Solid-state metathesis reactions under pressure: A rapid route to crystalline gallium nitride

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High pressure chemistry has traditionally involved applying pressure and increasing temperature until conditions become thermodynamically favorable for phase transitions or reactions to occur. Here, high pressure alone is used as a starting point for carrying out rapid, self-propagating metathesis reactions. By initiating chemical reactions under pressure, crystalline phases, such as gallium nitride, can be synthesized which are inaccessible when initiated from ambient conditions. The single-phase gallium nitride made by metathesis reactions under pressure displays significant photoluminescence intensity in the blue/ultraviolet region. The absence of size or surface-state effects in the photoluminescence spectra show that the crystallites are of micron dimensions. The narrow lines of the x-ray diffraction patterns and scanning electron microscopy confirm this conclusion. Brightly luminescent thin films can be readily grown using pulsed laser deposition. © 1998 American Institute of Physics. [S0003-6951(98)03705-X]

Gallium nitride (GaN) is important to the optoelectronics industry since thin films can be used to fabricate p-n junctions, quantum wells, lasers, and displays in the blue/ultraviolet region.[1–4] Light emitting diodes made with GaN are significantly brighter than conventional light bulbs and are up to 60 times brighter than the best known gallium phosphide materials.[1,3] Polycrystalline GaN may find use as a blue phosphor in display applications. GaN has generally been formed by heating Ga, Ga_2O_2, or gallium halides at elevated temperatures (>750 K) in an ammonia atmosphere for extended periods.[5–8] The materials produced are often poorly crystalline, contain impurities, and/or show weak photoluminescence. Other recent synthetic methods use polymeric and single-source precursors, microwave heating, and plasma assisted nitridation.[9–13] Single crystals of GaN are generally grown under high temperature (1700–1800 K)/high pressure conditions (>2 GPa for ~20 h) since GaN decomposes at ~1150 K under ambient pressure.[14–16] Recent experiments indicate sodium fluxes can be useful for crystal growth.[17]

Solid-state metathesis (SSM) reactions have developed over the past several years into an effective rapid method for producing materials such as nitrides that are difficult to make using conventional techniques.[18–20] Formation of very stable salt by-products drives these highly exothermic reactions. In contrast, elemental self-propagating high temperature synthesis (SHS) reactions are driven solely by product formation which for GaN synthesis ($Ga + 1/2N_2$, $\Delta H_{rxn} = -110$ kJ/mol) represents only 21% of the energy available in a comparable SSM reaction (e.g., $GaI_3 + Li_3N$, $\Delta H_{rxn} = -515$ kJ/mol). The intense heat of SSM reactions initiated from 298 K often generates temperatures of >1500 K (typically in <1 s) and has even yielded some high pressure/high temperature nitride phases such as cubic TaN.[21] Cubic TaN is normally made at more than 1900 K and 16 MPa of nitrogen pressure.[22] When carrying out a

SSM reaction between $TaCl_5$ and Li_3N [Eq. (1)] under ambient conditions, the product observed is the subnitride, Ta_2N, rather than nitrogen rich TaN

$$TaCl_5 + 5/3Li_3N \rightarrow TaN + 5LiCl + 1/3N_2. \tag{1}$$

Adding 12 moles of NaN_3 to this reaction increases the nitrogen overpressure enough to form some high temperature/high pressure cubic TaN along with the expected hexagonal Ta_2N.[20] Recent experiments carried out under 4.5 GPa of pressure without NaN_3 demonstrate that cubic TaN can be produced directly as the major product. The maximum adiabatic reaction temperature (T_{ad}) achieved if all the enthalpy of this reaction is used to heat the products at constant pressure is 1681 K which is less than the 1900 K normally required to form cubic TaN. Therefore, applying pressure to SSM reactions can lead directly to high pressure/high temperature phases.

The synthesis of cubic TaN suggests that other nitrides could also be made using SSM reactions under appropriate pressures from metal halides and Li_3N. Unfortunately, reactions between gallium halides and Li_3N fail under ambient conditions even though they are very favorable thermodynamically (>500 kJ/mol).[23] Therefore, these reactions appear to be good candidates for synthesis under pressure.

