применения. Сб. науч. тр. – Выпуск 22. – Киев: ИСМ им. В.Н. Бакуля НАН Украины, 2019. – С, 317–327.

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References

1. Lavrinenko, V.I., Poltoratskiy, V.G., Pasichnyi O.O., et al. (2019). Analiz naiavnoho zviazku mizh fizychnymy vlastyvostiamy oksydiv dlia otrymannia modyfikovanykh termostiikymy oksydamy almaznykh shlifporoshkiv z metoiu dopravlennia oksydnykh materialiv v zonu obrobky [Analysis of the existing relationship between the physical properties of oxides to obtain diamond grinding powders modified with heat-resistant oxides to deliver oxide materials to the treatment area]. *Porodorazrushaiushchii i metalloobrabatyvaiushchii instrument – tekhnika i tekhnolohiia eho izhotovleniia i primeneniia – Rock Destruction and Metal-Working Tools – Techniques and Technology of the Tool Production and Applications, 22,* 436–440 [in Ukrainian].
2. Oki T., Fukuta Y., Hisada E., & Aoki S. (1993). Patent of USA 5230718.
3. Skorina T., Adefris N. B. (2021). Patent Application of USA 2021/0002533.
4. Boldyrev V.V. (2006). Mehanohimiia i mehanicheskaia aktivatsia tverdyh veshchestv [Mechanochemistry and mechanical activation of solid substances]. *Uspehi himii – Advances in chemistry, 75, 3,* 203–216 [in Russian].
5. Poltoratskiy, V.G., Bochechka, O.O., Lavrinenko, V.I., et al. (2019). Modifitsirovanie shlifporoshkov sinteticheskoho almaza i kompaktov na osnove mikroporoshkov cBN termostoikimi oksidami i khloridami metodom zhidko-faznoho naneseniia [Modification of synthetic diamond grinding powders and compacts based on cBN micropowders with heat-resistant oxides and chlorides by the method of liquid-phase deposition]. *Porodorazrushaiushchii i metalloobrabatyvaiushchii instrument – tekhnika i tekhnolohiia eho izhotovleniia i primeneniia – Rock Destruction and Metal-Working Tools – Techniques and Technology of the Tool Production and Applications, 22,* 317–327 [in Russian].

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THERMODYNAMIC CALCULATION OF Ga–N MELTING DIAGRAM UNDER ATMOSPHERIC AND HIGH PRESSURES

It was done melting diagram calculation of Ga–N system at atmospheric pressure (0,1 MPa) and at high pressures (1; 4; 6 GPa) within the phenomenological thermodynamics models. It is shown that increasing of pressure up to 6 GPa doesn't lead to the new phases formation, but allows to extend the temperature range of gallium nitride wurtzite modification stability up to 2615 K (the temperature above which the gas-peretechnic reaction (2GaN $\leftrightarrows$ *2*Ga_L + N_2↑*) occurs).*

Key words: *GaN, high pressures, thermodynamic calculations, ThermoCalc*

Introduction

GaN is an extremely important material for many applications in electronics and optoelectronics. The technology of fabrication of such optoelectronic or high speed electronic devices involve processes that require the direct contact of the solid, liquid and gas phase near equilibrium conditions [1]. Knowledge of thermal stability and phase diagram «pressure-temperature-composition» is important for under-standing the boundary conditions for obtaining high-quality gallium nitride single crystals using various methods (HVPE, CVD, HPHT, etc.), as well as for understanding the boundary conditions for stable operation of devices where GaN crystals used as semiconductor elements. Therefore, in this work, Ga–N diagram thermodynamic calculations at different pressures (0.1 MPa, 1 GPa, 6 GPa) were performed in order to solve this class of problems and to find optimal conditions for growing high-quality GaN single crystals.

Thermodynamic calculations

Experimental data analysis (the compound formation and appearance of the liquid phase temperatures) published in [2, 3] showed that GaNw is a constant composition phase, and in the liquid phase there is no stratification. When was done the behavior describing of nitrogen and gallium at high temperatures, it was also necessary to take into account that at high pressures nitrogen is a supercritical fluid, and gallium is a metal with the widest temperature of liquid phase range (from 302 to 2400 K) [4].

To describe the dependence of Gibbs free energy on the nitrogen concentration in solid gallium it was used the model with two sublattices. To describe the dependence of Gibbs free energy on the nitrogen concentration in liquid gallium it was used the subregular solutions model. Wurtzite gallium nitride described as a phase with constant composition in the CEF approximation [5]. The models parameters for calculating of Ga–N system phase diagram under atmospheric pressure are involved from [1].

