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## Piezoelectric coefficients of GaN determined by hopping conduction of carriers

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Using resonant ultrasound spectroscopy, we monitored the resonance-frequency and internal-friction behaviors of a GaN monocrystal at elevated temperatures. An internal-friction peak appears with increasing temperature, at which reduction of frequency occurs. The frequency shift reflects the disappearance of the apparent piezoelectricity due to hopping conduction of carriers, allowing us to accurately determine the piezoelectric coefficients  $e_{ij}$ . We measured the frequency decrements of eight vibrational modes to inversely determine three independent  $e_{ij}$ : Our values are  $e_{15} = -0.22 \pm 0.02$  C/m<sup>2</sup>,  $e_{31} = -0.14 \pm 0.02$  C/m<sup>2</sup>,  $e_{33} = 1.15 \pm 0.05$  C/m<sup>2</sup>. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4966995>]

Gallium nitride (GaN) is a promising material for piezoelectric resonators such as a film-bulk-acoustic resonator because of its high  $Q$  value.<sup>1,2</sup> Design of the resonators requires the piezoelectric coefficients  $e_{ij}$  as well as the elastic constants  $C_{ij}$  because they dominate the mechanical resonance frequencies of piezoelectric materials. The piezoelectricity of GaN is also important in high-frequency and high-power electronic devices such as a high-electron-mobility transistor,<sup>3,4</sup> where piezoelectric polarization of GaN produces the two-dimensional electron gas,<sup>4-6</sup> through which the high-speed transportation of electrons is achieved. Thus,  $e_{ij}$  of GaN are essential to develop and optimize these devices.

Wurtzite GaN belongs to crystals with 6mm point-group symmetry and exhibits three independent piezoelectric coefficients,  $e_{15}$ ,  $e_{31}$ , and  $e_{33}$

$$[e_{ij}] = \begin{bmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{bmatrix}. \quad (1)$$

Previously,  $C_{ij}$  and  $e_{ij}$  of piezoelectric materials have been measured with the plate-thickness resonance method<sup>7,8</sup> and the pulse-echo method.<sup>9-11</sup> However, these conventional methods need many independent measurements on many specimens with different crystallographic orientations to determine a complete set of the coefficients through solving labyrinthine simultaneous equations. They are, therefore, inapplicable to GaN because a high-quality GaN monocrystal specimen is limited to a thin-plate shape ( $\sim 500$   $\mu\text{m}$  thick), and it is difficult to machine it into many different-orientation specimens.

Recently, these material constants are determined using resonant ultrasound spectroscopy (RUS) from a single small specimen.<sup>12-14</sup> RUS deduces  $e_{ij}$  and  $C_{ij}$  inversely by seeking an optimal set of them, minimizing the errors between measured and calculated resonance frequencies. However, the RUS method requires measurements of resonance frequencies, specimen dimensions, and mass density with extraordinarily

high precision to determine reliable  $e_{ij}$  because contributions of  $e_{ij}$  to resonance frequencies are considerably smaller than those of dimensions and mass density.<sup>14,15</sup> For example, determination of  $e_{ij}$  of a 500- $\mu\text{m}$ -thick GaN specimen within 10% error needs measurements of thickness and mass density within  $\sim 500$  nm and  $\sim 6$  kg/m<sup>3</sup> errors ( $\sim 0.1\%$  errors), because their contributions to resonance frequencies are larger than those of  $e_{ij}$  by a factor of  $\sim 100$  as shown in the [supplementary material](#), Figure S1. Consequently, it is very difficult to accurately determine  $e_{ij}$  of GaN with the existing methods. A few experimental studies<sup>16-18</sup> showed the piezoelectric coefficients as shown in Table I. Guy *et al.*<sup>16</sup> statically measured only  $d_{33}$  and estimated  $e_{33}$  and  $e_{31}$ . Nakamura *et al.*<sup>17</sup> estimated the three  $e_{ij}$  using the RUS method, but their specimen involved many free carriers (nearly conductive), where the piezoelectricity becomes quite low, and the deduced  $e_{ij}$  are highly underestimated. Ogi *et al.*<sup>18</sup> roughly estimated only  $e_{15}$  using the RUS method with a single resonance frequency. Thus, no study succeeded in measuring all the three independent  $e_{ij}$  reliably.