To carry out SSM reactions under pressure a Bridgman-anvil cell, whose essential features are shown in Fig. 1, is used. A fine (0.15 mm) iron wire is threaded through a mixture of reactants and pre-compacted into a pellet (typically 4.8 mm diameter, 1.5 mm high, ~80 mg). An Inconel gasket is coated with an insulating alumina/magnesia paste, affixed to the bottom anvil and cured. The pellet is placed in the gasket and the top Bridgman anvil is placed above the sample aided by alignment guides (not shown). Copper leads are placed in contact with the electrically conducting tungsten carbide cores and held in place with thin sheets (2 mm) of polyvinyl chloride. This entire assembly, along with a calibrated load cell to monitor pressure by measuring the applied force, is placed in a hydraulic press which can generate pressures up to 10 GPa. After increasing the pressure, the reaction is initiated by passing a current through the an-
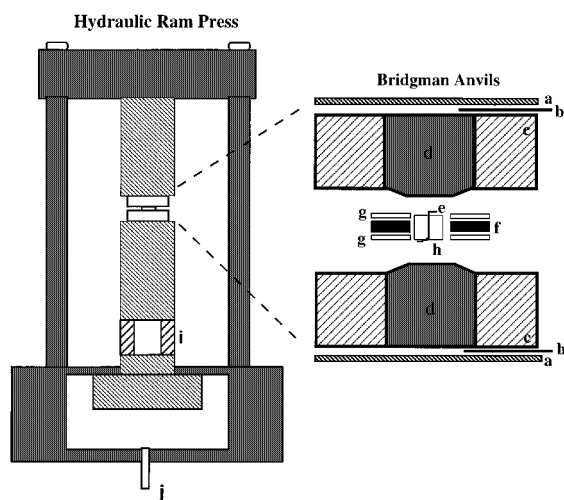
FIG. 1. A schematic diagram of the hydraulic press and the Bridgman anvils used for high pressure SSM reactions. The components include: (a) PVC sheets used for electrical insulation, (b) copper leads to pass current, (c) Bridgman anvils, (d) tungsten carbide cores, (e) iron wire for ignition of precursors, (f) Inconel gasket for lateral containment of reactants, (g) alumina/magnesia for electrical insulation, (h) solid reactants pre-pressed into a pellet, (i) strain gauge, and (j) inlet for hydraulic fluid.

FIG. 2. Powder x-ray diffraction patterns of the washed product formed from the reaction of GaI_3 and Li_3N under ambient conditions (top), with 1 GPa (middle), and with 4.5 GPa of applied pressure (bottom). The Miller indices for hexagonal GaN are indicated above the crystalline diffraction peaks.

vils, via the copper leads, which resistively heats the iron wire. The reaction time from ignition through propagation to completion is less than 1 s. After releasing the pressure, the products are collected and salt by-products washed away with alcohol and/or water. The volume of reactants can readily be increased in order to form bulk quantities of the desired material. For example, a modified belt apparatus with an internal cell volume of 0.48 cm^3 ($\sim$1.4 g of reactants) has been used to obtain $\sim$300 mg of GaN per reaction. Greater quantities can be synthesized by increasing the volume of the cell. Note that cubic boron nitride and diamond are produced commercially on a megaton scale each year using large volume presses.[24]

The reaction between GaI_3 and Li_3N produces GaN as given in Eq. (2)

$$GaI_3 + Li_3N \rightarrow GaN + 3LiI. \qquad (2)$$

This reaction is driven by salt formation ($\Delta H_{RXN} = -515$ kJ/mol) which accounts for 79% of the heat released. Assuming complete reaction and adiabatic conditions, a maximum reaction temperature, T_{ad}, of 1443 K is calculated. Since this temperature is above the melting point of lithium iodide (722 K), the reaction is expected to readily propagate.[18] Differential scanning calorimetry indicates that the reaction of GaI_3 and Li_3N initiates at 503.7 K, where a large irreversible exotherm is found. Other gallium halides could be used to produce GaN including $GaBr_3$ ($\Delta H_{RXN} = -611$ kJ/mol, $T_{ad} = 1593$ K), $GaCl_3$ ($\Delta H_{RXN} = -645$ kJ/mol, $T_{ad} = 1656$ K) or GaF_3 ($\Delta H_{RXN} = -627$ kJ/mol, $T_{ad} = 1954$ K). *Warning: Unfortunately, these gallium halides* ($GaBr_3$, $GaCl_3$ *and* GaF_3) *spontaneously detonate on mixing with lithium nitride which makes them unsuitable for pressing into pellets needed for carrying out reactions under pressure.*

