wang,¹ Xu He,¹ Hai-zhong Guo,^{1,a)} Can Wang,¹ Meng He,¹ and Guo-zhen Yang^{1,2}

¹*Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*

²*Collaborative Innovation Center of Quantum Matter, Beijing 100190, China*

(Received 17 August 2015; accepted 10 November 2015; published online 25 November 2015)

An intuitively persistent enhancement of the local surface potential of BiFeO₃ layers in both heterostructures of BiFeO₃/SrRuO₃/SrTiO₃ and BiFeO₃/Sr_{0.09}Nb_{0.01}TiO₃ was observed by the Kelvin probe force microscopy technique after the illumination of 375 nm laser. This photo-induced enhanced surface potential can maintain as long as 15 h after the illumination. We attributed this super-long-time relaxation of photo-induced influence to a photo-induced depolarization in the BiFeO₃ thin films, and our first-principles calculation of double-potential well further provides an instinct understanding on this depolarization process. Our findings provide a peculiar understanding into the photo-induced phenomena on the widely researched ferroelectric systems and offer an approach to tune their multifunctionality of the magnetization and polarization not only by applied magnetic and electric fields but also by optical filed. © 2015 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4936306>]

I. INTRODUCTION

As one of the most remarkable multiferroic materials, BiFeO₃ (BFO) has a relatively narrow band gap of approximately 2.2–2.7 eV, which is within the range of energy of the visible light^{1–3} in addition to its well-known large remnant polarization and high Curie temperature.⁴ Therefore, many attentions have been attracted on the photoelectric properties and applications of BFO. Above-band-gap photovoltage due to depolarization field and domain wall barrier, which is quite different from the conventional semiconductor photovoltaic devices,⁵ renders it a possible candidate for the next-generation photoelectric devices. However, photo-induced phenomena and the mechanisms behind BFO still remain unclear and very diversiform.⁶ Our previous works have shown a switchable photoelectric effect^{7,8} and a photo-assistant non-destructive readout.⁹ Besides, bulk BFO exhibits a large photostrictive response along the polarization direction due to a combination of photovoltaic and electrostrictive effects.^{10,11} The ultrafast lattice dynamics and localized inhomogeneous strain induced by photoexcitation in the BFO thin films have been observed by synchrotron-based x-ray diffraction.^{12,13} On the other hand, from the perspective of lifetime of photo-generated carriers, long-lived trapped photo-generated carriers, hundreds of ns,¹⁴ have been observed in the BFO films on SrTiO₃ (STO) and DyScO₃ substrates. More recently, several-hours-decay time of photoconductivity has been reported in the BFO films.¹⁵ The authors attributed this abnormally long decay time to a trapping character of sub-band levels, and announced that this effect was only observed in the strained BFO films which epitaxially grown on LaAlO₃ substrates with a *c/a* ratio of 1.23.

In this work, we observed a photo-induced change of the surface potential (SP) with a super-long relaxation time

(above 15 h) after the laser irradiation in both the heterostructures of the BiFeO₃/SrRuO₃ (SRO)/SrTiO₃ and BiFeO₃/Sr_{0.09}Nb_{0.01}TiO₃ (SNT0). Since that the BFO layers in both of the two heterostructures are almost strain-free,¹⁶ and photo-generated carriers are not supposed to have such abnormally long lifetime,^{14,15} we believe that the observed photo-induced change of SP with super-long relaxation time is attributed to the photo-induced depolarization with excited localized-states. Our first-principles calculation further explained how the photo-induced depolarization happens.

II. EXPERIMENTAL DETAILS

High-quality epitaxial BFO films were fabricated on (001)-oriented STO substrates covered with SRO bottom electrode (BiFeO₃/SrRuO₃/SrTiO₃, BFO/SRO/STO) and directly on the conductive SNT0 substrates (BFO/SNT0), respectively, by the laser molecular-beam epitaxy (laser-MBE). BFO for both the BFO/SRO/STO and BFO/SNT0 heterostructures were deposited at 580 °C with the oxygen pressure of 10 Pa. The thicknesses of BFO layers are 50 and 34 nm for BFO/SRO/STO and BFO/SNT0¹⁷ heterostructures, respectively. An XeCl 308 nm excimer laser was used with an energy density of 1.5 J cm⁻² and a repetition rate of 4 Hz. After deposition, the samples were *in situ* annealed for 20 min, and then cooled down to room temperature. Surface topography and surface potential were measured simultaneously by the non-contact atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) technique¹⁸ with a commercial test instrument (Asylum Research MFP3D). Domain structure was acquired by the piezoresponse force microscopy (PFM) mode using the same instrument to definitize the spontaneous polarization. The relative humidity and temperature remained unchanged in the measurement process. Pt-coated conductive tips (Olympus AC240, a spring constant of ~2 N m⁻¹ and a free air resonance frequency of ~70 kHz) were used for the scanning.

