

Epitaxy control and interfacial Coulomb's potential of LiNbO_3 thin films on R-cut sapphire.

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Formation mechanism of LiNbO_3 film with a new epitaxial orientation, $(10\bar{1}0)$, on R-cut sapphire was studied. The $(01\bar{1}2)$ textured film changed to $(10\bar{1}0)$ through $(11\bar{2}0)$ one by increasing Li concentration in films. The $(01\bar{1}2)$ and $(10\bar{1}0)$ textured films were epitaxial films. Based on the consideration of degree of freedom in sharing of octahedron containing Li and Nb, sufficient Li concentration and effect of interfacial restriction are considered to promote the formation of the $(10\bar{1}0)$ epitaxial film. If deposition is performed under the conditions which $(10\bar{1}0)$ epitaxial film is formed, excellent epitaxial film can be formed because the interface between $(10\bar{1}0)$ LiNbO_3 and $(01\bar{1}2)$ sapphire has larger cohesive energy.

1. INTRODUCTION

LiNbO_3 thin films on sapphire are very attractive composites for use in surface acoustic wave (SAW) device [1]. Although there are many reports about crystal growth of LiNbO_3 thin films using various techniques from the '70's [2], there are few reports which describe crystallographic evaluation in detail. Furthermore, there is no report about control of epitaxial orientation without changing the substrate. We have succeeded in controlling the epitaxial orientation of ionically bonded LN films on R-cut, $(01\bar{1}2)$, sapphire [3]. That is, we formed $(01\bar{1}2)$ and $(10\bar{1}0)$ epitaxial films. Recently, Shibata et al. formed $(10\bar{1}0)$ textured film on R-cut sapphire, though they do not control the preferred orientation [4]. As the new epitaxial relationship, $(10\bar{1}0)$ LN/ $(01\bar{1}2)$ sapphire, is very important for the SAW device application, we have performed further studies to understand the formation mechanism.

This paper describes the mechanism on controlling the epitaxial growth of LiNbO_3 thin films deposited on R-cut sapphire.

2. EXPERIMENTAL PROCEDURE

LN films were prepared by an rf-magnetron sputtering apparatus. To change Li/Nb ratio widely, composition in target, rf power, substrate temperature (T_s), total sputtering gas ($\text{Ar}+\text{O}_2$)

pressure, and the gas composition ($\text{Ar}:\text{O}_2$) were widely changed, because it has been understood that Li concentration in the film was changed by changing these parameters [3,5]. To evaluate the preferred orientation parallel to the film surface and film stress, X-ray diffractometer (XRD) was used. Reflection of high energy electron diffraction (RHEED) and X-ray Laue method (back-reflection) were used to confirm the epitaxial relationships in the growth plane. The composition of the films was measured by using secondary ion mass spectroscopy (SIMS). The crystallinity of the films was evaluated by rocking curve (R.C) method using X-ray double crystal spectrometer (XDCS).

3. RESULTS AND DISCUSSION

As mentioned above, we have confirmed that increasing the Li concentration in the target, rf power, total gas pressure, and O_2 concentration in sputtering gas, and decreasing the T_s , promotes the increasing the Li concentration in the film. The $(01\bar{1}2)$ textured film changes to $(10\bar{1}0)$ through $(11\bar{2}0)$ textured one by increasing Li concentration in the films [3]. Relationships among change in the texture of LN films, Li concentration in the film and deposition conditions are listed in Table 1.

Table 1 Change in the texture of LN film by varying the sputtering conditions.

Li concentration in targets	Low \longleftrightarrow High
rf power	Low \longleftrightarrow High
total sputtering gas pressure	Low \longleftrightarrow High
Oxygen partial pressure	Low \longleftrightarrow High
substrate temperature	High \longleftrightarrow Low
Li concentration in films	Low \longleftrightarrow High
epitaxial orientation	(01 $\bar{1}$ 2) \longleftrightarrow (10 $\bar{1}$ 0)

As films obtained so far displayed some texture, we attempted to find the optimum conditions to form the (01 $\bar{1}$ 2) and (10 $\bar{1}$ 0) epitaxial films. Figure 1 (a) shows the XRD spectrum from the (01 $\bar{1}$ 2) film. Only {012} diffraction lines are observed. The deposition conditions are the Li:Nb in the target of 3:1, rf power of 75 W, T_s of 700 °C, Ar:O₂ of 1:2 and total gas pressure of 25 mTorr. LN film with (10 $\bar{1}$ 0) preferred orientation is obtained under the deposition conditions of the Li:Nb in the target of 3:1, rf power of 75 W, T_s of 650 °C, Ar:O₂ of 1:2 and total gas pressure of 15 mTorr as shown in fig.1 (b).