Here, we propose a methodology that determines all the  $e_{ij}$  of a thin GaN specimen with the high-temperature RUS method using the piezoelectricity-disappearance phenomenon due to hopping conduction. Free carriers are trapped by deep acceptors such as Fe ions in a semi-insulating GaN,<sup>19</sup> where the conduction is mainly achieved by hopping of the trapped carriers between the sites with assistance of phonons.<sup>20</sup> The hopping conduction is a thermally activated phenomenon, and the hopping rate increases as the temperature increases.<sup>21</sup> The periodic carrier movement is also induced by the dynamic polarization change caused by mechanical vibrations via piezoelectricity. Thus, the hopping conduction is enhanced when the hopping rate matches with the vibration frequency, at which the internal friction shows a peak, because the acoustic energy is spent on the carrier movement.<sup>22</sup> Above the internal-friction peak temperature, the carriers move faster than the piezoelectric polarization change, and the apparent piezoelectricity disappears, resulting in a decrease in the resonance frequency (disappearance

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TABLE I. Piezoelectric coefficients  $e_{ij}$  (C/m<sup>2</sup>) of wurtzite GaN and elastic  $C_{ij}$  (GPa) and dielectric  $\epsilon_{ij}/\epsilon_0$  constants used in the inverse calculation ( $\epsilon_0$  represents the dielectric constant of vacuum). The local-density-approximation (LDA) or generalized-gradient-approximation (GGA) potential was used in the *ab-initio* calculation.

		$e_{15}$	$e_{31}$	$e_{33}$	$C_{11}$	$C_{13}$	$C_{33}$	$C_{44}$	$C_{66}$	$\epsilon_{11}$	$\epsilon_{33}$
Meas.	This work	$-0.22 \pm 0.02$	$-0.14 \pm 0.02$	$1.15 \pm 0.05$							
	Guy <i>et al.</i> <sup>16</sup>		-0.55	1.12							
	Nakamura <i>et al.</i> <sup>17</sup>	0.10	0.17	0.29							
	Ogi <i>et al.</i> <sup>18</sup>	$-0.332 \pm 0.03$									
	Ref. 27				359.7	104.6	391.8	99.6	114.9		
Calc.	Refs. 28 and 29									5.35	5.8
	LDA <sup>26</sup>	-0.38	-0.45	0.83							
	LDA <sup>31</sup>		-0.49	0.73							
	LDA <sup>32</sup>		-0.44	0.86							
	GGA <sup>32</sup>		-0.34	0.67							
	LDA <sup>33</sup>		-0.45	0.76							

of the piezoelectric stiffening). The resonance-frequency change  $\Delta f$  and the corresponding internal friction  $Q^{-1}$  are described by the Debye-type relaxation model<sup>23</sup>

$$\frac{\Delta f}{f} = \frac{\Delta_M}{2} \times \frac{1}{1 + (\omega\tau)^2}, \quad (2)$$

$$Q^{-1} = \Delta_M \times \frac{\omega\tau}{1 + (\omega\tau)^2}, \quad (3)$$

$$\Delta_M = \frac{e^2}{C\epsilon}. \quad (4)$$

Here,  $\Delta_M$  denotes the strength of relaxation, and  $e$ ,  $C$ , and  $\epsilon$  are the effective piezoelectric, elastic, and dielectric constants governing the vibrational mode, respectively. (The *effective* coefficient is expressed by a combination of the independent coefficients.)  $\omega$  and  $\tau$  denote the angular frequency and relaxation time for the carrier hopping, respectively. The internal friction thus shows a peak at  $\omega\tau = 1$ , across which the resonance-frequency shift occurs due to disappearance of the apparent piezoelectricity. There are numerous vibrational modes in a solid, and each has its own  $\Delta_M$  value, which can be accurately calculated with the Ritz method as shown below. Because contributions of the three  $e_{ij}$  to  $\Delta_M$  are different depending on the resonant mode, it is possible to determine all the three  $e_{ij}$  by measuring the frequency shift of various vibrational modes and comparing them with calculations. This approach requires the measurement of the *relative*

frequency change, allowing us to cancel out the measurement errors in the specimen dimensions and mass density as shown in the [supplementary material](#). Thus, this proposed method is sensitive only to the piezoelectricity of the material and can determine the  $e_{ij}$  even for a small GaN specimen much more accurately than the previous methods.

