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Oxygen vacancies induced enhancement of photoconductivity of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin film

R L Gao[1], C L Fu[1], W Cai[1], G Chen[1], X L Deng[1], H W Yang[2], J R Sun[2], Y G Zhao[3] and B G Shen[2]

[1] School of Metallurgy and Materials Engineering, Chongqing University of Science and Technology, Chongqing, 401331, People's Republic of China
[2] Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Science, Beijing 100190, People's Republic of China
[3] Department of Physics and State Key Laboratory of Low-Dimensional Quantum Physics, Tsinghua University, Beijing 100084, People's Republic of China
E-mail: gaorongli2008@163.com

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Abstract

Effects of light and electrical current on the electrical transport properties and photovoltaic properties of oxygen-stoichiometric $La_{0.5}Sr_{0.5}CoO_3$ and oxygen-deficient $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ films prepared by pulsed laser deposition have been investigated. Oxygen-deficient films annealed in a vacuum show an obvious increase of resistance and lattice parameter. Besides, a direct correlation between the magnitude of the photoconductivity and oxygen vacancies in $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ films has been observed. The light illumination causes a resistance drop to show the photoconductivity effect. Moreover, the photoconductivity can be remarkably enhanced by increasing the electrical current, that is, it exhibits current-enhanced photoconductivity (CEPC) effect. Oxygen deficiency in the annealed film leads to the formation of a structural disorder in the Co–O–Co conduction channel due to the accumulated oxygen vacancies and hence is believed to be responsible for the increase in higher photoconductivity. These results may be important for practical applications in photoelectric devices.

Keywords: oxygen vacancies, $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, photoconductivity, transport properties

1. Introduction

Cobaltates have attracted enormous scientific interest over decades not only due to their rich physical properties but also because of potential applications such as electrode materials in fuel cells, membranes for oxygen separation, and ferroelectric memory devices [1–4]. Among the cobaltates, highly strontium-doped lanthanum–cobalt oxides, such as $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) have been extensively investigated because of their properties of high electrical and excellent ionic conductivity. Besides, unlike the other transition metal oxides, LSCO can exhibit a unique property with reference to spin state transition, which can be tailored by external parameters, such as electric field, temperature, pressure, and magnetic field [5–7]. It is well known that the oxygen content of LSCO is also an important factor that can strongly affect their physical properties such as the crystal structure as well as the electrical transport and magnetic properties [8–12]. However, although many studies have been reported on the photoinduced effects in the oxygen-deficient doped manganites and multiferroic $BiFeO_3$ films [13–17], also as transition metal perovskite oxides, few studies have been reported on the photoinduced effects in the oxygen-deficient lightly doped cobaltates. In this letter, we report studies of the photoconductivity and its current enhancement in oxygen-deficient $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ ($LSCO_3$) thin films. We found that light illumination induced a resistance drop that was remarkably enhanced by electrical current.

2. Experimental process

The LSCO thin films were grown epitaxially on (001)-oriented $SrTiO_3$ (STO) substrates by pulsed laser deposition from the stoichiometric targets. Deposition was carried out using a 248 nm KrF excimer laser, which was operated at 3 Hz with a substrate temperature of 650 °C and an energy density of $2\,J\,cm^{-2}$, in an atmosphere of 35 Pa O_2. During deposition, the substrate holder rotated slowly in order to reduce the thickness variation of the film. The as-deposited oxygen stoichiometric $La_{0.5}Sr_{0.5}CoO_3$ films were *in situ* annealed in 500 Pa oxygen pressure and cooled down slowly at $2\,°C\,min^{-1}$ to room temperatures to avoid the effect of deficient oxygen. As comparison, $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ films were post-annealed *in situ* in a 10^{-5} Pa oxygen atmosphere at 400 °C for 1 min. The as-grown films have a typical thickness of about 120 nm by controlling deposition time. Structural characterization of the films was carried out using an x-ray diffractometer at room temperature. The surface morphology of the films was obtained using an atomic force microscopy. The temperature dependence of the magnetization of the films was measured using a commercial superconducting quantum interference device with an applied field of 200 Oe. For the conductive characteristics measurements, silver electrodes on the surface of LSCO films were deposited using thermal evaporation. Green laser with wavelength of 532 nm was used as excitation light source for the photoconductivity (PC) measurement. Current-voltage characteristics were measured using a Keithley 2611 source meter.

