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The origin of photovoltaic responses in BiFeO$_3$ multiferroic ceramics

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Abstract
Multiferroic BiFeO$_3$ (BFO) ceramics with electrodes of indium tin oxide (ITO) and Au thin films exhibit significant photovoltaic effects under near-ultraviolet illumination ($\lambda = 405$ nm) and show strong dependences on light wavelength, illumination intensity, and sample thickness. The correlation between photovoltaic responses and illumination intensity can be attributed to photo-excited and thermally generated charge carriers in the interface depletion region between BFO ceramic and ITO thin film. A theoretical model is developed to describe the open-circuit photovoltage and short-circuit photocurrent density as a function of illumination intensity. This model can be applied to the photovoltaic effects in p–n junction type BFO thin films and other systems. The BFO ceramic exhibits stronger photovoltaic responses than the ferroelectric Pb$_{1−x}$La$_x$(Zr$_x$Ti$_{1−x}$)$_{1−y/4}$O$_3$ (PLZT) ceramics under near-ultraviolet illumination. Comparisons are made with other systems and models for the photovoltaic effect.

(Some figures may appear in colour only in the online journal)

1. Introduction
Photovoltaic and photostrictive effects have been extensively investigated in antiferromagnetic/ferroelectric BiFeO$_3$ (BFO) thin films and crystals [1–13]. Several mechanisms were proposed for the photovoltaic responses in BFO thin films and crystals, including asymmetric ferroelectric photovoltaic effect (bulk photovoltaic effect) [7, 14], domain-wall model [8], and semiconductor-like p–n junction model [13]. The domain walls in rhombohedral BFO thin films exhibit a p–n junction-like potential step, whose value is theoretically higher in the 109° domain walls (~0.15 V) compared to the 71° domain walls (~0.02 V) [9]. The effects of electric (E)-field poling [2], illumination wavelength and intensity [2, 5], substrate [4], and electrode [5, 6] on photovoltaic responses and optical properties of BFO films have also been explored. In addition, the photostrictive effect in BFO crystal can reach 10$^{-5}$ with response time less than 0.1 s, which depends on light polarization and magnetic field [11].

A p-type semiconductivity was found in BFO film with impurity density of $n_p \sim 10^{23}$ m$^{-3}$ [13]. The photovoltaic responses were attributed to a p–n junction layer at the ITO–BFO interface. ITO film has been reported as being a n-type semiconductor with carrier concentration of $n_n \sim 10^{20} - 10^{27}$ m$^{-3}$ [15, 16]. Photovoltaic responses were also observed in the p–n depletion layer of a LaMnO$_3$/Nb-doped SrTiO$_3$ structure, in which LaMnO$_3$ plays the role of p-type semiconductor [17]. The photovoltaic responses of ferroelectric/piezoelectric PLZT ceramics and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_{1−x}$Ti$_x$O$_3$ (PMN–PT) crystals are sensitive to thickness and grain size [18–21]. A photovoltaic mechanism associated with charge distributions (polarization charge, Schottky space charge, and screening charge) was proposed for PLZT thin films and its efficiency can be improved with reduced thickness [22].

Most photovoltaic studies and proposed mechanisms in BFO films have been focusing on the current–voltage correlation under a constant light intensity. In this work,
a theoretical model was first proposed to describe the correlation between photovoltaic responses and illumination intensity in the ITO film/BFO ceramics/Au film capacitor configuration.

2. Experimental details

The BiFeO$_3$ (BFO) ceramics were prepared by the solid state reaction method. In the synthesis, Bi$_2$O$_3$ and Fe$_2$O$_3$ powders (purity ≥ 99.0%) were weighed in 1.1:1 ratio to compensate the loss of Bi during the sintering process. The powders were mixed in an agate mortar for more than 24 h using alcohol as a medium. The mixture was dried before calcining at 800 °C for 3 h. The calcined powder was then pressed into a disk before sintering at 830 °C for 10 h. ITO and Au films were deposited on the BFO ceramic as electrodes by dc sputtering. Two intensity-adjustable diode lasers of $\lambda$=405 and 532 nm were used for photovoltaic effects. The laser beam was incident perpendicular to the sample surface with ITO film.

