High rectification and photovoltaic effect in oxide nano-junctions

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Abstract. Polar oxide-based heterostructures composed of ferroelectric PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and hole-doped La$_{0.8}$Sr$_{0.2}$MnO$_3$ ultrathin epitaxial films were fabricated on Nb : SrTiO$_3$ substrates to check the viability of all oxide-based photovoltaic (PV) nano-junctions. We observed clear diode-like behavior, yielding a rectification ratio up to $\sim$1000. This large enhancement could be attributed to the presence of an ultrathin ferroelectric layer ($<$ 10 nm) that greatly contributed to the improved PV performance by promoting carrier separation, as compared with oxide junctions without the ferroelectric layer. Therefore, our results provide useful information for developing highly efficient ferroelectric oxide-based PV devices.
1. Introduction

Interfaces in a heterostructure are an important ingredient of modern microelectronic devices [1]. While current technologies largely rely on semiconductor-based heterostructures, there are a number of intriguing phenomena found in complex oxide-based heterostructures owing to the many electronic properties offered by transition metal oxides [2]. These include ferroelectricity, magnetism and superconductivity, spawning a huge potential for realizing oxide electronics. Moreover, because of recent advances in thin film synthesis, high-quality epitaxial oxide heterostructures have attracted much attention owing to their exciting interface-related physics [3, 4] and excellent performances over polycrystalline materials, e.g. in tunnel junctions [5–8], thermoelectrics [9] and transistors [10]. Perovskite oxide-based heterostructures including Schottky junctions and p–n diodes have also shown promising potential for photovoltaic (PV) applications [4, 11–13].

When light with photon energy greater than the band gap is absorbed in a junction, electron–hole pairs are generated and then separated from the interface by the strong internal electric field generated by the band offset. During these processes, the short-circuit photocurrent density \(J_{sc}\) is often limited by the diffusion of the photocarriers, and the open-circuit photovoltage \(V_{oc}\) is usually governed by the junction’s band alignment, which cannot exceed the built-in potential of the junction. The PV effect in oxide junctions has been mainly investigated with heterostructures composed of manganites and Nb : SrTiO\(_3\) (Nb : STO), an n-type degenerated semiconductor with a band gap of 3.2 eV. However, those manganite-based heterostructures exhibited a relatively low photovoltage (< 0.1 V) and a high dark saturation current owing to tunneling [14–16]. On the other hand, the ferroelectric PV effect, which was associated with the electric polarization, has been observed under light illumination with ferroelectric perovskite oxides, such as LiNbO\(_3\), BiFeO\(_3\), Pb(Zr, Ti)O\(_3\) and (Pb, La)(Zr, Ti)O\(_3\) [17–19]. While the PV process in ferroelectrics is different from that in junction-based heterostructures, ferroelectric oxide heterostructures can be useful for photoelectric device applications.

In ferroelectrics, the spontaneous polarization can separate the photogenerated electron–hole pairs by the internal electric field, which is about one order of magnitude larger than that in a conventional semiconductor p–n junction [20]. Recently, it was shown that ferroelectric domain walls could generate a high photovoltage, much larger than the band gap [19]. The observed photocurrent, however, turned out to be minuscule (of the
order of nano-amperes), mainly because of the short lifetime of photocarriers or poor carrier conduction. Moreover, oxide junctions with an ultrathin ferroelectric layer have not been extensively studied because of the difficulty of growing high-quality ultrathin films with good ferroelectric property. Thus, ultrathin ferroelectric films used as interfacial layers offer promising potential for achieving an enhanced PV output for the following reasons: firstly, the ultrathin insulating layers can effectively reduce the dark saturation current \(I_0\), which depends on the recombination rate of photogenerated carriers in a photodiode. This ultimately leads to a higher open-circuit photovoltage \(V_{oc}\) derived from the Shockley diode equation, i.e.
\[
V_{oc} = \left(\frac{Nk_B T}{q}\right) \ln\left(\frac{I_L}{I_0} + 1\right),
\]
where \(N\) is the ideality factor, \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(q\) is the charge and \(I_L\) is the light-generated current. Accordingly, the PV efficiency is enhanced logarithmically with decreasing thickness of the ferroelectric layer. Secondly, carrier recombination can be decreased, resulting in a higher photocurrent, since carriers need only travel a short distance to be collected at the junction. Moreover, the carrier transport becomes dominated by drift due to an increase in the effective electric field, originating from the ferroelectric polarization, which promotes carrier separation. As a result, oxide p–f–n junctions with ultrathin ferroelectric layers could render an enhanced PV response and a higher rectification compared with those of oxide p–n junctions. In this paper, we report on a high rectification and enhanced PV response found in ferroelectric oxide-based p–f–n nano-junctions. We have focused on using ultrathin ferroelectric thin films for constructing the junctions and explored their thickness-dependent diode behavior and PV performances.

