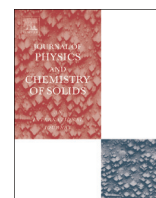




ELSEVIER

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

The challenge of decomposition and melting of gallium nitride under high pressure and high temperature

S. Porowski^a, B. Sadovyi^{a,c}, S. Gierlotka^a, S.J. Rzoska^{a,d,*}, I. Grzegory^a, I. Petrusha^b, V. Turkevich^b, D. Stratiichuk^b^a Institute of High Pressure Physics “Unipress”, Polish Academy of Sciences, ul. Sokołowska 29/37, 01-142 Warsaw, Poland^b V. Bakul Institute for Superhard Materials of the National Academy of Sciences of Ukraine, Avtozavodska str. 2, Kyiv 04074, Ukraine^c Department of Physics, Ivan Franko National University of Lviv, Dragomanova str. 50, Lviv UA 79005, Ukraine^d SMCEBI&Institute of Physics, University of Silesia, ul. 75 Pułku Piechoty 1, 41-500 Chorzów, Poland

ARTICLE INFO

Article history:

Received 22 November 2014

Received in revised form

21 April 2015

Accepted 8 May 2015

Available online 18 May 2015

Keywords:

Semiconductors

High pressures

Phase equilibria

Phase transitions

Crystal growth

ABSTRACT

Gallium nitride (GaN) is considered to be one of the most important semiconductors nowadays. In this report a solution of the long standing puzzle regarding GaN decomposition and melting under high pressure and high temperature is presented. This includes the discussion of results obtained so far. The possibility of a consistent parameterisation of pressure (P) evolution of the melting temperature (T_m) in basic semiconductors (GaN, germanium, silicon...), independently from signs of dT_m/dP is also presented.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Melting of basic semiconductors constitutes a long-standing challenge, due to its puzzling fundamental characteristics matched with a great practical importance [1–5]. Silicon, germanium and semiconducting compounds from the A^{III}B^V homologous series can be encountered to the most important materials employed in modern civilisation [4–6]. Recently, an exceptional position gained gallium nitride (GaN) as the base for innovative light sources, blue lasers, high power and high frequency transistors and converters [5–10]. The pressure evolution of the melting temperature $T_m(P)$ contains the message on fundamental properties of neighbouring solid and liquid phases [11,12]. The knowledge of $T_m(P)$ behaviour is also important for the development of new crystal growth technologies [2,5,7].

For decades, the Simon–Glatzel (SG) equation has served as the basic tool for portraying $T_m(P)$ evolution [11–13]:

$$T_m(P) = T_{ref} \left(1 + \frac{P}{\Pi} \right)^{1/b} \quad (1)$$

* Corresponding author at: Institute of High Pressure Physics “Unipress”, Polish Academy of Sciences, ul. Sokołowska 29/37, 01-142 Warsaw, Poland.

E-mail address: sylwester.rzoska@gmail.com (S.J. Rzoska).

where T_{ref} denotes the melting temperature under atmospheric pressure, b and Π are empirical, fitted parameters.

For the SG Eq.(1) always $dT_m/dP > 0$, i.e. compressing can solely increase the melting temperature. In fact, this is the typical pattern for the vast majority of materials tested so far [11]. However, for semiconductors surprisingly often $dT_m/dP < 0$, i.e. the melting temperature decreases with rising pressure [1]. This is the case for basic materials such as germanium and silicon where the clear experimental evidences for $dT_m/dP < 0$ in the whole range of experimentally available pressures exist [14,15]. Consequently, the question of the description of $T_m(P)$ evolution in such materials arises. For GaN the situation is even more puzzling, namely:

- (1) For decades semiconductors from the A^{III}B^V homologous series were described via the ‘classical’ theoretical model introduced by van Vechten (1971, [16]). For GaN a linear decrease of $T_m(P)$ described by $dT_m/dP \approx -19 (\text{K} \times \text{GPa}^{-1}) = \text{const}$ for $0.1 \text{ MPa} < P < 60 \text{ GPa}$ was predicted [16]. Such behaviour resulted from the *a priori* assumption that melting always takes place from the less dense tetrahedrally coordinated semiconductor to a higher coordinated metallic liquid. The available experimental results for silicon, i.e. linear $T_m(P)$ decrease with rising pressure, was taken as the general scaling reference.
- (2) In 2003, the ‘canonical’ nowadays reference for GaN melting appeared in the experimental report by Utsumi et al. [17]. It

was concluded: "... applying high pressure completely prevents the decomposition and allows the stoichiometric melting of GaN. At pressures above 6.0 GPa, congruent melting of GaN occurred at about 2220 °C, and decreasing the temperature allowed the GaN melt to crystallize to the original structure". The congruent melting at constant temperature $T_m \approx 2220$ K, i.e. $dT_m/dP \approx 0$, was suggested for $P > 6$ GPa up to at least 10 GPa. Notable is the confirmation of these results by Saitoh et al. [18], who carried out supplementary single-crystal-growth study of GaN between 2000–2400 °C at 6.5 GPa, using GaN powder as a starting material. Utsumi et al. [17] also indicated *ad hoc* the decomposition domain at the P – T plane. Notwithstanding, this suggestion coincides with earlier state-of-the-art studies by Karpinski et al. ([19]) who showed experimentally the clear decomposition up to $P \sim 5$ GPa and $T \sim 2600$ °C.

