High Thermal Conductivity of Gallium Nitride (GaN) Crystals Grown by HVPE Process

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1. Introduction

Silicon carbide (SiC) is utilized for many applications because of its high thermal conductivity. A thermal conductivity of over 360 W/mK at room temperature has been reported for SiC. This intrinsic thermal property of SiC allows us to fabricate devices such as thyristors for high power switching. Gallium nitride (GaN) has also received attention for many years due to its unique electrical properties. Since it has a large and tunable band gap of 3.4 eV at room temperature, GaN finds application in injection lasers and light-emitting diodes in the visible and ultraviolet regions. GaN is also used in high-electron-mobility transistors, quantum wells, photodetectors, and display devices.

On the other hand, the thermal properties of GaN are very important to make the devices work properly. In particular, the thermal conductivity of GaN is an essential property for estimating the suitability of devices. To the best of the authors knowledge, Sichel and Pankove were the first to report (1977) that the measured thermal conductivity of bulk GaN of 400 μm thickness at room temperature is 130 W/mK. This is not far from the upper limit of 170 W/mK for a perfect GaN crystal, as predicted by Slack. In 1998, Witek had theoretically estimated the value of the thermal conductivity of GaN as 410 W/mK, which is considerably higher than that predicted by Slack. The experimental thermal conductivity values of GaN obtained at room temperature, using a scanning thermal microscope, are scattered in the range of 50 to 210 W/mK. This is attributed to the effects of impurities and dislocations on the thermal properties. Luo et al. reported the thermal conductivity value of 155 W/mK using a third-harmonic electrical technique. Slack et al. studied the effect of oxygen on thermal conductivity and obtained an approximate value of 200 W/mK at 300 K for a flat plate-shaped sample, which was 200 μm thick and 3 mm wide. In 2003, Jezowski et al. also obtained the value of 226 W/mK for a bulk-shaped sample with a thickness of 100 μm and lateral dimensions of a few millimeters at 300 K. It is understood that the defects in GaN as well as impurities in it should be minimized in order to use the material in thyristors for manufacturing high-power-switching devices and high-brightness light-emitting diodes. It may also be suggested that a large bulk-shaped sample is strongly required for measuring the thermal properties of GaN in order to reduce the experimental uncertainties in the measurements. However, it was previously not an easy task to produce large bulk-shaped samples. In this regard, a bulk-shaped sample of single-crystal GaN with a relatively large size can now be prepared using the hydride vapor phase epitaxy (HVPE) process. This prompts us to measure the thermal properties of GaN again for checking the possibility of the application of GaN in high-power-switching devices.

The purpose of this study is to report the experimental results of thermal diffusivity of single-crystal GaN using a laser flash method in the temperature range of 298 to 849 K. The thermal diffusivity of single-crystal SiC was also measured for the purpose of comparison. The specific heat capacity of GaN was also measured using a differential scanning calorimeter, and its thermal expansion coefficient was measured by a thermal dilatometer in order to estimate the value of the thermal conductivity with sufficient accuracy.

2. Experimental

2.1 Thermal diffusivity measurement

The single-crystal GaN sample was grown on a sapphire
substrate in a conventional vertical-type HVPE reactor at the Optoelectronics Laboratory, Mitsubishi Chemical Corporation. The growth rate of GaN was approximately 120 \mu m/h, and the temperature at a reactor wall was maintained between 1248 and 1293 K. A free-standing GaN sample was spontaneously separated from the sapphire substrate. The high crystalline quality of the free-standing GaN crystal was supported by X-ray diffraction (XRD) analysis. The measured full width at half maximum (FWHM) of X-ray \omega -rocking curves were 62.0 and 98.8 arcsec for the (002) and (102) reflections, respectively. The impurity concentration was investigated using secondary-ion mass spectroscopy (SIMS). The GaN crystal was unintentionally doped with a silicon impurity of concentration 2.1 \times 10^{17} \text{ cm}^{-2}. The concentration of the other impurities (H, Li, Be, B, C, O, F, Na, Mg, Al, Cl, K, Fe, Cu, Zn, As, Br, I, and At) was below the detection limit. The dislocation density was determined from the dark spot density, which was obtained by the cathode luminescence method. The typical value of the dark spot density was approximately 5 \times 10^6 \text{ cm}^{-2}. The sample used in the present study was octagonal in shape with a thickness of 1 mm along the c axis. The radius of the inscribed circle of the octagonal-shaped sample was 5 mm. This sample was used for measuring the thermal diffusivity in the temperature range of 298 to 849 K.

