# Temperature-dependent rectifying and photovoltaic characteristics of an oxygen-deficient $Bi_2Sr_2Co_2O_y$/Si heterojunction*

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A $Bi_2Sr_2Co_2O_y$/Si heterojunction is obtained by growing a layer of p-type oxygen-deficient $Bi_2Sr_2Co_2O_y$ film on a commercial n-type silicon wafer by pulsed laser deposition. Its rectifying and photovoltaic properties are studied in a wide temperature range from 20 K to 300 K. The transport mechanism under the forward bias can be attributed to a trap-filled space-charge-limited current conduction mechanism. Under the irradiation of a 532-nm continuous wave laser, a clear photovoltaic effect is observed and the magnitude of photovoltage increases as the temperature decreases. The results demonstrate the potential application of a $Bi_2Sr_2Co_2O_y$-based heterojunction in the photoelectronic devices.

**Keywords:** $Bi_2Sr_2Co_2O_y$/Si heterojunction, rectifying characteristics, photovoltaic effect, space-charge-limited current

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## 1. Introduction

In recent years, heterostructures fabricated from transition metal oxides have aroused a great deal of interest, particularly for oxide electrical applications in which artificial multi-functionalities are used to realize novel devices.[1,2] $Bi_2Sr_2Co_2O_y$ (BSCO), a newly discovered strongly correlated transition metal oxide, has recently attracted great attention as a promising p-type thermoelectric material because of its good thermoelectric performance and chemical stability in air.[3–6] In addition to its good thermoelectric performance, BSCO has many other remarkable properties, for example, anisotropic electrical and magnetic properties, low temperature negative magnetoresistance effects, photoelectric effects, etc.[7–9] Such intriguing properties motivate us to exploring the BSCO-based heterojunction and utilizing its novel properties at the interfaces.

In this work, we demonstrate a new p–n heterojunction comprised of a p-type BSCO film deposited on commercial n-type silicon wafers, and investigate its electrical properties and photovoltaic effect. The result suggests the possibility of using available state-of-the-art silicon fabrication technology to create BSCO-based photoelectric devices besides the thermoelectric one.

## 2. Experiments

The BSCO/Si heterojunction was fabricated by growing a layer of p-BSCO film ($\sim$ 270 nm) on commercial n-type Si (001) wafers (carrier concentration: $2.2\times10^{18}$ cm$^{-3}$) without any chemical pre-treatment of the substrate or buffer layers. An excimer laser with 308-nm radiation was used for pulsed laser deposition (PLD) with a laser energy density of 1.5 J/cm$^2$ and a repetition rate of 3 Hz. An oxygen pressure of 10 Pa was maintained during the film growth at a substrate temperature of 650 °C. After the deposition, the film was cooled to room temperature within 10 min under the same oxygen pressure.

The current–voltage ($I$–$V$) curves and photovoltaic response curves of the BSCO/Si junction were measured by the two-probe method in a wide temperature range from 20 K to 300 K in a cryogenic refrigerator. In order to attain Ohmic contact, gold electrodes and silver paint electrodes each with a diameter of 0.5 mm were deposited on the film and substrate, respectively. The bias voltage directing from the BSCO film to the Si substrate is defined to be positive in the $I$–$V$ property measurement. To investigate the photovoltaic effect, a 532-nm continuous wave (cw) laser was used as a light source and the photovoltage was recorded by a 2700 Keithley source meter.

