Calibration of Curie Temperatures for LiTaO$_3$ Single Crystals by the LFB Ultrasonic Material Characterization System

Jun-ichi Kushibiki, *Member, IEEE*, Yuji Ohashi, and Naoyuki Mishima

Abstract—The line-focus-beam ultrasonic material characterization (LFB-UMC) system is applied to a standardized comparison and evaluation of the Curie temperatures, T_C, exclusively used in evaluating the chemical compositions of commercial LiTaO$_3$ crystals by measuring the velocities of Rayleigh-type leaky surface acoustic waves (LSAWs), V_{LSAW}. We measured V_{LSAW} and T_C(standardized) under the same T_C measurement conditions for $36°YX$-LiTaO$_3$ single-crystal wafers produced by four manufacturers and related the results to the T_C(individual) measured by the individual manufacturers. The relationships between V_{LSAW} and T_C(individual) varied from one company to another, and a single straight line of the proportional relationship between V_{LSAW} and T_C(standardized) was obtained for all wafers regardless of the manufacturer. These experimental results clarify that the problem associated with T_C measurements lies in the measurement conditions and the absolute accuracy of the measurement instruments. Measurements of the center frequencies of the actual SH-type surface acoustic waves (SAW) filter devices fabricated also are compared with V_{LSAW} measurements. A method of calibrating T_C using this ultrasonic system is proposed to establish standardized specifications of SAW-device crystal wafers.

I. INTRODUCTION

THE demand for surface acoustic wave (SAW) devices has been rapidly increasing in association with the recent proliferation of mobile communications systems. Growing homogeneous crystals in a chemical composition ratio is important for realizing high-performance SAW devices; the performance of SAW devices depends on the chemical and physical properties of the substrate materials as well as on the device fabrication processes. A working group in the International Electrotechnical Commission (IEC) is currently developing standardized specifications of piezoelectric single-crystal SAW wafers [1]. More stringent quality control for single crystals, particularly their chemical compositions, will be required when the specifications are established. Dependable specifications associated

with the chemical compositions of crystal wafers and the measuring methods must be set to ensure the crystal quality. However, single crystals are evaluated and selected after the mass production process of single crystals because growing all crystals with the same chemical composition ratio is technically very difficult and costly. The Curie temperature, T_C, is closely related to the chemical composition ratio and has been widely used as an indicator for evaluating the chemical composition ratios of LiNbO$_3$ and LiTaO$_3$ single crystals. Almost all manufacturers presently evaluate crystals by measuring T_C using differential thermal analysis (DTA) [2] or differential scanning calorimetry (DSC) [3].

It is fundamentally important in material evaluations to consistently obtain the same measured values for identical specimens, even when different measurement instruments or systems are used. Therefore, the same measurement conditions, superior system stability (or measurement reproducibility), and calibration accuracy must be ensured. We have been developing and applying accurate material evaluation techniques using the line-focus-beam ultrasonic material characterization (LFB-UMC) system [4], [5]. We have improved the system [6], developed its calibration method [7], [8], and applied it to evaluating LiNbO$_3$ and LiTaO$_3$ single crystals [9]–[16]. The LFB-UMC system was applied to measure LSAW velocities, V_{LSAW}, for 42°-rotated Y-cut X-propagating ($42°YX$-) LiTaO$_3$ wafers [17] in one of our previous reports [6]. Its relationships to other chemical and physical properties (T_C, lattice constant a, Li$_2$O concentration M(Li$_2$O), and SH-type SAW velocity V_{SAW}) were clarified, and a standardized evaluation of the chemical compositions was demonstrated. We then suggested that T_C values for wafer substrates measured by different crystal manufacturers possibly differed even though their elastic properties (V_{LSAW}) were nearly equal. This was considered to have resulted from either crystals grown with the same chemical composition ratio (or T_C) but different elastic properties or crystals evaluated by different measurement instruments and/or conditions for T_C. The primary cause of the former is associated with an insufficient poling process [9], [12], [18], [19]; however, it is unlikely that single-crystal manufacturers presently encounter this problem in view of their extensive knowledge and experience. The latter problems are very important factors in standardizing SAW wafer specifications, but we know of no experiments that focus on this difficulty. The relationship between Rayleigh-

Authorized licensed use limited to: TOHOKU UNIVERSITY. Downloaded on February 4, 2010 at 01:40 from IEEE Xplore. Restrictions apply.

type V_{LSAW} and SH-type V_{SAW} also was obtained theoretically for $42°YX$-LiTaO$_3$ wafers in the previous paper [6]. However, it is important that the relationship between V_{LSAW} and V_{SAW} is investigated experimentally because V_{SAW} was not studied directly.

This paper performs a standardized comparison and evaluation of T_C to evaluate the chemical compositions of LiTaO$_3$ crystals through the V_{LSAW} measured by the most recently developed LFB-UMC system. The specimens evaluated are SH-type $36°YX$-LiTaO$_3$ single-crystal wafer substrates [20] produced by four different manufacturers. Commercially available ultra-high-frequency (UHF) SAW filters with interdigital transducers (IDTs) [21], [22] on the wafer substrates then are fabricated, and the relationship between their center frequencies and V_{LSAW} is investigated.

II. LFB-UMC System

The measurement principle of the LFB-UMC system is described in detail in the literature [4]. The mechanical system, including the ultrasonic device and specimen, in the recently developed systems is installed in a temperature-controlled chamber to stabilize the measurement environment, i.e., the temperature of the water couplant [5]. A specimen transfer system, a temperature-controlled pure-water supply/drain system, and an automatic specimen tilting stage also are provided. With this system, loading, changing, and aligning specimens are performed by remote control to ensure efficient measurements by not disturbing the stabilized measurement environment.

In this study, we use the latest LFB-UMC system we have developed; this system has achieved the highest accuracy [6]. The system maintains a resolution of $\pm0.0013\%$ for $\pm2\sigma$ (σ: standard deviation) in V_{LSAW} measurements at an arbitrarily chosen single point on a specimen surface and of $\pm0.003\%$ over a two-dimensional scanning area of 75 mm × 75 mm. The absolute accuracy of the V_{LSAW} values is about $\pm0.01\%$ after system calibration [7], [8] using a standard specimen of $36°YX$-LiTaO$_3$ plate prepared from a crystal ingot grown with 48.50 Li$_2$O-mol% [23], [24].

