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FERROELECTRIC POLARON IN LAYERED PEROVSKITE FERROELECTRIC THIN FILMS

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Abstract: High quality $SrBi_2Ta_2O_9$ (SBT) ferroelectric thin films were fabricated on platinized silicon substrate by PLD. Electronic transport properties of $SrBi_2Ta_2O_9$ ferroelectric thin films in temperature range of 10 to 300K were studied. The conduction mechanisms in the thin films were analyzed. The results indicate the existence of two conduction mechanisms in SBT ferroelectric thin films. Due to the SBT layered structure, the carrier transport can be divided into two parts: internal transport, which is between the $(Bi_2O_2)^{2+}$ layers, and external transport, which is across the $(Bi_2O_2)^{2+}$ layers. Especially, behavior of electric transport of the polaron as an internal transport carrier is first observed in the $SrBi_2Ta_2O_9$ ferroelectric thin films. Activation energy of the internal transport carriers is $E_a \sim 0.0556$ eV. The results can be helpful in understanding the low DC leakage in SBT films at room temperature.

Key words: ferroelectric; polaron; electronic transport

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层状钙钛矿铁电薄膜中铁电极化子研究

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摘要:用 PLD 方法在铂金硅衬底制作了高质量的 $SrBi_2Ta_2O_9$(SBT)铁电薄膜样品.在 10 到 300 K 的低温范围,研究了 SBT 薄膜的电子输运特性,分析了其传导机制.结果显示在 SBT 铁电薄膜中存在两种导电机制.根据 SBT 层状结构,两种导电机制分为:被限制在 Bi-O 层内的内输运,和能够穿过 Bi-O 层的外输运.首次观察到作为内传导载流子的铁电极化子的电输运行为.在 SBT 薄膜中铁电极化子的热激活能 $E_a \sim 0.0556$ eV.研究结果为 SBT 薄膜具有极低漏电流提供了一种解释.

关 键 词:铁电;极化子;电子输运

Introduction

Ferroelectric thin films have tremendous potential application for data storage, sensors, uncooling infrared detectors, various tunable microwave devices, and microelectromechanical system technologies. Carrier transport plays an essential role in determining some characteristics of ferroelectric thin films such as fatigue and leakage to meet commercial requirements. In recent years, different transport mechanisms in ferroelectric materials, such as space charge limited conduction (SCL), thermionic emission limited conduction (TEL), and Poole-Frenkel emission limited conduction (PFL) have been reported [1-2]. Further, current-voltage (IV) characteristics may contain contributions from SCL and PFL conductions, and even TEL conduc-

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tion at high direct current (DC). The latter TEL part can usually be distinguished by its dependence on the selection of electrode material. To date, most of the studies on the transport properties of ferroelectric films are based on DC measurements, such as DC IV measurements. In direct current conductivity measurements, all types of carrier contributions to conductance are superposed. Thus, various transport mechanisms can't be easily distinguished. It is well known, however, that each type of carrier (or mechanism) possesses an independent relaxation time. Based on this feature, it is easy to distinguish the contributions of various mechanisms of electrical transport from frequency dependent conductivity measurements. However, there has been little experimental work on alternating current (AC) transport properties of the thin films below room temperature, although data collected at a broader temperature range would be helpful in understanding the conduction mechanisms of these films.

The electrical properties of ferroelectrics are known to be closely associated with its crystallographic structure. An important example is $SrBi_2Ta_2O_9$ (SBT), a representative of a new class of ferroelectrics in which the structure is based on perovskite octahedron layers $(SrTa_2O_7)^{2-}$ sandwiched between $(Bi_2O_2)^{2+}$ layers. SBT exhibits almost no fatigue and low DC leakage on Pt electrodes at room temperature (up to 10^{12} cycles at saturation), accompanied by other superior properties[3-4]. These unusual properties have generated tremendous interests in the fundamental conduction mechanisms of SBT.

In this work, we report the AC transport properties from 100 Hz to 15 MHz of SBT ferroelectric thin films in temperature range of 10 to 300 K. The dominant conduction mechanisms at different frequency ranges were analyzed. Most importantly, our results indicate the existence of conduction through the perovskite octahedron layers of the SBT structure.