## 3. Result and discussion

Figure 1(a) shows a typical XRD pattern of BSCO film on Si substrate, measured using a Philips X'Pert 4-circle diffractometer. Apart from Si (002) diffraction peak, the main peaks in the pattern can be indexed to the (00l) diffractions of BSCO, indicating that a single phase BSCO film with $c$-axis orientation is formed. Hall measurement reveals that BSCO is p-type conducting with a carrier density of about $2.9\times10^{19}$ cm$^{-3}$ at room temperature. Figure 1(b) displays an $R$–$T$ curve of

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BSCO thin film on Si. It exhibits a semiconductor conducting behavior in the whole measured temperature range from 20 K to 300 K. This conducting behavior is quite different from those reported for BSCO bulks or films in the literature in which a transition from metal to insulator was clearly observed at about 100 K–150 K.[10–12] We suggest that this discrepancy is mainly due to the difference in oxygen content between the samples. In this work, the BSCO film is fabricated under low oxygen pressure and thus a lot of oxygen vacancies will be present in the film.[13] In addition, defects at the interface between BSCO film and Si substrate, induced by the innative insulating $SiO_2$ layer on Si surface, are also likely to be responsible for this different electric transport behaviors.

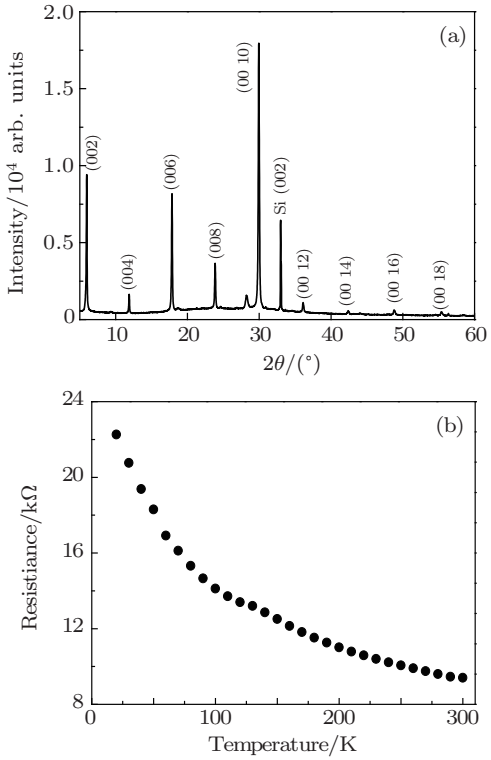



**Fig. 1.** (a) A typical XRD $\theta$–$2\theta$ scan and (b) plot of resistivity versus temperature of a 270-nm-thick BSCO film on the n-type Si substrate.

Figure 2(a) illustrates the current–voltage ($I$–$V$) curves of the BSCO/Si heterojunction, measured by tuning the applied voltage in a temperature range of 20 K to 300 K. As shown in the inset of Fig. 2(a), the contacts between Au and BSCO and between Ag and Si are Ohmic, which indicates that the asymmetric rectifying behavior is the intrinsic property of the heterojunction. Figure 2(a) shows that with temperature decreasing, the leakage currents decrease gradually at reverse bias curves and the forward biased curves shift toward higher voltage, and that no obvious change in the general $I$–$V$ relations is observed at low temperature despite the great resistance change of BSCO shown in Fig. 1(b). Diffusion voltage ($V_d$), defined as the voltage value of the forward current instantaneously increases, is obtained by fitting the forward $I$–$V$ curve as shown in Fig. 2(b), and $V_d$ increases almost linearly from 0.5 V to 0.72 V as temperature decreases from 300 K to 20 K. This $V_d$–$T$ behavior is quite different from that of BSCO/Nb-doped $SrTiO_3$ heterojunction previously reported by Wang *et al.*,[12] where $V_d$ deviated from the linear growth at a temperature of above 150 K at which a metal–insulator transition was also observed on the corresponding $R$–$T$ curve. Considering the fact that the BSCO layer reported in Wang *et al.*'s work was deposited at an oxygen pressure of 40 Pa and then cooled under an oxygen pressure of about 1 atm (1 atm = $1.01325\times10^5$ Pa), we think that the different $V_d$–$T$ curve observed in this BSCO/Si heterojunction is mainly caused by a large number of oxygen vacancies in the BSCO layer due to its lower deposition oxygen pressure.

