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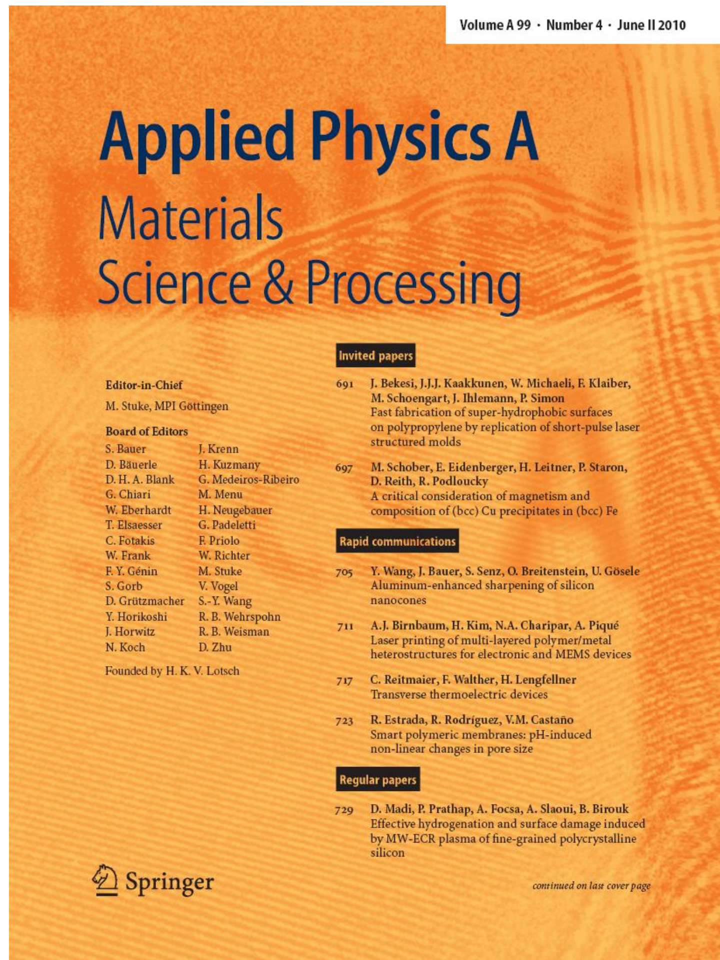

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Pyroelectric properties of $CaCu_3Ti_4O_{12}$ thin films grown by pulsed laser deposition

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Abstract A pyroelectric behavior was observed in $CaCu_3Ti_4O_{12}$ films and the pyroelectric coefficient was measured to be 1.35×10^{-7} C/cm^2 K for a film with thickness of 700 nm from 295 K to 340 K, larger than those of most pyroelectric materials. It was observed that the pyroelectric coefficient increased with the thickness of films from 300 to 700 nm. The origin of pyroelectric effect is proposed to depend on the distortion of the Ti–O octahedron due to the presence of Ti^{3+} ions. Comparing with the measurement result of an unpolarized film, our study strongly supports the interpretation of relaxor ferroelectric behavior in $CaCu_3Ti_4O_{12}$.

1 Introduction

Pyroelectric material for infrared sensors has generated much interest since uncooled infrared sensors are being increasingly demanded for many applications such as plant monitoring, gas detection, fire monitoring and security system [1]. Especially, more and more attention has been paid to fabricate excellent pyroelectric thin films which could be integrated with other silicon charge coupled devices together on Si wafers [2, 3]. The pyroelectric coefficient is an important parameter for pyroelectric material because it is proportional to detectivity and merit figures. Though pyroelectric thin films are expected to yield better sensitivity and faster response [4], it is difficult to prepare excellent thin films with large pyroelectric coefficient and stable characteristic due to the influence of surface and size effects [5, 6]. The value of the pyroelectric coefficient of the reported pyroelectric materials usually varies from 10^{-9} to 10^{-8} C/cm^2 K or even smaller, including $Ba_{0.8}Sr_{0.2}TiO_3$ thin films [7], non-crystalline $BaTiO_3$ thin films [8], $Pb(Zr_xTi_{1-x})O_3$ and $(Pb,La)(Zr,Ti)O_3$ thin films grown on crystalline substrates, etc. [9–14]. Since $CaCu_3Ti_4O_{12}$ (CCTO) was reported as a giant-dielectric-constant material in 2000 [15], many efforts have been devoted to study its dielectric properties [16–18]. A pyroelectric behavior has been observed in the bulk CCTO in 2007 [19], while a detailed study of its pyroelectric properties has not been reported yet, especially in thin films.

