Enhancement of Ferroelectric Photovoltaic Effect in
Bismuth Ferrite (BiFeO$_3$) through Doping

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In conventional junction-based photovoltaic cells, the photovoltage is usually smaller than the semiconductor band gap, due to the limitation of the energy barrier at the interface. Contrarily, ferroelectric photovoltaic effect is a bulk effect of which the photovoltage is not limited by the energy barrier. BiFeO3 (BFO), a multiferroic material with robust ferroelectric and magnetic orders at room temperature and a band gap within visible light range, provides a unique opportunity for ferroelectric photovoltaic effect study. Previous study has shown that chemical substitution in BFO has been a subject of much interest since it usually results in improved ferroelectric properties and enhancement in piezoelectric and dielectric performance. In this work, the role of chemical substitution on the ferroelectric and photovoltaic properties of epitaxial BiFeO3 films was investigated. It is found that doping indeed helps to enhance photovoltaic responses in BFO. As the doping concentration increases, the ferroelectric photovoltaic response of BFO is enhanced accordingly. Once the doping concentration reaches a threshold value, the ferroelectric polarization in the films disappear and consequently, there will be very small photovoltaic responses in doped BFO. The dependence of photovoltaic properties on La doping concentration suggests contributions to the improved photovoltaic properties from both the ferroelectric polarization and enhanced dielectric constant of doped BFO films. Finally, we studied the application of the photovoltaic effect of BFO films in memory device. The photovoltaic effect could be used to read the polarization status of BFO films non-destructively.

I. INTRODUCTION

Ferroelectric materials possess spontaneous polarization. Under external electric field, the polarization can be switched along the direction of the field. One of the most interesting properties in ferroelectric materials is switchable photovoltaic effects, which has been intensively investigated recently. In particular, BiFeO$_3$ (BFO), a ferroelectric material with robust ferroelectric orders at room temperature [1] and a band gap ($\sim$ 2.7 eV) within visible light range [2], provides a unique opportunity for ferroelectric photovoltaic effect study and applications.

Solar energy is a promising form of renewable and sustainable energy nowadays. Using semiconducting materials with photovoltaic effects, the solar energy can be converted to direct current electricity. Compared to conventional solar cells, the ferroelectric photovoltaic effects in BFO are switchable, making it particularly fascinating. In BFO heterostructures, switchable photovoltaic effect was mainly explained by the polarization dependent band modification of the BFO capacitor (Pt and La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) are top and bottom electrode respectively) in Figure 1. The unscreened polarization charge bends the electronic band and thus generates the built-in electric field of which the direction depends on the polarization direction. Once the polarization direction is switched, the built-in field reverses its direction. As a result, both open-circuit voltage (Voc) and short-circuit current (Isc) will change their signs.
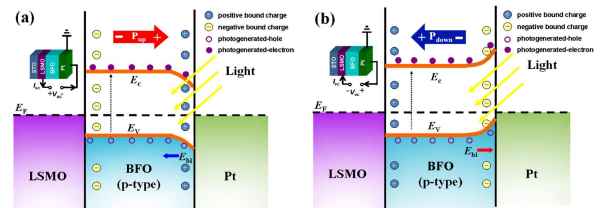

Figure 1: schematic of energy band diagrams and photovoltaic mechanism in Pt/BFO/LSMO heterostructure. (a) The upward polarization with downward built-in electric field and (b) the downward polarization with upward built-in electric field.

In ferroelectric random access memory (FeRAM), the logic states, "1" and "0", are represented by the two different polarization directions. Compared to other non-volatile memories such as hard disk drive and flash memory, FeRAM has shown advantages in speed and energy saving [3]. However, in conventional FeRAM, to read the information stored, a bias is applied to the ferroelectric capacitor, and the polarization switching current is detected in order to read the information. This process is destructive and rewrite steps are needed, which leads to high energy consumption and reduced FeRAM lifespan. Alternative non-destructive read-out process is of great interest. In 2013, the read-out process based on switchable photovoltaic responses in BFO was proposed [4]. As mentioned above, with their switchable nature, both signs of Voc and Isc can be used to non-destructively detect the polarization direction (i.e. the logic state in FeRAM).

