

Thermoelectric Properties of Hot-Pressed GaN and InN

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An attempt was made to obtain bulk III-nitride semiconductors such as InN, GaN and In_xGa_{1-x}N alloy using hot-press method in order to test their high temperature thermoelectric properties. The Seebeck coefficient and the resistivity were $-10\mu\text{V/K}$ and $1.8 \times 10^{-6} \Omega\text{m}$ for InN, and $-50\mu\text{V/K}$ and $1.9 \times 10^{-4} \Omega\text{m}$ for GaN at 300K, respectively. Thermal conductivity determined by laser flash method with porosity correction was 17W/mK for InN and 2.6W/mK for GaN. For InN the Seebeck coefficient and the resistivity increased monotonously with increasing temperature, which indicates that InN is metal or degenerated semiconductor. The power factor and the figure of merit were $2.1 \times 10^{-4} \text{ W/mK}^2$ and $1.5 \times 10^{-5} \text{ K}^{-1}$ for InN and $6.9 \times 10^{-5} \text{ W/mK}^2$ and $2.6 \times 10^{-5} \text{ K}^{-1}$ for GaN at 650K, respectively.

Key words: III-nitrides, Seebeck coefficient, thermal conductivity, thermoelectric energy conversion

1. INTRODUCTION

Thermoelectric power generation is a unique technology, which converts thermal energy into electrical energy directly using a monolithic semiconductor device. Functional materials used in the device for this purpose is called as thermoelectric materials and should possess large electrical conductivity and Seebeck coefficient, and very low thermal conductivity like a glass at the same time in order to maximize the thermal-to-electrical conversion efficiency. The best thermoelectric materials have been found in metal chalcogenides system such as Bi₂Te₃ [1] and PbTe[2] and metal pnictides systems, such as Zn₄Sb₃ [3], CoSb₃ [4,5] and Ce(Fe_{1-x}Co_x)₄Sb₁₂ [6], where the heavy metal elements play a important role to suppress the lattice thermal conductivity. One of the most important subjects in this research field is to find out a new potential thermoelectric material without using such a toxic elements since the energy applications, in which vast amount of materials are used, dose not accept any expensive and harmful components. Findings of oxide thermoelectric materials [7] are good demonstration of environment-conscious materials development.

Currently, III-nitrides semiconductors (GaN, AlN, InN, and their alloys) have high prospects for applications in opt-electronics such as light-emitting devices. The electrical transport and microscopic parameters such as effective mass, band gap and Hall nobilities have been deeply investigated[8], however, very limited number of research has been conducted to evaluate the thermoelectric properties of III-nitride. The system has advantages for such target mainly since they are composed of Al, Ga, In and N, which do not stress the environment.

Among them, Yamaguchi et al. reported

thermoelectric properties of InN based ternary alloy film [9] and related III-oxynitride thin film [10] prepared by reactive magnetron sputtering. The resistivity and the Seebeck coefficient of Al_{0.55}In_{0.45}N in the report are $2\text{m}\Omega\text{cm}$ and $-70\mu\text{V/K}$ at 900K, which are comparable with those of oxide materials being currently under development. Therefore further investigation on this system is desired not only for thin films but also for bulk materials.

In this study we made an attempt to prepare bulk III-nitrides compounds using hot-press method to evaluate the thermoelectric transport properties of InN and GaN at elevated temperature.

2. EXPERIMENTAL

InN and AlN (Toshima Chem. Co. Ltd.) and GaN(Furuuchi Chem. Co. Ltd) fine powders prepared on the route of pyrolysis reaction of ammonium fluoride compound of metals were used as starting materials in this study. Fig.1 shows electron microscopy pictures of the GaN and the InN powder and the particle sizes are estimated of the order of micrometers for the InN and much finer for the GaN from the picture. These nitride compound powders were examined by a powder X-ray diffraction and confirmed that both of them belonged to Wurtzite crystal structures. A small peak corresponds to In metal was detected in the InN powder pattern, whereas a trace of contamination phase was found in the GaN powder. The powders were charged in a 15mmφ graphite die cavity, and sealed with two graphite spacers and 2mm thick PBN powder surrounding the target powder. After an evacuation of the chamber down to 10 Pa and a purge with Ar gas, hot- pressing were carried out in a Ar gas flow under the condition of 100MPa uniaxial pressure, 773-973K x 120min for InN, In_{0.8}Ga_{0.2}, In_{0.8}Al_{0.2} and 1273K x 120min. for GaN, respectively.

