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doi: 10.1063/1.108282

Elastic properties of 5-mol % MgO doped $LiNbO_3$ crystals measured by line focus beam acoustic microscopy

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(Received 26 May 1992; accepted for publication 3 September 1992)

An ultrasonic method of line focus beam (LFB) acoustic microscopy is applied to quantitative characterization of $LiNbO_3$ wafers destined for optical use. Commercial *Z*-cut wafers obtained from two optical grade $LiNbO_3$ crystals, with and without 5-mol % MgO doping, are evaluated by measuring the leaky surface acoustic wave (LSAW) velocities. Doping of 5-mol % MgO to $LiNbO_3$ results in an increase of about 1% in the LSAW velocities and in a decrease of about 0.1% in density. Fewer elastic inhomogeneities are observed in the undoped wafer than in the MgO doped wafer. The measured LSAW velocities are compared with the chemical and physical properties, chemical composition, density, lattice constant, refractive index, and Curie temperature. It is shown that the LFB system has a much greater sensitivity and resolution in the determination of these properties than do other analytical methods. It is suggested that this method should be adopted as a new analytical technique for establishment of the crystal growth conditions and for evaluation of optical grade $LiNbO_3$ wafers.

Lithium niobate ($LiNbO_3$) is currently the most attractive ferroelectric material for integrated optoelectronic devices because of its favorable piezoelectric, acousto-optic, electro-optic, and nonlinear optical properties. It is one of the more important industrial subjects to provide high quality large-diameter substrates of the 5-mol % MgO doped $LiNbO_3$[1–5] with optically homogeneous properties, which are optical damage resistant. Much effort has been expended for establishing the crystal growth conditions for mass production and the evaluation procedures of crystals/wafers. Material analyses and evaluation have been conventionally conducted by measuring the chemical composition, the lattice constant, and imperfection in crystals by x-ray techniques, the Curie temperature by differential temperature analysis, the refractive index by the prism coupler method, the phase-matching temperature for second harmonic generation, and the distribution of MgO by electron probe microanalysis.[2–5] It might be considered that the variations in optical properties are mainly due to the distribution of chemical composition ratios of Mg/Li/Nb on a wafer and among wafers/crystals. Recently, a new method of quantitative material characterization, viz., line focus beam (LFB) acoustic microscopy[6] has become available and has been applied to studies of $LiNbO_3$ and $LiTaO_3$ crystals for surface acoustic wave (SAW) devices.[6–9] It has been demonstrated, from the investigation of the congruent chemical composition of $LiNbO_3$, that the LFB system exhibits resolution better than 0.005 mol % of Li_2O, which corresponds to 0.2 °C in the Curie temperature.[9] Thus an ultrasonic method using LFB acoustic microscopy has been newly proposed for characterization of optical-use $LiNbO_3$ and $LiTaO_3$ crystals and of Ti-diffused and proton-exchanged layers in device fabrication processes.[8,9]

The purpose of this letter is to demonstrate that this ultrasonic method is a promising candidate for a new characterization technique for optical material problems. Studies involving velocity measurements have been carried out for commercially available optical grade $LiNbO_3$ wafers with and without 5-mol % MgO dopant. The results are compared with the chemical and physical properties obtained by the other analytical methods.

The method and the system of LFB acoustic microscopy have been described in detail elsewhere.[6,7] Leaky surface acoustic waves (LSAWs), excited on the boundary between the solid specimens and the coupling liquid of distilled water, are employed for measurements. The phase velocities are determined through the $V(z)$ curve analysis.[6] Material anisotropy is measured as variations of LSAW velocities as a function of the wave propagation direction. The 225-MHz system employed is applicable to two-dimensional inspection of elastic inhomogeneities on a wafer. More recently, the relative accuracy of the LSAW velocity measurements has been estimated to be better than $\pm 0.005\%$ for a single measurement at a chosen position and $\pm 0.01\%$ over the entire scanning of a 75×75 mm area.

Z-cut $LiNbO_3$ wafers, with 3 in. diam, 1 mm thickness, and the orientation flat perpendicular to the crystallographic *y* axis, were obtained from the Yamaju Ceramics Co., Seto, Japan. Two optical grade $LiNbO_3$ crystals with and without 5-mol % MgO dopant were grown along the *z* axis having a crystal length of about 50 mm. Two wafers, taken at the wafer positions of 12 mm from the crystal head of each boule, were used for measurements of LSAW velocities, densities, and lattice constants, and another two wafers obtained at 16.5 mm wafer position were used for measurements of chemical compositions, refractive indices, and Curie temperatures.