1 Experiment

The samples were fabricated on platinized silicon ($Pt/Ti/SiO_2/Si$) by using pulsed laser deposition (PLD). The laser used for SBT thin film deposition was an XeCl (Lambda Physik LPX220icc, wavelength 308 nm) excimer laser with 5Hz repetition frequency, 17ns pulse duration and an energy of 160 mJ/pulse. The output laser beam was focused onto a rotating target at an angle of 45° by UV lens with a focal length of 50 cm. The stability of the incoming beam was monitored with an energy meter.

The SBT target was processed by mixing $SrCO_3$, Bi_2O_3 and Ta_2O_5 powders in a stoichiometric ratio by ball milling, followed by calcination of the mixed powders at 940 ℃. The calcined powders were then pressed at 800 kg/cm^2 in a circular die and the pressed pellets were sintered at 1200 ℃ for 2h in a regular box furnace. The target was freshly polished to produce uniform plasma cloud and mounted on a motor-driven rotary shaft.

The platinized silicon ($Pt/Ti/SiO_2/Si$) substrates were prepared from wafers of (111) oriented Si with a layer of thermally grown SiO_2, then coated with 10 nm Ti and 800 nm Pt using UHV electron beam evaporator (Balzers UMS500p) and Ti and Pt targets, respectively. The substrates, whose temperature was at 400 ℃ during deposition, were mounted onto a heated substrate holder and placed parallel to the target at a distance of 4 ~ 5 cm.

Before deposition, the chamber was initially pumped down to 5 Pa by a mechanical pump, and high purity oxygen was then introduced with a mass flow controller at a flow rate of 20 cm^3/min, until an approximate pressure of 20 Pa was obtained. The films were deposited on the platinized silicon substrates at 400 ℃, and annealed at 750 ℃ for 90 min in oxygen.

The crystallographic structure of the SBT films was characterized by x-ray diffraction (XRD) with CuK_α radiation. The microstructure of the films was observed by atomic force microscopy (AFM). The ferroelectric behavior and fatigue endurance were investigated by using RT66A (Radiant Technologies). Electrical conductivity of SBT thin films was measured by HP4194A Impedance/Gain-Phase Analyzer in the temperature range of 10 to 300 K. These measured values of conductivity between 100 Hz and 15 MHz were simulated by an equivalent circuit with an ideal capacitor shunted by an ideal resistor.

2 Results and discussion

2.1 Microstructure

The crystallographic structure of SBT films is characterized by x-ray diffraction (XRD) with CuK_α radiation and the results are shown in Fig. 1. The XRD pattern shows that the dominant orientations of the films on platinized silicon are (008) and (115).

The AFM images of the films's surface morphology are displayed in Fig. 2. The surface of films is smooth, and the morphology displays a homogeneous crack-free appearance in all scanned areas of the sample in Fig. 2 (a). The observed microstructure is very dense. This may be the result of modifying the growth kinetics by the discharge plasma. The large average kinetic energy of the depositing species inherent in pulsed laser deposition and high density target also likely contribute to the dense microstructure. The surface shows a mean grain size of about 300 nm. Moreover, the SBT film exhibits a columnar structure in Fig. 2 (b) of three-dimensional topography, indicating that the grain growth process is dictated by nucleation at the substrate surface, as observed previously for SBT films by transmission electron microscopy[4]. This is an expected result for films prepared by physical vapor deposition processes.

In order to examine the quality of the thin films further, the ferroelectric characteristics were measured. The samples for ferroelectric property investigation were typical sandwich structure Pt/SBT/Pt capacitor devices and a representative hysteresis loop is shown in Fig. 3. The remanent polarization (P_r) and coercive voltage (V_c) are approximately 10.46 $\mu C/cm^2$ and 1.2 V, respectively. These values are typical of SBT films that have been prepared previously by PLD. A 1kHz bipolar square wave with a magnitude of 3 V was used to fatigue the films. Excellent fatigue resistance was observed; the P_r during 10^{10} switching cycles did not show significant reduction.