Compacted bulk pellets were examined with X-ray diffraction and the density was determined with the volume and the weight. The pellets were cut into

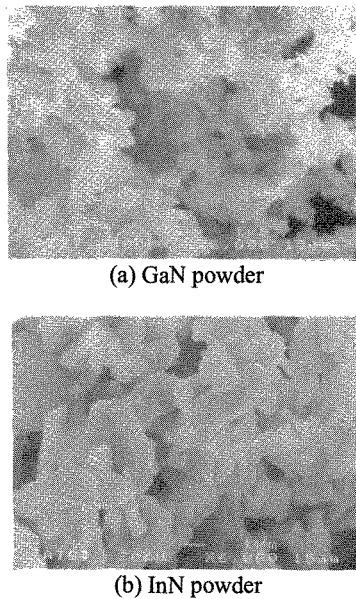


Fig.1 SEM pictures of GaN powder (a) and InN (b)

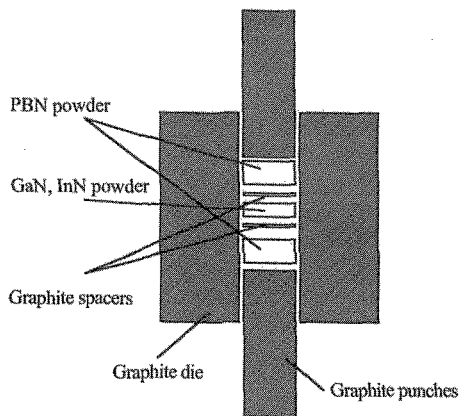


Fig.2 Schematic drawing of hot-press dies setup

1x1x15mm rectangular shaped samples, then resistivity and Seebeck coefficient measurement were carried out using ZEM-1 (ULVAC-RIKO Co. Ltd.) for temperature range from 310K to 650K. Thermal conductivity was determined from room temperature up to 673K with 1mm thick, 10mm ϕ small pellet by using laser flash apparatus, TC-7000 (ULVAC-RIKO Co.Ltd.)

3. RESULTS

From preliminary tests to tune the hot-pressing temperature for InN, it was found that temperature below 823K is too low for necking formation, and 973K is too high, which leads rapid decomposition of InN into nitrogen and metal In. The optimized hot-pressing temperature to maximize the density of InN sample in this study was supposed to be in the vicinity of 873K and the density was 4.66g/cm³, which was 68% of theoretical density of 6.81g/cm³. Decomposition of In took place even at 873K, and this was confirmed by X-ray diffraction as shown in Fig.3. As seen in the peak pattern in Fig.3 (a), relative peak height of metal In is

increased than that of starting powder. Estimated volume fraction of metal In was less than 20%.

For samples of nominal alloy composition, In_{0.8}Al_{0.2}N and In_{0.8}Ga_{0.2}N, we obtained 4.16 g/cm³ and 4.20 g/cm³, corresponding to 69% and 62% of the theoretical density, respectively. From X-ray diffraction data, it was revealed that there is no shift in the lattice constant and InN and GaN did not form isomorphous alloy under this process conditions. Separate distribution of GaN and InN was clearly observed by optical microscope in these samples.

The GaN samples prepared at 1273K was not fully dense, rather porous, and the estimated relative density was about 48% of the theoretical value, however the sample had a enough mechanical strength to be handled in post cutting process.

Fig.4, 5 show temperature dependences of electrical resistivity and Seebeck coefficient of all samples. InN and its composite with GaN and AlN show relatively low resistivity as a semiconductor, of the order of 10⁻⁶ Ω m. The resistivity and absolute value of Seebeck coefficient monotonously increase together with increasing temperature, which means the samples are metallic or degenerated semiconductors with high carrier concentration. On the other hand, GaN has two orders higher resistivity than that of InN, and the value decreases with increasing temperature. But the slope is not fitted to Arrhenius plot, and the decrease of the resistivity is supposed to be a complex reflection of its semiconducting nature and macroscopic changes of the texture in its porous structure. The absolute value of Seebeck coefficient increased monotonously from 50 μ V/K to 100 μ V/K in measured temperature range.

Fig. 6 shows the power factor value, $PF=S^2/\rho$, calculated from Fig.4 and Fig.5. A maximum power factor value of 1.2 μ W/cmK² is observed in InN sample at 650K. There observed a tendency that an addition of GaN and AlN to InN decreases the power factor.

