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Supporting Information

Effect of Temperature and Pressure on GaN Crystals by Na-Flux Method

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The article provides the following information on the boundary conditions and calculation process.

In this work, its boundary is defined as adiabatic and the corresponding conditions are expressed by the following equations.

$$\frac{\partial \mu}{\partial t} = \nabla(k\nabla T) + Q$$

where μ,t,k,T, Q and ∇ are the system energy, time, thermal conductivity of the material, temperature, heat source term per unit volume and gradient operator respectively. To ensure an adiabatic boundary, conditions must be set on the boundary to ensure that there is no heat flow (q) on the boundary. The calculation of heat flow (q) can be achieved by using the following equation:

$$q = -k\frac{\partial T}{\partial n}$$

The heat flow (q) and the unit normal vector (n) pointing out of the boundary are related. To ensure that $\frac{\partial T}{\partial n} = 0$, it is necessary to set $q = 0$. This ensures that no heat passes through the boundary, making it adiabatic.

The growth environment of GaN crystals grown by Na fluxes is extremely complex and the growth system consists of gas phase, solid phase and liquid phase environments. Therefore, its simulation requires the consideration of nitrogen dissolution under a variety of conditions. In the case considered, the total Gibbs energy G of the Ga-Na-N system is written as

$$G = x_{Ga}^{sol}\left[RT\ln\left(\gamma_{Ga}x_{Ga}^{sol}\right) + \mu_{Ga}^{(l)}\right] + x_{Na}^{sol}\left[RT\ln\left(\gamma_{Na}x_{Na}^{sol}\right) + \mu_{Na}^{(l)}\right] + x_{N}^{sol}$$

where the deviation of the total Gibbs energy from the ideal case is given by

$$\Delta G^{ex} = x_{Ga}^{sol}RT\ln\gamma_{Ga} + x_{Na}^{sol}RT\ln\gamma_{Na} + x_{N}^{sol}RT\ln\gamma_{N}$$

ΔG^{ex} is referred to as the excess Gibbsenergy. Here, x_{I}^{sol} , γ_I and $\mu_i^{(l)}$ are the equilibrium mole fraction, the activity coefficient and the standard Gibbs' energy of i-th component in the solution of arbitrary composition, respectively; R is the gas constant, T is the

temperature. After the introduction of the Redlich-Kister polynomials, which are used for the description of the excess Gibbs energy in the liquid phase and in the solid solution, we obtain

$$\Delta G^{ex} = x_{Ga}^{sol} x_{Na}^{sol} L_{Ga-Na} + x_{Na}^{sol} x_{N}^{sol} L_{Na-N} + x_{Ga}^{sol} x_{N}^{sol} L_{Ga-N}$$

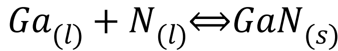
where L_{Ga-Na}, L_{Na-N}, L_{Ga-N} are the experimentally measured parameters of the interaction for the binary systems Ga-Na, Na-N and Ga-N. Finally, the activity coefficients are expressed by the Gibbs-Duhem equation as

$$RT\ln\gamma_N = \Delta G^{ex} - x_{Ga}^{sol}\frac{\partial \Delta G^{ex}}{\partial x_{Ga}^{sol}} - x_{Na}^{sol}\frac{\partial \Delta G^{ex}}{\partial x_{Na}^{sol}}$$

$$RT\ln\gamma_{Ga} = \Delta G^{ex} + (1 - x_{Ga}^{sol})\frac{\partial \Delta G^{ex}}{\partial x_{Ga}^{sol}} - x_{Na}^{sol}\frac{\partial \Delta G^{ex}}{\partial x_{Na}^{sol}}$$

$$RT\ln\gamma_{Na} = \Delta G^{ex} - x_{Ga}^{sol}\frac{\partial \Delta G^{ex}}{\partial x_{Ga}^{sol}} + (1 - x_{Na}^{sol})\frac{\partial \Delta G^{ex}}{\partial x_{Na}^{sol}}$$

The occurrence of GaN crystallisation at the seed crystal can be expressed in terms of



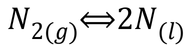
$$Ga_{(l)} + N_{(l)} \Leftrightarrow GaN_{(s)}$$

When the reaction has reached an equilibrium

$$RT\ln\left(\gamma_{Ga} x_{Ga}^{GaN}\right) + \mu_{Ga}^{(l)} + RT\ln\left(\gamma_N x_N^{GaN}\right) + \mu_N^{(l)} = \mu_{GaN}^{(s)}$$

where x_N^{GaN} is the molar fraction of nitrogen at reaction equilibrium. x_{Ga}^{GaN} is the equilibrium molar fractions of gallium in solution in a GaN crystal. $\mu_{Ga}^{(l)}$, $\mu_N^{(l)}$ and $\mu_{GaN}^{(s)}$ are the standard Gibbs energies of the gallium melt, N_2 and GaN crystals respectively.

For modelling at the gas-liquid interface, it is necessary to consider the free decomposition of nitrogen molecules at the interface to reach equilibrium.



$$N_{2(g)} \Leftrightarrow 2N_{(l)}$$

Taking into account the effect of nitrogen pressure, the equilibrium state of the gas and liquid phases can be expressed by the following equation

$$RT\ln\left(\frac{p_{N_2}}{P_a}\right) + \mu_{N_2}^{(g)} + B_{N_2} p_{N_2} + \frac{C_{N_2} - B_{N_2}^2}{2RT} p_{N_2}^2 = 2\left[RT\ln\left(\gamma_N x_N^{fs}\right) + \mu_N^{(l)}\right]$$

x_N^{fs} is the mole fraction of nitrogen in the equilibrium state. The standard Gibbs energy of the $\mu_N^{(l)}$ is given by the following equation

$$\mu_N^{(l)} = \mu_{GaN}^{(s)} - \mu_{Ga}^{(l)} - \left\{RT\ln\left[\gamma_{Ga}(1 - x_N^{sol})\right] + RT\ln\left(\gamma_N x_N^{sol}\right)\right\}$$

$$x_N^{sol} = \left(\frac{T}{2733.168}\right)^{13.82558} \textit{in pure gallium melt at Ga}_{\mathrm{N}}$$

p_{N_2} and $\mu_{N_2}^{(g)}$ are the pressure and standard Gibbs energy of the N_2 above the melt respectively. B_{N_2} and C_{N_2} are virial coefficients allowing for deviations from ideal gas. Pa is atmospheric pressure.

