# Deposition of Lithium Niobate Thin Films by the Rf Ion-plating Method

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We used the ion-plating apparatus for deposition of lithium niobate, making it possible to initiate a negative bias on the substrate and melt two targets simultaneously. We demonstrated the effect of negative rf bias on the substrate on the crystallinity of the film. We have obtained Li-Nb-O crystalline thin films at 3nm/s in average. The dominant crystalline phases of the films were LiNbO<sub>3</sub> and Li<sub>3</sub>NbO<sub>4</sub> at the high flux of Li onto substrate.

Keywords: lithium niobate, thin film, ion-plating, rf substrate bias

#### 1. INTRODUCTION

Lithium niobate is a ferroelectric material with great piezoelectric, electrooptic and photorefractive characteristics. It is widely used as surface acoustic wave filters and optical wave guides in the form of single crystals. Due to the miniaturization of electronic devices, lithium niobate thin films of a few  $\mu$ m in thickness are now in great demand. There have been many reports of deposition of lithium niobate on sapphire or LiTaO<sub>3</sub> substrates by pulse laser deposition (PLD)(1,2), chemical vapor deposition(3,6) or magnetron sputtering method(4,5), but few have achieved deposition rates of over 1nm/s(6). Deposition of lithium niobate thin films at a fast rate has been a long objective for many ferroelectric thin film researchers. The reason for the need of fast rate deposition lies in the practical use.

The object of this experiment is to deposit thin films on a Si substrate over 1nm/s deposition rate. In this paper, we use a negative rf bias on the substrate to improve the crystallinity of the film.

#### 2. EXPERIMENTAL

The experimental apparatus is shown in Fig1. In order to initiate a negative bias on an insulator film such as LiNbO<sub>3</sub>, a 13.56MHz rf power (<300W) must be used. A two source crucible allows the independent melting of two sources simultaneously. In order to experiment depositions at high temperatures, a PC/PBN heater ( $\phi$ 25mm) was placed 3mm above the substrate holder.

After the chamber was evacuated up to  $1 \times 10^{-6}$  Torr, the 15mm squared (100) Si substrate was pre-sputtered for 5minutes under a -500V bias in the Ar ( $2 \times 10^{-4}$ Torr) plasma before deposition. The plasma was induced by 13.56MHz rf power which also empowered a negative bias on the substrate at the same time.  $Li_2O$  powder and NbO<sub>2</sub> grains were independently melted by a 10kV electron beam.

We measured the temperature of the evaporation sources in the crucible at various electron beam currents by using a two-color pyrometer. From the temperature of each source, both the vapor pressures and the source fluxes onto substrate were estimated. By changing the scanning time of the electron beam current of both sources independently, we controlled the vapor fluxes onto the substrate; thus controlling the film composition.

Although Nb<sub>2</sub>O<sub>5</sub> is generally used for LiNbO<sub>3</sub> fabrication in single crystals(7), because of its thermodynamic stability, the solid-liquid phase area is too small in the Nb-O phase diagram shown in Fig.2(8). In order to secure a stable flux, NbO<sub>2</sub> was used in this paper.

The film thickness and surface roughness were analyzed by a surface profiler (DEKTAK). The film density was estimated using the film thickness and the intensity of Nb detected by the X-ray Fluorescence Analyzer (XRF). X-ray Diffraction (XRD) patterns (Cu K $\alpha$  radiation) were also taken.

In this paper, V and I each correspond to negative rf bias and the electron beam current, respectively. T corresponds to the substrate temperature.

## 3. RESULTS AND DISCUSSION

3.1 Preliminary experiments

Given the difficulty of measuring lithium concentration in the films, niobium oxide films were deposited by melting only the NbO<sub>2</sub> source in order to determine the suitable conditions for film crystallization. Depositions were done at the following conditions; electron



Fig.1 Experimental apparatus.

beam currents of I=200~ 400mA and negative bias of V=-250~-400V at T=600K. The deposition rates and the density of films are shown in Fig.3. The density was calculated at the presumption that the film was the single phase of Nb<sub>2</sub>O<sub>5</sub>.

At I=200mA, the deposition rate was 0.5nm/s, and the density was below  $3g/cm^3$ . The low deposition rate and the density for I=200mA were due to the low temperature of the NbO<sub>2</sub> source in the crucible. Its temperature lies right above the NbO<sub>2</sub> liquid-solid phase (T=2270K in Fig.2)

The films over I=200mA had a density between 5.1g  $/\text{cm}^3$  and 5.9g/cm<sup>3</sup>, which is in good accordance with the density of Nb<sub>2</sub>O<sub>5</sub> (=5.5~5.9mg/cm<sup>3</sup>). The deposition rates were also above 1nm/s. Films deposited at I= 400mA had deposition rates as high as 8nm/s.

We concluded that the temperature of the source at I=250mA was high enough to enable a fast deposition rate, and also achieve a dense film.