III. Experiments

A. Specimens

Two $36°YX$-LiTaO$_3$ single-crystal ingots chosen randomly from each of four manufacturers, A, B, C, and D, were prepared for specimens. The ingots were grown by the Czochralski method. Table I provides the dimensions of the ingots produced by each manufacturer. The diameters of the ingots of manufacturers A and B were 76 mm, and those of manufacturers C and D were 100 mm. Three wafers were sliced out of the top, middle, and bottom of each ingot. Two of the three wafers cut from each part were used for V_{LSAW} measurements, and the other was

TABLE I
DIMENSIONS OF $36°YX$-LiTaO$_3$ SINGLE-CRYSTAL INGOTS FOR
MANUFACTURERS A, B, C, AND D.

Crystal No.	Diameter [mm]	Length [mm]
A-1	76	65
A-2	76	65
B-1	76	102
B-2	76	86
C-1	100	80
C-2	100	94
D-1	100	78
D-2	100	79

used for SAW device fabrication. The wafers were approximately 0.35-mm thick with only one side optically polished. Manufacturers A and C regularly measure T_C at the top and bottom parts of their crystals, and manufacturer C additionally measured it at the middle part specifically for these experiments. Manufacturer B normally does not make T_C measurements, but the manufacturer had them conducted at the top, middle, and bottom parts of the crystals by a third party for these experiments. Manufacturer D usually measures T_C only at the bottom. The specimens used for the T_C measurements by individual manufacturers were taken out of the parts of the ingots either next to or close to the parts from which the wafers for the V_{LSAW} measurements were sliced.

B. LSAW Velocities

We measured the velocities of LSAWs propagating along the crystallographic X axis with the LFB-UMC system at five measurement points positioned at intervals of 10 mm over a range of ±20 mm in a diameter direction parallel to the X axis for the two wafer specimens sliced from the top, middle, and bottom parts of each crystal ingot. The specimens used for this measurement were thin, approximately 0.35 mm; serious effects of the waves reflected from the back surface of the specimens could thus occur in the V(z) curve measurements [25]. Moving average processing was applied to the frequency dependence of V_{LSAW} measured at 0.5-MHz steps over a range of 215 to 235 MHz to eliminate these effects, and the system was subsequently calibrated [7] to obtain the final measured values.

Fig. 1 shows the results of V_{LSAW} distributions measured on the wafers of each manufacturer. Very small V_{LSAW} variations were observed in each crystal ingot between two wafers that were cut adjacently at the top, middle, and bottom parts of the crystal, exhibiting very similar profiles. However, relatively large differences were detected between the two wafers from the middle part of the D-2 ingot. The V_{LSAW} variation on each wafer was within 0.3 m/s except on the middle-1 wafer of the D-2 ingot. The differences among the wafers of the four manufacturers were about 5 m/s. A small V_{LSAW} distribution difference of less
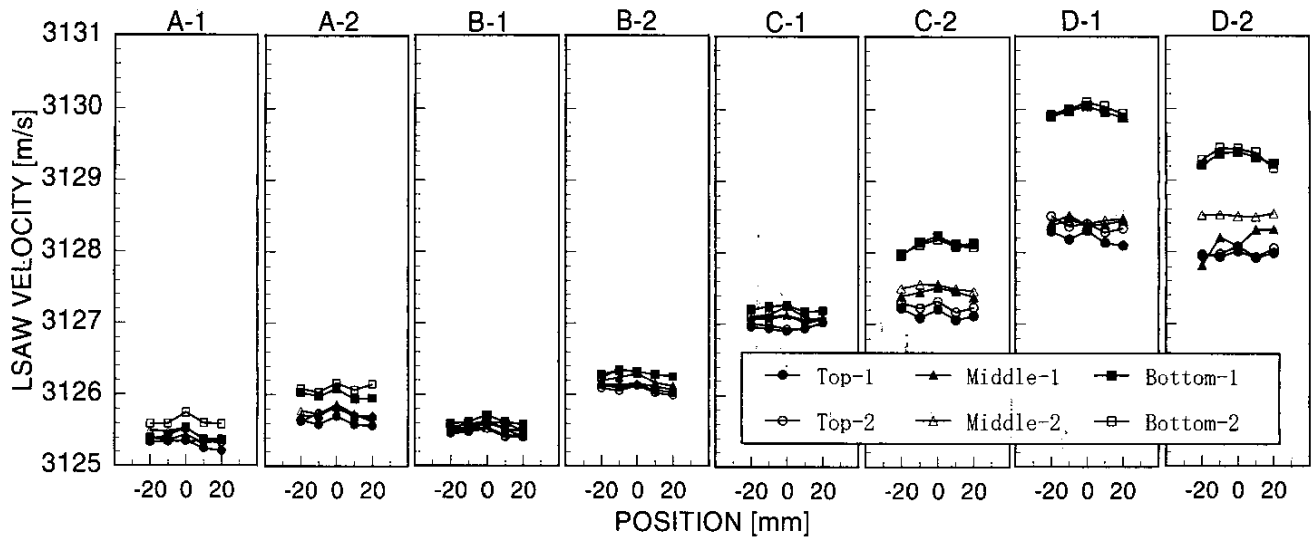
Fig. 1. LSAW velocity distributions for $36°YX$-LiTaO$_3$ wafers prepared from eight ingots produced by manufacturers A, B, C, and D, provided in Table I.

than 0.5 m/s was observed for the ingots of manufacturers A and B; but significant differences of about 1.0 m/s and 1.8 m/s were obtained for the ingots of manufacturers C and D. The measured V_{LSAW} for almost all the ingots tended to increase from the top to the bottom wafers. Significant V_{LSAW} differences between the middle and bottom wafers were observed in the D-1 and D-2 ingots in particular.

C. Curie Temperatures

1. Conditions of Individual Manufacturers: Table II shows the measurement systems and conditions of T_C for individual manufacturers. Manufacturers A, B, and C use thermal analysis methods; manufacturer D adopts a capacitance (permittivity) measurement method. The heating rate and weight and particle size of the samples also vary from one manufacturer to another. The T_C was measured for the samples taken from the parts of ingots close to the wafers used for V_{LSAW} measurements. The sampling was made at two positions (top and bottom) of the ingots from manufacturer A, at three positions (top, middle, and bottom) for those from manufacturers B and C, and only at the bottom for those from manufacturer D.