2. Nano-junction fabrication with ultrathin ferroelectric layers

Thin film hetero-junctions were fabricated by growing ferroelectric \(\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3\) (PZT) and hole-doped \(\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3\) (LSMO) epitaxial thin films on 0.5 wt% \(\text{Nb:STO}\) (100) single crystal substrates using pulsed laser epitaxy. Details on the growth of thin films and their ferroelectric properties can be found elsewhere \[21\]. The \(\text{Nb:STO}\) substrates were chemically and thermally treated for achieving atomically flat, \(\text{TiO}_2\)-terminated surfaces. The junctions were composed of a PZT ultrathin layer (1–16 nm in thickness) and an LSMO layer (5 or 10 nm). As shown in figure 1(a), all samples revealed atomically smooth surfaces with a typical root-mean-square roughness below 0.2 nm. X-ray diffraction (XRD) scans from thicker films confirmed the epitaxial growth with good crystallinity (FWHM <0.05° in \(\omega\) rocking-curve scans). The electrical transport and PV properties were characterized by a semiconductor characterization system (Keithley 4200-SCS) in the dark and under light illumination. Piezoresponse force microscopy (PFM) was used to confirm the ferroelectricity of ultrathin PZT layers. Figure 1(b) shows surface morphology (upper panel) and out-of-plane PFM phase images (lower panel) of a 5 nm-thick PZT film on an \(\text{Nb:STO}\) substrate covered with an LSMO (5 nm) film after poling at ±1.5 V. The rectangular patterns with phase contrast clearly indicate that the two opposite polarizations were achieved by switching the ferroelectric polarization, confirming that our ultrathin PZT films persistently maintain the ferroelectricity.

3. Electrical transport properties of nano-junctions and their rectification behaviors

Figure 2(a) shows the typical current density \((J)\–\)voltage \((V)\) characteristics of p–n (LSMO/\(\text{Nb:STO}\)) and p–f–n (LSMO/PZT/Nb:STO) nano-junctions with two different LSMO thicknesses (5 and 10 nm). Note that the polarization in a ferroelectric junction can influence

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Figure 1. Sketch of the setup for $J(V)$ measurement under light illumination on an ultrathin oxide p–f–n junction (LSMO/PZT/Nb : STO) with an atomically flat surface. Semitransparent Au electrodes were used as top contacts for PV measurements. (b) Topographic image (upper panel) and PFM phase image (lower panel) of a 5 nm thick PZT film on LSMO/Nb : STO after poling. The PFM phase image $(7 \times 4 \, \mu m^2)$ shows clear evidence of ferroelectricity. The white contrasts correspond to the ‘down’ polarization state, while the dark ones represent the polarization ‘up’ state.

Figure 2. (a) $J(V)$ curves of oxide p–n and p–f–n nano-junctions with LSMO ultrathin films (5 and 10 nm). The thickness of f-PZT layer is fixed at 5 nm. $N$ indicates the ideality factor. The p–f–n junctions show higher ideality factors than those of p–n junctions. (b, c) Different plots of the $E$ dependence of current density for various conduction mechanisms: (b) Schottky emission and (c) FN tunneling of LSMO (10 nm)/PZT (5 nm)/Nb : STO structures.

the charge transport due to the modified band alignments and carriers’ population depending on the direction of the ferroelectric polarization (see also figure 3). All p–f–n nano-junctions were pre-poled to have a down polarization state. The $J–V$ curves were highly nonlinear, and there existed significant asymmetry with respect to the polarity of $V$, indicating good rectification behavior. The ideality factor $(N)$ was in the range of 1.3–3.3. However, the p–n junctions,
Figure 3. Block charge diagrams of a p–f–n junction with the polarization pointing down (left) and up (right). Both polarization directions can be switched by applying positive and negative biases to the top (LSMO) layer. Due to the nature of the majority carriers, holes for LSMO and electrons for Nb : STO, the up-polarization state after applying a negative bias induces depleted layers, yielding a low current flowing across the junction.

