Preparation and Characterization of LiTaO₃ Films Derived by an Improved Sol-Gel Process

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In this paper, an improved sol-gel method was suggested to obtain high-concentration LiTaO₃ precursor solution for simplified experimental conditions and thicker films, by mixing lithium acetate and tantalum ethoxide in a 1, 2-Propylene glycol solution. Compared to traditional methods, the process was done without weak acidic solution and absolute dry experimental condition. Results of a comparative study of LiTaO₃ thin films derived by the improved sol-gel process and a traditional process using 2-methoxy ethanol as solvent were presented. Nano-crystalline LiTaO₃ films with rhombohedral structures were formed in both methods after annealing at 650 ° for 5 min. The thickness of each LiTaO₃ layer coated onto the substrate increased from 25 nm to 110 nm when 2-methoxy ethanol was replaced by 1, 2-Propylene glycol. LiTaO₃ films with a stronger preferential orientation were obtained in 1, 2-Propylene glycol due to its higher boiling point and slower volatilization rate. On the other hand, the diffraction peak intensity of LiTaO₃ thin films prepared using 1, 2-Propylene glycol was weaker than that of the films prepared using 2-methoxy ethanol due to decreased times of annealing.

KEY WORDS: LiTaO₃; Thin film; Sol-gel; Crystallization

1. Introduction

LiTaO₃ is an excellent and proven ferroelectric material due to its pyroelectric, electrooptic, nonlinear optic, and photorefractive properties. These properties make it useful in pyroelectric detectors, optical waveguide, surface acoustic wave guides, holographic memory, and so on^[1–3]. For most of the applications in these areas, high quality thin films are required to produce miniaturized and integrated devices^[4]. Recently, several methods such as RF sputtering^[5], pulsed laser deposition (PLD)^[6], metal organic chemical vapor deposition (MOCVD)^[7], molecular beam epitaxy (MBE)^[8], and sol-gel process^[9–12] have been employed to deposit LiTaO₃ thin films. Compared to the other dry deposition methods, sol-gel process is

advantageous from processing costs, processing temperature, large area fabrication, and stoichiometric composition control. In most of the available reports, LiTaO₃ thin films are derived from double alkoxide prepared by hydrolysis of lithium acetate (CH₃COOLi) and tantalum ethoxide (Ta(OC₂H₅)₅) in 2-methoxy ethanol (CH₃OCH₂CH₂OH)^[13–14]. Use of lithium 2, 4-pentanedionate (LiC₅H₇O₂) and tantalum isopropoxide (Ta[OCH(CH₃)₂]₅) in 1, 3-propanediol (HO(CH₂)₂OH) is also investigated^[15]. The processes should be precisely controlled for metal alkoxides are very vulnerable to hydrolysis.

In this paper, we provide an improved sol-gel process by mixing lithium acetate and tantalum ethoxide in a 1, 2-propylene glycol (CH₂OHCHOHCH₃) solution to obtain high-concentration LiTaO₃ precursor solution for simplified experimental conditions and thicker films. In the experiments, LiTaO₃ thin films were prepared by the improved sol-gel process and a traditional process using 2-methoxy ethanol as solvent. The structures, morphologies and crystallinities of the obtained LiTaO₃ thin films were examined and com-

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Fig. 1 Flow diagram for preparation of LiTaO_3 films: (a) flow diagram of method A for preparing LiTaO_3 precursor solution; (b) flow diagram of method B for preparing LiTaO_3 precursor solution; (c) flow diagram of spin-coating and heat treatment for preparing LiTaO_3 crystalline films

pared through scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction (XRD).

2. Experimental

Fig. 1 shows the flow diagrams for preparation of LiTaO_3 films. Precursor solutions were prepared by two methods in the experiments. In both methods, Lithium acetate (LiAc) and tantalum ethoxide were used as the source materials. 2-methoxy ethanol was used as solvent in method A, as shown in Fig. 1(a). Lithium acetate was added into 2-methoxy ethanol in a mol ratio of 1:60. The solution was magnetic stirred at 120 °C until LiAc was completely dissolved and then cooled to 60 °C. Acetic acid was added to adjust the pH of the solution to 5–6. Tantalum ethoxide was then added in a 1:1 molar ratio of Li to Ta. The solutions were refluxed at 130 °C for 4 h and 110 °C for 12 h. The process was carried out in N_2 .

Fig. 1(b) shows an improved process for preparing LiTaO_3 precursor solution. 1, 2-Propylene glycol was used as solvent. The mol ratio of LiAc to solvent was reduced to 1:15. After LiAc completely dissolving, tantalum ethoxide was added and the solution was refluxed by the same method in Fig. 1(a). The process was carried out in air and no acid was used. After hydrolysis and polycondensation, brown-like LiTaO_3

precursor solutions were obtained with a concentration of 0.2 and 1 mol/L, respectively.