- (3) In 2007 Sokol et al. [20] presented evidence for the incongruent 'melting' of GaN at $P = 7.5$ GPa and $T \approx 2300$ K, i.e. well above the terminal pressure for the congruent melting indicated by Utsumi et al. [17,18].
- (4) The situation became even more intriguing when taking into account results of Molecular Dynamics (MD) simulations by Harafuji et al. (2004, [21]). They determined a nonlinear increase of $T_m(P)$ up to at least $P \approx 8$ GPa, with $dT_m/dP \approx +160$ (K \times GPa $^{-1}$) for $P \rightarrow P_{\text{atm}}$.

The great importance of ultimate explaining the mystery of GaN melting was stressed by Utsumi et al. [17]: "...such results have great potential in providing high-quality bulk single crystals of GaN". Hence, getting ultimate insight into melting and decomposition of GaN in the P – T plane may be essential for further development of GaN based devices. It is notable that GaN crystals cannot be grown by the classical Czochralski [22] or Bridgman [23] methods from a stoichiometric melt since GaN decomposition occurs prior to melting at high temperatures under atmospheric pressure as well at moderate pressures [6,19]. However, the decomposition of GaN can be limited by applying high hydrostatic pressures [6,19,24]. This in turn is inherently associated with the knowledge of the pressure dependence of the decomposition as well as the onset of the congruent melting [6]. In this context worth indicating is the recent discussion on GaN thermochemical and related kinetics of crystals formation and decomposition at HP – HT conditions [6,25]. Notable are also innovative HP – HT solutions in which the process is developed using a solid-phase nitrogen source to form GaN crystals in a Ga metal melt [6,26].

From the general fundamental point of view the knowledge of the phase diagram in the P – T plane is essential for an ultimate thermodynamic picture of any material [11,12].

This report shows the clear experimental evidence that undermines both the 'canonical' experimental conclusions by Utsumi et al. [17] and theoretical predictions by van Vechten [16]. A new procedure for estimating hypothetical GaN melting loci, determined despite decomposition occurring a priori, is proposed. A possible consistent parameterisation of $T_m(P)$ behaviour for basic semiconductors characterized both by $dT_m(P)/dP > 0$ and $dT_m(P)/dP < 0$ is also proposed.

2. Materials and methods

2.1. High-pressure and high-temperature treatment of GaN samples

A high pressure (HP) toroid-type apparatus DO-043 supported by a 2000 t hydraulic press, developed for growing diamond crystals, was applied [27]. A typical sample for high pressure and high temperature (HP – HT) experiments was composed of three platelets of GaN single crystals [28], (lateral size ca. 0.7 cm),

obtained by Hydride Vapour Phase Epitaxy (HVPE) and surrounded by GaN powder. The powder of maximal grain size 80 μm was prepared by milling the same type of GaN single crystals. The samples were placed in two-layer tantalum-graphite cylindrical capsules and then pressurised and heated up to the required P – T conditions in the range $P = 6 - 9$ GPa and $T = 2500 - 3400$ K. The volume of GaN samples was equal to $V \approx 0.76$ cm 3 . The latter value was about x100 larger than ones used in ref. [17]. This fact improved the quality of the detection of relevant features of HP – HT treated samples and the analysis of the decomposition. Moreover, the impact of parasitic reactions at the surface of the sample could be qualitatively reduced.

The apparatus was calibrated using well known melting temperatures in P – T plane: for Mo, Mo–C [29,30] and carbon [31]. The resulted experimental errors $\pm 5\%$ for pressure and less than ± 50 K for temperature. These values are within the 'state-of-the-art' range for such extreme conditions experiments [1,2,17–20].

Two types of output results were observed after the HP – HT treatment. For the first one, GaN sample was not decomposed after annealing under high pressure and temperature (Fig. 1). Moreover, high resolution X-ray diffraction studies confirmed that GaN crystals remained single crystalline after the experiment. For the second one, GaN samples totally decomposed during heating and a mixture of liquid gallium and newly grown crystals was observed. Powder X-ray diffraction confirmed that GaN crystals grown during cooling. The measured mass of these new crystals as well as the mass of gallium allowed to determine the solubility of nitrogen in gallium by the method developed in ref. [23]. The increase of solubility with rising pressure, correlated with increasing temperature and pressure, up to the value $x \sim 17$ at% was noted, namely: $x = 3.7$ at% at $P = 6$ GPa and $T = 2800$ K, $x = 11$ at% at $P = 8$ GPa and $T = 3150$ K, $x = 17$ at% at $P = 9$ GPa and $T = 3400$ K. In this sequence of tests only the decomposition of GaN was observed. These results are presented and confronted with earlier ones below.

2.2. The estimation of hypothetical congruent melting loci from solubility data

The existing evidence for solubility of GaP and GaSb can be well portrayed by the relation based on the ideal solution model [11,24,32], which can be rewritten in the following scaling form:

$$\frac{T}{T_m}(x) = \frac{\Delta S^F}{\Delta S^F - R \ln 4x(1-x)} \quad (2)$$

where x denotes the concentration (solubility) of B^V component and R is for the gas constant and ΔS^F is the entropy of fusion.

