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High optical transmittance and anomalous electronic transport in flexible transparent conducting oxides $Ba_{0.96}La_{0.04}SnO_3$ thin films

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A B S T R A C T

Wide bandgap semiconducting perovskite La:$BaSnO_3$ is a promising candidate for next-generation transparent conducting oxides due to its high electron mobility and excellent oxygen stability. In this work, in order to realize flexible optoelectronics, an epitaxial growth of $Ba_{0.96}La_{0.04}$ SnO_3 (BLSO) film on a flexible mica via van der Waals epitaxy is established. The high quality heteroepitaxy and crystallinity of BLSO films are confirmed by a combination of X-ray diffraction and atomic force microscopy. Results show that the flexible BLSO films not only retain a high transmittance of more than 85% in the visible region under unbending conditions, but also exhibit a remarkable transmittance of 90% under bending conditions. Due to the fixed lattice mismatch and misfit strain, an anomalous electronic transport behavior, showing as a continuous enhancement of resistivity dependence on the decreasing temperatures from high to low, was observed for all BLSO films. Although the resistivity of flexible BLSO films is a slight larger than that of growth on rigid counterparts, the resistivity of 7–10 mΩ cm is also satisfied with actual application for optoelectronic devices at room-temperature. Our study marks that the technological advancements toward realizing flexible optoelectronics are promising by utilizing perovskite oxides La-doped $BaSnO_3$ and mica substrate.

1. Introduction

Over the past few years, transparent conducting oxides (TCO) have attracted a great deal of interests owing to increasing demands for the widespread application of current optoelectronic devices, e.g. solar cells, flat panel displays, light emitting diodes, and transparent logic devices, and so on. [1–5] Many binary oxide materials including the pure and impurity doped ZnO, In_2O_3, as well as SnO_2 were studied for these purposes, successfully demonstrating passive transparent conductive windows to active semiconducting devices, such as *pn* junctions, field effect transistors, and UV lasers [5–8]. However, with the ongoing development of optoelectronic technology, exploration of new alternative transparent materials but with more outstanding performance or special properties are becoming more and more important. In view of actual applications, most of TCO films are generally required to have a wide band gap of more than 3.0 eV, necessary for high transmittance in the visible region [6]. Meanwhile, wide band gap semiconductors with the perovskite structure are becoming the favorable TCO due to their rich physical properties and compatibility for multilayer structures together with the potential applications in high-temperature and high-power electronics. For example, La(In,Sb)-doped $SrTiO_3$ and Nb-doped $CaTiO_3$ have been reported in the context of new TCO materials [9–12].

In this work, we focus on another wide band gap semiconductor, perovskite barium stannate oxide $BaSnO_3$ (BSO). BSO is known to form an ideal cubic perovskite structure in which the Sn-O-Sn bonding angle is close to 180 °. The pristine BSO can be regarded as an insulating material since for its negligible conductivity. Its conduction band is mainly Sn 5*s* orbitals, and the valence band is mainly oxygen 2*p* orbitals with a large bandgap of 3.4 eV [13]. For the enhancement of conductivity, some different doped elements have been substituted, such as La and Gd doping on Ba site, Sb doping on Sn site [14–17]. In particular, La-doped BSO (BLSO) has been recently gained numerous attentions due to its excellent electron mobility and high chemical stability. Kim et al. reported that BLSO film and single crystal have high carrier mobility of 70 and 320 $cm^2/V\,s$ at room temperature, respectively [15]. Recent investigations have proved that such a high mobility is due to its smaller carrier effective mass ($m^* = 0.40\ m_e$) and longer

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carrier relaxation time [18,19]. The high mobility and a wide band gap indicate that BLSO is a promising candidate for transparent conductor applications. Furthermore, Wadekar et al. found that the room temperature resistivity could be effectively decreased from 7.8 to 4.4 mΩ cm by choosing $SmScO_3$ substrate comparing with $SrTiO_3$ substrate [20]. The main reason has been attributed to reduction in dislocation density due to the lower lattice mismatch. In addition, epitaxial growth BLSO film on the other variety of substrates, including $PrScO_3$ [21], $LaAlO_3$ [22], $BaSnO_3$ [23], MgO [24], have been also reported.

We noticed that all reported substrates were rigid wafers instead of flexible substrates. In present, flexible devices, i.e., devices fabricated on flexible substrates, are very attractive in application due to their stretchable, biocompatible, light-weight, and portable [25–29]. Therefore, in order to further expand the application scope and give rise to new functionalities of BLSO film on optoelectronic field, it is necessary to study the BLSO film growth on the flexible substrates. Here, we reported our recent results about the epitaxial growth BLSO film on flexible mica substrates, including detailed fabrication conditions, optical transmittance spectra of unbending and bending conditions, as well as electronic transport properties. The obtained results indicate that BLSO films have excellent optical transmittance as high as more than 85% in the visible region regardless of under bending or unbending state. Different from the conductivity properties of BLSO films grown on $SrTiO_3$ substrate, an anomalous electronic transport showing as the enhancement of resistivity with the decrease of temperature occurred in all of present films. The experiments confirmed that this behavior was unrelated to the inserted buffer layer but depended on misfit strain due to lattice mismatch. Although BLSO films grown on the flexible mica substrate show a larger resistivity than that grown on rigid $SrTiO_3$(001) substrate, the value of 7–10 mΩ cm is also satisfied with actual application in optoelectronic devices at room temperature. Our work will pave a way for the future development of flexible TCO film.

