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Microstructure, colossal magnetoresistance effect and thermal infrared property of annealed $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ thin films on Si(100)

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ABSTRACT

The $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ thin films were deposited on Si(100) by DC magnetron sputtering followed by annealing at 973 K for 0.5~2 h in air/oxygen. The microstructure, room temperature reflectance and magnetoresistance (MR) of the annealed films were investigated using Glancing angle X-ray diffraction (GXRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) analyses and resistivity measurement. The results indicate that the films are single perovskite phase with distorted cubic structure. All the films show (100) preferred orientation and the degree of (100) preferred orientation depends on the annealing time and ambience. The films with highly (100) preferred orientation have a shorter Mn–O bond length. With the increase of temperature, the MR% of the films first decreases slowly in a wide temperature range, then increases and, finally, decreases rapidly. The maximum MR% of the films at 10 K and room temperature is about 73% and 7.9%, respectively. Lengthening annealing time in air cannot ensure the increase of metal-insulator transition temperature (T_{MI}) of the films. Suitable lengthening of annealing time is propitious to the improvement of temperature stability of magnetoresistance for the films annealed in air. The higher the value T_{MI}, the lower the room temperature emittance of the films evaluated based on reflectance.

1. Introduction

Doped perovskite manganites $RE_{1-x}A_xMnO_3$, where RE is a trivalent rare earth element and A is a divalent alkali earth element, have attracted tremendous attention in recent decades due to their colossal magnetoresistance (CMR) effect [1–3], variable emittance property [4,5] and other extraordinary magnetic and electric properties [6–8]. The CMR effect makes these materials very interesting due to their potential applications such as infrared detectors, magnetic field sensors and high-density memory cells [9]. Meanwhile, they are also regarded as a promising candidate for smart thermochromic variable emittance thermal control materials, which can be used to adjust the temperature of the elements of spacecraft systems automatically [10]. Up to now, however, the electrical transport behavior and mechanisms of variable emittance of these materials have not been understood very well. Their CMR effect and variable emittance property have the characteristics of a particular temperature dependence. It is also not clear if there is a certain relationship between CMR and variable emittance property. Therefore, more work should be done to understand CMR effects and mechanisms of this variable emittance and to effectively adjust the properties by changing the preparation process, all of which is beneficial to widening the application of these materials.

With the miniaturization and micro-scaling of electron devices for most technological applications, it is desirable to grow thin films of these materials and integrate them into Si-based microelectronic devices. However, the physical properties of $RE_{1-x}A_xMnO_3$ films are very sensitive to their structure [11,12]. Different deposition methods and growth conditions such as substrate temperature, working pressure, annealing temperature and annealing time, can result in different structures, which further affect the properties of $RE_{1-x}A_xMnO_3$ films. Therefore, a stable and controllable preparation process is a prerequisite for the further research of $RE_{1-x}A_xMnO_3$ film materials and their applications. At present, perovskite manganite films are prepared mainly by physical methods (such as pulsed laser deposition, molecular beam epitaxy, magnetron sputtering) and chemical methods (including sol–gel,

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metal organic compound decomposition methods) [13–16]. The films deposited by physical methods usually have higher density and better bonds between the film and substrate than the films deposited by chemical methods. Compared with the pulsed laser deposition method and molecular beam epitaxy method, magnetron sputtering method can be used to prepare large area film materials with high quality at low cost and is easy to be used in commercial scale production. So, it is important to study the magnetron sputtering preparation process of $RE_{1-x}A_xMnO_3$ films and their structure and properties for promoting the application of these materials. Due to low oxygen pressure during the magnetron sputtering process, the $RE_{1-x}A_xMnO_3$ films have a certain degree of oxygen vacancies. In order to improve this situation, an annealing treatment usually is needed.

In this work, the $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ thin films were deposited on Si(100) by DC magnetron sputtering followed by annealing at 973 K for 0.5~2 h in air/oxygen ambient. The microstructure, magnetoresistance and room temperature thermal infrared property of the annealed films have been investigated.

2. Experimental

The $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ thin films were grown on Si(100) by DC magnetron sputtering. The target, with nominal composition $La_{0.7}Sr_{0.3}MnO_3$, was prepared using a solid state reaction method [17]. The Si(100) substrate was cleaned with acetone in an ultrasonic cleaner for 15min and then was etched by Ar ions in chamber for 20min before deposition. The deposition was carried out in Ar(75vol.%)+O_2(25vol.%) at a total pressure of 0.1Pa. The Si(100) substrate temperature was kept at 853 K during the deposition. The deposition power was about 30 W. The deposition rate was about 4.4 nm/min and the thickness of the films was about 795 nm. After deposition, the films were annealed at 973 K, followed by furnace cooling in atmosphere. According to the annealing time and ambience, the annealed films were identified by f1 (annealing at 973 K/0.5 h in air), f2 (annealing at 973 K/1 h in air), f3 (annealing at 973 K/2 h in air) and f4 (annealing at 973 K/1 h in 110Pa O_2), respectively.