We used high-resistance and high-quality wurtzite GaN, where a small amount of Fe ions ( $\sim 80$  ppm) are doped as deep acceptors to achieve the semi-insulating state. Three rectangular-parallelepiped specimens were prepared, and their dimensions along the three principal axes are about 3.5 mm, 3.0 mm, and 0.4 mm. (The  $c$  axis is along the 0.4-mm side.) The mass density determined by the Archimedes method is 6080 kg/m<sup>3</sup>.

To measure the resonance frequencies and internal friction of various vibrational modes at elevated temperatures, we developed the tripod-type RUS<sup>13,14,24</sup> system as shown in Fig. 1(a). The specimen is put on a tripod, consisting of two fused-silica needle buffer rods and one needle-thermocouple support for measuring the specimen temperature. The two rod-type ultrasonic transducers are attached to the silica buffer rods for excitation and detection of free vibrations. Heating of the specimen is achieved by inserting it into a cylindrical heater. Because no external force was applied to the specimen, except for gravity, and no coupling agent was used, it is possible to measure the resonance frequencies of ideal free vibration. The weak acoustic contacts realize the accurate internal-friction measurement;<sup>25</sup> the vibration energy of the specimen leaks to

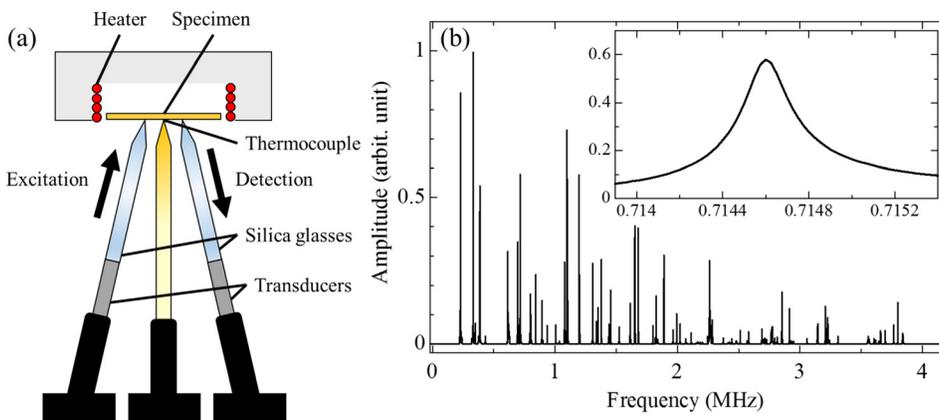


FIG. 1. (a) Measurement setup of the high-temperature RUS method and (b) resonant spectra of GaN measured by the measurement system at room temperature. The inset enlarges a resonant peak.

contacting transducers in conventional contact methods, causing an increase in the apparent internal friction. Figure 1(b) shows an example of the measured resonance spectrum of the GaN specimen, showing many fine resonance peaks. We used eight peaks among them to determine the three  $e_{ij}$ ; they show large contributions of  $e_{ij}$ , and they are completely isolated from neighboring peaks (non-overlapping peaks).

The present technique determines  $e_{ij}$  inversely by comparing the measured and calculated resonance-frequency shifts, which are equivalent to the frequency shifts from the non-piezoelectric state ( $e_{ij}=0$ ): The resonance frequencies were computed using the Ritz method, where the displacement and electric potential were expanded by linear combinations of normalized Legendre polynomial, involving the maximum degree of 24. In the inverse calculation, we used the initial  $e_{ij}$  values in the theoretical study<sup>26</sup> with *ab-initio* calculation, and used  $C_{ij}$  values<sup>27</sup> from our recent measurements and reported dielectric constants<sup>28,29</sup> as shown in Table I.

Figure 2(a) shows an example of the temperature behavior of resonant spectrum of  $B_{1g}$ -2 mode (the mode denotation follows Mochizuki<sup>30</sup>). (The detailed change appears in the [supplementary material](#), Movie.) The resonance frequency decreases as temperature increases, and the peak becomes broader and then sharp again with further increasing temperature, indicating the internal-friction peak in this temperature range. Figure 2(b) shows the resonance-frequency change in this mode. Resonance frequencies usually decrease linearly with increasing temperature because of the stiffness decrease. It indeed decreases linearly below  $\sim 80^\circ\text{C}$ , but significantly drops at  $\sim 110^\circ\text{C}$ , and then decreases linearly again above  $\sim 150^\circ\text{C}$ . The linear decreases at low and high temperature regions occur with the same rate and correspond to the usual frequency change. We then subtracted it from the temperature response as shown in Fig. 2(c). Also, the temperature behavior of internal friction of this mode is plotted in Fig. 2(c), which shows a peak at  $\sim 110^\circ\text{C}$ . These behaviors are consistent with the relaxation phenomenon caused by the hopping conduction of carriers, and they are expressed by Eqs. (2)–(4). Because the relaxation time is inversely proportional to the Boltzmann

