HEAT CAPACITY OF CRYSTALLINE GaN

Iwona Zięborak-Tomaszkiewicz, Ewa Utzig and P. Gierycz[*]

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

The heat capacity of gallium nitride has been measured by DSC method using DuPont Thermal Analyst 2100, DSC 951 unit in the temperature range (300–850 K). The temperature dependence of the heat capacity can be presented in the following form: $C_p = 32.960 + 0.162 \cdot 10^{-1}\,T + 2360170\,T^{-2} - 775370000\,T^{-3}$.

Introduction

Nitride semiconductor and specially GaN are widely investigated, from many years, in highly developed countries as USA and Japan [1]. Many methods for formation of crystalline layers of these semiconductors have been elaborated but most important seem to be the hetero- and homoepitaxial methods as well as the synthesis of the group III-nitrides from pure components under high pressure and temperature developed in the Institute of High Pressure Research, Polish Academy of Sciences [2–7]. Crystalline gallium nitride GaN(cr) is the most important from the semiconductors of the group-III nitrides that over a time of few recent decades have been played very radical role in research and development of the modern optoelectronics. Of all the materials of importance in solid-state devices, none is more ubiquitous than gallium nitride. So, our results of GaN(cr) were executive of the heat capacity C_p by scanning calorimetry (DSC), and also the standard molar enthalpy of formation $\Delta_f H_m^0$ (298.15 K)=—163.7+4.2 kJ mol^{-1}, that have been concluded by fluorine combustion calorimetry [8]. The heat capacity of the solid GaN has been measured before by calorimetry in the low-temperature range of 5–60 [9] and 55–300 K [10] by Koschenko *et al.* Recently, the heat capacities of GaN single crystal were measured by Kremer *et al.* [11] in the low-temperature range of 15–400 K using a system calorimeter (Quantum Design, 6325 Lusk Boulevard, San Diego, CA) and in the range of 300–750 K with a Perkin-Elmer DSC. Chen *et al.* [12] measured the heat capacity of GaN in the temperature range of 113–1073 K and Itagaki *et al.* [13] as well as Leitner *et al.* [14] in the high temperature range of 812–1034 and 673–1173 K, respectively.

Experimental

Materials

Gallium nitride sample of monocrystalline in hexagonal wurzite structure received from High Pressure Research Center PAS (Warsaw, Poland) was very pure (>99.99%). The purity of the sample was confirmed by X-ray diffraction, thermogravimetry (TG) and the Perkin-Elmer Elemental Analyser.

Methods

Heat capacity of crystalline gallium nitride GaN was determined by DSC method [15] using DuPont Thermal Analyst 2100, DSC 910 unit. The measurements were carrier out in the temperature range 300–850 K at heating rate 5 K min^{-1}, in the atmosphere of dry, pure argon at flow rate 100 mL min^{-1}. The calorimeter was calibrated on the indium sample and the open aluminum pans were applied for the measurements.

Determination of the experimental data based on three DSC runs:

- first with empty pan
- second with reference material of well known C_p – in this case we used the synthetic sapphire (2-Al$_2$O$_3$ pellet)
- third with the sample of crystalline GaN (mass 18–24 mg).

Reproducibility of DSC signals in the range 300–850 K both for empty pan and containing sapphire pellet were confirmed. On the basis of these recorded DSC signals for each measurement as well as the known values of $C_p = f(T)$ for the sapphire the values of heat capacity of the GaN as a function of temperature has been determined by the use of the following equation:

* Author for correspondence: gierycz@ichf.edu.pl

$$C_p = C_{p_{sap}} \frac{\Delta_{sam}}{\Delta_{sap}} \frac{m_{sap}}{m_{sam}}$$

where C_p – the measured value of GaN heat capacity, $C_{p_{sap}}$ – the known value of sapphire GaN heat capacity, Δ_{sam} – the signal difference between the GaN sample and empty pan, Δ_{sap} – the signal difference between the sapphire sample and empty pan, m_{sam}, m_{sap} – the mass of GaN and sapphire sample, respectively.

The measured, in such a way, values of heat capacities as a function of temperature are shown in Table 1 and Fig. 1.

