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Tunable photovoltaic effects in transparent $Pb(Zr_{0.53},Ti_{0.47})O_3$ capacitors

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We report an investigation on optical, ferroelectric, and photovoltaic properties of transparent Sn-doped In_2O_3 (ITO)/$Pb(Zr_{0.53},Ti_{0.47})O_3$ (PZT)/ITO thin film capacitors. The ferroelectric PZT sandwiched structures grown on glass substrates exhibit a transmittance of 65% in the visible light range. The current-voltage characteristics show that the transparent PZT capacitors possess a significant photovoltaic response under a light illumination. Moreover, the photovoltaic response can be well tuned by an external electrical field, which can be understood by considering the tunable depolarized field in the PZT capacitors. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4709406]

Multi-field couplings of functional materials under coupled thermal, magnetic, electric, optical, and mechanical loads have attracted extensive attention.[1] The coupled electro-optic effect, i.e., photovoltaic effect, which has been applied for various optoelectronic devices, optical sensors, and solar cells, has been observed in various materials including ferroelectrics.[2–6] The photovoltaic effect typically involves two basic processes, including the generation of electron-hole pairs under light irradiation and the separation of electrons and holes under an internal electrical field. Consequently, the net electric current flow is formed in a particular direction.[7] For a conventional semiconductor p-n junction, the internal electric field exists only in the depletion layer of p-n junctions.[8] In contrast, the internal electric field in the ferroelectric thin films extends over the whole volume of the films after the electric poling process.[9] In addition, the internal electric field in ferroelectric materials is nearly an order of magnitude higher than that in a p-n junction.[9] Hence, the bulk photovoltaic effects can be achieved in ferroelectric film capacitors without constructing complicated junction structures.[9] In recent years, the photovoltaic effect in ferroelectric materials have drawn intensive attentions.[4–6,9–12] A great deal of experimental and theoretical works have been done to improve the photovoltaic response in ferroelectric devices.[5,9–12] The photovoltaic responses achieved in single crystal and epitaxial thin films of $BiFeO_3$ can be modulated by controlling the interface barrier as well as domain configuration.[13–16] Zheng *et al.* found that the photocurrent is related to the Schottky barrier and the ferroelectric polarization in ferroelectric capacitors.[12] Due to the switchable polarization states, the photovoltaic responses in ferroelectric capacitors are expected to be tuned by controlling the external electric field.[17] Therefore, it is important to study the relationship between ferroelectric polarization states and the photovoltaic response in ferroelectric capacitors.

Recently, the transparent photovoltaic modules, which can be integrated into building as roofs or windows to create power, have attracted much attention and already been realized in a service stations by BP Solar.[18] Notably, although both the optical properties and the photovoltaic effect of ferroelectric films have been investigated separately,[12,19] the photovoltaic effect of transparent ferroelectric film capacitors has not yet been studied so far. In this letter, we investigated the photovoltaic response in transparent $Pb(Zr_{0.53},Ti_{0.47})O_3$ (PZT) film capacitors, which can be well tuned by an external electric field. The experimental observation can be explained by considering the tunable depolarization field in PZT capacitors.

Polycrystalline PZT thin films with 400 nm in thickness were deposited onto commercial glass substrate coated with 150 nm thick Sn-doped In_2O_3 (ITO) thin films by means of pulsed laser deposition (PLD) technique at an oxygen partial pressure of 10 Pa. A low temperature of 580 °C was chosen for the PZT deposition because the ITO-coated glass cannot endure a temperature higher than 600 °C.[19] The arrays of circular ITO top electrodes with 150 nm in thickness and 100 μm in diameter were deposited on the PZT layer using a metal shadow mask. The crystalline structure of the films was characterized by x-ray diffraction (XRD). As shown in Fig. 1(a), PZT thin films are in single phase with a perovskite structure. The ferroelectric properties of ITO/PZT/ITO capacitors were examined using a radiant precision ferroelectric analyzer system (see Fig. 1(b)). The optical properties were investigated at room temperature by a UV/Vis/NIR Spectrometer (Lambda 950, Perkin Elmer). The current-voltage (*I-V*) behaviors were characterized using a Keithley 4200 Semiconductor Characterization System equipped with a He-Ne light source. The photovoltaic response as a function of wavelength of emitted light at zero-bias voltage was obtained by an Oriel IQE-200 measurement system

