Effect of cooling oxygen pressure on the photoconductivity in Bi$_{0.9}$La$_{0.1}$FeO$_3$ thin films

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**Abstract**

A direct correlation is observed between the magnitude of the photoconductivity and cooling oxygen pressure in Bi$_{0.9}$La$_{0.1}$FeO$_3$ films. With lower oxygen vacancies ($V_{O_5}$) films cooled in higher oxygen pressure show obviously decrease in leakage current. Higher level of $V_{O_5}$ led to higher free carrier concentration and hence is believed to be responsible for the increase in higher photoconductivity. It is evident that BLFO films with higher $V_{O_5}$ cooled in lower oxygen pressure and/or light illumination induce a higher carrier injection, $n_i$ and thus the conductive mechanism is dominated by space-charge-limited conduction.

**1. Introduction**

Multiferroic materials combine two or more properties of ferromagnetism, ferroelectricity, and ferroelasticity. Such materials offer extra degrees of freedom in the information storage process, which may either simplify the operation of present device structures or offer new architecture [1,2]. Among them, single-phase multiferroic BiFeO$_3$ (BFO) is the most extensively investigated due to its high ordering temperatures of ~1100 K and an antiferromagnetic Néel temperature of ~640 K [3,4]. Robust ferroelectricity ($P_r \sim 100 \mu C/cm^2$), relatively smaller band gap near 3 eV compared to other ferroelectrics and its lead-free nature make BFO a prime candidate for next-generation devices including nonvolatile memories and sensor [4–8]. In addition to the band gap of BFO in or near the visible range, BFO has the added intriguing possibility that it might posses an anomalous photovoltaic effect. Since the 1960s, the anomalous photovoltaic effect has been observed in a number of ferroelectric materials and the effect has been characterized in detail [9]. For photovoltaic ferroelectrics, it has been observed that a homogeneous short circuit crystal displays a photocurrent in the direction of spontaneous polarization under uniform illumination. The non equilibrium photo excited carriers are effectively driven by the ferroelectric polarization and therefore the ferroelectric polarization is a main driving force for the photovoltaic effect in BiFeO$_3$. Besides, it well known that defects, such as oxygen vacancies also contribute to the photovoltaic effect in BFO [10–13]. Finally, the ability to tune the oxygen vacancies in BFO may enable researchers to engineer the band gap and conductivity to enhance the photo ferroelectric properties. Up to now, there are only few studies regarding the effect of oxygen vacancies on the photoconductivity in BFO [14].

This paper is mainly to report the influence of cooling oxygen pressure on the photoconductivity in Bi$_{0.9}$La$_{0.1}$FeO$_3$ (BLFO) thin films. Here, the small amount of La is added to stabilize the perovskite structure. The photoconductivity in BLFO thin films was found to be strongly dependent on the oxygen vacancy concentration, which is very sensitive to the cooling oxygen pressure of the BLFO thin films.

**2. Experimental process**

500 nm thick BLFO thin films were grown epitaxially on (001) SrTiO$_3$ (STO) substrates using pulsed laser deposition method (PLD) with 30 nm thick La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) as bottom electrode. The conductive metallic oxide LSMO was chosen as bottom electrode because its lattice parameter is very close to STO and BFO, and therefore, with small lattice parameter mismatch and stress. First LSMO thin films were deposited on STO substrates under a deposition temperature of 700 °C and an oxygen pressure ~50 Pa. Then, the BLFO thin films were grown at 650 °C under a low oxygen pressure of 15 Pa. The other laser parameters during depositions were (i) laser source: KrF excimer laser with $\lambda = 248$ nm, (ii) repetition frequency: 5 Hz, (iii) energy density was about 1.5 J/cm$^2$. Typical film growth rate was around 9 nm per minute. To investigate the effect of oxygen vacancies on the conductivity, the as deposited BLFO films were slowly cooled to room temperature (2 °C/min) in the oxygen atmosphere of 500, 20 and 0.5 Pa, respectively. For the conductive characteristics measurements, 200 nm thick Ag layer as the top electrodes was...
deposited by PLD through a shadow mask with an area of $3 \times 10^{-4}$ cm$^2$. Structural characterization of the BLFO films was performed using X-ray diffraction (XRD), using M$\mu$s Bruker make D8-Discover system at 40 kV and 40 mA power settings. Green laser with wavelength of 532 nm (100 mW/cm$^2$) was used as excitation light source for the photoconductivity (PC) measurement. Current-voltage characteristics were measured using a Keithley 2611 source meter. The polarity of bias is defined as negative or positive according to the negative or positive voltage applied to the Ag top electrode.

