

Thermodynamic Assessment of the Gallium–Nitrogen System

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(Received July 16, 2001; accepted July 16, 2001)

Subject classification: 64.30.+t; 64.70.Dv; 64.70.Hz; S7.14

Thermochemical and phase diagram data for the Ga–N system were assessed by employing the CALPHAD method. A consistent model representation of available thermodynamic properties agrees well with the critically evaluated experimental data. Thermodynamic extrapolation/interpolation of these data was applied to estimate the sublimation and melting characteristics of the GaN compound: at atmospheric pressure of nitrogen, gallium nitride sublimates incongruently by decomposing into nitrogen-rich gas and gallium-rich liquid, but can melt congruently at high nitrogen pressure (≈ 4.9 GPa).

Introduction Development of group-III nitride electronic and optoelectronic devices is hindered by several materials issues: challenges in synthesizing quality bulk single crystal substrates; degradation of device structures during processing and/or operation caused in part by thermal decomposition of group-III nitrides. Knowledge of the pressure–temperature–composition (P – T – x) phase diagrams and thermochemical properties of the group-III–nitrogen systems can provide guidance in optimizing the crystal growth parameters and establishing the thermal processing limits of nitride compounds and alloys. An experimental determination of the III–N phase diagrams is experimentally challenging given the high melting temperatures of the nitrides and extremely high equilibrium nitrogen pressures encountered in these systems [1]. Thus, a thermodynamic assessment of the sparse experimental data is attractive.

This paper reports a thermodynamic calculation of the Ga–N system employing the CALPHAD (CALculation of PHase Diagrams) procedure [2, 3]. The effect of pressure on phase equilibria in the Ga–N system was computed by introducing non-ideal pressure dependence of the Gibbs energy for the N_2 gas. Consistent model representation of all thermodynamic properties in this system allowed calculation of the full P – T – x phase diagram including the sublimation and melting parameters of GaN compound, and the equilibrium partial pressures in the system.

Evaluation of Experimental Data Critical evaluation of experimental thermochemical and phase diagram data was described in detail previously [4]. The evaluation of experimental information has revealed considerable discrepancy in both thermochemical and phase diagram data. For example, the reported enthalpy of formation values for GaN vary by more than 40% [5–7]. The decomposition temperatures of GaN into gallium-rich liquid and nitrogen-rich gas at atmospheric nitrogen pressure are also highly uncer-

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tain and vary from 993 K [8] to 1223 K [9] and even higher for annealing epitaxial films. The discrepancies could be associated with: a) possible contamination of GaN; b) large kinetic barrier to the decomposition of this compound [10], especially for the epilayers. For the latter reason, only phase diagram data that represented three-phase equilibria (liquid + GaN + gas) were selected for the assessment. It was believed that this type of experimental data was collected at the conditions close to equilibrium, as opposed to the possibly metastable two-phase (GaN + gas) data for which the kinetic barrier might have prevented or delayed formation of liquid gallium droplets.

Results The wurtzite structure was assumed to be the only stable solid form of GaN in the temperature–pressure range of interest ($T = 298$ K to 2792 K and $P = 0.1$ MPa to 7.6 GPa). Thermodynamic models and their parameters for the condensed phases, GaN compound and liquid phase, were summarized in previous work [4]. To account for non-ideal behavior in the gas phase at high pressures, the Gibbs energy for the N_2 gas was re-assessed in the present study by fitting to the equation of state of nitrogen [11] as follows:

$$G_{N_2}(T, P) = G_1(T) + G_2(P, T), \quad (1)$$

where

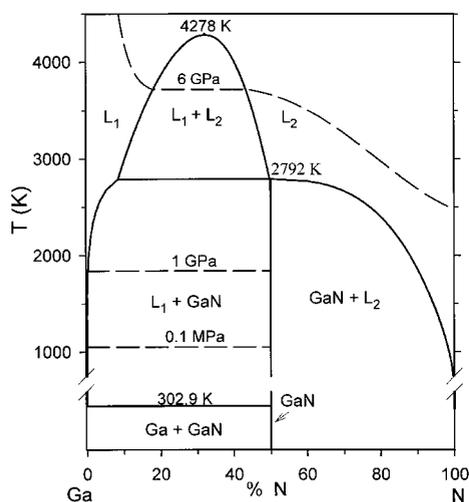
$$G_1(T) = -35378.55 + 205.4282T - 56.03704T \ln(T) + 8.246216 \times 10^{-3} T^2 - 6.3897 \times 10^{-7} T^3 + 3146190/T,$$

and

$$G_2(P, T) = RT \ln(P/P_0) + 2.6954947 \times 10^{-5} (P - P_0) - 1.02167 \times 10^{-15} (P - P_0)^2,$$

where T is in K and P is in Pa with $P_0 = 101325$ Pa.

Model parameters from [4] together with Eq. (1) were used to calculate thermochemical and phase diagram properties of the Ga–N system. Figure 1 shows the calculated T – x projection of the phase diagram with superimposed isobaric lines. The diagram is similar to that of Al–N [12] and features



a steep liquidus on the Ga-rich side and a predicted miscibility gap in the liquid. The calculated GaN congruent melting temperature of 2792 K at a nitrogen pressure of 4.9 GPa fits well with the melting point predicted from the semi-empirical theory of electronegativity [13].