The analysis of experimental results under atmospheric pressure yielded $\Delta S^F \approx 12.7$ cal/(mole K) for GaSb and 12.3 cal/(mole K) for GaP (Fig. 2) [6,24,32]. For GaN the decomposition into $\text{Ga} + \text{N}_{\text{atomic}}$ solution and N_2 gas also takes place but the solubility under atmospheric pressure remain extremely low even at very high temperatures. It becomes detectable only if pressure is significantly increased. Under such restrictions for a given pressure there is only one 'decomposition' temperature at which the solubility can be determined. However, even for $P = 1.5$ GPa nitrogen solubility in gallium is still low (< 0.5 at%) [24,27]. These data are shown in the inset in Fig. 2. Despite the fact that each solubility is determined for different pressures the parameterisation via Eq. (2) with $\Delta S^F \approx 12.5$ cal/(mole K) appeared to be possible. This fact as well as similar values of ΔS^F for GaSb, GaP and GaN can suggest the pressure invariance of this parameter for this 'homologous' series of compounds. However, we would like to recall the statement from ref. [32] regarding GaP and GaSb " ΔS^F differs considerably from the entropies of solution measured experimentally", so

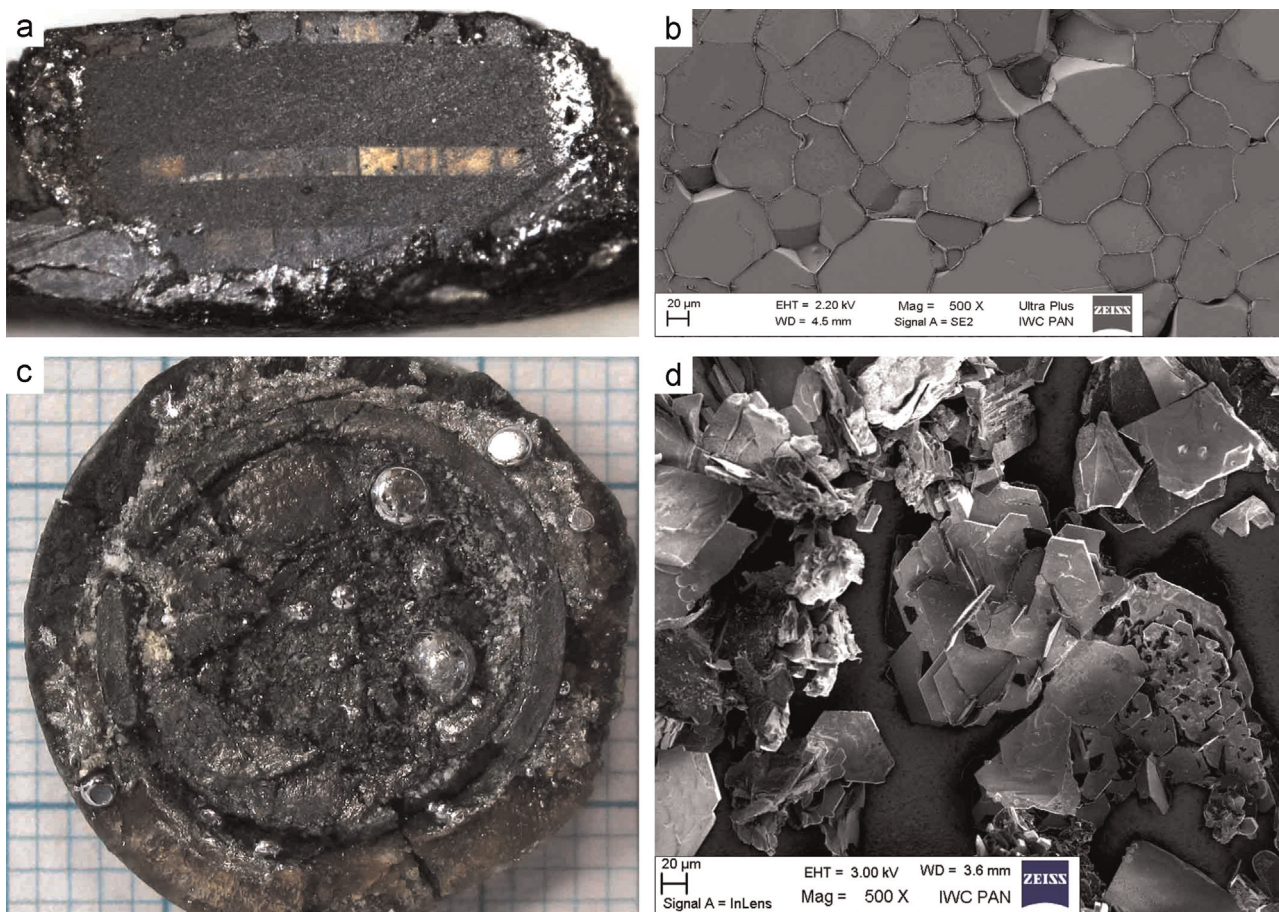


Fig. 1. Optical microscopy and SEM pictures of GaN samples after HP-HT treatment revealing two types of behaviour. Type I: in Fig. 1a there are visible changes in the shape of GaN crystals and in Fig. 1b there are hallmarks of GaN powder sintering. Type II: in Fig. 1c the whole sample is decomposed and gallium droplets are visible whereas in Fig. 1d newly grown crystals appear after the removal (etching) of gallium.