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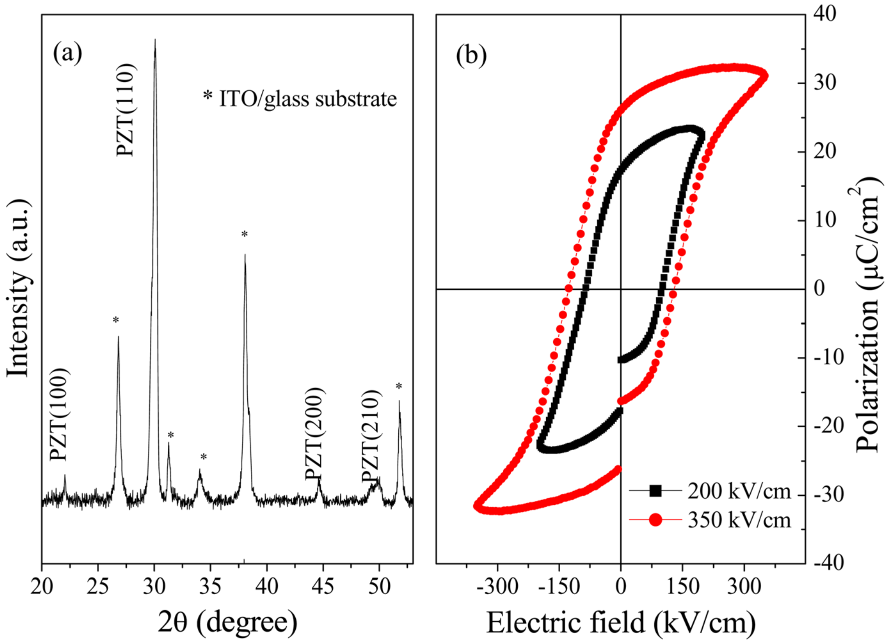

FIG. 1. (a) XRD patterns for a PZT film grown on ITO/glass substrates. (b) Polarization-electric field (P-E) hysteresis loops for the transparent ITO/PZT/ITO capacitors measured at various electric fields.

(Newport). In order to check the effect of the external stimuli on the photovoltaic effect in ferroelectric materials, external electric voltages were used to tune the polarization state of the PZT capacitors. dc electric voltages varying from -3 to $+3$ V at a step of 1.0 V are applied on the PZT cells. Each poling voltage was kept for 30 s, and then the photocurrent-voltage curves were measured at small voltages between -0.5 and $+0.5$ V to avoid disturbing the poling state. It should be noted that even though the poling field is smaller than the coercive field, 30 s of the poling time is long enough for the ferroelectric polarization switching.[20]

Figure 2(a) shows the dark and illuminated *I-V* curves for the transparent ITO/PZT/ITO capacitors, which indicates a significant photovoltaic effect. The asymmetric dark *I-V* curves in symmetric sandwiched structures are induced by the internal strain, interface barrier states, and domain states of the ITO/PZT/ITO capacitors.[13,14,21] The open circuit photo voltage (V_{OC}) and the short circuit current (I_{SC}) are defined as the intersections of the illuminated *I-V* curves with the axis of voltage and photocurrent. Under a light intensity of 450 μW/cm^2, V_{OC} and I_{SC} are obtained as -0.25 V and 0.4 pA, respectively. Figure 2(b) shows the temporal dependence of the photocurrent for a transparent ITO/PZT/ITO capacitor at various incident light intensity and a zero-bias voltage, indicating a repeatable and stable photocurrent response to the light illumination. In addition, there is no decay of photocurrent when the I_{SC} was measured during 50 on-off cycles of the illumination light.