3. Results and discussion

Fig. 1 reveals high quality, epitaxial films that appear to be single phase regardless of the cooling pressure. Only a small shoulder can be found from the (002) peaks of LSMO after cooling in 20 and 500 Pa, respectively. Noticeable shift of the BLFO (002) diffraction peak is observed with varying cooling pressure, pointing to the ability to tune oxygen stoichiometry with affecting the BLFO structure as can be seen from the inset of Fig. 1. The out-of-plane c parameter for these BLFO films increases from 0.397 to 0.399 nm with the cooling oxygen pressure decreasing from 500 to 0.5 Pa. Yuan et al. have observed the c parameter increasing after cooling BFO/SRO/STO (001) with the oxygen pressure from 760 to 0.01 Torr [15]. However, Basu et al. demonstrated that no noticeable shift of the BFO (222) diffraction peak is observed with varying cooling pressure from 760 to 0.01 Torr in the [1 1 1] oriented BFO/SRO/STO heterostructures [14]. Generally, this noticeable diffraction peak shift is always observed in oxygen deficient perovskite manganite such as LSMO and LCMO films [16–19]. As the LSMO layer is so thin that no clear peak shift can be seen under different cooling oxygen pressures. Therefore, it is unknown whether the variation of c parameter is resulted from the oxygen vacancies in BLFO films or by the compressive stress of LSMO bottom electrode.

Fig. 2 shows the leakage current as a function of electric field for the BLFO thin films cooled under different oxygen pressures. It clearly shows that, with decreasing cooled oxygen pressure, the leakage current of the thin film increases evidently. Inset of Fig. 2 shows the data for both positive and negative biases have been graphed on the same axis. The (I–V) characteristics of the films both at negative and positive bias are asymmetric for the 500 Pa oxygen pressure cooling, this may originate from the different work functions of Ag and LSMO electrodes [20,21]. However, the I–V curve shows less asymmetric under lower oxygen pressure cooling. The conductivty at room temperature calculated by the leakage current at $-3$ V is about 9.8 $\times$ $10^{-10}$ (cm$^2$ V$^{-1}$ s$^{-1}$), 1.13 $\times$ $10^{-8}$ (cm$^2$ V$^{-1}$ s$^{-1}$), and 5.39 $\times$ $10^{-8}$ (cm$^2$ V$^{-1}$ s$^{-1}$) for the thin film cooled at 500, 20 and 0.5 Pa, respectively. The dependence of leakage current of the BLFO thin film on cooling oxygen pressure is consistent with that of the BFO thin film reported by Basu et al. [14]. Basu et al. have investigated the leakage currents of BFO thin films grown by pulsed laser deposition under different cooling oxygen pressures, and their results also show that as the oxygen pressure varying from 760 to 0.1 Torr the conductivity increases with decreasing cooling oxygen pressure, but the conductivity decreases again while the cooling oxygen pressure is 0.01 Torr, which has not been observed in our BLFO thin films even the cooling oxygen pressure is low to 0.5 Pa (~0.00375 Torr). Many studies have shown that oxygen vacancies in ferroelectric thin film can be reduced by annealing the film in oxygen [22,23]. This may explain the result that the higher leakage current density of the cooled BFO in lower cooling oxygen pressure than that of higher pressure. It is worth noting that the conductivity of BLFO films cooled in 0.5 Pa oxygen pressure is 55 times larger than that with 500 Pa cooling, indicating obvious effect of oxygen vacancies on the leakage current.