Under ambient conditions, the reaction of GaI_3 and Li_3N produces a small amount of poorly crystalline GaN (Fig. 2, top) along with gallium metal (visible as gallium spheres),
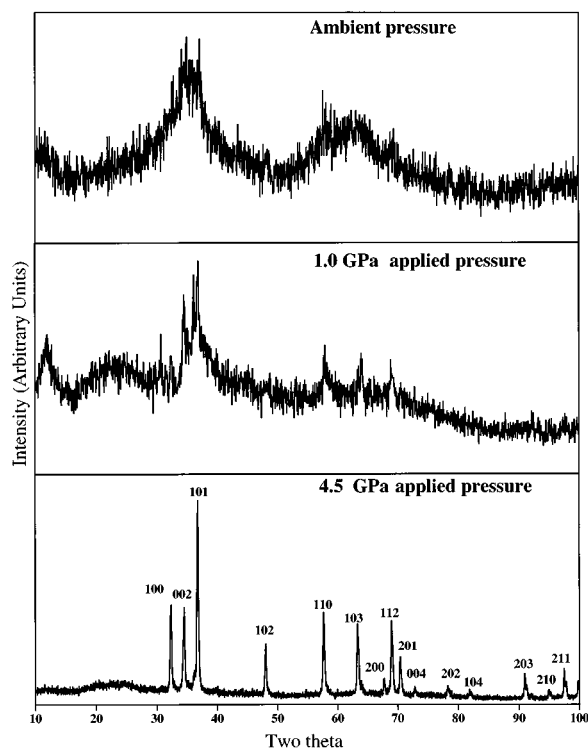
nitrogen gas, and lithium iodide. At higher pressures, both the crystallinity and yield of GaN increases. At 1 GPa partially crystalline GaN forms (Fig. 2, middle). The reaction appears complete with little evidence of Ga metal formation. Increasing the pressure to 4.5 GPa leads to highly crystalline GaN (Fig. 2, bottom). A least squares refinement of the x-ray data indicates that $a = 3.188(4)$ Å and $c = 5.18(1)$ Å, which is comparable to literature values for hexagonal GaN of $a = 3.1879 - 3.1894$ Å and $c = 5.1856 - 5.1865$ Å.[25] The LiI is removed by washing with water and yields of GaN of up to 87% are obtained. Losses are simply due to handling the material. The GaN produced by the 4.5 GPa metathesis reaction is single phase, according to the x-ray powder diffraction pattern and contains no detectable iodine by energy dispersive spectroscopy. The Ga content of the GaN is 51 mol % (50% expected) as calculated by thermal gravimetric analysis carried out in air to 1273 K, which converts all of the GaN to Ga_2O_3. X-ray photoelectron spectroscopy indicates the presence of some surface oxidation which can be reduced by washing with nonaqueous solvents or by a brief plasma nitridation.[13]

