Diffusion of Aluminum, Scandium and Gallium Ions into Lithium Niobate Single Crystals

Hajime HANEDA, Joyce K. YAMAMOTO[†], Kenji KITAMURA and Shigeyuki KIMURA

National Institute for Research in Inorganic Materials, 1-1, Namiki, Tsukuba-shi, Ibaraki 305

ニオブ酸リチウム単結晶中の Al, Sc 及び Ga イオンの拡散

羽田 肇・Joyce K. Yamamoto[†]・北村健二・木村茂行

無機材質研究所, 305 茨城県つくば市並木 1-1

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Diffusion of aluminum, scandium and gallium ions in single crystals has been studied. Stoichiometric crystals have been grown by the Czochralski method using a double crucible and automatic powder supply system. Diffusant concentration profiles were measured by secondary ion mass spectrometry. The diffusivities of all ions depended on the Li/Nb ratio of single crystals. The diffusion coefficients were larger in the samples with lithium deficient composition than in that with stoichiometric composition. This behavior was explained by a cation vacancy model in the lithium niobate lattice.

Key-words: Lithium niobate, Diffusion, Impurity, Stoichiometry, Defect structure, Aluminum, Gallium, Scandium

1. Introduction

LiNbO₃ is an opto-electronic material of current interest for the fabrication of waveguide device. Opto-electric switches, modulators and SHG devices have been demonstrated in this materials.¹⁾ The phase diagram of Li₂O-Nb₂O₅ system shows a single phase LiNbO₃ region extending toward a Li₂O-deficient phase boundary.²⁾ It has been revealed that some optical properties are sensitive to the Li/Nb ratio and dopants in the crystal.³⁾ A large disadvantage of this material is the low optical damage threshold against laser radiation. A recent study on laser radiation effect has indicated that the optical damage of 1 mol% Sc₂O₃ doped LiNbO₃ is approximately two times smaller than undoped crystal.⁴⁾

On the other hand most waveguides in LiNbO₃ are fabricated by patterning of an evaporated Ti layer into a desired configuration by photolithography, so some studies on Ti diffusivity in LiNbO₃ crystal have been carried out.^{5),6)} Generally, diffusion coefficients depends on the composition of the host materials. However surface reaction and doping effect have prevented understanding the clearly compositional effect in the previous studies because of heavily dop-

ing.

Difficulties in growing noncongruent melting crystals of sufficient size and of reasonable homogeneity have discouraged investigation into the effect of variations in the Li/Nb ratio. However, stoichiometric single crystals with reasonable size and homogeneity were, recently, grown by means of the Czochralski method using a double crucible and automatic powder supply system.⁷⁾ The present report focuses the compositional effect on diffusions in LiNbO₃ lattice of trivalent ions, which are aluminum, scandium and gallium. The chemical analysis was carried out by means of a secondary mass spectrometer, so the diffusion measurement could be done in the condition of low concentration of diffusants.

2. Experimental

A single crystal with the chemical composition close to the stoichiometric (hereafter denoted as SLN) was grown by the Czochralski method using a double crucible and automatic powder supply system. These procedure was described elsewhere in detail.⁷⁾ A single crystals with congruent composition (denoted; CLN) was grown by the ordinary Czochralski method. The Curie temperature measurements and chemical analysis revealed that SLN and CLN crystals have the Li₂O compositions with 49.8±1 mol% and 48.5±1 mol%, respectively.

The diffusion experiment was carried out under the condition of thin film source for diffusion species. The grown crystal was cut with a (001) plane. Surface were polished with diamond paste to mirror quality. The thin film was prepared by a dipping method.⁸⁾ The coating solution for diffusion coupling was mixed with nitrate of gallium, aluminum and scandium, diethylene glycol, and water, where metal concentration was 0.05 mol/kg. The crystals were dipped in these solutions, and dries in air at 120°C for 1 day, and then calcined at 600°C for 10 min. After these processes the oxide films with about 10 nm order thickness was formed at surface.

The diffusion annealing was carried out in air for desired duration. After diffusion annealing the depth profiles of diffusion species were evaluated by means

[†] Present Address: Mitsui Mining and Smelting Co., Ltd., Corporate Research and Development Center, Optical Crystals Research Group, 1333-2, Haraichi, Ageo-shi, Saitama 362

of a secondary ion spectroscopy (SIMS, CAMECA, IMS4f). The cesium positive ions were used as primary ions. The primary ions were accelerated with 10 keV and bombarded at the surface of sample. To maintain the constant electric field at sample surface the platinum films with 40 nm thickness were deposited at crystal surfaces by sputtering. To eliminate excess electric charge the normal incident electron gun was used at analysis. The secondary ions were detected as a form of oxide molecular negative ion (e.g. GaO^- for Ga-ion detection). An electron multiplier was used as a detector of secondary ions.

3. Results and discussion

Typical diffusion profiles of diffusion species are shown in Fig. 1. As seen in this figure, the diffusivities of all species in CLN crystals (Nb excess samples) are always larger than that in SLN crystals (stoichiometric samples). Diffusion coefficients, D , were calculated using the depth profile and following equation,⁹⁾

$$(C(x) - C_1) / (C_0 - C_1) = \text{erfc}(x / (2(Dt)^{1/2})) \quad (1)$$

where, $C(x)$ is concentration of diffusing species at depth, x and diffusion duration time, t . C_1 is initial concentration (the background intensity, chosen in present study) in solid, and C_0 , constant surface concentration. In the present calculation, concentrations were assumed to be proportional to relative secondary ion intensities. For SIMS analysis, this relation is valid in the range of under few percent of concentration in same matrix.