First, measurements of the angular dependence of the LSAW velocities were made at the center of the negative *z* surfaces for two undoped and 5-mol % MgO doped $LiNbO_3$ wafers, in order to observe the effect of doping on the elastic properties, as shown in Fig. 1. Reflecting the crystal symmetry, the observed velocities vary remarkably with wave propagation direction and the same velocity values are obtained at 60° intervals for each sample, which

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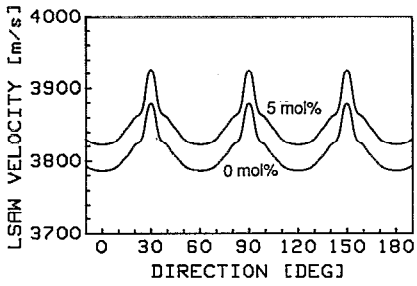

FIG. 1. Measured LSAW velocities for z-cut $LiNbO_3$ wafers with and without 5-mol % MgO dopant.

means that both samples are prepared with just the z-cut crystal surface. The propagation directions of 0° and 90° in Fig. 1 correspond to the x and y axes, respectively, on the z-cut $LiNbO_3$ surface. The doping of 5-mol % MgO results in the velocity increasing in all the directions. For example, the average increases are measured to be 35.96 m/s (0.95%) between 3786.21 and 3822.17 m/s for the equivalent x-axis directions and to be 46.52 m/s (1.20%) between 3879.18 and 3925.70 m/s for the equivalent y-axis directions, as given in Table I. Measurements of the densities of the wafers showed that the 5-mol % MgO doping reduced the density by 4.5 kg/m^3 (0.097%), from 4647.3 to 4642.8 kg/m^3.

As seen from our previous investigation of $LiNbO_3$ crystals for SAW devices, elastic inhomogeneities are in general observed on commercial $LiNbO_3$ wafers.[7] For this reason, LSAW velocity measurements for the x- and y-axis propagation directions were performed by scanning the undoped and 5-mol % MgO doped $LiNbO_3$ wafer surfaces in 1 mm steps over a distance of 66 mm along the diameter directions, parallel and perpendicular to the orientation flat. The results measured along the x-axis scanning line, when LSAWs propagate in the y-axis direction for the undoped and doped wafers, are typically presented in Figs. 2(a) and 2(b), respectively. For the undoped specimen, the velocity variations are fairly small: The average velocities are 3878.66 m/s with a maximum difference of 0.59 m/s (0.015%) for the x-scanning and 3878.96 m/s with 0.63 m/s (0.016%) for the y-scanning. On the other hand, for the doped specimen, relatively large variations in the velocity, decreasing gradually in the outer regions, are observed with the slightly different profiles: The average velocities are 3924.57 m/s with a maximum difference of 2.59 m/s (0.066%) for the x-scanning and 3924.66 m/s with 2.32 m/s (0.059%) for the y-scanning. In addition to the velocity variations due to the doping effect illustrated in

TABLE I. LSAW velocities and densities of z-cut $LiNbO_3$.

Specimen	LSAW velocity v_{lsaw}(m/s) x-axis	y-axis	Density ρ(kg/m^3)
undoped	3786.21	3879.18	4647.3
doped	3822.17	3925.70	4642.8
difference	+35.96	+46.52	−4.5

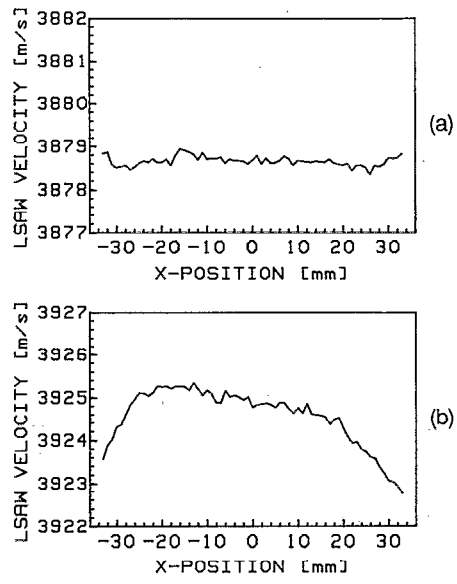

FIG. 2. LSAW velocity variations along x-axis diameter direction for zy $LiNbO_3$ wafers. (a) Undoped, (b) 5-mol % MgO doped.

Fig. 1, the velocity variations for the MgO doped specimen are clearly larger than those for the undoped specimen. Even for LSAWs propagating in the x-axis direction, similar profiles of the velocity variations, as seen for the y-axis wave propagation direction, were observed for the corresponding scanning lines. The same level of elastic inhomogeneities was obtained in these experiments for both the x- and y-axis wave propagation directions.

Changes in the LSAW velocities and densities due to the doping of 5-mol % MgO to $LiNbO_3$ must be related to changes of the other chemical and physical properties. The chemical compositions of Mg/Li/Nb, the c-axis lattice constant, the ordinary and extraordinary refractive indices n_o and n_e, and the Curie temperatures T_c were measured, in order to be able to discuss the sensitivity of the LFB system. These measured data are tabulated in Table II. Chemical analysis made the compositional differences quantitatively clear with a measurement accuracy around 1 mol %. The effect of the doping appears in the expansion of c by 0.0044 Å, in the decrease of n_e by 0.0097, which is larger than that for n_o, and in the increase of T_c by 78 °C. Taking the larger velocity change, as shown in Table I, of 46.52 m/s along the y-axis wave propagation direction, the sensitivities to the compositions are calculated to be 0.105 mol %/(m/s) to MgO, 0.0559 mol %/(m/s) to Li_2O, and 0.0494 mol %/(m/s) to Nb_2O_5, respectively, under the linear approximation in the chemical and physical parameters between the two states, viz., with and without the 5-mol % MgO dopant. With the system stability in measurements, the resolutions can be estimated to be better than 0.02 mol % to MgO, 0.01 mol % to Li_2O, and 0.01 mol % to Nb_2O_5. In a similar way, the sensitivities to the physical parameters are calculated as presented in Table III, and finally the resolutions are determined as better than 0.02 kg/m^3 for ρ, 2×10^{-5} Å for c, 4×10^{-5} for n_e, and 0.3 °C for T_c. Considering the measurement errors to

TABLE II. Changes of other chemical and physical properties by 5-mol % MgO doping to $LiNbO_3$.

