High Nitrogen Pressure Solution (HNPS) growth method

Method and Experimental Setup

It is a temperature gradient method based on a direct reaction between gallium and nitrogen at a high temperature (up to 2000 K) and high nitrogen pressure (up to 1 GPa).

Nitrogen molecules dissociate on gallium's surface and dissolve in the metal. Therefore, the crystals are grown from the solution of atomic nitrogen in liquid gallium.

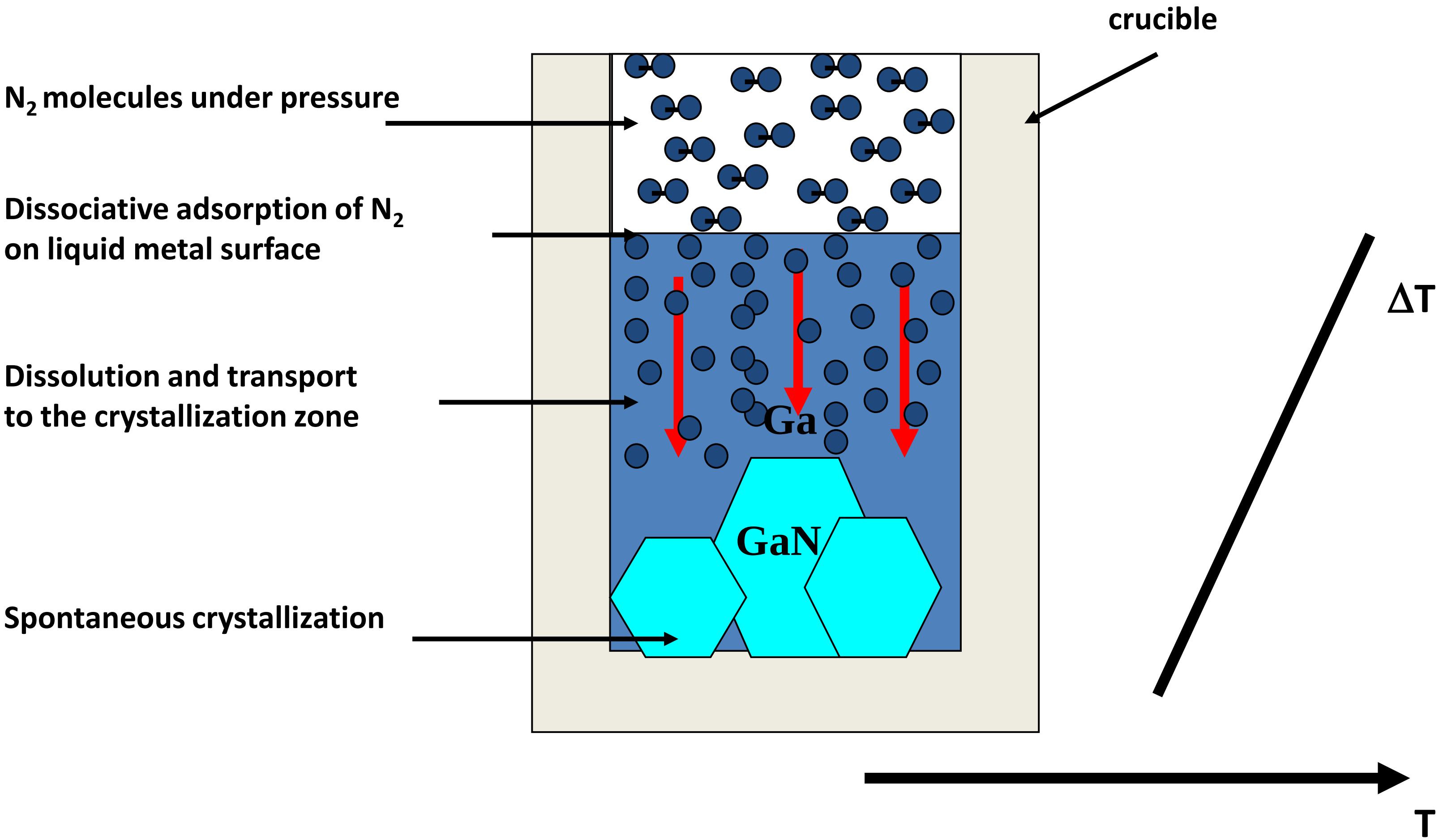
Supersaturation is created by the application of temperature gradient along the liquid gallium.

Due to the temperature gradient in the system, the atomic nitrogen is transported from the hot end of the solution to the cooler part.

The solution at the cold part is supersaturated.

