Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thermochimica Acta 401 (2003) 169–173

thermochimica acta

www.elsevier.com/locate/tca

High temperature enthalpy and heat capacity of GaN

J. Leitner[a,*], A. Strejc[b], D. Sedmidubský[b], K. Růžička[c]

[a] Department of Solid State Engineering, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic
[b] Department of Inorganic Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic
[c] Department of Physical Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

Received 17 September 2002; received in revised form 30 September 2002; accepted 15 November 2002

Abstract

The heat capacity and the heat content of gallium nitride were measured by calvet calorimetry (320–570 K) and by drop calorimetry (670–1270 K), respectively. The temperature dependence of the heat capacity in the form $C_{pm} = 49.552 + 5.440 \times 10^{-3}T - 2.190 \times 10^{6}T^{-2} + 2.460 \times 10^{8}T^{-3}$ was derived by the least squares method. Furthermore, thermodynamic functions calculated on the basis of our experimental results and literature data on the molar entropy and the heat of formation of GaN are given.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gallium nitride; Heat capacity; Heat content; Thermodynamic functions

1. Introduction

Gallium nitride (GaN) and other nitrides of the group III elements are important materials for the fabrication of various semiconductor devices such as light emitting diodes, lasers, photodetectors or metal-semiconductor field effect transistors and high electron mobility transistors [1]. Various methods are utilized for the deposition of epitaxial layers and the heterostructures of these materials. Metalorganic vapor phase epitaxy (MOVPE) has some advantages over other techniques and it became the leading epitaxial technology in the last decade.

A number of papers have recently been published dealing with the thermodynamic analysis of the deposition of GaN, (Al, Ga)N, (Ga, In)N as well as (Al, Ga, In)N epitaxial layers by metalorganic vapor phase epitaxy. Such theoretical calculations yield accurate results provided they are based on reliable thermodynamic data. Thermodynamic data for solid GaN are quoted in tables [2,3] and they have recently been assessed [4,5]. Unfortunately, the data show a large scatter and that is why new investigations should be performed.

The heat capacity of the solid GaN was measured by Koshchenko et al. [6] in the temperature range of 5–330 K using an adiabatic calorimeter. Chen et al. [7] have measured the heat capacity of GaN for temperatures from 113 to 1073 K. They obtained the temperature dependence of C_{pm} in the form:

$$C_{pm}\ (\mathrm{J\,mol^{-1}\,K^{-1}}) = 30.310 + 25.203 \times 10^{-3}T - 285603T^{-2} - 6.523 \times 10^{-6}T^{2} \qquad (1)$$

Itagaki and Yamaguchi [8] have measured the heat content of GaN in the temperature range of 812–1034 K. The experimental data were fitted by the

---

[*] Corresponding author. Fax: +420-2-243-10337.
E-mail address: jindrich.leitner@vscht.cz (J. Leitner).

0040-6031/03/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(02)00547-6

following equation:

$$H_T - H_{298}\ (\mathrm{J\,mol^{-1}}) = 43.6T + 4.31\times10^{-3}T^2 + 4.84\times10^{5}T^{-1} - 15,000 \quad (2)$$

from which heat capacity can be obtained by differentiating with respect to temperature:

$$C_{\mathrm{pm}}\ (\mathrm{J\,mol^{-1}\,K^{-1}}) = 43.6 + 8.62\times10^{-3}T - 4.84\times10^{5}T^{-2} \quad (3)$$

The results of the calorimetric investigation on GaN are presented in this paper. Furthermore, thermodynamic functions calculated on the basis of our experimental results and literature data on the molar entropy [6] and the heat of formation [9] of GaN are given.