Supplementary Figures S1–S18

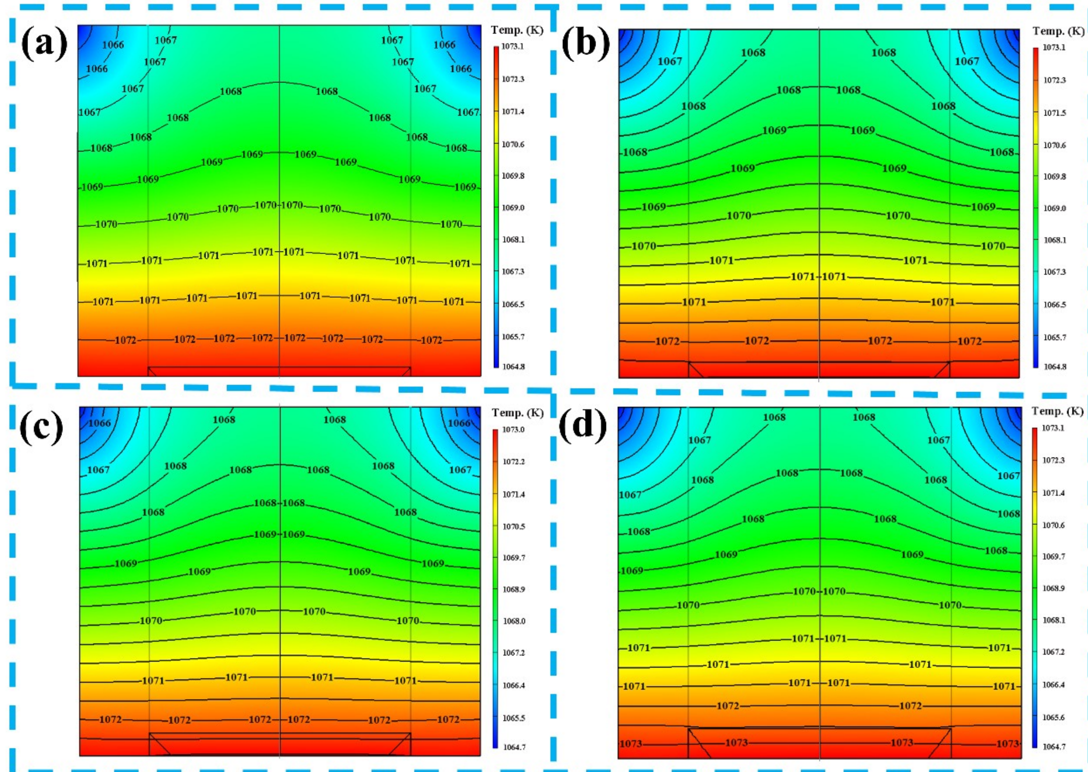


Figure S1. Temperature gradient diagrams at various time points. (a) 5 hours, (b) 20 hours, (c) 40 hours, and (d) 60 hours.

