Thin Solid Films 600 (2016) 1–5

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

The effect of La doping concentration on optical and electrical properties of $La_xSr_{1-x}TiO_3$ thin film fabricated by sol–gel process

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ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form 29 December 2015
Accepted 5 January 2016
Available online 7 January 2016

Keywords:
$La_xSr_{1-x}TiO_3$thin films
Sol–gel method
Optical and electrical properties

ABSTRACT

Strontium titanate ($SrTiO_3$), a typical wide-band-gap perovskite oxide, is a promising candidate for the application of thin film transistor (TFT). In this paper, the $La_xSr_{1-x}TiO_3$ thin films with different doping concentration are fabricated by sol–gel method. X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscope (AFM), UV–Vis-NIR transmission spectroscopy and four point probe instrument are employed to characterize the crystal structure, surface profile, transmittance and resistivity of $La_xSr_{1-x}TiO_3$ thin films. The results show that $La_xSr_{1-x}TiO_3$ (x = 0.5 at.%, 1 at.%, 1.5 at.%, 2 at.%, 4 at.%, 6 at.%, 8 at.%, 10 at.%) thin films are single $SrTiO_3$ cubic phase after La doping. Additionally, the SEM and AFM observation reveal dense grains and smooth surface. $La_xSr_{1-x}TiO_3$ film possesses high transmittance in visible region. The conductivity of $La_xSr_{1-x}TiO_3$ thin films is improved tremendously after La doping. The resistivity of $La_{0.04}Sr_{0.96}TiO_3$ is 11.7×10^{-3} Ω·cm and its transmittance is 88.66%.

1. Introduction

Panel display (PD) has replaced the role of traditional cathode-ray tube (CRT) attributed to its attractive advantages, such as high-resolution, ultra-thins, fast-response time, low-power costing and perfect viewing angle experience. Thin-Film Transistor (TFT) is the core component of PD, whose quality greatly affects the display performance. Traditional materials for TFT are amorphous silicon (α-Si) and polycrystalline silicon (p-Si). However, α-Si-TFT suffers from low-mobility, strong-photosensitiveness and poor-stability. The p-Si-TFT bears the drawbacks of poor-uniformity, high-cost, and complex production process. Therefore, a new kind of material is demanded for this field.

It has been demonstrated that strontium titanate ($SrTiO_3$) [1–4], a typical wide-gap perovskite oxide, is a promising candidate for the application of TFT. It is transparent in the visible region [5,6]. Properly doping with impurity, $SrTiO_3$ turns to a good semiconductor or conductor. These characteristics have great advantages when $SrTiO_3$ is used in the field of thin film transistor (TFT) [7]. In particular, the electronic performance of the all-$SrTiO_3$ structure thin film transistor (TFT), in which La-doped $SrTiO_3$ has been used as the semiconducting channel while intrinsic polycrystalline $SrTiO_3$ is used as a gate insulator, is superior to that of the conventional α-Si-TFT and p-Si-TFT [8]. Thus, $La_xSr_{1-x}TiO_3$ thin film is a promising candidate for the application of TFT.

There are many methods to prepare $La_xSr_{1-x}TiO_3$ thin film such as vertical pulsed laser deposition (VPLD) [11], laser molecular beam epitaxy (LMBE) [12], chemical vapor deposition (CVD) [13] and sol–gel [9,10]. VPLD, LMBE and CVD suffer from complex process and high cost. However, sol–gel method has a lot of advantages, such as simple technology, low cost, low firing temperature, easy to achieve quantitative doping, easy to prepare uniform multicomponent films, effectively control films' elements and large area deposition. Therefore, we prepare $La_xSr_{1-x}TiO_3$ thin films by sol–gel method and we further study the effect of the La doping concentration on the optical and electrical properties of $La_xSr_{1-x}TiO_3$ thin films in this paper.

2. Experiment details

In this work, the raw materials for the solution synthesis were strontium nitrate [$Sr(NO_3)_2$], tetrabutyl titanate [$Ti(OC_4H_9)_4$] and lanthanum nitrate hexahydrate [$La(NO_3)_3 \cdot 6H_2O$]. In detail, $Sr(NO_3)_2$ and $Ti(OC_4H_9)_4$ were used as the Sr and Ti precursor, respectively. The molar ratio of $Ti(OC_4H_9)_4$ and $Sr(NO_3)_2$ was 1:1. $La(NO_3)_3 \cdot 6H_2O$ was the dopant. Methoxyethanol ($C_3H_8O_2$) was the main solvent. Glacial acetic acid (CH_3COOH) was used as the accessories solvent and the catalyst. Acetylacetone ($C_5H_8O_2$) and polyvinyl pyrrolidone [PVP, $(C_6H_9NO)_n$] were used as the chelating agent and surfactant, respectively. n(PVP): n(Ti) = 3:400.The molar ratio of CH_3COOH and $Sr(NO_3)$ was 30:1. The molar ratio of $Ti(OC_4H_9)_4$ and $C_5H_8O_2$ was 1:1. The volume ratio of CH_3COOH and $C_3H_8O_2$ was 2:3.

