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Photovoltaic effects and its oxygen content dependence in $BaTiO_{3-\delta}$/Si heterojunctions

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Three oxide heterojunctions made of $BaTiO_{3-\delta}$/Si have been fabricated under various oxygen pressures by laser molecular beam epitaxy. They all exhibited nonlinear and rectifying *I-V* characteristics but with a large difference in the rectification behaviors. Their photoelectric properties and dependences on oxygen contents in $BaTiO_{3-\delta}$ films have been experimentally studied. We found that the photovoltaic effects depended strongly on the oxygen contents of the $BaTiO_{3-\delta}$ films. The possible mechanism was proposed based on the band structure of the *p-n* heterojunctions. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2884320]

Perovskite-type oxide thin films are very attractive due to their multifunctional properties such as ferroelectric, colossal magnetoresistance, and optical properties.[1–4] $BaTiO_3$, as a member of perovskite family, is one of the most extensively investigated oxide material because of its abundant physical properties and potential applications. A large amount of work has been focused on the structural, transport, ferroelectric, dielectric, and optical properties of $BaTiO_3$ films.[5–9] Especially transitional metal oxide materials integrated on silicon substrate show a rich variety of electronic and magnetic properties.[10–13] As we all know, oxygen content plays a very important role in almost all properties of these materials or heterostructures. Stoichiometric barium titanate is insulating, however, electrical conduction will be induced if grown in deoxidization environment.[14,15] In this paper, we report a systematic study on the oxygen content dependent rectification and photovoltaic characteristics of $BaTiO_{3-\delta}$ (BTO)/Si junctions under illumination by different light sources. By controlling the oxygen pressure, the physical properties of BTO/Si junctions are found to be varied greatly.

BTO thin films were grown on *p*-type Si (100) by a laser molecular beam epitaxy system under different oxygen pressures. The three typical samples were named as HOP (fabricated under high oxygen pressure), MOP (fabricated under middle oxygen pressure), and LOP (fabricated under low oxygen pressure) according to their fabrication oxygen pressure at 1×10^{-1}, 5×10^{-2}, and 1×10^{-4} Pa, respectively. The substrate temperature was kept at 620 °C. The three BTO films were all 5×10 mm^2 large with the thickness of ~200 nm. A detailed deposition procedure can be found in our previous report. Both reflection high-energy electron diffraction patterns and x-ray diffraction measurements have confirmed that the BTO films were epitaxially grown on the Si substrates.[10,16] The electrical characteristics were measured by a Keithley 2400 current source. The photoelectric properties were investigated by using different light sources including a 632.8 nm HeNe laser, a 253.65 nm Hg lamp, and a 308 nm XeCl pulsed laser. The photoelectric signals were recorded by a 500 MHz digital oscilloscope with an input impedance of 1 MΩ.

Figure 1 shows the *I-V* characteristics of samples HOP, MOP, and LOP measured at room temperature. Similar to the traditional semiconductor *p-n* junction, the three samples all exhibited asymmetry for the positive and negative biases but with quite different rectification behaviors. With decreasing oxygen pressure, the leakage current of BTO thin film increased steeply due to more oxygen vacancies acting as electron donors. The diffusion voltages were 2, 1.2, and 0.1 V for samples HOP, MOP and LOP, respectively.

Figure 2 displays the *I-V* behaviors in semilogarithmic plot of the three BTO/Si junctions at 300 K under HeNe laser illumination. Solid and open symbols denote the data in the dark and under illumination, respectively. For samples MOP and LOP, the *I-V* curves showed great photocurrents in the reverse bias. However, for sample HOP, the two curves in the dark and under illumination were with little difference, which indicated that sample HOP was not so active under the illumination of HeNe laser.

Figure 3(a) shows the photovoltaic signals under HeNe laser illumination (power density of 1 mW/mm^2). As expected from the *I-V* curves in Fig. 2, we did not observe the photovoltaic signals of sample HOP. For samples MOP and

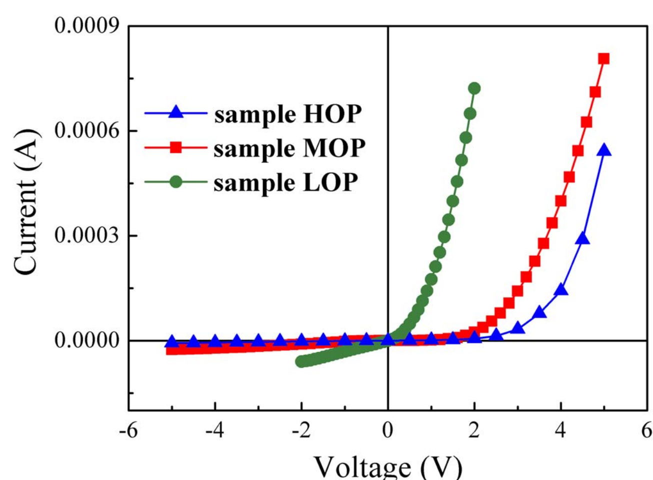

FIG. 1. (Color online) The rectifying properties of samples HOP, MOP, and LOP at room temperature in the dark.