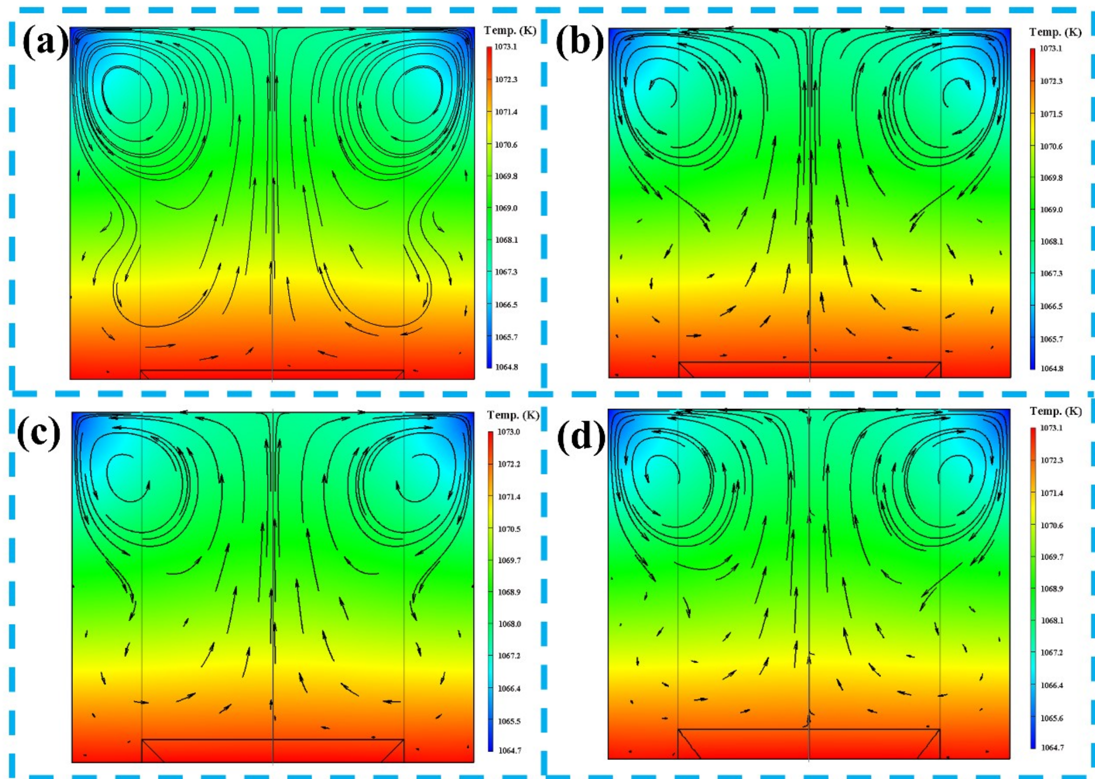


Figure S2. Stream function diagrams at various time points: (a) 5 hours, (b) 20 hours, (c) 40 hours, and (d) 60 hours.

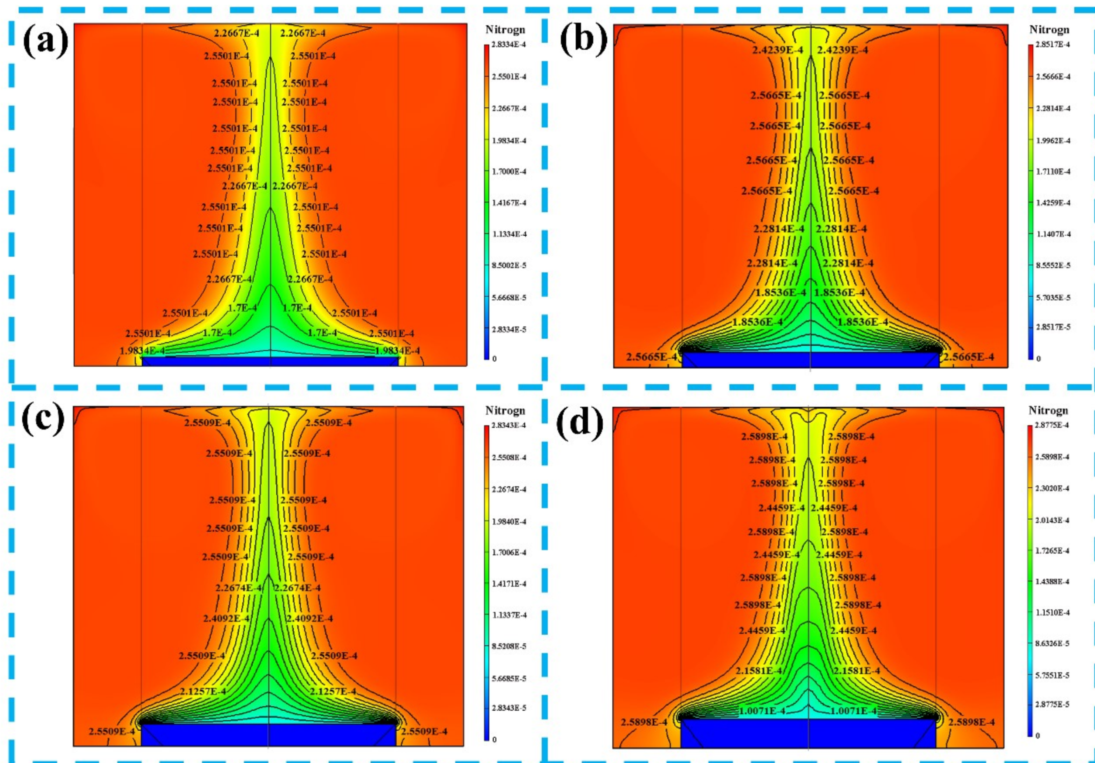


Figure S3. N^{3-} concentration distribution diagrams at different time points: (a) 5 hours,

(b) 20 hours, (a) 40 hours, (a) 60 hours.

