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Evidences for the depletion region induced by the polarization of ferroelectric semiconductors

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Ferroelectric materials possess spontaneous polarization pointing from negative to positive bound surface charges. When a ferroelectric semiconductor is polarized, the induced electric field can drive free carriers, e.g., electrons in an n-type material, to neutralize surface charges until such field becomes zero. Such diffusion of free carriers induces a depletion region. Polarization switch can move the depletion region to the opposite surface, thus it can be used to manipulate any properties that are affected by such depletion region, such as unidirectional current and photovoltaic current. © *2009 American Institute of Physics*. [doi:10.1063/1.3268783]

Switch of ferroelectric polarization (P_{FE}) can be used to manipulate many semiconductor properties in a slightly leaky ferroelectric sample, i.e., a ferroelectric semiconductor. Most applications of ferroelectric materials are based on their P_{FE}, which needs to be switched by a large enough electric field. Although only $\sim 10^{-9}$ s is needed to switch a ferroelectric domain, far longer period is commonly used to fully polarize ferroelectric samples, especially polycrystalline samples.[1] High resistivity has been crucial for the study and applications of ferroelectric materials.[2–4] With the development of advanced characteristic techniques, domains of ferroelectric semiconductors can be switched by electric field pulses and then their electrical properties can be studied by scanning probe based techniques and so on.[5] Thus the interaction between P_{FE} and semiconductor properties should be investigated in details.

P_{FE} has already been used to manipulate the unidirectional current and photovoltaic current of polarized ferroelectric semiconductors, though it is not clear how these properties couple with P_{FE}. Choi *et al.*[5] recently reported that P_{FE} can switch the directions of unidirectional current and photovoltaic current and the latter varies with the electric polarization of incident light beam (P^{ω}, ω is the frequency) in a single domain $BiFeO_3$ crystal. Besides, the dependence of photovoltaic voltage on P_{FE} was also observed in WO_3-doped $(Pb_{0.97}La_{0.03})(Zr_{0.52}Ti_{0.48})O_3$ (W-PLZT) films.[6,7] These observations open the door to the application of ferroelectric semiconductors in microelectronic or photoelectric devices. How photovoltaic voltage is induced in ferroelectrics has been studied extensively.[6–12] However, it is not clear why these unidirectional current and photovoltaic current depend on the P_{FE} direction in many ferroelectric materials. Traditionally, such behaviors come from a depletion region which exists in p-n/Schottky junctions or is induced by photorefractive effect or high-density surface states.[8–11] However, the photovoltaic current induced by these factors should not reverse its direction upon P_{FE} switch. It is necessary to study whether and how a depletion region depends on P_{FE} in a ferroelectric semiconductor.

In this letter, a P_{FE}-induced depletion region is proposed to explain the dependence of unidirectional current and photovoltaic current on P_{FE} direction in a polarized ferroelectric semiconductor.

Many factors can lead to depletion regions in a ferroelectric semiconductor, including (i) depolarization field (E_{FE}) due to incomplete screening of the polarization charge, (ii) Schottky barriers at the electrode/ferroelectric interface due to different work functions, and (iii) surface states of the semiconductor or other special factors.[6–11] All of them can generate photovoltaic response, but only that generated by depletion regions due depolarization field can be reversed upon polarization switching. The P_{FE} dependent current and photovoltaic responses can only be observed if factor (i) dominates over (ii) and (iii), thus the dependence on electrode materials. Please note that the width of such depletion regions depends on the P_{FE}, band gap and doping concentration of the ferroelectric semiconductor. If the doping concentration is higher, the depletion region can be limited to a region next to the surface. It can also extend throughout the whole sample if the doping concentration is low, the ferroelectric layer is thin and/or the remnant P_{FE} is large.