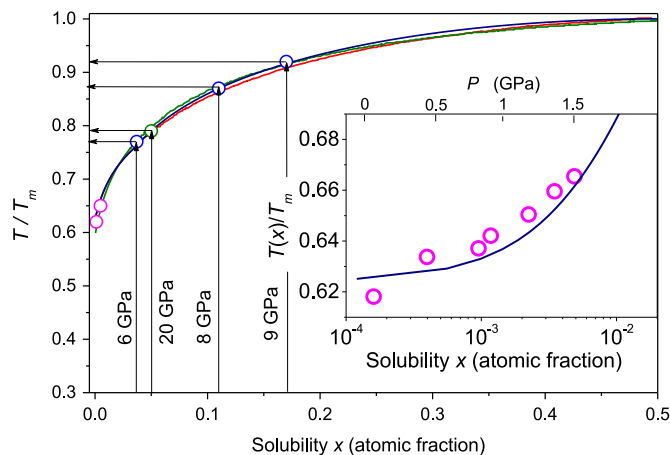


Fig. 2. Liquidus curves for GaSb, GaP and GaN for different pressures (a) and scaled liquidus curves for these compounds (b). — is for GaSb, — for GaP (based on data from refs. [2,16,32]) and — for GaN in this work. ○ – Experimental solubility values obtained by Grzegory et al. [24], ○ – theoretical solubility value obtained by Nord et al. [33], ○ – experimental solubility values from this work. The inset shows the parameterisation of solubility via Eq. (2), basing on data from ref. [19,24]. Each solubility is determined at the decomposition, for different temperatures and pressures (see the upper scale).

in fact ΔS^F should be considered only as the adjustable model parameter: ‘the apparent effective entropy of fusion’. So far, determining of the real value of ΔS^F for GaN in (very) extreme HP-HT conditions remains a strong challenge for future experiments. One of possible indirect ways can be based on measurements of volume

changes as the function of pressure and the application of the Clapeyron equation.

It should be stressed that for a given isobar in GaN one can determine a single experimental point located at $T(x, P_0)$ curve at the decomposition loci (Fig. 2) [6,24].

In this report the scaling Eq. (2) was used to estimate $T_m(P)$ behaviour from solubility data. This analysis based on: (i) experimental values obtained in this work (for $P=6-9$ GPa), (ii) values reported in ref. [24] (for 0.81 GPa and 1.5 GPa) and (iii) the theoretical value for $P=20$ GPa obtained via MD and Monte-Carlo calculations [30]. On increasing pressure, the solubility at equilibrium conditions increases. However, the scaling form of Eq. (2) causes that for each isobar one can extrapolate it up to the congruent solubility limit at $x = 0.5$, determining in this way $T_m(P)$ value for the given isobar P . Applying such a procedure for subsequent tested isobars one can determine $T_m(P)$, despite the fact that melting is hidden by the decomposition occurring prior to melting

2.3. Invariant parameterisation of the pressure evolution of melting temperature

The key tool for describing the pressure evolution of melting temperature is the Simon–Glatzel (SG) Eq. (1), which reflects the fact that for the vast majority of materials tested so far compressing increases the melting temperature [11,12]. Regarding implementations, Eq. (1) it is simply fitted to a given set of $T_m(P)$ experimental data [11,12]. However, such ‘typical’ method of analysis has two drawbacks: (i) *a priori* the validity of SG Eq. (1) in an arbitrarily selected

range of pressures is assumed, (ii) the nonlinear fitting via Eq. (1) matched with experimental errors of (T_m, P_m) data can lead to a notable uncertainty of output parameters. To overcome these basic problems in ref. [34,35] the transformation of experimental data $T_m(P) \rightarrow [d(\ln T_m)/dP]^{-1}$ prior to the fitting was proposed. It resulted from the derivative of Eq. (1), namely:

$$[d(\ln T_m)/dP]^{-1} = A + BP \quad (3)$$

Hence, the lack of linearity at $[d(\ln T_m)/dP]^{-1}$ versus P plot should yield a linear dependence if SG Eq. (1) is valid in the given range of pressures. The lack of such behaviour denotes the formal inadequacy of SG equation for describing of the given set of $T_m(P)$ experimental data. In such a case fitting via Eq. (1) can yield only ‘apparent and effective’ values of parameters. A ‘non-linearity’ appearing at the plot defined by Eq. (3) can indicate the existence of a reversal melting, i.e. the transformation: $dT_m/dP > 0 \rightarrow (\text{compression}) \rightarrow dT_m/dP < 0$ for the given material. To portray such behaviour Drozd–Rzoska (DR) derived the relation [34,35]:

$$T_m(P) = T_{ref} \left(1 + \frac{\Delta P}{\Pi} \right)^{1/b} \times \exp\left(\frac{\Delta P}{c}\right), \text{ for } \Delta P = P - P_{ref}. \quad (4)$$

where $\Pi = \pi + P_{ref}$, $-\pi$ is the extrapolated, negative pressure for which $T_m(P \rightarrow -\pi) \rightarrow 0$. The parameter $-\pi$ can be considered as the onset of the absolute stability limit spinodal in negative pressures domain. One can assume arbitrary values of parameters (P_{ref}, T_{ref}) along the melting curve, starting from $-\pi$.

The domain of adequacy of Eq. (4) can be estimated from the transformation of experimental data defined by the dependence easily obtained via derivative of Eq. (4) and subsequent linearization [34]:

$$[d(\ln T_m)/dP + c^{-1}]^{-1} = A + BP \quad (5)$$

The simple regression fit can yield A and B coefficients and subsequently optimal values of all relevant parameters (π, b, c) . Their substitution into Eq. (4) should yield an equation able to portray experimental data without any further fitting.

