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Preparation and Characterization of Lithium Tantalate Thin Films using a High-concentration Precursor Solution

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An improved method of preparing lithium tantalate ($LiTaO_3$) precursor solution has been developed using 1,2-Propylene glycol solution instead of 2-methoxy ethanol. The $LiTaO_3$ film thickness produced by each coating process was about 110nm after annealing at 700°C, which is much thicker than that produced by the normal method (25nm). Using the improved method, the preferred orientation of the film was (012) and the size of a typical crystallite was about 15nm. Studies of the surface morphologies of the fabricated $LiTaO_3$ film showed little surface roughness and high uniformity. The dielectric constant and dielectric loss factor of the annealed film were 45 and 0.006 at high frequency, respectively.

Key words: Lithium tantalate thin film, Sol-gel method,
high-concentration precursor solution, detectors, Dielectric constant.

Lithium tantalate ($LiTaO_3$) is an excellent ferroelectric material, due to its pyroelectric, electro-optical, nonlinear optical, and photorefractive properties[1,2]. These properties make it useful in terahertz wave detectors, infrared detectors, optical waveguides, surface acoustic wave guides, holographic memory, and so on[3-5]. When used as a detector, a few absorption layers are coated on to the $LiTaO_3$ layer in order to absorb the incident radiation and allow heat to diffuse into the pyroelectric material. The resulting temperature change in the $LiTaO_3$ can cause changes in crystal lattice spacing, consequently changing the magnitude of the spontaneous polarization. This produces an accumulated transient excess of free surface charges on the surface and bottom electrodes, which can be sensed as an output current, which flows into an external preamplifier circuit, generating an output voltage signal[6]. The key parameter for the $LiTaO_3$ detector is therefore voltage responsivity, defined as the ratio of output voltage signal to the modulated incident radiation power; this is very sensitive to the thickness of the $LiTaO_3$ [7]. The smaller the thickness of the detector, the larger is the voltage responsivity. $LiTaO_3$ in bulk form has limited applications in high-performance systems because the voltage responsivity of detectors prepared with bulk material is limited by geometrical thickness[8]. In addition, it is difficult to integrate the $LiTaO_3$ bulk to a read-out integrated circuit. This is the reason why the thin film form of the $LiTaO_3$ device has many advantages over the bulk device.

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Considerable effort has been spent trying to improve the properties of the $LiTaO_3$ thin film device by using different thin film preparation processes, such as RF sputtering[9], pulsed laser deposition[10], metal organic chemical vapor deposition[11], molecular beam epitaxy[12], and the sol-gel process[13-15]. Compared to the other dry deposition methods, the sol-gel process presents some advantages with regard to processing costs, ease of doping, low processing temperature, ease of fabricating large areas and stoichiometric composition control. For example, $LiTaO_3$ thin films have been derived from a double alkoxide prepared by the hydrolysis of lithium acetate (CH_3COOLi) and tantalum ethoxide ($Ta(OC_2H_5)_5$) in 2-methoxy ethanol ($CH_3OCH_2CH_2OH$) [16]. The use of Lithium 2,4-pentanedionate ($LiC_5H_7O_2$) and tantalum isopropoxide ($Ta[OCH(CH_3)_2)]_5$) in 1,3-propanediol ($HO(CH_3)_2OH$) has also been investigated[8]. However, the processes have to be precisely controlled because metal alkoxides are very vulnerable to hydrolysis. In addition, the film coating procedure needs to be repeated several times in order to obtain a device film of suitable thickness, because each single coating produces a very thin layer of $LiTaO_3$.

This paper describes an improved sol-gel process produced by mixing lithium acetate and tantalum ethoxide in 1,2-Propylene glycol ($CH_2OHCHOHCH_3$) solution. This gives a high-concentration $LiTaO_3$ precursor solution that can, using a simple experimental procedure, produce thicker films. $LiTaO_3$ thin films were prepared using both the improved sol-gel process and the previously reported method, with 2-methoxy ethanol as solvent. Some characteristics of the obtained $LiTaO_3$ thin films were examined including morphology, crystallinity and hysteresis loops. The results indicate that the improved sol-gel method is suitable for detector fabrication.