However, in both two possible applications, it is suggested that the switchable photovoltaic response of BFO heterostructures is too small. Thus, improving the photovoltaic effect of BFO thin film capacitors becomes a critical issue. Our project aims to enhance the ferroelectric photovoltaic effect of BFO by chemical doping.

II. HYPOTHESIS

Chemical substitution in BFO has been a subject of much interest since it usually results in improved ferroelectric properties and enhancement in piezoelectric and dielectric performance [5]. Here, we plan to conduct a systematic study of the effect of rare earth substitution on the photovoltaic properties of BFO. The substitution can be achieved by A-site doping ($Bi_{1-x}La_xFeO_3$, $Bi_{1-x}Sm_xFeO_3$ and $Bi_{1-x}Dy_xFeO_3$). A series of doped BFO thin films will be deposited by pulsed laser deposition (PLD) and then the devices can be prepared using standard photolithography and lift off process. Finally, the photovoltaic properties of various samples will be tested to investigate the dependence of photovoltaic properties on doping concentration.

III. MATERIALS AND METHODOLOGY

A. Preparation of BFO capacitors

We prepared BFO capacitors (Pt/BFO/LSMO/SrTiO3, in which Pt and LSMO are top and bottom electrodes) with various doping concentration of different dopants using PLD. As shown in Figure 2, during PLD, a pulsed laser beam is focused onto the targets. When the laser energy density is above a threshold value, the target materials will be evaporated, forming a plasma plume. The plume travels normal to the target surface until it reaches the heated substrate surface, and film growth occurs. It preserves the complex stoichiometry of target material and thus especially suitable for the deposition of films with complex compositions [6]. Optimized parameters (temperature of 670℃ with the oxygen partial pressure of 300 mTorr) were used to obtain films with reduced roughness and increased quality. Fabrication of BFO films were done by our mentors.
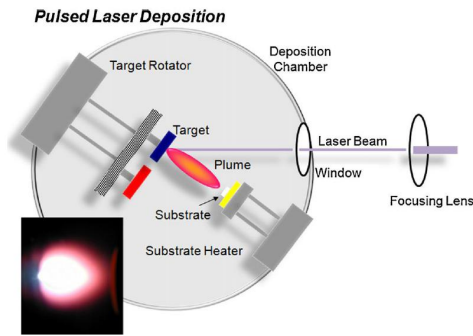
Figure 2: schematic illustration of a pulsed laser deposition system. The inset shows the plume during deposition. The deposition chamber is equipped with target holder, substrate heater, rotators, windows, and vacuum pumps.

B. Characterization details of BFO Films

Ferroelectric properties were characterized using a commercial ferroelectric tester (Precision LC, Radiant Technologies). The current-voltage (I-V) behavior of the films was obtained using a low-noise probe station and a pA meter/direct current (DC) voltage source (Hewlett Package 4140B) under the illumination of a Halogen lamp (energy density ~20 mW cm^{-2}) through the top electrodes. The experimental setup is schematically shown in Figure 3.
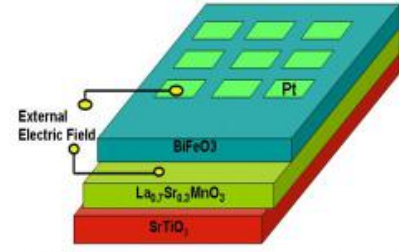
Figure 3: experimental setup for the electrical characterizations of Pt/ BFO/LSMO heterostructure