irrespective of the LSMO thickness, exhibited a relatively small rectification effect although $N$ was close to unity. It could be attributed to the high reverse saturation current owing to tunneling. With applying a reverse bias, electrons in the valence band on the p-side can directly tunnel to the empty states in the n-side with their energy lying between the top of the valence band in the neutral region of the p-side and the Fermi level in the neutral region of the n-side. Because the barrier width decreases with increasing reverse bias voltage, the tunneling current increases rapidly with the reverse bias voltage. It has been reported that the trap-assisted tunneling and the interband Zener tunneling are dominant junction transport mechanisms at reverse bias in perovskite-type oxide p–n junctions [15]. In contrast, our p–f–n nano-junctions of LSMO/PZT/Nb : STO showed rather high rectifying behavior due to the fact that the reverse saturation current density was significantly reduced. The current levels were at least four orders of magnitude less than those of p–n junctions. The maximum rectification ratios, i.e. the ratio between the forward and reverse currents at a certain voltage, of p–n junctions with LSMO (5 nm) and LSMO (10 nm) were 79 (at $\pm 0.35$ V) and 8.7 (at $\pm 0.35$ V), respectively. Higher maximum rectification ratios were obtained from p–f–n junctions, i.e. 103 (at $\pm 1.5$ V) and 1388 (at $\pm 0.85$ V) with 5 and 10 nm thick LSMO layers, respectively. Thus, the results imply that introducing a ferroelectric layer for p–f–n junctions gives rise to a high rectification effect due to the reduced dark saturation current.

In order to understand the underlying electronic transport mechanism in the highly rectifying LSMO (10 nm)/PZT (5 nm)/Nb : STO structure, we fitted the $J–V$ curves. Conventional conduction mechanisms in ferroelectric thin films include the interface-limited Schottky emission, Fowler–Nordheim (FN) tunneling, space-charge-limited bulk conduction (SCLC) and bulk-limited Poole–Frenkel (PF) emission. Note that we have excluded the bulk-limited conduction mechanisms, i.e. SCLC and PF, because they are not usually considered as dominant transport mechanisms in ultrathin films. Moreover, direct tunneling is only applicable when the thickness of a wide-band-gap oxide is below $\sim 2$ nm [22]. Therefore, we fitted the data for the Schottky emission and FN tunneling, as shown in figures 2(b) and (c).
In general, the Schottky emission can be examined from the linear behavior in a $\ln(J/T^2)$ versus $E^{1/2}$ plot, and the magnitude of the linear slope is proportional to $1/(T\sqrt{\varepsilon})$, where $\varepsilon$ is the optical dielectric constant and $T$ is the temperature. As shown in figure 2(b), the plot certainly exhibits linear regimes. It turns out that the only $\varepsilon$ estimated from the slope in the reverse bias region is not unreasonable, i.e. $\varepsilon \approx 10.5$, which is even slightly larger than that from a polycrystalline PZT film ($\varepsilon \approx 6$) [23]. Thus, we conclude that the Schottky emission plays a dominant role in the reverse bias region at low electrical fields. On the other hand, a good linear fit in the $\ln(J/E^2)$ versus $1/E$ plot (see figure 2(c)) seems to indicate that the FN tunneling is dominant in the high electric field regime. As represented in figure 2(c), two linear regions with different onset fields exist for forward and reverse biases. The onset fields ($E_{FN}$) were 270 and 1420 kV cm$^{-1}$ for forward and reverse biases, respectively. These observations suggest that both Schottky emission and FN tunneling are mainly responsible for the transport process in ferroelectric p–f–n nano-junctions. Furthermore, we carefully investigated thickness-dependent transport mechanisms of p–f–n junctions. The total current density decreased for thicker ferroelectric layers. Below 5 nm thicknesses of PZT layers, the Schottky emission plot yielded an unreasonable fitting both for forward and reverse biases. Instead, it appeared that tunneling was predominant in the entire voltage regions. In contrast, p–f–n junctions with PZT thicker than 5 nm showed that the Schottky emission and FN tunneling played a major role in low-voltage and high-voltage regions, respectively, for forward and reverse biases.

The role of ferroelectric layers in transport properties of p–f–n junctions can be understood with the charge distribution in p–f–n junctions with up- and down-polarization states. Figure 3 shows block charge diagrams of a p–f–n junction. The two different polarization directions can induce two different charge states, i.e. accumulation and depletion for down- and up-polarization states, respectively, which lead to different electrostatic potential profiles at the interfaces. For example, the potential barriers for the down-polarization state are lower than those for the up-polarization state both for forward and reverse biases as also seen from a thick PZT capacitor [24]. However, when a forward bias was applied to the p–f–n junction, a significant change in current flow by reversing the polarization direction was observed due to the carrier population change. Therefore, it is worthy of note that the polarization direction not only influences the transport properties, but also modifies the PV characteristics.