Method and Experimental Setup

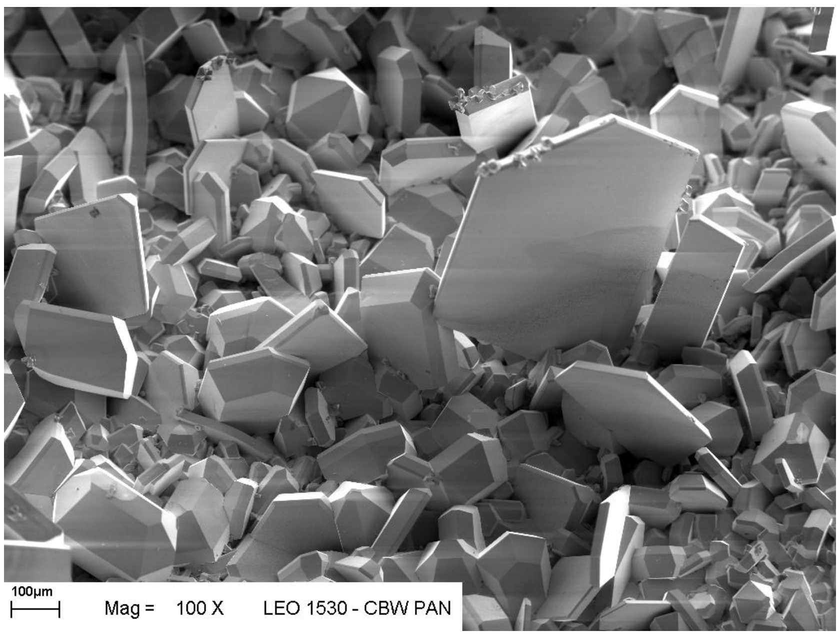
$$Ga + 1/2 N_2 \rightarrow GaN$$

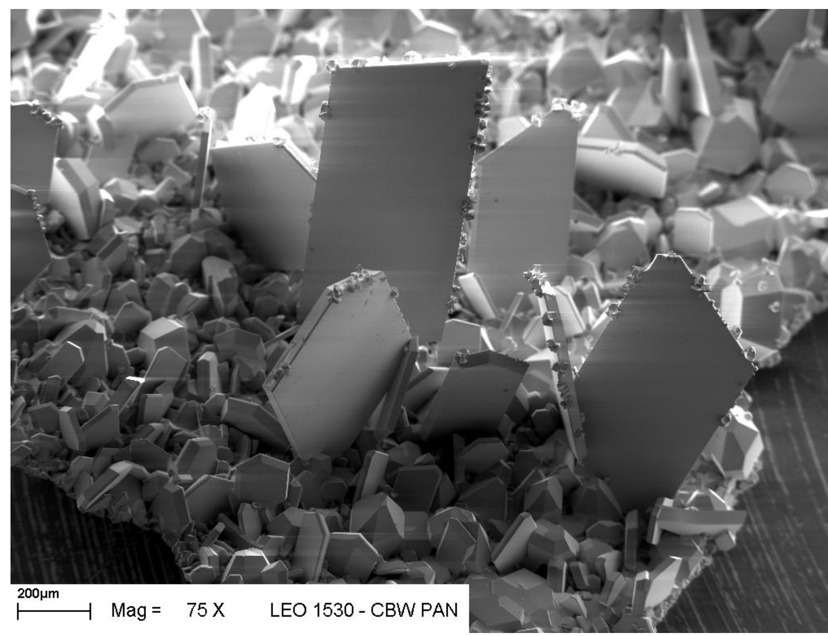


Method and Experimental Setup

The GaN crystals are grown spontaneously from the wall of the crucible, from the GaN polycrystalline layer (film) created on the surface of the liquid metal.