It is notable that relations resembling Eq. (4) were proposed earlier by Rein and Demus ([36]) and a decade later by Kechin ([37]). However, they assumed reference values (T_{ref}, P_{ref}) related to atmospheric pressure ($T_{ref} = T_m(P_{ref} \approx 0)$) or to the triple point, which is not always known. Neither negative pressures domain nor resulted of the meaning if coefficient Π were not considered [36,37]. Consequently, values of parameters have to depend on the selected values of $T_{ref}(P_{ref})$. The proposed in refs. [34,35] preliminary transformation and analysis of experimental data via Eqs. (3) and (5) and the inclusion of negative pressures domain lead to ‘pressure-invariant’ values of parameters. This yields the possibility of a reliable extrapolation of the description via DR Eq. (4) beyond the domain of experimental data [34,35]. It is worth recalling that for solids and liquids neither atmospheric pressure nor $P \approx 0$ do not constitute a specific reference. One can pass $P=0$ without any physical hallmark and enter the negative pressure domain via isotropic stretching, down to the absolute stability limit (spinodal) [11,38]. DR Eq. (4) can describe $T_m(P)$ behaviour both in the negative and ‘positive’ pressures domains [34,35].

3. Results and discussion

Fig. 3 shows the first ever compilation of existing experimental and theoretical data regarding decomposition and melting for gallium nitride (GaN). It also presents new experimental results

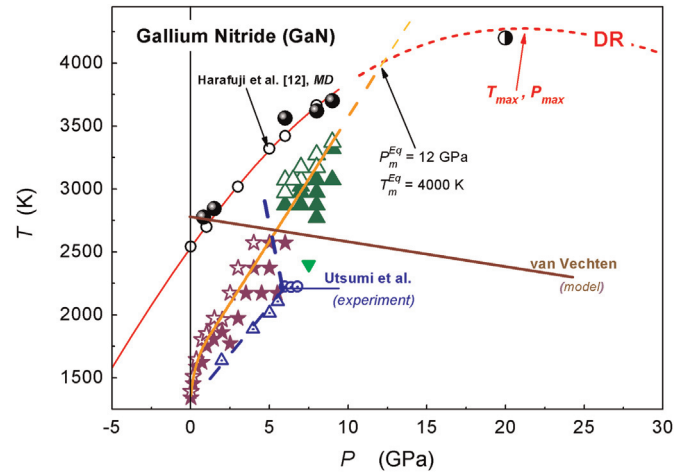


Fig. 3. Pressure dependence of GaN melting and GaN P - T decomposition equilibrium curves (EQ). The experiment based evidence by Utsumi et al. [17] is presented via: Δ and \circ for experimental data regarding decomposition and melting, respectively. The general behaviour suggested on this base in ref. [17], is given via solid (melting) and dashed (decomposition) lines in blue. The melting line predicted by van Vechten model as shown by straight line in wine [16]. MD simulation results by Harafuji et al. [21] are given as \circ . Solid symbols \blacktriangle , \star are for GaN stable conditions and \triangle , \star denote GaN decomposed to $(\text{Ga}+\text{N})_{\text{liq}}$ and N_2 . Experimental data denoted as \star and \star are taken from ref. [19] by Karpinski et al. The experimental result by Sokol et al. [20] is denoted by ∇ . Experimental decomposition data obtained within the given research are shown as \blacktriangle and \triangle . Hypothetical ‘hidden’ melting temperatures calculated on the basis of these values, via scaling procedure proposed in the given report, are denoted as \bullet . The symbol \circ is for the hypothetical melting temperature calculated from theoretical solubility estimated in ref. [30]. --- is for the equilibrium curve (guide for eyes) and --- is for $T_m(P)$ curve determined via DR Eq. (4) [34,35], with parameters given in Fig. 4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

obtained by the authors. There is a clear correlation with earlier results by Karpinski et al. [19], who noted the decomposition up to $P \sim 4$ GPa as well as with measurements by Sokol et al. [20] for higher pressure. Results presented show an unequivocal decomposition up to at least $P=9$ GPa. The presented evidence does not support results reported by Utsumi et al. [17], who excluded decomposition for $P > 6$ GPa. The theoretical behaviour suggested by van Vechten [16] (solid ‘wine’ line in Fig. 3) is clearly non-correlated with the presented experimental results. Fig. 3 presents also $T_m(P)$ data obtained by Harafuji et al. [21] via MD approach (open circles). They are located above the decomposition domain. Hypothetical melting temperatures obtained via the novel protocol described above (Section 2.2 and Fig. 2) are shown as ‘semi-solid circles’. The coincidence with MD estimations by Harafuji et al. [21] is visible.

Results of the derivative-based and distortions-sensitive analysis via Eqs. (3) and (5) for GaN are presented in Fig. 4. It is visible that the description of experimental data via the basic SG Eq. (1) is possible only in the limited range of pressure, $P < 3$ GPa. The substitution of parameters obtained via the analysis presented Fig. 4 to DR Eq. (4) yields the ‘red’ curve in Fig. 3, covering the full set of data. Notable is fair agreement both with semi-empirical experimental data associated with given report as well as with MD simulation results by Harafuji et al. [21].