Fig.7 and Fig.8 show temperature dependences of heat capacity and thermal conductivity. In laser flash method, thermal conductivity is given as a product of measured density D , thermal diffusivity α and heat capacity C_p , where the α and C_p are determined simultaneously analyzing thermal responses of the pellet-like sample. In general the error in thermal conductivity determined in this method mainly attributed to error of heat capacity. In this study, the measured heat capacity of InN showed a good agreement with the literature value[11] as plotted in Fig.7. The thermal conductivity decreases with increasing temperature accompanying a sharp drop at 400K for InN and InN based composition. As mentioned earlier, In metal phase was detected from InN sample by X-ray diffraction, and the drop in thermal conductivity is possibly related to metal In. All of the thermal conductivity data are temperature independent above 400K.

The figure of merit Z , a measure of performance of the thermoelectric material defined as $Z=S^2/(\rho \kappa)$, was calculated using data plotted in Fig.2, Fig.3 and Fig.8. At room temperature, we obtained $Z=3.4 \times 10^{-6} \text{ K}^{-1}$ and $5.6 \times 10^{-6} \text{ K}^{-1}$ for InN and GaN; respectively. The figure of merit increases with increasing temperature and showed maximum Z of $1.5 \times 10^{-5} \text{ K}^{-1}$ and $2.6 \times 10^{-5} \text{ K}^{-1}$ at 650K in this study.

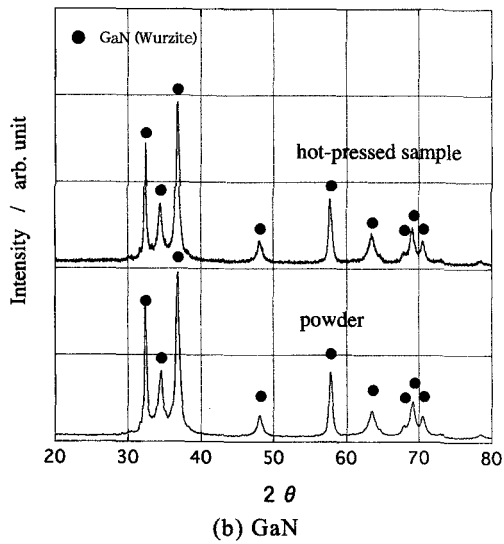
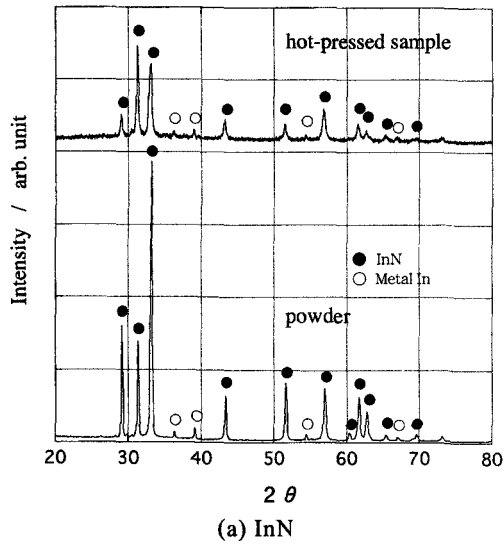


Fig.3 X-ray diffraction pattern of starting powder and hot-pressed sample of InN and GaN.

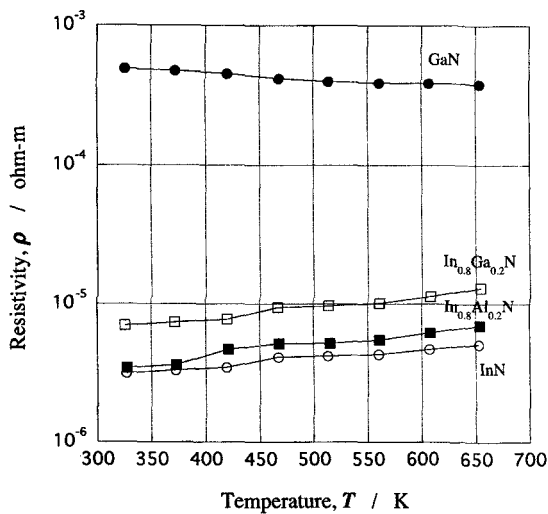


Fig. 4 Temperature dependence of electrical resistivity of InN, In_{0.8}Al_{0.2}N, In_{0.8}Ga_{0.2}N and GaN.