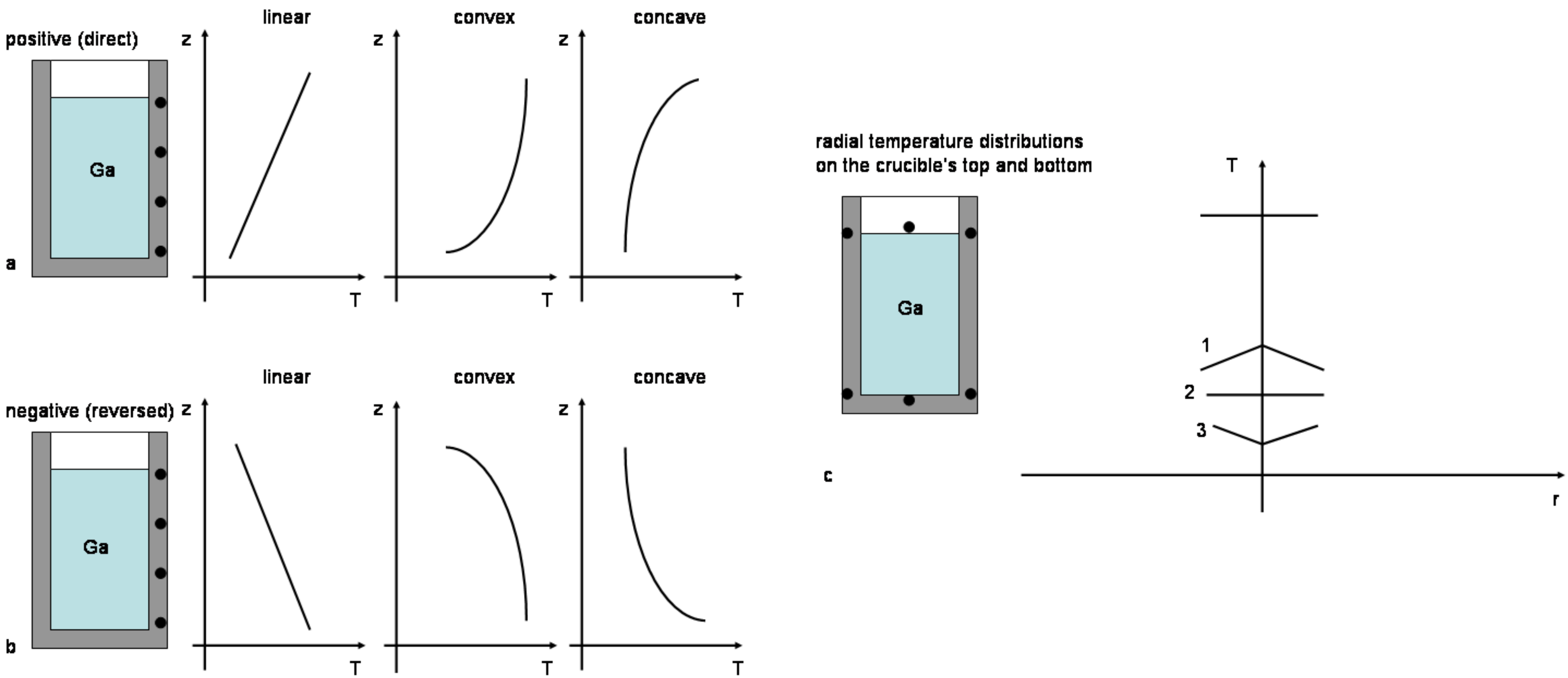
The GaN crystals are distributed randomly in the supersaturated cold zone of the solution.





Method and Experimental Setup

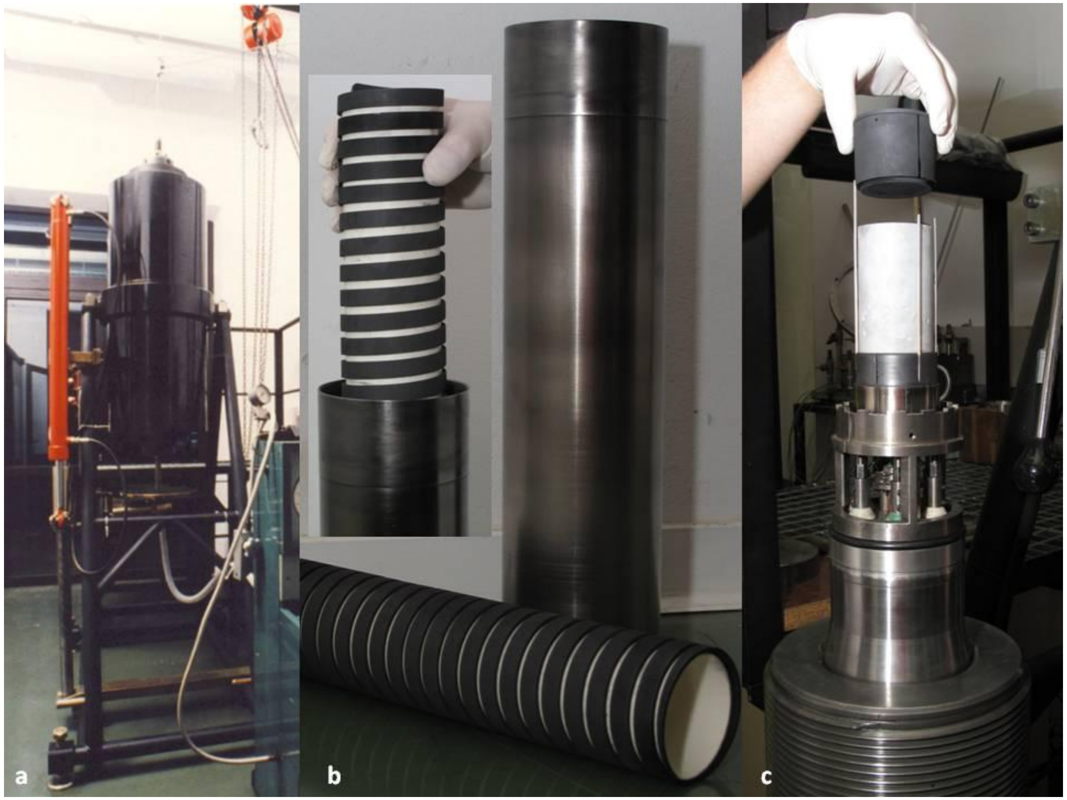
Typical crystal growth experiment is when the metal (Ga), placed in the crucible, is heated in the furnace inside the high pressure reactor with a constant rate to given axial and radial temperature profiles.