IV. RESULTS AND DISCUSSION

A. $Bi_{1-x}La_xFeO_3$ Characterization

After using the ferroelectric tester to test the ferroelectric properties of various $Bi_{1-x}La_xFeO_3$ films (BLFO$_x$, x=0, 0.1, 0.2, 0.3 and 0.4), the polarization-voltage (P-V) loops are shown in Figure 4.1 to Figure 4.5.
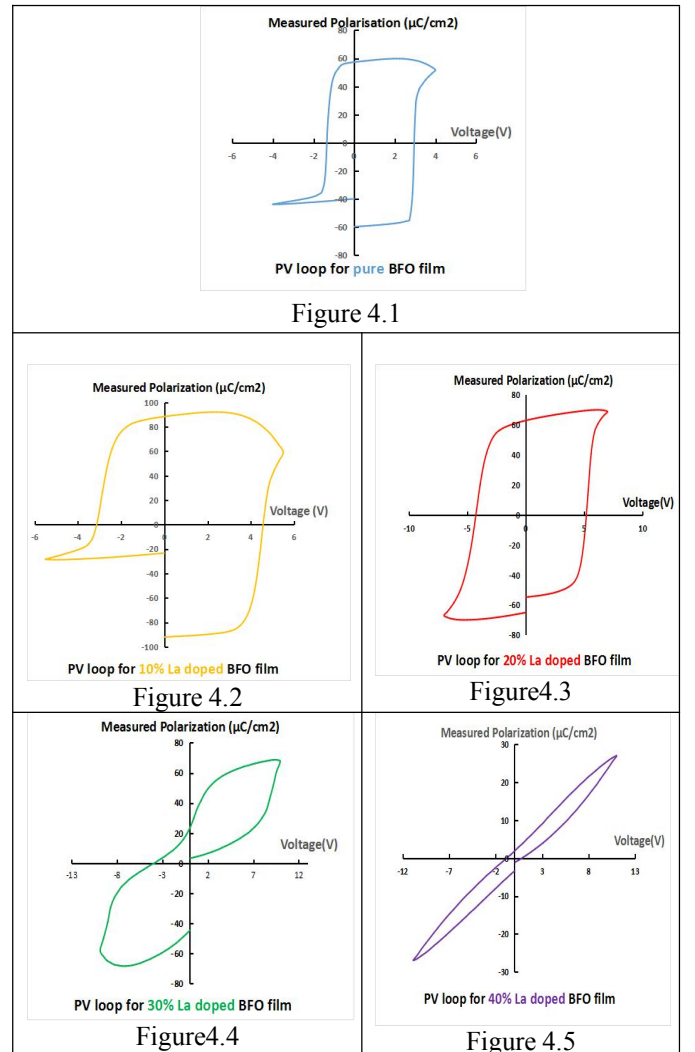
Figure 4.1

Figure 4.2

Figure4.3

Figure4.4

Figure 4.5

Figure 4.1-4.5: The P-V loops of the Pt/BLFO$_x$/LSMO heterostructure with different concentration of La

As mentioned in the introduction, ferroelectric polarization is the driving force of the photovoltaic effects in ferroelectrics; we firstly investigated the ferroelectric properties of these devices. As shown from the Figure4.1, *P-V* curves of BLFO$_x$ from x=0 to 0.2 have clear hysteresis loops, demonstrating strong ferroelectric polarization. However, no spontaneous polarization was observed from 30% La onwards.

Secondly, we checked the photovoltaic properties of fabricated BLFO thin films and the results are shown in Figures 5 and 6.
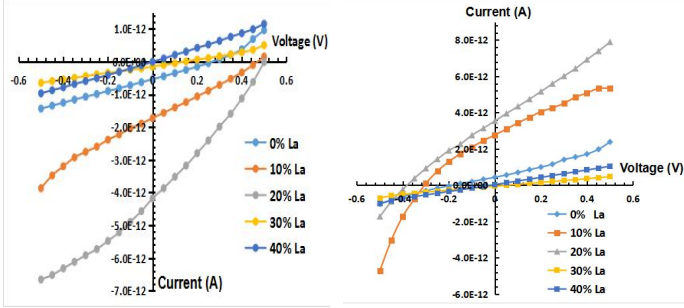
Figure 5, the *I-V* curves of Pt/BLFO$_x$/LSMO heterostructure with different concentration of La at the status of upward polarisation

Figure 6, the *I-V* curves of Pt/BLFO$_x$/LSMO heterostructure with different concentration of La at the status of downward polarization

Indeed, both Voc and Isc values become much larger when the doping concentration increases from 0% to 20%. The signs of Voc and Isc are different for upward and downward polarisation, implying the switchable photovoltaic responses of BFO under different polarisation direction. Moreover, corresponding to the disappearance of ferroelectric properties from 30% onwards, both values of Voc and Isc drop drastically, nearly to zero, from 30% La onwards, which further supports the claim that ferroelectric polarization is the driving force of the photovoltaic effects.