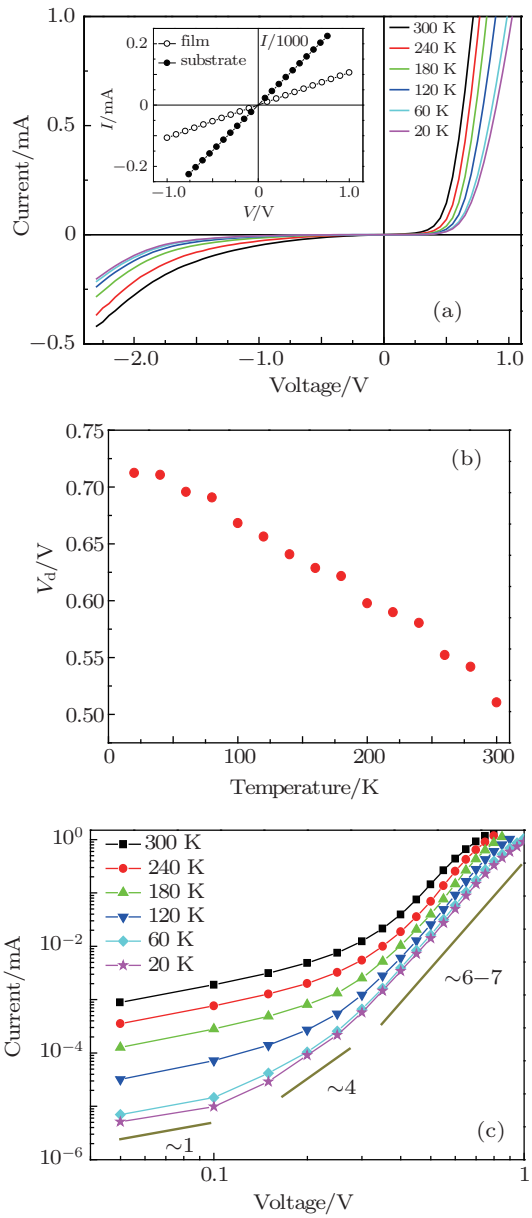



**Fig. 2.** (color online) (a) $I$–$V$ curves of BSCO/Si heterojunction, measured from 20 K to 300 K. The inset shows the $I$–$V$ curves of the two Au contacts on the BSCO film as well as Ag contacts on Si substrate at 300 K. (b) Temperature-dependent diffusion voltage ($V_d$) of the $Bi_2Sr_2Co_2O_y$/Si heterojunction. (c) The positive branches of $I$–$V$ curves in a log–log scale.

To further understand the transport mechanism, we have re-plotted the positive branches of $I$–$V$ curves in a log–log scale as shown in Fig. 2(c). The slope of $I$–$V$ curve increases from 1 to 6–7 with the increase of forward bias voltage. Similar characteristics have been observed in many other transition metal oxide heterojunctions and can be attributed to a trap-filled limit space-charge-limited current (SCLC) conduction mechanism.[14–17] It should be mentioned here that the slope of $I$–$V$ curve governed by the typical SCLC conduction usually has a slope of 2, but if there exist defects at the junction interface the slope will be larger than 2.[18] Figure 2(c) shows that at lower applied bias voltage, the thermally excited free carriers are dominant and the $I$–$V$ curves each follow the Ohm's law with slope about 1. When the applied bias voltage reaches up to a threshold voltage $V_{\rm T}$, the number of injected carriers exceeds that of thermally excited free carriers and a trap-filled SCLC conduction occurs in the $I$–$V$ curves with slope larger than 2, indicating that the oxygen vacancies or other interface defects-related trap centers are distributed in the space-charge region of the BSCO/Si heterojunction.