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: kjjin@iphy.ac.cn and hguo@iphy.ac.cn

The sample was illuminated by a continuous laser (Oxxius, power density of $0\text{--}80\text{ mW cm}^{-2}$) of 375 nm wavelength ($h\nu = 3.31\text{ eV}$) which focused into a circle spot with a diameter of 0.3 mm .

The band structures of the as-grown BFO layers on SNTN and on SRO/STO are schematically shown in Figs. 1(a) and 1(b), respectively.^{8,19,20} We took the work functions of BFO, SNTN, and SRO as 4.7 , 4.0 , and 5.2 eV , respectively.^{21,22} We propose the effects of polarization field and interfacial Schottky barrier on band bending is coexisting in the BFO thin films. However, the quantitative barrier height and the exact band bending cannot be given because we cannot evaluate the contribution of the non-complete polarization in the as-grown thin films and the interfacial trapped charges. We used the continuous laser with the wavelength of 375 nm as the excitation light source in the measurement. It has been demonstrated that the photo-generated carriers in BFO layers can be separated by the internal field and accumulated at the surface, which can be detected and analyzed using KPFM.¹⁸ Figures 1(c) and 1(d) show the KPFM images measured in the dark and under the illumination of the 375 nm laser for the as-grown BFO layers in these two heterostructures, respectively. The KPFM images in Figs. 1(c) and 1(d) were scanned line by line from up to down while the laser was alternately turned on and off, during this real-time scan process. Therefore, the KPFM images are alternately dark (light) and light (dark) corresponding to the laser-on and off conditions, respectively. The difference of the surface potential in the BFO layer between in the dark and under illumination was regarded as the photovoltage in the previous reports.²³ The arrows denote the order of scan progression. We can plot the corresponding time-resolved SP with alternatively laser-on and off conditions, by considering the longitudinal scan rate of 10 nm/s and the scan extent of $5\text{ }\mu\text{m}$. Figures 1(e) and 1(f) show the corresponding time-resolved SP with alternatively laser-on and off conditions obtained from Figs. 1(c) and 1(d), respectively. As noted in Fig. 1(e), SP falls immediately with laser turning on, and then rebounds as soon as laser turning off. We

attribute this to the negative photovoltaic effect in the as-grown BFO/SRO junction, as the direction of the built-in electric field is from the surface of BFO to the interface of BFO/SRO, consistent with the reported band structures.^{19,24} This phenomenon can be understood easily based on the schematic band structure shown in Fig. 1(a). The photon-generated electron-hole pairs can be separated by the internal electric field in BFO of BFO/SRO/STO, and the electrons move to the BFO surface, while holes move to the interface of BFO/SRO/STO, and therefore SP drops. When we turned off laser, the photon-generated electron-hole pairs recombine, leading to the rapid rebound of SP. For the similar reason, we can understand the opposite phenomenon shown in Fig. 1(f), as the internal electric field in BFO of BFO/SNTN is in the opposite direction with that in BFO/SRO/STO. From Figs. 1(e) and 1(f), we can conclude that the photo-generated voltage is approximately -0.04 V for BFO/SRO/STO and $+0.06\text{ V}$ for BFO/SNTN, respectively. Therefore, we can confirm that the type of the photon-generated carriers moved to the surface of BFO film in the BFO/SNTN heterostructures is opposite with that in the BFO/SRO/STO heterostructures.

A slick test procedure was implemented to obtain a local SP distribution map containing both illuminated and unilluminated regions. The schematic diagram is shown in Figs. 2(a)–2(c). Blue arrows in Fig. 2(a) schematically show an approximate preferred direction of spontaneous polarization in BFO/SRO/STO which has also been reported elsewhere.²⁵ Uniform grayness on the sample surface in Fig. 2(a) represents a roughly uniform spatial distribution of SP on the as-grown BFO film. The Pt-coated conductive tip (Olympus AC240) used here has a height of $14\text{ }\mu\text{m}$, which means that the cantilever of probe is approximate to $14\text{ }\mu\text{m}$ above the sample surface, and a width of $40\text{ }\mu\text{m}$, close and large enough to shade the light for the under area of the sample. When we turned on the 375 nm laser and let it illuminate the sample surface perpendicularly, the region under the cantilever of probe was shaded by the cantilever itself as shown in the dark gray in Fig. 2(b). This shaded region is named