3. Results and discussion

Figures 1 and 2 show open-circuit photovoltage ($V_{oc}$) and short-circuit photocurrent density ($J_{sc}$) as light was switched on and off under illuminations of $\lambda$ = 405 and 532 nm for thicknesses of $t_D$: 2, 0.3, and 0.5 mm. Both $V_{oc}$ and $J_{sc}$ exhibits strong and nonlinear dependences on light intensity ($I$) and wavelength ($\lambda$). The intensity-dependent $V_{oc}$ and $J_{sc}$ are plotted in figures 3 and 4. Compared with $\lambda$ = 532 nm, the illumination of $\lambda$ = 405 nm ($E_{ph}$ ≈ 3.06 eV) induces much stronger photovoltaic responses. These results agree with the optical band gap of ~2.74 eV in BFO [2, 12]. The $J_{sc}$ for $t = 0.2$ mm can reach ~0.23 A m$^{-2}$ for $I \sim 1.9 \times 10^3$ W m$^{-2}$ under illumination of $\lambda = 405$ nm. This $J_{sc}$ is much stronger than in the poled PLZT(3/52/48) ceramics, whose $J_{sc}$ ($t = 50 \mu$m) shows a linear increase with $I$ and is ~0.2 mA m$^{-2}$ for $I \sim 2 \times 10^3$ W m$^{-2}$ under illumination of $\lambda = 366$ nm [18].

To understand the light intensity-dependent $V_{oc}$ and $J_{sc}$, a theoretical model is derived as follows. We consider a p-type BFO slab on the right and an n-type ITO slab on the left. Electrons will diffuse right, and holes diffuse left, annihilating each other and leaving a depletion region. The first task is to find the open-circuit voltage step $U_o$ going from left to right across the p–n junction under no illumination. For no illumination there can be no net current. The compensating current is from holes from the non-depleted p-type BFO diffusing ‘uphill’ in electrostatic energy to the non-depleted n-type ITO and from electrons from the non-depleted n-type ITO diffusing ‘uphill’ in electrostatic energy to the non-depleted BFO.

In addition to the thermally generated electron–hole pairs with $I$ and $\lambda$, many additional electron–hole pairs will be generated optically under illumination. These additional holes will flow right, and the electrons left, thereby decreasing the depletion-region width. However, the decreased width will lower the retarding voltage that limits the leftward hole and electron diffusion currents, thus increasing these currents. The decreased width decreases the downward voltage step from the depletion region, to magnitude $U < U_o$, and so the measured open-circuit...
The voltage is

\[ V_{oc}(I) = U_o - U_{oc}(I). \]  (1)

There are three contributions to the total current density \( J \). The first contribution \( J_1 \) is from thermally stimulated electron–hole pairs created in the depletion region. The number density \( n_t \) of electrons close enough to the top of the valence band so that they have a chance to be excited to the conduction band is assumed to be 

\[ n_t = N kT/E_{cn}, \]

where \( N \) is the density of electrons in the valence band, \( k \) is Boltzmann’s constant, \( T = 300 \text{ K} \) is chosen as room temperature, and \( E_{cn} \) is the top energy of the valence band. The thermal excitation probability \( p_v \) per unit time per electron is 

\[ p_v = \nu \exp(-E_{cn}/kT), \]

where \( \nu \) is the attempt frequency and \( E_{cn} \) is the bottom energy in the conduction band. Considering both the n- and p-type regions, we multiply \( n_t p_v \) by the depletion-region width \( d \) and by the carrier charge \( q \) to find \( J_1 \),

\[ J_1 = qkTv[(d_n N_n/E_{cn})e^{-E_{cn}/kT} + (d_p N_p/E_{vp})e^{-E_{vp}/kT}]. \]  (2)

The second contribution to \( J \) is the \( J_e \) from existing carriers that are close to the depletion region and have enough thermal energy to jump across it against the coulomb force. The dopant concentration \( n \) is assumed to be independent of position. The holes (or electrons) that are close enough to the depletion region so that when thermally excited they do not lose much energy to other carriers, are assumed to come from a plane of thickness corresponding to the mean spacing between acceptors (or donors). The number density per unit area of these potentially excited carriers accordingly is 

\[ n_{t}^{2/3} \]

(or \( n_{e}^{2/3} \)). The probability per unit time per carrier that such a carrier obtains enough energy to cross the depletion region is 

\[ \nu \exp(-qU/kT). \]