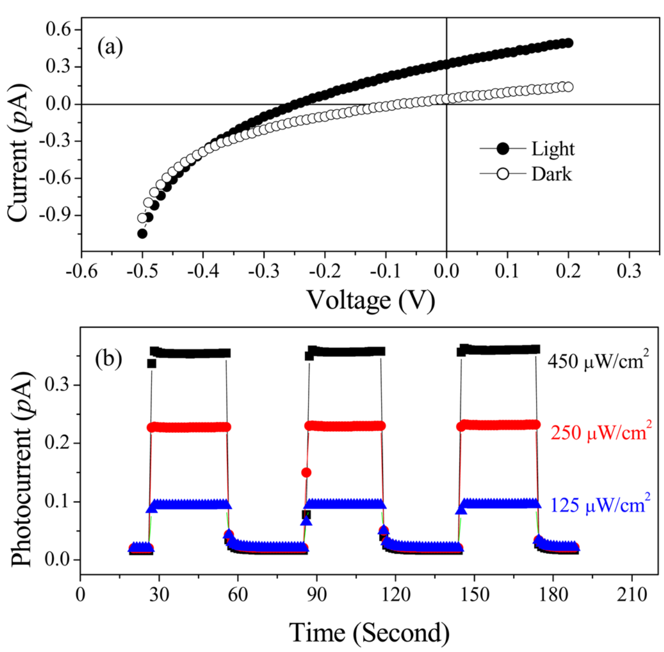

FIG. 2. (a) *I-V* characteristics for the transparent ITO/PZT/ITO capacitor in dark and illumination conditions. (b) Temporal dependence of the photocurrent at a zero-bias voltage and various incident light intensities.

All components in our layered structures are transparent, so that the logo (NIMTE CAS) can be clearly seen through the transparent PZT capacitors, as shown in the inset of Fig. 3(a). The optical transmittance spectra as a function of the wavelength for both PZT capacitors and blank ITO/glass substrates are measured. In the visible region (400-800 nm), the transmittance of the PZT capacitor is about 65%, while that for a blank ITO/glass substrate is around 80%, as shown in Fig. 3(a). In general, the high transmittance of ITO/PZT/ITO capacitors is a disadvantage for photovoltaic devices, since a high photovoltaic efficiency usually requires most of the incoming lights could be adsorbed and transferred into electric energy. However, in some specific cases, for example, a roof or window glass serving as an electric power supplier for a building, the transparent photovoltaic modules which possess both a high transmittance and a high photovoltaic efficiency become very useful.[22] The transparent ferroelectric capacitors provide an alternative candidate for solar cells with multi-functionalities.

The wavelength dependence of V_{OC} for the transparent ITO/PZT/ITO capacitors is shown in Fig. 3(b). The observed photovoltaic effect strongly depends on the wavelength of illumination. The maximum V_{OC} of 0.165 V is obtained at

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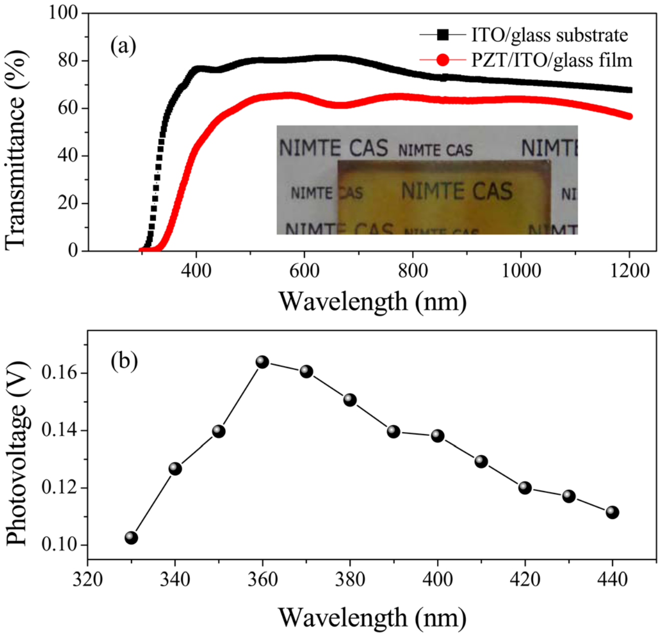

FIG. 3. (a) Optical transmission spectra for a transparent ITO/PZT/ITO capacitor and a blank ITO/glass substrate in the visible region. The inset shows that a logo (*NIMTE CAS*) is placed under the transparent ITO/PZT/ITO capacitor. (b) Wavelength dependence of the open circuit voltage, V_{OC}, for transparent ITO/PZT/ITO capacitors.