First, strontium nitrate, lanthanum nitrate hexahydrate and polyvinyl pyrrolidone were dissolved into glacial acetic acid. Methoxyethanol was mixed into glacial acetic acid. The solutions were then mixed and stirred in 80 °C water bath to form Sr precursor solution A. Tetrabutyl titanate, acetylacetone and methoxyethanol were mixed, heated and stirred to form Ti precursor solution B. Then, solution A was added into solution B and the mixture was heated and stirred for 60 min.

http://dx.doi.org/10.1016/j.tsf.2016.01.008
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The clear yellowish solution was prepared. After that, the solution was put in an ambient atmosphere at 30 °C for 72 h, then the clear yellowish stable sol was finally prepared.

Spin-coating was employed to deposit the sol at 2100 rpm onto the quartz substrates. The wet films were pyrolyzed at 180 °C for 10 min after deposition and then annealed at 950 °C. The $La_xSr_{1\text{-}x}TiO_3$ films were obtained by multiple repetitions of the deposition.

The crystal structure of the film was analyzed by Japan Shimadzu XRD-7000 XRD diffractometer. The microstructure of the $La_xSr_{1\text{-}x}TiO_3$ film was investigated using a JSM-6390 A scanning electron microscope (SEM) and Japan Shimadzu SPM-9500 J3 atomic force microscope (AFM). Optical properties including transmittance and reflectance were measured with an Aquila nkd-8000 spectrophotometer [14–16] in the spectral range from 350 to1000 nm. It is noteworthy to mention that the optical transmittance is given for the thin film alone by normalization to a bare substrate. On the basis of transmittance and reflectance spectra, refractive index (n), extinction coefficient (k) and physical thickness (d) of the films were estimated based on reverse engineering method using FTG FilmStar software. Fitting of experimental results was made using Drude-Lorentz dispersion model with 5 oscillators and Powell's analysis method. As well as, the electrical property was determined with a Four-Point Probes.

3. Results and discussion

3.1. Structural characterization

The XRD patterns of $La_xSr_{1\text{-}x}TiO_3$ thin film with different doping concentration are presented in Fig. 1. It is observed that all of the diffraction peaks can be well indexed to a cubic structure of $SrTiO_3$ (JCPDSeardNo.79–0176). In addition, what we find from the XRD patterns is that there do not appear any impure peaks when the doping concentration is less than 8 at.%. However, with the further increasing of doping concentration, that is, when the doping concentration is 10 at.%, the diffraction peaks begin moving to small angle direction and some TiO_2 impurity phase peak appears. It is well known that $SrTiO_3$ and $LaTiO_3$ make a complete solid solution [17]. The probable explanation for the appearance of TiO_2 phase when the doping concentration exceeds 10 at.% can be as follows. In general, depending on the growth conditions, different defects can exit in $SrTiO_3$ materials, and they often affect the doping, conductivity, compensation, minority carrier lifetime, and so on. For example, Sculling et al. [18] reported that the La-doped $SrTiO_3$ thin film grown at low growth pressure has lower resistivity than that grown at higher growth pressure. In the sol–gel process, two major reactions occur in the high temperature annealing:

$$SrCO_3 \rightarrow SrO + CO_2 \tag{1}$$

$$SrO + TiO_2 \rightarrow SrTiO_3 \tag{2}$$

Although the extent of substitution of La^{3+} to Sr^{2+} could be very high, higher La doping will lead to the formation of strontium vacancies defects which will reduce the Sr/Ti mol ratio [19]. Therefore the surplus of TiO_2 will be precipitated. Furthermore, as can be seen in Fig. 1, the Full width at half maximum (FWHM) of all samples is large, and it accounts for that LaxSr1-xTiO3 thin films are polycrystalline. When the doping concentration is 4 at.%, not only the intensity of (110) diffraction peak of La0.04Sr0.96TiO3 thin film is relatively high, but also other diffraction peaks of La0.04Sr0.96TiO3 are sharper than others. Hence, the crystal quality of La0.04Sr0.96TiO3 thin film is the best.