Fig. 2 shows the results of the measured T_C(individual) by the manufacturers, plotted against the average V_{LSAW} obtained in the preceding section for corresponding wafers sliced from nearly the same crystal ingot parts as the T_C was sampled. Approximated straight lines for each set of the samples of individual manufacturers were derived as the solid lines by the least-squares method, and an approximated straight line fitted to the data for the entire set of samples is represented by a dotted line. Fig. 2 indicates that T_C(individual) measured by each manufacturer is proportional to V_{LSAW} measured on the corresponding wafers produced by the same manufacturer, although the
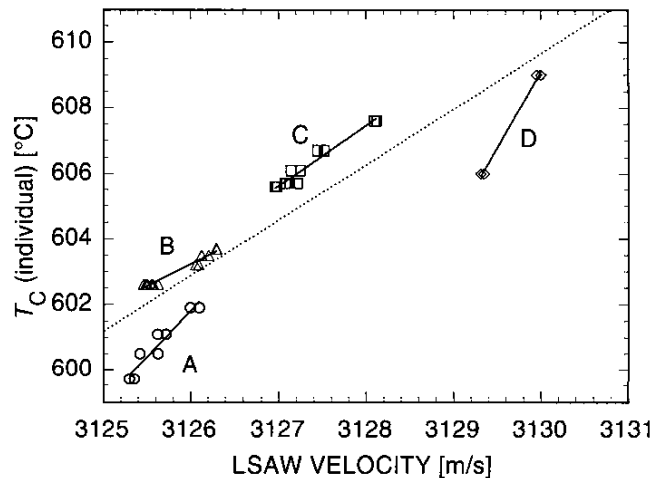

Fig. 2. Measured relationship between LSAW velocities, V_{LSAW}, and Curie temperatures, T_C(individual), measured by individual manufacturers for $36°YX$-LiTaO$_3$ wafers produced by manufacturers A, B, C, and D. Approximated lines obtained by the least-squares fitting are shown as solid lines in each set of results and as a dotted line in all results.

slopes of the approximated straight lines differ. The single straight line, $T_C = 1.6936 \cdot V_{LSAW} - 4691.2$, for the data of all four manufacturers is represented with temperature deviations of $-2.5°C$ to $1.4°C$.

2. Standardized Conditions: The T_C(standardized) was measured under the standardized conditions presented in Table III for one of the two top, middle, and bottom wafers of each manufacturer for which V_{LSAW} was measured. The wafers around the central part in an area approximately 10 mm × 10 mm were ground into powder, and the powder was passed through a 100-mesh sifter. Fifty milligrams of the sifted powder was used for the measurement. The relationship between T_C(standardized) and

TABLE II
MEASUREMENT SYSTEMS AND CONDITIONS OF T_C(INDIVIDUAL) FOR MANUFACTURERS A, B, C, AND D.

	A	B	C	D
Method	DTA	DSC	DTA	Capacitance measurement
Instrument	Rigaku TG-810	Mac Science DSC 3100S	Rigaku TG-8120	Seiko Instruments TMA-300
Heating rate	10°C/min	20°C/min	40°C/min	3°C/min
Atmosphere	N_2	Air	Air	Air
Weight or size of sample ($LiTaO_3$)	15 mg	104 mg	112 mg	$3 \times 10 \times 0.5$ mm
Particle diameter of sample	As powdered	520 μm (35 mesh)	As powdered	—
Weight of reference (Al_2O_3)	15 mg	104 mg	51 mg	—

TABLE III
MEASUREMENT SYSTEM AND CONDITIONS OF T_C(STANDARDIZED) FOR A STANDARDIZED EVALUATION.

Method	DSC
Instrument	Seiko Instruments DSC6200
Heating rate	10°C/min
Atmosphere	N_2 flow (100 ml/min)
Weight of sample ($LiTaO_3$)	50 mg
Particle diameter of sample	180 μm (100 mesh)
Weight of reference (Al_2O_3)	27 mg

Fig. 3. Measured relationship between LSAW velocities, V_{LSAW}, and Curie temperatures, T_C(standardized), measured under the standardized measurement conditions shown in Table III for $36°YX$-$LiTaO_3$ wafers produced by manufacturers A, B, C, and D. Approximated lines obtained by the least-squares fitting are shown as solid lines in each set of results and as a dotted line in all results.

the average V_{LSAW} is shown in Fig. 3. In contrast to the results given in Fig. 2, the relationship obtained for all the manufacturers is represented by a single straight line, $T_C = 1.7317 \cdot V_{LSAW} - 4809.6$, with temperature deviations of $-0.5°C$ to $0.9°C$. The results obtained for manufacturer D in Fig. 3 deviated somewhat from the line due to the greater distributions in the ingots compared with those from the other manufacturers. These results clarify that the differences among the manufacturers seen in Fig. 2 are caused by different measurement conditions and/or measurement systems for T_C(individual).