We use an n-type ferroelectric semiconductor as an example in the following discussion, where a depletion region can be induced near the negative bound surface charges. Oxygen vacancies of ABO_3-type ferroelectrics are the main reason for them to become n-type semiconductors,[13–15] as demonstrated in the oxygen-deficient $BaTiO_3$ and Ca-doped $BiFeO_3$.[13,16] This means that oxygen vacancies can be donors in Fig. 1. A neutral oxygen vacancy (V_O) easily releases electron(s) to conduction band (CB) and becomes positively charged ($V_O^{\bullet}$ or $V_O^{\bullet\bullet}$).[13–15] The E_{FE} can activate electrons of oxygen vacancies and then drive them to neutralize positive bound surface charges.[1] At one surface a narrow electron region is formed to neutralize the positive bound surface charges, resulting in the downward-bend CB and valence band (VB), and at the opposite surface V_O loses electrons and becomes $V_O^{\bullet}$ or $V_O^{\bullet\bullet}$. Different from free electrons in CB,

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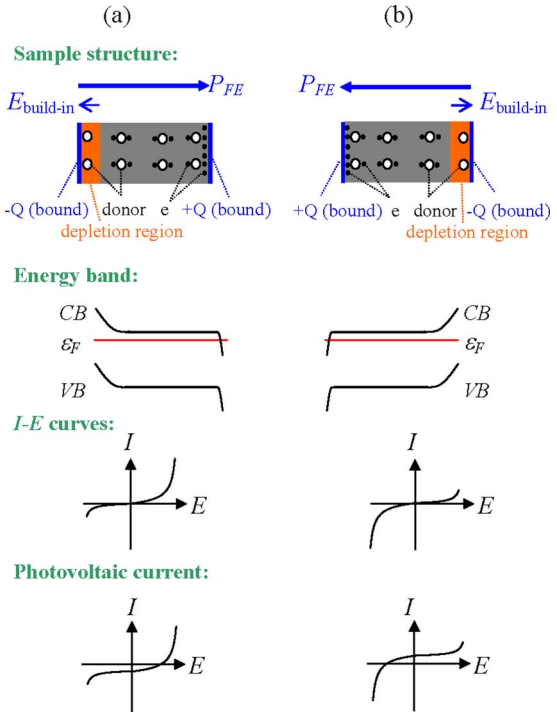

FIG. 1. (Color online) The schematic map of sample structures, energy bands, *I-E* curves and photovoltaic currents for some n-type semiconductor with a P_{FE} directing to (a) right or (b) left, where the right electrode of sample is zero-volt ground and the positive current is defined to pass through crystal from left to right.

$V_O^{\bullet}$, or $V_O^{\bullet\bullet}$ can be treated as fixed charges under small field.[13] As a result, near negative bound surface charges, a depletion region contains the fixed $V_O^{\bullet}$ or $V_O^{\bullet\bullet}$, resulting in the upward-bend CB and VB. The thickness of depletion region should depend on both the P_{FE} and the concentration of oxygen vacancies,[13,16] and a build-in electric field ($E_{build\text{-}in}$) should direct from the depletion region to the negative bound surface charges. In a word, a depletion region can be induced near the negative bound surface charges in n-type ferroelectric semiconductor, being similar to that induced by the high-density surface states of n-type semiconductors.

The P_{FE} induced depletion region can explain the observed unidirectional current (I) which depends on the orientation of P_{FE}, temperature, and light illumination. Being similar to any other depletion region, it introduces a unidirectional current and its forward bias occurs when an external small field (E) is applied along P_{FE}, i.e., against the direction of $E_{build\text{-}in}$, as shown in Fig. 1(a). Since such a depletion region does not come from a Schottky junction, its properties do not depend on the type of electrodes (e.g., Au and Ag). When the temperature increases or a light beam illuminates the crystal, electrons from oxygen vacancies or even some electrons in VB can be promoted to CB,[17] thus the resistivity inside the semiconductor decreases and the depletion region becomes thinner, both of which contribute to a larger I under the same E. The switch of P_{FE} moves negative bound surface charges and the neighboring depletion region from one surface to the opposite surface, thus directions of $E_{build\text{-}in}$ and forward bias of unidirectional current also reverse simultaneously, as shown in Figs. 1(a) and 1(b). The above conclusion is consistent with the experimental results reported in Ref. 5. Since the I at the forward bias (i.e. E parallel to P_{FE}) is far larger than that at the reverse bias (i.e. E anti-parallel to P_{FE}) in Fig. 1, this difference can be used to nondestructively read-out P_{FE} direction that is important for ultrahigh-density information storage.[18]