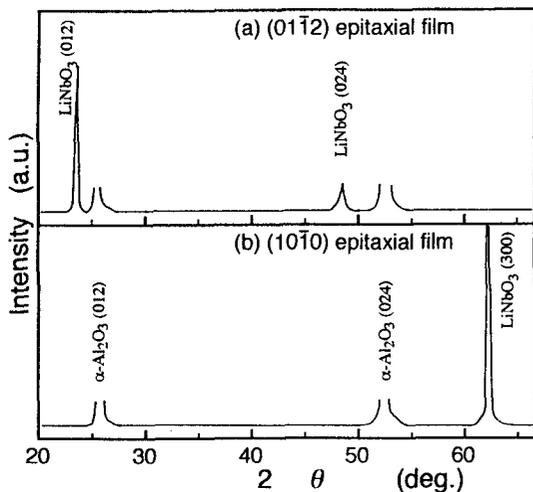


Fig.1 XRD spectra from the (01 $\bar{1}$ 2), (a), and (10 $\bar{1}$ 0), (b), epitaxial films.

We succeeded in controlling the preferred orientation of LN film on R-cut sapphire and obtaining films with a preferred orientation. However, we do not aware whether these films are epitaxial films. Then, we confirm the epitaxial

relationships in the growth plane using RHEED and X-ray Laue method. At first, the (10 $\bar{1}$ 0) epitaxial film was seemed to be a excellent single crystalline LiNbO₃. Furthermore, the crystallinity and the roughness of (10 $\bar{1}$ 0) epitaxial film surface was better than those of (01 $\bar{1}$ 2) film surface from the RHEED analyses. However, it was revealed that these epitaxial films have double positioning structure (180° domain structure) by detailed analysis using X-ray Laue method. That is, each epitaxial film has two epitaxial relationships with respect to the substrate, [01 $\bar{1}$ 1] LN//[01 $\bar{1}$ 1] sapphire and [0 $\bar{1}$ 11] LN//[01 $\bar{1}$ 1] sapphire for (01 $\bar{1}$ 2) LN, and [0001] LN//[2 $\bar{1}$ 10] sapphire and [000 $\bar{1}$] LN//[2 $\bar{1}$ 10] sapphire for (10 $\bar{1}$ 0) LN. We did not aware this fact from RHEED analyses because diffraction patterns by the incident directions of electron beam we used do not change if the sample has double positioning structure.

R.C. measurements were performed to evaluate the crystallinity of the each epitaxial film using XDCS with and without detector slit. The comparison of the FWHMs of R.C.s leads to that the (10 $\bar{1}$ 0) film has better crystallinity. However, as the decrease of FWHM of (01 $\bar{1}$ 2) film when detector slit with 150 μm width is used is larger than that of (10 $\bar{1}$ 0) film, (10 $\bar{1}$ 0) film has larger distribution of lattice spacing.

We have also obtained the film stresses of both films as -1.37×10^{10} dyn/cm² for (01 $\bar{1}$ 2) film and of -1.68×10^{10} dyn/cm² for (10 $\bar{1}$ 0) film.

Generally, interfacial restriction, interfacial energy, E_v at hetero interface is expressed as $E_i = \sigma_s + \sigma_f - \gamma$. The σ_s and the σ_f are the surface free energies of the substrate and the film, respectively. The γ is the cohesive energy resulted from forming the interface. Thus, the interface with larger γ has an advantage in forming epitaxial film. We calculated the cohesive energies at (10 $\bar{1}$ 0) and (01 $\bar{1}$ 2) epitaxial film/(01 $\bar{1}$ 2) sapphire interfaces to evaluate the interfacial restriction. The cohesive energy was estimated by only Coulomb's potential. We used the rigid-lattice approximation, and each atomic site was substituted by a point ionic charge. The energy was calculated using hemispherical film with

the diameter of 22~60Å which contains about 1300~8000 ions and the substrate with sufficiently larger diameter than that of films. At first, to seek the most stable position of the film hemisphere, translation operation was performed. Then, to find the stable epitaxial relationship, the film hemisphere was rotated on the substrate.