D. Center Frequencies of SAW Filters

We fabricated 1.9 GHz-band SAW filters [26] on the third wafers sliced from the crystal positions next to the other wafers used for the V_{LSAW} measurements described in Section III-B. The devices were 2628 chips on the 76-mm$^\phi$ wafers produced by manufacturers A and B, and 4428 chips on the 100-mm$^\phi$ wafers produced by manufacturers C and D. Al films with a nominal thickness of 145 nm were deposited by direct current (DC) magnetron sputtering as electrode material. The center frequencies, f_c, defined as the mean frequency between two lower-side (f_L) and upper-side (f_U) frequencies at a 15-dB down level with reference to the minimum insertion loss in the frequency characteristics, that is, $f_c = (f_L + f_U)/2$, were measured for each SAW filter chip. Measured f_c values
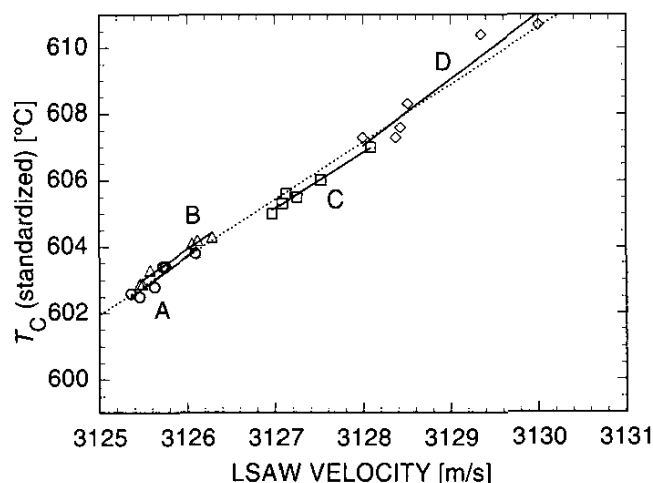
were distributed from $\pm 2\sigma = \pm 2.32$ MHz to ± 3.86 MHz for all the wafers, although the measurement reproducibility of f_c for one chip was $\pm 2\sigma = \pm 0.14$ MHz. Fig. 4 depicts the relationship between the average center frequency of the SAW devices on each wafer and the average value of the measured V_{LSAW} obtained for the other two adjacent wafers. An approximated straight line was obtained by the least-squares fitting to each set of the results and is represented by a solid line, and that for all the data, by a dotted line. The slopes of the solid lines for the individual manufacturers range from 0.72 MHz/(m/s) to 1.00 MHz/(m/s), and that for the dotted line is 0.52 MHz/(m/s); the data for the wafers of manufacturer D are more broadly distributed. One wavelength of the SAW filters was about 2.18 μm; thus, the relationship of the ratio of a change in f_c to a unit change in V_{SAW} at an ultrasonic frequency around 1880 MHz is approximately 0.46 MHz/(SH-SAW-m/s). The relationship between the effective V_{SAW} (the intermediate velocity between the short and open

states) and V_{LSAW} for $36°YX$-LiTaO$_3$, 1.47 (SH-SAW-m/s)(LSAW-m/s), was converted to the relationship between V_{LSAW} and f_c through calculations that resulted in 0.67 MHz/(LSAW-m/s). The slopes of the dotted and solid lines in Fig. 4 are close to this value, thus indicating that the center frequency of the filter varies with the acoustic properties (V_{SAW} or V_{LSAW}) of the substrates. It can be understood that the homogeneity in the acoustic properties, corresponding to the chemical composition, is one of the important factors for improving the device yields.

The average measured values appeared to vary significantly (from -0.72 MHz to 1.64 MHz) from the dotted line, compared to the results for T_C(standardized) in Fig. 3. Furthermore, there were much greater distributions of f_c on the wafers (maximum $2\sigma = 3.86$ MHz). The V_{LSAW} variations of $\pm 2\sigma = \pm 0.06$ m/s to ± 0.20 m/s measured on each wafer of the individual manufacturers yielded corresponding f_c variations of $\pm 2\sigma = \pm 0.03$ MHz to ± 0.10 MHz, converted by using the relationship of 0.52 MHz/(LSAW-m/s) in Fig. 4. This indicates that the variations of f_c of the inhomogeneity of the wafer substrates themselves as well as of the measurement reproducibility ($2\sigma = 0.14$ MHz) contribute less to the measurements. Therefore, the substantial f_c variations obtained on the wafers in Fig. 4 are considered to be primarily associated with the device fabrication processes, such as distributions in the thickness of Al films and in the electrode width.

IV. DISCUSSIONS

A. Evaluations of Crystals by Individual Manufacturers

Table IV presents the relationships between V_{LSAW} for $36°$ YX-LiTaO$_3$ wafers and the values of other chemical and physical properties. These were obtained using the chemical composition dependences of the acoustical physical constants for LiTaO$_3$ crystals reported in the literature [23], [24] and the relationship between M(Li$_2$O) and T_C in the literature [27]. The measured V_{LSAW} distributions in Fig. 1 and the distributions of M(Li$_2$O) and V_{SAW} calculated from the conversion coefficients in Table IV are summarized in Table V. The V_{LSAW} variations on the wafers were within 0.27 m/s, except for the value of 0.49 m/s for manufacturer D. The maximum V_{LSAW} variations in the crystal ingots produced by manufacturers A and B were about 0.5 m/s; the larger V_{LSAW} distributions were obtained in the crystal ingots produced by manufacturers C and D, with maximum variations of 0.95 m/s and 1.80 m/s. The V_{LSAW} distributions for wafers of manufacturers A, B, and C were about 1 m/s, and the distribution among the wafers of manufacturer D was significantly larger, almost twice that of the other manufacturers. A tolerance of $\pm 0.04\%$ for SAW velocities [28] corresponds to a tolerance of ± 1.69 m/s for SH-type V_{SAW} (surface-free velocity 4214 m/s) for $36°YX$-LiTaO$_3$ wafers. The distributions for the wafers produced by each manufacturer, the distribu-
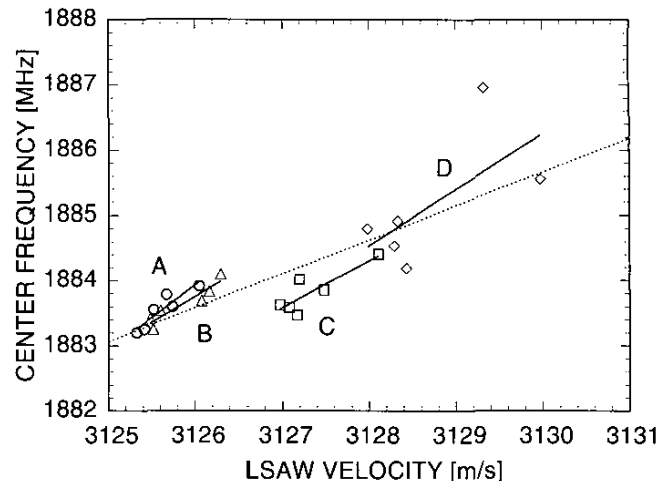

Fig. 4. Measured relationship between LSAW velocities and the center frequencies of SAW filters for $36°YX$-LiTaO$_3$ wafers produced by manufacturers A, B, C, and D. Approximated lines obtained by the least-square fitting are shown as solid lines in each set of results as a dotted line in all results.

TABLE IV
RELATIONSHIPS BETWEEN LSAW VELOCITIES AND OTHER CHEMICAL AND PHYSICAL PROPERTIES FOR $36°YX$-LiTaO$_3$ WAFERS.