The system is annealed under high nitrogen pressure for 100–500 h. After that, the furnace is cooled down at a constant rate, the system is decompressed, and the metal with GaN crystals inside is removed.

Method and Experimental Setup

Vertically positioned technological gas pressure chambers of internal diameters up to 10cm are used. The multizone cylindrical graphite furnaces, capable of reaching the maximum temperature of 2073 K, are placed inside the gas pressure reactors. To register the temperature, PtRh6%–PtRh30% thermocouples are used. They are arranged along the furnace and coupled with the input power control electronic systems. The pressure is measured by manganine gauges positioned in the low temperature zones of the reactors.



Thermodynamic and Kinetic Aspects

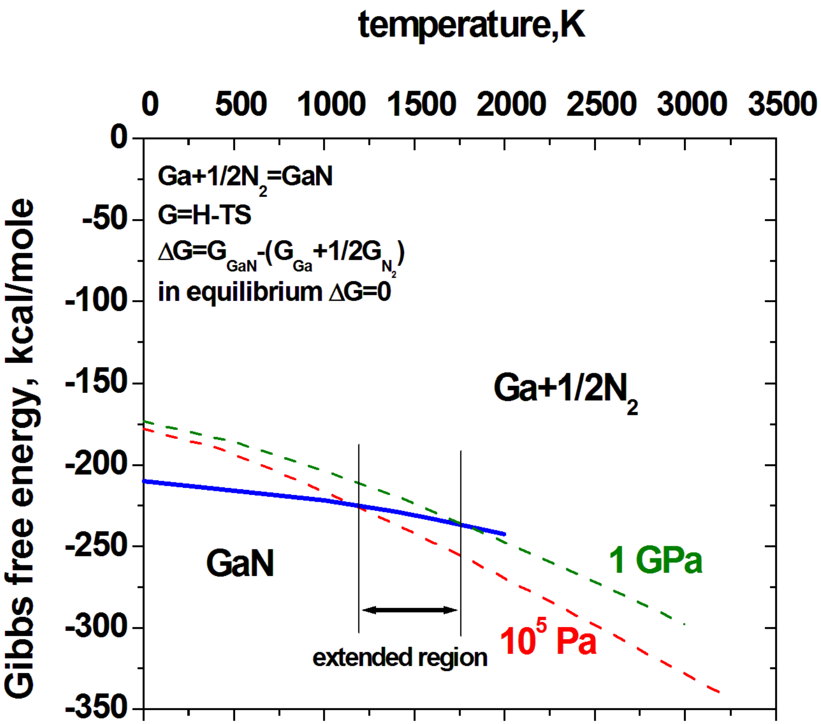
The analysis of thermodynamics properties of GaN and the system of its constituents explains the role of high pressure.

Since gallium nitride is a strongly bonded compound, the free energy of the crystal is very low in relation to the reference state of free N and Ga atoms.

The N_2 molecule is also strongly bonded.

GaN	**8.92 eV/molecule**
N_2	**9.8 eV/molecule**
GaAs	**6.52 eV/molecule**
ZnSe	**5.16eV/molecule**

The free energy *G* of GaN constituents in their normal states becomes close to the crystal's one.



S. Porowski, I. Grzegory, J. Cryst. Growth, 178, 174 (1997)

Thermodynamic and Kinetic Aspects

With an increase of the temperature, Gibbs free energy of the constituents decreases faster than the free energy of the crystal.