High pressures cause a free Gibbs energy increase for the each phase by the $\int_0^p V_m^{ph} dp$, value, where V_m^{ph} is the molar volume of the phase with the structure Ph. Bulk modules, thermal expansion coefficients (CTE), phases' molar volumes and molar volumes' changes from temperature, for solid phases (gallium and gallium nitride) were taken from the literature summarized in the publication [6], and the bulk modules of liquid phases were described in such a way as to minimize deviations from experimental data (namely: melting temperatures dependences on pressure). The liquid phase volume calculated by the formula:

$$V_m^L = x_{\mathrm{Ga}} V_{Ga}^L + x_{\mathrm{N}} V_N^L + x_{\mathrm{Ga}} x_{\mathrm{N}} V^{mix},$$

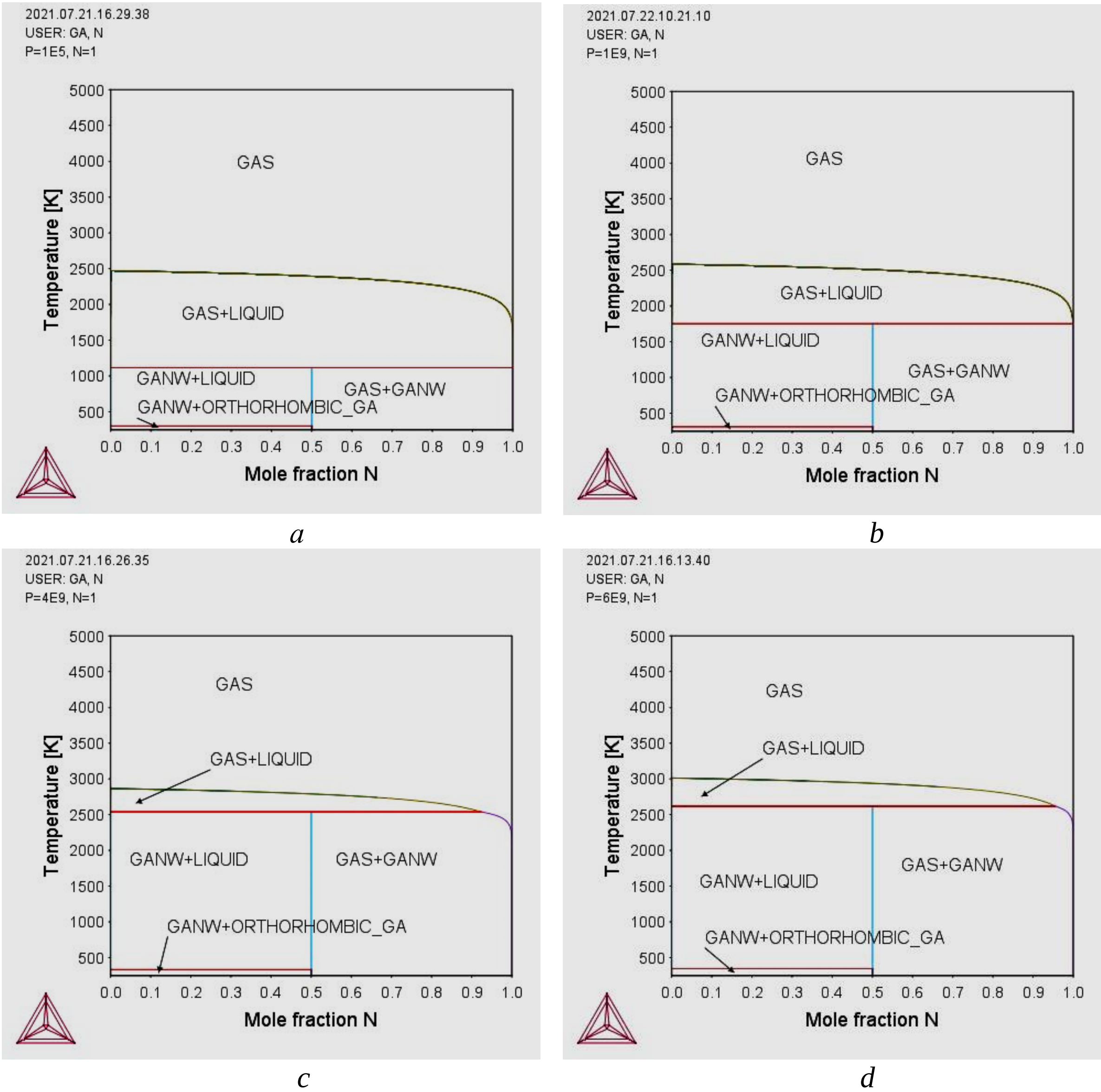
where V_m^L, V_{Ga}^L, V_N^L, V^{mix} – the volumes of liquid phase, liquid gallium, liquid (fluid) nitrogen and the mixing volume respectively, m^3/mol; x_{Ga}, x_N – the mole fractions of gallium and nitrogen respectively.