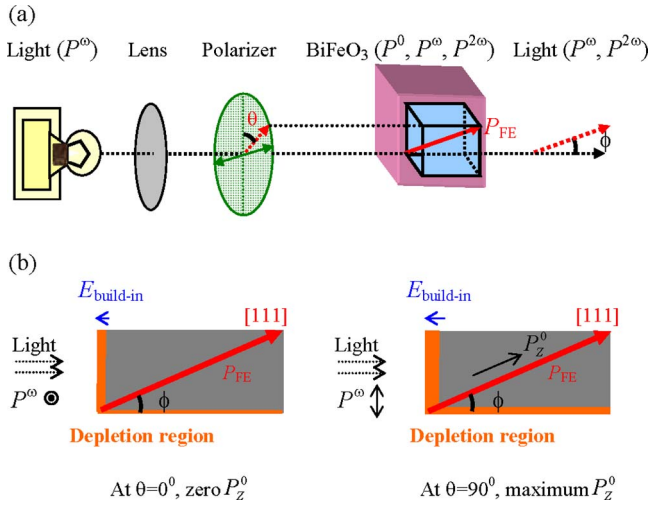

FIG. 2. (Color online) (a) A single-ferroelectric-domain $BiFeO_3$ crystal produces P^0 and $P^{2\omega}$ when a light beam with P^{ω} illuminates the crystal. (b) (Left) The depletion region isn't influenced by P^{ω} and photovoltaic current is small at $\theta=0°$ (i.e., $P^{\omega} \perp P_{FE}$), or (Right) such region becomes thicker and photovoltaic current becomes larger because of maximum P_Z^0 at $\theta=90°$.

The P_{FE} induced depletion region can also explain the photovoltaic current which depends on the P_{FE} orientation. When the depletion region is illuminated by a light beam with photon energy larger than the band gap,[13,14] electron-hole pairs can be generated and holes/electrons drift toward/against the surface with negative bound surface charges under the $E_{build\text{-}in}$. Such diffusion results in a photovoltaic current along the direction of $E_{build\text{-}in}$, i.e., against the orientation of P_{FE}. This photovoltaic current induced by the light beam from near-depletion-region side should be stronger than that by the light beam from the opposite side, since most light should be absorbed as it passes through the sample, such as the ≥ 70 μm thickness $BiFeO_3$ crystal used in Refs. 5 and 19. When the depletion region moves from one surface to its opposite surface of samples because of P_{FE} switch, photovoltaic current also switches its direction to be against the orientation of P_{FE}, as shown in Figs. 1(a) and 1(b). This conclusion is again consistent with the experimental results reported in Ref. 5.

The photovoltaic current may be weakly influenced by the P^{ω} of the incident light beam because the optical rectification disturbs the depletion region in a single domain crystal. In Fig. 2, we use a single domain $BiFeO_3$ semiconductor discussed in Ref. 5 as an example. The coordinates defined according to $BiFeO_3$ pseudocubic crystal axes are $x \| [1\ -1\ 0]$, $y \| [1\ 1\ -2]$, and $z \| [1\ 1\ 1]$ (i.e., along P_{FE}), ϕ is defined as the angle between the P_{FE} and the propagation direction of light beam, and θ is defined as the angle that light polarizer rotates around this propagation direction.[20] The induced nonlinear polarization (P^{NL}) includes the zero-frequency P^0 due to optical rectification and the 2ω-frequency $P^{2\omega}$ due to second harmonic generation when the light beam with a P^{ω} and a density of I_0 illuminates the $BiFeO_3$ crystal.[19,20] $BiFeO_3$ belongs to the 3 m point group and thus there are only four independent nonlinear optical coefficients, i.e., d_{22}, d_{31}, d_{15}, and d_{33}.[20] Both P^0 and $P^{2\omega}$ can be exactly calculated according to the left hand side of Eq.