Several isobaric sections of the phase diagram are shown in Figs. 2a–d. They illustrate the effect of increasing pressure on phase equilibria, including the thermal be-

Fig. 1. T – x projection of the P – T – x phase diagram calculated at equilibrium pressure of nitrogen (with isobaric dashed lines)

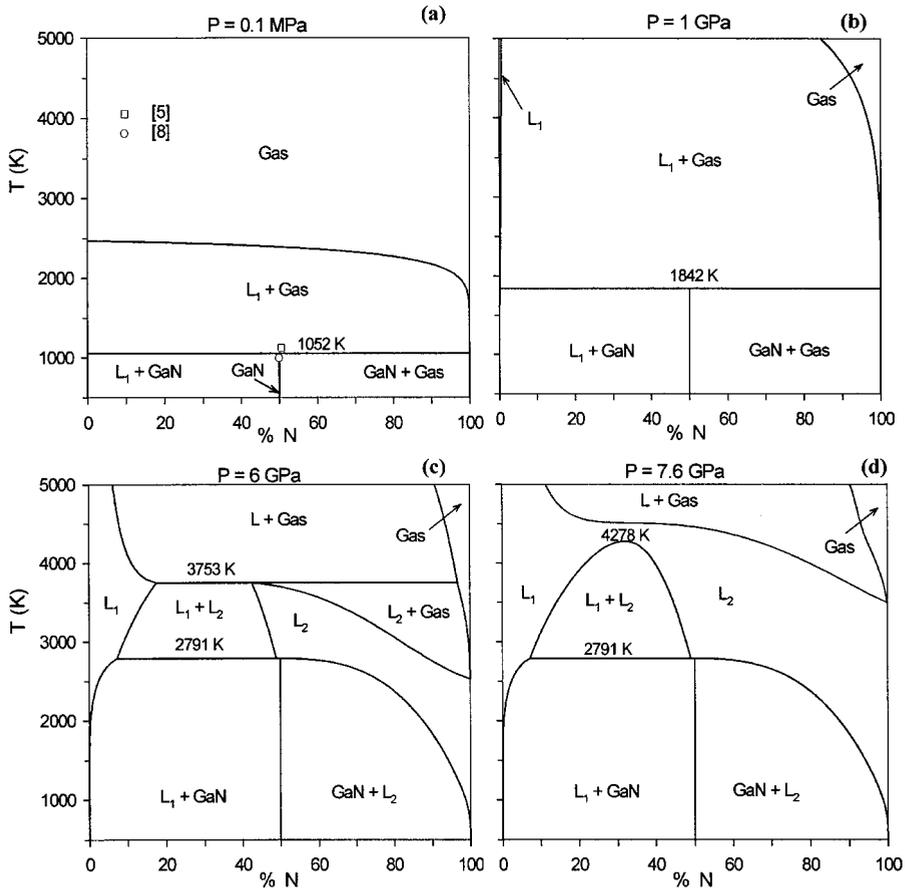


Fig. 2. Calculated $(T-x)_P$ sections of the $P-T-x$ diagram illustrating the effect of pressure, particularly, on the thermal stability of GaN. Note that raising $P(N_2)$ from 0.1 MPa to 7.6 GPa increases the decomposition/melting temperature of GaN from 1052 K to 2792 K

havior of GaN. Figure 2a shows that at standard pressure of 0.1 MPa GaN should sublimate incongruently by decomposing into a Ga-rich liquid and a N-rich gas at 1052 K. It should be noted that the calculated decomposition temperature of GaN at atmospheric pressure can only be achieved when the kinetic barrier to this process is removed [8, 14]; otherwise, superheating can occur. In Figs. 2b–d, GaN is shown to become more stable with increasing pressure and melts congruently at pressures in excess of 4.9 GPa.

Figure 3 summarizes calculated and experimental data for the thermal stability of GaN as a function of N_2 partial pressure. It clearly demonstrates that the N_2 pressure in excess of its equilibrium values should be applied during thermal processing of GaN to suppress the decomposition. Taking into account the thermodynamics of the $N_2(\text{gas}) \rightarrow 2N(\text{gas})$ reaction, it seems even more effective to maintain an over-pressure of atomic nitrogen or other activated N-species (e.g., NH_3) over GaN at elevated temperatures.

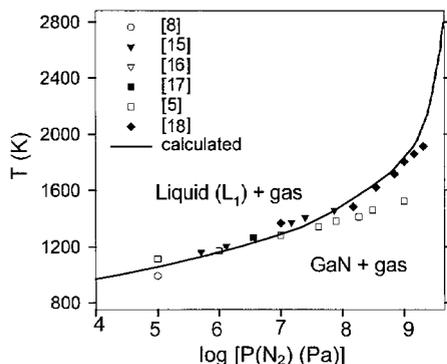


Fig. 3. Pressure dependence of GaN thermal stability. Solid line and symbols represent calculated and experimental three-phase (GaN + liquid + gas) equilibrium, respectively

To further improve the thermodynamic description of the Ga–N system, we plan to critically evaluate and add thermochemical information [6, 19, 20] that was not available at the time of assessment of work [4], and to introduce the pressure dependence to the Gibbs energy of the GaN compound and Ga–N melt.

Conclusion Critically evaluated thermodynamic data were used to calculate the P – T – x phase diagram of the Ga–N system. The pressure-temperature parameters of thermal stability of the GaN compound were successfully derived. Sublimation of GaN was found to be incongruent and should be taken into consideration during thermal processing.

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