In this letter, the pyroelectric properties of the polycrystalline CCTO thin films with different thicknesses have been investigated by dynamic method [20]. The largest value of pyroelectric coefficient is determined to be 1.35×10^{-7} C/cm^2 K, which presents great potential applications in the uncooled infrared detections.

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2 Experimental

A series of CCTO thin films with different thicknesses were prepared on Nb:$SrTiO_3$ (100) (NSTO) conductive substrates by the pulsed laser deposition (PLD) at 800°C under an oxygen pressure of 10 Pa. The beam of a Lambda Physik XeCl excimer laser (308 nm, 20 ns, 4 Hz) was focused on a sintered CCTO target with an energy density of about 2 J/cm^2. The thicknesses of the CCTO films were measured to be

300, 400, 500 and 700 nm, respectively, by a surface profile measuring system (DEKTAK, USA). Au film dots with a thickness of 50 nm and a diameter of 1 mm were deposited on CCTO films through a mask at 600°C under 3×10^{-3} Pa. The Au dots and NSTO conductive substrate serve as top and bottom electrodes, respectively. The crystalline structure of the CCTO film was analyzed by X-ray diffraction (XRD) with Cu Kα radiation at 1.54 Å.

The pyroelectric coefficient from 295 K to 340 K was investigated by dynamic method. This measuring system was calibrated by using $BaTiO_3$ (100) single crystal as a reference. The samples were heated by a heat source which was kept at a constant temperature, and then they were cooled by a cold source. During the heating and cooling processes, the values of temperature and corresponding current were recorded every two seconds by Fluke 8840 A multimeter and Keithley 2400 sourcemeter, respectively. Before the measurement of pyroelectric coefficient, a dc electric field of 20000 V/cm was applied between the two electrodes for 24 hours at room temperature to ensure that the electrical dipole moments in CCTO film would be fully polarized, and then the two electrodes were shorted directly to discharge for half an hour in order to eliminate the initial potential difference. An unpolarized CCTO sample was also investigated as a comparison.

3 Results and discussion

The XRD result of the 400-nm-thick CCTO film on NSTO substrate is shown in Fig. 1. There are four CCTO diffraction peaks, which means that the structure of CCTO in the films is single phase but polycrystalline. Figure 2 shows the time evolutions of the temperature and corresponding current for the polarized sample of CCTO film with a thickness of 700 nm, while no obvious current signal was observed for the unpolarized sample. As shown in Fig. 2, the value of current stayed around zero when the temperature was changeless. It jumped to a maximum abruptly as the temperature began to increase. Then it decreased slowly as the temperature increased not so quickly. A negative current signal with about the same magnitude emerged during the cooling process. These phenomena mean that the current is proportional to the change rate of the temperature, which is the behavior of the pyroelectric current. Since the pyroelectric current is caused by the variation of spontaneous polarization, the negative current during the cooling process indicated that the change of spontaneous polarization in CCTO film was reversible within this temperature range.

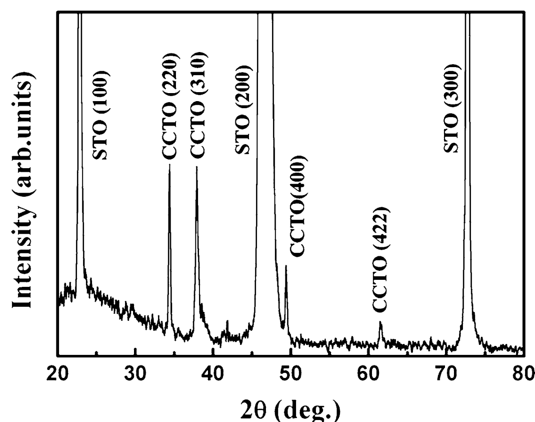

Fig. 1 XRD spectra of CCTO film with thickness of 700 nm on $Nb{:}SrTiO_3$ (100)