Fig. 1(c) shows the flow diagram for preparing LiTaO_3 crystalline films from the precursor solutions. Spin technique was used to form thin films of gel on p-type (111) silicon substrates at a speed of 3000 r/min for 45 s. The films were then heat treated in air in three steps with different temperatures and durations: the films were firstly dried at 180–200 °C for 5 min to remove water and organic solvents, then pyrolyzed at 400–450 °C for 30 min, a final step of annealing was carried out to densify and crystallize the films at 650–750 °C for 5 min, followed by a furnace cooling to the room temperature. Spin-coating/heat treatment operations were repeated to obtain LiTaO_3 films with desired thickness.

3. Results and Discussion

Experiments suggested that moisture content and ambient humidity should be precisely controlled which had a great influence on the synthesis of LiTaO_3 . N_2 or other inert gas was crucial for vapor isolation when 2-methoxy ethanol was used as solvent. Acetic acid was also used to keep the precursor solutions acidic and stable. Otherwise, the solution would become opaque white after a few hours because of uncontrolled hydrolysis of tantalum ethoxide. By con-

Fig. 2 Structural formulas of 2-methoxy ethanol (a) and 1, 2-Propylene glycol (b)

trast, tantalum ethoxide and LiTaO_3 precursor were much more stable in 1, 2-Propylene glycol. Fig. 2 shows the structural formulas of 2-methoxy ethanol and 1, 2-Propylene glycol. It was suggested that more hydroxyl groups were contained in 1, 2-Propylene glycol, which could combined with Li^+ to form lithium alkoxide and contributed to the solubility of LiAc . At the same time, the viscosity of 1, 2-Propylene glycol was $60.5 \times 10^{-3} \text{ Pa}\cdot\text{s}$ at 20°C , which was much higher compared to that of 2-methoxy ethanol ($1.72 \times 10^{-3} \text{ Pa}\cdot\text{s}$) at the same temperature. The process could therefore be done in air and the LiTaO_3 precursor solutions could be preserved for a longer time without acetic acid when 1, 2-Propylene glycol was used as solvent due to its higher solubility and viscosity.

The thicknesses of the obtained LiTaO_3 films were measured by SEM. The 10-layer- LiTaO_3 thin film prepared by method A was about 250 nm. In method B, a LiTaO_3 thickness of about 670 nm was achieved when only 6 layers were coated onto the substrate, as shown in Fig. 3. The thickness of each layer increased from 25 nm to 110 nm when 2-methoxy ethanol was replaced by 1, 2-Propylene glycol as the solvent. This was attributed to the high concentration of precursor solution due to higher solubility of lithium acetate in 1, 2-Propylene glycol. The times of spin-coating and heat treatment could be greatly reduced to obtain desired thickness of LiTaO_3 films. Fig. 3 also suggested that the film was dense and had good adhesion with the substrate.

Three-dimensional (3-D) AFM pictures of LiTaO_3 thin films in a scan area of $5000 \text{ nm} \times 5000 \text{ nm}$ prepared by the two methods are shown in Fig. 4(a) and Fig. 4(b) respectively. The films were annealed

Fig. 3 SEM image of the cross-section of 6-layer- LiTaO_3 thin film prepared by method B

at 700°C for 5 min. The AFM pictures indicate that the LiTaO_3 film obtained by method B had a much smaller surface roughness. Fig. 4(c) shows the SEM image of surface morphologies of the film and indicated a particle size of about 15 nm.

XRD analysis with $\text{CoK}\alpha$ radiation was carried out to study the crystalline phase formation and the preferred orientation of crystal growth. Fig. 5 shows the XRD patterns of LiTaO_3 thin films deposited on p-type (111) silicon substrates with different methods and annealing temperatures (650 , 700 and 750°C in method A, 700 and 750°C in method B). 8-layer- LiTaO_3 and 4-layer- LiTaO_3 thin films were coated onto the substrates in method A and method B, with thicknesses of about 200 nm and 450 nm, respectively. The XRD patterns suggested that the films could be crystallized at 650°C . Polycrystalline films with rhombohedral structures were formed in both methods after the annealing (compared with Joint Committee on Powder Diffraction Standards, JCPDS). When the annealing temperature increased from 650°C to 750°C in method A, the diffraction peak intensity of LiTaO_3 thin films increased and the half peak width decreased. An appropriate annealing temperature for LiTaO_3 thin films is 700°C because the diffraction peak intensity of LiTaO_3 was strong while that of the impurities (for example at $2\theta=26.595^\circ$) was weak.