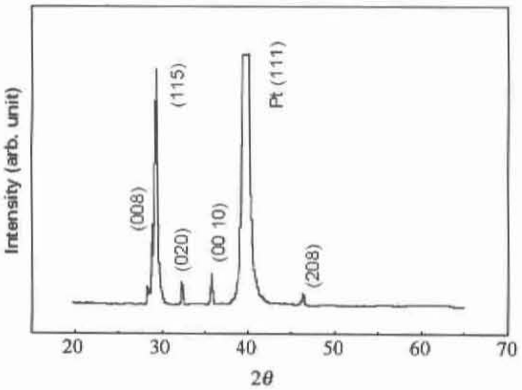

Fig. 1 X-ray diffraction pattern of SBT films on platinized silicon (Pt/Ti/SiO2/Si) substrates with pulsed laser deposition of dc glow discharge plasma.
图 1 在铂金硅衬底上 SBT 薄膜的 X 光衍射花样

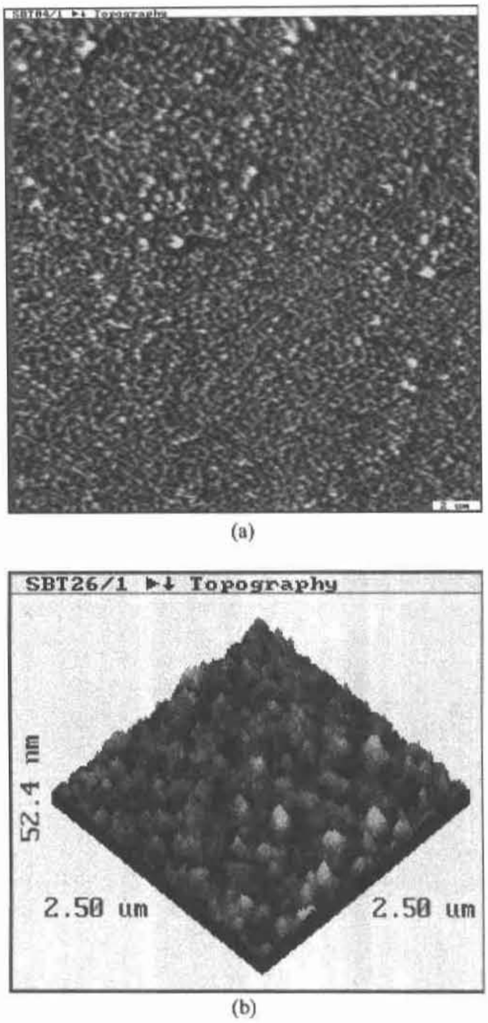

Fig. 2 The AFM images of SBT films's (a) surface morphology (b) three-dimensional topography
图 2 SBT 薄膜的原子力显微形貌. (a) 表面形貌, (b) 立体形貌

2.2 Electrical conductivity

The frequency dependence of the electrical conductivity is illustrated in Fig. 4 with temperature as a parameter (10 to 300 K). The behavior of the curves can be divided into three regions.

Region Ⅰ is from 100 Hz to 1.5 MHz, where the

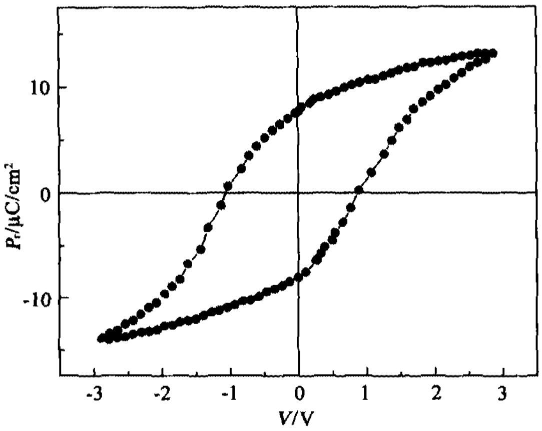

Fig. 3 Polarization - electric field hysteresis loop of a SBT thin film.
图3 SBT薄膜的电滞回线

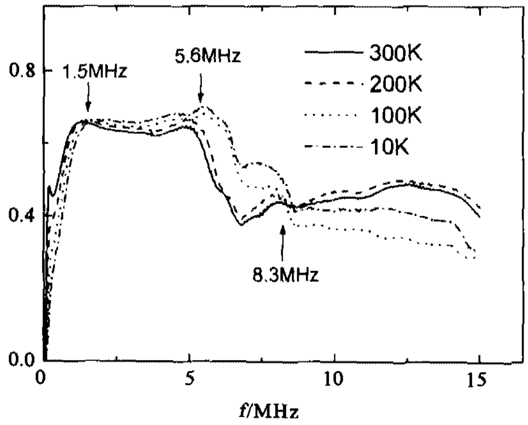

Fig. 4 The frequency dependence of conductivity in SBT films as a function of temperature (from 10 to 300 K)
图4 温度作为参数的SBT薄膜电导与频率的关系

electrical conductivity rises rapidly, and the electrical conductivity in the region increases linearly with temperature. This is the typical feature of space charge (electrons or holes) conduction in ferroelectric thin films. This transport mechanism in ferroelectric thin films has been studied by other authors, and some models have been proposed [1].

