Doping Dependence Of The Thermal Conductivity Of Hydride Vapor Phase Epitaxy Grown *n*-GaN/Sapphire (0001) Using A Scanning Thermal Microscope

D.I. FLORESCU*, V.A. ASNIN*, L.G. MOUROKH*, FRED H. POLLAK*, and R. J. MOLNAR**

* Physics Department and New York State Center for Advanced Technology in Ultrafast Photonic Materials and Applications, Brooklyn College of CUNY, Brooklyn, NY 11210

** Massachusetts Institute of Technology, Lincoln Laboratory, Lexington, MA 02420-9108

ABSTRACT

We have measured the doping concentration dependence of the room temperature thermal conductivity (κ) of two series of *n*-GaN/sapphire (0001) fabricated by hydride vapor phase epitaxy (HVPE). In both sets κ decreased linearly with log *n*, the variation being about a factor two decrease in κ for every decade increase in *n*. $\kappa \approx 1.95$ W/cm-K was obtained for one of the most lightly doped samples ($n = 6.9 \times 10^{16}$ cm^{-3}), higher than the previously reported $\kappa \approx 1.7$-1.8 W/cm-K on lateral epitaxial overgrown material [V.A. Asnin *et al*, Appl. Phys. Lett. **75**, 1240 (1999)] and $\kappa \approx 1.3$ W/cm-K on a thick HVPE sample [E.K. Sichel and J.I. Pankove, J. Phys. Chem. Solids **38**, 330 (1977)]. The decrease in the lattice component of κ due to increased phonon scattering from both the impurities and free electrons outweighs the increase in the electronic contribution to κ.

INTRODUCTION

Despite the considerable body of work, both experimental and theoretical, on the electronic, optical, and structural properties of group III nitrides [1] relatively little work has been reported on thermal conductivity κ. This quantity is of importance from both fundamental and applied perspectives. The lattice thermal conductivity is a function of the mean free path of the phonons and hence is determined by both intrinsic (phonon-phonon Umklapp scattering) and extrinsic (phonon-"defect", phonon-carrier scattering) factors [2]. Sichel and Pankove [3] determined κ of "bulk" hydride vapor phase epitaxy (HVPE) GaN as a function of temperature (25K<T<360K) with $\kappa \approx 1.3$ W/cm-K at 300K. More recently Asnin *et al* [4] have performed high spatial resolution measurements on several lateral epitaxial overgrown (LEO) GaN/sapphire (0001) samples using a scanning thermal microscope (SThM) and found $\kappa \approx 1.7$-1.8 W/cm-K [4]. Slack has estimated an upper limit of 1.7 W/cm-K at 300K for GaN [5].

We report high spatial resolution determination of κ at 300K on two sets of HVPE *n*-GaN/sapphire (0001) samples as a function of *n*. The measurements were made using a ThermoMicroscope's SThM Discoverer system [6], with a spatial resolution of ≈ 2-3 μm. Values of *n* were deduced from both 300K Hall effect and micro-Raman [longitudinal optical phonon-plasmon (LPP)] measurements. In both sets of samples κ decreased linearly with log *n*, the variation being about a factor two decrease in κ for every decade increase in *n*. $\kappa \approx 1.95$ W/cm-K was obtained for one of the most lightly doped samples ($n = 6.9 \times 10^{16}$

https://doi.org/10.1557/S1092578300004476 Published online by Cambridge University Press

cm^{-3}), higher than previously reported κ [3,4].

Sample set A had unintentional n (6-800x10^{16} cm^{-3}) and thicknesses (t) in the range of 5-74 μm. For sample set B t was constant≈10 μm and 15x10^{16} cm^{-3}< n < 300x10^{16} cm^{-3}.

Our observation also helps to explain the results on the LEO material [4], which had $n \approx$ (10-20)x10^{16} cm^{-3} [7]. The decrease in the lattice component of κ due to increased phonon scattering from both the impurities and free electrons outweighs the increase in the electronic contribution to κ.

EXPERIMENTAL DETAILS

The GaN films were grown by the HVPE method in a vertical type reactor [8]. During this process, gallium monochloride is synthesized upstream by reacting HCl gas with liquid Ga metal at 800-900^{0}C.The GaCl is transported to the substrate where it is reacted with NH_3 at 1000-1100 ^{0}C forming GaN. All films were grown on (0001) sapphire. The carrier concentration n_H was determined by 300K Hall effect measurements. Several characteristics of the samples are listed in Table I.