As is known, the pyroelectric coefficient p is defined as follows [21]

$$p = \left(\frac{\partial D}{\partial T}\right)_E = \frac{\partial P_s}{\partial T} + E\varepsilon_0 \frac{\partial \varepsilon_r}{\partial T} \quad (1)$$

where D is the dielectric displacement, T is temperature, E is applied electric field, P_s is spontaneous polarization, ε_0 is the permittivity of free space, and ε_r is the permittivity of pyroelectric material. When there is no applied electric field, (1) could be simplified as follows

$$p = \frac{dP_s}{dT} \quad (2)$$

In pyroelectric material, the change of temperature will cause the variation of spontaneous polarization which will produce a displacement current I parallel to the polar axis given by [22]

$$I = A\frac{dP_s}{dt} = A\frac{dP_s}{dT}\frac{dT}{dt} = Ap\frac{dT}{dt} \quad (3)$$

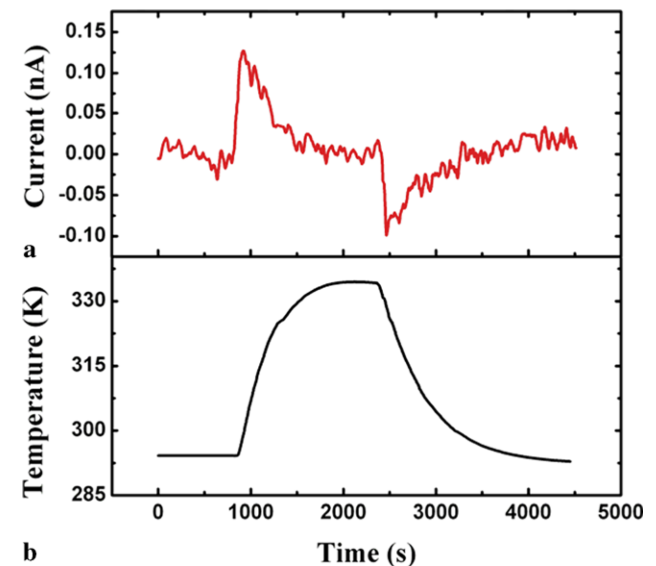

Fig. 2 The time evolutions of the temperature (**a**) and corresponding current (**b**) for the polarized sample with CCTO film thickness of 700 nm during the heating and cooling process

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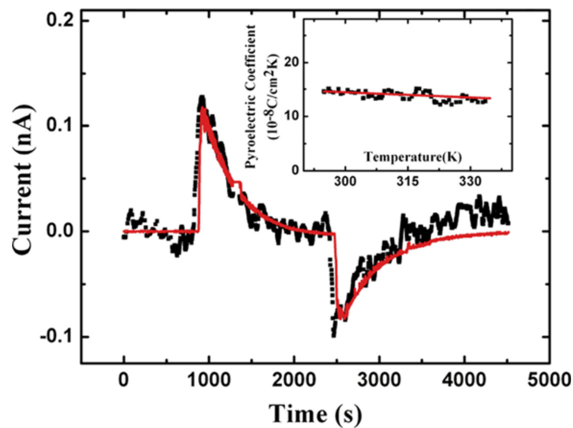

Fig. 3 The fitting of pyroelectric current according to the temperature evolution by $I = ApdT/dt$. The *inset* shows the variation of the pyroelectric coefficient dependent on the temperature

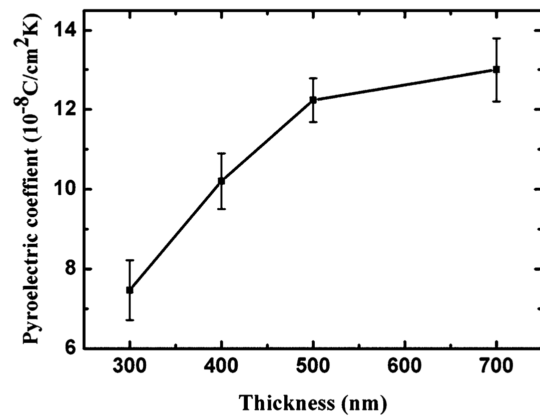

Fig. 4 The relationship between the pyroelectric coefficient and the thickness of CCTO film. The error of the points is determined by repeated measurement

where A is the area of the top electrode, and dT/dt is the temperature change rate.