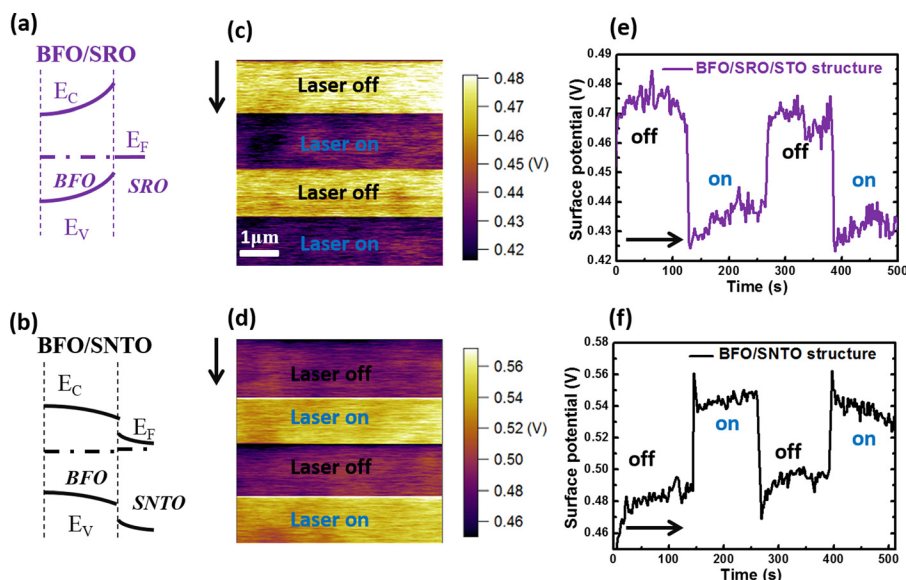


FIG. 1. Schematic interfacial band diagrams of (a) the BFO/SNTN structure and (b) the BFO/SRO/STO heterostructure. (c) and (d) Corresponding KPFM images measured in the dark and under illumination of the 375 nm laser for the BFO films in these two structures, respectively. The arrows denote the scan progression. (e) and (f) The corresponding time-resolved SP profile obtained from (c) and (d), respectively, by considering the scan rate 10 nm/s .