Region Ⅱ is from 1.5 to 8.3 MHz, in which a flat plateau is found from 1.5 to 5.6 MHz, and the curves drop steeply above 5.6 MHz. In this frequency range, the relationship of temperature dependent conductivity of SBT films is nonlinear. This indicates a relaxation conduction mechanism in the thin films.

Region Ⅲ includes data above 8.3 MHz. Over the frequency of 8.3 MHz, the conductivity changes slowly with measured frequency. However, the temperature dependence of the conductivity shows an unusual behavior in this frequency range. As shown in Fig. 5, the conductivity decreases with temperature at first, reaching its lowest value at about 85 K, then it begins to rise. At last almost no dependance on temperature is observed near room temperature. It should not be from impurities and defects due to no volatile component in SBT, which is one of reason for SBT fatigue-free, not like Pb-based ferroelectric materials. [3] This indicates the existence of a new conduction mechanism in SBT thin films.

SBT has the bismuth-containing layered perovskite structure where double layers of Ta-O octahedra are sandwiched between $(Bi_2O_2)^{2+}$ layers. It is widely accepted that the $(Bi_2O_2)^{2+}$ layers prohibit carriers from coming into the perovskite layers because their positioning in the lattice is self-regulated to compensate for the charge, which should make SBT fatigue-free[3]. When carriers are in the perovskite layers, in contrast, they are also prevented from escaping, thus they would be captured between the $(Bi_2O_2)^{2+}$ layers. For carriers moving, the $(Bi_2O_2)^{2+}$ layers are like high transport barriers. Due to the SBT structure above, we can divide carrier transport into two parts; internal transport, which is between the $(Bi_2O_2)^{2+}$ layers, and external transport, which is across the $(Bi_2O_2)^{2+}$ layers. Evidently, the internal transport can not be seen in DC measurements because of the low activation energy of internal transport carriers, but it may exhibit its behav-

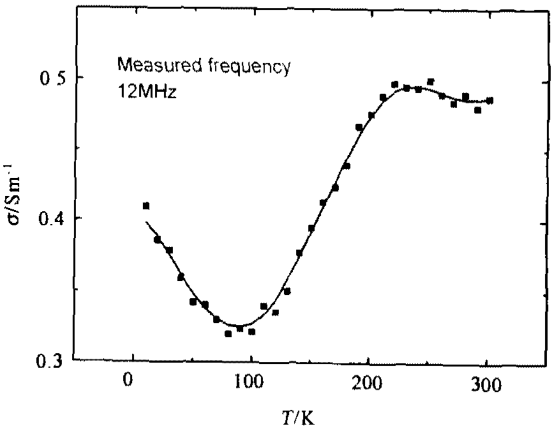

Fig. 5 The conductivity of SBT films versus temperature above 8.3 MHz frequency
图5 在8.3MHz频率以上,SBT薄膜电导与温度的关系

ior in AC measurement. The interaction of free carrier with spontaneous polarization (P), or a ∇P effect has been discussed[2]. In the ferroelectric materials, it is found that the transfer of static charge, defined as an intuitive concept in the usual way based on partitioning the ground-state electronic density into contributions attributed to different atoms, is incomplete. Due to a narrow Ta d band in SBT, we can consider the coupling of the spontaneous polarization fields of perovskite lattice between the $(Bi_2O_2)^{2+}$ layers and electrons from incomplete static charge transfer as a quasi-particle, or ferroelectric polaron, which may be the origin of the internal transport carries. In fact, the quasi-particle in layered perovskite ferromagnetic thin films has been reported.

