

Preparation of LiTaO₃ Thin Film by Sol-Gel Method.

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Lithium tantalate thin film was fabricated by sol-gel method. Two kinds of sol were prepared from the mixture of the constituent metal alkoxides and the double-alkoxide synthesized. The solvent used was 2-ethoxyethanol and coating was conducted by dip-coating method. The coating film from double-alkoxide was crystallized by heating at 600°C. But quality of the film from double-alkoxide was too poor to measure the dielectric properties. An addition of diethanolamine (DEA) into the sol from the mixture of alkoxides lowered the crystallization temperature as low as 550°C and the resultant film was suitable for the dielectric measurements. The values $\epsilon_r=20$ and $\tan\delta=0.07$ were obtained.

1. Introduction

Lithium tantalate and lithium niobate are very attractive materials having excellent combination of ferroelectric, pyroelectric, electrooptic, and acoustic properties. For high performance application, the preparation of thin film of lithium tantalate material have been studied extensively¹⁻⁵. Among the various methods of preparing thin films, the sol-gel method is an excellent method and lithium tantalate films were also fabricated by this method. The sol-gel methods used for the preparation of lithium tantalate films and powders employed acetic acid^{1,3,6-8} to stabilize the sol.

We have fabricated many oxide thin films from metal alkoxides and acetates using ethanolamine as a sol stabilizer⁹⁻¹². The ethanolamines, such as diethanolamine and triethanolamine, are very effective for alkoxides to avoid from precipitation and/or gelation when they were exposed to humidity.

This paper contains the result of investigation on the preparation of lithium tantalate thin films using the sol-gel method and ethanolamine as a sol stabilizer. The microstructure and dielectric properties of the resultant thin films are also described.

2. Experimental

The starting reagents used for the experiment was tantalum pentaethoxide and lithium metal. We prepared two kinds of sol using the reagents. One was that from synthesized double-alkoxide and the other was that from the mixture of two metal alkoxides.

The double-alkoxide was synthesized as follows; proper amounts of tantalum pentaethoxide and lithium were mixed into dehydrated ethanol, which was solvent and reactant to synthesize lithium alkoxide. After refluxing the solution for 24h at 100°C, the solvent was removed. The alkoxide was then distilled at about 220°C under 0.1mmHg. Since this boiling temperature is close to the published data¹³ of lithium tantalum double alkoxide, i.e., 230°C under 0.2mmHg, and Ta(OEt)₅ has a boiling temperature of 146 °C under 0.15mmHg¹³, the alkoxide synthesized here should be LiTa(OEt)₆.

For the preparation of another sol, lithium isopropoxide was synthesized by a reaction of lithium with large amount of isopropanol dehydrated. After removal of the excess isopropanol, lithium isopropoxide was obtained as white powder.

For the preparation of both of the sols, 2-ethoxyethanol was used as a solvent. The concentration of sols was 0.2M as lithium tantalate. After dip-coating, the film was dried. This coating-drying procedure was repeated for 5 and 10 times. Then the film was crystallized by heating at 500 to 700°C. The substrate used was ITO sputtered glass substrate. The crystallization of the films was measured by XRD. The microstructure of the thin film was observed by TEM.

After gold was vacuum evaporated on the film surface as an upper electrode of 1.4 mm in diameter, dielectric properties of the films was measured at a range between room temperature and 300°C.

3. Results and Discussion.

3-1. Crystallization of the film.

The thin film coated with sol from double-alkoxide was amorphous by heating at 500 °C and was crystallized at 600 °C when they were coated for 3 times. The coated films were translucent and fine cracks were observed. When gold electrode was deposited, current leakage between top and bottom electrodes through the cracks occurred and the films were not able to measure the dielectric properties. To avoid the formation of cracks, two methods were tried. Firstly we increased the repetition number of coating from 3 to 10 times. Secondary, since thick coating sometimes causes the formation of cracks, the film thickness of each coating was decreased by decreasing the drawing speed of substrate during dip-coating procedure from 18 to 6 cm/min. The two attempts, however, were in vain.

The sol from the mixture of lithium and tantalum alkoxides, then, was used for the fabrication of the film. Since the film from this sol was not crystallized by heating at 600 °C and some moisture in air caused hydrolysis of the alkoxides, double-molar of diethanolamine (DEA) was added into the sol. Figure 1 shows XRD patterns of films prepared with and without DEA at 600 °C for 5 coating. It is very interesting that the addition of DEA accelerated the crystallization of lithium tantalate by heating at 600 °C. Further investigation revealed that lithium tantalate was crystallized at 550 °C. This should be caused by the change in the sol and/or gel structure. We tried to

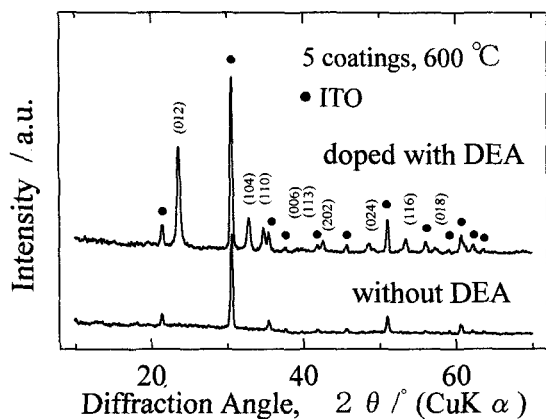


Fig. 1 XRD patterns of LiTaO_3 films doped with DEA and blank heated for 650 °C.

determine the change in sol structure by NMR. The results, however, were not enough to clarify the change in the structure.