The thermal diffusivity measurement of single-crystal GaN was performed using a vertical-type laser flash method.\textsuperscript{10–14} The single-crystal GaN is transparent for an Nd:glass laser; hence, a thin gold layer of approximately 100 nm thickness was sputtered on both the sides of the GaN sample. One layer acts as an absorber for the pulsed laser beam and the other acts as an emitter of infrared rays. Carbon powder was also sprayed on both the surfaces of the sample in order to increase the absorbance of the heating laser pulse and the emissivity of infrared rays for detecting the change in temperature of the sample after the laser irradiation. Such metal coating with carbon was found to work well for measuring the thermal diffusivity of the transparent samples.\textsuperscript{10,11}

Figure 1 shows a schematic diagram of the sample arrangement used for measuring the thermal diffusivity in this study. The front surface of the sample was irradiated with a pulse of Nd:glass laser as the heat source (output 7 J) with a beam diameter of approximately 10 mm. The beam diameter was large enough to homogeneously heat the octagonal-shaped sample surface. Therefore, the heat flow along the c axis of the sample is one-dimensional. To prevent a fracture in the thin metal film coating, an optical filter was inserted in the path of the laser beam to reduce the intensity of the laser beam. An InSb infrared detector was employed to measure the temperature response from the rear surface of the sample. The measurements were carried out under vacuum to minimize the heat leakage from the sample to its surroundings. The thermal diffusivity (\(\alpha\)) of the sample can be readily obtained using the following equation:\textsuperscript{15}

\[
\alpha = 0.1388 \frac{d^2}{t_{1/2}}
\]

where \(d\) is the sample thickness and \(t_{1/2}\) is the time required for the rear surface of the sample to reach half the value of the maximum temperature rise.

### 2.2 Thermal expansion measurement

In order to examine the effect of the sample thickness and temperature on thermal diffusivity, the thermal expansion coefficient of GaN was measured using a conventional thermal dilatometer at the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. This dilatometer allows measuring the size variation within 1 \mu m. A rectangular sample of single-crystal GaN was prepared and used for the thermal expansion measurement. The temperature during the experiments was varied between 298 to 473 K.

### 2.3 Specific heat capacity measurement

The specific heat capacity was measured using a conventional differential scanning calorimeter (DSC) at the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. The measurement was made under an atmosphere of high purity nitrogen with a flow rate of 50 ml/min. The specific heat capacity of sapphire was used as a reference. The DSC curve was analyzed by the enthalpy method. The experimental details and the data processing of DSC measurements have been reported elsewhere\textsuperscript{14} and are not repeated here.

### 3. Results and Discussion

Figure 2 shows the typical temperature response curve for single-crystal GaN obtained in this study. The temperature increases rapidly and reaches a maximum value within 7 ms. The time required to reach half the value of the maximum
temperature rise, \( t_{1/2} \), is estimated to be 1.64 ms, which is very short and is approximately twice the laser pulse width. This phenomenon is known as the pulse width effect and is a typical characteristic of laser flash measurements of high thermal diffusivity samples.\(^{16} \) In such a case, equation (1) gives an overestimation of the thermal diffusivity value. For this reason, we also carried out thermal diffusivity measurements of pure copper (thermal conductivity = 398 W/mK) with different thicknesses in the range of 0.889 to 3.179 mm. The pulse width effect was found to be insignificant in the measurement of copper disks with a thickness larger than 2.44 mm. On the basis of these results, a correction factor could be determined for thin samples with a thickness of less than 1 mm. Hence, the pulse width effect for the measurements of GaN was corrected with reference to copper.