factor ( $\tau = A \exp(E/kT)$ ) with the activation energy  $E$  and the proportionality constant  $A$ , we fitted Eq. (2) to the measured frequency change ratio with the fitting parameters  $\Delta_M$ ,  $E$ , and  $A$ . The result is shown with the solid line in Fig. 2(c), showing good agreement with the measurements. Furthermore, we calculated the internal-friction change using Eq. (3) with the same parameters, which consistently explains the internal-friction measurements, confirming that the observed frequency shift is caused by the hopping conduction of carriers.

The frequency shifts are important to determine  $e_{ij}$ , and we measured them for eight modes for each specimen, which are enough to inversely determine the three independent  $e_{ij}$ . Figure 3(a) shows some of such measurements with the fitted theoretical curves, and Fig. 3(b) compares the measured and calculated frequency shifts after the convergence; the typical rms error between them was 8%. Our approach obtains the  $e_{ij}$  values at  $\sim 110^\circ\text{C}$  because the frequency shifts occur near this temperature as shown in Fig. 3(a). However, we expect an insignificant difference between the values determined at  $110^\circ\text{C}$  and room temperature because of very high thermal stability of GaN with a high Debye temperature of 636 K.<sup>27</sup> Magnitudes of temperature coefficients of  $C_{ij}$  and  $e_{ij}$  are comparable with each other for piezoelectric materials, including quartz<sup>11</sup> and lithium niobate.<sup>9</sup> The temperature coefficients of  $C_{ij}$  of GaN are reported to be of the order of 10 ppm/ $^\circ\text{C}$ ,<sup>27</sup> and we expect the similar temperature coefficients for  $e_{ij}$ , predicting only 0.1% (or less) difference between  $e_{ij}$  at  $110^\circ\text{C}$  and room temperature.

Table I shows averages of the  $e_{ij}$  of the three specimens together with previously reported values, including theoretical studies.<sup>26,31–33</sup> Our  $e_{33}$  favorably agrees with that by Guy *et al.*<sup>16</sup> They determined it from  $d_{33}$  directly obtained by measuring the out-of-plane displacement of the surface when an electric field was applied along the  $c$  axis. Thus, the value is reliable. By contrast,  $e_{33}$  deduced by Nakamura *et al.*<sup>17</sup> is much lower than our value, but they used specimens involving many free carriers, causing underestimation of  $e_{ij}$ . It is noted that theoretically calculated  $e_{33}$ <sup>26,31–33</sup> are significantly lower than the experiments: The difference is between 25% and 42%. As for  $e_{31}$ , our result is highly different from the

