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TECHNICAL ARTICLE

Debye temperature of wurtzite AlN determined by X-ray powder diffraction

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The Debye temperature of wurtzite aluminum nitride (AlN) was determined by the Rietveld refinement method based on the room-temperature X-ray powder diffraction data. The refined lattice parameters are $a = 3.11139(1)$ Å, $c = 4.978\,43(3)$ Å; the refined positional parameter for N is $z = 0.384\,59(33)$ Å; and the refined temperature factors of Al and N were 0.442(12) Å^2 and 0.559(33) Å^2, respectively. Using this refined temperature factor, the Debye temperature was evaluated as 971 K through the Debye approximation. © *2014 International Centre for Diffraction Data.*
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Key words: AlN, Debye temperature, powder diffraction, X-ray

I. INTRODUCTION

The wurtzite III-nitride semiconductor, aluminum nitride (AlN), finds more and more applications in the next generation electronic and optical devices, owing to the excellent thermal conductivity, high electrical resistivity, high resistance to chemicals, wide direct band gap (6.2 eV), and transparency in the ultraviolet (UV) range. In addition, the small mismatch in thermal expansion coefficients and lattice constants with GaN makes the bulk AlN single crystal, an ideal substrate for GaN-based devices.

The Debye temperature, which indicates the effective cut-off phonon energy of a material, is a basic physical quantity but cannot be obtained directly from the experimental measurements. In general, the Debye temperature is estimated either by low-temperature specific heat or by elastic constants of materials or by the quasi-harmonic Debye model (Blanco *et al.*, 2004). The specific heat method is to measure the heat capacity and deduce the Debye temperature according to the Debye model. As to the elastic constants method, the Debye temperature can be estimated using the Anderson method (Anderson, 1963) once the elastic constants are obtained through experimental measurements or theoretical calculations. The quasi-harmonic Debye model is a theoretical calculation method adopting thermodynamic equations.

Despite several methods accessible to the Debye temperature, most of the works (Kato and Hama, 1994; Wright, 1997; Shimada *et al.*, 1998; Yonenaga *et al.*, 2002; Saib and Bouarissa, 2006; Kazan *et al.*, 2007; Sotnikov *et al.*, 2010; Wang *et al.*, 2010) focus mainly on the elastic constants, bulk moduli, or shear moduli rather than the Debye temperature, and no Debye temperatures for AlN have been further deduced. Furthermore, the data of Debye temperature for AlN obtained from different samples or based on the known calculation methods are scattered (Slack *et al.*, 1987; Nipko and Loong, 1998; Dodd *et al.*, 2001; Wang *et al.*, 2007, 2008; Peng *et al.*, 2008). It is worth mentioning that more precise Debye temperature can be obtained using quality samples, especially single crystals. Following Lu and Liang (1981), by utilizing of the method based on the X-ray powder diffraction using powder samples, the Debye temperature can also be derived. The effectiveness and reliability of this method have been confirmed in GaN (Chen *et al.*, 1999) and SiC (Peng *et al.*, 2009). To the best of our knowledge, the Debye temperature of AlN has not been estimated by this way. In this work, we first obtained high-purity and high-crystalline AlN powder samples by grinding AlN crystal prepared through the physical vapor transport (PVT) method. Then we employed the method of the X-ray powder diffraction to obtain the Debye temperature of AlN at 298 K for the first time.

II. EXPERIMENTAL

Growths of the AlN crystal were carried out by the PVT method in an inductively heated furnace. AlN polycrystalline wafer was selected as seed. Experimental details can be found elsewhere (Zuo *et al.*, 2012). Pre-sintered source was held into a TaC crucible, which was encased by a graphite crucible. The TaC crucible is 30 mm in internal diameter and 60 mm in length. The seed–source distance was kept at 12 mm and appropriate temperature field was controlled by tailoring graphite insulating material. This temperature field made the temperature of seed about 50 °C lower than that of the source. Before heating, the growth chamber was evacuated to a vacuum of about 6.0×10^{-4} Pa, and then it was filled into high purity N_2 (99.999%) of about 0.6 atm. In succession, the source materials were heated and maintained at about 2200 °C for 80 h, and then slowly cooled down to room temperature. Finally, AlN crystal boules were obtained through the aforementioned growth procedure. The AlN crystal was sliced, and then was treated by ultrasonic cleaning in anhydrous alcohol and de-ionized water for 30 min, respectively. High-quality AlN crystal was selected and grinded to fine powder. The ground AlN fine powders were sifted through a 400 mesh sieve (grain size <38 μm) before used for the X-ray powder diffraction analysis. The impurities in the AlN

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crystal were analyzed by Glow Discharge Mass Spectroscopy (GDMS) and Instrumental Gas Analysis (IGA). The X-ray powder diffraction analysis was performed on a Panalytical X'Pert diffractometer operated at 40 kV and 40 mA using Cu$K\alpha_1$ radiation at room temperature (298 K). The diffraction data were collected by step-scanning mode with steps of 0.02° (2θ). An angular range from $2\theta = 20°$ to 135° and a measuring time of 5 s per step were applied. The Rietveld refinement was carried out using the computer program FULLPROF (Rietveld, 1967, 1969; Rodriguez-Carvajal, 1990, 2003).