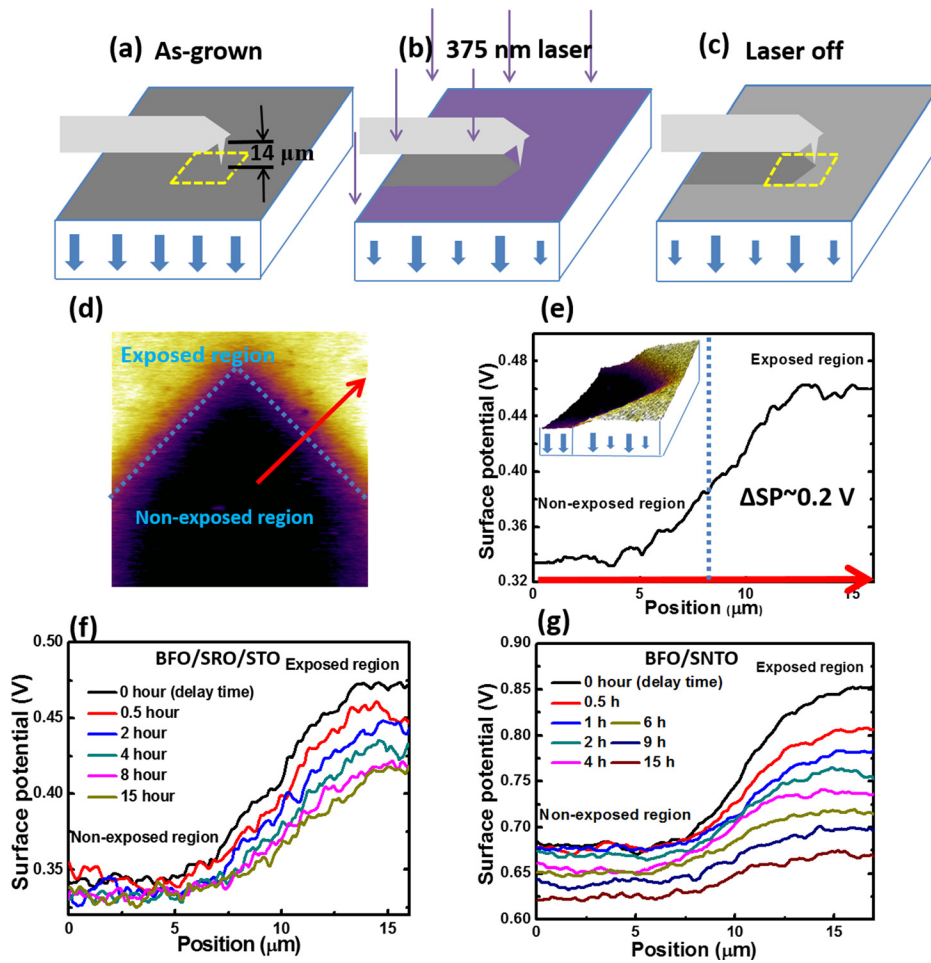


FIG. 2. Schematic diagram of the test procedure in the cases of (a) as-grown condition, (b) laser-on condition, and (c) laser-off condition, respectively. The width of the cantilever here is $\sim 40\ \mu\text{m}$ and the tip height is $\sim 14\ \mu\text{m}$. (d) KPFM image of the BFO/SRO/STO heterostructure after perpendicular illumination of the 375 nm laser for 30 min. (e) SP profile obtained from the KPFM image. The position axis from 0 to $15\ \mu\text{m}$ is corresponding with the red arrow marked in (d) from tail to head. Inset is SP distribution accompanied with the schematic diagram of domain structure. (f) SP profiles obtained from the KPFM images of the BFO/SRO/STO heterostructure after turning off the laser for various delay times. (g) SP profiles obtained from the KPFM images of the BFO/SNTO heterostructure after turning off the laser for various delay times.

non-exposed region in this paper, different from the exposed region directly illuminated shown in purple in Fig. 2(b), although slight scattered light should unavoidably illuminate on the non-exposed region. After keeping the 375-nm laser with $\sim 40\ \text{mW cm}^{-2}$ power density on for 30 min, we turned it off, and scanned a larger area covering the non-exposed region as marked by the yellow dashed box schematically in Figs. 2(a) and 2(c). And the SP distribution map (KPFM images) of BFO/SRO/STO is shown in Fig. 2(d).

III. RESULTS

From Fig. 2(d), we can see a clear boundary between the non-exposed and exposed regions from the SP distribution map, meaning that SP of the exposed region has enhanced after exposure. It is necessary to reiterate that Fig. 2(d) and the photo-induced phenomena hereinafter were measured with laser off, which is different from the measurement of photo-generated voltage by real-time scan of SP mentioned earlier. The black curve in Fig. 2(e) shows the SP values versus positions along the red arrow marked in Fig. 2(d). As we know, the absolute value of the potential is not so important comparing to the difference of the potential; therefore, we just pay attention to the difference of SP (ΔSP) between the exposed and non-exposed regions and the change of SP in this work. From Figs. 2(d) and 2(e) we can see that SP keeps increasing along the red arrow from

the non-exposed region to the exposed region, and ΔSP between the two regions is about 0.2 V. Then we did another comparing measurement, after keeping illuminating for 30 min, we turned off laser and scanned the spatial distribution of SP continuously with 0.5 Hz scan rate. The SP distributions for various delay times are plotted in Fig. 2(f). It can be seen from Fig. 2(f) that we can still clearly distinguish the non-exposed region and the exposed region from the SP profiles even after 15 h relaxation, since SP of the exposed region is maintained at higher value than that of the non-exposed region. It is noteworthy that the illumination for several minutes can lead to the enhancement of SP lasting for a dozen or more hours. To our best knowledge, this relaxation time is much longer than that in most of photo-induced phenomena observed in ferroelectrics,^{10–12,14,20} even two times longer than the decay time of persistent photoconductivity in the strained BFO films on LaAlO_3 substrates, which was ascribed to a long-lived trapping levels of the BFO films.¹⁵

We also performed the similar measurements on the BFO/SNTO heterostructures, and obtained exactly the same SP enhancement on the exposed region of the BFO/SNTO heterostructures. The SP profiles of the BFO/SNTO heterostructures after turning off laser for various delay times are shown in Fig. 2(g). We can also clearly distinguish the non-exposed region and the exposed region from the SP profiles after 15 h relaxation.