From results above, we concluded that the ferroelectric photovoltaic properties of BFO can indeed be enhanced through doping. However, once the doping concentration is more than the threshold concentration, no more ferroelectric and photovoltaic effect can be detected.

B. $Bi_{1-x}Dy_xFeO_3$ (BDFO$_x$) and $Bi_{1-x}Sm_xFeO_3$ (BSFO$_x$) Characterization

This enhancement of ferroelectric photovoltaic properties through doping is further proved by *P-V* and *I-V* characterisation of BDFO$_x$ and BSFO$_x$ thin films respectively, shown in Figure 7. Therefore, we conclude that it is a universal phenomenon that, within a doping concentration range, doping helps enhance the ferroelectric photovoltaic effect of BFO. The larger the concentration is, the larger the enhancement of photovoltaic effect.
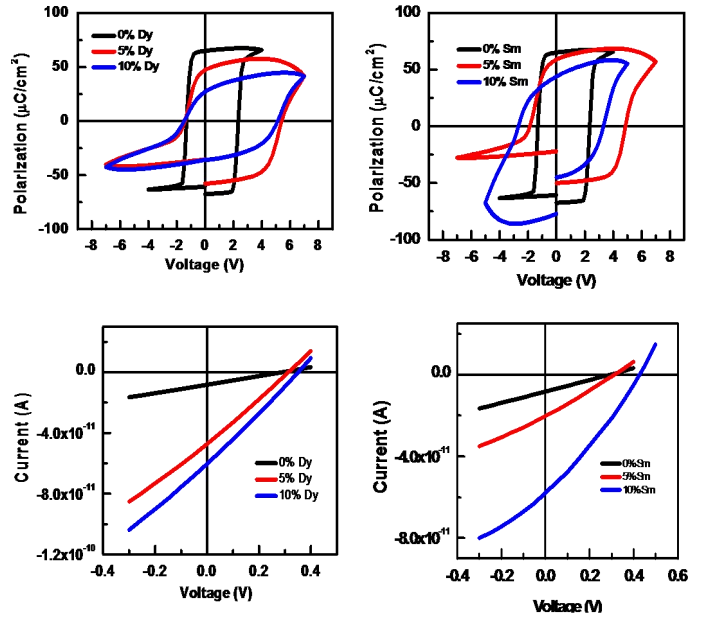

Figure 7, the ferroelectric and photovoltaic properties of Dy and Sm doped BFO films.

V. DISCUSSION OF ORIGIN OF THE ENHANCEMENT

To find out the origin of the enhancement, we look into the band structure and analyse the possible factors such as band gap, height and width of the band bending.

From the band theory, the smaller the band gap, the greater the electrical conductivity of semiconductors has. Reduced band gap would certainly improve the photovoltaic responses. Hence, we checked the absorption spectrum of BFO with doping concentration of 0 and 20% La (Figure 8). These two similar curves indicate that the energy level of doped BFO and pure BFO films are nearly the same, their band gaps are thus of no large difference. Hence, the enhancement is not likely to be the reduced band gap.
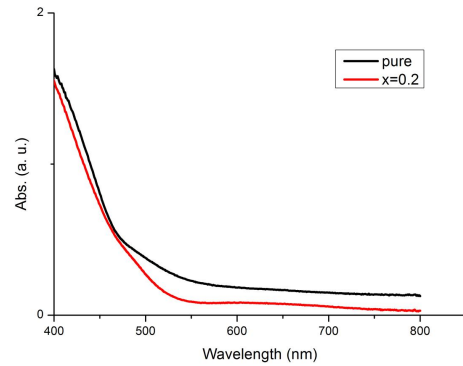