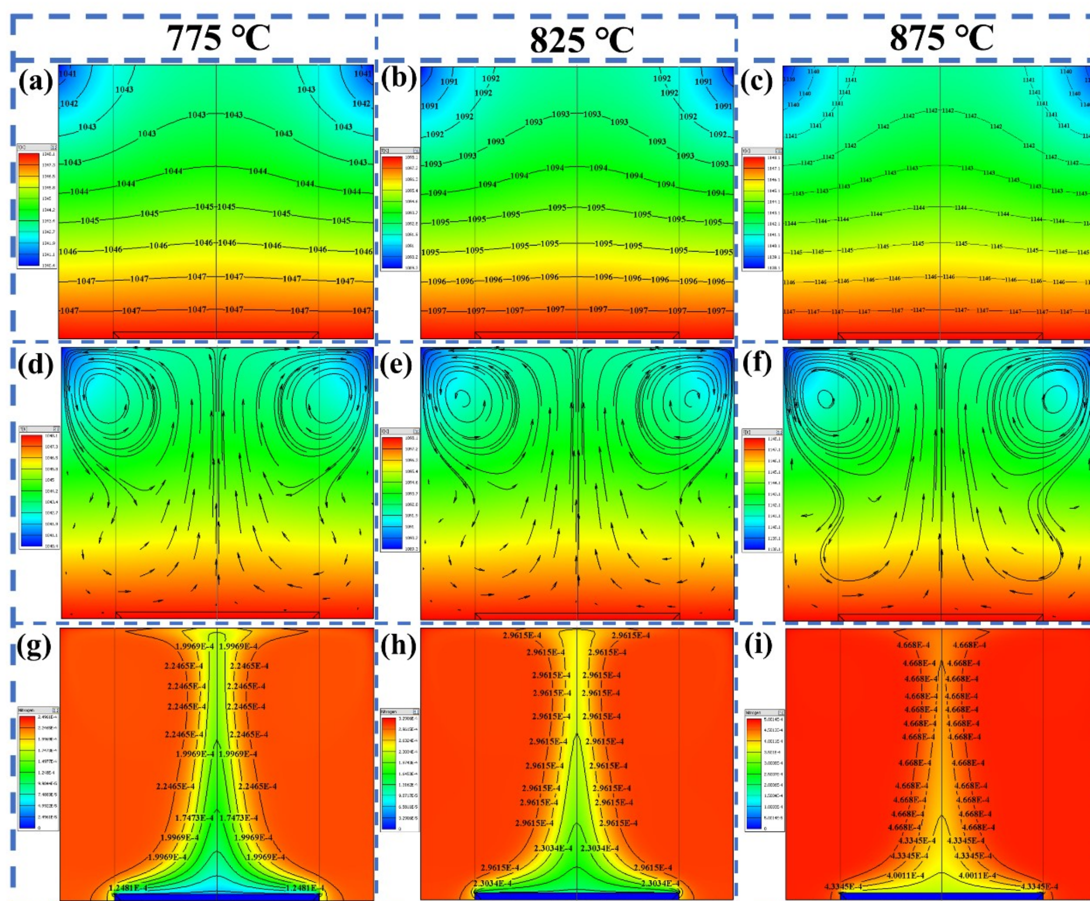


Figure S4. Simulation results under the temperatures of 775, 825 and 875 ℃, temperature gradient (a-c), stream function (d-f) and N^{3-} concentration distribution. (g-i).

In addition, due to the high solubility of Gallium Nitride, the seed crystals are partially dissolved. As a result, gallium nitride can only be partially grown at 875°C.

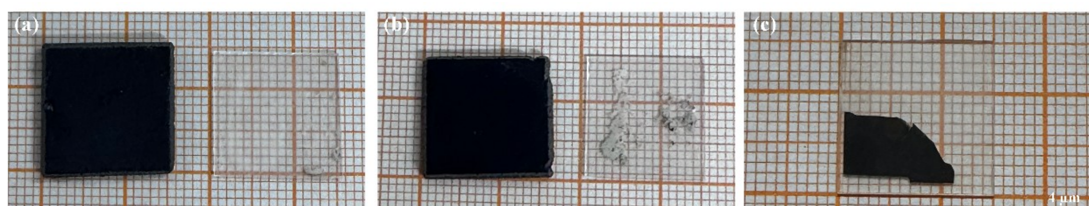


Figure S5. Optical images of GaN crystals at increasing temperature, (a) 775, (b) 825 and (c)875 ℃.

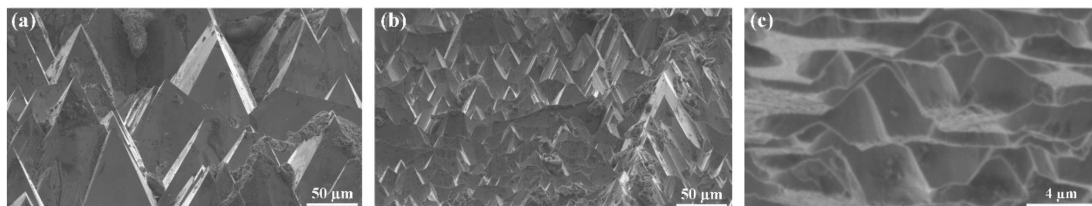


Figure S6. SEM images of surfaces, (a) 775, (b) 825 and (c)875 ℃.

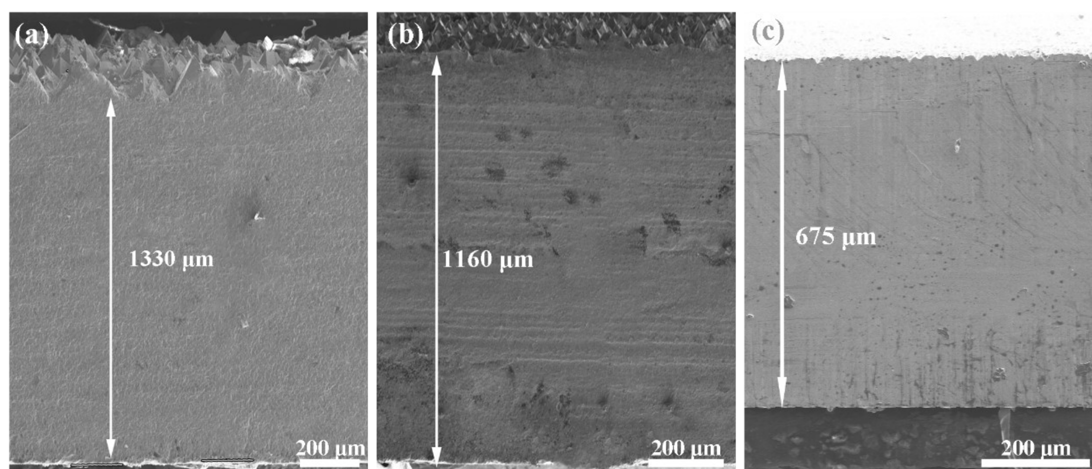


Figure S7. SEM images of cross-sections, (a) 775, (b) 825 and (c)875 ℃.