3. Results and discussion

Figure 1(a) reveals high quality, epitaxial LSCO films that appear to be single phase regardless of the oxygen content. There are no secondary phases visible. Typical rocking curves show a

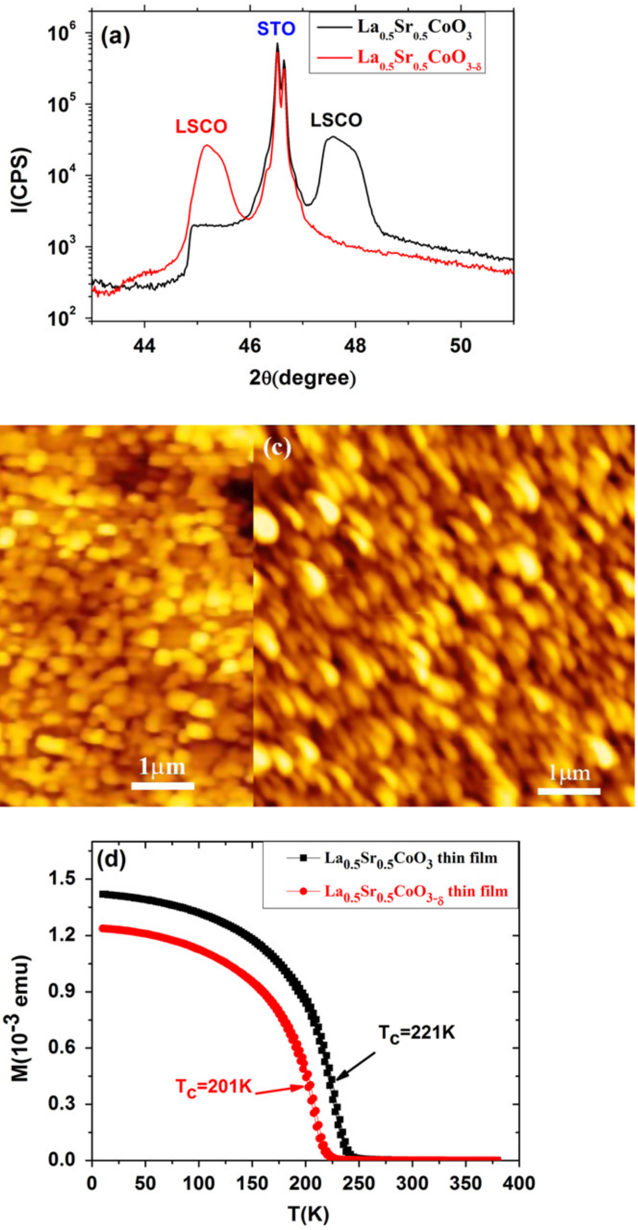

Figure 1. (a) XRD spectrum of $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ films deposited on STO substrates. (b) AFM images of $La_{0.5}Sr_{0.5}CoO_3$ and (c) $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ films. (d). The ZFC and FC temperature dependence of magnetization for the $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ films.

full width at half-maximum of 0.3°, indicating good crystallinity. A noticeable shift of the LSCO (002) diffraction peak is observed after annealing, pointing to the ability to tune oxygen stoichiometry and affect the LSCO structure. The out-of-plane *c* parameter for these LSCO films increases from 0.381 nm to 0.396 nm with the annealing oxygen pressure decreasing from 500 Pa to 10^{-5} Pa. Generally, this noticeable diffraction peak shift is always observed in oxygen deficient transition metal perovskite oxide such as $La_{1-x}Sr_xMnO_3$, $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xCoO_3$ films [18–23]. Figures 1(b) and (c) show the topography of LSCO films. It can