The extrapolation beyond the ‘experimental’ domain ($P < 9$ GPa) correlates with $T_m(P \approx 20$ GPa) where the results were estimated using MD simulation data reported by Nord et al. [33] (open star-half-filled circle). Such extrapolation can be justified by the mentioned pressure invariance of parameters in Eq. (4). In this respect, the hypothetical maximum at $P_{\text{max}} \approx 22$ GPa as well as the subsequent reversal melting associated with $dT_m(P)/dP < 0$ is notable.

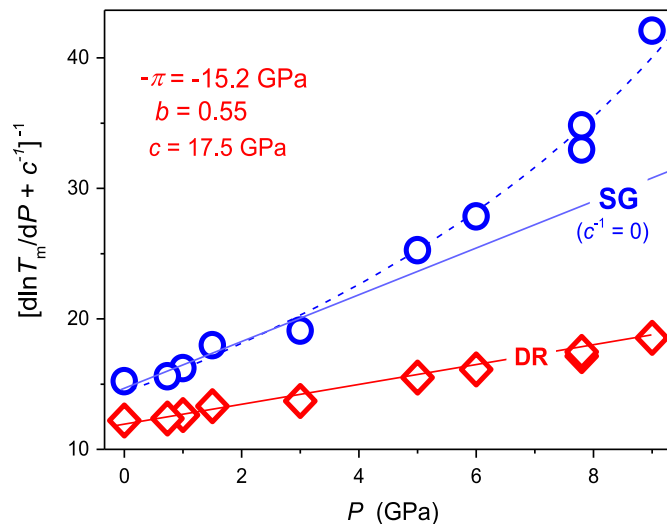


Fig. 4. Results of the derivative-based analysis, via Eq. 5, indicated the domain of validity of SG [11,13] (blue line, Eq. (1)) and DR [34,35] (red line, Eq. (4)) equations as well as yielding optimal values of parameters, given in the figure. It is visible that the reliable SG description is limited to ca. 3 GPa. The extension beyond this domain leads to the “effective” and approximate SG parameterisation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

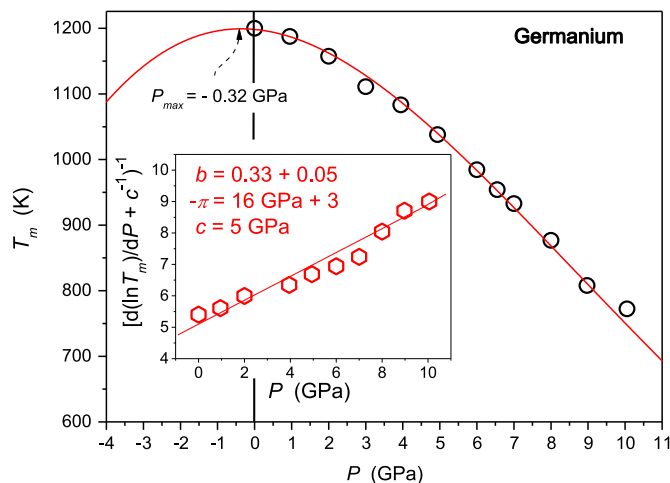


Fig. 5. Pressure dependence of melting temperature of germanium. Experimental data are from [14,35,37] and parameterisation (red curve) is related to Eq. (4). The inset shows results of analysis of experimental data transformed via Eq. (5), yielding input parameters for basic DR Eq. (4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Melting of such basic semiconductors as silicon and germanium is not disturbed by the decomposition occurring in prior and ‘direct’ $T_m(P)$ experimental data can be obtained and analysed.

Fig. 5 presents experimental melting data for germanium [14,35,37]. The transformation of $T_m(P)$ experimental data via Eq. (5), shown in the inset in Fig. 5. It enables determining of parameters which substitution into Eq. (4) yields the red curve in the main part of Fig. 5. Its extension into the negative pressure domain revealed the ‘crossover to the ‘typical’ behaviour described by $dT_m(P)/dP > 0$. For silicon the situation is less clear: numerical models suggest a nonlinear decrease of melting temperature on compressing, which extends into the negative pressures domain yielding a maximum for

$P \sim -2$ GPa [39–42]. However, the experimental evidence indicates a notably linear decrease of the melting temperature down to $P \sim 11$ GPa, with $dT_m/dP = -63$ K/GPa [15].

4. Conclusions

The target of this report is the melting of basic semiconductors under pressure, particularly regarding gallium nitride (GaN). For GaN experimental tests were carried out up to $P=9$ GPa, with a pressurised sample ca. 100 x larger than in studies carried out so far [17,18]. This feature of the experiment notably reduced the experimental uncertainty and parasitic artefacts. It is particularly notable, that up to $P=9$ GPa only decomposition of GaN was observed. Such behaviour is well correlated with earlier studies by Karpinski et al. [19]. Results obtained do not support the ‘canonical’ experimental evidence by Utsumi et al. [17], who suggested solely congruent melting for $P > 6$ GPa.