The carrier concentration for $n \geq$ 40x10^{16} cm^{-3} was also determined from the LPP modes observed in Raman scattering [9] and compared to the Hall effect results. Raman microprobe (≈ 2μm) measurements were made in the backscattering geometry using a triple grating spectrometer (Jobin-Yvon model T64000) and the 488 nm line of an Ar-ion laser as excitation. The Raman system was equipped with an Olympus BH2 microscope. Values of the carrier concentration (n_R) were deduced from Eqs. (2) and (3) in Ref. [8] (see Table I), using an electron effective mass (m_e^*) of 0.22 (in units of the free electron mass) [10] and a high frequency dielectric constant (ε_∞) of 5.5 [11].

The probe tip of the SThM system consists of a "V" shaped resistive thermal element incorporated at the end of a cantilever that enables atomic force microscopy-type feedback, as shown schematically in Fig. 1a. The arms of the cantilever are made of Wollaston process wire consisting of silver wire ≈ 75μm in diameter containing a platinum/10% rhodium core ≈ 3μm in diameter. The resistive element at its end comprises a 200μm length of platinum that has been exposed by removal of the silver and bent into a "V" shape (radius of curvature ≈ 1μm), which acts as the probe. The resistive element forms one leg of a Wheatstone bridge, as shown in Fig. 1b. A current is passed through the probe so that in air its temperature is about 40-50°C above ambient. There is a feedback loop to adjust the bridge voltage as necessary to keep the bridge balanced thus keeping the temperature of the probe constant. When the probe contacts the sample heat flows from the probe to the material, as shown in Fig. 1c. In the absence of feedback, this flow of heat would reduce the probe temperature, decreasing the resistance and causing the bridge to shift. The feedback senses this shift and increases the voltage applied to the bridge (U_{out}), returning the resistance to its set point. The thermal conductivity κ is proportional to the heat flow or $(U_{out})^2$, as shown in Fig. 1c.

Although initially designed to measure only relative spatial variations in U_{out}, Ruiz *et al* [12] developed a calibration procedure that makes is possible to evaluate absolute values of κ. Based on the results of Ref. [13] we estimate that the lateral/depth resolution is about 2 – 3 μm for materials with $\kappa \approx$ 1.5-2 W/cm-K.

https://doi.org/10.1557/S1092578300004476 Published online by Cambridge University Press

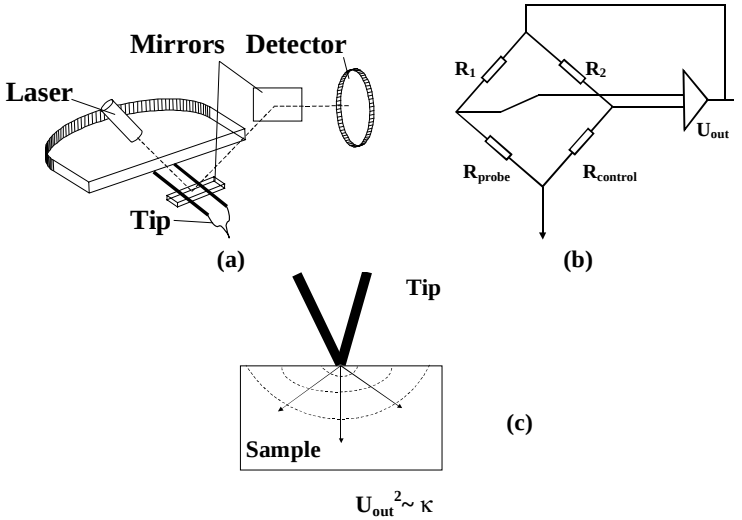


Fig. 1 (a) Schematic diagram of the SThM probe, (b) circuit diagram of the probe control, and (c) heat flow from the tip into the sample.

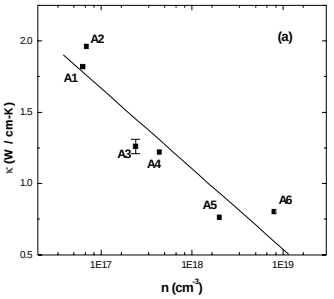
Table I Summary of t, n_H/n_R, μ and κ of the two sets of samples.