Dark-light I–V characteristics were measured to investigate if a change in conductivity appeared under illumination. The resulting current of photoexcited carriers, driven by the intrinsic polarization, can be described by the following equation [24]:

$$j = (\sigma_d + \sigma_{ph}) \rho$$

(1)

which is typical of photoferroelectric materials. Where $\sigma_d$ and $\sigma_{ph}$ represent the dark and light components of the conductivity, respectively. The photo conductivity can be expressed as [25]

$$\sigma_{ph} = q(\Delta n\mu_n + \Delta p\mu_p)$$

(2)

where $q$ is the electron charge, $\Delta n$ and $\Delta p$ are the photo-induced electron and hole density, and $\mu_n$ and $\mu_p$ is the electron and hole mobility, respectively. Under illumination with wavelength equal to or larger than the band gap, photo generated carriers are added up to dark ones and a larger current is expected, therefore the conductance is increased and the resistance is thus decreased. Noting that large leakage currents in BFO have typically been attributed to the presence of oxygen vacancies [25]. Therefore, we proceeded to investigate a series of samples grown at 850 °C and 15 Pa partial pressure of O$_2$ and then cooled to room temperature at varying pressures in order to control the oxygen stoichiometry. The presence of oxygen vacancies effectively introduces electrons into the lattice and increases the free carrier concentration.

Fig. 1. XRD spectrum of BLFO/LSMO/STO films cooled under different oxygen pressure, inset shows the (002) BLFO peaks shift.

Fig. 2. I–V characteristics of BLFO/LSMO/STO (001) thin films cooled at 500, 20 and 0.5 Pa, respectively. Inset shows the data for both positive and negative biases have been graphed on the same axis.
Fig. 3 shows I–V characteristics taken in dark and 100 mW cm$^{-2}$ green light illumination of 500 nm thick BFO films. Figs. 3(a–c) refer to dark and light I–V curves taken on samples cooled in 500, 20, and 0.5 Pa, respectively. At an applied field of 60 kV/cm ($V = -3$ V). Illuminated conductivities of $6.62 \times 10^{-9}$ ($\Omega \cdot \text{cm}$)$^{-1}$, $2.7 \times 10^{-8}$ ($\Omega \cdot \text{cm}$)$^{-1}$, and $1.03 \times 10^{-7}$ ($\Omega \cdot \text{cm}$)$^{-1}$ were measured for samples cooled at 500 Pa Fig. 3(a), 20 Pa Fig. 3(b), and 0.5 Pa Fig. 3(c), respectively. Moreover, with the decrease in cooling oxygen pressure, an obvious increase in the conductivity is observed at all applied fields. The corresponding photoconductivity $\sigma_{\text{ph}}$ is $5.64 \times 10^{-9}$ ($\Omega \cdot \text{cm}$)$^{-1}$, $1.57 \times 10^{-8}$ ($\Omega \cdot \text{cm}$)$^{-1}$ and $4.91 \times 10^{-8}$ ($\Omega \cdot \text{cm}$)$^{-1}$, respectively. Indicating that $\sigma_{\text{ph}}$ increases with oxygen vacancies. Similar and huge enhancement of the conductivity induced by oxygen vacancies was reported in single domain of BFO crystals [11].

It is worth noting that the photon energy 2.33 eV (with $\lambda = 532$ nm) is smaller than the band gap of BLFO ($\sim 3$ eV) [26–29]. Therefore, it is difficult for the green light to induce the photo excited carriers based on the intrinsic absorption of BLFO film. The main reasons may be that, on the one hand, there exist a small number of defects such as oxygen vacancies, locating at the grain boundaries. On the other hand, oxygen vacancies should lead to the creation of some states inside the band gap, the ionization energy of impurities is usually smaller than the band gap of the materials. Besides, defect absorption is weaker than intrinsic absorption since the concentration of defects is several orders of magnitude smaller than that of the main crystal lattice atoms and therefore the conductivity increases. Thus, lower oxygen pressure means more oxygen vacancies, which induces the enhancement of leakage current density. In addition, nearly symmetric dark I–V behavior Fig. 3(d) indicates that the change in conductivity upon illumination is not simply the result of excitation across a Schottky barrier with either contact. The possible origin is the photo induced carrier generation in the film plays a major role for the behavior. When illuminated with energies below the band gap of BLFO film, as the thickness of the film is thinner than the absorption length of light in the wavelength range used in the present experiments, some photons could pass through the BLFO film and be absorbed by the electrode LSMO, which induced more carriers in LSMO electrode. By using different electrodes, Basu et al. [14] showed that it is intrinsic to the BFO. Besides, oxygen vacancies in BFO are known to electromigrate [26]. Therefore, one possible intrinsic origin could be the change in the oxygen vacancies distribution through BLFO induced by the different cooling pressures or by the carriers in LSMO electrode.

