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Preliminary study on pyroelectric lithium tantalite by a novel electrostatic spray pyrolysis technique

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Abstract

In this paper, we report the first results obtained for pyroelectric $LiTaO_3$ thin films prepared on silicon substrates by electrostatic spray pyrolysis (ESP), a simple, low cost and efficient technique not widely used for $LiTaO_3$ deposition, using lithium acetylacetonate and tantalum ethoxide in a mixture of methanol. The effect of the growth and annealing temperature on the structural and optical properties has been investigated. X-ray diffraction measurements have shown that $LiTaO_3$ thin films became preferentially oriented in the (0,1,2) plane after annealing treatment in an oxygen environment using the rapid thermal processing. On the other hand, a thermal stress's modeling is performed to observe the effect of growth temperature on the as-deposited films and the substrates. The SEM images have shown that the film heat-treated at 600 °C became more homogeneous and smoother than that before annealing. The optical phonon modes of the $LiTaO_3$ thin films have been also investigated using infrared reflectivity (FTIR) and Raman spectroscopy.

Keywords: $LiTaO_3$; Pyrolysis; X-ray diffraction; Stresses; Characterization

1. Introduction

Lithium tantalite ($LiTaO_3$) is a well-known ferroelectric material that exhibits unique electro-optical, acoustic, piezoelectric, pyroelectric, and non-linear optical properties combined with good mechanical and chemical stability and wide transparency range making it a suitable material for applications in electro-optic, surface acoustic wave devices, and pyroelectric detectors [1–3].

However, in bulk form it has limited applicability for high performance system. Therefore, the thin film forms of the material with high quality increase its potential and availability for pyroelectric applications [4].

The $LiTaO_3$ thin films have been prepared by several growth techniques on various substrates, such as RF-magnetron sputtering [5–7], thermal evaporation [8], laser ablation [9], sol gel process, and metal-organic chemical vapor deposition (MOCVD) [10–13]. A simple, cheap, and efficient technique called ESP was used to deposit $LiTaO_3$ thin films. In this paper, we report the first results on $LiTaO_3$ films prepared by ESP using lithium acetylacetonate and tantalum ethoxide as sources compounds. In this technique, the growth of the films is controlled by reaction kinetics. The most important parameter for reaction kinetics is the temperature. In the spray pyrolysis process, ideal conditions of deposition are obtained when the droplet approaches the substrate just as the solvent is completely vaporized. When a non-uniform droplet size is generated, the consequence is a change in the thermal behavior depending on the mass of droplets. The deposition process is then affected by the differences in the size of droplets (the decomposition temperature depends

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on the droplets size). This thermal behavior of the droplets size has been discussed by several authors [14,15]. The as-deposited films were heated using the rapid thermal annealing (RTA) technology to avoid strains or reactions at the film-substrate interface.

The structural and optical properties of $LiTaO_3$ thin films are investigated through the X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared reflectivity (FTIR) and Raman spectroscopy.

2. Experimental procedure

The setup used for ESP is presented elsewhere [16]. The substrate temperature (T_s) was controlled using a chromel–alumel thermocouple (placed above the substrate) to an accuracy of 2 °C. $LiTaO_3$ thin films were deposited on heated corning silicon (1 cm × 1 cm) substrates by electro spraying aqueous solutions containing 10^{-2} mol/l lithium acetylacetonate ($Li[CH_3COCHCOCH_3]$) and tantalum ethoxide ($Ta[OC_2H_5]_5$), respectively, in a mixture of methanol. The deposition time was fixed at 180 min for all the films. As the substrate front side on which lithium tantalite is deposited was faced to a droplets flux and since the thickness of corning silicon substrate was 1.2 mm, the actual estimated temperature at which the film was formed might be 100 °C lower than the temperature of the back side where the thermocouple was placed. The nozzle diameter was 1 mm and the high voltage was kept constant at 12 kV for a substrate–nozzle distance of 3, 4.5, and 6 cm. The liquid flow through the nozzle was controlled by a low-flow peristaltic pump, and it is maintained at 220 μl min^{-1}. Study of structural properties of the films was carried out using an XRD type gonio with monochromatic CuKα radiation. The surface morphology of the films was observed by SEM.