Figure 2 is TG-DTA curves of powders, or gels, prepared from sols doped with and without DEA by drying at 110 °C. The weight loss of the powder without DEA up to 1000 °C was about 18 %. Tantalum hydroxide is known to have formula of HTaO_3 after drying at 100 °C¹⁴ and lithium hydroxide easily absorbs H_2O and CO_2 from air to convert $\text{LiOH}\cdot\text{H}_2\text{O}$ and Li_2CO_3 , respectively. Since the total weight loss during conversion from the mixture of HTaO_3 and Li_2CO_3 into LiTaO_3 is about 13% and this value is fairly close to the present weight loss, the tantalum and lithium alkoxides were both hydrolyzed during drying the film. The exothermic reaction at 620 °C was not assigned.

On the other hand, the DEA added gel has larger weight loss of about 48 %. This value is approximately the same value as the loss of two molar of DEA leaving from one molar of lithium tantalate, 47%. From the results of TGA it was concluded that the strong coordination of nitrogen atom in DEA molecule to metals prevented removal of ligands by heating and, therefore, protected alkoxides from hydrolysis-condensation to form individual hydroxide or carbonate. Consequently, the distribution of cations in the gel doped with DEA should be the same as they in the sol. This random distribution of cations in the gel led crystallization of lithium tantalate as low as 550 °C.

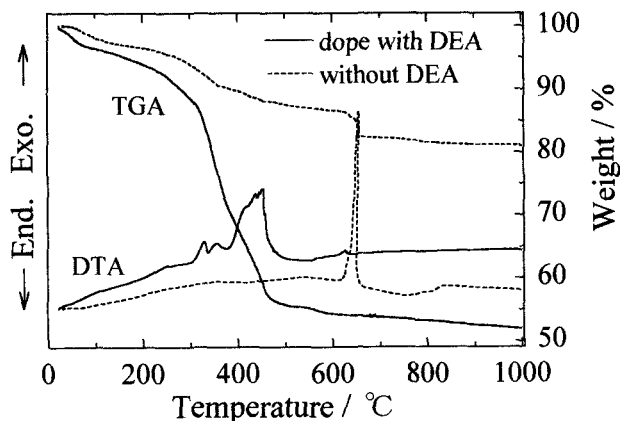


Fig. 2 DTA and TGA curves of gels with and without DEA.

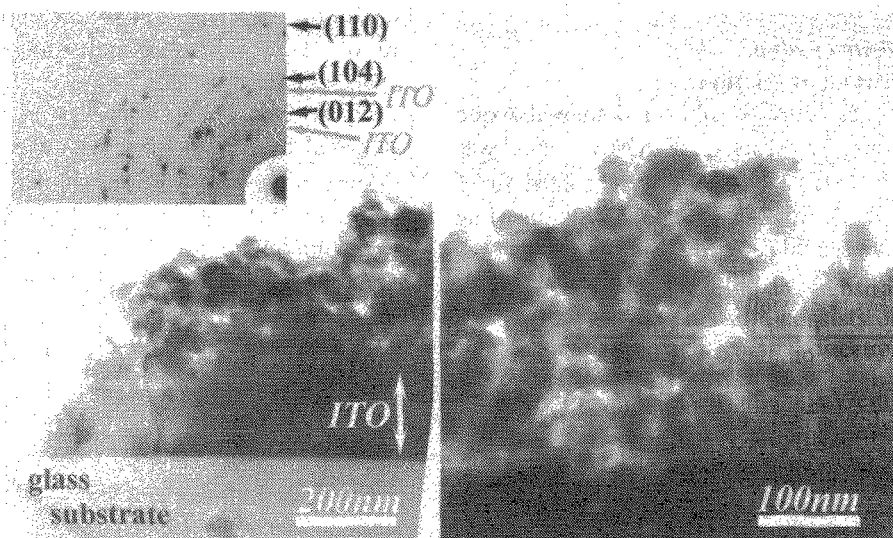


Fig.3 TEM photographs and SAD pattern of LiTaO_3 film coated 10 times and heated at 650°C

3-2. Microstructure of the film.

The films prepared from the mixture of lithium and tantalum alkoxides were translucent. The thickness of the films after heating was about 120 nm for 5 times coatings. The crystallite size of lithium tantalate crystal was calculated from peak width of XRD using a Scherrer's equation to be about 20 nm. The crystallite size calculated did not change among the films of different heating temperature and coating numbers.