The calculated diffusion coefficients were shown in Fig. 2 as a function of reciprocal temperature. The reported values for Ti-diffusion are also represented in Fig. 2. The diffusion coefficients in CLN crystals (nonstoichiometric composition) are larger than SLN (crystals stoichiometric).

Gallium, aluminum and scandium ions are in aliovalent state in LiNbO_3 , so the substitution of these ions to any cation site changes the defect concentration in LiNbO_3 . It is difficult that the doping effect is distinguished from the compositional effect in heavily doped samples. SIMS analysis has an advantage to analyze low level impurity in the ppm-range. However, the concentrations can not be directly obtained from the secondary ion intensities. In the present case, the concentration was estimated using the amount of initial thin film. Figure 3 shows the estimated concentration as a function of depth, that indicates that the concentration is under few percent. This level is smaller than the excess amount of niobium ions. The actual concentration is considered to be less than the value in Fig. 3 due to the solid solubility. Measured values agree with calculated values in the range of ppm order. If a dissolving effect of gallium ion on the cation defect structure exists, the depth profile are not fitted at the whole

Fig. 1. Depth profiles of secondary ion intensities. Closed circles: obsd. data in CLN samples, open circles: obsd. data in SLN samples and solid lines: cald. values using Eq. (1).
 (a) ScO^- at 1073 K,
 (b) GaO^- at 1073 K,
 (c) AlO^- at 873 K.

Fig. 2. Temperature dependences of diffusion coefficients. Closed : obsd. date in CLN samples, open: obsd. data in SLN samples.

Circle, for Al diffusion, triangle, for Sc diffusion, and rectangle, for Ga diffusion, respectively.

Solid line : Ti diffusion coefficient in congruent lithium niobate (Ref. 13).

Dotted line : Ti diffusion coefficient in congruent lithium niobate (Ref. 5).

Dashed line : Ti diffusion coefficient in congruent lithium niobate (Ref. 6).

Dot and dashed line : Ti diffusion in stoichiometric lithium niobate (Ref. 6).

Fig. 3. Ga concentration as a function of depth in CLN sample, calcd. with the thickness of the dipped thin film. Closed circles, obsd. data and solid line calcd. data.

range to ppm order concentration. The compositional dependence of diffusion coefficient is, therefore, caused by the original amounts of cation defects.

The variation of Nb concentration can be understood to be a Li_2O loss process from the stoichiometric composition. For this process three defect models are proposed as follows,

<Model I>

<Model II>

<Model III>

Equation (2) is for assuming the existence of oxygen and Li-site vacancy, Eq. (3) and Eq. (4), Li-site and Nb-site, respectively. Lerner et al. have claimed that the cation vacancy model without oxygen vacancy (Eq. (3) or Eq. (4)) is a reasonable interpretation more than oxygen vacancy model according to the result of density measurement.¹⁰⁾ Recent X-ray and neutron diffraction analysis of the defect structure of lithium niobate has indicated that vacancies exist on the Li-site and the Nb cation lattice is complete¹¹⁾ (model II), what is harmony with the theoretical calculation of defect.¹²⁾

According to the model II, the trivalent ions diffuse through the lithium vacancies. Although the diffusing ions preferentially substitute for any cation site, the diffusivity along *c*-axis increases with the vacancy concentration at any cation site, that causes the increasing of diffusivity in Nb rich composition.

The levels of diffusion coefficient of aluminum and scandium ions are almost same as Ti diffusion coefficient. The gallium ion has a tendency with higher diffusivity than titanium ion. The degree of discrepancy between CLN and SLN of trivalent ions is greater than that of titanium. This suggests the difference of preferentiality for cation site among these ions.

References

- 1) R. C. Alferness, *IEEE J. Quantum Electron.*, QE-17, 946-59 (1981).
- 2) J. R. Carruthers, G. E. Peterson, M. Grasso and P. M. Bridenbaugh, *J. Appl. Phys.*, 42, 1846-51 (1971).
- 3) for example, B. Chen and A. C. Pastor, *Appl. Phys. Lett.*, 30, 376-79 (1977).
- 4) J. K. Yamamoto, K. Kitamura, N. Iyi, S. Kimura, Y. Furukawa and M. Sato, to be published in *Appl. Phys. Lett.*
- 5) W. K. Burns, P. H. Klein, E. J. West and L. E. Plew, *J. Appl. Phys.*, 50, 6175-82 (1979).
- 6) R. J. Holmes and D. M. Smyth, *J. Appl. Phys.*, 55, 3531-35 (1984).
- 7) K. Kitamura, J. K. Yamamoto, N. Iyi, S. Kimura and T. Hayashi, *J. Cryst. Growth*, 116, 327-32 (1992).
- 8) M. Takakamo, H. Terada, A. Watanabe, H. Haneda, T. Mitsuhashi and S. Shirasaki, Proc. 2nd Japan Int. SAMPE Symp., 264, Nikkan Kogyo Shinbun (1991).
- 9) J. Crank, "Mathematic of Diffusion", Oxford Press (1955) pp. 26-41.
- 10) P. Lerner, C. Legras and J. P. Duman, *J. Cryst. Growth*, 3/4, 231-35 (1968).
- 11) N. Iyi, K. Kitamura, F. Izumi, J. K. Yamamoto, H. Hayashi, H. Asano and S. Kimura, to be published in *J. Solid State Chem.*
- 12) H. Donnerberg, S. M. Tomlinson, C. R. A. Catlow and O. F. Schirmer, *Phys. Rev. B* 40, 11909-16 (1989).
- 13) M. Fukuma, J. Noda and H. Iwasaki, *J. Appl. Phys.*, 49, 3693-98 (1978).