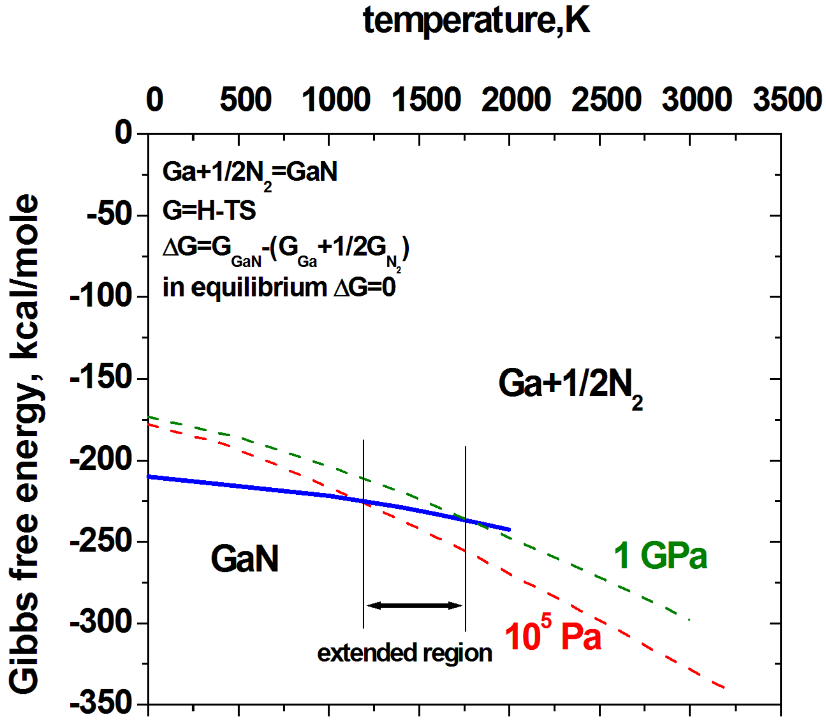
At higher temperatures nitride becomes thermodynamically unstable.

The crossing of *G*(*T*) curves determines the equilibrium temperature where GaN coexists with its constituents at a given N_2 pressure.

The application of pressure increases the free energy of the constituents to a much higher degree than the Gibbs free energy of the crystal.

The equilibrium point shifts to higher temperatures and the GaN stability range extends.

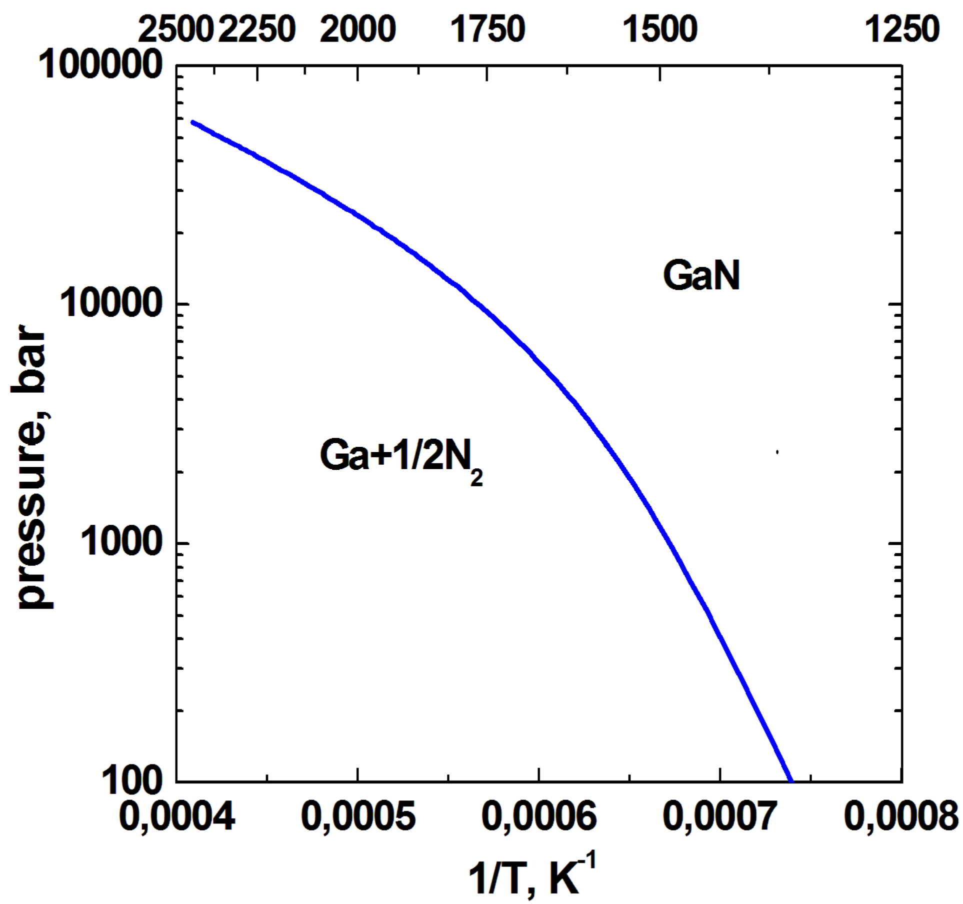
This extension allows the growth of GaN crystals from solution in liquid Ga.



