



Nucleation and crystallization of $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ ternary compound thin films co-sputtered from LiNbO_3 and Li_2O targets



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ARTICLE INFO

Article history:

Received 24 March 2013

Received in revised form 6 January 2014

Accepted 6 January 2014

Available online 15 January 2014

Keywords:

Nucleation

Crystallization

Lithium Niobate

Lithium Oxide

Niobium pentoxide

Solid Phase Epitaxy

Sputtering

ABSTRACT

$\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ ternary compound thin films were deposited by dual sputtering from LiNbO_3 and Li_2O targets to cover a wide range of Li/Nb molar ratios. When all parts of the films were crystallized during sputtering at elevated temperatures, pyrochlore phase crystallites of Li_3NbO_4 , LiNbO_3 , and LiNb_3O_8 were preferentially oriented toward their respective (222), (006), and ($\bar{6}02$) directions. These closely packed crystallographic planes having the lowest surface free energies were initially created under exposure to the plasma and the crystallization that followed proceeded exclusively on these seed planes. The volume fraction of each crystalline component as a function of the Li/Nb molar ratio obeyed the established phase diagram. In contrast, solid-phase crystallization of pre-deposited amorphous films through post annealing exhibited a non-equilibrium nature, and the volume fraction of each crystalline component depended on the crystallization rate rather than the Li/Nb molar ratio. Solid-phase crystallization decelerated when excess Li_2O was contained in the film. Specifically, LiNbO_3 crystallites with near-stoichiometric compositions were randomly oriented without the operating mechanism of preferential orientation toward c-planes. In certain situations, crystalline domains were spatially of inhomogeneous composition, resulting in the simultaneous coexistence of Li_3NbO_4 , LiNbO_3 , and LiNb_3O_8 .

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1. Introduction

LiNbO_3 single crystal is a representative opto-electronic material [1] and its bulk crystal growth has long been studied [2–6]. LiNbO_3 crystals are endowed with various functional properties such as having ferroelectric, pyroelectric, electro-optic, and nonlinear optical effects [7]. The electro-optic effect is the operating principle for high-frequency modulators, fast optical switches, and Pockels sensors [8]. The nonlinear optical effect is responsible for frequency-doubled lasers and wavelength converters [9–11]. The feasibility of the pyroelectric effect [12] has been demonstrated for compact X-ray sources [13]. Except for these stand-alone devices, promising applications of LiNbO_3 crystals can be developed for integrated systems [14,15], for instance, in combination with silicon photonics [16]. If a LiNbO_3 layer is overlaid on a SiO_2 layer, the sharp refractive index profile between the core (LiNbO_3) and cladding (SiO_2) layers enables propagating light to be efficiently confined within the LiNbO_3 waveguide [17–22]. We can thus impart active functions to the optical circuit by placing LiNbO_3 segments in the mid-section of silicon-based passive waveguides, which are typically made of SiO_x , SiON , and Si_3N_4 [23].

Featuring single crystals ensures basically the same electro-optic and frequency conversion coefficient of the LiNbO_3 crystal. To make hybrid systems, however, wafer bonding [24,25] and thinning processes incur

a great deal of cost. The product is a single optical component. In contrast, depositing LiNbO_3 film is a convenient approach for inserting LiNbO_3 segments in advantageous places. It is compatible with patterned substrate and multiple layers can be formed if necessary. The problems accompanied with employing LiNbO_3 polycrystalline films are their inferior properties compared with those of single crystals due to defects. In our previous attempts by using electron cyclotron resonance (ECR) plasma sputtering with a single LiNbO_3 target [26], the O_2 flow rate for a single phase with a molar ratio of Li:Nb = 3:1 to nucleate was between 0.5 and 1 sccm. However, films grown under such a low O_2 flow rate were slightly oxygen-deficient LiNbO_{3-x} . If the O_2 flow rate was higher than 1 sccm, Li atoms, in contrast, reacted with oxygen radicals that were generated in the plasma, and the volatile Li_2O molecules desorbed into the vacuum at high temperatures. This led to the formation of $\text{Li}_{1-x}\text{NbO}_3$ films. Although the standard approach for growing films with a molar ratio of Li:Nb:O = 1:1:3 is employing Li-excess targets, it is difficult to predict the exact target composition that will result in a stoichiometric composition. Moreover, the composition of deposited films may vary depending on the growth temperature, deposition rate, and other plasma parameters [27–30]. It is not guaranteed that a stoichiometric composition will be obtained within a parameter range by only adjusting the O_2 flow rate. Notwithstanding this background, the composition should preferably be variable to meet diverse demands in the actual process. Depending on the application for the device, the factors affecting priority may be crystallinity, the domain structure, surface roughness, or the deposition rate rather than stoichiometry.