MATERIALS AND METHODS

Two methods of preparing $LiTaO_3$ film precursor solutions are shown in Figure 1. In both methods, lithium acetate (LiAc) and tantalum ethoxide were used as the source materials. 2-methoxy ethanol was used as the solvent in method 1, as shown in Figure 1(a). LiAc was added to 2-methoxy ethanol in a mole ratio of 1:20. The solution was magnetic stirred at 120 °C until the LiAc had completely dissolved and was then cooled to 60 °C. Acetic acid was added to adjust the pH of the solution to 5-6. Tantalum ethoxide was then added to give a 1:1 molar ratio of Li to Ta. The solutions were refluxed at 130 °C for 4h and 110 °C for 12h. The process was carried out in a N_2 environment. Figure 1(b) shows the improved method (method 2) for preparing the $LiTaO_3$ precursor solution. In this method, 1,2-Propylene glycol was used as solvent. The mole ratio of LiAc to solvent was reduced to 1:5. After the LiAc had completely dissolved, tantalum ethoxide was added to give a precise molar ratio of 1:1 and the solution was refluxed by the same method. The process was carried out in air and no acid was added. After hydrolysis and polycondensation, brownish $LiTaO_3$ precursor solutions were obtained with a concentration of 0.2mol/L and 1mol/L for methods 1 and 2, respectively.

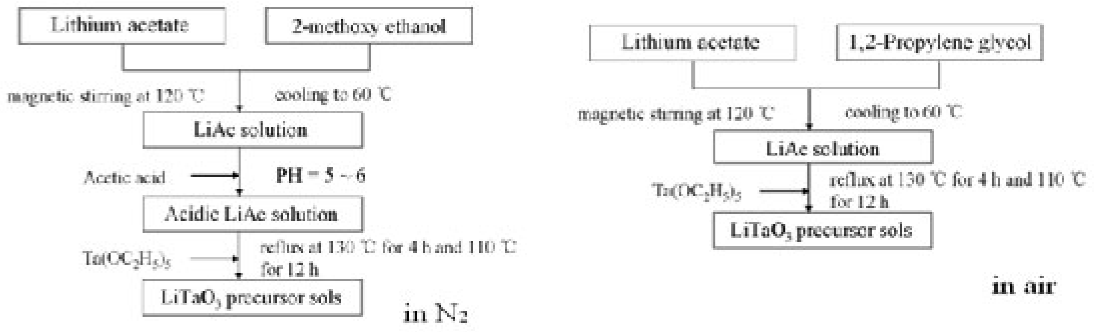
P-type (111) silicon substrate was used to coat the $LiTaO_3$ precursor solutions, to form $LiTaO_3$ films. The two precursor solutions were spun coated on the silicon substrate at a speed of 3000rpm for 45s. The films were then heat treated in air in three steps, with different temperatures and durations: the films were first dried at 180 °C - 200 °C for 5min to remove water and organic solvents, then pyrolyzed at 400-450 °C for 30min. A final annealing step was carried out to densify and crystallize the films at 650-750 °C for 5min, followed by cooling of the furnace to room temperature. Spin-coating/heat treatment operations were repeated several times to obtain $LiTaO_3$ films of the desired thickness.

RESULTS AND DISCUSSIONS

The film cross-sections were measured using a scanning electron microscope (SEM). Results showed that the average film thickness produced from a single coating using methods 1 and 2 were 25nm and 110nm, respectively. In other words, the thickness of the annealed $LiTaO_3$ film produced by a one time coating process increased from 25nm to 110nm when the solvent was changed from 2-methoxy ethanol to 1,2-Propylene glycol. This must be attributed to the high concentration of Li in the precursor solution due to the higher solubility of lithium acetate in 1,2-Propylene glycol.