To investigate the effect of cooling oxygen pressure on the conductive mechanisms and nearly symmetric dark I–V behavior of BLFO films cooling in low oxygen pressure, we consider the

![Fig. 3](image-url)

Fig. 3. Light and dark current as a function of applied field for BLFO/LSMO/STO (001) films cooled at (a) 500 Pa, (b) 20 Pa, (c) 0.5 Pa partial pressure of oxygen.
bulk-limited space-charge-limited conduction (SCLC) leakage mechanisms because the SCLC mechanism is considered as a normal leakage behavior and correlates with oxygen vacancies in BFO materials [11]. The limitation arises from a current impeding space charge forming as charges are injected into the film from the electrode at a rate faster than they can travel through the film. The current density for SCLC is [30–34].

\[ J_{\text{SCLC}} = \frac{9}{8} \epsilon_0 \epsilon_r \mu V^2 \frac{d^3}{3} \]  

where \( \epsilon_0 \) is the permittivity of vacuum, \( \epsilon_r \) is the dielectric constant of the film, \( \mu \) is carrier mobility, \( V \) is the applied voltage, and \( d \) is the sample thickness.

Fig. 4 shows \( \log(J) \) versus \( \log(E) \) characteristics of the BLFO films cooled in 500 and 0.5 Pa oxygen pressure at negative bias. For the BLFO films cooled in 500 Pa oxygen pressure, the slopes are close to 1 and the leakage currents show Ohmic behavior at relatively lower electric fields. In the high electric field range of 27 kV/cm (dark) and 19.5 kV/cm (light), the \( \log(J) \)-log(\( E \)) plots are linear and the slopes are close to 2, which agree well with the SCLC mechanism. For the BLFO films cooled in 0.5 Pa oxygen pressure, the \( \log(J) \)-log(\( E \)) plots are linear and the slopes are close to 2 in the electric field range of 11.8 kV/cm (dark), and 6 kV/cm (light), indicating the SCLC mechanism. Therefore, we can conclude that SCLC conductive mechanism is more dominated in lower cooling oxygen pressure (with high oxygen vacancies concentration) and light illumination.

Oxygen vacancies have been related to the origin of space charges in some ferroelectric materials [35]. Oxygen vacancies create deep-trap energy levels in the band gap for activated electrons to be mobile. Therefore, more oxygen vacancies mean more free carriers generated in the films. Qi et al. demonstrated that in the BFO films space charges originated from deep-level traps in the band gap which induced by \( V_{oa} \) [36]. Thus, a higher density of \( V_{oa} \) contributes directly to the high free carrier concentration, which, in return, leads to a higher leakage current density in the low oxygen cooled BLFO films with high density of oxygen vacancies. On the other hand, the SCLC originates from the density of free carriers due to the carrier injection, \( n_i \), becoming greater than the density of volume-generated free carriers, \( n_v \) [36]. The limitation of SCLC arises from a current impeding space charge forming as charges are injected into the film from the electrode at a rate faster than they can travel through the film. Therefore, more carrier injection rate will result a faster rate than they can travel through the film, which in turn makes the SCLC be dominated. It is evident that the higher \( V_{oa} \) in lower oxygen pressure cooled BFO and/or under light illumination induce a higher \( n_i \) consist of oxygen vacancies or photo-induced electron–hole pairs, and therefore the conductive mechanism is dominated by SCLC with higher carrier injection.

4. Conclusions

In summary, the effect of cooling oxygen pressure on the photoconductivity in \( \text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3 \) films under illumination from a 100 mW/cm\(^2\) green light source was studied. X-ray diffraction analysis revealed noticeable shift of the BLFO (002) diffraction peak is observed with varying cooling pressure, pointing to the ability to tune oxygen stoichiometry with affecting the BLFO crystal structure. A direct correlation is observed between the magnitude of the photoconductivity and post growth cooling pressure. The BLFO films cooled in higher oxygen pressure show obviously decrease in leakage current than that of low oxygen cooled, dark conductivities increased by 55 times of magnitude when comparing films cooled in 500 and 0.5 Pa. Large increases in photoconductivity are observed in light, a higher level of oxygen vacancies led to the high free carrier concentration and hence is believed to be responsible for the increase in higher photoconductivity. It is evident that the higher \( V_{oa} \) in lower oxygen pressure cooled BFO and/or light illumination induce a higher carrier injection, \( n_i \), and hence the conductive mechanism is dominated by SCLC.

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