	Conversion coefficient
Li$_2$O content	0.044 mol%/(LSAW-m/s)
Curie temperature	1.71°C/(LSAW-m/s)
SAW velocity	1.87 (SAW-m/s)/(LSAW-m/s)

tions in the ingots of each manufacturer, and the distributions among the wafers of manufacturers A, B, and C were all within this tolerance, but the distributions among the wafers produced by manufacturer D exceeded it.

We assessed the distributions in the ingots, i.e., the distributions along the pulling axis. The V_{LSAW} in any ingot tended to increase from the top part of the crystal to the bottom. This tendency indicates that M(Li$_2$O) increases from top to bottom, considering the relationship between the V_{LSAW} and M(Li$_2$O), 0.044 (Li$_2$O-mol%)/(LSAW-m/s), in Table IV. The increases in M(Li$_2$O) were estimated to be the smallest in the ingots of manufacturer B (0.007 mol% to 0.011 mol%), and the largest in the ingots of manufacturer D (0.061 mol% to 0.080 mol%), as indicated in Table V. These results signify that the M(Li$_2$O) in the melts is greater than that corresponding to the true congruent composition, and that the melt composition differs significantly from the congruent composition, particularly in the ingots of manufacturer D [15]. The compensation of M(Li$_2$O) in the melt compositions of each manufacturer was estimated in order to make the chemical composition of crystal ingots produced by each manufacturer as close to the congruent composition as possible.

TABLE V

VARIATIONS OF MEASURED LSAW VELOCITIES, V_{LSAW}, ESTIMATED SAW VELOCITIES, V_{SAW}, AND ESTIMATED Li_2O CONTENTS, $M(Li_2O)$, FOR $36°YX$-$LiTaO_3$ WAFERS.

Sample		V_{LSAW} [m/s]	V_{SAW} [m/s]	$M(Li_2O)$ [mol%]
On wafers	A	$0.08 \sim 0.23$	$0.15 \sim 0.43$	$0.004 \sim 0.010$
	B	$0.08 \sim 0.20$	$0.15 \sim 0.37$	$0.004 \sim 0.009$
	C	$0.07 \sim 0.27$	$0.13 \sim 0.50$	$0.003 \sim 0.012$
	D	$0.05 \sim 0.49$	$0.09 \sim 0.91$	$0.002 \sim 0.022$
In ingots	A	$0.33 \sim 0.48$	$0.61 \sim 0.89$	$0.015 \sim 0.021$
	B	$0.17 \sim 0.24$	$0.32 \sim 0.45$	$0.007 \sim 0.011$
	C	$0.26 \sim 0.95$	$0.48 \sim 1.78$	$0.011 \sim 0.042$
	D	$1.38 \sim 1.80$	$2.58 \sim 3.36$	$0.061 \sim 0.080$
Among wafers	A	0.80	1.50	0.035
	B	0.84	1.57	0.037
	C	1.14	2.13	0.050
	D	2.04	3.80	0.090

TABLE VI

COMPENSATION OF Li_2O CONTENT IN THE MELT COMPOSITIONS TO GROW A MORE HOMOGENEOUS CRYSTAL FOR EACH INGOT.

Crystal No.	$dM(Li_2O)/dL$ [$\times 10^{-3}$ mol%/mm]	$C(Li_2O)$ [Li_2O-mol%]
A-1	0.224	−0.034
A-2	0.325	−0.049
B-1	0.073	−0.011
B-2	0.123	−0.019
C-1	0.144	−0.022
C-2	0.449	−0.068
D-1	1.021	−0.155
D-2	0.774	−0.117

The estimation method proposed in the literature [29] is given in the following equation:

$$C(Li_2O) = \alpha \times dM(Li_2O)/dL, \tag{1}$$

where α is the coefficient of 152 Li_2O-mol%/(Li_2O-mol%/mm) and $dM(Li_2O)/dL$ is the derivative of $M(Li_2O)$ with respect to the crystal ingot length L from top to bottom in each ingot along the pulling axis. The results are given in Table VI. The negative signs indicate decreasing $M(Li_2O)$. The very minor compensations of less than 0.02 Li_2O-mol% required for the ingots of manufacturer B, as well as the substantial compensations of more than 0.1 Li_2O-mol% for manufacturer D, were determined through highly accurate evaluations using the LFB system, which is a very reliable feedback guideline for producing more homogeneous crystals.

Crystals A-1 to C-1 exhibited relatively small V_{LSAW} variations along the crystal pulling axis, as clarified by the distributions in Fig. 1. However, V_{LSAW} variations greater than 1 m/s were observed in crystals C-2 to D-2 along the crystal pulling axis as V_{LSAW} increased. It is very interesting to note that, among these tendencies, the crystal ingots of manufacturer A seem to exhibit slightly greater variations along the crystal pulling axis than those of manufacturer B, for which the V_{LSAW} values were slightly smaller

than those for manufacturer A. The ingots of manufacturer D exhibit remarkable variations along the pulling axis and the diameter axis. These observations may indicate that factors other than the melt composition, such as differences in the growth conditions or furnaces, are involved in producing slightly different acoustic properties in crystals.

B. Calibration of Curie Temperatures

The measured T_C values obtained through thermal analysis methods are thought to be affected by two factors: system calibration accuracy, such as the absolute accuracy of thermocouples in temperature measurements, and the measurement conditions, such as the heating rate and the particle diameter and weight of powdered specimen and reference materials. In general, the measured T_C increases as the heating rate increases. A temperature distribution is thus created in the specimen as all the reactions are observed with a time delay. In addition, the measured temperatures shift higher as the weights of specimens increase [2]. Comparing the heating rates of each manufacturer and the weights of powdered specimens and reference materials given in Table II leads us to expect that the T_C measured for identical samples will increase in the order of manufacturers A, B, and C. This trend among the results for the three manufacturers can certainly be seen in Fig. 2 by a comparison with the dotted line representing the linear relationship between V_{LSAW} and T_C. In contrast, a comparison of the measurement conditions (i.e., heating rate and the sample weight) of each manufacturer in Table II with standardized conditions in Table III suggests that T_C measured under the conditions of manufacturer A will be lower than that under the standardized conditions, and that T_C measured under the conditions of manufacturers B and C will be higher than that measured under standardized conditions. From Figs. 2 and 3, the results for manufacturers A and C are as we expected. However, the results for manufacturer B are contrary to the trend expected from the measurement conditions, indicating that T_C for manufacturer B in Fig. 2 is slightly lower than that

in Fig. 3. The causes of this result probably include the calibration accuracy of the instruments used as well as the measurement conditions. A different measurement method adopted by manufacturer D (a capacitance measurement) also is considered to cause some differences in the absolute accuracy of T_C.