III. RESULTS AND DISCUSSION

Figure 1 shows the optical photo of the typical AlN crystal boule obtained by the PVT method. The size of the AlN crystal boule is 29 mm in diameter and 18 mm in height. Because of the rough surface and selective absorption, the AlN crystal shows non-transparent and brown color. To evaluate the purity of the AlN crystal we obtained, the impurities in the AlN crystal were analyzed by GDMS and IGA methods. The concentrations of the elements that could be detected were listed in Table I. The results show that oxygen, carbon, and silicon are the primary impurities, and their concentrations are 240, 300, and 260 ppm wt, respectively. The total impurity concentrations are <1000 ppm wt, which shows our samples are high-purity AlN.

For Rietveld refinement, the initial structural model was built according to the space group of AlN $P6_3mc$. The Al atom was set at (1/3, 2/3, 0) and the N at (1/3, 2/3, z/c), respectively. The z-parameter of the N atom was refined freely. By successively refining the parameters for the N atomic position and the isotropic temperature parameters, the isotropic Debye–Waller factors (B factors) of Al and N were converged to 0.442(12)and 0.559(33) Å^2, respectively. The agreement factors converged to $R_p = 6.33\%$ and $R_{wp} = 8.19\%$. The result of the final Rietveld refinement was plotted in Figure 2, and the final refined structural parameters and temperature factors were given in Table II.

Using the obtained temperature factors, the Debye temperature can be calculated according to the Debye approximation (Lu and Liang, 1981). In the approximation, the



Figure 1. (Color online) Photo of the typical AlN crystal boule obtained by the PVT method.

TABLE I. Impurity concentrations of AlN crystal analyzed by IGA and GDMS.

O	C	Si	Ti	V	Ta		Method
240	300	–	–	–	–	(ppm wt)	IGA
–	–	260	20	0.11	Electrode	(ppm wt)	GDMS

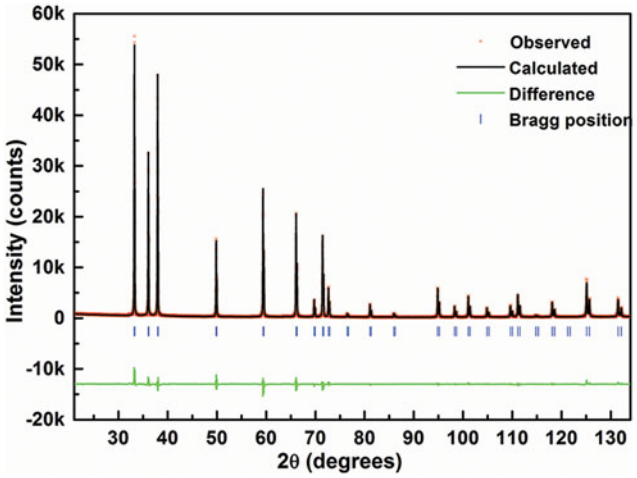


Figure 2. (Color online) Rietveld refinement of the X-ray diffraction pattern of AlN. Red small points represent the experimental values, black solid line is the calculated pattern, green solid line is the difference between the experimental and calculated values, and blue vertical bars are the Bragg positions.

TABLE II. Final refined parameters from powder X-ray diffraction data of AlN, $a = 3.111\ 39(1)$ Å, $c = 4.978\ 43(3)$ Å, space group $P6_3mc$, $R_p = 6.33\%$, $R_{wp} = 8.19\%$, and $R_{exp} = 3.66\%$.