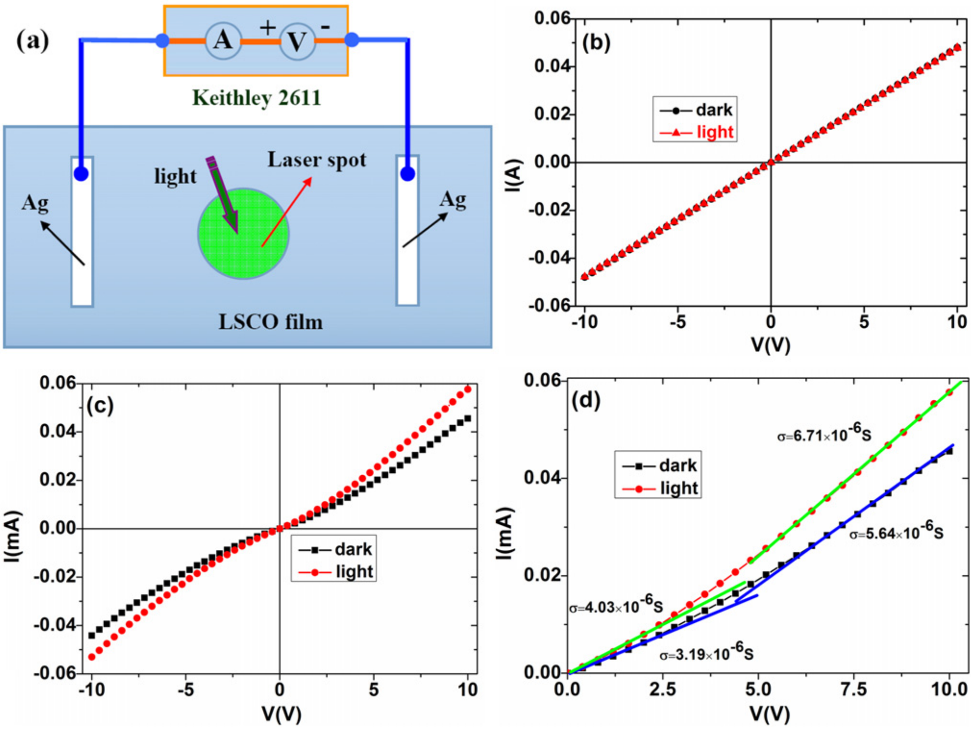

Figure 2. (a) The experimental current and voltage contact configuration with respect to the illuminated region. (b) *I-V* characteristics of $La_{0.5}Sr_{0.5}CoO_3$ and (c) $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ films in darkness and under illumination. (d) The conductivity as a function of voltage of the positive biases from figure 2(c).

be seen that the roughness and the grain sizes of oxygen-deficient $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ are greater than that of oxygen-stoichiometric $La_{0.5}Sr_{0.5}CoO_3$ films, indicating the effect of annealing on the microstructures. Figure 1(d) shows the zero-field-cooled (ZFC) and field-cooled (FC) temperature dependence of magnetization for the oxygen-stoichiometric and oxygen-deficient LSCO thin films. Measurements were performed with a field of 0.02 T applied in the plane of the films. As seen in figure 1(d), the paramagnetic (PM) to FM transition can be observed and the Curie temperatures (T_C) for the two samples are distinctly different. $La_{0.5}Sr_{0.5}CoO_3$ film has a higher intensity of *M*, and its Curie temperature (221 °C) is also slightly higher than that of $LaSrCoO_{3-\delta}$, suggesting that this sample has a higher spin order. The slight variation of T_C in LSCO films should be related to the oxygen vacancies, which in turn may be related to the microstructures of the films. Generally, oxygen vacancies in the doped cobaltates would lead to a negative electric charge deficiency which is compensated by a Co^{4+} decrease to keep charge neutrality. So the oxygen vacancy will reduce the Co^{4+}/Co^{3+} ratio to change the mixed Co valence and hole-doping level [24]. The magnetic, transport, and structural properties strongly depend on the hole-doping level [25]. The FM correlation and the associated T_C increase monotonically with the hole-doping level [25]. The decrease of the hole-doping level in the oxygen-deficient LSCO thin film would weaken the FM correlations to result in the decrease of T_C.

Figure 2 depicts the effect of light illumination on the electric transport properties of the LSCO thin film. The experimental current and voltage contact configuration with respect to the