It is difficult to compare the chemical compositions of crystals produced by different manufacturers on the same T_C scale because the manufacturers adopt different measurement methods and various measurement conditions, and the absolute accuracy of their systems is insufficient. However, it is very important to identify the primary factors that affect the measured T_C values and to establish specific measurement conditions for T_C in order to standardize the specifications of piezoelectric single-crystal wafers for SAW devices. It is particularly impracticable to establish specifications for supplying wafers to users who design and produce SAW devices when the measurement conditions may introduce an uncertainty of a few degrees centigrade while the tolerance of T_C is $\pm 3°C$, as seen in Fig. 2. It is also important to establish measurement procedures for a proper system calibration method to obtain an accurate, absolute temperature, including use of a thermocouple, and to calibrate the system regularly.

Although absolute accuracy is important in calibrating a system, ensuring sufficient measurement reproducibility is even more important. The total measurement error probably will increase when the measurement reproducibility of T_C is about $\pm 1°C$, considering absolute accuracy. In contrast, the measurement reproducibility for V_{LSAW} exceeds $\pm 0.002\%$ and the absolute accuracy is about $\pm 0.01\%$, which correspond to $\pm 0.1°C$ and $\pm 0.5°C$ for T_C. The relative accuracy and absolute accuracy of V_{LSAW} are considerably greater than those of T_C. Therefore, individual T_C measurement systems can be accurately calibrated using T_C converted from V_{LSAW} measured by the LFB-UMC system as the reference. Specifically, this can be done by measuring V_{LSAW} with the LFB-UMC system and measuring T_C with the instruments to be calibrated, such as DTA and DSC systems, to evaluate single crystals grown by individual manufacturers. The relationship between the two measurement results (the calibration line) then can be obtained. Calculations can be made to convert V_{LSAW} into V_{SAW}, if necessary, as described in Section IV-A. The conversion coefficient between V_{LSAW} and T_C is given in Table IV. Grown crystals can be evaluated by the velocities of V_{SAW} or V_{LSAW} converted from the measured T_C by using the relationship between T_C determined in this way and V_{SAW} (or V_{LSAW}). The specimens used to determine the previous relationships can be used thereafter as reference specimens. The availability of multiple instruments for T_C measurements enables us to measure the differences in T_C values with different instruments to be calibrated by measuring the reference specimens. The total performance of T_C measurement instruments probably will vary with time. It is thus necessary to calibrate systems regularly using the reference specimens discussed previously.

C. Evaluation of the Fabrication Process Conditions of SAW Devices

The results in Section III-D indicated some serious problems associated with device fabrication processes other than the chemical composition problem of the wafer substrates. The device fabrication processes are roughly divided into two categories, the metal film formation process and the electrode pattern formation process, which are directly related to the metal film thickness and the electrode width. The distribution of Al film thickness after film formation was examined by X-ray fluorescence analysis. Measurements were conducted at five positions (the center of the wafer, the upper and lower sides, and the right and left sides 20 mm from the center) for a 20-mm$^\phi$ area. The measurement reproducibility was estimated to be $\pm 2\sigma = \pm 0.5$ nm. The average Al film thickness was about 135 nm, and the thickness distributions were $\pm 2\sigma = \pm 1.0$ nm on the wafers and ± 1.8 nm among the wafers. We calculated the V_{SAW} dispersion characteristics for the Al film on $36°YX$-LiTaO$_3$ substrate using the acoustical physical constants in the literature for LiTaO$_3$ [23], [24] and Al [30], according to the analytic procedures [31]–[33], to estimate the contribution of the film thickness distribution. The velocity variation to the thickness was -0.28 (m/s)/nm around $f_H = 254$ Hz·m for $f = 1883$ MHz and $H = 135$ nm; a thickness variation of ± 1.8 nm corresponds to a measured f_c variation of ± 0.24 MHz. This value is very small compared to the f_c variations (maximum 1.64 MHz) from the dotted line in Fig. 4 and the f_c distributions (maximum 3.86 MHz) on the wafers. This indicates that we should consider the influence of distributions in the electrode width in the IDTs on each wafer as another factor. The distributions in electrode width are related to changes in the process conditions (exposure, development, and etching) when forming electrode patterns. Therefore, variations in the measurements are primarily problems associated with slightly different IDT fabrication process conditions.

The f_c distributions on the wafers described previously ($\pm 2\sigma = \pm 2.32$ MHz to ± 3.86 MHz) correspond to about a 90% to 70% yield when a rigorous tolerance for f_c, for example, $\pm 0.1\%$ (± 1.9 MHz), is required for the devices. However, the variations in the chemical composition of the wafer substrates actually reduce the yield, as seen in Figs. 3 and 4. Wafer substrates with elastic inhomogeneities within $\pm 0.04\%$ (1.69 m/s) in V_{SAW} (surface-free velocity), which corresponds to ± 0.90 m/s in V_{LSAW}, also might contribute an f_c distribution of ± 0.47 MHz on the measurements. The additional f_c distribution can be estimated to be ± 0.91 MHz, which is almost twice as large as that previously, if we use wafer substrates with a tolerance of $\pm 3°C$ in T_C [1], corresponding to ± 1.75 m/s in V_{LSAW}. From the technical aspect of designing and producing devices, it is important to establish the crystal growing conditions around the true congruent composition reported in a previous paper [29] and also discussed previously. Device makers then will not need to concern themselves with the

elastic properties of the crystals and will be able to concentrate on improving the device fabrication conditions, particularly the electrode patterning process, which is the primary factor in f_c distributions.

V. CONCLUSIONS

This paper compared and evaluated the conditions for measuring T_C, which is widely used to evaluate the chemical compositions of LiTaO$_3$ single crystals, using Rayleigh-type V_{LSAW} measured by the LFB-UMC system.