The full width at half maximum (FWHM) of the $SrTiO_3$ (1 1 0) peaks with different La doping concentration is depicted in Fig. 2. It is observed that crystallinity of the $La_xSr_{1\text{-}x}TiO_3$ thin film is improved with the La doping concentration until 4 at.%. Nevertheless, as the La concentration further increase, the FWHM increases. This indicates that the crystallinity is deteriorated. The probable explanation for the above changes of crystallinity can be as follows. In the sol–gel process, there are lots of strontium vacancies in the as-prepared undoped $SrTiO_3$ thin films [20,21]. Due to the fact that the radius of La^{3+} (0.115 nm) is similar to that of Sr^{2+} (0.113 nm), with moderate quantity of La doping, the doped La atom can occupy the position of strontium vacancies and hence improve the crystallinity. However, with the further increasing of La doping concentration, local lattice deformation is formed and hence the crystallinity gets worse. The same trend was also observed in Cu and Ag-doped ZnO films [22,23]. Moreover, the good uniformity of $La_xSr_{1\text{-}x}TiO_3$ film doped with 4 at.% La atoms have also been observed by the SEM image shown in Fig. 3. It is evident that the $La_{0.04}Sr_{0.96}TiO_3$ film exhibits dense grains and smooth surface.

Fig. 3 displays the scanning electron micrographs of 0.5 at.%, 4 at.%, 10 at.% $La_xSr_{1\text{-}x}TiO_3$ and intrinsic $SrTiO_3$. The surface characterization of $La_xSr_{1\text{-}x}TiO_3$ films (x = 0.5 at.%, 4 at.%) shows dense grains and smooth surfaces. However, an uneven and coarse surface is distinctly shown in $La_{0.1}Sr_{0.9}TiO_3$.

The AFM micrographs are shown in Fig. 4. The surface roughness Ra of 0.5 at.%, 4 at.%, 10 at.% $La_xSr_{1\text{-}x}TiO_3$ thin films is 3.052, 3.452 and 6.618 nm, respectively. There is little difference of surface roughness for the $La_{0.005}Sr_{0.995}TiO_3$ and $La_{0.04}Sr_{0.96}TiO_3$ thin films. However, there appear cracks on surface of 10 at.% $La_xSr_{1\text{-}x}TiO_3$. The surface roughness

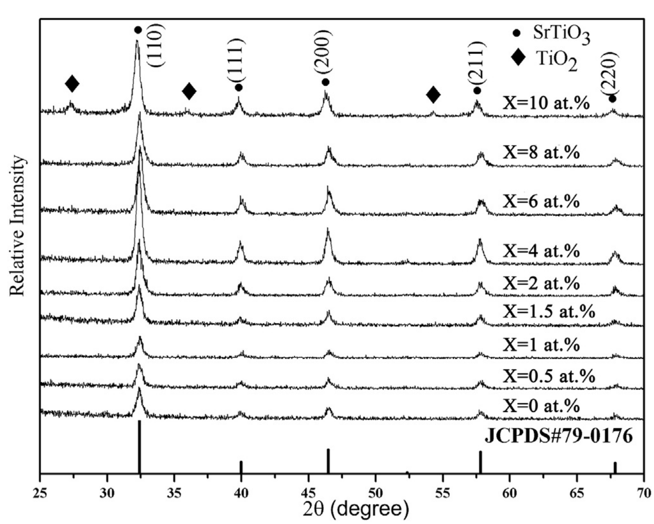

Fig. 1. XRD patterns of LaxSr1-xTiO3 thin films.

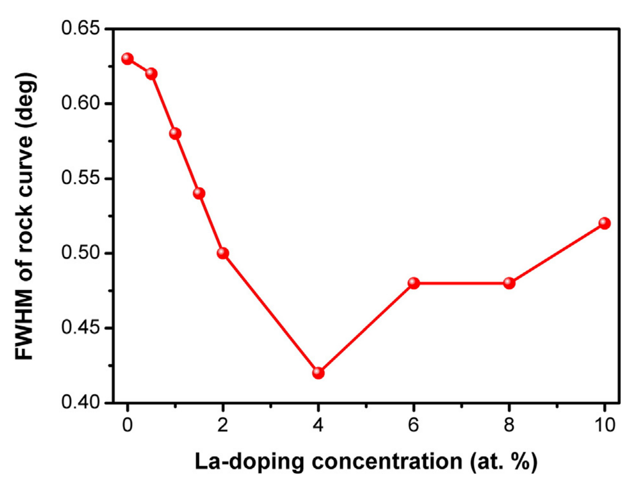

Fig. 2. FWHM of the $La_xSr_{1\text{-}x}TiO_3$ (1 1 0) peaks with different La doping concentration.