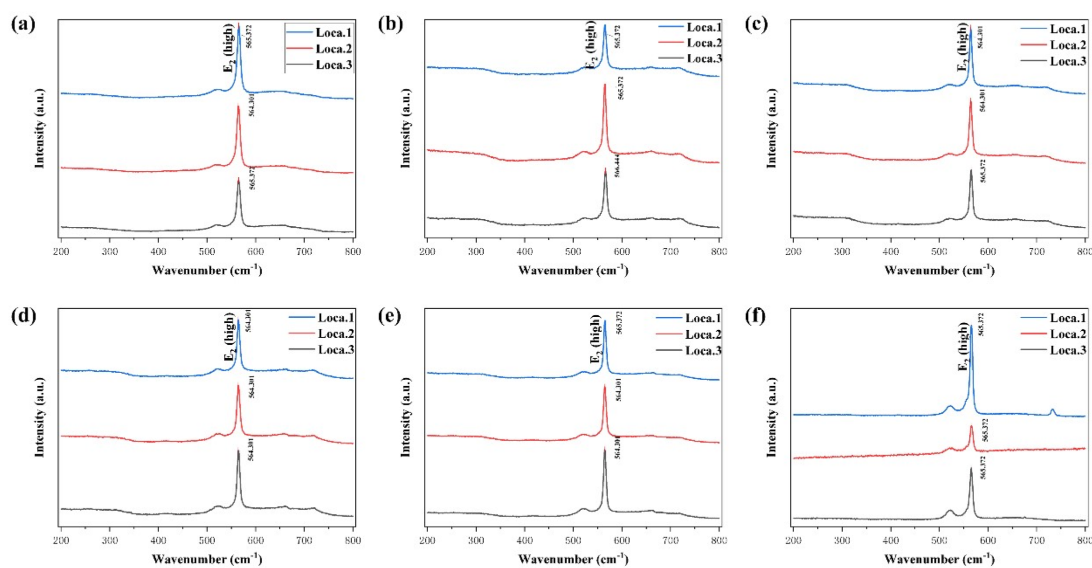


Figure S8. Raman tests of gallium nitride crystals at different temperatures. (a) 750, (b) 775, (c)800, (d) 825, (e)850 and (e) 875 ℃.

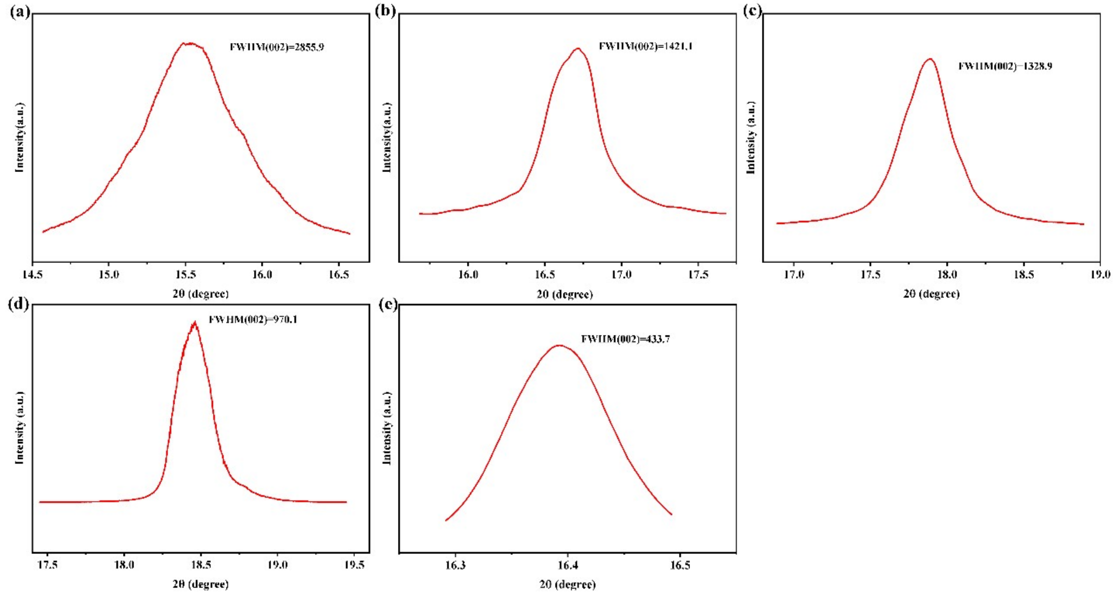


Figure S9. XRD test results of GaN crystals at different temperatures (002). (a) 775, (b) 800, (c)825, (d) 850, and (e)875 °C.

The quality of the GaN crystals obtained by growth at 750°C was poor and the XRD tests were inconclusive.

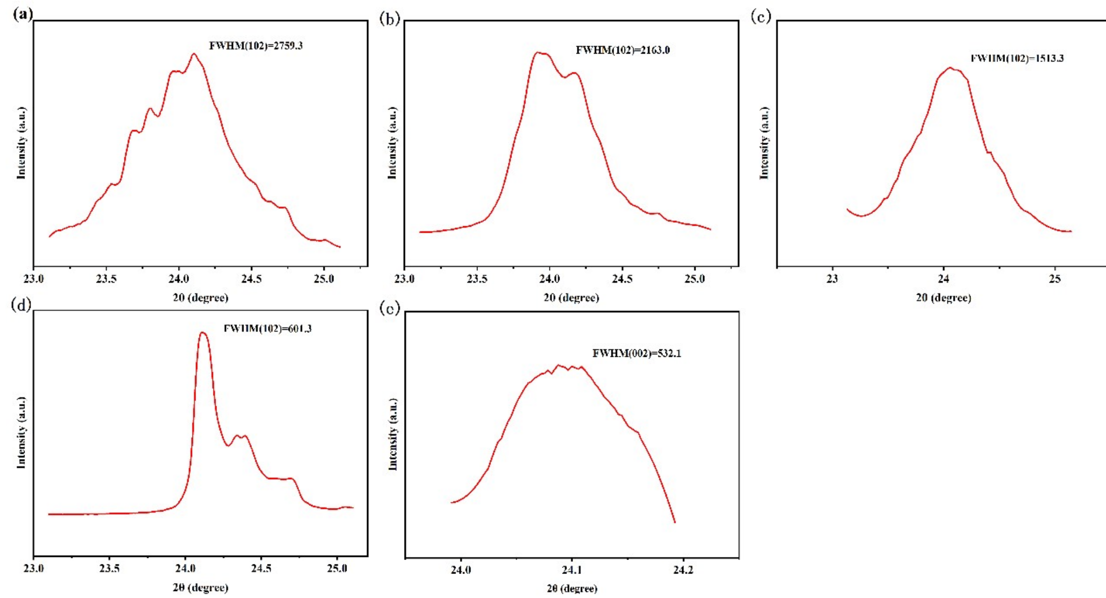


Figure S10. XRD test results of gallium nitride crystals at different temperatures (102). (a) 775, (b) 800, (c)825, (d) 850, and (e)875 °C.