The V_{LSAW} distributions were first measured for $36°YX$-LiTaO$_3$ wafers produced by four different manufacturers for SH-type SAW devices. Our measurements revealed the relationships between T_C(individual) measured by the individual manufacturers and V_{LSAW} to be linear. However, the proportional coefficients and absolute accuracies of T_C(individual) differed among the manufacturers. The relationship between T_C(standardized) and V_{LSAW} was expressed by a single straight line when T_C(standardized) was measured under constant measurement conditions, with no significant differences among manufacturers. These results experimentally verify that problems in T_C measurements arise from the measurement conditions and/or the absolute accuracy of the measurement instruments.

Unsolved problems concerning evaluations of crystals through current T_C measurements were identified with accurate standardized evaluations using the LFB-UMC system. The criteria for the chemical composition ratios of crystals must correspond to the tolerance of T_C to standardize the specifications of piezoelectric single-crystal wafers for SAW devices. The results of the experiments in this paper demonstrate that it is crucial to not only establish the T_C tolerance, but also to institute a proper T_C calibration method to ensure the absolute accuracy of measured data. The ultrasonic technology of the LFB-UMC system is capable of measuring V_{LSAW} (or converted V_{SAW}) with excellent measurement reproducibility. Thus, it will play a key role in realizing future SAW devices at higher frequencies with superior performance, not only by evaluating and selecting better wafer substrates but also by calibrating measurement systems for T_C data needed for chemical composition analyses.

To better evaluate the wafer substrates for SAW devices using the LFB-UMC system, we compared the relationship between the Rayleigh-type V_{LSAW} and SH-type V_{SAW} obtained through experiments fabricating commercial SAW filters and measuring their center frequencies and through numerical calculations and found that they coincided well. This indicates that SH-type V_{SAW} variations caused by changes in the chemical composition ratio in crystal substrates can be detected and accurately evaluated as V_{LSAW} variations. We also verified that changes in the chemical composition ratio in the substrate and changes due to differences in the device fabrication process (thickness or width of the electrode) can be detected separately by

accurately obtaining the elastic property (V_{LSAW}) of each substrate in advance. This indicates that problems in the production process for SAW devices exert the most influence on the device characteristics in a practical production line, rather than problems associated with the elastic inhomogeneities of wafers. This information will be very useful for improving device fabrication conditions and increasing productivity.

REFERENCES

[1] IEC-PAS, "Single Crystal Wafers Applied for Surface Acoustic Wave Device—Specification and Measuring Method," IEICE/Std-0002, Apr. 17, 2001.

[2] C. B. Murphy, "Differential thermal analysis," *Anal. Chem.*, vol. 30, pp. 867–872, Apr. 1958.

[3] E. S. Watson, M. J. O'Neill, J. Justin, and N. Brenner, "A differential scanning calorimeter for quantitative differential thermal analysis," *Anal. Chem.*, vol. 36, pp. 1233–1238, June 1964.

[4] J. Kushibiki and N. Chubachi, "Material characterization by line-focus-beam acoustic microscope," *IEEE Trans. Sonics Ultrason.*, vol. SU-32, pp. 189–212, Mar. 1985.

[5] J. Kushibiki, Y. Ono, Y. Ohashi, and M. Arakawa, "Development of the line-focus-beam ultrasonic material characterization system," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 49, pp. 99–113, Jan. 2002.

[6] J. Kushibiki, Y. Ohashi, and T. Ujiie, "Standardized evaluation of chemical compositions of LiTaO$_3$ single crystals for SAW devices using the LFB ultrasonic material characterization system," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 49, pp. 454–465, Apr. 2002.

[7] J. Kushibiki and M. Arakawa, "A method for calibrating the line-focus-beam acoustic microscopy system," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 45, pp. 421–430, Mar. 1998.

[8] J. Kushibiki, M. Arakawa, and R. Okabe, "High-accuracy standard specimens for the line-focus-beam ultrasonic material characterization system," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 49, pp. 827–835, June 2002.

[9] J. Kushibiki, H. Takahashi, T. Kobayashi, and N. Chubachi, "Quantitative evaluation of elastic properties of LiTaO$_3$ crystals by line-focus-beam acoustic microscopy," *Appl. Phys. Lett.*, vol. 58, pp. 893–895, Mar. 1991.

[10] J. Kushibiki, H. Takahashi, T. Kobayashi, and N. Chubachi, "Characterization of LiNbO$_3$ crystals by line-focus-beam acoustic microscopy," *Appl. Phys. Lett.*, vol. 58, pp. 2622–2624, June 1991.

[11] J. Kushibiki, T. Kobayashi, H. Ishiji, and N. Chubachi, "Elastic properties of 5-mol% MgO doped LiNbO$_3$ crystals measured by line focus beam acoustic microscopy," *Appl. Phys. Lett.*, vol. 61, pp. 2164–2166, Nov. 1992.

[12] J. Kushibiki, H. Ishiji, T. Kobayashi, N. Chubachi, I. Sahashi, and T. Sasamata, "Characterization of $36°YX$-LiTaO$_3$ wafers by line-focus-beam acoustic microscopy," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 42, pp. 83–90, Jan. 1995.

[13] J. Kushibiki, T. Kobayashi, H. Ishiji, and C. K. Jen, "Surface-acoustic-wave properties of MgO-doped LiNbO$_3$ single crystals measured by line-focus-beam acoustic microscopy," *J. Appl. Phys.*, vol. 85, pp. 7863–7868, June 1999.

[14] J. Kushibiki, Y. Ono, and I. Takanaga, "Ultrasonic microspectroscopy of LiNbO$_3$ and LiTaO$_3$ single crystals for SAW devices," *IEICE Trans. Electron.*, vol. J82-C-I, pp. 715–727, Dec. 1999.

[15] J. Kushibiki, T. Okuzawa, J. Hirohashi, and Y. Ohashi, "Line-focus-beam acoustic microscopy characterization of optical-grade LiTaO$_3$ single crystals," *J. Appl. Phys.*, vol. 87, pp. 4395–4403, May 2000.

[16] J. Kushibiki, Y. Ohashi, and Y. Ono, "Evaluation and selection of LiNbO$_3$ and LiTaO$_3$ substrates for SAW devices by the LFB ultrasonic material characterization system," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 47, pp. 1068–1076, July 2000.