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In the work reported in this paper, we found adaptive control of the film composition to be close to that of the stoichiometric one. Prior to approaching this goal, we studied the manner in which phases were formed in the $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ ternary compound system over a wide range of Li/Nb molar ratios. We employed dual sputtering from a LiNbO_3 main target and a Li_2O sub-target to tailor the film composition. Li and O atoms sputtered from the Li_2O target supplemented Li atoms that were lost in the form of Li_2O from the film and from the LiNbO_3 target surface due to the impact with argon ions. We could vary the Li/Nb molar ratio (x) in deposited films between 0.4 and 2, while maintaining sufficiently oxidized conditions.

The crystal growth sequence is composed of two steps, i.e., initially assembling atoms to create crystalline seeds (nucleation) and following this with growth on the seed crystal surfaces (crystallization) [31]. Bulk crystal growth from melts proceeds by extending the front of seed crystal at the liquid/solid interface. The nucleation step is skipped if a seed crystal is provided. In contrast, crystal growth by molecular-beam epitaxy, chemical vapor deposition, and sputtering proceeds at the vacuum/solid interface. If an epitaxial substrate is not used, the initial nucleation process may govern the following crystallization step. Solid-phase crystallization is another route forming crystalline thin films, where nucleation begins not only at the solid–solid interface but also at the surface and inside the film under non-equilibrium conditions. The crystallization step will be greatly affected by the location where nucleation occurs. Against this background, we tried to characterize the crystal growth process during deposition (as-crystallization) as well as the solid-phase crystallization of pre-deposited amorphous films (post-crystallization). In the latter case, we found that the migration activity of constituent atoms was the primary parameter affecting phase formation and crystallization.

2. Experimental details

The geometrical configuration for our dual target sputtering system is in Fig. 1. It is based on an ECR plasma sputtering system combined with an RF magnetron gun. In the ECR plasma source, transmitting microwaves (500 W) through double facing windows generated remote plasma from Ar/O_2 gas mixtures when an external magnetic field was applied. We fixed the Ar flow rate at 8 sccm and the O_2 flow rate at 3 sccm. Li, Nb, and O atoms were sputtered by applying RF voltage (500 W) to the cylindrical LiNbO_3 target. Deposition from the LiNbO_3 target alone at this O_2 flow rate formed $\text{Li}_{1-x}\text{NbO}_3$ films. Hence, we supplied Li and O atoms from the RF magnetron gun that was equipped with a Li_2O target under an operating power between 0 and 100 W.

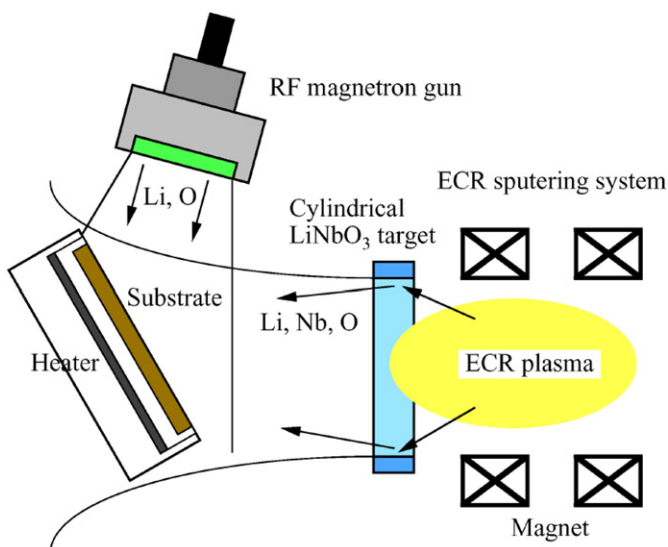


Fig. 1. Geometrical configuration for ECR sputtering and RF magnetron sputtering.