The hole and electron contributions to \( J_e \) are negative, so \( J_e \) is given by

\[ J_e = -q\nu(n_{t}^{2/3} + n_{e}^{2/3}) \exp(-qU/kT). \]  (3)

The third contribution is the photo-excited current density \( J_p \). The light intensity is assumed to decay exponential in the BFO-side depletion region with a general form of \( I(z) = I \exp(-z/\beta) \), where \( \beta \) is the attenuation length. The ITO layer absorbs little light because its optical band gap is larger than the photon energy. The absorbed intensity \( I_0 \) in the depletion region can be estimated by 

\[ I_0 = I_d/\beta. \]

The creation rate of electron–hole pairs can be estimated to be 

\[ I_d/(hc/\lambda), \]

then \( J_p \) is given by

\[ J_p = qdI_\lambda/(hc\beta). \]  (4)

We now find an expression for the p–n junction voltage step \( -U \) in terms of the depletion-region widths \( d_n \) and \( d_p \), which are parameters of light intensity. Let position coordinate \( x \) be zero at the interface of the p–n junction. In the depletion region of 

\[-d_n < x < 0, \]

\( \rho_n = qn_n \) comes from the ionized donors each of which has donated one electron to the conduction band. Similarly, in the depletion region of 

\[ 0 < x < d_p, \]

\( \rho_p = qn_p \) comes from the acceptors each of which has accepted one electron from the valence band. Using Gauss’ law for the region \(-d_n < x < 0\), the position-dependent E-field is,

\[ E(x) = \int_{-d_n}^{x} (\rho_n/\varepsilon_o \varepsilon_n) \, dx' = (\rho_n/\varepsilon_o \varepsilon_n)(x + d_n). \]  (5)

Then the contribution from the n-type material to \(-U\) is,

\[ -U_n = -\int_{-d_n}^{0} E(x) \, dx = -(\rho_n/\varepsilon_o \varepsilon_n)d_n^2/2. \]  (6)
Similarly, \( V_{sc} = (\rho_p/\varepsilon_o \varepsilon_p) d_p^2 / 2 \) is from the p-type material. The total contributions for \( -U \) are

\[-U = (\rho_p/\varepsilon_o \varepsilon_p)d_p^2 / 2 - (\rho_n/\varepsilon_o \varepsilon_n)d_n^2 / 2 \]

\[= -(q/2\varepsilon_o)(n_p d_p^2 / \varepsilon_p + n_n d_n^2 / \varepsilon_n) \]

Equation (7) yields

\[-U = -(q^2/2\varepsilon_o)(n_p d_p^2 / \varepsilon_p + n_n d_n^2 / \varepsilon_n) = -Bd^2; \]

\[B = (q^2\varepsilon_o/2\varepsilon_p)(n_p d_p^2 / \varepsilon_p + n_n d_n^2 / \varepsilon_n). \]

We use the condition of no illumination to solve for \( U_{sc} \) and designate \( d \) as \( d_0 \). For no illumination we have \( J_{io} + J_{eo} = 0 \), i.e.

\[qkT/(n_p n_p/\varepsilon_o \varepsilon_p + n_n d_n^2 / \varepsilon_n) \exp(-E_{gsc}/kT) + (n_p/\varepsilon_p) \exp(E_{gsc}/kT) \]

\[\exp(2/3) + (q^2/2\varepsilon_p) \exp(-Bd_0^2/2kT) = 0. \]

Before solving \( d_0 \) and \( U_{sc} \), it is worthwhile to know how \( J_{io} \) is related to the diode reverse saturation current \( I_{sc} \). We rewrite equation (9), still for no illumination, but now with an applied voltage \( V_{sc} \) given by \( V_{sc} = U_{sc} - U \). From equation (8), we have \( d = (U_{sc} - V_{sc})/B \). Inserting this \( d \) value in place of \( d_0 \) in equation (9) gives the current density \( J_a \) resulting from \( V_{sc} \):

\[J_a = J_{io}[(1 - V_{sc}/U_{sc})^{1/2} - \exp(V_{sc}/V_c)], \]

where \( V_c \equiv kT/q \). The diode current–voltage characteristic as given by Shockley et al [23] is

\[J_a = (I_0/A)[1 - \exp(V_{sc}/V_c)], \]

where \( A \) is junction area. As increasingly negative voltage is applied, the exponential term quickly approaches zero, before the square root term in equation (10) changes appreciably from unity, so \( J_a \) becomes \( J_{io} \) in equation (10) and \( I_0/A \) in equation (11).