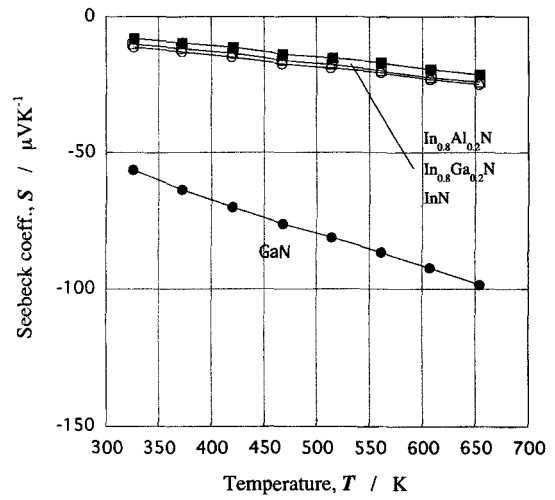


Fig. 5 Temperature dependence of electrical resistivity of InN, In_{0.8}Al_{0.2}N, In_{0.8}Ga_{0.2}N and GaN.

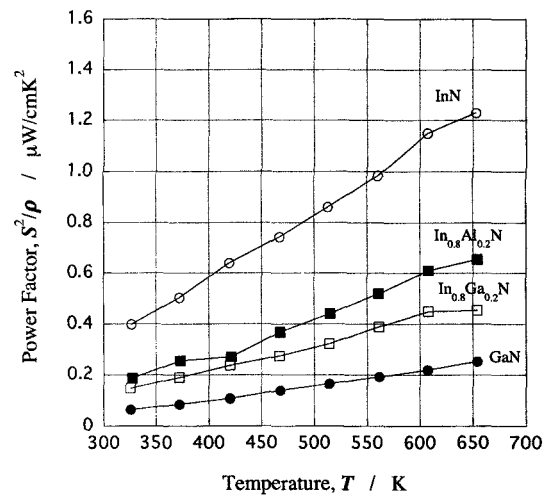


Fig. 6 Temperature dependence of power factor of InN, In_{0.8}Al_{0.2}N, In_{0.8}Ga_{0.2}N and GaN.

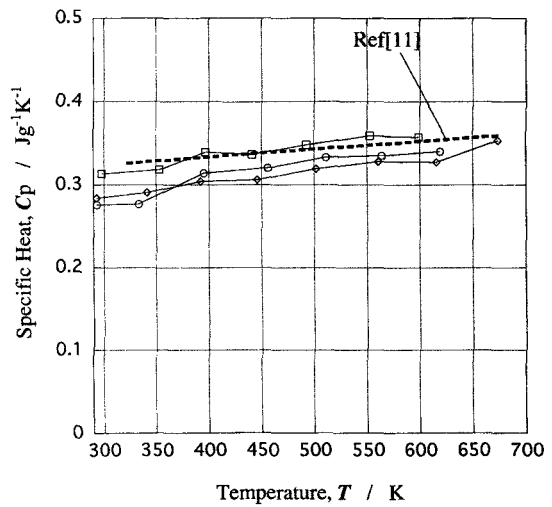


Fig.7 Temperature dependence of heat capacity of InN. Dotted line is taken from Ref[11].

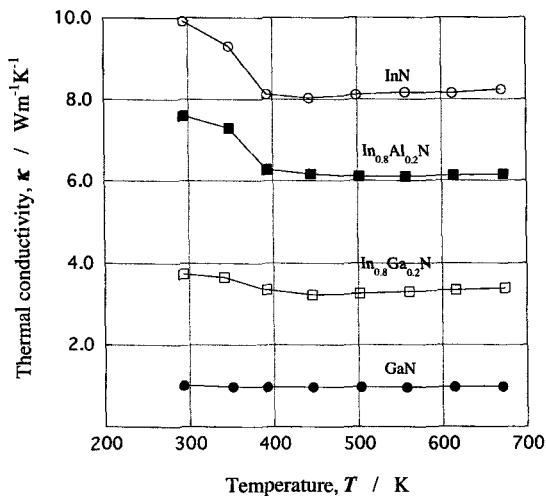


Fig. 8 Temperature dependence of thermal conductivity of InN, $\text{In}_{0.8}\text{Al}_{0.2}\text{N}$, $\text{In}_{0.8}\text{Ga}_{0.2}\text{N}$ and GaN.

4. DISCUSSIONS

The density of the sample was 68% for InN and 48% for GaN in this study. In order to estimate the thermoelectric transport properties of a fully dense material, we made a correction in the resistivity and the thermal conductivity depending on the density using Maxwell's equation[12]. For the case of porous media, the equation is expressed as

$$\kappa_m = \frac{2+e}{2(1-e)} \kappa_{\text{eff}}$$

where e , κ_m and κ_{eff} are porosity, conductivity of media, and effective conductivity, respectively. Seebeck coefficient doesn't change by volume fraction of macroscopic pore. The corrected data at 300K are summarized in Table I. We should note that the power factor of InN is consistent with that reported for InN based thin film.