Hypothetical values of melting temperature were determined via novel procedure from scaled analysis of solubility (Section 2.2): for GaN melting is hidden by the decomposition occurring in prior. The obtained ‘semi-experimental’ values $T_m(P)$ data correlated with MD simulation estimations by Harafuji [21] and Nord et al. [33]. All these indicate that for GaN $dT_m/dP \approx +160$ (K x GPa⁻¹) for $P \rightarrow P_{\text{atm}}$, and the congruent melting may be expected for $P > 12$ GPa. It is notable that van Vechten [16] suggested a similarity in melting for gallium nitride (GaN) and boron nitride (BN). Originally, he predicted $dT_m/dP \approx -19$ (K x GPa⁻¹) = const up to ca. 60 GPa for both materials [16]. However, for BN a clear evidence of crossover $dT_m/dP > 0 \rightarrow dT_m/dP < 0$ on rising pressure was reported [28]. This paper indicates that such behaviour is may take place also for GaN. It is noteworthy that such qualitative impact of pressure on the phase transition temperature is not restricted solely to melting, but is was detected also for solid–solid transitions. However, in situ measurements assisting such process are still very rare due to great experimental difficulties under extreme pressure and even more under extreme temperatures and pressures.

Worth stressing is the significance of results obtained for the general discussion on the melting phenomenon [11,12] as well as their possible impact on the future development of GaN crystal growth technologies [5–7,43], which subsequently can create a new basis for innovative electronic devices. Notable is the possible importance of the presented way of analysis for material engineering [44] and geophysics [45], where the interplay between high pressures, high temperatures, melting and decomposition takes place.

Acknowledgements

The research was supported by FP7 START Project “Boosting EU-Ukraine cooperation in the field of Superhard Materials” Ref. 295003, Polish Grant MNiSW “Kwantowe nanostruktury półprzewodnikowe do zastosowań w biologii i medycynie” POIG 01.01.02-008/08-00, Grant NCN (Poland) Ref. UMO-2012/05/N/ST3/02545. SJR was supported by the National Science Centre (Poland) 2011/03/B/ST3/02352. The Authors would like to thank Jörg Neugebauer and Martin Albrecht for their critical discussion, Adam Presz and Igor Dzieciolewski for SEM tests and Jan Weyher for etching the samples.

References

- [1] T. Suski, W. Paul, *High Pressure in Semiconductor Physics II*, Academic Press,