#### 3.2 Effect of negative bias

Using the facts from section 3.1, LiNbO<sub>3</sub> depositions were done at  $I_{Li}$ =50mA,  $I_{Nb}$ =250mA, V=0~-500V and T=300K in order to confirm the effect of rf bias on the film crystallinity. Film surface was smooth and deposition rates of over 1nm/s were obtained for all films. The NbO phase was clearly confirmed from the XRD patterns in Fig.4. Although crystalline Li-Nb-O phases



Fig.2 Nb-O phase diagram (8)



Fig.3  $Nb_2O_5$  Density and deposition rate of films deposited at T=600K at various I(mA)

were not confirmed, the NbO (002) peak intensity was clearly increasing with rf bias.

The rf bias could enhance the crystallinity of the film. But also note that the excess bias resulted in the degradation of the film crystallinity. It is clear that a high negative bias near V=-350V was suited to crystallize the film.



3.3 Effect of substrate temperature

Despite the high lithium flux at  $I_{Li}=60~120$ mA, Li-Nb-O phases were not confirmed at T=300K. The low substrate temperature may have been responsible for this. In this section, we conducted experiments at almost the same conditions as the previous section but at a higher substrate temperature, in order to verify the effect of the temperature on the film crystalline phase. In Fig.5, we show the XRD patterns of films deposited at T= 600K. The crystalline phase in deposited films changes from NbO to Li<sub>2</sub>CO<sub>3</sub> with the gradual increase of I<sub>Li</sub>. Since no lithium niobate crystalline phase was confirmed in XRD patterns, the lithium oxide and the niobium oxide could not have been incorporated into the film at the same rate. The high temperature might be responsible for this segregation.

The film was transparent and the surface was smooth for  $I_{Li}=35$ mA, while the films which contained  $Li_2CO_3$  had rough surfaces. Although the deposition rate was >3nm/s for all the samples, the lithium niobate phase which we had expected, was not formed. The  $Li_2CO_3$  could be formed by reacting amorphous lithium oxide in films with the  $CO_2$  in the atmosphere, after the films were taken out of vacuum ( $Li_2O + CO_2 = Li_2CO_3$ ). It was demonstrated by the fact that the transparent film surface gradually turned white and crumbled.

In order to incorporate the lithium oxide into the film with the niobium oxide, we conducted depositions at a higher temperature T=700K. The other conditions are as follows; V=-400V,  $I_{Nb}$ =250 mA,  $I_{Li}$ =60~120mA. We obtained films with smooth surfaces at a deposition rate of over >1nm/s at all the  $I_{Li}$ . We show the XRD patterns of deposited films in Fig.6. All the samples showed the diffraction peaks of Li<sub>3</sub>NbO<sub>4</sub>. At  $I_{Li}$ =120mA, LiNbO<sub>3</sub> (006) and (122) peaks were also confirmed. There was no dramatic change in the crystal phase of the film, despite the difference in lithium flux. The crystal-





Fig.6 XRD patterns of films deposited at I<sub>Nb</sub>=250mA V=-400V T=700K Ar=2x10<sup>-4</sup>Torr at various I<sub>L1</sub> (mA)

linity of  $Li_3NbO_4$ , however, improved gradually with additional Li vapor flux.

It is clear that both the high  $I_{Li}$  and the high substrate temperature were needed to incorporate  $Li_2O$  into the film. The sticking coefficient of Li was much lower than that of Nb, considering the facts that Li atom has a lighter mass than Nb atom and that the Li melting point (454K) is lower than Nb (2750K). Therefore, Li would be more likely to re-evaporate from the film at high substrate temperatures. Moreover, in the other previous reports of LiNbO<sub>3</sub> deposition(9), Li rich targets were used for PLD and sputtering methods. Thus, the need of high  $I_{Li}$  was probably responsible for the deposition of crystalline phase of lithium niobate.

### 4. CONCLUSION

We obtained films with smooth surfaces at a fast deposition rate of over 1nm/s for all samples deposited at  $I_{Nb}>250$ mA, excluding films containing  $Li_2CO_3$ . The negative bias was an important factor in film crystallinity.

The crystalline phase in the films changed from NbO to  $Li_2CO_3$  and then to  $Li_3NbO_4$  and  $LiNbO_3$  with gradual increase of lithium flux. Furthermore, the crys-

tallinity of  $Li_3NbO_4$  improved with the increase of the electron beam current of lithium source.

At room temperature, there were no crystalline phases containing lithium. At 600K, crystalline phases containing Nb or Li were confirmed, but lithium oxides and niobium oxides might be segregated. At higher 700K,  $LiO_2$  was incorporated into the film and  $Li_3NbO_4$  and  $LiNbO_3$  were confirmed as the dominant crystal phase at  $I_{Li}$ =120mA.

These results indicate that a high Li flux at a high temperature (T=700K) and high negative bias (V= -400V) was suited for the fabrication of LiNbO<sub>3</sub>.

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