Atoms	Site	x/a	y/b	z/c	B(Å^2)
Al	2b	1/3	2/3	0	0.442(12)
N	2b	1/3	2/3	0.384 59(33)	0.559(33)

temperature factor can be described as

$$B = \frac{6h^2T}{Mk\Theta_D^2}\left\{\phi(x) + \frac{x}{4}\right\} \quad (1)$$

where B is the average temperature factor for Al and N, $x = \Theta_D/T$, Θ_D is the Debye temperature, T is the experimental temperature, h is Planck's constant, k is Boltzmann's constant, M is the reduced atomic mass of Al and N, and ϕ(x) is the Debye integral function, which is defined as

$$\phi(x) = \frac{1}{x}\int_0^x \frac{y}{e^y - 1}dy \quad (2)$$

By defining

$$G = \frac{BMkT}{6h^2} \quad (3)$$

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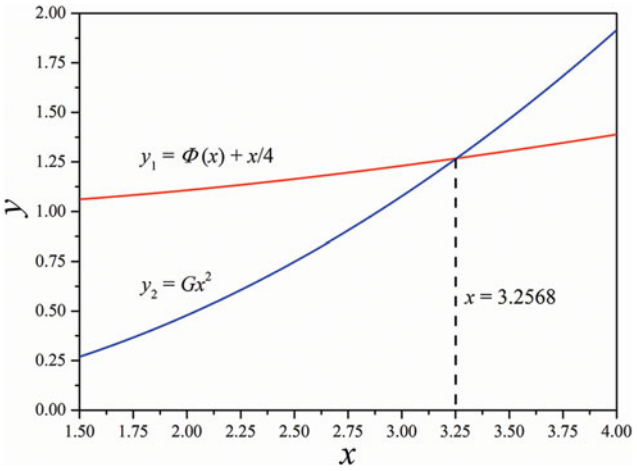


Figure 3. (Color online) Numerical solution for Eq. (4).

then Eq. (1) is reduced to

$$\phi(x) + \frac{x}{4} = Gx^2 \tag{4}$$

According to Eq. (3), the calculated value of G is 0.1196. Inserting $G = 0.1196$ into Eq. (4), and solving numerically the equation, as shown in Figure 3, we can get $x = 3.2568$. Then the Debye temperature can be obtained as $\Phi_D = 971$ K.

Our result together with other available experimental and theoretical calculation values of Debye temperature of AlN is summarized in Table III. As can be seen that our result of 971 K is in agreement with the results of 980 K (Dodd *et al.*, 2001), 975.97 K (Wang *et al.*, 2008), and 950 K (Slack *et al.*, 1987), but deviates from others. For the result of 903 K (Slack *et al.*, 1987), which is obtained by measuring surface acoustic velocity on the films prepared using metalorganic chemical vapor deposition (MOCVD) on sapphire, the existing stress and enhanced dislocation density because of the mismatch of lattice constants and thermal expansion coefficients between AlN and sapphire might be a source for underestimation. The result of 800 K (Nipko and Loong, 1998) corresponds to the Debye temperature at 0 K. The values of 1015.58 K (Wang *et al.*, 2007) and 1028 K (Peng *et al.*, 2008) are calculated results by adopting the quasi-harmonic Debye model on the basis of the thermodynamic theory and the ideal crystal structure of AlN, which are quite close to our result.

By the way, we have also tried to obtain the Debye temperature by measuring the low-temperature specific heat of the AlN single-crystal samples. However, the deduced Debye temperature from the specific heat experimental result is 458.39 K, which is much lower than the reported data. The similar phenomenon was observed in measuring the Debye temperature of GaN (Song *et al.*, 2004). We think that the large underestimation is probably because of heat loss between the testing sample and sample holder.

TABLE III. Experimental and theoretical calculation values of Debye temperature.

Θ_D(K)	Method	Sample	Reference
971	Exp.	Ground crystal	Present work
903	Exp.	Film	Slack *et al.* (1987)
950	Exp.	Polycrystalline	Slack *et al.* (1987)
980	Exp.	Ceramic	Dodd *et al.* (2001)
800	Cal.	–	Nipko and Loong (1998)
975.97	Cal.	–	Wang *et al.* (2008)
1015.58	Cal.	–	Wang *et al.* (2007)
1028	Cal.	–	Peng *et al.* (2008)

IV. CONCLUSION

High-purity and -quality AlN sample were prepared by the PVT method. The Debye temperature of wurtzite AlN was determined by the Rietveld refinement method based on the room-temperature X-ray powder diffraction data. The refined lattice parameters are $a = 3.111\ 39(1)$ Å, $c = 4.978\ 43\ (3)$ Å; the refined positional parameter for N is $z = 0.384\ 59\ (33)$ Å; and the refined temperature factors of Al and N were $0.442(12)$ Å^2 and $0.559(33)$ Å^2, respectively. Using these refined temperature factors, the Debye temperature has been evaluated as 971 K through the Debye approximation.

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SUPPLEMENTARY MATERIALS AND METHODS

The supplementary material refered to in this paper can be found online at journals.cambridge.org/pdj.

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