Now we use equation (9) to solve \( d_0 \). We can use equations (2), (3), and (8) to find \( U_{sc} \), \( J_{io} \), and \( J_{eo} \). To find \( V_{sc} \), we start by finding the \( d \) that gives \( J_1 + J_e + J_p = 0 \). Then we find \( U \) corresponding to this \( d \), and use \( V = U_{sc} - U \). We set \( D = d/d_0, \alpha = qd_0/hc B J_{sc} \), and \( C = qd_0^2/kT = qU_{sc}/kT \). For the open-circuit case, the illumination intensity-dependent \( D_{oc} \) is \( d_{oc} / d_0 \) can be obtained by

\[J_1 + J_p + J_e = J_{io} D_{oc} + J_{eo} D_{oc} \alpha \]

\[-J_{io} \exp(C(1 - D_{oc}^2)) = 0. \]

Then the \( V_{oc} \) can be obtained by using equation (8), i.e.

\[V_{oc} = U_{sc} - BD_{oc}^2 U_{sc} = U_{sc}(1 - D_{oc}^2). \]

Now we investigate the total short-circuit current density \( J_{sc} \) and area-specific resistance \( R_{sc} = RS \) of the BFO thin films, whose \( R_{sc} \) is zero in the short-circuit case. The resistivity of semiconductors typically decreases as temperature is increased. If the temperature due to laser illumination does not vary too much, a linear approximation between resistance and intensity can be used, i.e. \( R_{sc} = R_{sc0}(1 - \eta \theta) \). \( \eta \) is the intensity coefficient of resistance. The emf driving the \( J_{sc} \) through the source area-specific \( R_{sc} \) is \( U_{sc} - U_{sc0} \). Here, the \( J_{sc} \) is.

\[J_{sc} = (U_{sc} - U_{sc0})/R_{sc0} = U_{sc0}(1 - D_{oc}^2)/R_{sc0}. \]

From equation (12), modified for the short-circuit case, we have

\[J_{sc} = J_{io}[D_{sc}(1 + \alpha I) - \exp[C(1 - D_{sc}^2)]]]. \]

We subtract equation (14) from equation (15) and use \( F \equiv U_{sc}/R_{sc}J_{sc} \). We then obtain

\[D_{sc}(1 + \alpha I) - \exp(C(1 - D_{sc}^2)) - (1 - D_{sc}^2) = 0. \]

The short-circuit \( D_{sc} = d_{sc}/d_0 \) as a function of \( I \) can be obtained from equation (16). Then, the \( J_{sc} \) can then be obtained from equation (15). In the fitting, a weak intensity-dependent resistance was used in \( F \), i.e. \( F \equiv U_{sc}/R_{sc}J_{sc} \).

The solid lines in figures 3 and 4 are fits of \( V_{oc} \) and \( J_{sc} \) as a function of intensity \( I \) by using equations (12)–(16) with parameters given in table 1. The experimental results and theoretical fits agree reasonably well. The insets of figures 3 and 4 show the correlation between the ratio \( d/d_0 \) and light intensity for the open-circuit and short-circuit cases. The measured \( V_{oc} \) are comparable with the BFO thin films, whose \( V_{oc} \) varies in the range of 0.3–0.5 V [2, 6]. The measured \( V_{oc} \) was predicted by our model if values for \( E_{gsc}, E_{gsc}, E_{gsc}, E_{gsc} \) from the literature are used in equations (8), (9), and (12) to find \( d_0, d_{oc} \) and \( U_{sc0} \), and then equation (13) is used to find \( V_{oc} \). In fact, our model using these parameters predicts \( V_{oc} \) in the 0.3–0.5 V range found in BFO thin-film-based structures as well as in common photovoltaic junction materials like Si and Ge.

