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Photodiode properties of epitaxial Pb(Ti,Zr)O_3/$SrTiO_3$ ferroelectric heterostructures

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A substantial photovoltaic effect is found in heterostructures of typical ferroelectric oxides. Pb(Ti,Zr)O_3/Nb-doped $SrTiO_3$, especially, exhibits current–voltage characteristics of the photovoltaic effect of a typical *pn* junction (*p*: hole carrier type, *n*: electron carrier type). A preliminary nonoptimized device shows high performance such as open circuit voltage of 0.7–0.8 V, external conversion efficiency of 0.6%–0.8%, and response time faster than 20 μs for ultraviolet light at room temperature, suggesting the potential of this diode as a new class of photodiode. The results support the formation of a *pn* like junction by ferroelectric oxides. Additionally, the photovoltaic characteristics are tuned by the application of short pulse voltages and retained. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1357807]

The photovoltaic effect has been reported for *pn* junctions of Ge and Si (*p*: hole carrier type, *n*: electron carrier type) as well as for various semiconductors and, also, at Schottky contacts. In principle, the photovoltaic effect can be observed when an illuminated part sandwiched by conducting parts possesses a built-in potential. Therefore, it has also been reported for various oxide/metal Schottky contacts[1] including those of ferroelectric materials.[2,3] However, the effect has been small, and few studies have reported current–voltage (*IV*) characteristics comparable with those of typical semiconductor junctions under illumination.

Ferroelectric oxides are usually regarded as insulators having spontaneous polarization P_S. Accordingly, the leakage current in metal/ferroelectric/metal capacitor structures is sometimes interpreted as dielectric relaxation. On the other hand, ferroelectric oxide films often exhibit *p* or *n* type conduction. Empirically, the barrier height of an oxide semiconductor correlates well with the work function,[4] which has also been experimentally confirmed in epitaxial ferroelectric films on the macroscopic and nanometer scales.[5] These observations indicate the possibility of the formation of *pn* junction by ferroelectrics.[5,6] If ferroelectric oxides form a *pn* junction, it can be useful as a transparent semiconductor, due to the mechanical strength, the radiation hardness, and the ferroelectricity such as the pyroelectric infrared detection. Additionally, it would provide a basis for understanding of the interaction between the photon and the ferroelectricity. To explore this, we have studied the photovoltaic effect in epitaxial heterostructures of typical ferroelectric oxides.

$PbTi_{0.8}Zr_{0.2}O_3$ (PZT) films are epitaxially grown on 0.5 wt % Nb-doped $SrTiO_3$ (STON) substrate by pulse laser deposition and are 200 nm thick. According to x-ray diffractometry the films are *c* axis oriented, and the lattice axes are three dimensionally aligned with those of the substrate. The lattice mismatch between PZT and the STON substrate is estimated to be 1%. The PZT films and STON exhibit a *p*-type and an *n*-type conduction, respectively. The PZT films showed reasonable polarization hysteresis loops at 200 kHz. Additionally, some other epitaxial structures such as $BaTiO_3$ (BTO, *n*-type conduction)/STON were formed. Approximately 20-nm-thick Pt or Au films with surface areas from 0.1 to 0.3 mm^2 are sputter deposited as top electrodes. The bottom electrode was pasted silver. The light source was a 150 W Xe–Hg lamp with a heat-absorption glass filter and it had intense emission near 3.40 eV (365 nm). The spectrometer was the McPherson 257 with resolution of 4–20 nm. The radiation power was measured by an optical powermeter with a Si photodiode and an energy powermeter.

Figure 1 shows typical *IV* hysteresis of a Pt/PZT/STON diode illuminated by 3.44 eV photons in a quasistable state. Well-defined *IV* characteristics of a photodiode are evident. For photon energy higher than 3.2 eV, the conductance of the diode and the photocurrent increases slowly with time for 1 h. This effect continued after turn off of the light. This slow component is 10%–20% of the total photocurrent, and the photovoltaic current reaches a quasistable state in 20–30 s. The quasistable value of the open-circuit photovoltage increases with the light power and is 0.7 V at light power of 4 $mW\,cm^{-2}$. The maximum external power conversion efficiency is 0.6%, which is reached at the applied voltage $V = 0.55$ V. The efficiency increases up to 0.8% with the light power, at least until it reaches the instrumental limit of 60 mW/cm^2. Another diode having a lower efficiency yielded 4

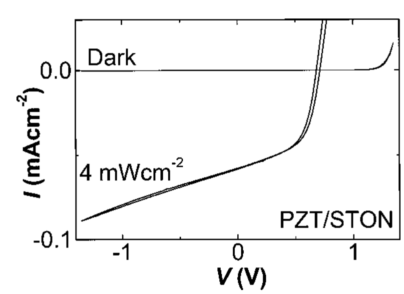

FIG. 1. *IV* characteristics of a PZT/STON junction diode under illumination by 3.44 eV photons and in the dark at 300 K. The voltage polarity is defined at the top electrode on PZT.