S. Porowski, I. Grzegory, J. Cryst. Growth, 178, 174 (1997)

Thermodynamic and Kinetic Aspects

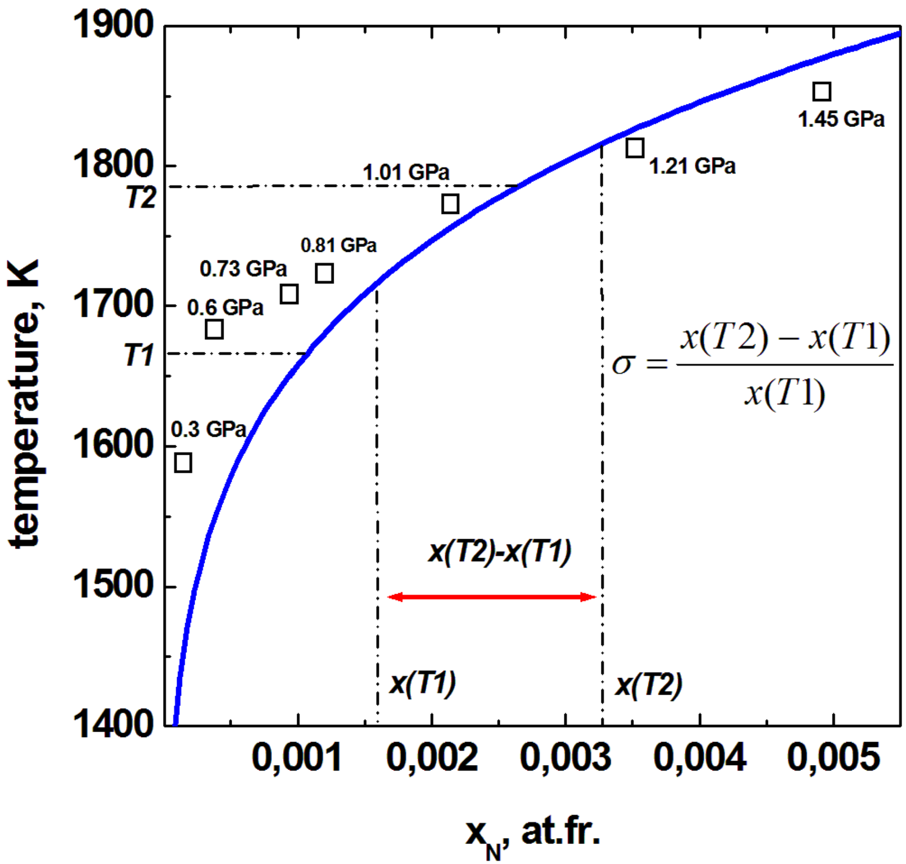
The equilibrium p_{N2} –T conditions for GaN were determined by direct synthesis and decomposition experiments performed by both: gas-pressure technique and high-pressure anvil technique.



J. Karpinski, et al., J. Cryst. Growth, 66, 1 (1984)

Thermodynamic and Kinetic Aspects

The experimental nitrogen solubility data result from annealing of Ga in N_2 atmosphere at three phase Ga-N_2-GaN equilibrium conditions.



The solid line is the liquidus line for Ga-GaN system calculated in ideal solution approximation.