The thermal diffusivity values of GaN and SiC at room temperature are shown in Fig. 3 together with those of sapphire and pure copper, which are known as high thermal conductivity materials.\(^{17} \) The thermal diffusivity of GaN obtained in this study is 98.6 \( \times 10^{-6} \) m\(^2\)/s at room temperature, whereas the thermal diffusivity of 6H-SiC is 198 \( \times 10^{-6} \) m\(^2\)/s at room temperature.

The thermal diffusivity measurements were also made above the room temperature up to 849 K. The thermal expansion coefficient of 3.53 \( \times 10^{-6} \) K\(^{-1}\) was obtained for GaN along the c axis. This clearly indicates that the change in the thickness of GaN due to thermal expansion is negligible and thus no correction due to the sample thickness is needed for estimating the thermal diffusivity using equation (1) at elevated temperatures. The thermal diffusivity of GaN is plotted in Fig. 4 as a function of temperature. The measurements are repeated five times at the measured temperature. From this figure, one can clearly see a good reproducibility in the results. The thermal diffusivity of GaN is found to decrease with increasing temperature and it may be represented with an uncertainty of \( \pm 1.8\% \)\(^{13} \) by the following equation:

\[
\alpha = \frac{939}{T - 201} \times 10^{-5} \text{ m}^2/\text{s}
\]

The measured DSC signal of GaN is shown in Fig. 5 along with two other curves of the reference material sapphire and an empty cell. It may be noted that the value of the specific heat capacity of the sample, \( C_p,\) can be estimated using the following equation:

\[
C_p = \frac{C_{ps} W_c S_c}{W_s S_r}
\]

where \( W_c \) is the weight of the sample and \( S_c \) is the area between the DSC curves of GaN and the empty cell. The subscripts \( r \) denotes the reference material, which is sapphire in this case. \( S_r \) is the area between the DSC curves of the reference material and the empty cell. The data obtained for the specific heat capacity of GaN are shown in Fig. 6 as open circles. Recently, Jacob et al.\(^{18} \) have obtained an empirical equation to calculate the heat capacity of GaN above room temperature. This equation is valid in the temperature range of 350 to 1075 K and is represented as

\[
C_p = 74.424 - 0.00106 T + 46720/T^2 - 685.9/T^{0.5}\text{J/molK}
\]

Equation (4) has also been plotted in Fig. 6 as a solid line for the purpose of comparison. The measured values in this study are well represented by eq. (4). Therefore, in order to obtain the value of the thermal conductivity of GaN, equation (4) was used to estimate the value of the specific heat capacity for temperatures ranging from room temperature to 849 K.

The thermal conductivity \( \lambda \) can be estimated using thermal diffusivity \( (\alpha) \) and specific heat capacity \( (C_p) \) data with the help of the following equation (5):

\[
\lambda = \alpha \rho C_p
\]

where \( \rho \) is the density of the material. As the value of the thermal expansion coefficient of GaN is very small (3.53 \( \times 10^{-6} \) K\(^{-1}\)), a constant density \( (6.15 \text{g/cm}^3) \)\(^1\) has been used to estimate the thermal conductivity by using equation (5). The calculated thermal conductivities of GaN, for comparison, are shown in Fig. 7 as a function of the temperature along with the results of SiC. The thermal conductivity of GaN decreases almost exponentially with increase in temperature. This is obvious because the density and specific heat are almost constant; however, thermal diffusivity changes exponentially with temperature (Fig. 4), as mentioned before. The thermal conductivity of GaN is found to rapidly decrease with increasing temperature. The data obtained by Sichel and Pankov\(^2\) also suggests the decreasing trend in thermal conductivity with increasing temperature above room temperature. Slack et al.\(^3\) and Jezowski et al.\(^9\) have presented a negative temperature coefficient of thermal conductivity above approximately 20 and 45 K, respectively, since the contribution of the Umklapp
Fig. 7 Thermal conductivity values of GaN as a function of temperature together with the values reported by Sichel and Pankove. The filled square mark shows the thermal conductivity of SiC-6H estimated from the measured thermal diffusivity data in this study. The broken line is the data from Nilsson et al. given by $\lambda = \frac{6111}{T+55}$ W/mK.