Figure 2 shows the calculated cohesive energy against the relative angle between $[0\bar{1}11]$ LN and $[0\bar{1}11]$ sapphire for the $(01\bar{1}2)$ film, and $[0001]$ LN and $[0\bar{1}11]$ sapphire for the $(10\bar{1}0)$ film.

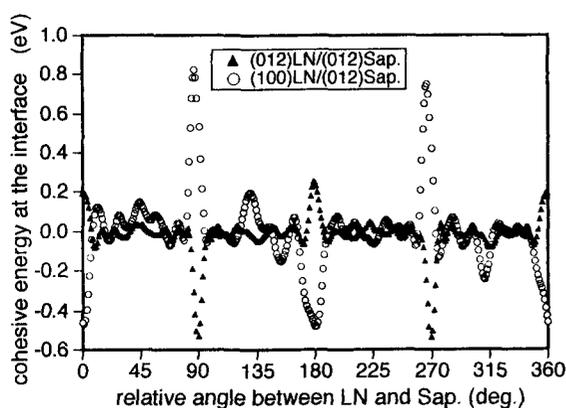


Fig.2 Change in cohesive energy at the $(10\bar{1}0)$ and $(01\bar{1}2)$ LN / $(01\bar{1}2)$ sapphire interfaces against the relative angle between $[0\bar{1}11]$ LN and $[0\bar{1}11]$ sapphire for the $(01\bar{1}2)$ film, and $[0001]$ LN and $[0\bar{1}11]$ sapphire for the $(10\bar{1}0)$ film.

In this calculation, film hemispheres with about 35Å of diameter were used. In this system, that is, there are two stable epitaxial relationships, and they coincide with the experimental result. For the $(10\bar{1}0)$ LN/ $(01\bar{1}2)$ sapphire interface, the stable angles also coincide with the experimental result. Furthermore, it is revealed that the $(10\bar{1}0)$ LN/ $(01\bar{1}2)$ sapphire interface is stabler, because the maximum cohesive energy at the interface is much larger than that at the $(01\bar{1}2)$ LN/ $(01\bar{1}2)$ sapphire interface. Therefore, it is considered that the crystallinity of the $(10\bar{1}0)$ LN film was better.

As there are large lattice mismatches at the $(01\bar{1}2)$ LN/ $(01\bar{1}2)$ sapphire interface, the increasing the film diameter causes the decreasing the cohesive energy. Figure 3 shows the diameter

dependence of the cohesive energy at the $(01\bar{1}2)$ LN/ $(01\bar{1}2)$ sapphire interface. In this system, the film with the diameter of larger than 60Å does not grow epitaxially on the $(01\bar{1}2)$ sapphire, if the film had the rigid-lattice without any defects. Of course, the decreasing the cohesive energy by increasing the film diameter is relieved by stress in the film.

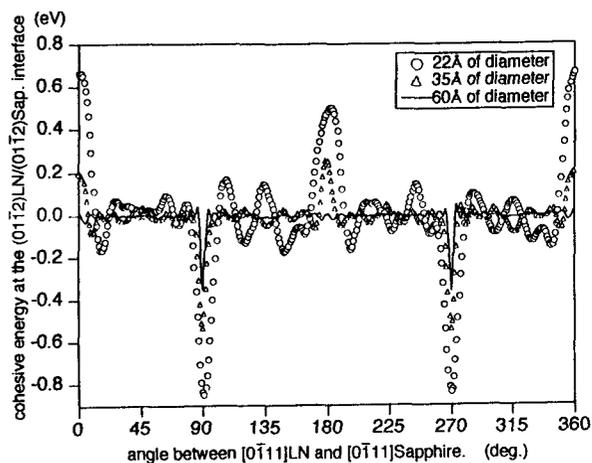


Fig.3 Film diameter dependence of the cohesive energy at the $(01\bar{1}2)$ / $(01\bar{1}2)$ sapphire interfaces.

Figure 4 shows change in the cohesive energy at the $(10\bar{1}0)$ LN/ $(01\bar{1}2)$ sapphire interface by increasing the film diameter (number of ions contained in the film). Open circles represent the cohesive energy at the rigid film/substrate interface, and closed circles represent that using about 8% stressed film.