We should note that the evolution of the photo-induced SP persistent change is the same for both structures, although the type of the photon-generated carriers moved to the surface of the BFO film in BFO/SNTO heterostructures is opposite to that in the BFO/SRO/STO heterostructures. In addition, the relaxation of the SP enhancement ($\sim$ hours) is much longer than the lifetime of photo-generated charges (about 100–200 ns)¹⁴ in the strain-free BFO film on the STO substrates. We believe that when we turn off the light and do the KPFM scan, the photo-generated charges have almost diffused away and completely recombined. Therefore, the observed SP enhancement should not result from the photo-generated carriers, but results from some other charges with super-long lifetime ($\sim$ hours). And that charges should be the bounded charges and the corresponding screening charges. Screening charges, which can be reflected on SP, are inevitably accumulated on the surface of ferroelectrics to balance the bound charges of polarization. The screening charges come from adsorbates, H^+ and OH^- ions, or artificial injected electrons and holes.^{18,26} In some cases, the screening charges are in tiny excess of the bound charges, then they are named as overscreened charges. These overscreened non-equilibrium charges would diffuse away along the surface or desorb from the surface till to a screened equilibrium state due to the coulomb repulsion. This diffusion or desorption of overscreened charges is very slow ($\sim$ several hours) due to the trapping effect of polarization.^{9,27} Therefore, we propose that the photons with energy above the band gap of BFO have some long-term influence on the polarization of BFO, and further change the balance between the surface-adsorbed screening charges and the bound charges. More specifically, it should be the photo-induced depolarization that leads to overscreening of surface-adsorbed charges, which can be maintained for hours after the illumination. In fact, the photo-induced depolarization has also been proposed from the observation of THz emission on BFO by the illumination of femtosecond laser pulses.^{28,29}

To further understand the mechanism of the enhanced SP of the BFO films induced by the depolarization, the polarization of the as-grown BFO/SRO/STO and BFO/SNTO heterostructures were evaluated. Two rectangular regions were scanned by using the contact-AFM mode with applied biases of ± 8 V for BFO/SRO/STO and ± 9 V for BFO/SNTO, respectively, both higher than the coercive voltages of the BFO films. Out-of-plane PFM phase images of the BFO/SRO/STO and BFO/SNTO heterostructures are shown in Figs. 3(a) and 3(b), respectively. The bright region noted by the yellow dashed box corresponds to the upward polarized domains on which a negative bias was applied. Conversely, the adjacent left region applied by a positive bias corresponds to the downward polarized domains. The surface morphology of the corresponding written area is shown in Figs. 3(c) and 3(d). It can be seen from Figure 3 that the applied bias did not impact the surface morphology, and therefore only induced the domain switching. From Figs. 3(a) and 3(b) it can be seen that the phase images of the regions with positive biases applied are as same as that of the as-grown regions both in the BFO/SRO/STO and BFO/SNTO heterostructures, suggesting that the as-grown BFO

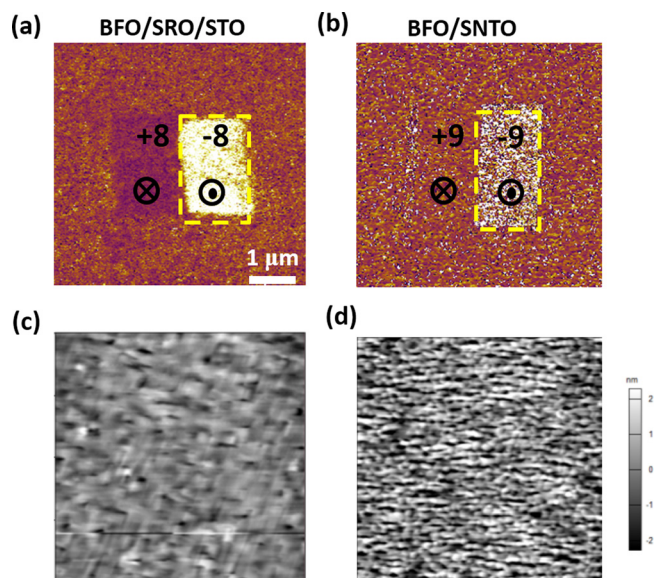


FIG. 3. Out-of-plane PFM phase images of (a) the BFO/SRO/STO and (b) BFO/SNTO structures after application of two opposite biases higher than the coercive voltage on two rectangular regions. Corresponding surface morphology of the written area of (c) the BFO/SRO/STO and (d) BFO/SNTO structures.