(1) as discussed in Ref. 20. The $d_{22}(2\omega)$, $d_{31}(2\omega)$, $d_{15}(2\omega)$, and $d_{33}(2\omega)$ of $BiFeO_3$ epitaxial thin film show absolute values of about 298, 104, 60, and 3401 pm/V, respectively.[20] Besides, there are $d_{ij}(0)/d_{ij}(2\omega) \sim [n_{ij}^2(0)-1]/[n_{ij}^2(2\omega)-1]$, where $n(0)$ and $n(2\omega)$ are the refractive indices at zero frequency and 2ω, respectively. Therefore, we can conclude that $|d_{33}| \gg |d_{22}|$, $|d_{33}| \gg |d_{31}|$, and $|d_{33}| \gg |d_{15}|$ for both P^0 and $P^{2\omega}$. As a result, P^{NL} can be roughly approximated as shown in the right hand side of Eq. (1).

$$P_x^{NL} = I_0 f_x \sin 2\theta (d_{15} f_z \sin\phi - d_{22} f_y \cos\phi) \approx 0,$$

$$P_y^{NL} = I_0 (-d_{22} f_x^2 \cos^2\theta + d_{22} f_y^2 \cos^2\phi \sin^2\theta + d_{15} f_y f_z \sin 2\phi \sin^2\theta) \approx 0,$$

$$P_Z^{NL} = I_0 (d_{13} f_x^2 \cos^2\theta + d_{31} f_y^2 \cos^2\phi \sin^2\theta + d_{33} f_z^2 \sin^2\phi \sin^2\theta) \approx I_0 d_{33} f_z^2 \sin^2\phi \sin^2\theta, \quad (1)$$

where f_x, f_y, and f_z are effective linear Fresnel coefficients for transmission that shouldn't differ much from each other, and ϕ is ~54.74° as in Ref. 5.

Different from $P^{2\omega}$, P_z^0 has a dc trait when the light beam pulse is not short enough to induce strong radiation. According to the right hand side of Eq. (1), the P_z^0 has a period of 180°, a zero value at θ=0° (i.e., $P^{\omega} \perp P_{FE}$) and a maximum value at θ=90° (i.e., P^{ω} is parallel to the in-plane component of the P_{FE}) in Fig. 2(b).[20] With the proper sign of d_{33}, the P_z^0 can produce a maximum photovoltaic current at θ=90° and a minimum photovoltaic current at θ=0. It should be noted that optical rectification cannot influence photovoltaic effect in multiferroelectric-domains samples because both ϕ and θ in Eq. (1) are random. Optical rectification is a possible mechanism to explain the weak dependence of photovoltaic current on the polarization direction of incident P^{ω} observed by Choi *et al.*[5]

Again, we emphasize that a depletion region can be introduced by many factors, such as p-n junction, Schottky junction,[8,9,12] high-density surface states of semiconductor, photorefractive effect,[11] and/or P_{FE} of the ferroelectric semiconductor. However, it is argued here that only the P_{FE} induced depletion region can be moved upon P_{FE} switching and so does the corresponding photovoltaic current. In cases where more than one factors coexist, detailed experimental conditions are important to analyze which factor dominates. For example, when ferroelectric films are grown on bottom electrodes followed by the deposition of top electrode, the bottom electrode/film interface has a longer heating history than the top interface. Thus the Schottky barrier-induced photovoltaic effects at the two electrode/ferroelectric interfaces may not cancel each other, and the P_{FE}-induced photovoltaic effect may not dominate the overall response. This can also happen when two different electrode materials are used. Even in this case, the P_{FE} switch could still slightly adjust the photovoltaic current as observed in W-PLZT and $BiFeO_3$ films.[8,9,12] When the two interfaces are perfectly symmetric, e.g., the same metal electrodes on $BiFeO_3$ crystal or the in-plane sandwich structure of W-PLZT, the Schottky barrier-induced effect cancels and the P_{FE}-induced effect dominates the device response.[5–7]