The quality of the GaN crystals obtained by growth at 750°C was poor and the XRD

tests were inconclusive.

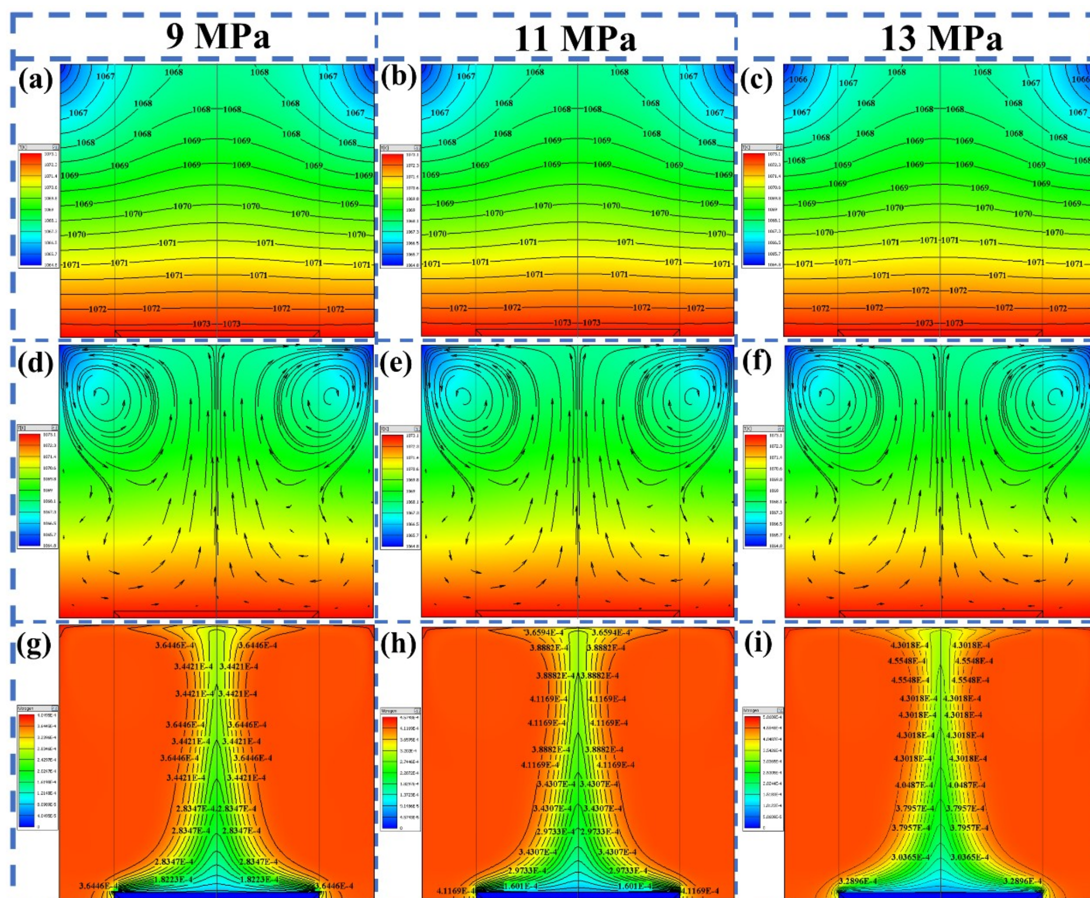


Figure S11. Simulation results under the pressure of 9, 11 and 13MPa, temperature gradient (a-c), stream function (d-f) and N^{3-} concentration distribution. (g-i).

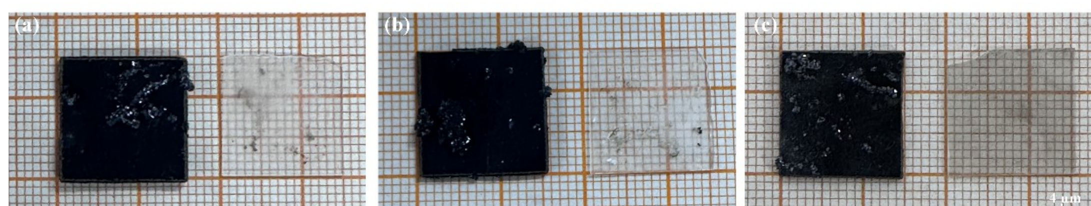


Figure S12. Optical images of GaN crystals at increasing pressure, (a) 9, (b) 11 and (c)13 MPa.

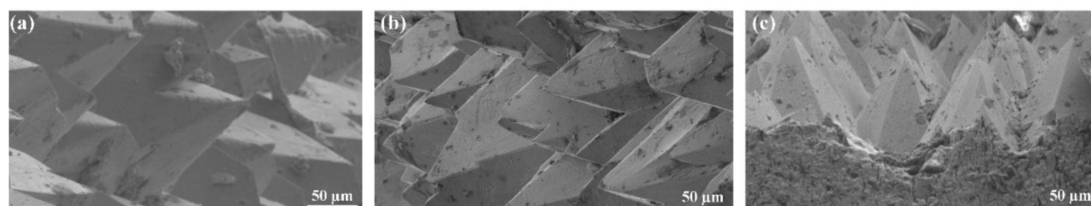


Figure S13. SEM images of surfaces, (a) 9, (b) 11 and (c)13 MPa.