Figure 8, absorption spectra of a pure BLFO film and BLFO$_{x=0.2}$

Then we look into the height of the band bending. Increased height would result in larger built-in field and

consequent enhanced photovoltaic properties. From Figure 9, the remnant polarisations of BFO with doping concentration of 0, 10, 15 and 20% La are similar when the leakage voltage is taken account. Since the number of polarised charges is unchanged, the height of the band bending is most likely unchanged as well. The height of the band bending is therefore not the factor that causes the enhancement.
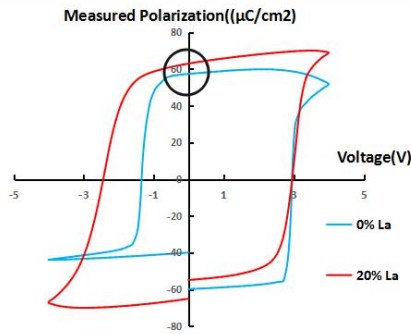

Figure 9: P-V loops of 20% doped and pure BFO films, with remnant polarisation being circled.

Lastly, the width of band bending is then discussed.
Using the formula of depletion width W derived from Poisson equation,

$$W = \sqrt{\frac{2\varepsilon_0 \varepsilon_r \phi}{e N_D}}$$

where, ε_0 is the permittivity of free space,
ε_r is the dielectric constant of the semiconductor,
e is the electronic charge,
ϕ is the Schottky barrier height,
and N_D is the carrier density.

Since La is isovalent dopant for Bi in BFO, it is reasonable to assume that the carrier density is almost unchanged, which was also confirmed in Gd doped BFO films [7], Schottky barrier height is reasonably assumed to be the same for pure and doped BFO samples from previous discussion.

Figure 10 shows the dielectric constant of BFO films with various doping concentration of La. It is observed that the dielectric constant of the films increases significantly due to La doping. At 1 kHz, the dielectric constant is about 70 for pure BFO, which increases to ~ 130 for $BLFO_x$=0.2, and ~ 220 for $BLFO_x$=0.4.
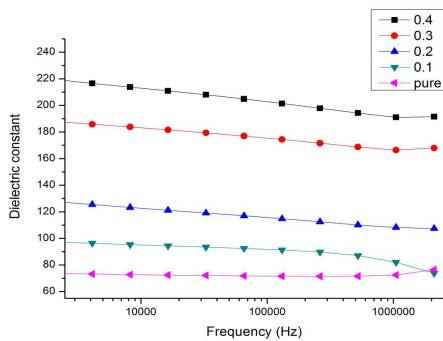

Figure 10: the dielectric constant of $BLFO_x$ thin films for x=0, 0.1, 0.2, 0.3 and 0.4 at different frequencies

When ε_0, N_D and ϕ are constant, substituting ε_r into the formula given above, it shows that the depletion width increases as doping concentration of La increases

With this evidence, it is appropriate to say that the enhancement of ferroelectric photovoltaic performance of BFO through doping is due to the increased depletion width, which allows greater number of photocarries to be separated. These photocarries are responsible for photovoltaic effect of BFO. When the number of effective charge carries at the built-in field increases, photovoltaic response would then be improved.

VI.   CONCLUSION

In conclusion, doping indeed helps to enhance photovoltaic effect of BFO. As the doping concentration increases, the ferroelectric photovoltaic response of BFO is enhanced accordingly. However, once the doping concentration reaches a threshold value, there will be no more increment in photovoltage of BFO under light illumination. Instead, when the doping concentration exceeds the threshold value of its BFO films, the ferroelectric photovoltaic response is deteriorated drastically. Regarding the origin of enhancement, we found out that depletion width is the key factor. Depletion width increases as the doping concentration increases; the increased depletion width allows greater number of photocarriers to be separated at the depletion region by bound charge, leading to more effective moving photocarriers, which thus enhances the photovoltaic performance of BFO.

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