2. Experimental

Powdered GaN (Aldrich, >99.99%) was used in all experiments. A heat conduction Setaram C-80 calorimeter was used for the heat capacity determination. The measurements were carried out in incremental temperature scanning mode with a number of 5–10 K steps (heating rate 0.2 K min^{-1}) followed by isothermal delays of 9000 s. Three runs had to be performed—with empty crucible (blank), with the reference material (synthetic sapphire, NIST Standard reference material no. 720) and with the sample. For the heat capacity of the sample the following relation holds:

$$C_{\mathrm{pm,s}}(T_i \rightarrow T_{i+1}) = \frac{Q_{\mathrm{s}} - Q_{\mathrm{blank}}}{Q_{\mathrm{ref}} - Q_{\mathrm{blank}}}\, c_{\mathrm{p,ref}}\, \frac{m_{\mathrm{ref}}}{m_{\mathrm{s}}} M_{\mathrm{s}} \quad (4)$$

where Q is the relevant peak area for the sample (s), the reference material (ref) and blank, $C_{\mathrm{p,ref}}$ the mean specific heat capacity of the reference material in the temperature range $T_i - T_{i+1}$, m the mass and M the molar mass. The typical mass of samples was approximately 6 g. The accuracy of DSC measurements is estimated to be better than ±2%.

Heat content determinations were carried out by the drop method using the high temperature calorimeter Setaram (Multi HTC 96). Isothermal measurements were made in the nitrogen atmosphere by alternate dropping of the reference material (small pieces of synthetic sapphire, NIST Standard reference material no. 720) and the sample (GaN pellets, 5 mm in diameter, thickness of 2–3 mm) from the feeding chamber held at room temperature (T_0) through a lock into the working cell of the preheated calorimeter. Endothermic effects are detected and the relevant peak area $Q(T)$ is proportional to the heat content of the dropped specimen $\Delta H(T)$:

$$Q(T) = ST\frac{m}{M}\,\Delta H(T), \qquad \Delta H(T) = \int_{T_0}^{T} C_{\mathrm{pm}}\,\mathrm{d}T \quad (5)$$

where m and M are the mass and the molar mass of the specimen, respectively. The sensitivity of calorimeter $S(T)$ at temperature T is determined from the known heat content of the standard. The measurements were performed at temperatures 673–1173 K on samples with the masses 90–180 mg. The delays between two subsequent drops were 40–50 min. In order to check the accuracy of the present measurement, the heat content of platinum was measured first. The values $\Delta H = 18.76$ and 18.78 kJ mol^{-1} were observed at 970 K which differ approximately 0.8% from the recommended SGTE data [10].

3. Results and discussion

The molar heat capacity data are plotted in Fig. 1. The heat content data are listed in Table 1 and shown in Fig. 2. The raw data were treated simultaneously using the least square method with different weights for individual points. As the heat content data by Itagaki and Yamaguchi [8] are in good agreement with our values, they were taken into account during the optimization too. In order to smoothly link our temperature dependence to the low-temperature data of Koshchenko et al. [6] six points, namely C_{pm} (200 K) = 26.8 J mol^{-1} K^{-1}, C_{pm} (210 K) = 27.8 J mol^{-1} K^{-1}, C_{pm} (230 K) = 29.5 J mol^{-1} K^{-1}, C_{pm} (250 K) = 31.1 J mol^{-1} K^{-1}, C_{pm} (273.15 K) = 32.9 J mol^{-1} K^{-1} and C_{pm} (298.15 K) = 34.9 J mol^{-1} K^{-1} were included in the regression procedure. A four-parameters fitting equation with the T^{-3} term was used to reach higher flexibility around the room temperature. Thus, the temperature dependence of the molar heat capacity of solid