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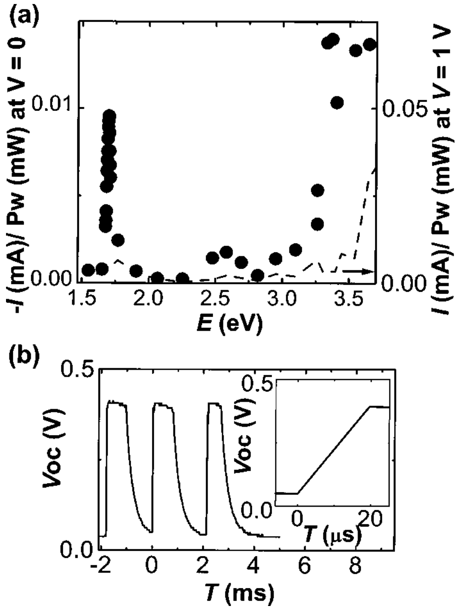

FIG. 2. (a) Spectral sensitivity of the photovoltaic effect of the PZT/STON junction diode at 300 K. The closed circles and the dashed lines show the short-circuit photocurrent divided by the light power *Pw* and the photocurrent at 1 V divided by the light power, respectively. (b) The photovoltaic response to the chopped UV light by measuring the voltage of a 1 MΩ load resistor. The inset shows an expanded view. The photovoltaic open-circuit voltage V_{OC} decreases gradually with the chopping frequency. The difference between the V_{OC} in Fig. 1 and that here in (b) is mainly due to this frequency dependence.

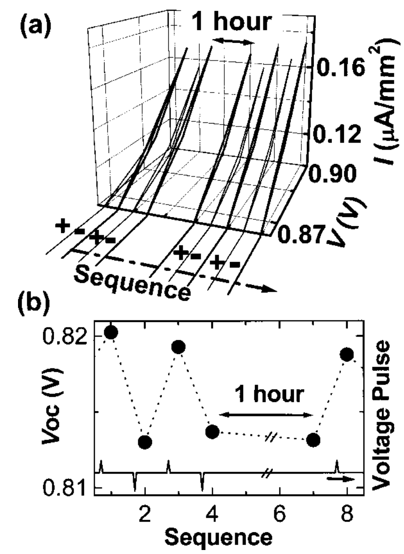

FIG. 3. (a) *IV* characteristics of the PZT/STON diode near the maximum applied voltage of 0.9 V under UV light after short pulses of +3 and −6 V in the dark. (b) Open-circuit voltage V_{OC} after each short pulse.

μW/cm^2 under outdoor sunlight around 1 p.m. on a hazy day (March 2000, 20, Kitakyushu, Japan).

The spectral response was studied by measuring the photocurrent at $V=0$ during a sweep of the light wavelength and by measuring the *IV* characteristics at different wavelengths. The dependence of the photocurrent at $V=0$ on photon energy estimated by these methods was qualitatively similar. The closed circles in Fig. 2(a) show the spectral response estimated from the first method. The large increase of the photovoltaic effect at 3.2 eV is evident, and is attributed to the band to band transition that corresponds to the band gaps of the PZT and STON. A narrow peak is located at 1.7 eV. The sharpness of the spectral response indicates that this peak is probably due to impurity-related absorption. In principle, the optical transition from the metal to PZT can contribute to the photovoltaic response that should have a broad spectral response starting from 0.5 to 1 eV. Such a response is not clearly visible in Fig. 2(a), suggesting that the photovoltaic effect at the Schottky barrier is secondary.

The response time of the present diode is intrinsically limited by the large resistance and the dielectric constant as well as by the large electrode size of 0.5 mm^2. Nonetheless, the photovoltaic response to the chopped light shows that the response time is shorter than the instrumental limit of 20 μs [Fig. 2(b)]. This also supports the fact that the observed phenomena are not of chemical or structural origin but of electrooptic origin.

P_S or carrier injection can change the band bending of the junction.[5,7] Therefore, the photovoltaic characteristics of the present diodes can be controlled by voltage pulses. Indeed, a 10 μs pulse of −6 V applied in the dark enhances the forward bias current under light by 10%, and a 10 μs pulse of +3 V applied in the dark restores it to its original value [Fig. 3(a)]. The modulation is retained at least for 1 h. Furthermore, the open-circuit voltage, i.e., the voltage at zero current, is repeatedly changed by 10% and is retained [Fig. 3(b)]. On the other hand, the effect of the voltage pulse on the short-circuited photocurrent, i.e., the current at zero voltage, is only vaguely observed. This is probably because the short-circuit photocurrent is expected to depend mostly on the generation and the recombination process but not much on details of the transport process near the *pn* junction. If the primary origin of pulse modulation is carrier injection, modulation would be difficult to observe, because ultraviolet (UV) light changes the distribution of the injected carriers. This inference, the modulation of the diode characteristics by low-voltage low-current short pulses, and its retention favor partial switching of P_S as the origin, although the P_S effect is observed only under very limited conditions and most of the *IV* hystereses, reported in the literature seem to be due to charge injection.