The Fourier transform infrared (FTIR) measurements were performed at room temperature in vacuum to minimize the effect of atmospheric water-vapour absorption. The FTIR measurements were performed in the 80–550 cm^{-1} frequency range, using an IFS 66 V/s spectrometer equipped with a globar source, a Tylar 6μ separatist and a GAT SN detector.

The Raman measurements in the backscattering geometry were performed at room temperature using the 514.5 nm light from a mixed Ar/Kr ion laser of ~100 mW. A double monochromator was used to analyze the scattered radiation with a resolution of less than 1 cm^{-1}. The spot size on the samples was ~2 μm.

3. Experimental results and discussion

3.1. Structural analysis of the $LiTaO_3$ thin films

The crystalline quality and orientation of the $LiTaO_3$ thin films deposited on Si (1 0 0) substrates have been investigated, before and after annealing under oxygen atmosphere at 600 °C, by XRD. Fig. 1a shows the XRD pattern of the as-deposited lithium tantalite films for a growth temperature of 350 °C. It is observed that before annealing treatment, the thin films are not of good crystalline quality. The peaks at about 48.6°, 53.5°, and 56.3° correspond, respectively, to the orientation in the (0,2,4), (1,1,6), and (1,2,2) planes. The peaks at about 33° and 69.12° correspond to the diffraction from the silicon substrate.

After annealing treatment at 600 °C in a flowing oxygen atmosphere, additional $LiTaO_3$ peaks at about 23.7°, 34.8°, and 42.6° appear (see Fig. 1b). These peaks are, respectively, attributed to the $LiTaO_3$ (0,1,2), (1,1,0), and (2,0,2) orientation. One can observe clearly (Fig. 1b) that the intensity of the peaks corresponding to the lithium tantalite orientation increases after annealing and the diffraction orientations are sharpened by the thermal treatment, which is due to an improvement of the crystal quality of the films. The clear appearance after annealing of the peak of highest intensity at about 23.7° indicates that the annealed films became preferentially oriented in the (0,1,2) plane. During annealing treatment in an oxygen environment, $LiTaO_3$ thin films have been oxidized, the tantalum–oxygen ratio, and the lithium–oxygen ratio have decreased, the impurity

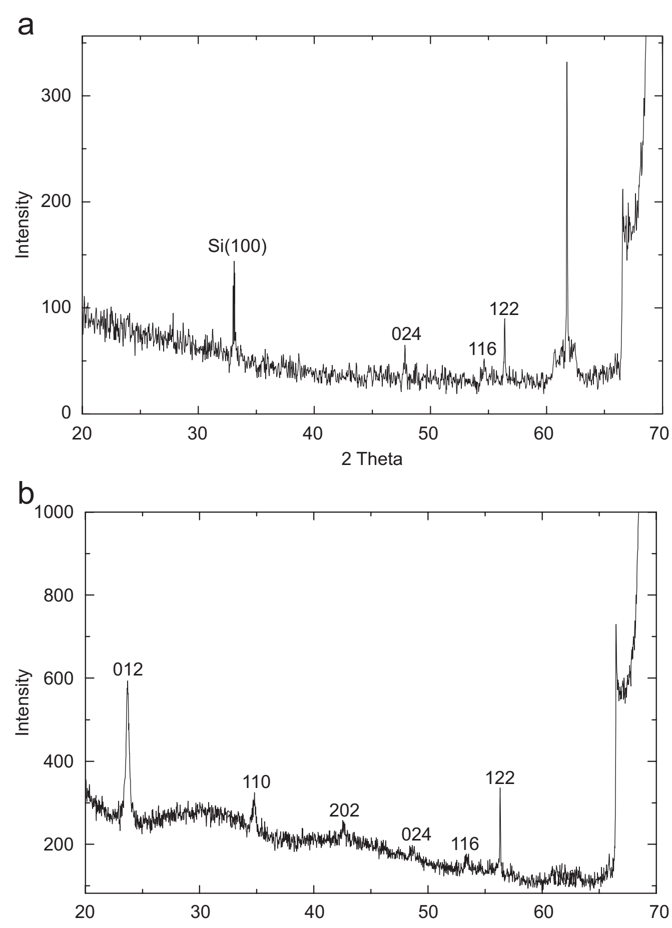

Fig. 1. XRD spectra of $LiTaO_3$ thin films (a) as grown at 350 °C and (b) after annealing treatment at 600 °C in an oxygen environment.