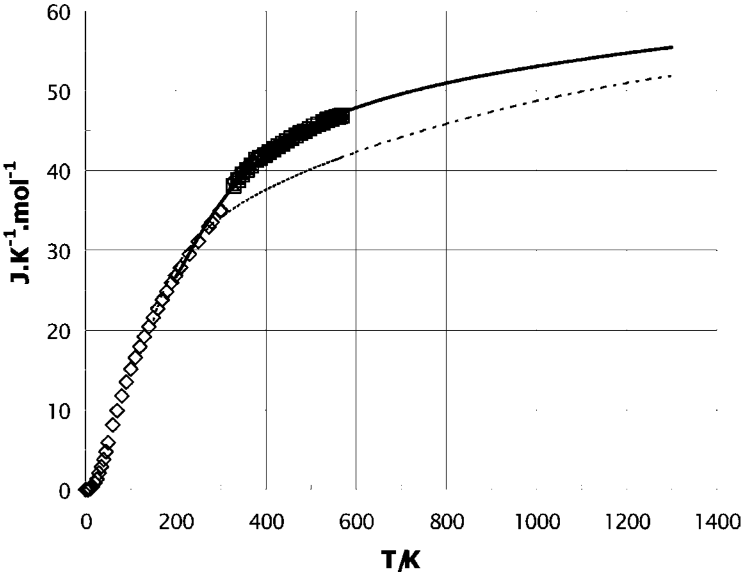

Fig. 1. Temperature dependence of molar heat capacity of solid GaN: (○, △, □) experimental points (calvet); (◇) [6]; (- - -) [7]; (—) fitted curve (Eq. (6)).

GaN can be expressed by the following equation ($T = 200$–$1300\,\mathrm{K}$):

$$C_{\mathrm{pm}}\,(\mathrm{J\,mol^{-1}\,K^{-1}}) = (49.552 \pm 2.279) + (5.440 \pm 2.936) \times 10^{-3}T - (2.190 \pm 0.288) \times 10^{6}T^{-2} + (2.460 \pm 0.459) \times 10^{8}T^{-3} \qquad (6)$$

Temperature dependence of the heat content is derived by integration of Eq. (6) with respect to temperature as follows:

$$H_T - H_{298}\,(\mathrm{J\,mol^{-1}}) = (49.552 \pm 2.279)T + (2.906 \pm 1.468) \times 10^{-3}T^{2} + (2.190 \pm 0.288) \times 10^{6}T^{-1} + (1.230 \pm 0.459) \times 10^{8}T^{-2} - (20976.1 \pm 1295.5) \qquad (7)$$

The mean absolute deviation δ ($\delta = \Sigma\mathrm{abs}(\Delta H_{T,\mathrm{calculated}} - \Delta H_{T,\mathrm{experiment}})/n$) between the

Table 1
Heat content of solid GaN

T (K)	ΔH (kJ mol^{-1}) experiment	ΔH (kJ mol^{-1}) calculated Eq. (7)	T (K)	ΔH (kJ mol^{-1}) experiment	ΔH (kJ mol^{-1}) calculated Eq. (7)
670.5	17.081	16.463	920.1	29.291	29.153
670.5	17.273	16.463	920.3	29.374	29.164
670.8	17.152	16.478	970.2	32.432	31.785
720.9	19.851	18.960	970.3	32.406	31.791
721.0	19.492	18.965	1069.3	37.425	37.057
770.1	21.667	21.433	1069.4	26.834	37.062
770.1	21.278	21.433	1168.1	42.929	42.398
820.0	23.533	23.972	1168.0	42.996	42.395
820.0	24.212	23.972	1271.5	50.015	48.069
869.9	26.668	26.542	1271.7	49.156	48.080
870.0	26.852	26.547			