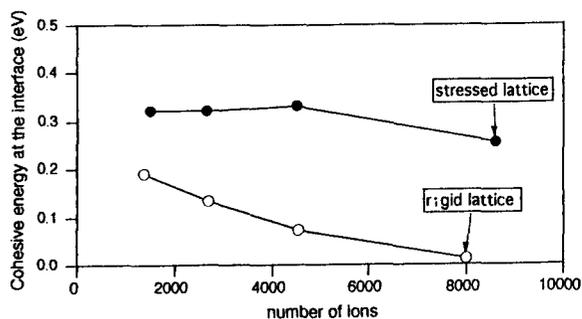
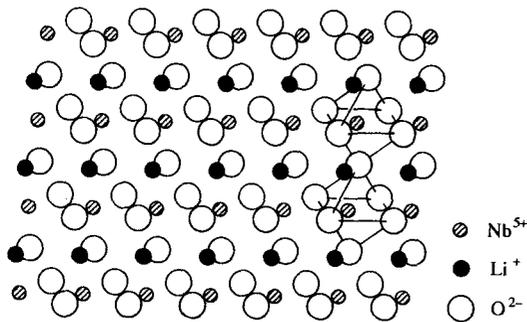


Fig.4 Change in cohesive energy at the $(01\bar{1}2)$ LN/ $(01\bar{1}2)$ sapphire by increasing the film diameter (number of ions contained in the film).

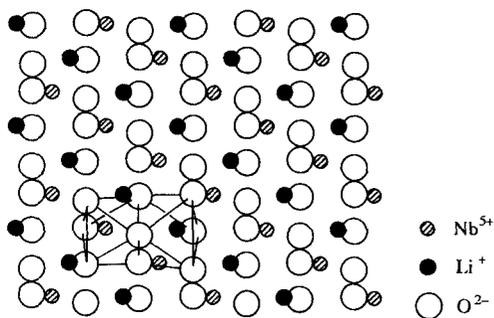
We can understand why the (10 $\bar{1}$ 0) LN on (01 $\bar{1}$ 2) sapphire has better crystallinity. Then, why does the (01 $\bar{1}$ 2) textured film change to (10 $\bar{1}$ 0) through (11 $\bar{2}$ 0) one by increasing Li concentration in the films?

The ionic arrangement of LN was calculated by using its space group and the atomic position to consider the formation mechanisms of (01 $\bar{1}$ 2) and (10 $\bar{1}$ 0) epitaxial films.

Figure 5 represents a cross sectional view of each plane. LiNbO₃ consists of octahedra containing a Li ion and those containing a Nb ion, and the degree of freedom in sharing between each octahedron changes depending on the crystal orientation. For example, sharing corner has the largest degree of freedom in the sharing, and the sharing face the least degree of freedom.



(a) Cross sectional view of (01 $\bar{1}$ 2) plane



(b) Cross sectional view of (10 $\bar{1}$ 0) plane

Fig.5 Cross sectional views of LN films

In the case of (01 $\bar{1}$ 2) epitaxial film formation, each ion forms a line, which makes a layered structure along the growth orientation. Also, octahedra containing each cation make a layered structure. That is, octahedron containing Nb can link the next octahedron containing Nb by shar-

ing corner passing over the octahedron containing Li. Therefore, the (01 $\bar{1}$ 2) epitaxial film can be formed under Li-poor conditions. For (10 $\bar{1}$ 0) epitaxial films, both octahedra coexist in a same plane, and they link by sharing face to each other. Both octahedra link by sharing edge toward the growth orientation. It seems that it is therefore difficult to form the (10 $\bar{1}$ 0) epitaxial film without the stoichiometric Li concentration.

4. CONCLUSION

We succeeded in controlling the preferred orientation of LN film on R-cut sapphire, and (01 $\bar{1}$ 2) and (10 $\bar{1}$ 0) epitaxial films were obtained. Their experimental epitaxial orientations coincide with the calculated results of the cohesive energy at both interfaces.

Based on the consideration of degree of freedom in sharing of octahedron containing Li and Nb, it is considered that the (01 $\bar{1}$ 2) epitaxial film can be formed even under Li poor condition, however, sufficient Li concentration needs to form the (10 $\bar{1}$ 0) epitaxial film. If deposition is performed under the conditions which (10 $\bar{1}$ 0) epitaxial film is formed, excellent film can be formed because the interface between (10 $\bar{1}$ 0) LN and (01 $\bar{1}$ 2) sapphire has larger cohesive energy.

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