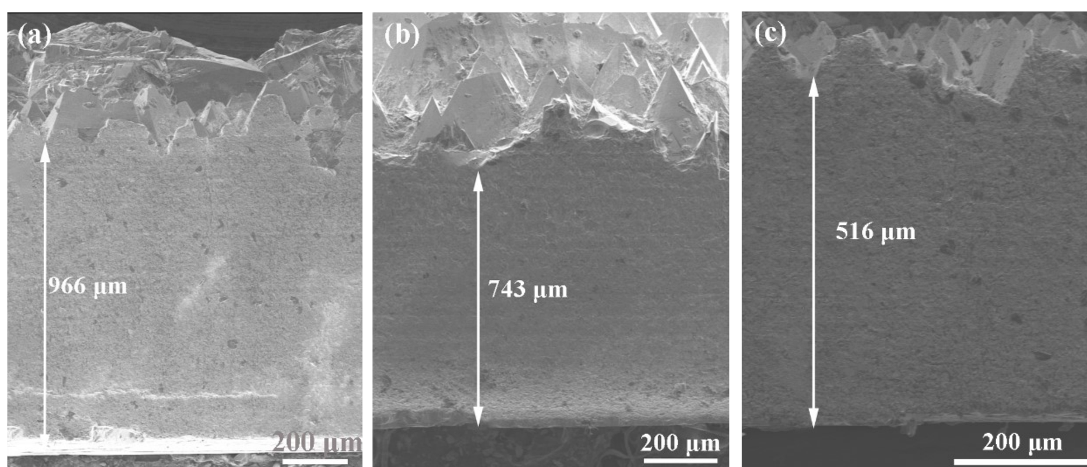


Figure S14. SEM images of cross-sections, (a) 9, (b) 11 and (c)13 MPa.

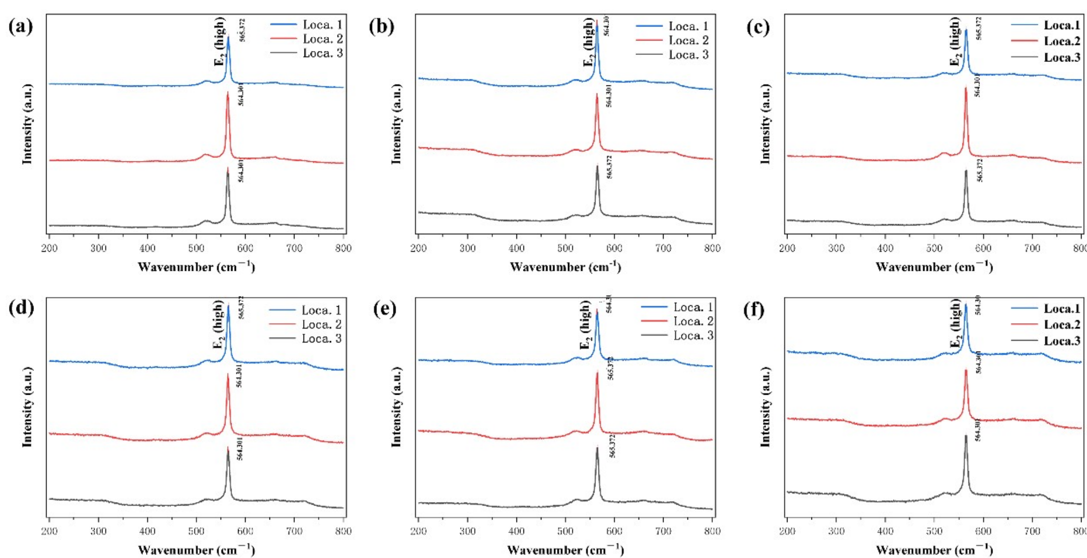


Figure S15. Raman tests of gallium nitride crystals at different pressures. (a) 3, (b) 5, (c)7, (d) 9, (e) 11 and (f) 13MPa.