The estimated thermal conductivity is 16.7 W/mK for InN and 2.6W/mK for GaN at 300K, and these are much smaller than reported values, 45W/mK[13] and 130W/mK[14], respectively.

The reason of the discrepancy may be partially due to difference in grain size of the samples. The smaller grain size is known to be effective to scatter propagating phonon and to reduce the thermal conductivity. The hot-pressed samples in this study have a size of several micrometers and that is probably the main reason of low thermal conductivity. The value of GaN is doubly checked by steady state relative method at room temperature, and the result supports very low thermal conductivity around 1W/mK. It seems that there is other microscopic phonon scattering mechanism in addition to grain size effect, and this remains as an open question in this study.

5. CONCLUSIONS

In this study we made an attempt to obtain bulk III-nitride semiconductors such as InN, GaN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy using hot-press method in order to test their high temperature thermoelectric properties. The Seebeck coefficient and the resistivity were $-10\mu\text{V/K}$ and

Table I Summary of thermoelectric properties of fully dense III-nitrides estimated with density correction.

Sample	Relative density	Seebeck coeff. $\mu\text{V/K}$	Thermal conductivity $\text{Wm}^{-1}\text{K}^{-1}$	Resistivity $\text{m}\Omega\text{-m}$	Figure of Merit Z (300K) K^{-1}	Figure of Merit Z (650K) K^{-1}
InN	68%	-10	16.7	1.76	3.4×10^{-6}	1.5×10^{-6}
GaN	48%	-50	2.6	190	5.6×10^{-6}	2.6×10^{-6}
$\text{In}_{0.8}\text{Ga}_{0.2}\text{N}$	62%	-10	7.1	3.53	4.0×10^{-6}	1.4×10^{-6}
$\text{In}_{0.8}\text{Al}_{0.2}\text{N}$	69%	-10	12.7	2.01	3.9×10^{-6}	1.4×10^{-6}

$1.76 \times 10^{-6} \Omega\text{m}$ for InN, and $-50\mu\text{V/K}$ and $1.9 \times 10^{-4} \Omega\text{m}$ for GaN at 300K, respectively. Thermal conductivity determined by laser flash method with porosity correction was 17W/mK for InN and 2.6W/mK for GaN. For InN the Seebeck coefficient and the resistivity increased monotonously with increasing temperature, which indicates that InN is metal or degenerated semiconductor. The maximum power factor and figure of merit within the measured temperature range were $2 \times 10^{-4} \text{W/mK}^2$ and $1.5 \times 10^{-5} \text{K}^{-1}$ at 650K, respectively.

References

- [1] H.J. Goldsmid, J. Appl. Phys., 32 2198 (1961)
- [2] V.Fano, in CRC Handbook to Thermoelectrics, Ed. by D.M. Rowe, CRC Press, p.257 (1995)
- [3] T.Caillat et al., J. Phys. Chem. Solid. **58**, p.1119 (1997)
- [4] L.D.Dudkin, et al., Zh. Neorg. Khim 1 p.2096 (1956)
- [5] G.S. Nolas, J. Sharp and H.J.Goldsmid Eds., Thermoelectrics -Basic Principles and New Materials Developments" Springer, p.178 (2001)
- [6] B. C. Sales, D. Mandrus, and R. K. Williams, Science **272**, 1325(1996)
- [7] I. Terasaki, Y. Sasago and K. Uchinokura: Phys. Rev. B56 (1997) R12685
- [8] P.Ruterana, M.Albrecht, J.Neugebauer Eds., Nitride Semiconductors, WILEY-VCH,(2003)
- [9] S.Yamaguchi, Y.Iwamura, A.Yamamoto, Appl. Phys. Lett., **82** p.2065-2067 (2003)
- [10] S.Yamaguchi, Y.Iwamura, A.Yamamoto, Jpn. J. Appl. Phys., **41** L1354-1356 (2003)
- [11] Thermochemical Properties of Inorganic Substances, Springer, (1977)
- [12] Maxwell, J.C., A Treatise on Electricity and Magnetism, Clarendon Press, Oxford, (1904)
- [13] S.Krukowski, et al., J. Phys. Chem. Solid., **59**, p.289 (1998)
- [14] E.K.Sichel and J. I. Pankove, J. Phys. Chem. Solid., **38**, p.330, (1977)

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