Specimen	Composition (mol %) MgO	Li_2O	Nb_2O_5	Lattice constant c(Å)	Refractive index at 6328 Å n_o	n_e	Curie temperature T_c(°C)
undoped	0	48.4	51.6	13.8659	2.2880	2.2031	1132
doped	4.9	45.8	49.3	13.8703	2.2829	2.1934	1210
difference	+4.9	−2.6	−2.3	+0.0044	−0.0051	−0.0097	+78

be about ± 0.2 kg/m^3 for the density, about $\pm 3\times 10^{-4}$ Å for the lattice constant, about $\pm 2\times 10^{-4}$ for the refractive index, and ± 2 °C for the Curie temperature, we can say that this ultrasonic method has a much greater sensitivity and resolution than any present systems.

This study has demonstrated successfully that LFB acoustic microscopy is very useful as a new quantitative evaluation method for evaluating $LiNbO_3$ wafers/crystals produced for integrated optoelectronic devices, through measurements of the elastic properties, which are directly interrelated to the other chemical and physical properties of the ferroelectric materials. It has been clarified for the first time that the 5-mol % MgO doping for $LiNbO_3$ provides the elastic properties with increases of about 1% in LSAW velocities for all wave propagation directions and with decreases of 0.097% in density. Some significant inhomogeneities of the LSAW velocity variations of about 0.066% for the doped specimen do exist. Such inhomogeneities may be a final point for discussing mass production of the devices for high reproducibility of properties. Homogeneity of the chemical composition distribution in the crystal is essentially dependent upon the crystal growth conditions such as the chemical composition of the melt and the rotating and pulling speeds. Therefore, information of inhomogeneities among wafers/crystals obtained from this kind of evaluation can be fed back to adjustment of the conditions, leading to a superior product.

TABLE III. Sensitivity and resolution to other chemical and physical properties for zy MgO:$LiNbO_3$ by LSAW velocity measurements.

Property	Sensitivity	Resolution
MgO	0.105 mol %/(m/s)	0.02 mol %
Li_2O	0.0559 mol %/(m/s)	0.01 mol %
Nb_2O_5	0.0494 mol %/(m/s)	0.01 mol %
ρ	0.0967 kg/m^3/(m/s)	0.02 kg/m^3
c	9.46×10^{-5} Å/(m/s)	2×10^{-5} Å
n_e	2.09×10^{-4} 1/(m/s)	4×10^{-5}
T_c	1.68 °C/(m/s)	0.3 °C

The authors would like to thank T. Sannomiya for his helpful discussions, I. Sahashi and T. Sasamata, Yamaju Ceramics Co., for providing the wafers used in these experiments and for providing the data of the optical refractive indices obtained by the prism coupler method and the Curie temperatures by differential temperature analysis, and K. Masuda, Shimazu Corp., for the measurement of the chemical compositions by sequential plasma spectrometry. This work was supported in part by Research Grant-in-Aids from the Ministry of Education, Science and Culture of Japan and from the Toyota Physical and Chemical Research Institute.

[1] G. G. Zhong, J. Jin, and Z. K. Wu, Proc. 11th International Quantum Electronics, IEEE Cat. No. 80CH1561-0, 631 (1980).
[2] D. A. Bryan, R. R. Rice, R. Gerson, H. E. Tomaschke, K. L. Sweeney, and L. E. Halliburton, Opt. Eng. **24**, 138 (1985).
[3] B. C. Grabmaier and F. Otto, J. Cryst. Growth **79**, 682 (1986).
[4] G. E. Peterson and S. R. Lunt, Ferroelectrics **75**, 99 (1987).
[5] Y. Furukawa, M. Sato, F. Nitanda, and K. Ito, J. Cryst. Growth **99**, 832 (1990).
[6] J. Kushibiki and N. Chubachi, IEEE Trans. Sonics Ultrason. **SU-32**, 189 (1985).
[7] J. Kushibiki, H. Asano, T. Ueda, and N. Chubachi, Proc. IEEE Ultrasonics Symp., IEEE Cat. No. 86CH2375-4, **2**, 783 (1986).
[8] J. Kushibiki, H. Takahashi, T. Kobayashi, and N. Chubachi, Appl. Phys. Lett **58**, 893 (1991).
[9] J. Kushibiki, H. Takahashi, T. Kobayashi, and N. Chubachi, Appl. Phys. Lett. **58**, 2622 (1991).