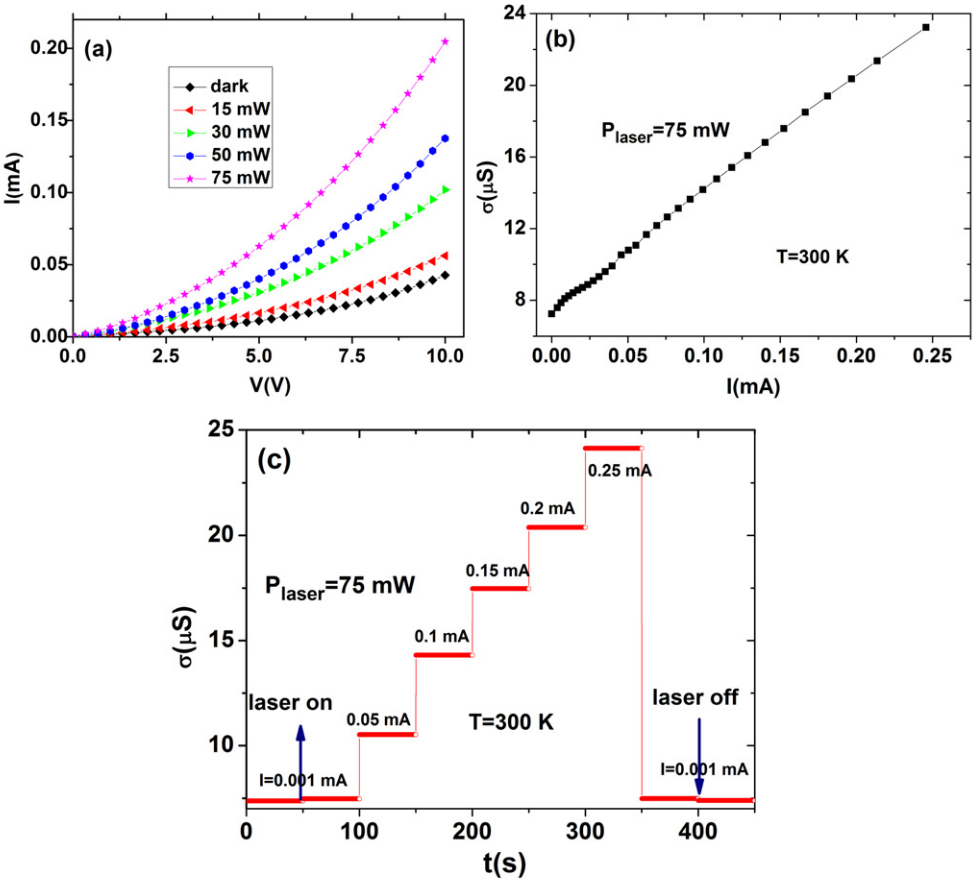

Figure 3. (a) *I–V* characteristic at 300 K of the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin film under different intensity of light illumination. (b) Photoconductivity of the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin film as a function of electrical current under light illumination of 75 mW. (c) Time dependence of conductivity of the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin film with light illumination of 75 mW and various electrical currents at 300 K.

illuminated region are shown in figure 2(a). It can be seen from figure 2(b) that whether in darkness or under light illumination of 15 mW, the $LaSrCoO_3$ film is only slightly resistive and exhibits Ohmic contact behavior and no photoconductivity can be observed. In contrast, the resistance of $LaSrCoO_{3-\delta}$ film increases three orders of magnitude and the *I–V* curve slightly deviated from linearity, as seen in figure 2(c). Besides, it is interesting to note that obvious photoconductivity can be observed and the photoconductivity can be strongly enhanced by increasing the voltage (or electric current), both in darkness and under illumination. For instance, the conductivities increase from 3.19×10^{-6} s to 5.64×10^{-6} s in darkness while from 4.03×10^{-6} s to 6.71×10^{-6} s under illumination, respectively, as shown in figure 2(d).

Figure 3(a) shows the *I-V* characteristic of the oxygen-deficient LSCO thin film at 300 K under light illumination with different intensity. The *I–V* curve was almost linear in darkness, which indicates that the resistance of the oxygen-deficient LSCO thin film was independent of the electrical current without light illumination. The electrical current alone did not cause the decrease of the resistance of the oxygen-deficient LSCO thin film. In contrast, light illumination greatly modified the *I–V* characteristic of the oxygen-deficient LSCO thin film. The slopes of the *I–V* curves increased because the resistance decreased under light illumination. A decrease in resistance by more than one order of magnitude is observed at 10 V and the photoconductivity becomes evident in the whole studied voltage range when the light intensity is increased to 75 mW. Furthermore, it is interesting to note that the *I–V* curve under light illumination deviated from linearity. In other words, the transport properties of the oxygen-deficient LSCO thin film under light illumination strongly depended on the electrical current, which exhibits a current-enhanced photoconductivity (CEPC) effect. Figure 3(b) shows the conductivity of the $LaSrCoO_{3-\delta}$ thin film at 300 K as a function of various electrical currents. It was found that conductivity shows linearity with current (*I*), in other words, the $LaSrCoO_{3-\delta}$ thin film exhibits CEPC effect and this effect is strengthened and more obvious with increasing light intensity. Figure 3(c) shows the conductivity of $LaSrCoO_{3-\delta}$ thin film at 300 K as a function of elapsed time upon the applications of light illumination of 75 mW and various electrical currents. The arrows pointing down and up indicate the switching on and off of the light illumination. The conductivity of the film increases to a higher value when the illumination is switched on. Moreover, the conductivity enhancement induced by the illumination becomes more dramatic with the increase of the electrical current showing the CEPC effect. Finally, the conductivity recovers the original value when the light illumination is switched off and the electrical current is decreased to 1 μA. This means that the photoconductivity and the CEPC effects are both transient.