The dependence of Gibbs free energy on pressure calculated in the approximation [7]. Thermodynamic parameters that affect the change in the Gibbs free energy under pressure for the phases of Ga–N system shown in the Table.

Phases' thermodynamic parameters in Ga–N system

Phase	Molar volume, m^3/mol	Bulk modulus, GPa	Dependence coefficient of bulk modulus versus pressure	CTE, K^{-1}
GaL	$11.85\cdot10^{-6}$	48	9,1	$11,4\cdot10^{-5}$
Gag	$11.8\cdot10^{-6}$	48	9,1	$5,4\cdot10^{-5}$
GaNw	$13.72\cdot10^{-6}$	207	3,0	$1,85\cdot10^{-5}$
N	$170.0\cdot10^{-6}$	1,77	0,1	$14,8\cdot10^{-5}$

Ga–N system's melting diagrams at different pressures, calculated using the above model representations using the software package ThermoCalc [8] shows at Figure. Thus, the calculations showed no transition of wurtzite gallium nitride to cubic modification at these pressures. Analysis of the obtained data shows that for all pressures up to 6 GPa is characterized by the presence of a gas-peretictic reaction with the formation of liquid gallium and molecular nitrogen, which coincides with the experimental data in [9]. In this work, it was showed that Ga–N system is characterized by the passage of this reaction even at a pressure of 9 GPa, without the formation of a cubic modification of GaN. Moreover, pressure increasing leads to a passage temperature increase of this reaction: for instance, at atmospheric pressure, this reaction occurs at a temperature of 1115 K, at 1 GPa – at a temperature of 1750 K, at a pressure of 4 GPa – 2550 K, and at a pressure of 6 GPa the reaction is already occurs at 2615 K.



Phase diagrams of Ga–N system at 0,1 MPa (a), 1 GPa (b), 4 GPa (c) ma 6 GPa (d)

At the same time, the temperature range of liquid gallium existence increase insignificantly, which is associated with a small difference between the molar volumes of solid and liquid gallium.

Thus, the combination of the two above effects that appear in the Ga–N system with increasing pressure (namely, a slight increase in the temperature of liquid gallium existence, and a signifi0cant increase in the decomposition temperature of gallium nitride to liquid gallium and molecular nitrogen) leads to a significant expansion of the temperature range of stability of gallium nitride in the Ga–N system, which coincides with the literature data [10]. Most likely, this is because pressure increasing in Ga-N system allows increasing the nitrogen solubility in liquid gallium, and therefore, to activate the interaction of gallium and nitrogen with gallium nitride formation according to the equation:

$$Ga+0{,}5N_2 \rightarrow GaN$$

Conclusions

A pressure increasing up to 6 GPa expands the temperature range of gallium nitride existence and increases the solubility of nitrogen in liquid gallium. Under such conditions, the addition of one more element that dissolves GaN in the liquid state will ensure the existence of a liquid solution saturated with a significant amount of nitrogen and gallium, which, in turn, will provide the possibility of gallium nitride crystallization at high pressures and temperatures from molten solution.

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ТЕРМОДИНАМІЧНИЙ РОЗРАХУНОК ДІАГРАМИ ПЛАВКОСТІ
СИСТЕМИ Ga–N ЗА АТМОСФЕРНОГО ТА ВИСОКИХ ТИСКІВ

В межах моделей феноменологічної термодинаміки виконаний розрахунок діаграми плавкості системи Ga–N при атмосферному тиску (0,1 МПа) та при високих тисках (1; 4; 6 ГПа). Показано, що підвищення тиску до 6 ГПа не приводить до утворення нових фаз, проте дозволяє розширити температурний інтервал стабільності вюрцитної модифікації нітриду галію аж до 2615 К за умови збереження газоперитектичної реакції $2GaN \leftrightarrows 2Ga_L + N_2\uparrow$.

Ключові слова: *GaN, високі тиски, термодинамічні розрахунки, ThermoCalc*

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СИСТЕМЫ Ga–N ПРИ АТМОСФЕРНОМ И ВЫСОКОМ ДАВЛЕНИЯХ

В рамках моделей феноменологической термодинамики выполнен расчет диаграммы плавкости системы Ga–N при атмосферном давлении (0,1 МПа) и при высоких давлениях (1; 4; 6 ГПа). Показано, что повышение давления до 6 ГПа не приводит к образованию новых фаз, однако позволяет расширить температурный интервал стабильности вюрцитной модификации нитрида галлия до 2615 К при сохранении газоперитектичной реакции $2GaN \leftrightarrows 2Ga_L + N_2\uparrow$.