Table 1 Experimental values of GaN heat capacities

T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}
313.15	36.951	573.15	45.288
333.15	38.523	593.15	45.625
353.15	39.662	613.15	45.935
373.15	41.103	633.15	46.221
393.15	42.113	653.15	46.485
413.15	42.993	673.15	46.730
433.15	43.366	693.15	46.957
453.15	43.374	713.15	47.168
473.15	43.701	733.15	47.366
493.15	43.860	753.15	47.550
513.15	44.081	773.15	47.723
533.15	44.520	793.15	47.884
553.15	44.921	813.15	48.037
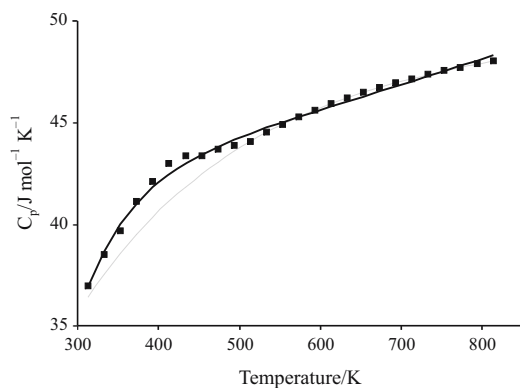
Fig. 1 Comparison of the experimental data of GaN with the results of their correlation and prediction;
■ – experimental data, —— – Leitner *et al.* – corr [14].,
- - - - – Kremer *et al.* – pred.[14]

Calculation of heat capacity data

The experimental data have been correlated by four different equations describing the heat capacity in the solid phase:
- the three polynomial equations:
  a) in the form proposed by Chen *et al.* [12]:

$$C_p = C_1 + C_2 T + C_3 T^{-2}$$

  b) in the form proposed by Itagaki and Yamaguchi [13]:

$$C_p = C_1 + C_2 T + C_3 T^{-2} + C_4 T^2$$

  c) in the form proposed by Leitner *et al.* [14]:

$$C_p = C_1 + C_2 T + C_3 T^{-2} + C_4 T^{-3}$$

- the equation proposed by Kremer *et al.* [11] in the form:

$$C_p = 6R\left(1 - \frac{\Theta_\infty^2}{20T^2} + \frac{\Theta_\infty^4}{560T^4}\right) + C_1 T$$

where C_p – heat capacity, J mol^{-1} K^{-1}; T – temperature, K; R – the gas constant; Θ_∞ – the Debye temperature, $\Theta_\infty = 863$ K; $C_1 \ldots C_4$ – adjustable parameters.

The minimization function (F) was defined as follows:

$$F = \min \sum_{i=1}^{n}(C_{p_i}^{exp} - C_{p_i}^{cal})^2$$

where $C_{p_i}^{exp}$, $C_{p_i}^{cal}$ – the experimental and calculated heat capacities, respectively, n – the number of experimental data points and for each equation the adjustable parameters were calculated using the Levenberg–Marquardt algorithm [16].

The results of correlation ($D(C_p)$ and $DR(C_p)$ – the absolute and relative root mean square deviations of heat capacity, respectively) as well as the obtained values of adjustable parameters are shown in Table 2.

$$D(C_p) = \left[\frac{\sum_{i=1}^{n}(C_{p_i}^{exp} - C_{p_i}^{cal})^2}{n-m}\right]^{0.5}$$

$$DR(C_p) = \left[\frac{\sum_{i=1}^{n}\left(\frac{C_{p_i}^{exp} - C_{p_i}^{cal}}{C_{p_i}^{exp}}\right)^2}{n-m}\right]^{0.5}$$

where $C_{p_i}^{exp}$, $C_{p_i}^{cal}$ – the experimental and calculated heat capacities, respectively, n – the number of experimental data points, m – the number of adjustable parameters.

The results of correlation of heat capacities experimental data (average error about 0.22 J mol^{-1} K^{-1} – 0.7%) obtained by the use of the first three equations are on the level of the experimental accuracy (1%).