Figure 3 is TEM photographs of the film coated 10 times and heated at 650°C . The selected area electron diffraction indicated that the lithium tantalate was crystallized with random orientation of crystalline direction on the surface of the ITO electrode. The grain size was about 30-50 nm. This value was a little larger than that estimated by XRD. As the film thickness of 5 times coatings was about 120nm, the films consisted of only a few grains packing through the film thickness. The grains are round in shape and the grain-boundary seemed to be sintered not tightly. The film contained pores and the density was not so high. The interface between ITO electrode and lithium tantalate grain was rather clear, suggesting no chemical reaction between them seems, which was confirmed by the measurement using XPS.

3-3. Electrical properties.

The dielectric constant of films fabricated by 5 coatings and heated at $600\text{-}700^\circ\text{C}$ was low and

dielectric loss of those was large. The poor dielectric properties of the 5 times coating films were attributed to the porous structure of the films, as described above. The dielectric properties of 10 times coating films were improved. The relative dielectric constants of films coated 10 times and heated at 600 , 650 , and 700°C were 12, 20, and 15, and the values of $\tan\delta$ of those were 9, 7, and 10%, respectively. In the present study, the film heated at 650°C exhibited the highest dielectric constant and lowest dielectric loss.

The temperature dependence of the dielectric properties of the film fabricated by heating at 650°C was measured up to 300°C and is shown in Fig. 4. The dielectric constant gradually increased up to 200°C . The dielectric loss was rapidly increased when the measuring temperature became $>100^\circ\text{C}$ and exhibited thermal hysteresis on measuring cycle.

3-4. Effect of addition of Mn.

It is well known that the addition of manganese improves dielectric properties of ferroelectric ceramics. We also investigated the effects of doping of manganese on dielectric properties of present lithium tantalate film. The manganese was doped as the solution of manganese 2-ethylhexanoic acid, which was synthesized from manganese acetate. The amounts of manganese were 1 and 2 %.

The addition of manganese did not affect crystallization of lithium tantalate, but crystallite size became a little smaller than that of non-doped film.

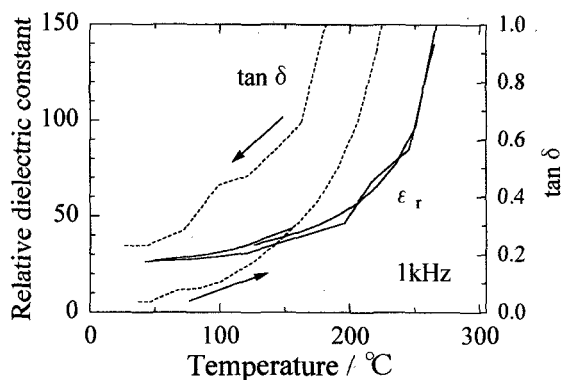


Fig.4 Dielectric properties of LiTaO_3 film with elevated temperature.

The thickness of lithium tantalate films doped with manganese, heated at 650°C and coated 10 times was 260 and 310 nm for doping of 1 and 2%, respectively. The relative dielectric constant at room temperature of the films doped with 1 and 2% manganese are 25 and 20, respectively. The dielectric loss, $\tan\delta$, of those were 11 and 2%, respectively.

Figure 5 is the measuring temperature dependence of dielectric constant and $\tan\delta$ of the film doped with 2% manganese, heated at 650°C and coated 10 times. The dielectric constant of the manganese added specimens was almost the same as that of the non-doped ones at room temperature, whereas $\tan\delta$ and the change in the dielectric properties at elevating temperature became smaller than those of the blank specimens. The addition of manganese into lithium tantalate improved dielectric properties at high temperature and suggested possibility to use the film at higher temperatures.

4. Conclusion.

The lithium tantalate thin film was prepared by the sol-gel method. The addition of diethanolamine into the mixed solution of alkoxides of lithium and tantalate enhanced the crystallization and avoid the alkoxide from hydrolysis. The crystallized lithium tantalate had grain size of 30-50 nm in diameter and the films was rather porous. The addition of manganese improved dielectric loss, especially at a higher temperature.

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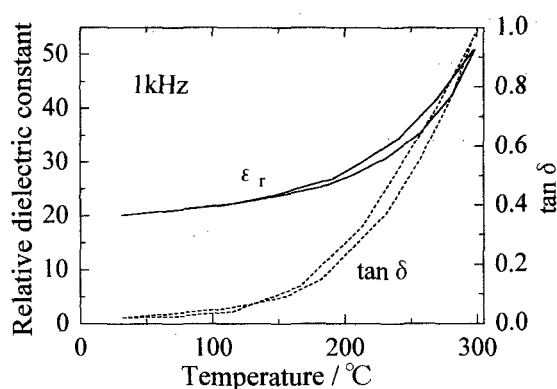


Fig.5 Dielectric properties of Mn doped LiTaO_3 film with elevated temperature.

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