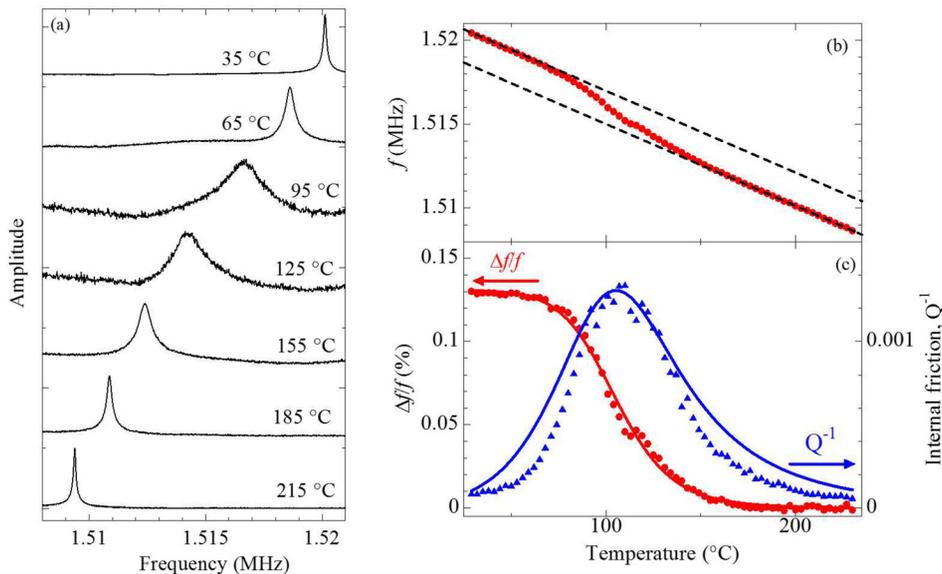


FIG. 2. (a) Resonant spectra of  $B_{1g}$ -2 mode at several temperatures and (b) the resonance-frequency change of the resonant mode versus temperature. The broken lines represent usual temperature dependencies of the resonance frequency. (c) The baseline-subtracted fractional frequency change and the corresponding internal friction. The solid lines show fitted theoretical curves in Eqs. (2) and (3), where the parameters are determined by fitting them to the measured frequency change.

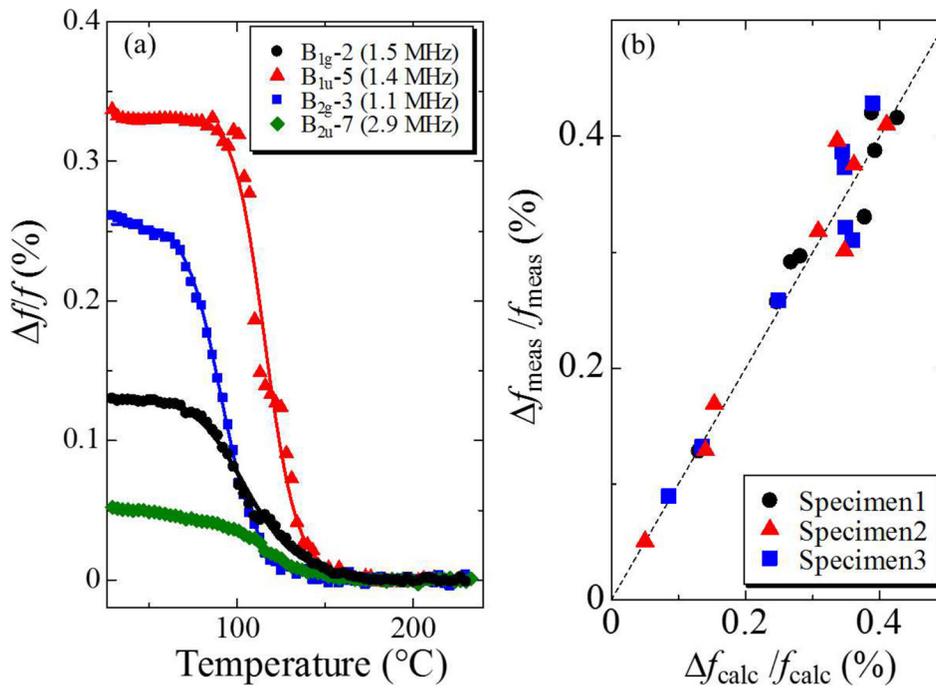


FIG. 3. (a) Temperature behaviors of some resonant modes. The solid lines show the fitting curves of Eq. (2). (b) Correlation between the measured and calculated frequency shifts after convergence of the three specimens.

measurement by Guy *et al.*,<sup>16</sup> but they extracted  $d_{31}$  from  $d_{33}$  using a simple assumption  $d_{31} = -\frac{1}{2}d_{33}$  and did not measure it. An experimental value of  $e_{15}$  is recently reported,<sup>18</sup> but it was roughly deduced from a single frequency shift with fixing other  $e_{ij}$  using the unreliable theoretical values, making the resultant value unreliable as well. Therefore, our present value for  $e_{ij}$  are the most reliable from the point of measurement principle.

In summary, we determined all the three piezoelectric coefficients of GaN by measuring free-vibration resonance-frequency shifts at elevated temperatures caused by disappearance of the apparent piezoelectricity due to the hopping conduction of carriers. Our proposed method does not need accurate measurements of specimen dimensions and mass density, and is sensitive only to the piezoelectric coefficients even for a thin-plate specimen with high precision, because the *relative* frequency changes are used. Because there is no experimental report on the complete set of reliable  $e_{ij}$  of GaN, our measurement values will be highly important for studying calculation conditions in theories.

See [supplementary material](#) for the resonance-spectrum change during temperature increase (movie). Also, see [supplementary material](#) for the contributions of thickness, mass density, and piezoelectric coefficients to resonance frequencies and for insensitivity of the present method to thickness and mass density of the specimen.

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