Ключевые слова: *GaN, высокие давления, термодинамические расчеты, ThermoCalc*

Література

1. Unland J., Onderka B., Davydov A., Schmid-Fetzer R. Thermodynamics and phase stability in the Ga–N system // Journal of Crystal Growth – 2003. – V. 256. – P. 138–143; doi:10.1016/S0022-0248(03)01352-6.
2. Congruent melting of gallium nitride at 6 GPa and its application to single-crystal growth / W. Utsumi; H. Saitoh; H. Kaneko, et. al. // Nature Materials. – 2003. – V. 2, N 11. – P. 735–738; doi:10.1038/nmat1003.
3. The new insight into gallium nitride (GaN) melting under pressure / S. Porowski, B. Sadovyi, S. Gierlotka, et. al. // arXiv preprint arXiv:1408.3254
4. CRC handbook of chemistry and physics, 85th Edition / under Lide, D. R. edition – CRC press. – 2712 p.
5. Hillert M. The compound energy formalism // J. Alloys Compd. – 2001. – V. 320, N 2. – P. 161–176; doi: 10.1016/S00925-8388(00)01481-X**.**
6. Springer Nature Switzerland AG, Part of Springer Nature [Electronic resource]. – Access mode: https://www.springernature.com/gp/products/ journals.
7. Murnaghan F. D. The compressibility of media under extreme pressures // Proc. Nation. Acad. Sci. USA. – 1944. – V. 9, N 30 – P. 244–247; https://doi.org/10.1073/pnas.30.9.244.
8. Thermo-Calc & DICTRA, computational tools for materials science / J-O. Andersson, T. Helander, L. Höglund et. al. // Calphad. – 2002. – V. *2*, N 26. – P. 273–312; https://doi.org/10.1016/S0364-5916(02)00037-8.
9. Physical properties of Ga-Fe-N system relevant for crystallization of GaN–Initial studies. / B. Sadovyi, P. Sadovyi, I. Petrusha, et. al. // Journal of Crystal Growth. – 2019 – V. 507 – P. 77–86; https://doi.org/10.1016/ j.jcrysgro.2018.10.035.
10. The challenge of decomposition and melting of gallium nitride under high pressure and high temperature / S. Porowski., B. Sadovyi., S. Gierlotka, et. al. // J. Phys. Chem. Solids. – 2015. – V. 85. – P. 138–143; doi.org/10.1016/j.jpcs.2015.05.006.

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References

1. Unland, J., Onderka, B., Davydov, A., & Schmid-Fetzer, R. (2003). Thermodynamics and phase stability in the Ga–N system. *Journal of Crystal Growth*, *256*, 33–51.
2. Utsumi, W.; Saitoh, H.; Kaneko, H.; Watanuki, T., et. al. (2003). Congruent melting of gallium nitride at 6 GPa and its application to single-crystal growth. *Nature Materials, 2, 11,* 735–738.
3. Porowski, S., Sadovyi, B., Gierlotka, S., Rzoska, S. J., et.al. (2014). The new insight into gallium nitride (GaN) melting under pressure. *arXiv preprint arXiv:*1408.3254.
4. Lide, D. R. (Ed.). (2004). *CRC handbook of chemistry and physics (V. 85*). CRC press.
5. Hillert, M., (2001). The compound energy formalism. *J. Alloys Compd., 320, 2,* 161–176.
6. Springer Nature Switzerland AG, Part of Springer Nature. *www.springernature.com*. Retrieved from https://www.springernature.com/gp/products/ journals.
7. Murnaghan, F.D. (1944). The compressibility of media under extreme pressures. *Proc. Nation. Acad. Sci. USA*, *9*, 30, 244–247.
8. Andersson, J-O., Helander, T., Höglund, L. et. al. (2002). Thermo-Calc & DICTRA, computational tools for materials science. *Calphad*, *2*, *26*, 273–312.
9. Sadovyi, B., Sadovyi, P., Petrusha, I., et. al. (2019). Physical properties of Ga–Fe–N system relevant for crystallization of GaN–Initial studies. *Journal of Crystal Growth*, *507*, 77–86.
10. Porowski, S., Sadovyi, B., Gierlotka, S., et al. (2015). The challenge of decomposition and melting of gallium nitride under high pressure and high temperature. *J. Phys. Chem. Solids*, *85*, 138–143.