The obtained LiTaO_3 films were polycrystalline in

Fig. 4 AFM and SEM images of LiTaO_3 films: (a) AFM image of LiTaO_3 film prepared by method A; (b) AFM image of LiTaO_3 film prepared by method B; (c) SEM image of LiTaO_3 film prepared by method B

Fig. 5 XRD patterns of LiTaO₃ thin films deposited on p-type (111) silicon substrates with different methods and annealing temperatures

both methods. It is suggested by Fig. 5 that the films derived by method B had a stronger (012) preferential orientation. By contrast, high diffraction peak intensity on (100) and (116) planes besides (012) plane was observed in method A. The difference of preferential orientation intensity was relevant to the structures of gel films derived from different solvents. It was also reported that the films with stronger preferential orientation could be obtained when using solvent with higher boiling point in the preparation^[16]. The boiling point of 2-methoxy ethanol and 1, 2-Propylene glycol were 124.5 °C and 188.2 °C, respectively. In the deriving process, volatilization of the organic solvent and polymerization of long-chain Li-O-Ta proceeded simultaneously. Due to slower volatilization rate of 1, 2-Propylene glycol, the polymerization was promoted to obtain LiTaO₃ films with bigger grain size in method B. Fig. 5 also suggested that the diffraction peak intensity of LiTaO₃ thin films prepared by method B was weaker in general than that of the films prepared by method A. In the past, we have reported that the diffraction peak intensity of LiTaO₃ was proportional to the times of annealing^[17]. In the experiments, each spin-coating step was followed by an annealing process, so 8 and 4 times of annealing were done in method A and method B, respectively. The diffraction peak intensity difference appeared to be due to the different times of annealing in the two methods.

4. Conclusions

LiTaO₃ nano-crystalline thin films were prepared by a traditional sol-gel process and an improved sol-gel process using lithium acetate and tantalum ethoxide as starting materials. 2-methoxy ethanol and 1, 2-Propylene glycol were used as solvent, respectively. Nano-crystalline LiTaO₃ films with rhombohedral structures were obtained in both methods after annealing at 650 °C for 5 min. When 2-methoxy ethanol was used, the experiments should be done in N₂ or other inert gas for absolute dry condition and acetic acid was used to keep the precursor solution acidic and stable. 25 nm LiTaO₃ thin film was obtained when each layer was coated onto the substrate

by the LiTaO₃ precursor solution with a concentration of 0.2 mol/L. When 2-methoxy ethanol was replaced by 1, 2-Propylene glycol as the solvent, the process could be done in air and without acid for tantalum ethoxide and LiTaO₃ precursor were much more stable in 1, 2-Propylene glycol due to its high solubility and viscosity. The LiTaO₃ precursor solution reached a concentration of 1 mol/L and the thickness of each layer increased to 110 nm, which greatly reduced the times of spin-coating and heat treatment to obtain LiTaO₃ thin films with a desired thickness. The LiTaO₃ films had a stronger preferential orientation due to higher boiling point and slower volatilization rate of 1, 2-Propylene glycol. On the other hand, the diffraction peak intensity of LiTaO₃ thin films prepared using 1, 2-Propylene glycol was weaker than that of the films prepared using 2-methoxy ethanol due to decreased times of annealing.

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REFERENCES

- [1] T. Sokoll, V. Norkus and G. Gerlach, *Surf. Coat. Technol.* **97** (1997) 469.
- [2] G. Fu, X.F. Qin and X.L. Wang, *J. Korean Phys. Soc.* **56** (2010) 1364.
- [3] W.T. Hsu, Z.B. Chen, C.C. Wu, R.K. Choubey and C.W. Lan, *Materials* **5** (2012) 227.
- [4] D.Y. Zhang, D.G. Huang, J.H. Li, K. Li, D.D. Dan and Z. Dong, *J. Infrared Millim. Waves* **26** (2007) 170 (In Chinese).
- [5] C.H. Kohli, J. Moser, K. Prasad, P.E. Schmid, F. Levy and G. Burri, *Microelectron. Eng.* **29** (1995) 201.
- [6] L.S. Hung, J.A. Agostinelli, J.M. Mir and L.R. Zhang, *Appl. Phys. Lett.* **62** (1992) 3071.
- [7] T. Yamamoto, N. Wakiya, N. Mizutani and K. Shinozaki, *Key Eng. Mater.* **320** (2006) 57.
- [8] Z. Sitar, F. Gitmans, W. Liu and P. Günter, *MRS Proc.* **401** (1995) 255.
- [9] S. Hirano and K. Kato, *J. Non-Cryst. Solids* **100** (1988) 538.
- [10] S.L. Young, M.C. Kao and H.Z. Chen, *J. Electroceram.* **17** (2006) 799.
- [11] M.C. Kao, H.Z. Chen, C.M. Wang, Y.C. Chen and M.S. Lee, *Appl. Phys. A* **79** (2004) 103.
- [12] Z.X. Cheng, H. Kimura, K. Ozawa, A. Miyazaki and C.V. Kanna, *J. Alloys Compd.* **402** (2005) 208.
- [13] J. H. Jean, *J. Mater. Sci.* **25** (1990) 859.
- [14] D.Y. Zhang, D.G. Huang and Z. Dong, *Proc. SPIE* **6149** (2005) 614911.
- [15] M.C. Kao, M.S. Lee, C.M. Wang, H.Z. Chen and Y.C. Chen, *Jpn. J. Appl. Phys.* **41** (2002) 2982.
- [16] H. Huang, M.W. Zhu, J. Gong and C. Sun, *Acta Metall. Sin.* **43** (2007) 1043. (in Chinese)
- [17] J. Gou, J. Wang, Z.H. Huang and Y.D. Jiang, *Key Eng. Mater.* **531–532** (2013) 446.