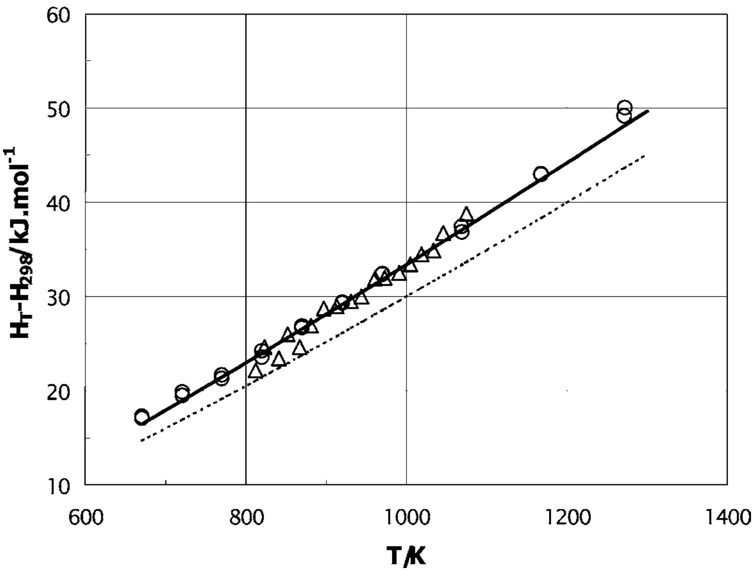

Fig. 2. Temperature dependence of heat content of solid GaN: (○) experimental points (drop); (△) [8]; (- - -) [7]; (—) fitted curve (Eq. (7)).

Table 2
Thermodynamic functions of solid GaN

T (K)	C_{pm} (J mol^{-1} K^{-1})	H_m (kJ mol^{-1})	S_m (J mol^{-1} K^{-1})	G_m (kJ mol^{-1})
298.15	35.819	−156.800	36.500	−167.682
300	35.962	−156.734	36.722	−167.750
400	41.884	−152.815	47.954	−171.997
500	45.480	−148.433	57.717	−177.292
600	47.872	−143.759	66.233	−183.499
700	49.608	−138.881	73.749	−190.505
800	50.963	−133.850	80.465	−198.222
900	52.082	−128.696	86.534	−206.577
1000	53.048	−123.438	92.073	−215.511
1200	54.702	−112.659	101.895	−234.933
1400	56.140	−101.572	110.437	−256.184

calculated (Eq. (7)) and experimental values of $\Delta H_T = H_T - H_{298}$ is 0.53 kJ mol^{-1} with the maximum value of 1.89 J mol^{-1} at 1272.45 K.

Our results are in good agreement with the high-temperature heat-content data of Itagaki and Yamaguchi [8]. On the other hand, there are relatively large differences (more then 10% in the temperature range 400–800 K) between the temperature dependence of the heat capacity assessed in this work and published in literature [7].

Thermodynamic functions of solid GaN calculated on the basis of our temperature dependence of the heat capacity and literature data on the molar entropy [6] and the heat of formation [9] of GaN are given in Table 2.

Acknowledgements

This work was supported by the GACR (Grant no. 106/00/0568) and the Ministry of Education of the Czech Republic (Research Projects no. MSM 223100002 and 223400008).

References

[1] P. Kung, M. Razeghi, Opto-Electron. Rev. 8 (2000) 201.

[2] O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, 2nd ed., Springer, Berlin, 1991.

[3] I. Barin, Thermochemical Data of Pure Substances, 2nd ed., VCH, Weinheim, 1993.

[4] I.N. Przhevalskii, S.Yu. Karpov, Yu.N. Makarov, MRS Internet, J. Nitride Semicond. Res. 3 (1998) 30.

[5] A.V. Davydov, T.J. Anderson, in: T.D. Moustakas, S. Mohney, S.J. Pearton (Eds.), Electrochemical Society Proceedings on III–V Nitride Materials and Processes III, vol. 98–18, Boston, 1998, p. 38.

[6] V.I. Koshchenko, A.F. Demidenko, L.D. Sabanova, V.E. Yachmenev, Yu.M. Gran, A.F. Radchenko, Izv. Akad. Nauk SSSR, Neorg. Mater. 15 (1979) 1686.

[7] X. Chen, Y. Lan, J. Liang, X. Cheng, Y. Xu, T. Xu, P. Jiang, K. Lu, Chin. Phys. Lett. 16 (1999) 107.

[8] K. Itagaki, K. Yamaguchi, Thermochim. Acta 163 (1990) 1.

[9] M.R. Ranade, F. Tessier, A. Navrotska, V.J. Leppert, S.H. Risbud, F.J. DiSalvo, C.M. Balkas, J. Phys. Chem. B 104 (2000) 4060.

[10] A.T. Dinsdale, CALPHAD 15 (1991) 317.