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Band gap determination using Tauc's plot for $LiNbO_3$ thin films

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Abstract: $LiNbO_3$ thin films were deposited using RF magnetron sputtering technique. Structural studies confirmed the formation of $LiNbO_3$ phase with minor Li deficiency. The RMS roughness and average grain size of the crystallized thin films was found to be in the range of 5.74 -26nm and 26 -152nm respectively. From Tauc's plot, it can be seen that the band gap energy is decreasing with increase in annealing temperature till 700°C. At 750°C, band gap is shifted towards blue end. The variation in band gap is primarily due to the Li vacancies and grain size effects which are explained by quantum confinement model.

Introduction and Experimental:

Lithium Niobate ($LiNbO_3$) is widely studied material for exploring its large non-linear optic, ferroelectric and piezoelectric properties [1]. Although, well studied by several researchers, consistent literature on band gap of $LiNbO_3$ is meagre. From both theoretical and experimental estimates, direct and indirect band gap energy of $LiNbO_3$ is reported to be in the range of 3.5 - 4.7eV. These changes are attributed to several parameters like grain size, composition and defects [1-3].

In this article, we tried to explore the effect of ex-situ annealing on structural, morphological and band gap characteristics.

$LiNbO_3$ thin films were deposited on fused silica substrate by RF magnetron sputtering technique using a 2 inch $LiNbO_3$ ceramic target. The sputtering target is prepared using $LiNbO_3$ powder with 5wt% excess Li content. The films were deposited at a sputtering pressure of 20mTorr in 100% Ar gas. After deposition, the films were annealed in tubular furnace in flowing oxygen atmosphere at different temperatures.

The crystallographic structure was analyzed by the X-ray diffractometer (XRD). The surface morphology was examined using atomic force microscopy (AFM). The transmission spectra for the same were recorded using UV-Visible spectrometer.

Results and Discussion:

The XRD spectra of $LiNbO_3$ thin films annealed at different temperatures are shown in figure 1. Indexing of diffraction peaks have been done based on the standard $LiNbO_3$ and $LiNb_3O_8$ XRD pattern (JCPDS diffraction file # 880289 and #752154). For the films annealed at 700°C, all planes are well matched with

$LiNbO_3$ except one at 72.89° which corresponds to $LiNb_3O_8$. Films annealed at 600°C and 650°C have secondary phases at higher angles which are clearly indicated with *. Also the film annealed at 750°C have dominated phase of $LiNb_3O_8$.

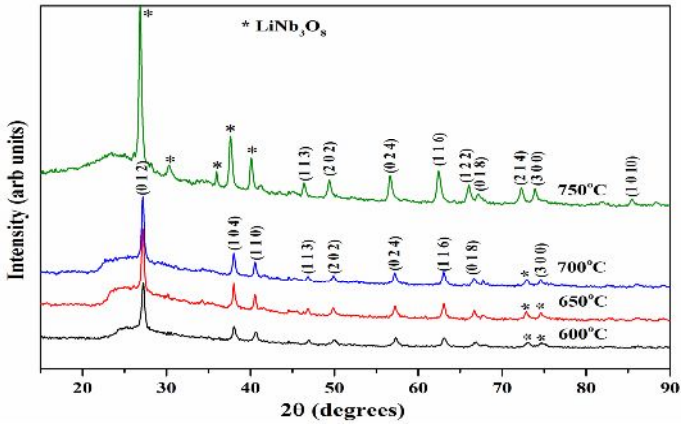

Figure 1. XRD patterns of $LiNbO_3$ thin films.

This might be due to the evaporation of Li at such high temperature. With increase in temperature, shift is observed towards the lower angle in the XRD peak position in comparison with standard $LiNbO_3$, indicating the presence of strain in film. The strain is mainly due to the nature of the substrate. Since fused silica is amorphous, growth in a preferred direction is not possible.

Fig. 2(a)-(d) shows atomic force microscopy (AFM) micrographs (3 × 3 μm) of $LiNbO_3$ thin films deposited on fused silica after annealing at different temperatures. From fig. 2(a), the grains are clustered and agglomerated like separate islands. With increase in annealing temperature, the grains coalesce to form larger grains as shown in fig. 2(c) and (d). The grains with distorted triangular shape have their size exponentially increased with annealing temperature. The porosity also decreased with increase in annealing temperature. This is due to the increase in grain size. The average grain size and RMS roughness values are given in table 1.