Table 1 Summary of the thermal properties of GaN and 6H-SiC at room temperature obtained in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific heat capacity (J/gK)</th>
<th>Density (g/cm$^3$)</th>
<th>Thermal diffusivity ($\times 10^{-6}$ m$^2$/s)</th>
<th>Thermal conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN (along the c axis)</td>
<td>0.417*</td>
<td>6.15**</td>
<td>98.6</td>
<td>253</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>0.69**</td>
<td>3.21**</td>
<td>198</td>
<td>438</td>
</tr>
</tbody>
</table>

*obtained from equation (4) and **taken from Ref. 1.

processes may dominate in this temperature range. The value of thermal conductivity obtained in the present study has been compared with the reported values of the free-standing bulk-shaped samples. The obtained thermal conductivity of 253 W/mK in this study at room temperature is higher than those previously reported. The major impurity in the present sample is silicon ($2.1 \times 10^{17}$ cm$^{-3}$), and the dislocation density is approximately $5 \times 10^6$ cm$^{-2}$. However, the sample used by Sichel and Pankove, which has a thermal conductivity value of approximately 130 W/mK, had many impurities as pointed out by Slack et al. The thermal conductivity value of 200 W/mK was obtained by Slack et al. for a GaN sample with impurities of oxygen ($2.1 \times 10^{16}$ cm$^{-3}$) and silicon ($0.37 \times 10^{16}$ cm$^{-3}$). Jezowski et al. reported the impurities and Ga vacancy (O: $1 \times 10^{20}$ cm$^{-3}$, Si: $1 \times 10^{17}$ cm$^{-3}$, H: $7 \times 10^{17}$ cm$^{-3}$, C: $1 \times 10^{19}$ cm$^{-3}$, Mg: $1 \times 10^{18}$ cm$^{-3}$, Ga vacancy: $1 \times 10^{18}$ cm$^{-3}$) in their sample and reported a thermal conductivity of approximately 226 W/mK. Florescu et al. reported a carrier concentration of $6.9 \times 10^{16}$ cm$^{-3}$ in the sample and a thermal conductivity of approximately 195 W/mK. The data on the impurities, dislocation density, and Ga vacancy in all the reported samples, which show high thermal conductivity, are not sufficient to make a quantitative comparison among the measured values of thermal conductivity. However, it may be concluded that the high thermal conductivity value of GaN, which has been obtained in this study, is attributed to the low concentration of impurities and low dislocation density. It should be noted, as shown in Fig. 7, that the temperature variation of SiC reported by Nilsson et al. is close to the GaN case.

4. Summary

The thermal diffusivity of single-crystal GaN grown by the HVPE process was measured not only at room temperature but also at high temperatures of up to 849 K using the vertical-type laser flash method. The results were summarized as a function of the temperature. The measurement of the thermal expansion of GaN along the c axis clearly indicates that no correction due to the sample thickness is needed for estimating the thermal diffusivity value; this is because the thermal expansion coefficient of GaN is very low ($3.53 \times 10^{-6}$ K$^{-1}$).

The specific heat capacity of GaN was also measured using a differential scanning calorimeter in order to obtain the values of the thermal conductivity of GaN as a function of temperature. The thermal properties of single-crystal GaN at room temperature, which are obtained in this study, are summarized in Table 1 together with those of SiC for comparison. The thermal conductivity value of 253 W/mK for GaN along the c axis is the highest reported value among the previously reported ones for single-crystal GaN; this corresponds to approximately 60% of the value reported for SiC. Although thermal properties of single-crystal GaN are known to be very sensitive to defects, the present results at least suggest that the thermal conductivity value of single-crystal GaN could be significantly improved when a perfect crystal is produced, which is the case in the current study. It is also worth mentioning that GaN is undoubtedly one of the candidates for next generation high-power-switching devices due to its high thermal conductivity.

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REFERENCES