Sample	t (μm)	n_H/n_R (10^{16} cm^{-3})	μ (cm^2/V-s)	κ(W/cm-K)
A1	74±5	6.3/-	921	1.82±0.1
A2	57±4	6.9/-	850	1.95±0.1
A3	23±2	24/-	633	1.26±0.07
A4	6±1	44/35	207	1.23±0.07
A5	13±2	190/150	300	0.76±0.04
A6	5±1	800/500	841	0.80±0.04
B1	10±1	14/-	470	1.62±0.08
B2	10±1	15/-	418	1.68±0.08
B3	10±1	16/-	485	1.65±0.08
B4	10±1	59/50	423	1.72±0.08
B5	10±1	100/85	369	1.38±0.07
B6	10±1	197/140	309	1.12±0.06
B7	10±1	300/250	276	1.10±0.05

https://doi.org/10.1557/S1092578300004476 Published online by Cambridge University Press

EXPERIMENTAL RESULTS

Shown in Table I are the measured values of κ at 300K for samples A1-A6 and B1-B7. Note that samples A1 and A2 with $n = 6.3\text{x}10^{16}$ cm^{-3} and $n = 6.9\text{x}10^{16}$ cm^{-3} have $\kappa = 1.82\pm0.05$ W/cm-K and 1.95±0.05 W/cm-K, respectively; the latter is the highest value of this parameter observed to date. Plotted in Figs. 2a and 2b are κ as a function of log n for the two sets of samples, respectively. Representative error bars are shown. The solid lines in the figure are least-square fits to a linear function. For both sets of samples $\kappa(n)$ is essentially the same.



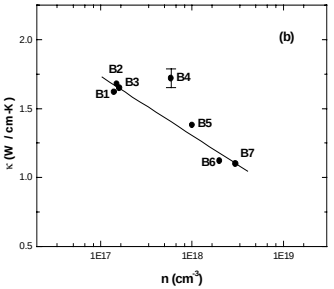


Fig. 2 Thermal conductivity as a function of carrier concentration, n, for samples (a) A1-A6 and (b) B1-B7.

DISCUSSION OF RESULTS

From kinetic theory the lattice κ is given by [2]:

$$\kappa(T)=(1/3)v_s c(T)\ell(T)=(1/3)v_s^2 c(T)\tau(T) \qquad (1)$$

where v_s is the average velocity of sound (with only a weak temperature dependence), $c(T)$ is the lattice specific heat, $\ell(T)$ is the phonon mean free path, and $\tau(T)$ is the lifetime.

In almost all materials $\kappa(T)$ first increases with temperature, reaches a maximum (κ_{max}) at some characteristic temperature T_{ch}, and then decreases [4]. At low temperatures ℓ is relatively long and is dominated by extrinsic effects such as "defects" and/or finite crystal size and $c(T)\propto(T/\Theta_D)^3$, where Θ_D is the Debye temperature. As the temperature increases $c(T)$ begins to saturate and intrinsic temperature dependent Umklapp processes become dominant, thus causing a decrease in ℓ. For GaN $T_{ch} \approx 200$K [3] and $\Theta_D \approx 600$K [14].

For $T<T_{ch}$ κ is very sensitive to "defect" density but still has some dependence in a range of T above T_{ch}. Since at 300K we are close to T_{ch}, the thermal conductivity will still be a function of n.

The observed dependence of κ on log n, as shown in Fig. 2, is difficult to account for in detail since we are in a regime where both extrinsic and intrinsic scattering processes are important. The scattering of the phonons from the impurity atoms can be described on the basis of mass-difference scattering, the relaxation time being given by [2]:

$$\tau_{imp}^{-1} \propto n(1\text{-}M_{imp}/M_{av}) \qquad (2)$$

where M_{imp} is the mass of the impurity atoms and M_{av} is the average mass of the atoms in the

https://doi.org/10.1557/S1092578300004476 Published online by Cambridge University Press

material. Thus there will certainly be a dependence of κ on n. However, because of the Umklapp contribution, phonon scattering from the free carriers, and the contribution of the free carriers to the electronic component of κ; the particular function form is not immediately evident. Clearly more work in this area needs to be done.

Slack has estimated an upper bound of $\kappa \approx 1.7$ W/cm-K for GaN at 300K from the relation [5]:

$$\kappa = BM_{av}\delta\Theta_D^3/T\gamma^2 \qquad (3)$$

where B is a constant, δ is the average volume occupied by one atom in the crystal, and γ is the Grüneisen parameter. By using the factor $M_{av}\delta\Theta_D^3$ as a scaling parameter he deduced the above value of κ for GaN at 300K. However, this analysis is limited since the above expression is applicable only for $T >> \Theta_D$ ($\approx$ 600K in GaN).

Our observation also helps to explain the observed values of $\kappa \approx 1.7$-1.8 W/cm-K on the LEO material [6], which had $n \approx (10\text{-}20)\text{x}10^{16}$ cm^{-3} [7] (see Fig. 2).