For an ideal solution:

$$x = x_0 \exp\left[-\frac{\Delta H_{sol}}{RT}\right]$$

For GaN **ΔH_{sol}=44.7 kcal/mol**

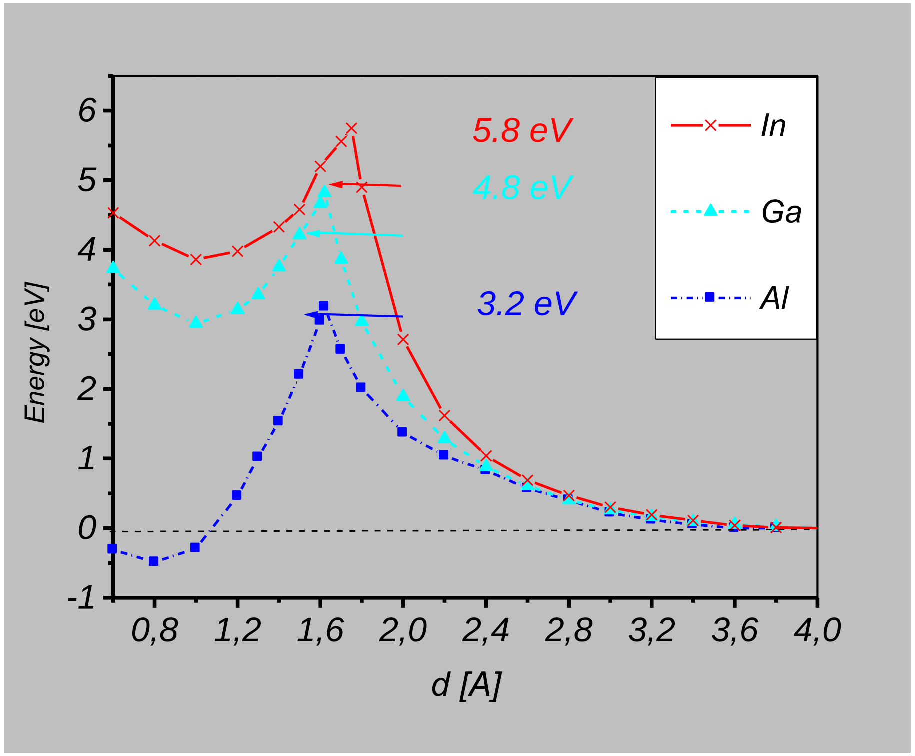
$$\sigma = \frac{\Delta x}{x_e} = \frac{\Delta H_{sol} \Delta T}{RT^2} \leq 30\%$$

X_N < 1 at%

I. *Grzegory et al. in Bulk Crystal Growth of Electronic, Optical and Optoelectronic Materials, Wiley&Sons, (2005), 173*

Thermodynamic and Kinetic Aspects

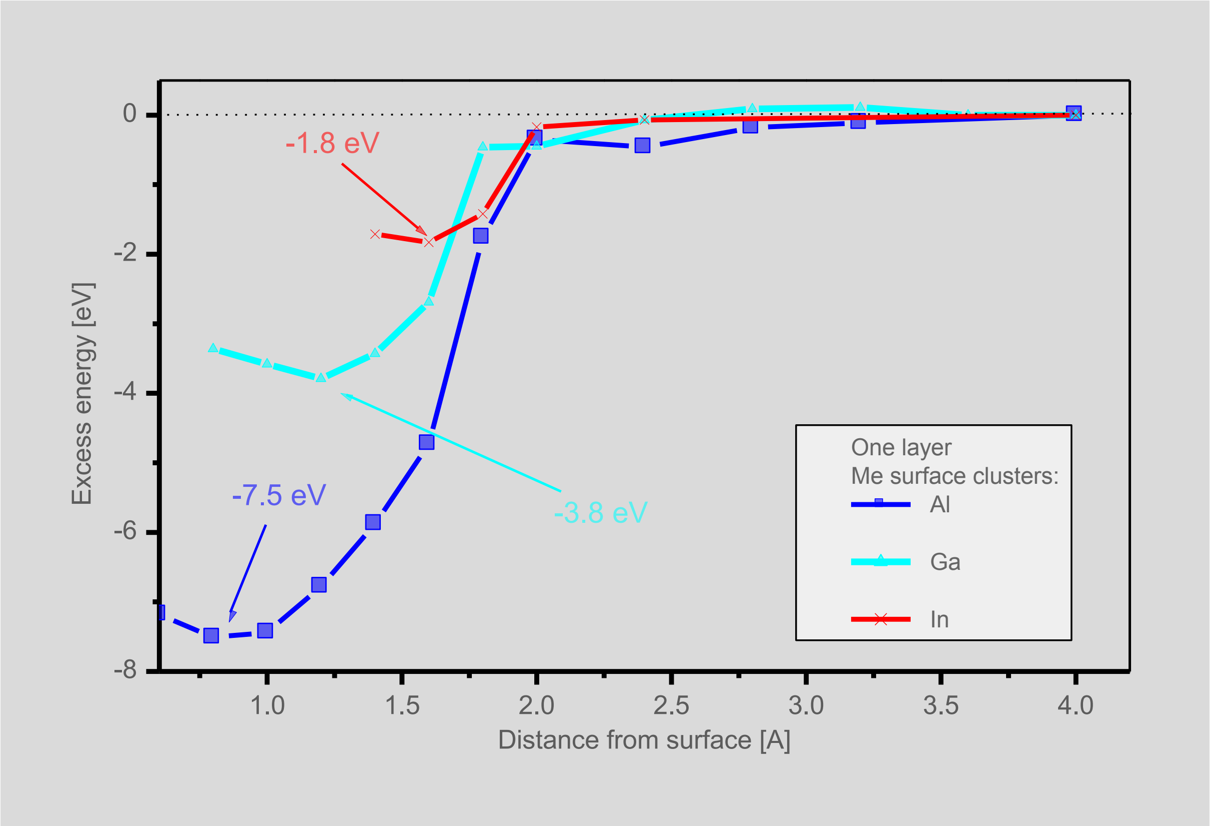
The nitrogen pressure is important for the kinetics of the GaN synthesis. The synthesis of GaN from its constituents is possible due to dissociative chemisorption of N_2 molecules on gallium's surface. The nitrogen molecule dissociates on the surface only if the potential barrier, lower than the bonding energy in the nitrogen molecule, can be overcome. However, the value of the potential barrier seems to be quite high. Therefore, the density of the interacting gas (thus its pressure) is of crucial importance.