films have a downward preferred spontaneous polarization in both the BFO/SRO/STO and BFO/SNTO heterostructures. This conclusion is in accordance with previous reports.^{9,25} It has been reported that epitaxial BFO films grown on a conductive substrate,³⁰ especially with a $SrRuO_3$ bottom electrode, exhibit a downward preferred direction of polarization, also named as self-polarized.²⁵

Since that 0.02%–0.07% overscreening of polarization charges will lead to a considerable change of SP (hundreds of millivolt),^{26,27} photo-induced unobservable small change of internal polarization can be clearly reflected in the SP measurement. In this case, even if the depolarization is very tiny ($\sim$ just a few percent), SP will increase hundreds of millivolts due to the excess positive screen charges on the surface of the BFO films as schematically shown in Fig. 4(a). Then these excess positive charges serve as the overscreened charges and lead the surface to an overscreened non-equilibrium state. And this non-equilibrium state will induce the diffusion of the adsorbed overscreened positive charges with several hours relaxation time to a re-equilibrium state,^{9,18,27,31} which is exactly contribute to our measured long relaxation time of SP. So far, it seems that we can explain the entire experimental phenomena as follows. First, we illuminated the BFO films by a 375 nm laser, and the photo-generated charges are separated by the built-in electric field. This process is the reason to induce the photo-generated voltage and was measured by the real-time SP scan. Meanwhile, laser induces some tiny modulation of polarization which is regarded as depolarization. Second, laser was turned off and the photon-generated electron-hole pairs rapidly recombine. However, the tiny modulation of polarization did not come back to the non-illuminated state due to the ferroelectricity. The overscreened positive charges make SP higher than the initial state. Third, the diffusion of the overscreened positive charges with several hours relaxation time leads SP to slowly reduce.

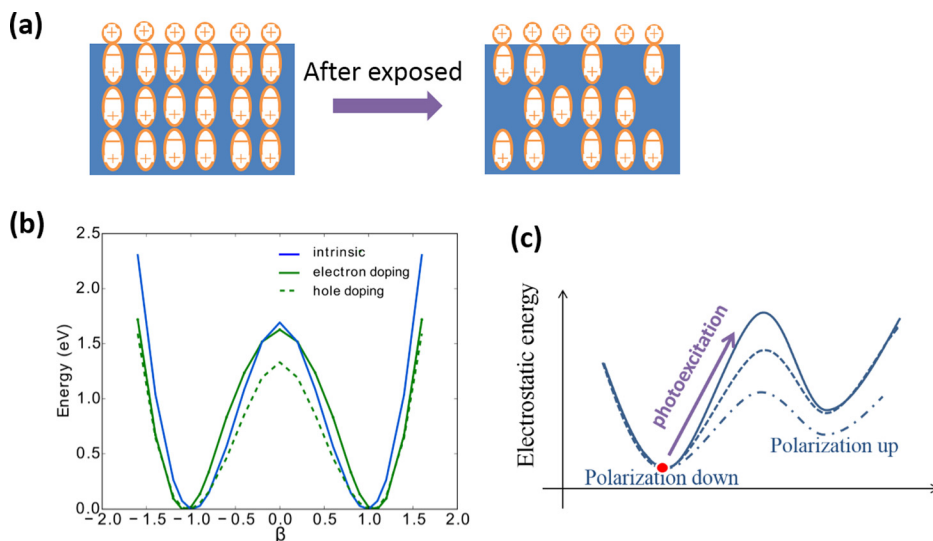


FIG. 4. (a) Schematic diagram of photo-induced depolarization in macroscopic perspective. (b) Calculated ferroelectric double well with an electron or a hole added to the BFO primitive cell. (c) Schematic graphic of the asymmetric double potential well corresponding to the two spontaneous polarized states. Solid line denotes the as-grown state, dashed line denotes the barrier reducing effect, and dotted dashed line denotes the anisotropy suppressing effect.

IV. DISCUSSION

There are two possible mechanisms for the decrease of the macroscopic polarization revealed by the long-time relaxation of SP. One is that some parts of the ferroelectric domains are reversed. The other is that the polarization is screened by charge, which needs to have long lifetime so the time scale can fit. Though Bhatnagar *et al.* proposed that the long lifetime trapped carriers only exist in compressive strained BFO films,¹⁵ we do not fully rule out the possibility that the decrease of the polarization is due to the trapped carriers, which screens the polarization.