Certain GaN devices, such as high power field effect transistors, laser diodes, etc., would benefit greatly from GaN with higher thermal conductivity, as heat extraction from the device becomes more efficient with higher κ. Also, GaN has many potential applications in the area of high temperature electronics, where a large κ is very advantageous [15]. Our highest observed value of $\kappa \approx 1.95$-1.85 W/cm-K is somewhat smaller than single crystal AlN ($\approx$2.85 W/cm-K) [16] and is considerably higher than that of sintered AlN material [5]; the latter is often used as a heat sink material. Thus GaN based devices could be fabricated on HVPE GaN/sapphire material with the above thermal conductivities, thus avoiding costly processing steps.

SUMMARY

The doping dependence of the room temperature κ of two series of HVPE n-GaN/sapphire (0001) has been measured using a SThM. κ decreased linearly with log n, the variation being about a factor two decrease in κ for every decade increase in n in both sets of samples. The general behavior of $\kappa(n)$, i.e., decrease with increasing n, is similar to other semiconductors in a comparable temperature range. For one of the most lightly doped samples ($n = 6.9\text{x}10^{16}$ cm^{-3}) $\kappa \approx 1.95$ W/cm-K, higher than the previously reported κ on several LEO samples and a thick HVPE material. The decrease in the lattice component of κ due to increased phonon scattering from both the impurities and free electrons outweighs the increase in the electronic contribution to κ. The implications of these findings for device applications and design are discussed.

ACKNOWLEDGEMENTS

The Brooklyn College work was supported by Office of Naval Research contract N00014-99-C-0663 (administered by Dr. Colin Wood) and the New York State Science and Technology Foundation through its Centers for Advanced Technology program. The Lincoln Laboratory work was sponsored by the US Air Force under Air Force contract #F19628-95-C-002. Opinions, interpretations, conclusions, and recommendations are those of the authors

and are not necessarily endorsed by the US Air Force.

REFERENCES

[1] See, for example, *Group III Nitride Semiconductor Compounds*, ed. by B. Gil (Clarendon, Oxford, 1998).

[2] See, for example, *Thermal Conduction in Semiconductors* by C.M. Bhandari, and D.M. Rowe (Wiley, New York, 1988)

[3] E.K. Sichel and J.I. Pankove, J. Phys. Chem. Solids **38**, 330 (1977).

[4] V.A. Asnin, F.H. Pollak, J. Ramer, M. Schurman, and I. Ferguson, Appl. Phys. Lett. **75**, 1240 (1999).

[5] G.A. Slack, J. Phys. Chem Solids **34**, 321 (1973).

[6] ThermoMicroscopes, 1171 Borregas Avenue, Sunnyvale, CA 94089.

[7] M. Pophristic, F.H. Long, M. Schurman, J. Ramer, and I.T.Ferguson, Appl. Phys. Lett. **74**, 3519 (1999).

[8] R.J. Molnar, W. Gotz, L.T. Romano, and N.M. Johnson, J.Crystal Growth **178**, 147 (1997).

[9] P.Perlin, J. Camassel, W. Knap, T. Taliercio, J.C. Chevin, T. Suski, I. Gregory, and S. Porowski, Appl. Phys. Lett. **67**, 2524 (1995).

[10] M. Suzuki, and T. Uenoyama in *Group III Nitride Semiconductor Compounds*, ed. by B. Gil (Clarendon, Oxford, 1998), p. 307.

[11] G. Popovici, H. Morkoç, and S.N. Mohammad in *Group III Nitride Semiconductor Compounds*, ed. by B. Gil (Clarendon, Oxford, 1998), p. 19.

[12] F.Ruiz,W.D. Sun, F.H. Pollak, and C.Venkatraman, Appl. Phys. Lett. **73**, 1802 (1998).

[13] A. Hammiche, H.M. Pollack, M. Song, and D.J. Hourston, Meas. Sci. Technol. **7**, 142 (1996).

[14] I. Akasaki, and H. Amano in *Properties of Group III Nitrides*, ed. by J.H. Edgar (INSPEC, London, 1994) p. 30.

[15] J.T. Torvik, M. Leksono, J.I. Pankove, and B. Van Zeghbroeck, MRS Internet J. Nitride Semicond. Res. **4**, 3 (1999).

[16] G.A. Slack, R.A. Tanzilli, R.O. Pohl, and J.W. Vandersande, J. Phys. Chem. Solids **48**, 641 (1987)