4. Photovoltaic properties of ferroelectric nano-junctions

We note that similar transport behavior has recently been reported from ferroelectric tunnel junctions. Pantel et al [25] reported that a high electroresistance effect across a fully depleted ferroelectric tunnel junction can be achieved by a change in the transport mechanism from direct tunneling to FN tunneling. Thus, since FN tunneling depends strongly on the effective thickness of the ferroelectric layer, the latter plays an important role in determining the overall transport properties of ultrathin ferroelectrics-based junctions. The observed high rectifying behavior indeed implies enhancement of the PV performance in oxide p–f–n nano-junctions. The ultrathin oxide Schottky or p–n junctions often present both rectification and PV effects. However, there are technical drawbacks for their practical solar cell applications, including low open-circuit voltages and high dark saturation currents caused by tunneling. In fact, ultrathin LSMO (<10 nm in thickness) and 0.5 wt% Nb : STO, which has a carrier concentration of the order of $10^{19}$–$10^{21}$ cm$^{-3}$, yields an ultrathin depletion layer in a p–n junction. However, our p–f–n nano-junctions with insulating PZT layers can provide a thicker...
Figure 4. $I_{sc}$ and $V_{oc}$ as a function of time under UV light on and off. The PV performance with the down-polarization state was superior to the up-polarization state due to the carrier accumulation.

active layer for absorbing light. In ultrathin ferroelectric PZT films, the polarization appears to be still comparable to the bulk value and remains constant across the junctions, while the neighboring layers can suffer from interfacial modification in local structures and electronic properties [21, 26]. Note that, for all p–f–n junctions, a pre-poling process was performed in order to direct the polarization towards the forward direction of a diode.

In order to clarify the role of ferroelectric polarization, we investigated polarization orientation dependence of the PV performance. Figure 4 shows changes in photocurrent at zero bias and open-circuit photovoltage with UV light on and off for an LSMO (5 nm)/PZT (5 nm)/Nb : STO structure. When the internal field due to the band alignment and polarization-induced electric field were incorporated with the same direction across the p–f–n junction, i.e. down-polarization state, we obtained a higher short-circuit current and a higher open-circuit voltage than those with the up-polarization state. This result suggests that the enhanced PV performance can be attributed to the ferroelectric polarization. Thus, an increase in the internal field across the p–f–n junction reinforced by the ferroelectric polarization led to the effective carrier separation.

Figure 5 depicts the PV characteristics of an Au/LSMO (10 nm)/PZT (5 nm)/Nb : STO structure under light illumination with 1.5 Sun (150 mW cm$^{-2}$) and UV (10 mW cm$^{-2}$, $\lambda = 350–400$ nm). Illumination on the surface of the sample induced substantial photoconduction. As shown in figures 5(a) and (b), the illuminated $J(V)$ curves shift toward the negative photocurrent and positive photovoltage, typical of conventional semiconductor photodiodes. However, there was a noticeable difference in the magnitude of photocurrent and photovoltage between UV and solar light illumination. This indicates that the photo-carriers across the band gaps of the PZT ($\sim 3.4$ eV) and Nb–STO (3.2 eV) contribute to the PV responses. Figure 5(b) shows a time-dependent $J_{sc}$ with light on and off. The steady-state photocurrents at zero bias are evident due to the band-to-band transition of charge carriers by absorbing photon. Under UV and solar illumination, this junction exhibited, respectively, $J_{sc}$ of $-114$ and $-1.4 \mu$A cm$^{-2}$ at 0 V, $V_{oc}$ of +0.3 and +0.2 V, and fill factor (FF) of 40 and 45%. We have also studied the
Figure 5. \( J(V) \) curves of highly rectifying LSMO (10 nm)/PZT (5 nm)/Nb : STO junctions in the dark and under illumination with solar light (intensity: 1.5 Sun = 150 mW cm\(^{-2}\)) and UV light (\( \lambda = 350-400 \text{ nm} \), 10 mW cm\(^{-2}\)). (b) The short-circuit photocurrent density (\( J_{sc} \)) as a function of time with light (UV and 1.5 Sun) on and off, clearly showing the steady-state photocurrent. (c) Light intensity dependence of \( J_{sc} \) and \( V_{oc} \) under solar light illumination. (d) Illuminated \( J(V) \) curves of p–n and p–f–n junctions with different LSMO thicknesses (5 and 10 nm).