- London, 2006.
- [2] P.Y. Yu, High pressure semiconductor physics: looking toward the future on the shoulder of the past, *Phys. Stat. Sol.* 248 (2011) 1077–1082.
 - [3] P. Bhattacharya, R. Fornari, H. Kamimura, *Comprehensive Semiconductor Science and Technology*, Elsevier, Amsterdam, 2011.
 - [4] P.A. Gargini, Challenges for the semiconductor industry in the 21st century, *ECS Trans.* 50 (2013) 3–11.
 - [5] S. Adachi, *Properties of Group-IV, III-V and II-VI Semiconductors*, Wiley and Sons, Chichester, 2005.
 - [6] D. Ehrentraut, E. Meissner, M. Bockowski, *Technology of Gallium Nitride Crystal Growth*, Springer Verlag, Dordrecht, 2010.
 - [7] H. Morkoc, *Handbook of Nitride Semiconductors and Devices: GaN-based Optical and Electronic Devices*, Vol. 3, Wiley-VCH, Weinheim, 2008.
 - [8] B. Gil, *III-Nitride Semiconductors and Their Modern Devices*, Oxford Univ. Press, Oxford, 2013.
 - [9] F. Roccaforte, O. Fiorenza, G. Greco, R.L. Nigro, F. Giannazzo, A. Patti, M. Saggio, *Challenges for energy efficient wide band gap semiconductor power devices*, *Phys. Stat. Solidi* 111 (2014) 2063–2071.
 - [10] http://www.nobelprize.org/nobel_prizes/physics/laureates/2014/: The Noble Prize in Physics 2014 was awarded jointly to Isamu Akasaki, Hiroshi Amano and Shuji Nakamura 'for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources'.
 - [11] V.P. Skripov, M.Z. Faizulin, *Crystal-Liquid-Gas Phase Transitions and Thermodynamic Stability*, Wiley-VCH, Weinheim, 2004.
 - [12] E.I. Estrin, *Phase Transitions in Solids Under High Pressure*, CRC Press, Boca Raton, 2014.
 - [13] F.E. Simon, G. Glatzel, Bumerkungen zur schmelzdruckkurve, *Z. Anorg. (Allg.) Chem.* 178 (1929) 309–316.
 - [14] S.N. Vaidya, J. Akella, G.C. Kennedy, Melting of germanium to 65kbar, *J. Phys. Chem. Solids* 30 (1969) 1411–1413.
 - [15] A. Kubo, Y. Wang, C.E. Runge, T. Uchida, B. Kiefer, N. Nishiyama, T.S. Duffy, Melting curve of silicon to 15GPa determined by two-dimensional angle-dispersive x-ray diffraction using a Kawai-type apparatus with X-ray transparent sintered, *J. Phys. Chem. Solids* 69 (2008) 2255–2560.
 - [16] J.A. Van Vechten, Quantum dielectric theory of electronegativity in covalent systems: III. Pressure temperature phase diagrams, heat of mixing and distribution coefficient, *Phys. Rev. B* 73 (1973) 1479–1507.
 - [17] W. Utsumi, H. Saitoh, H. Kaneko, T. Watanuki, K. Aoki, O. Shimomura, Congruent melting of gallium nitride at 6GPa and its application to single-crystal growth, *Nat. Mater.* 2 (2003) 735–738.
 - [18] H. Saitoh, W. Utsumi, H. Kaneko, K. Aoki, The phase and crystal growth study of group-III nitrides in 2000 °C at 20GPa region, *J. Cryst. Growth* 300 (2007) 26–31.
 - [19] J. Karpiński, J. Jun, S. Porowski, Equilibrium pressure of N₂ over GaN and high pressure solution growth of GaN, *J. Cryst. Growth* 66 (1984) 1–7.
 - [20] A.G. Sokol, Yu.N. Palyanov, N.V. Survtsev, Incongruent melting of gallium nitride at 7.5GPa, *Diamond Relat. Mater.* 16 (2007) 431–434.
 - [21] K. Harafuji, T. Tsuchiya, K. Kawamura, Molecular dynamics simulation for evaluating melting point of wurtzite-type GaN crystal, *J. Appl. Phys.* 96 (2004) 2501–2512.
 - [22] J. Czochralski, Ein neues ferverfahren zur Messung des Kristallisationsgeschwindigkeit der Metalle, *Z. Phys. Chem.* 92 (1918) 219–221.
 - [23] P.W. Bridgeman, Various physical properties of rubidium and caesium and the resistance of potassium under pressures, *Roc. Am. Acad. Arts. Sci.* 60 (1925) 305–309.
 - [24] I. Grzegory, J. Jun, M. Boćkowski, S.T.K. Krukowski, M. Wróblewski, B. Łuczniak, III-V Nitrides – thermodynamics and crystal growth at high N₂ pressure, *J. Phys. Chem. Solids* 56 (1995) 639–644.
 - [25] T.J. Peschek, J.C. Angus, K. Kash, Thermodynamic properties of gallium nitride, *J. Cryst. Growth* 322 (2011) 114–116.
 - [26] D.R. Gilbert, A. Novikov, N. Patrin, J.S. Budai, F. Kelly, R. Chodelka, R. Abbaschian, S.J. Pearton, R. Singh, High-pressure process to produce GaN crystals, *Appl. Phys. Lett.* 77 (2000) 4172–4174.
 - [27] L.G. Khvostantsev, V.N. Slesarev, Large-volume high-pressure devices for physical investigations, *Phys. Uspekhi.* 51 (2008) 1059–1063.
 - [28] A. Mujica, A. Rubio, A. Munoz, R.J. Needs, High-pressure phases of group-IV, III-V, and II-VI compounds, *Rev. Mod. Phys.* 75 (2003) 863–892.
 - [29] T.Y. Velikanova, V.Z. Kublii, B.V. Khanenko, *Sov. Powder Metall* 24 (1988) 291–296.
 - [30] N.S. Fateeva, L.F. Vereshchagin, Melting curve of molybdenum up to 60kbar, *JETP Letters* 14 (1971) 153–154.
 - [31] S.C. Kennedy, G.C. Kennedy, The equilibrium boundary between graphite and diamond, *J. Geophys. Res.* 81 (1976) 2467–2470.
 - [32] N.N. Sirota, *Semiconductors and Semimetals, Physics of III-V Compounds*, Vol. 4, Academic Press Inc., New York, 1968.
 - [33] J. Nord, K. Albe, P. Erhart, K. Nordlund, Modelling of compound semi-conductors: analytical bond-order for gallium, Nitrogen and gallium nitride, *J. Phys.: Condens. Matter* 15 (2003) 5649–5662.
 - [34] A. Drozd-Rzoska, Pressure dependence of the glass temperature in supercooled liquids, *Phys. Rev. E* 72 (2005) 041505.
 - [35] A. Drozd-Rzoska, S.J. Rzoska, A.R. Imre, On the pressure evolution of the melting temperature and the glass transition temperature, *J. Non-Cryst. Solids* 353 (2007) 3915–3923.
 - [36] C. Rein, D. Demus, Mathematical description of strongly nonlinear pressure dependence of phase transition temperatures, *Cryst. Res. Technol.* 28 (1993) 273–281.
 - [37] V.V. Kechin, Melting curve equation at high pressure, *Phys. Rev. B* 65 (2001) 052102.
 - [38] A.R. Imre, H.J. Maris, P.R. Williams, *Liquids Under Negative Pressures*, Kluwer, Dordrecht, 2003.
 - [39] M. Wilson, P.F. McMillan, Crystal-liquid phase relations in silicon at negative pressure, *Phys. Rev. Lett.* 90 (2003) 135703–135707.
 - [40] P.F. McMillan, M. Wilson, D. Daisenberger, D. Machon, A density-driven and metallic polyamorphs of silicon, *Nat. Mater.* 4 (2005) 680–684.
 - [41] C.C. Matthai, N.H. March, D. Lamoen, Supercooled molecular liquids and the glassy phases of chemically bonded N, P, As, Si and Ge, *Phys. Chem. Liq.* 47 (2009) 607–613.
 - [42] K.M.S. Garcez, A. Antonelli, Pressure effects on the transitions between disordered phases in supercooled liquid silicon, *J. Chem. Phys.* 135 (2011) 204508.
 - [43] I. Grzegory, Application of GaN pressure grown crystals for epitaxy of GaN-based structures, *Acta Phys. Polon.* 98 (2000) 183–193.
 - [44] T.S. Tsiklis, *Handbook of Techniques in High-Pressure Research and Engineering*, Springer, Berlin, 2010.
 - [45] J.-P. Poirier, *The Physics of the Earth Interior*, Cambridge Univ. Press, Cambridge, 2006.