However the best results of correlation have been obtained for the Leitner *et al.* [14] equation which has

Table 2 Results of correlation and prediction of the heat capacity experimental data of GaN

Equation	$D(C_p)$/J mol^{-1} K^{-1}	$DR(C_p)$/%	Adjustable parameters/J mol^{-1}
Correlation			
1) Chen *et al.* [12]	0.326	0.789	C_1=46.565 C_2=0.351·10^{-2} C_3= −998114
2) Itagaki and Yamaguchi [13]	0.258	0.589	C_1=63.674 C_2= −0.406·10^{-1} C_3= −1652880 C_4=0.305·10^{-4}
3) Leitner *et al.* [14]	0.220	0.505	C_1=32.960 C_2=0.162·10^{-1} C_3=2360170 C_4= −775300000
4) Kremer *et al.* [11]	0.711	1.677	C_1=0.155·10^{-2}
Prediction			
1) Kremer *et al.* [11]	1.088	2.553	C_1=0.00103 [104]

four adjustable parameters (Table 2) and gave results of 20–30% better than other of these equations.

The worst results have been obtained by the use of the Kremer *et al.* [11] equation elaborated for description of whole range of temperatures from 300 to 1400 K. The average error of correlation is 1.5 worse than the experimental accuracy and three times bigger (Table 2) than in the case of the best Leitner *et al.* [14] equation. It is caused by the fact that this equation has only one adjustable parameter and its flexibility is much poorer than others.

The discrepancy between the best correlation results and the experimental heat capacities data are plotted in Fig. 1.

Moreover the predictive abilities of the Kremer *et al.* [11] equation have been checked on prediction of heat capacity GaN data with the parameter C_1=0.00103 J mol^{-1} K^{-2} adjusted by least-squares fitting of all data from 300 to 1400 K [11]. The obtained prediction results are given in Table 2 and Fig. 1.

The predicted values of heat capacities lay below the experimental data in the whole range of investigation (from 300 to 850 K). The biggest gap, which mainly contributes to the overall error, has been found for the first region between 300–550 K. The second part of the range of experimental data is predicted quite well.

Conclusions

The experimental results which fully agree with those obtained in the best laboratories confirm the applicability of the used method for accurate measurement of heat capacities of GaN as well as other group-III nitrides.

All polynomial equations used for the correlation fit the heat capacities data with accuracy close to that obtained experimentally (<1%). The results obtained for the four parametric equations [13, 14] differ only slightly from the results obtained for three parametric equation [12].

The worst, worse than experimental, accuracy of correlation (1.7%) has been obtained by the use of the Kremer *et al.* [11] equation elaborated for description of whole range of temperatures from 300 to 1400 K.

The prediction of heat capacities by the use of this equation, with parameter adjusted from the whole range of experimental data from 300 to 1400 K, show a big gap between experimental and predicted values in the lower temperature range (300–550 K).

It is necessary to mention that the experimental data in the temperature range: 350–450 K (Fig. 1) seem to be saddled with biggest errors but not bigger than 0.6%. So, the prediction accuracy on the level of 2.6% (4.5 worse) in this region cannot be accepted and explained by the experimental errors.

The predicted values of heat capacities lay below the experimental data in the whole range of investigation (from 300 to 850 K) with the biggest gap in the temperature range between 300–550 K. The gap can be only slightly reduced by adjusting the C_1 parameter in the Kremer *et al.* [11] equation but still in this temperature range the fitting curve lays below the experimental data.

Concluding, we can say that this equation can not be recommended for accurate description of heat capacities of GaN in liquid phase.

List of symbols

C_p – heat capacity, J mol^{-1} K^{-1}

$C_{p_{sap}}$ – the known value of sapphire GaN heat capacity, J mol^{-1} K^{-1}

Δ_{sam} – the signal difference between the GaN sample and empty pan

Δ_{sap} – the signal difference between the sapphire sample and empty pan

m_{sam} – the mass of GaN sample, g

m_{sap} – the mass sapphire sample, g

T – temperature, K

R – the gas constant

Θ_{∞} – the Debye temperature, Θ_{∞}=863 K

$C_1 \dots C_4$ – adjustable parameters

$C_{\text{p}_i}^{\text{exp}}$ – the experimental heat capacity for 'i' experimental point, J mol^{-1} K^{-1}

$C_{\text{p}_i}^{\text{cal}}$ – the calculated heat capacity for 'i' experimental point, J mol^{-1} K^{-1}

n – the number of experimental data points

m – the number of adjustable parameters

Acknowledgements

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