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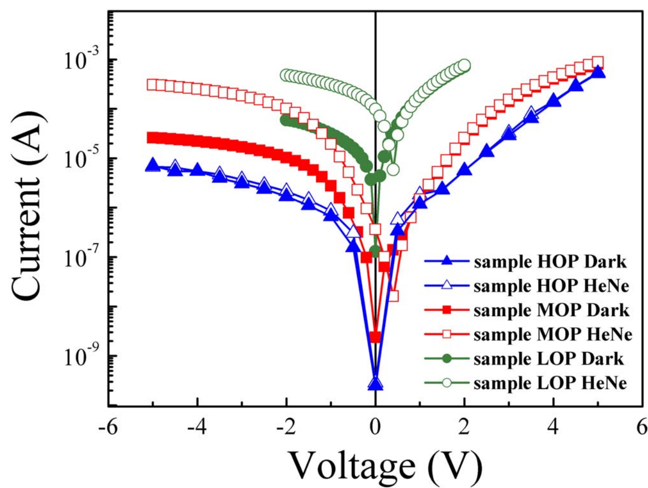

FIG. 2. (Color online) *I-V* relationships of samples HOP, MOP, and LOP under illumination (open symbols) compared with in the dark (solid symbols).

LOP, the photovoltages (PVs) were 115 and 400 mV, respectively. Figure 3(b) shows the photovoltaic responses of the three samples under the ultraviolet (UV) XeCl laser illumination. In this case, samples MOP and LOP showed the high PVs of 330 and 360 mV, respectively. Especially, sample HOP also showed the photovoltaic response of 53 mV to UV light irradiation. To further verify the results, we measured their UV response using a continuous Hg lamp with a power density of 0.53 mW/cm^2. The PVs for samples HOP, MOP, and LOP were 2, 15.4, and 37 mV, respectively, as shown in Fig. 3(c).

To understand the variation of above properties for samples HOP, MOP, and LOP, we plotted schematic energy band structures for samples HOP and LOP, as shown in Fig. 4. As we all know, samples fabricated at lower oxygen pressure have more oxygen vacancies so sample LOP has the most oxygen vacancies and sample HOP has the least oxygen vacancies. In forming a heterojunction of BTO/Si, electrons with higher density in *n*-type BTO film than those in Si should diffuse into Si and holes with higher density than those in BTO should diffuse into BTO. The diffusion causes a built-in electric field in the space charge region around the interface, which is how a barrier at the interface shown in Fig. 4 was built up.[17] With the illumination of light, photon-induced carriers were separated by the built-in field at the interface and, thus, caused a PV we measured. Sample HOP with the least oxygen vacancies can cause the least built-in field, as well as the least PV and photoconductivity, as shown in Figs. 2 and 3. As the photon energy from a HeNe laser (~2 eV) is less than the band gap of BTO (~3.2 eV) and the photon energy from a XeCl laser (~4 eV) is larger than the band gap of BTO, photon-induced carriers can be created not only in Si but also in BTO with the illumination of XeCl laser. We believe that it is the reason why the PVs for sample HOP can be observed, as shown in Figs. 3(b) and 3(c). It is easy to understand that much smaller PV is induced by Hg lamp than that induced by laser, as the illumination strength of Hg lamp is much smaller than that of laser. The mechanism for the different rectification behaviors of different samples shown in Fig. 1 is not so obvious, we speculate that it relates with the impurity levels in the band gap of BTO, as schematically plotted as the shadow part in Fig. 4. More oxygen vacancies in sample LOP should cause more impurity levels,[18] which can make the transport in sample LOP easier than that in sample HOP, as shown in Fig. 1.

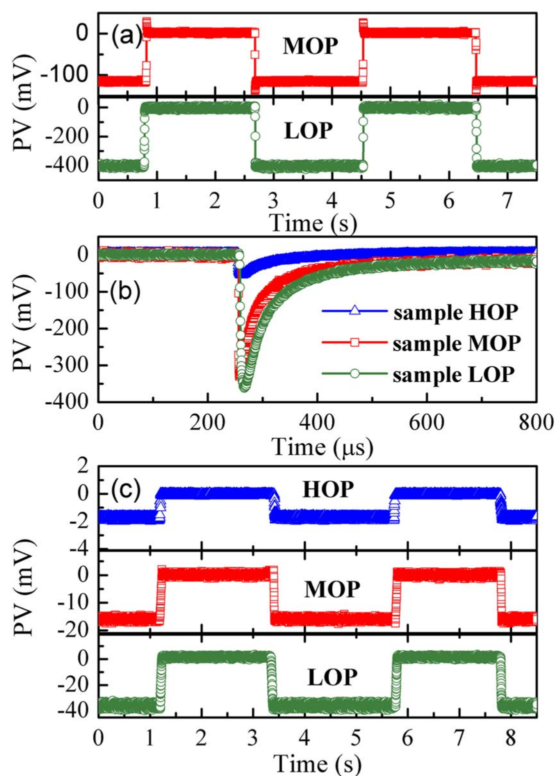

FIG. 3. (Color online) The photovoltages (PVs) of samples HOP, MOP, and LOP under the illumination of (a) HeNe laser, (b) XeCl laser, and (c) Hg lamp.

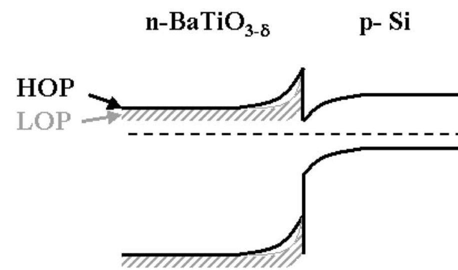

FIG. 4. The schematic band structures of *p-n* junctions of samples HOP and LOP. The conduction band and valence band of $BaTiO_{3-\delta}$ film in sample HOP were denoted by black lines and those of sample LOP were denoted by gray shadow lines.

In conclusion, the photovoltaic effects of the three samples of BTO/Si with various oxygen contents were investigated in detail. It is found that the heterostructure of BTO/Si with lower oxygen content has a larger PV and better photoconductivity. We believe that this kind of dependence is related with the charge transferring at the interface of the heterostructure. The impurity levels for BTO/Si with smaller oxygen contents should also play an important role in its photoelectric response and transport property.

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