One should point out that the CEPC effect observed in the $LaSrCoO_{3-\delta}$ thin film cannot be connected to heat-induced effects due to the electrical current and light illumination. Hu *et al* estimated that a light illumination of 56.7 mW cm^{-2} and an electrical current of 20 μA will give a temperature rise of only about 0.5 K [14]. Therefore, the remarkable CEPC effect cannot be explained by such a minute heating effect.

As can be seen from figure 2(b), no CEPC effect was observed in oxygen-stoichiometric LSCO films, implying that the CEPC effect in the oxygen-deficient LSCO thin film was closely associated with the oxygen vacancies. Generally, the resulting current of photo-excited carriers, driven by the electric field, can be described by the following equation: [26]

$$j = \left(\sigma_d + \sigma_{ph}\right)\xi \tag{1}$$

where σ_d and σ_{ph} represent the dark and light components of the conductivity, respectively. The photoconductivity can be expressed as [27]

$$\sigma_{ph} = q\left(\Delta n\mu_n + \Delta p\mu_p\right) \tag{2}$$

where q is the electron charge, Δn and Δp are the photo-induced electron and hole density, and μ_n and μ_p is the electron and hole mobility, respectively.

From equation (2) one can conclude that the photoconductivity is not only dependent on the density of electron and hole, but also on the mobility, because the oxygen vacancies in the oxygen-deficient film can trap the photoinduced electrons and the photoinduced holes become the extra carriers that produce the decrease of resistance [28, 29]. The oxygen deficiency in the annealed LSCO film leads not only to a change in the Co^{3+}:Co^{4+} ratio, but to formation of structural disorder in the Co–O–Co conduction channel due to accumulation of oxygen vacancies [24]. On one hand, more oxygen vacancies will induce a larger amount of electrons [30]. On the other hand, with higher light intensity illumination, the increased photons in the same area generate more carriers and create more Co–O–Co conduction channels. As a result, the oxygen vacancies in the LSCO thin film would cause Curie temperature shift and photoconductivity enhancement. Besides, oxygen vacancies with positive charges in LSCO films are naturally attracted to, and thus accumulate at, the negative electrode side when a high electric field is applied, which will affect the *I-V* curves deviated from linearity because the accumulation of oxygen vacancies induces a heavily doped n +layer and thus induce a Schottky barrier. Our result may be of significance from the viewpoint of application because a high photoconductivity sensitivity and tunability can be achieved in the oxygen-deficient LSCO thin film at moderate light intensity and low electrical current.

4. Conclusions

In summary, we have investigated the effects of light illumination and electrical current on the electrical transport properties and photovoltaic properties of oxygen-stoichiometric $La_{0.5}Sr_{0.5}CoO_3$ and oxygen-deficient $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ films prepared by pulsed laser deposition. The light illumination causes a resistance drop to show photoconductivity effect. Moreover, the photoconductivity can be remarkably enhanced by increasing the electrical current, that is, it exhibits current-enhanced photoconductivity effect. Oxygen deficiency in the annealed film leads to the formation of a structural disorder in the Co–O–Co conduction channel due to the accumulated oxygen vacancies and hence is believed to be responsible for the increase in higher photoconductivity. These results may be important for practical applications in photoelectric devices.