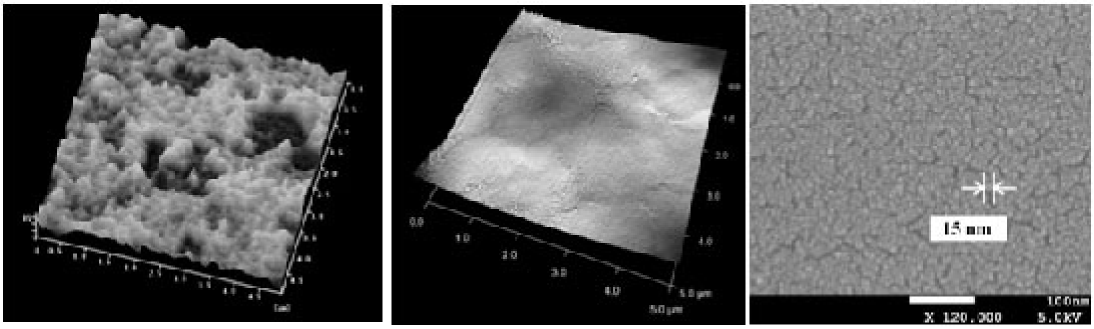
Therefore, the coating and annealing time can be significantly reduced using method 2. Three-dimensional atomic force microscope (AFM) pictures of $LiTaO_3$ thin films taken over a scan area of 5µm×5µm prepared by methods 1 and 2 are shown in Figures 2 (a) and (b), respectively. The films were annealed at 700 °C for 5min. The AFM pictures indicate that the $LiTaO_3$ film fabricated by method 2 has a much lower surface roughness than the film obtained using method 1. SEM surface morphology image of the film shown in Figure 2 (c), shows that the $LiTaO_3$ film heat treated at 700 °C has become crystalline and the typical size of the crystallites has increased to about 15nm. The crystallized $LiTaO_3$ particles covering the film surface are very uniform and compact.

In order to identify the crystallization state of the $LiTaO_3$ thin films, X-Ray Diffraction (XRD) analysis with Co $K_{\pm}$ radiation (»=1.54056Å, diffraction between 20°-80°, scanning rate at 0.025°/sec) was carried out to study the crystalline phase formation and the preferred orientation of crystal growth. The XRD analysis curves of $LiTaO_3$ thin films deposited on p-type (111) silicon substrates with methods 1 and 2 and annealing temperatures 650 °C, 700 °C and 750 °C are shown in Figure 3. The XRD patterns indicate that the films can be crystallized at 650 °C. Polycrystalline films with rhombohedral structures were formed in both methods after the annealing (results compared with JCPDS data) and the preferred orientations of the film were (012), (100) and (110). When the annealing temperature was increased from 650 °C to 750 °C with method 1, the diffraction peak intensity of the $LiTaO_3$ thin films increased and the half peak width decreased. There was no obvious difference between the XRD peaks and preferred orientation of the $LiTaO_3$ films fabricated using methods 1 and 2. From the SEM and XRD test results, we conclude that method 2 is an efficient method for the fabrication of $LiTaO_3$ films with low surface roughness and high uniformity.



(a) (b)

Fig. 1. Flow diagrams for preparation of precursor solutions: (a) Method 1; (b) Method 2



(a) (b) (c)

Fig. 2. Surface morphologies of $LiTaO_3$ films: (a) AFM picture of $LiTaO_3$ film prepared by method 1; (b) AFM picture of $LiTaO_3$ film prepared by method 2; (c) SEM picture of $LiTaO_3$ film prepared by method 2

$LiTaO_3$ thin film is a suitable material for pyroelectric detectors because of its high Curie temperature (620 ^{o}C), low dielectric constant and loss, and moderate pyroelectric constant. In order to measure the dielectric constant and dielectric loss parameters of the prepared material, a multilayer film is required with the structure Si/ SiO_2/ Pt/ $LiTaO_3$/ Al. In this structure, Si is the substrate, the SiO_2 layer is for insulation and the Pt and Al act as bottom and top electrodes, respectively. The cross-section of a multilayer without the covering top Al electrode was examined by SEM and is shown in Figure 4. The pyroelectric material $LiTaO_3$ film is compact and adheres tightly to the bottom Pt electrode. The top aluminum electrode, with a diameter of 0.8mm, was prepared by heat evaporation through a mask on to the surface of the film.

Before testing the electronic characteristics, the $LiTaO_3$ thin film was polarized at a low voltage (20V) for 30 min to achieve a polarised state. The dielectric constant and loss factor (tan´) was measured using a HP4294A impedance analyzer. The results are shown in Figure 5. The dielectric constant decreased from 73 to 48 as the frequency of impedance analyzer increased from 0.04 kHz to 2 kHz, but remained stable at approximately 45 at higher frequencies. Similarly, the dielectric loss factor was reduced from 0.03 to 0.009 as the frequency increased from 0.04 kHz to 2 kHz, remained below 0.006 when the frequency increased further, from 2k Hz up to 10 kHz. The lower values of dielectric constant and loss factor contribute significantly to an increase of the detectivity figure-of-merits for a detector.