[17] O. Kawachi, S. Mineyoshi, G. Endoh, M. Ueda, O. Ikata, K. Hashimoto, and M. Yamaguchi, "Optimum cut for leaky SAW on LiTaO₃ for high performance resonators and filters," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 48, pp. 1442–1448, Sep. 2001.

[18] I. Takanaga and J. Kushibiki, "Elastic constants of multidomain LiTaO₃ crystal," *J. Appl. Phys.*, vol. 86, pp. 3342–3346, Sep. 1999.

[19] I. Takanaga and J. Kushibiki, "Elastic constants of multidomain LiTaO₃ crystal (Erratum)," *J. Appl. Phys.*, vol. 87, p. 960, Jan. 2000.

[20] K. Nakamura, M. Kazumi, and H. Shimizu, "SH-type and Rayleigh-type surface waves on rotated Y-cut LiTaO₃," in *Proc. IEEE Ultrason. Symp.*, 1977, pp. 819–822.

[21] R. M. White and F. W. Voltmer, "Direct piezoelectric coupling to surface elastic waves," *Appl. Phys. Lett.*, vol. 7, pp. 314–316, Dec. 1965.

[22] K. Yamanouchi and K. Shibayama, "Elastic surface-wave excitation, using parallel-line electrodes above piezoelectric plates," *J. Acoust. Soc. Amer.*, vol. 41, pp. 222–223, Jan. 1967.

[23] J. Kushibiki, I. Takanaga, M. Arakawa, and T. Sannomiya, "Accurate measurements of the acoustical physical constants of LiNbO₃ and LiTaO₃ single crystals," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 46, pp. 1315–1323, Sep. 1999.

[24] J. Kushibiki, I. Takanaga, S. Komatsuzaki, and T. Ujiie, "Chemical composition dependences of the acoustical physical constants of LiNbO₃ and LiTaO₃ single crystals," *J. Appl. Phys.*, vol. 91, pp. 6341–6349, May 2002.

[25] J. Kushibiki, Y. Ohashi, and M. Arakawa, "Influence of reflected waves from the back surface of thin solid-plate specimen on velocity measurements by line-focus-beam acoustic microscopy," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 47, pp. 274–284, Jan. 2000.

[26] M. Koshino, K. Kanasaki, N. Akahori, M. Kawase, R. Chujyo, and Y. Ebata, "A wide-band balanced SAW filter with longitudinal multi-mode resonator," in *Proc. IEEE Ultrason. Symp.*, 2000, pp. 387–390.

[27] M. Sato, A. Iwama, J. Yamada, M. Hikita, and Y. Furukawa, "SAW velocity variation LiTaO₃ substrates," *Jpn. J. Appl. Phys.*, vol. 28, no. 28-1, pp. 111–113, 1989.

[28] K. Yamada, T. Omi, S. Matsumura, and T. Nishimura, "Characterization of 4-inch LiTaO₃ single crystals for SAW device application," in *Proc. IEEE Ultrason. Symp.*, 1984, pp. 243–248.

[29] J. Kushibiki, Y. Ohashi, Y. Ono, and T. Sasamata, "Evaluation and improvement of optical-grade LiTaO₃ single crystals by the LFB ultrasonic material characterization system," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 49, pp. 905–914, July 2002.

[30] O. L. Anderson, "Determination and some uses of isotropic elastic constants of polycrystalline aggregates using single-crystal data," in *Physical Acoustics.* vol. III, pt. B, W. P. Mason, Ed. New York: Academic, 1965, pp. 43–95.

[31] J. J. Campbell and W. R. Jones, "A method for estimating optimal crystal cuts and propagation directions for excitation of piezoelectric surface waves," *IEEE Trans. Sonics Ultrason.*, vol. SU-15, pp. 209–217, Oct. 1968.

[32] J. J. Campbell and W. R. Jones, "Propagation of surface waves at the boundary between a piezoelectric crystal and a fluid medium," *IEEE Trans. Sonics Ultrason.*, vol. SU-17, pp. 71–76, Apr. 1970.

[33] G. W. Farnell and E. L. Adler, "Elastic wave propagation in thin layers," in *Physical Acoustics.* vol. IX, W. P. Mason and R. N. Thurston, Eds. New York: Academic, 1972, pp. 35–127.

Jun-ichi Kushibiki (M'83) was born in Hirosaki, Japan, on November 23, 1947. He received the B.S., M.S., and Ph.D. degrees in electrical engineering from Tohoku University, Sendai, Japan, in 1971, 1973, and 1976, respectively.

In 1976 he became a research associate at the Research Institute of Electrical Communication, Tohoku University. In 1979, he joined the Department of Electrical Engineering, Faculty of Engineering, Tohoku University, where he was an associate professor from 1988 to 1993 and became a professor in 1994. He has been studying ultrasonic metrology, especially acoustic microscopy and its applications, and established a method of material characterization by line-focus-beam acoustic microscopy. He also has been interested in biological tissue characterization in the higher frequency range, applying both bulk and acoustic microscopy techniques.

Dr. Kushibiki is a Fellow of the Acoustical Society of America; a member of the Institute of Electronics, Information and Communication Engineers of Japan, of the Institute of Electrical Engineers of Japan, of the Acoustical Society of Japan, and of the Japan Society of Ultrasonics in Medicine.

Yuji Ohashi was born in Toyama prefecture, Japan, on August 27, 1973. He received the B.S. and M.S. degrees in electrical engineering from Tohoku University, Sendai, Japan, in 1996 and 1999, respectively.

He is currently studying toward the Ph.D. degree at Tohoku University. His research interests include development of line-focus-beam acoustic microscopy system and its applications to materials characterization.

Mr. Ohashi is a member of the Acoustical Society of Japan.

Naoyuki Mishima was born in Hiroshima, Japan, on December 15, 1956. He received the B.S., M.S., and Ph.D. degrees in physical science from Hiroshima University, Hiroshima, Japan, in 1979, 1981, 1984, respectively.

In 1984 he joined the Surface Acoustic Device (SAW) Engineering Division of Toshiba Corporation, Kawasaki, Japan. In 2002 he transferred to the SAW Engineering Division of Fujitsu Co. Ltd., Suzaka, Japan, where he is presently Director. He has been engaged in the research and development of producing and processing SAW devices.

Dr. Mishima is a member of the Institute of Electronics, Information and Communication Engineers of Japan.