Based on these arguments, we believe that the observed unusual behavior of the conductivity over 8.3 MHz in the films may result from the internal transport, ferroelectric polaron in SBT thin films. In Fig. 1, it is clear that the frequency dependence of the conductivity is divided into two branches in the high frequency range (over 8.3 MHz). For both of them, the conductivity decreases with frequency at low temperature and increases with frequency at high temperature. This is believed to be caused by two transport modes, i. e. tunneling and hopping, of the ferroelectric polarons in SBT. Tunneling is analogous to a wave-like motion, which decreases when frequency increases, while hopping is a phonon-activated process which is predominant at high temperature, and the conductivity increases with frequency, which have been observed in Fig. 4.

The conductivity *vs* temperature curve (Fig. 5) further demonstrates the two transport modes of ferroelectric polarons in the films. The temperature dependence of the conductivity, including both tunneling and hopping transport mechanisms, consists of a $T^{-1.5}$ temperature dependence and an $\exp(-E_a/kT)$ thermally activated process. At low temperatures the bandwidth becomes narrow and band-type transport is possible; the change of the conductivity with temperature has a predominant of $T^{-1.5}$ temperature dependence. With temperature increasing, a large number of highly excited vibrational levels are conducted so that the polaron motion which is greatly affected by interactions with vibrations becomes random and non-wave like, and hopping mode is mainly conductance; the temperature dependence of the conductivity is mainly $\exp(-E_a/kT)$, or the conductivity increases with temperature increasing. From fitting the experimental data by $\exp(-E_a/kT)$, the activation energy $E_a \sim 0.0556$ eV of the polaron in SBT thin films is estimated. Indeed, the activation energy of internal transport carriers is so small that it is not shown by DC measurement, as shown in Fig. 6.

Between the two transport modes, there is a critical temperature T_c. According to Holstein's estimation, at $T \le 0.4\hbar\omega_L/k$ a band-type conduction may be assumed, and at $T \ge 0.5\hbar\omega_L/k$ a hopping-type conduction may be assumed. In our previous work, ω_L of SBT film was 2.4×10^{13} Hz[5]. Temperature regions of $T \le$ 73K band-type and $T \ge$ 91K hopping-type conduction are estimated, respectively. From the experimental result in Fig. 5, the critical temperature of the two transport modes in SBT films is obtained about 85 K. This agrees very well with Holstein's estimation value.

It is also noted that the conductivity depends weakly on temperature 300 K in Fig. 5. This indicates that the carrier lies in the intermediate between the coherent and hopping transport at near room temperature. The conduction behavior has been observed at room temperature in other materials before[6].

3 Conclusions

High quality $SrBi_2Ta_2O_9$ (SBT) ferroelectric thin

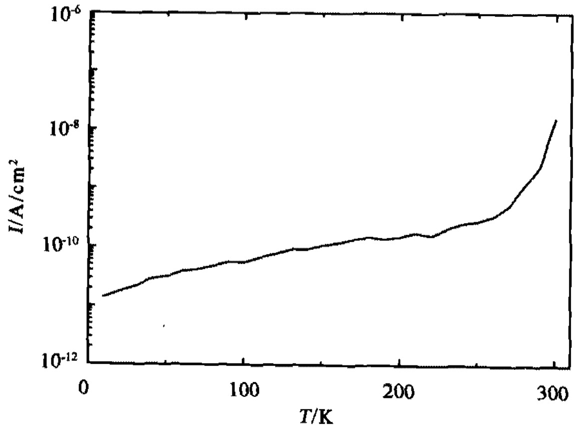

Fig. 6　Temperature dependence of the DC (leakage) current of a PLD-derived Pt/SBT/Pt sample at 3 V
图6　在3V下,SBT薄膜直流电流与温度的关系

films have been fabricated on platinized silicon by using PLD. The crystallographic structure of SBT films was characterized by x-ray diffraction and the most pronounced diffraction peaks were associated with the (008), and (115) reflections. The microstructure of the films was characterized by atomic force microscopy, indicating that the grain growth process is dictated by nucleation at the substrate surface. AC transport properties of $SrBi_2Ta_2O_9$ ferroelectric thin films in temperature range of 10 to 300K were studied. The conduction mechanisms in the thin films were analyzed. The results indicate the existence of three conduction mechanisms in SBT ferroelectric thin films. Specially, behavior of electric transport of the polaron is firstly observed in the $SrBi_2Ta_2O_9$ ferroelectric thin films. Activation energy of the internal transport carriers is so small that it is not shown by DC measurement, which can be helpful in understanding the fundamental origins of low DC leakage in SBT films at room temperature.

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