An improved method of preparing lithium tantalate thin film is described. A high-concentration $LiTaO_3$ precursor solution was obtained using 1,2-Propylene glycol solution instead of 2-methoxy ethanol and the film thickness obtained with each coating procedure was about 110nm, after annealing at 700^{o}C. AFM pictures

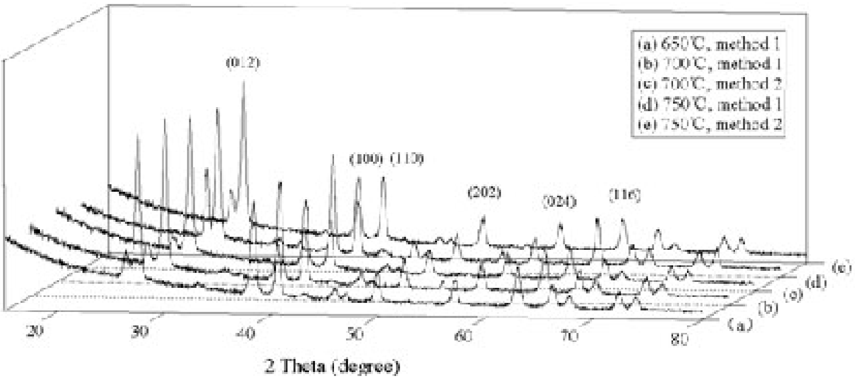


Fig. 3. XRD patterns of $LiTaO_3$ thin films deposited on silicon substrates using different methods and annealing temperatures

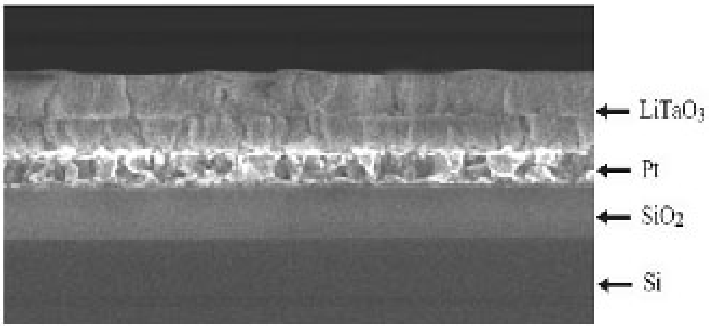


Fig. 4. SEM cross-section of $LiTaO_3$ thin films deposited on Pt/SiO_2/Si(111) substrates

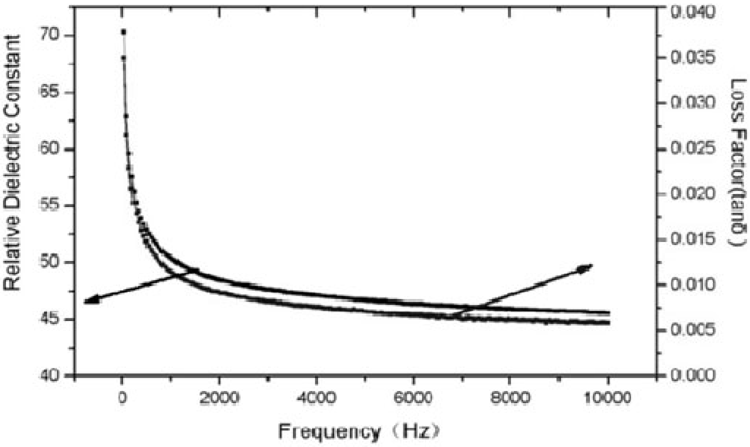


Fig. 5. The dielectric constant and dielectric loss factor at different frequency of $LiTaO_3$ film fabricated by method 2

indicated that the $LiTaO_3$ film fabricated by this improved method had much smaller surface roughness than the film obtained using the conventional 2-methoxy ethanol route. The typical crystallite size was about 15nm. XRD results suggested that the preferred orientations of the film were (012). The diffraction peaks of $LiTaO_3$ for thin films fabricated using both methods were nearly the same. The dielectric constant and dielectric loss factor of the annealed film, prepared using this novel procedure, were 45 and 0.006 at high frequency, respectively. Test results indicated that the $LiTaO_3$ thin film fabricated using the new method 2 was a pyroelectric material with great potential for infrared and terahertz detectors.

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