In choosing the fit parameters, we note that the carrier concentration \( n_p \) in the n-type ITO films is larger than \( n_p \) in the p-type BFO films [13, 15, 16]. Thus, from equation (8) we have \( B = U_{sc}/d_0^2 = qn_p/(2\varepsilon_o \varepsilon_p) \). The room-temperature dielectric permittivity \( \varepsilon_p \) in BFO ceramic is \(~10^2 \) [24]. We

| Table 1. The fitting parameters for the solid lines in figures 3 and 4. |
|-----------------|---|---|---|---|---|
| \( \lambda \) = 405 nm | \( U_{sc} \) (V) | \( C \) | \( \alpha \) (W m\(^{-2}\))\(^{-1}\) | \( R_{sc} \) (\( \Omega \) m\(^{-2}\)) | \( \eta \) (W m\(^{-2}\))\(^{-1}\) |
| \( t \) = 0.2 mm | 0.78 | 28 | 2.2 \times 10^8 | 9.4 | 0.001 |
| \( t \) = 0.3 mm | 0.59 | 23 | 1.0 \times 10^7 | 12 | 0.0008 |
| \( t \) = 0.5 mm | 0.57 | 23 | 1.0 \times 10^7 | 23 | 0.0004 |
use the carrier density $n_p \cong 10^{23} \text{ m}^{-3}$ as reported for BFO film [13]. For the case of $t = 0.2 \text{ mm}$, $d_o \cong (2e_0\epsilon_0 U_o/qm_p)^{1/2}$ was estimated to be $\approx 330 \text{ nm}$, which is consistent with the depletion layer in ITO–BFO films [13]. The parameters $C$ and $U_o$ are related by the carrier charge $q (=\text{CT}/U_o)$, where we chose $q$ as the electron charge $\approx 1.6 \times 10^{-19} \text{ C}$.

Finally, we consider three related questions. First, how do the shapes of our $V_{oc}$ and $J_{sc}$ curves versus $I$ compare with those for other $p$–$n$-junction-based photovoltaic systems? Second, how can our model account for the similarities and differences between those systems and ours? Third, how does our model for these intensity dependences compare with other models?

Other reports [25, 26] show curves for $V_{oc}$ versus $I$ with convex shape similar to ours. However [25], shows linear dependence of $J_{sc}$ on $I$, unlike our convex curves. Our model is able to account for this difference in $J_{sc}$ behavior, by analyzing the differences in the ratios $D_{sc}$ and $D_o$ shown in the insets of figures 3 and 4. Mathematically, from equations (12) and (16), one can think of $F$ as being a function of $D$, and we find that $\partial F/\partial D > 0$ and so also $\partial D/\partial F > 0$. This means that $D_{sc} > D_{oc}$. The crucial factor in $F \equiv U_o/R_A J_{sc}$ is the area-specific source resistance $R_A$. As $R_A$ becomes infinite, $D_{sc}$ and $D_{oc}$ become equal. If $R_A = 0$, $D_{oc} = 1$. Physically, this means that there is no hindrance for photo-generated electron–hole pairs to travel around the circuit until they recombine, whereas for nonzero $R_A$ this hindrance narrows the depletion-region width. For $R_A$ small but nonzero, the parameter $1 - D_{sc}$ becomes small. If we expand equation (15) in this small parameter, we arrive at the relation

$$J_{sc} \left( \text{small } R_A \right) \cong J_{0o} \alpha I.$$ (17)

This relation that is linear in $I$ can account for the linear dependence of $J_{sc}$ on $I$ observed by Cusano [25] if $R_A$ is small.

Cusano [25] has no expressions for $V_{oc}$ or $J_{sc}$. Rose [26] does not provide an expression for $J_{sc}$. Reference [26] shows a linear dependence in $V_{oc}$ at low intensity, followed by a convex curve that saturates into a horizontal line. If we take the low and high intensity limits for $D_{sc}$ in equation (12) and insert these values into equation (13), we obtain

$$V_{oc} \left( \text{low } I \right) \cong \alpha U_o J/(C + 1/2);$$
$$V_{oc} \left( \text{high } I \right) \cong U_o.$$ (18)

Accordingly, our model predicts the same linear, convex curve, constant $I$ dependence sequence that is presented by Rose [26].

4. Conclusions

The ITO film/BFO ceramic/Au film configuration exhibits significant photovoltaic effects under illumination of $\lambda = 405 \text{ nm}$, which strongly depend on light wavelength, illumination intensity, and thickness. The proposed model which includes both thermally generated and photo-excited electron–hole pairs, can reasonably describe the photovoltaic responses as a function of illumination intensity. This physical model can be applied to the photovoltaic effects in $p$–$n$-junction type BFO thin films and pother systems.

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References