365 nm, which approximately corresponds to the band gap of PZT films.[5]

The effect of external electric fields on the photovoltaic response in ferroelectric capacitors is investigated. Figure 4(a) shows the *I-V* characteristics of the transparent ITO/PZT/ITO capacitors under various external poling voltages. It can be observed from the figure that (i) the I-V curves are shifted towards the positive/negative field direction when a positive/negative external electric voltage is applied and (ii) *Voc* and *Isc* are varied with the poling voltage (as shown in Figs. 4(b) and 4(c)). Therefore, both *Voc* and *Isc* can be continuously tuned by applying an external poling voltage. When switching the external voltage from -3 to $+3$ V, I_{SC} and V_{OC} are varied from 0.6 to 0.15 pA and from -0.45 to -0.15 V, respectively. The temporal dependence of photocurrent for the transparent ITO/PZT/ITO capacitor under various poling voltages is presented in Fig. 4(e), which suggests that the instantaneous photocurrent response can be tuned by the electric poling field as well. Figure 4(d) shows the light-to-electricity power conversion efficiency of a transparent PZT capacitor at various external poling voltages. The power conversion efficiency can be calculated by the ratio of the output electrical power P_{out} to the incident optical power P_{in}, where $P_{out} = JV$, J, and V are photocurrent and photovoltage, respectively.[11] While switching the external voltage from -3 to $+3$ V, the maximum conversion efficiency value is changed from 0.02% to 0.22%. Although the present ITO/PZT/ITO capacitors possess the small conversion efficiency value of 0.22%, which is comparable with the previous experimental value,[23] the photovoltaic response of ferroelectric capacitors can be tuned by the external electric voltage.

Since the photovoltaic effect in ferroelectric materials is due to the separation of the light-induced carriers under an internal electric field,[5] the tunable photovoltaic effects in the ITO/PZT/ITO capacitors can be interpreted with considering the effect of the depolarization field. The total internal electric field, E, in ferroelectric capacitors consists of two independent components, the built-in field, E_{bi}, and the depolarization field, E_p. The E_{bi} in ferroelectric capacitors originates from various factors, including the oxygen-related strain gradient[24] and the effect of interfacial layer between the ferroelectric thin films and the substrates.[25] In the present ITO/PZT/ITO capacitors, E_{bi} may result from the effect of the interface layer between PZT films and ITO electrode.[26] The effect of E_{bi} on the photovoltaic response of ferroelectric capacitors deserves further research.[27] The E_p is proportional to the strength of ferroelectric polarization and therefore can be tuned by varying the external bias voltage.[28] It should be noted that the screening effects, which may suppress the depolarization field, need to be taken into account in metal electrode/ferroelectric/metal electrode structures. However, for oxide electrode/ferroelectric/oxide electrode structure, including our ITO/PZT/ITO capacitors, the screening effect is very weak and can be neglected.[10,11] When applying a positive/negative electric voltage to the ITO/PZT/ITO