We conclude that a depletion region can be induced by the bound surface charges in a polarized ferroelectric semiconductor. Such depletion region leads to asymmetric *I-E* curves, photovoltaic currents and so on. P_{FE} switching can move the bound surface charges and its neighboring depletion region, and adjust any semiconducting properties that are affected by such depletion region. Furthermore, a polarized light beam may influence the depletion region and photovoltaic current through optical rectification in a single domain ferroelectric semiconductor.

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[1] J. F. Scott, *Ferroelectric Memories* (Springer, Heidelberg, Germany, 2000).
[2] M. Fiebig, J. Phys. D: Appl. Phys. **38**, R123 (2005).
[3] K. F. Wang, J. M. Liu, and Z. F. Ren, Adv. Phys. **58**, 321 (2009).
[4] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **299**, 1719 (2003).
[5] T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin, and S.-W. Cheong, Science **324**, 63 (2009).
[6] K. Yao, B. K. Gan, M. Chen, and S. Shannigrahi, Appl. Phys. Lett. **87**, 212906 (2005).
[7] M. Qin, K. Yao, Y. C. Liang, and B. K. Gan, Appl. Phys. Lett. **91**, 092904 (2007).
[8] M. Qin, K. Yao, and Y. C. Liang, J. Appl. Phys. **105**, 061624 (2009).
[9] M. Qin, K. Yao, and Y. C. Liang, Appl. Phys. Lett. **95**, 022912 (2009).
[10] P. Poosanaas, A. Dogan, S. Thakoor, and K. Uchino, J. Appl. Phys. **84**, 1508 (1998).
[11] K. Peithmann, A. Wiebrock, and K. Buse, Appl. Phys. B: Lasers Opt. **68**, 777 (1999).
[12] S. Y. Yang, L. W. Martin, S. J. Byrnes, T. E. Conry, S. R. Basu, D. Paran, L. Reichertz, J. Ihlefeld, C. Adamo, A. Melville, Y. H. Chu, C. H. Yang, J. L. Musfeldt, D. G. Schlom, J. W. Ager III, and R. Ramesh, Appl. Phys. Lett. **95**, 062909 (2009).
[13] C.-H. Yang, J. Seidel, S. Y. Kim, P. B. Rossen, P. Yu, M. Gajek, Y. H. Chu, L.W. Martin, M. B. Holcomb, Q. He, P. Maksymovych, N. Balke, S. V. Kalinin, A. P. Baddorf, S. R. Basu, M. L. Scullin, and R. Ramesh, Nature Mater. **8**, 485 (2009).
[14] S. J. Clark and J. Robertson, Appl. Phys. Lett. **94**, 022902 (2009).
[15] C. Ederer and N. A. Spaldin, Phys. Rev. B **71**, 224103 (2005).
[16] J. Xing, K. J. Jin, H. B. Lu, M. He, G. Z. Liu, J. Qiu, and G. Z. Yang, Appl. Phys. Lett. **92**, 071113 (2008).
[17] S. 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).
[18] P. Maksymovych, S. Jesse, P. Yu, R. Ramesh, A. P. Baddorf, and S. V. Kalinin, Science **324**, 1421 (2009).
[19] D. Talbayev, S. Lee, S. W. Cheong, and A. J. Taylor, Appl. Phys. Lett. **93**, 212906 (2008).
[20] A. Kumar, R. C. Rai, N. J. Podraza, S. Denev, M. Ramirez, Y. H. Chu, L. W. Martin, J. Ihlefeld, T. Heeg, J. Schubert, D. G. Schlom, J. Orenstein, R. Ramesh, R. W. Collins, J. L. Musfeldt, and V. Gopalan, Appl. Phys. Lett. **92**, 121915 (2008).