The high quality of the GaN produced by metathesis under 4.5 GPa confining pressure is apparent in the photoluminescence spectra shown in Fig. 3. The excitation source is 5 ns, 20 μJ pulse of 266 nm radiation. The room temperature (300 K) spectrum (Fig. 3, bottom) reveals only the 3.38(3) eV band gap characteristic of bulk GaN.[26] The low temperature (20 K) spectrum (Fig. 3, middle) is also consistent with high quality bulk GaN with a sharp excitonic transition at 3.45(3) eV and lower energy features originating from
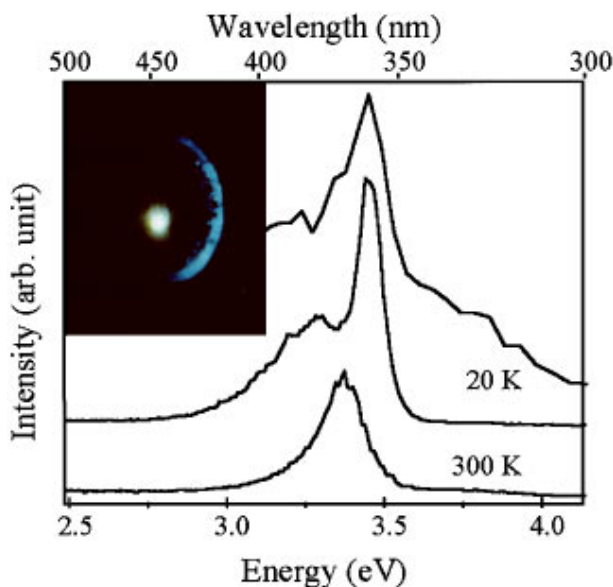
FIG. 3. Gated photoluminescence spectra of GaN produced by metathesis reactions carried out under 4.5 GPa of pressure. The room temperature (300 K) spectrum (bottom) exhibits the band gap of bulk GaN at 3.38(3) eV, while the lower temperature (20 K) spectrum (middle) has a sharp excitonic transition at 3.45(3) eV and emission due to donor-acceptor pair recombination at lower energies. The 20 K spectrum (top) is from a GaN film grown on a MgO substrate by pulsed laser deposition. The bright blue photoluminescence from the GaN film can be seen in the photograph.

known donor-acceptor pair recombination.[27] The photoluminescence measurements do not show either size effects or surface states, consistent with micron-scale, rather than nano-scale, crystallites. This is confirmed by scanning electron microscopy and a negligible amount of line broadening measured in the x-ray diffraction pattern (Fig. 2, bottom) when compared to an external silicon standard.

To demonstrate the potential for device fabrication, pulsed laser deposition of the powder was used to grow thin polycrystalline GaN films on MgO substrates.[28] A pressed pellet of GaN powder was used as a rotating target in a vacuum chamber with a pressure $\leq 5 \times 10^{-8}$ Torr during growth. The target was pre-ablated to remove any surface contaminants. A 150 mJ pulsed excimer laser (248 nm) with a fluence of ~ 2 J/cm^2 at a pulse repetition rate of 1 Hz for 4 h enables films of 800 Å thickness to be grown on a MgO substrate heated to 580 °C. The bright blue photoluminescence (Fig. 3, upper left) is a secondary reflection from the GaN. The white spot is the primary, bright reflection and has bleached the photographic film. Although the high energy pulsed laser caused irreversible damage to the thin film after 1000 laser shots, the photoluminescence spectrum (Fig. 3, top) reveals the signature of GaN with a good signal to noise ratio. Work on creating thin film devices with doped GaN is now in progress.

An equilibrium phase diagram for GaN suggests that at the calculated adiabatic temperature of 1443 K, below a pressure of 4 MPa, the formation of Ga plus nitrogen gas should be favorable relative to GaN.[14] However, above 4 MPa GaN is stable, in agreement with the observed SSM results under pressure. Inert additives such as salt have been used to lower the temperatures of other SSM reactions, leading to less crystalline products.[20] For the GaI$_3$/Li$_3$N reaction, salt additives are of interest not only to lower reaction temperatures and

product crystallinity, but potentially at lower temperature, reactions could be developed to produce GaN at lower pressures. In theory, addition of 6.2 or more moles of LiCl should lower the reaction temperature enough (≤ 940 K) to favor the formation of GaN under ambient pressure. However, this may simply lead to nanocrystalline GaN, as observed in metathesis reactions between GaCl$_3$ and Li$_3$N carried out in an autoclave with benzene at 553 K.[29]

The cell designed for igniting reactions under pressure can now be used for carrying out other SSM reactions. Since high quality mixed-metal solid solutions have been made by SSM reactions under ambient conditions,[30] experiments to produce GaN solid solutions, such as (Ga,Al,In)N from appropriate mixed-metal halide precursors are in progress. Recent work on another SSM reaction suggests that other high temperature/high pressure phases such as cubic boron nitride can be synthesized under appropriate conditions.[31]

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