Glancing angle X-ray diffraction (GXRD) was used to confirm the phase structure of the films, using Cu Kα radiation and 5° angle. The surface morphologies of the films were observed using a scanning electron microscope (SEM). The bond structure and IR reflectance spectra at room temperature of the films were examined using Fourier transform infrared spectroscopy (FTIR). The resistivity was measured as a function of the temperature using the standard four-probe method between 10 K and 325 K in zero field and at 3 T.

3. Results and discussion

3.1. Surface morphology of the films

Fig. 1 shows the surface morphologies of the as-grown and annealed $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ films. Clearly, the films regrow during the annealing process and become rougher after annealing. There are plenty of particles formed by regrowth in the films f2 and f4 annealed at 973 K for 1 h in air and O_2 respectively. In contrast, the latter has smaller regrown particles but a few similar particles can be observed on the surface of the films annealed at 973 K for 0.5 h and 2 h in air. It indicates that the changes of annealing time and ambience can result in obvious changes of the surface roughness, the particle size and particle morphology of the films. This is mainly because the oxygen content, regrowth mode and preferred orientation of grains change with the annealing time and ambient conditions.

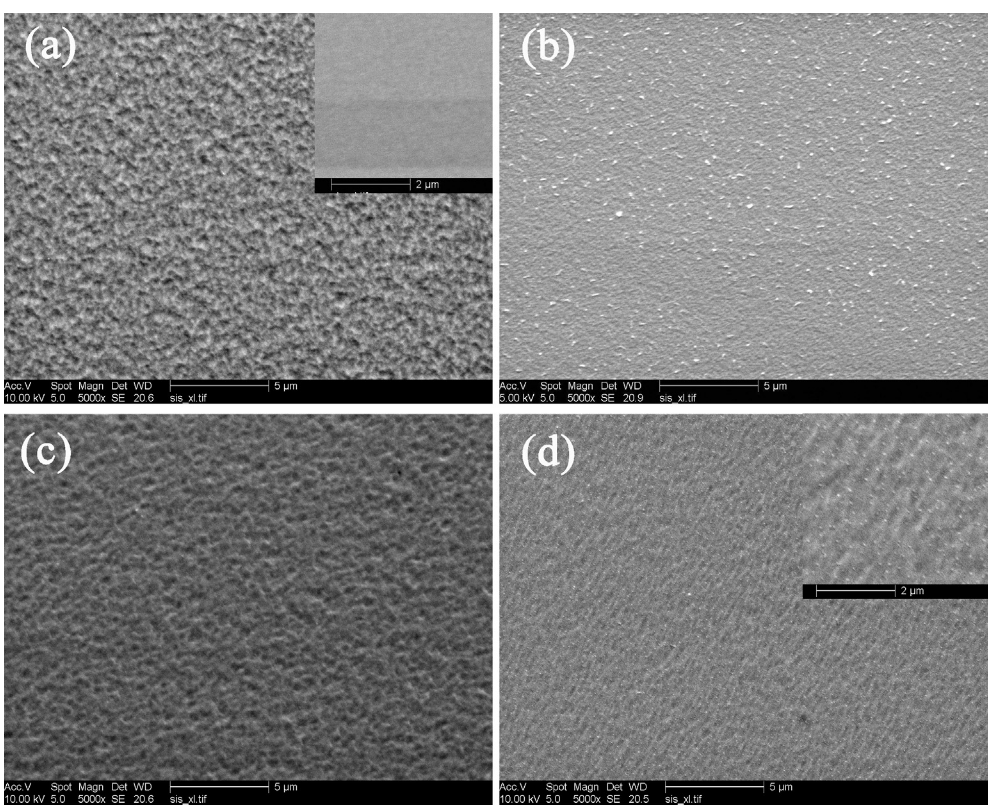

Fig. 1. Surface morphologies of (a) thin film f1 (annealing at 973 K/0.5 h in air), inset is the as-grown film; (b) thin film f2 (annealing at 973 K/1 h in air); (c) thin film f3 (annealing at 973 K/2 h in air) and (d) thin film f4 (annealing at 973 K/1 h in 110Pa O_2), inset is magnification of the part of the film f4.