evolution of \( J_{sc} \) and \( V_{oc} \) in our p–f–n junctions as a function of the incident solar light intensity, as shown in figure 5(c). Above a light intensity of 100 mW cm\(^{-2}\), \( V_{oc} \) increased linearly with the voltage responsivity-area product of \( \sim 0.2 \text{ V cm}^2 \text{ W}^{-1} \). Additionally, as was expected, \( J_{sc} \) showed a linear relationship with the light intensity. We have further investigated the influence of the thickness of p-LSMO and f-PZT on the PV output. Figure 5(d) presents a comparison of the PV response between p–n and p–f–n junctions with two different LSMO thicknesses (5 and 10 nm). Under UV light, the PV properties were clearly improved: \( J_{sc} = -90 \) and \(-114 \mu \text{A cm}^{-2}\) and \( V_{oc} = +0.4 \) and +0.3 V, respectively, from p–f–n junctions with 5 and 10 nm thick LSMO layers. These \( J_{sc} \) and \( V_{oc} \) are at least three times larger than those of p–n junctions (e.g. \( J_{sc} = -24 \) and \(-35 \mu \text{A cm}^{-2}\) and \( V_{oc} = +0.08 \) and +0.11 V). This improvement is attributed to the reduced saturation current and expanded depletion region as mentioned before.

5. Effect of ferroelectric layer thickness on photovoltaic performance

According to conventional semiconductor solar cell physics, \( V_{oc} \) depends on \( I_L \) and \( I_0 \) of a solar cell. \( I_0 \) is a more important factor because this can be changed by some orders of magnitude, while \( I_L \) varies only slightly. Figure 6(a) illustrates the PZT thickness-dependent
Figure 6. PV properties of p–f–n junctions as a function of PZT thickness: (a) open-circuit voltage ($V_{oc}$), (b) fill factor (FF) and (c) output power ($P_{out}$).

$V_{oc}$ in p–f–n junctions. It was found that the optimum thicknesses ($d_m$) with the maximum $V_{oc}$ were in the range of 5–10 nm. Below $d_m$, $V_{oc}$ rapidly increased with increasing thickness of PZT films, and then started to gradually decrease as the thickness further increased above $d_m$. This result can be understood by taking into account the fact that there exists an effective thickness of the ferroelectric layer to minimize the saturation current through tunneling and/or bulk recombination in the ferroelectric layer.

In PVs, the fill factor (FF) is a measure of energy yield and is defined as $(J_m V_m)/(J_{sc} V_{oc})$, where $J_m$ is the current density and $V_m$ is the voltage for a maximum power output. Therefore, we have extracted it from the $J$–$V$ curves. Figure 6(b) summarizes the overall change in FF as a function of PZT and LSMO thicknesses. The thickness-dependent FF is analogous to that of $V_{oc}$. From our $J$–$V$ data, the maximum value we obtained was FF = 45%, which was very similar to that from organic thin film solar cells [27]. Moreover, we also found that our nano-junctions could produce a maximum output power [$P_{out} = (J_{sc} V_{oc}) \times \text{FF}$] of 16 $\mu$W cm$^{-2}$ with an external energy conversion efficiency of 0.16% under UV illumination (10 mW cm$^{-2}$).

As one can see in figure 6(c), the performance of the junctions deteriorated when the thickness of the ferroelectric layer increased further beyond 5 nm. This might stem from the increased charge recombination and poor bulk conduction, which limits both the power output and the conversion efficiency. Moreover, the PV output also abruptly dropped when the ferroelectric film was too thin ($< 5$ nm). These results are in good agreement with a recent theoretical prediction for the PV effect in ferroelectric thin film heterostructures [28].

6. Conclusion

In summary, large dependence of the PV performance on the thickness of ferroelectric layers in oxide-based ultrathin p–f–n nano-junctions composed of p-LSMO and f-PZT was observed. We observed excellent diode-like behavior, yielding a rectification ratio up to $\sim 1000$ from a junction with an ultrathin (5 nm) PZT layer. Although the energy conversion efficiency was lower than the predicted value, our result implied that the use of high-quality ultrathin ferroelectric films could provide a route to highly efficient photodiodes. Further investigation on ferroelectric p–f–n nano-junctions, such as experiments including ferroelectrics with a low band gap, good carrier transport properties and large absorption of visible light as well as an efficient light trapping design, would help in developing highly efficient oxide-based PV devices.
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