S. Krukowski et al., J. Cryst. Growth 189/190 (1999) 159.

Thermodynamic and Kinetic Aspects

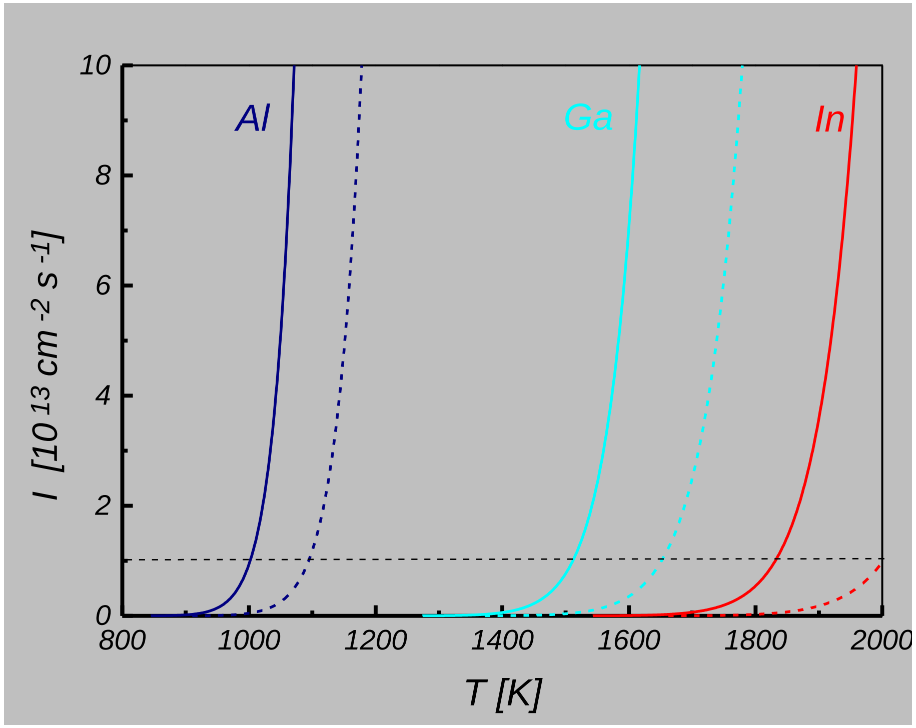
It should be mentioned that for oxygen interacting with gallium, there is no potential barrier. One can always expect the oxygen atoms in liquid gallium. This fact is very important for the properties of GaN crystals grown by the HNPS method.



S. Krukowski et al., J. Cryst. Growth 189/190 (1999) 159.

Thermodynamic and Kinetic Aspects

The high potential barrier for nitrogen dissociation on the liquid gallium's surface also suggests that this dissociation process is kinetically controlled even for relatively high temperatures. Determining the rate of dissociation at 2 GPa, it was shown that the rate of dissociation is not very fast. For an effective synthesis, the temperature ought to be higher than 1500 K. It may be concluded that only the application of the high nitrogen pressure allows the synthesis of gallium nitride from its constituents.



$$I = p/[2\pi mkT]^{1/2}[1+\Delta E/kT]\exp(-\Delta E/kT)$$

10 mg per cm^2 during 100h

S. Krukowski et al., J. Cryst. Growth 189/190 (1999) 159.