The value of the pyroelectric coefficient, as shown in the inset of Fig. 3, was calculated from the result of Fig. 2 by using (3). Though the pyroelectric coefficient is usually dependent on the temperature, the value of p changed slightly within the temperature range from 295 to 340 K. In order to eliminate the error caused by the thermal noise, the curve of current evolution can be fit by (3) as shown in Fig. 3 assuming that the value of p was constant within this temperature range. From the fitting result, the value of p for CCTO film was determined to be 1.35×10^{-7} C/cm^2 K, at least 2 times larger than that of most other reported pyroelectric materials such as BST [7], BTO [8], and PZT [9], etc. As a reference, the pyroelectric coefficient of $BaTiO_3$ single crystal was also measured to be 1.8×10^{-8} C/cm^2 K from 295 K to 340 K by the same measuring system, which is in agreement with the reported value of 2.0×10^{-8} C/cm^2 K [23].

Though there was no applied electrical field, a feeble potential difference existed between two electrodes when the temperature changed. Therefore the rationality of neglecting the second term of (1) should be doubted. The maximum pyroelectric current was about 0.15 nA. So the maximum potential difference between electrodes could not exceed $U = 0.15\ \text{nA} \times 50\ \Omega = 7.5$ nV, where 50 Ω is the resistance of Keithley 2400 sourcemeter. One can see that even for a very large value of $\partial\varepsilon_r/\partial T$, e.g., thousands of K^{-1}, the contribution to the pyroelectric coefficient (calculated as $E\varepsilon_0\partial\varepsilon_r/\partial T$) induced by the potential difference is much smaller than 10^{-7} C/cm^2 K.

The pyroelectric properties of the other three samples were also investigated by the same method. The relationship between pyroelectric coefficient and the thickness (d) of CCTO film is shown in Fig. 4. As can be seen, the value of the pyroelectric coefficient was nearly proportional to the thickness of CCTO film when 300 nm $\le d \le$ 500 nm and tended to saturation at a higher value of d. This phenomenon is probably caused by substrate-induced strains developed due to the lattice mismatch between the substrate and deposited material. The lattice structure and dielectric properties of films are influenced by the strains within certain thickness near the surface of substrates [24, 25]. As a result, the change of polarization in the films with the temperature may be frustrated due to the existence of substrate-induced strains. As the films become thicker, the strains would be relaxed beyond the critical thickness, and the pyroelectric properties of CCTO films will behave as a bulk material.

The lattice structure without any defect of CCTO belongs to the $Im\overline{3}$ symmetric space group. Since pyroelectricity is symmetric forbidden, we propose that the origin of the pyroelectric effect for CCTO could be explained by the distortion of the Ti–O octahedral due to the presence of Ti^{3+}. It is known that CCTO films deposited at high temperatures probably possess both Ti^{4+} and Ti^{3+}, which is caused by the presence of oxygen loss. Ti^{3+} is likely to distort the lattice because of its larger ionic radius (0.67 Å) than that of Ti^{4+} (0.605 Å), which places the Ti–O bonds under tension leading to the distortion of Ti–O octahedron. Then, the Ti^{3+} cation is displaced off center along their one threefold axis forming the electrical dipole moment. Since no obvious signal was observed for the unpolarized sample, there is no long-range order of the spontaneous polarization before being polarized, which is a good proof for the interpretation of relaxor ferroelectric behavior in CCTO [26]. Under the applied electric field of 20000 ∼ 30000 V/cm, the displacements of Ti^{3+} cations are adjusted to form a considerable component of polarization vector perpendicular to the surface of films. As the temperature changes, there are two different mechanisms which will change the original polarization. On one side, as the temperature increases, the lattice structure will expand and destroy the intrinsic distortion which leads to a change of the polarization of Ti–O octahedron. On the other side, the quantized energy level of

the Ti^{4+} will change (E_1 to E_n) within the well with the increase of the temperature [27]. Therefore its mean equilibrium position will be changed in the lattice which will give a change in the overall electrical dipole moment. The observed pyroelectric signal is the result of the two mechanisms working together.

4 Conclusion

In summary, the pyroelectric properties of CCTO films on Nb:$SrTiO_3$ (100) substrates was studied. The largest value of pyroelectric coefficient among the tested samples was determined to be 1.35×10^{-7} C/cm^2 K from 295 K to 340 K, larger than that of most other reported pyroelectric material. It is probably a good candidate for pyroelectric applications. The relationship between pyroelectric coefficient and the thickness of films was also discussed. The origin of the pyroelectric effect for CCTO film was proposed to depend on the distortion of Ti–O octahedron due to the presence of Ti^{3+} ions.

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