The substrate surface was tilted at 30° from the direction of the ECR plasma source and 50° from the RF magnetron gun.

We used four-inch $\text{Si}(100)$ wafers as substrates. Dipping them in a 2.5% HF solution removed the native oxide layer and prepared a hydrogen-terminated surface. The reason why non-epitaxial Si substrates were used was to investigate the manner of phase formation that was not guided by a crystalline template [26]. Deposition was done either at a substrate temperature of 510°C or 70°C . Irradiating the substrate surface with a plasma stream while the substrate was non-annealed with a heater raised the surface temperature up to 70°C . At 510°C , crystalline films were produced in their deposited state. Solid-phase crystallization of amorphous films that had been deposited at 70°C was driven by 3 h of post annealing at 600°C in a vacuum. Film thickness was measured by single-wavelength ellipsometry at a wavelength of 633 nm assuming that the extinction coefficient was negligibly small. The values we obtained were confirmed to agree with the differential thickness between bare (deposited) and masked (non-deposited) regions on a substrate surface, which was measured with a stylus step profiler. Although the Li/Nb molar ratio in lithium niobate films can be monitored by nondestructive optical measurement such as infrared absorption and Raman scattering spectroscopies [32–34], we employed inductively coupled plasma atomic emission spectroscopy (ICP-AES) for quantitative evaluation.

The crystal structures were determined by X-ray diffraction (XRD) (RINT1500, Rigaku) by using a $\text{Cu K}\alpha$ line as the primary X-ray beam. It is known that the $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ ternary compound system has four stable compounds: $3\text{Li}_2\text{O}\cdot\text{Nb}_2\text{O}_5$, $\text{Li}_2\text{O}\cdot\text{Nb}_2\text{O}_5$, $\text{Li}_2\text{O}\cdot 3\text{Nb}_2\text{O}_5$, and $\text{Li}_2\text{O}\cdot 14\text{Nb}_2\text{O}_5$ [35]. They correspond to the crystalline components of Li_3NbO_4 , LiNbO_3 , LiNb_3O_8 , and $\text{Li}_2\text{Nb}_{28}\text{O}_{71}$. Of these, $\text{Li}_2\text{Nb}_{28}\text{O}_{71}$ appearing at extremely Li deficient compositions was beyond the range of compositions that could be prepared in our deposition system. The other three components, if they were selectively orientated, could clearly be distinguished in terms of the primary XRD signals of $\text{Li}_3\text{NbO}_4(222)$, $\text{LiNbO}_3(006)$, and $\text{LiNb}_3\text{O}_8(602)$, which appear at respective 2θ angles of 37° , 39° , and 38° .

3. Results

3.1. Distribution of thickness and composition over 4-inch substrate surface

Fig. 2 plots the relation between RF magnetron sputtering power applied to the Li_2O target and Li_2O molar fraction in deposited $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ compound films at a fixed directory point on the 4-inch wafer surface. We confirmed that all parts of films were crystallized during deposition at 510°C since post annealing scarcely changed the XRD peak intensities. The Li_2O content linearly depended on the sputtering power down to 10 W. Sustaining the linear relation even at such low sputtering powers is because Li and O are light atoms. At Li_2O sputtering powers

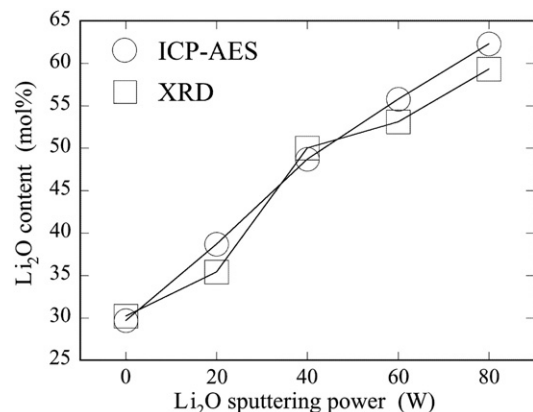


Fig. 2. Relation between RF magnetron sputtering power applied to Li_2O target and Li_2O mole% in deposited $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ thin films.

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