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References

[1] Kharton V V, Naumovich E N, Vecher A A and Nicolaev A V 1995 *J. Solid State Chem.* **120** 128
[2] Chueng J T, Morgan P T, Lowndes D H, Zhang X Y and Breen J 1993 *Appl. Phys. Lett.* **62** 2045
[3] Madlhukar S, Aggarwal S, Dhote A M, Ramesh R, Krishnan A, Keeble D and Poindexter E 1997 *J. Appl. Phys.* **81** 3543
[4] Ramesh R, Gilchrist H, Sands T, Keramidas V G, Haakenaasen R and Fork D K 1993 *Appl. Phys. Lett.* **63** 3592
[5] Raccah P M and Goodenough J B 1967 *Phys. Rev.* **155** 932
[6] Mydeen K, Mandal P, Prabhakaran D and Jin C Q 2009 *Phys. Rev.* B **80** 014421
[7] Kimura S, Maeda Y, Kashiwagi T, Yamaguchi H, Hagiwara M, Yoshida S, Terasaki I and Kindo K 2008 *Phys. Rev.* B **78** 180403(R)
[8] Raveau B, Pralong V, Caignaert V, Hervieu M and Maignan A 2005 *J. Phys.: Condens. Matter.* **17** 7371
[9] Kolesnik S, Dabrowski B, Mais J, Majjiga M, Chmaissem O, Baszczuk A and Jorgensen J D 2006 *Phys. Rev.* B **73** 214440
[10] Manna K, Samal D, Elizabeth S and kumar P S A 2013 *J. Appl. Phys.* **114** 083904
[11] Vanitha P V, Arulraj A, Santhosh P N and Rao C N R 2000 *Chem. Mater.* **12** 1666

[12] Haggerty R P and Seshadri R 2004 *J. Phys.: Condens. Matter.* **16** 6477
[13] Huhtinen H, Laiho R, Lahderanta E, Vlasenko L S, Vlasenko M P and Zakhvalinskii V S 2000 *Phys. Rev.* B **62** 11614
[14] Hu L, Sheng Z G, Huang Y N, Song W H and Sun Y P 2012 *Appl. Phys. Lett.* **101** 042413
[15] Gao R L, Yang H W, Chen Y S, Sun J R, Zhao Y G and Shen B G 2014 *Appl. Phys. Lett.* **104** 031906
[16] Gao R L, Yang H W, Chen Y S, Sun J R, Zhao Y G and Shen B G 2014 *J. Alloy. Comps.* **591** *346*
[17] Gao R L, Yang H W, Chen Y S, Sun J R, Zhao Y G and Shen B G 2014 *Physica* B **432** 111
[18] Sun J R, Yeung C F, Zhao K, Zhou L Z, Leung C H, Wong H K and Shen B G 2000 *Appl. Phys. Lett.* **76** 1164
[19] Sun J R, Yeung H W, Li H, Zhao K, Chan H N and Wong H K 2001 *Appl. Phys. Lett.* **90** 2831
[20] Yin Z Z, Gao G Y, Huang Z, Jiao X L, Liu Q Z and Wu W B 2009 *J. Phys. D: Appl. Phys.* **42** 125002
[21] Zhi B W, Gao G Y, Huang Z, Wang L F, Tan X L, Chen P F and Wu W B 2013 *J. Appl. Phys.* **113** 203701
[22] Gazquez J, Bose S, Sharma M, Torija M A, Pennycook S J, Leighton C and Varela M 2013 *APL Mater.* **1** 012105
[23] Manna K, Samal D, Elizabeth S and kumar P S A 2013 *J. Appl. Phys.* **114** 083904
[24] Prokhorov V G, Leea Y P, Kim K W, Ishchuk V M and Chukanova I N 2002 *Appl. Phys. Lett.* **80** 2353
[25] Abrikosov A A 1987 *Fundamentals of the Theory of Metals* (Amsterdam: North-Holland)
[26] Tabares-Munos C, Rivera J-P and Schmid H 1984 *Ferroelectrics* **55** 235
[27] Chen Y, Zang Y Y, Xie D, Wu X, Ren T L, Wei J Q, Wang K L, Wu D H and Zhu H W 2012 *Integr. Ferroelectr.* **134** 58
[28] Cauro R, Gilabert A, Contour J P, Lyonnet R, Medici M-G, Grenet J-C, Leighton C and Schuller I K 2001 *Phys. Rev.* B **63** 174423
[29] Sheng Z G, Sun Y P, Dai J M, Zhu X B and Song W H 2006 *Appl. Phys. Lett.* **89** 082503
[30] Yi H T, Choi T, Choi S G, Oh Y S and Cheong S-W 2011 *Adv. Mater.* **23** 3403