The efficiency of the Pt/PZT/STON is 10 times higher than that of Pt/BTO/STON, and the efficiency of the Pt/PZT/$(La, Sr)_2CuO_4$ (*p*-type) Schottky diode and Pt/BTO/$(La, Sr)_2CuO_4$ is low. This fact gives additional support for the view that the photovoltaic effect originates from the PZT/STON interface that is *pn* junction like. The band based on the work function difference (Fig. 4) is consistent with the conversion efficiency that is decreasing the order of Pt(Au)/PZT/STON (p/n), Pt/BTO/STON (n/n), Pt/PZT/$(La, Sr)_2CuO_4$ (p/p), and Pt/BTO/$(La, Sr)_2CuO_4$ (n/p). Additionally, the Pt/La-doped PZT (sol–gel method)/Pt capacitor exhibited only a very small photovoltaic current, a small open-circuit voltage, and an extremely slow response speed, consistent with previous reports.[2]

The preceding results consistently indicate that the photovoltaic effect in Fig. 1 originates at the PZT/STON interface. This is consistent also with the relatively small dependence of the photovoltaic characteristics on the electrode materials (Pt, Au) and the electrode material dependence of the dark current.[8] However, a closer examination of Figs. 1

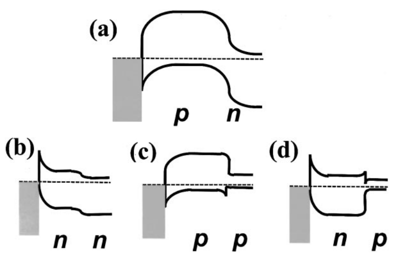

FIG. 4. Simplified band diagrams of the ferroelectric oxide heterostructures neglecting the band offset. (a) PZT/STON [1], (b) M/BTO/STON [0.1], (c) M/PZT/(La, Sr)$_2$CuO$_4$[≈ 0], and (d) M/BTO/(La, Sr)$_2$CuO$_4$[≈ 0]. The numbers in the square brackets are the observed approximate external energy conversion efficiency, and M represents the metal layer of a Schottky contact.

and 5 indicates a few characteristics that deviate from those of an ideal *pn* junction. They are (1) the incomplete saturation of the reverse bias current, (2) the light-enhanced forward bias current near +1.5 V, and (3) the current increase near +0.6 V (the threshold voltage for the diffusion current in the dark is +1.5 V). The second feature is often found in the photovoltaic effect at the *pn* junction and at Schottky contacts.[9] The first and the last features, which reduce the conversion efficiency, have often been attributed to series resistance and leakage current.[10]

The leakage current, i.e., the increase of the current near +0.6 V under illumination, shows a hump-shaped *IV* curve, and grows with the light power (Fig. 5). No corresponding current is observed near $V = +0.6$ V in the dark. This optical enhancement of the current at $V \geqslant 1$ V was observed for light having not only energy close to the band gap energy but also that of 1.7 eV as shown by the dashed lines in Fig. 2(b). The junctions of HgCdTe and CdS/Cu$_2$S exhibit a similar hump-shaped *IV* curve, which was attributed to the tunneling current.[11] Additionally, possible band to band tunneling through a PZT/STON junction was suggested,[6] and the

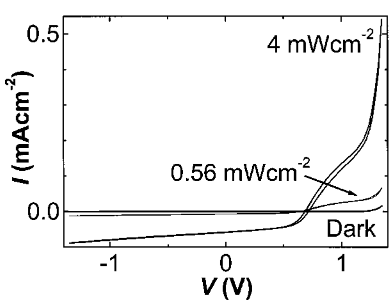

FIG. 5. Replot of Fig. 1 in an expanded ordinate range with another *IV* curve under UV illumination of 0.56 mW cm^{-2}. The threshold voltage of 1.5 V in the dark, the light-enhanced forward bias current near 1.5 V, and the light-induced current increase near 0.6 V are seen.

hump-shaped *IV* curve under illumination is only weakly dependent on temperature. Therefore, the current near +0.6 V showing a hump-shaped *IV* curve could be due to tunneling that may be associated with the trap levels detected in the spectral response. If this explanation is correct, the formation of an intrinsic layer between PZT and STON (*PIN*) would increase the open-circuit voltage and the conversion efficiency. Additionally, the optically enhanced forward bias current in Fig. 5 suggests that caution is needed in the vicinity of the leakage current measurements, especially, those using an atomic force microscope.

In conclusion a substantial photovoltaic effect is found in epitaxial ferroelectric heterostructures. The high performance of the PZT/STON ferroelectric diodes without an antireflection coating, any window layer, or the optimization of various parameters such as electrode materials and thickness of the layers proves the potential usefulness of the present diode. Their sensitivity to UV light and their radiation hardness can be beneficial in space. The present results support the formation of a *pn* like junction by ferroelectrics, which would be important in understanding of the ferroelectric surface. However, understanding of their detailed characteristics awaits further studies.

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