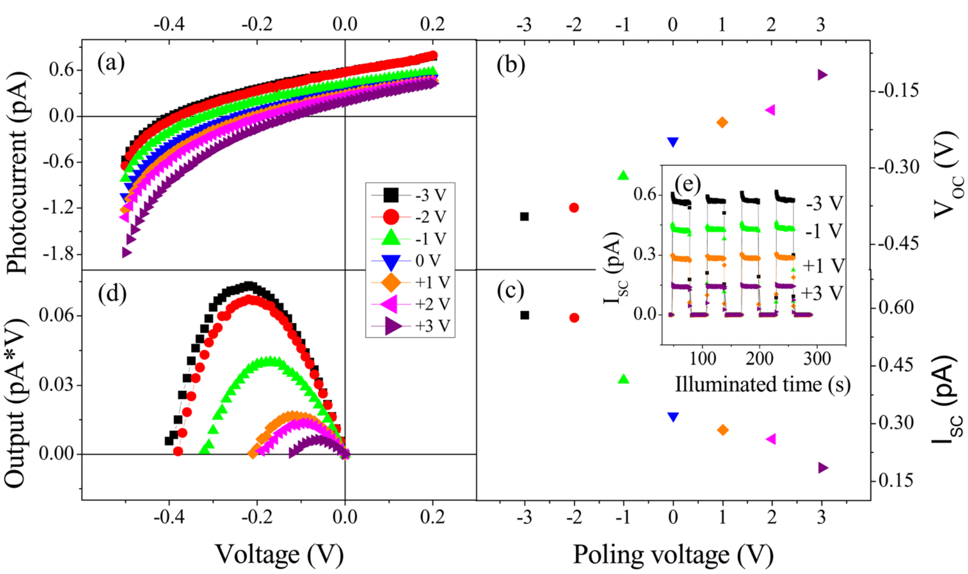

FIG. 4. (a) Illuminated *I-V* characteristics, (b) open circuit voltage (V_{OC}), (c) short-circuit current (I_{SC}), and (d) the corresponding photovoltaic output varied with the external electric voltages in the transparent ITO/PZT/ITO capacitors. (e) Temporal dependence of the photocurrent at various poling voltages.

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capacitor, E_p becomes negative/positive, and the effective electric field in the PZT capacitor is correspondingly reduced/enhanced, resulting in a reduced/enhanced photovoltaic response. In order to facilitate the discussion, the depolarized voltage V_p, i.e., $E_p \times d$, and the build-in voltage V_{bi}, i.e., $E_{bi} \times d$, are used, where d is the thickness of PZT films. Based on the method developed by Zheng *et al.*,[12] $|V_P|$ and $|V_{bi}|$ can be estimated by using the equations $V_p = \frac{1}{2}(V_+ - V_-)$ and $V_{bi} = \frac{1}{2}(V_+ + V_-)$, where V_+ and V_- are the open-circuit voltage after positively and negatively poling the samples, respectively. Similarly, the current $|I_P|$ contributed by the depolarized field and $|I_{bi}|$ contributed by the build-in field can be evaluated by using $|I_P| = \frac{1}{2}(I_+ - I_-)$ and $|I_{bi}| = \frac{1}{2}(I_+ + I_-)$, where I_+ and I_- are the short-circuit current for the positively and negatively poling states, respectively. Thus, $|V_{bi}| = |E_{bi} \times d| = 0.27\,\mathrm{V}$ and $|I_{bi}| = 0.38\,\mathrm{pA}$ can be obtained. The ferroelectric polarization dependent components $|V_P| = |E_p \times d|$ and $|I_P|$ are obtained as 0.05, 0.10, 0.14 V and 0.06, 0.16, 0.20 pA at an external applied electric voltage of 1, 2, and 3 V, respectively. Our experimental observations demonstrate that the external electric voltage can effectively tune the photovoltaic responses of ferroelectric ITO/PZT/ITO capacitors. As aforementioned, these photovoltaic responses are related with the variations of E_p in ferroelectric films.[7] On the other hand, the external applied voltage dependence of E_p exists in all ferroelectric materials.[28] Thus, the photovoltaic response for ferroelectric thin films is expected to be controlled by the external electric voltage. Although the present ITO/PZT/ITO capacitors possess the small conversion efficiency value of 0.22%, this new degree of control may find application in some novel ferroelectric-based solar cells since a large conversion efficiency value of 6.5% is reported recently in Pt/epitaxial Bi_2FeCrO_6/Nb-$SrTiO_3$ capacitors.[29]

In summary, we have investigated the ferroelectric properties and photovoltaic responses of the transparent ITO/PZT/ITO capacitors. The present results show that the photovoltaic response in ferroelectric capacitors can be controlled by an external electric field, which is explained by considering the variable depolarized field in ferroelectric capacitors. The ability to control photovoltaic effects by the external electric field in ferroelectric capacitors is important for developing intelligent ferroelectric-based optoelectronic devices and solar cells with multi-functionalities.

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