2. Experiment

A series of BLSO films with various thicknesses were fabricated on mica substrates using pulsed laser deposition (PLD) technique. Dense ceramics targets of $Ba_{0.96}La_{0.04}$ SnO_3 were prepared by standard solid state reactions. A 248 nm KrF excimer laser with the repetition rate of 4 Hz and laser energy density irradiated on the rotating targets of 1.6 J/cm^2 were used for the film fabrication. During deposition, the temperature of substrate was set in the range of 720–780 °C to change the quality of epitaxial films. Then, the films were in situ annealed before being cooled down in the same oxygen ambient. The crystalline structure and the epitaxial characteristics of the BLSO films were examined by X-ray diffraction (XRD, PANalytical) using Cu K_α radiation at room temperature. The surface morphology of the films was studied by atomic force microscopy (AFM) in the tapping mode. The optical transmittance were measured on a spectrophotometer UV3600 at the room temperature. Temperature-dependent resistivity was investigated by the standard four-terminal method.

3. Results and discussion

Up to present, BLSO films were mostly deposited on the rigid wafers $SrTiO_3$ (001) which is one of the most widely substrate for depositing perovskite oxides films [14,15]. Some reported results have confirmed that it is easy to realize epitaxial growth of BLSO films on $SrTiO_3$ (001) substrate with a superior crystalline quality due to both of all perovskite structures and an ignorable lattice mismatch. Here, we choose mica as the substrate mainly based on three reasons [30,31]: (i)Mica is a flexible material and has been extensively utilized to fabricate flexible devices; (ii) Mica is a transparent material which is beneficial for high light transmission; (iii) Mica can bear high temperature. During the deposition of BLSO films, the substrate was heated to high temperature more than 700 °C. The good chemical stability of mica under high temperature was very important for BLSO growth. However, mica wafers are non-perovskite substrate. The perovskite substrates are good in promoting the growth of perovskite type film. On the contrary, non-perovskite substrates difficultly achieve an ideal epitaxial growth of it. Therefore, BLSO can't be directly deposited on mica substrate (In fact, we have tried doing it but only polycrystalline film is obtained.). Thus, we need to first deposit one kind of perovskite materials as buffer layer and then deposit BLSO. In this paper, perovskite oxides $BaTiO_3$(BTO) was chosen to deposit on mica substrate as buffer layer through comparing different materials. We found BTO was easy to realize epitaxial growth on mica substrate along the direction of (111). In the following work for all BLSO films, before depositing BLSO, BTO buffer layer with the thickness near 30 nm was first deposited on mica substrate. In order to guarantee the epitaxial growth of BLSO films, some basic film properties of BTO buffer layer, such as its appropriate orientation, crystallinity, and smooth surface have been also checked beforehand. The super-smooth surface and high crystallinity of BTO buffer layer can be prepared by using the optimal growth condition.

As we know, many deposition conditions determine the growth quality of epitaxial films, including laser energy density, repetition rate (number of laser pulses per second), ambient gas and its pressure, target-substrate distance, substrate temperature, and annealing time. In this work, we found that the last two factors were more prominently related with the growth quality than others. Fig. 1(a) shows the XRD patterns of BLSO films deposited on mica (00*l*) substrate with the inserted buffer layer BTO as the substrate temperature is set in the range of 720–780 °C. We find that the BTO film exactly grows along the direction (111) on mica substrate and BLSO film epitaxially grows on top of BTO film. Both (111) and (222) peaks of BLSO film were clearly shown in Fig. 1(a). Two obvious characteristics can be also observed with the increase of substrate temperatures. (i) At T = 720 °C, except for the normal diffraction peaks of mica, BTO, and BLSO, its XRD pattern also exhibits many impurity peaks. As the substrate temperatures was increased to 780 °C, the impurity peaks significantly decrease and almost disappear. (ii) With the enhancement of substrate temperatures, the peak intensity of BLSO film (222) becomes stronger, indicating a better crystallization of BLSO film at 780 °C than 720 °C. The rise of substrate temperatures improves the mobility and diffusion of the adatoms, which is propitious for BLSO atoms to arrange themselves in highly ordered manner. Fig. 1(b) shows the magnified Bragg peaks of BLSO film (222) around $2\theta \sim 81^\circ$. Besides the rise of peak intensity, the full width at half-maximum of BLSO peak (222) also becomes smaller

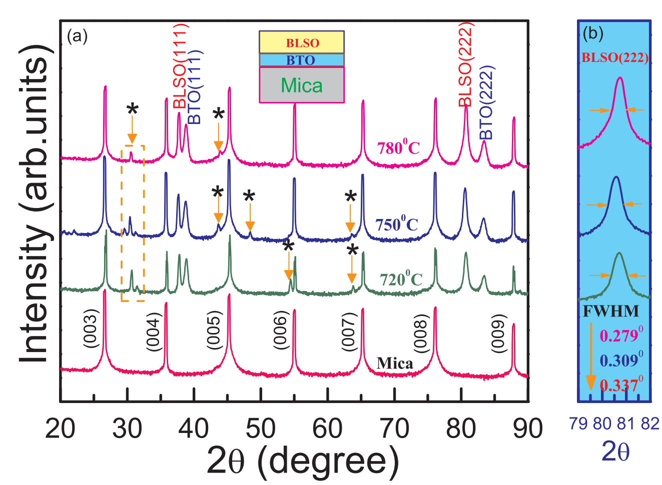

Fig. 1. (a) The X-ray θ-2θ profile of the grown BLSO/BTO/mica films at different substrate temperatures and the bottom XRD pattern is for empty mica (The symbol * indicates the diffraction peaks of impurity phase.). (b) The varied FWHM of (222) Bragg peaks at three various substrate temperatures.