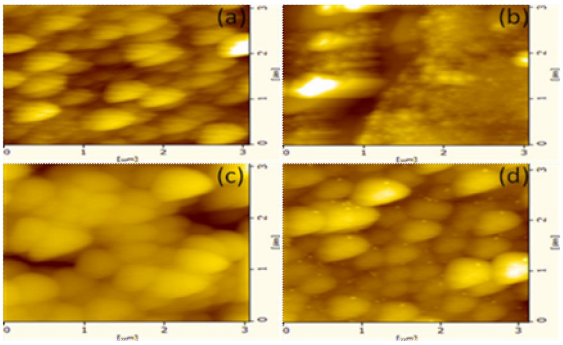

FIGURE 2. Morphology of films annealed at (a) 600°C (b) 650°C (c) 700°C (d) 750°C.

The determination of optical band gap is obtained by Tauc's equation [4],

$$\alpha h\nu = A(h\nu - E_g)^n. \qquad (1)$$

Where, A is a constant, hν is photon energy, Eg is the allowed energy gap, n = ½ for allowed direct transition and n = 2 for allowed indirect transition.

Figure 3(a) shows the absorption coefficient (α) and the two defined regions separated by the peak of derivative of absorption coefficient. The Tauc's region is extrapolated to $(\alpha h\upsilon)^2 = 0$. to obtain the band gap. The Urbach's region tells the structural and thermal disorder present in the film. Figure 3(b) shows the $(\alpha h\nu)^2$ vs. hν for films annealed at different temperatures. With increase in annealing temperature, the band gap is red shifted

till 700°C. For 750°C, the band gap again shifted towards blue end. The optical band gap is highly influenced by the chemical bonds of the constituent elements present in the structure. In $LiNbO_3$, interband transitions from O-2p to Nb-4d states involve electronic transitions. Structural defects like Li vacancies, Nb antisite defects, oxygen vacancies also results in band gap narrowing [4]. The range of band gap values reported in the present study is fairly lower than previous reports [4].

Band gap is also affected by grain size. In general, the band gap decreases with the increase in grain size. The band gap variation with grain size due to quantum confinement is given by

$$E_g^{nano} = E_g^{bulk} + \frac{\hbar^2 \prod^2}{2Mr^2} \qquad (2)$$

Where E_g^{nano} is the band gap of nanoparticle, E_g^{bulk} is the band gap of bulk material.

M is the effective mass of the system, r is the radius of the nanoparticle.

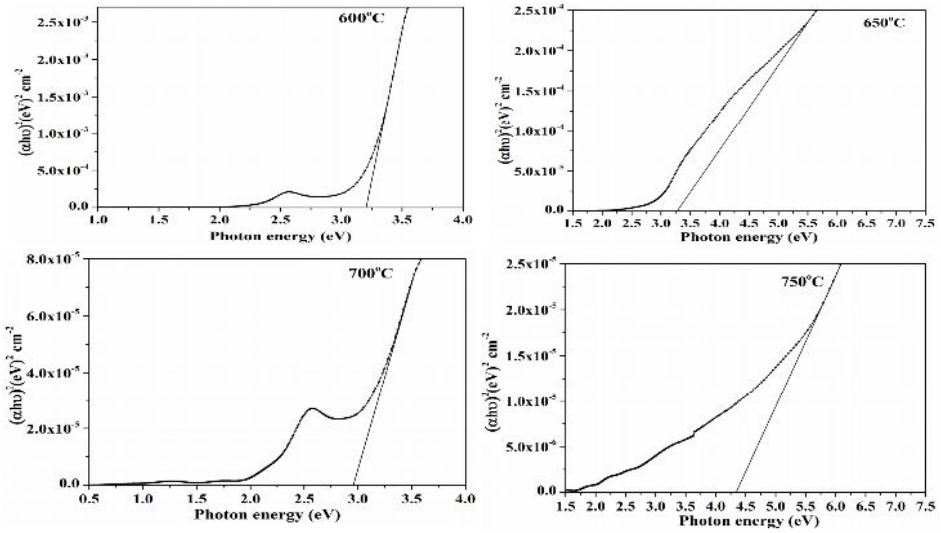

Fig. 3(a) **Fig. 3(b)**

Figure 3(a): Plot defining Urbach and Tauc regions. 3(b): Tauc's plot for $LiNbO_3$ thin films annealed at different temperatures.

From the above model, it is clear that band gap varies inversely with size of the particle [5]. The average grain sizes are 26nm, 36nm, 130nm and 152nm and their corresponding band gap 3.26nm, 3.17nm, 2.95nm and 4.34nm at 600°C, 650°C, 700°C and 750°C respectively. At 750°C, the increase in band gap is either due to the Li vacancies or the formation of larger particles from the sintering and recrystallization of smaller particles which is clear from AFM images.

In conclusion, $LiNbO_3$ thin films are deposited using RF magnetron sputtering technique at room temperature and ex-situ annealed at different temperatures. At 700°C, the film has dominant rhombohedral $LiNbO_3$ structure. With increase in annealing temperature, average grain size is found to be increasing and band gap shows an oscillatory behavior. This is either due to the intrinsic defects or effect of grain size which is explained by quantum confinement model.

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