Here we try to give possible reasons why light can help the reversing of ferroelectric polarization. The first reason is that the barrier between the opposite polarization state is reduced. For a unit cell in the ferroelectric structures, the polarization can be viewed as the spontaneous breaking of the centrosymmetry of the lattice structure, which is stabilized by the chemical bonds. Thus, the two spontaneous polarized states are in a double potential well with a barrier in between. In the ground state, the height of the barrier of the ferroelectric double well energy in bulk BFO is about 2 eV.³² We calculated the barrier with an electron or a hole added to the BFO primitive cell and found that both lead to the reduction of the height of the barrier as shown in Fig. 4(b). Our calculation is carried out with the assumption of isotropic structure, whereas in our heterostructures, the boundary conditions make the potential double well asymmetric as schematically show in Fig. 4(c). Despite this, the reduction of the barrier height shows increasing of possibility of polarization reversing. Another reason is that the Coulomb force, which can stabilize the long range ferroelectric order, is screened by the photo-generated carriers. The third reason is that the lattice gains energy when illuminated, which can also increase the possibility of polarization reversing. Our BFO films have a downward preferred spontaneous polarization. Thus, increasing of the possibility of reversing the local polarization orientation leads to the reduction of the overall polarization.

V. CONCLUSIONS

In conclusion, we have demonstrated a persistent photo-induced change of SP in the multiferroic BFO heterostructures

by means of the KPFM technique. Two heterostructures of BFO/SRO/STO and BFO/SNTO with reversed built-in electric fields in as-grown BFO films were investigated to eliminate the contribution of the photo-generated carriers on the SP change. The dependences of SP on relaxation time were investigated to evaluate contributions from the polarization bond charges and the corresponding screen charges. A photo-induced depolarization with excited localized states was proposed and further clarified by determination of polarization orientation in the films and first-principles calculations of double-potential well. We believe that a further diffusion of the adsorbed overscreened positive charges with several-hours-relaxation time to a re-equilibrium state contributes to our measured long-relaxation time of SP for BFO thin film in a depolarized state after the exposure. Our results will provide a deep insight into the widely researched photo-induced phenomena which is regarded as potentially new degrees of freedom and coupling mechanisms of the multifunctional BFO.

ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program of China (Nos. 2012CB921403 and 2014CB921001), the National Natural Science Foundation of China (Nos. 11134012, 11174355, 11574365, and 11474349), and the “Strategic Priority Research Program (B)” of the Chinese Academy of Sciences (No. XDB07030200).

¹S. R. Basu, L. W. Martin, Y. H. Chu, M. Gajek, R. Ramesh, R. C. Rai, X. Xu, and J. L. Musfeldt, *Appl. Phys. Lett.* **92**, 091905 (2008).

²J. F. Ihlefeld, N. J. Podraza, Z. K. Liu, R. C. Rai, X. Xu, T. Heeg, Y. B. Chen, J. Li, R. W. Collins, J. L. Musfeldt, X. Q. Pan, J. Schubert, R. Ramesh, and D. G. Schlom, *Appl. Phys. Lett.* **92**, 142908 (2008).

³H. T. Yi, T. Choi, S. G. Choi, Y. S. Oh, and S. W. Cheong, *Adv. Mater.* **23**(30), 3403 (2011).

⁴G. Catalan and J. F. Scott, *Adv. Mater.* **21**, 2463 (2009).

⁵S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C. H. Yang, M. D. Rossell, P. Yu, Y. H. Chu, J. F. Scott, J. W. Ager, L. W. Martin, and R. Ramesh, *Nat. Nanotechnol.* **5**, 143 (2010).

⁶J. Kreisel, M. Alexe, and P. A. Thomas, *Nat. Mater.* **11**, 260 (2012).

⁷L. Wang, K.-j. Jin, C. Ge, C. Wang, H.-z. Guo, H.-b. Lu, and G.-z. Yang, *Appl. Phys. Lett.* **102**, 252907 (2013).