Figure 3 shows the photovoltaic responses of BSCO/Si heterojunction when BSCO film surface is irradiated by a cw 532-nm laser at different powers at room temperature. As the laser power increases from 5 mW to 30 mW, the photovoltage increases from 13 μV to 51 μV. This can be well understood according to the theory of the conventional p–n junction. Since the 532-nm photon energy (∼ 2.3 eV) is larger than the band gap of BSCO (∼ 1.0 eV), photon-induced electron–hole pairs are created mainly in the BSCO layer. When these photo-induced nonequilibrium charge carriers, electrons, and holes, diffuse into the space-charge region, they will be separated by the built-in field and move to the Si region as well as BSCO region, generating the open circuit voltage ($V_{\rm oc}$) between the two electrodes. It is known that for a conventional p–n junction, the relation between $V_{\rm oc}$ and laser power $P$ at a constant temperature can be described by the equation of $V_{\rm oc} = (k_{\rm B}T/e)\ln(1+\beta P)$, where $k_{\rm B}$ is the Boltzmann constant, $e$ is the electron charge and $\beta \propto \exp(E_{\rm g}/(k_{\rm B}T))$ ($E_{\rm g}$ is the band gap).[19] The plot of $\exp((eV_{\rm oc})/(k_{\rm B}T))$ versus $P$ of the BSCO/Si heterjunction exhibits a straight line at room temperature as shown in the inset of Fig. 3, being coincident well with the predication of the equation.

Figure 4 displays the variation of $V_{\rm oc}$ with temperature at an irradiation power of 20 mW. It can be seen that $V_{\rm oc}$ increases monotonically with temperature decreasing. A similar behavior has been observed previously in many manganite heterojunctions and considered to be related to the change in the thickness of the depletion layer and the magnitude of the built-in field.[20–22] As temperature decreases, the depletion layer becomes thicker and the built-in field becomes higher, which indicates more photo-induced carriers accommodated by the space-charge region and a larger driving force for these carriers, and therefore leading to a higher $V_{\rm oc}$.

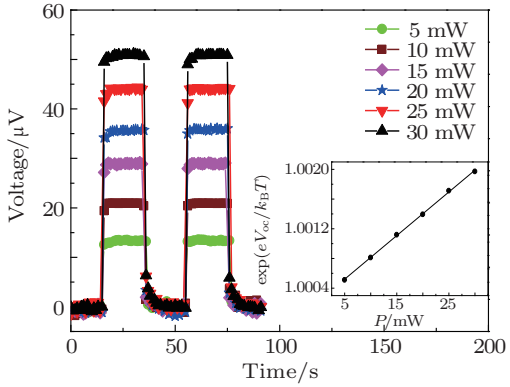



**Fig. 3.** (color online) Photovoltages of the heterojunction when BSCO film is illuminated by 532-nm laser at different power densities. The inset shows an exponential plot of $V_{\rm oc}$ against laser power.

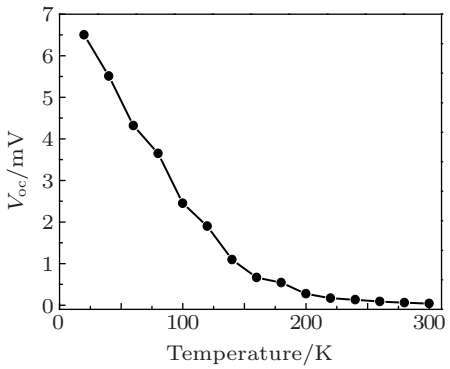



**Fig. 4.** Variation of $V_{\rm oc}$ with temperature.

## 4. Conclusions

In this paper, we prepare a BSCO/Si heterojunction by using PLD technology. The heterojunction exhibits a perfect rectifying characteristic, and its transport mechanism under the forward bias can be attributed to a trap-filled SCLC conduction mechanism. A clear photovoltaic effect is observed in this heterojucntion and the photovoltage increases monotonically with temperature decreasing. The result suggests potential applications of the BSCO-based heterojunction in optoelectronic devices.

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