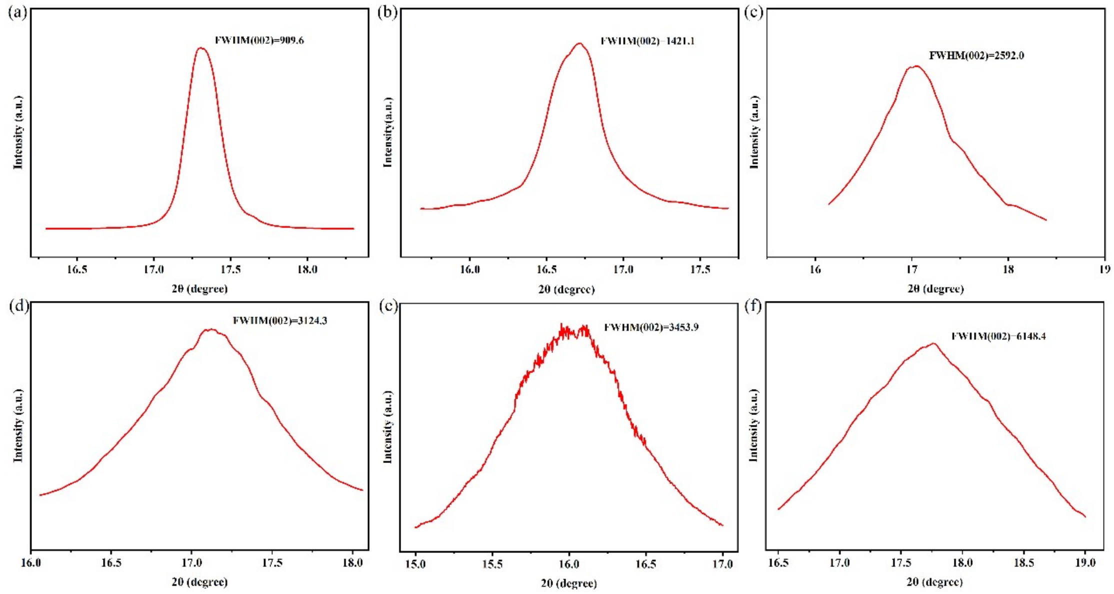


Figure S16. XRD test results of gallium nitride crystals at different pressures (002). (a) 3, (b) 5, (c)7, (d) 9, (e) 11 and (f) 13MPa.

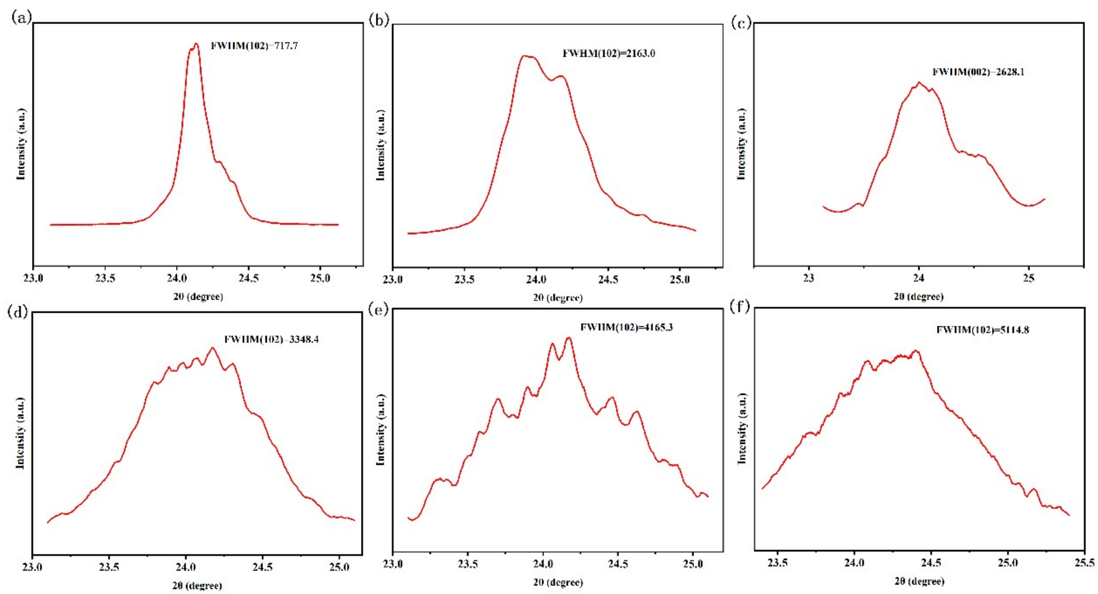


Figure S17. XRD test results of gallium nitride crystals at different pressures (102). (a) 3, (b) 5, (c)7, (d) 9, (e) 11 and (f) 13MPa.

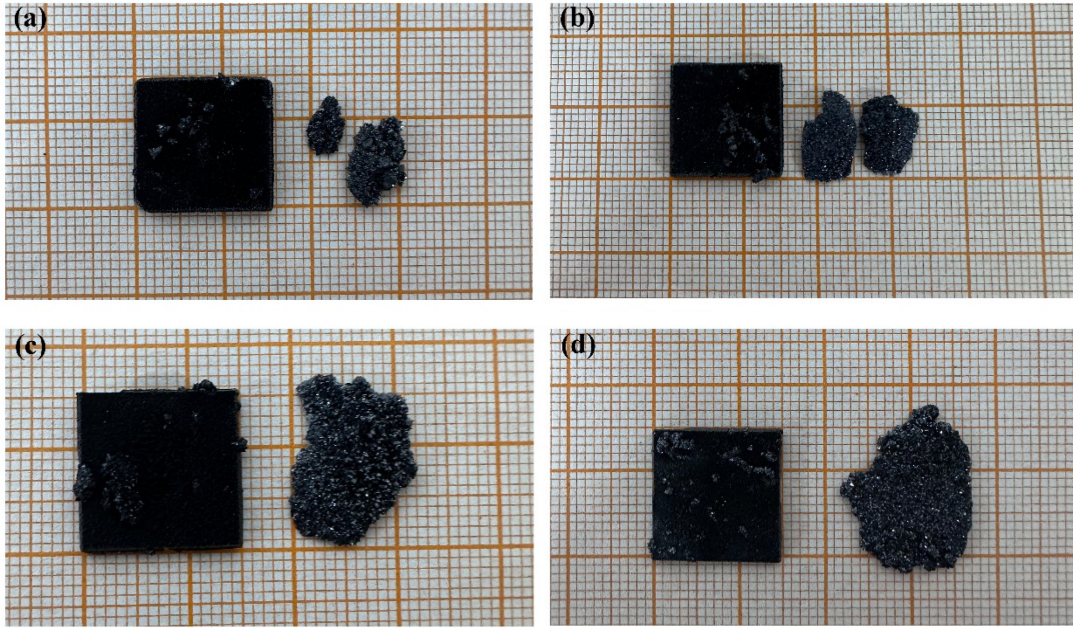


Figure S18. Image of polycrystalline under different pressures, (a) 7, (b) 9, (c) 11 and (d) 13MPa.