- ⁸C. Wang, K.-j. Jin, Z.-t. Xu, L. Wang, C. Ge, H.-b. Lu, H.-z. Guo, M. He, and G.-z. Yang, *Appl. Phys. Lett.* **98**, 192901 (2011).
- ⁹L. Wang, K. J. Jin, J. X. Gu, C. Ma, X. He, J. Zhang, C. Wang, Y. Feng, Q. Wan, J. A. Shi, L. Gu, M. He, H. B. Lu, and G. Z. Yang, *Sci. Rep.* **4**, 6980 (2014).
- ¹⁰B. Kundys, M. Viret, D. Colson, and D. O. Kundys, *Nat. Mater.* **9**, 803 (2010).
- ¹¹B. Kundys, M. Viret, C. Meny, V. Da Costa, D. Colson, and B. Doudin, *Phys. Rev. B* **85**, 092301 (2012).
- ¹²H. Wen, P. Chen, M. Cosgriff, D. Walko, J. Lee, C. Adamo, R. Schaller, J. Ihlefeld, E. Dufresne, D. Schlom, P. Evans, J. Freeland, and Y. Li, *Phys. Rev. Lett.* **110**, 037601 (2013).
- ¹³D. Schick, M. Herzog, H. Wen, P. Chen, C. Adamo, P. Gaal, D. G. Schlom, P. G. Evans, Y. Li, and M. Bargheer, *Phys. Rev. Lett.* **112**, 097602 (2014).
- ¹⁴Y. Yamada, T. Nakamura, S. Yasui, H. Funakubo, and Y. Kanemitsu, *Phys. Rev. B* **89**, 035133 (2014).
- ¹⁵A. Bhatnagar, Y. H. Kim, D. Hesse, and M. Alexe, *Nano Lett.* **14**, 5224 (2014).
- ¹⁶B. Dupé, I. C. Infante, G. Geneste, P. E. Janolin, M. Bibes, A. Barthélémy, S. Lisenkov, L. Bellaiche, S. Ravy, and B. Dkhil, *Phys. Rev. B* **81**, 144128 (2010).
- ¹⁷H. Guo, R. Zhao, K. J. Jin, L. Gu, D. Xiao, Z. Yang, X. Li, L. Wang, X. He, J. Gu, Q. Wan, C. Wang, H. Lu, C. Ge, M. He, and G. Yang, *ACS Appl. Mater. Interfaces* **7**, 2944 (2015).
- ¹⁸S. V. Kalinin and D. A. Bonnell, *Nano Lett.* **4**, 555 (2004).
- ¹⁹Z. Fan, K. Yao, and J. Wang, *Appl. Phys. Lett.* **105**, 162903 (2014).
- ²⁰F. Yan, G. N. Chen, L. Lu, and J. E. Spanier, *ACS Nano* **6**(3), 2353 (2012).
- ²¹X. Fang and T. Kobayashi, *Appl. Phys. A: Mater. Sci. Process.* **69**, S587 (1999).
- ²²H. Yang, H. M. Luo, H. Wang, I. O. Usov, N. A. Suvorova, M. Jain, D. M. Feldmann, P. C. Dowden, R. F. DePaula, and Q. X. Jia, *Appl. Phys. Lett.* **92**, 102113 (2008).
- ²³Y. Zhou, L. Fang, L. You, P. Ren, L. Wang, and J. Wang, *Appl. Phys. Lett.* **105**, 252903 (2014).
- ²⁴W. Ji, K. Yao, and Y. C. Liang, *Adv. Mater.* **22**, 1763 (2010).
- ²⁵Y. H. Chu, M. P. Cruz, C. H. Yang, L. W. Martin, P. L. Yang, J. X. Zhang, K. Lee, P. Yu, L. Q. Chen, and R. Ramesh, *Adv. Mater.* **19**, 2662 (2007).
- ²⁶F. Yan, G. Z. Xing, M. Islam, S. Li, and L. Lu, *Appl. Phys. Lett.* **100**, 172901 (2012).
- ²⁷X. Q. Chen, H. Yamada, T. Horiuchi, K. Matsushige, S. Watanabe, M. Kawai, and P. S. Weiss, *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.-Process., Meas., Phenom.* **17**, 1930 (1999).
- ²⁸K. Takahashi, N. Kida, and M. Tonouchi, *Phys. Rev. Lett.* **96**, 117402 (2006).
- ²⁹D. S. Rana, I. Kawayama, K. Mavani, K. Takahashi, H. Murakami, and M. Tonouchi, *Adv. Mater.* **21**, 2881 (2009).
- ³⁰F. Johann, A. Morelli, D. Biggemann, M. Arredondo, and I. Vrejoiu, *Phys. Rev. B* **84**, 094105 (2011).
- ³¹J. J. Segura, N. Domingo, J. Fraxedas, and A. Verdager, *J. Appl. Phys.* **113**, 187213 (2013).
- ³²D. Ricinchi, K. Y. Yun, and M. Okuyama, *J. Phys.: Condens. Matter* **18**, L97 (2006).