Acidic Ammonothermal Growth of Gallium Nitride in a Liner-Free Molybdenum Alloy Autoclave

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ABSTRACT

This paper discusses promising materials for use as internal, non-load bearing components as well as molybdenum-based alloys for autoclave structural components for an ammonothermal autoclave. An autoclave was constructed from the commercial titanium-zirconium-molybdenum (TZM) alloy and was found to be chemically inert and mechanically stable under acidic ammonothermal conditions. Preliminary seeded growth of GaN was demonstrated with negligible incorporation of transition metals (including molybdenum) into the grown material ($<10^{17} \text{ cm}^{-3}$). Molybdenum and TZM were exposed to a basic ammonothermal environment, leading to slight degradation through formation of molybdenum nitride powders on their surface at elevated temperatures ($T > 560^\circ\text{C}$). The possibility of a 'universal', inexpensive, liner-free ammonothermal autoclave capable of exposure to basic and acidic chemistry is demonstrated.

KEYWORDS

B1. Nitrides

A2. Ammonothermal

B1. Molybdenum Alloys

B1. GaN

A1. Corrosion

B1. Supercritical Ammonia

1. Introduction

In recent years, gallium nitride (GaN) has found significant use as an optoelectronic material for LEDs, lasers, as well as power electronics.[1–4] However, current GaN substrates are generally expensive. Growth of GaN from melt requires extreme conditions ($P > 12$ GPa, $T > 2000^{\circ}\text{C}$) and is thus not easily scalable, requiring alternative approaches.[5] One viable approach is the ammonothermal method, where GaN is dissolved in supercritical ammonia at lower temperatures and pressures. The ammonothermal method requires the use of mineralizers to dissolve appreciable amounts of GaN. Mineralizers can be basic (such as Na or K) which increase the concentration of NH_2^- ions or acidic (such as NH_4Cl or NH_4I) which increase the concentration of NH_4^+ ions. Acidic and basic ammonothermal environments cause different corrosion with autoclave components[6,7], so the mineralizer type must be considered when developing the autoclave.

Ammonothermal growth has demonstrated high quality single crystal GaN in basic and acidic chemistries.[8–12] Significant effort has already led to increased purity and growth rate.[11,13,14] Recently, ammonothermal acidic growth demonstrated high growth rates of up to $40\text{ }\mu\text{m/hr}$, making acidic growth attractive for industrial application.[15] However, even fundamental characteristics of the growth environment such as GaN solubility are still under investigation, indicating the necessity of further research.[16]

Acidic ammonothermal growth is particularly corrosive to most engineering metals and often requires expensive precious metal liners.[12,14] Recent work has indicated that molybdenum and its alloys may make suitable pressure bearing autoclave wall materials as they show little or no indication of corrosion in the ammonothermal environment with either fluoride or chloride chemistry.[7,17] An inert autoclave body would eliminate the need to integrate cumbersome and expensive liners, possibly reducing the cost for ammonothermal growth. Molybdenum and its alloys may be powder sintered to larger dimensions than ingot based nickel chromium super-alloy autoclaves which may open pathways to new industrial implementations for this growth method. The refractory nature of the metal also enables exploration of higher temperature regimes as compared to the nickel chromium superalloys. The suggested stability of molybdenum in basic environments also potentially enables corrosion resistant autoclaves for novel chemistries involving both basic and acidic mineralizers.[7]

In this paper, we present on the development of an externally heated, liner-free autoclave fabricated using load bearing, commercial titanium-zirconium-molybdenum (TZM) alloy and discuss

various challenges associated with integrating other chemically and mechanically stable materials. Successful operation under acidic ammonothermal conditions (addition of ammonium chloride powder) will be presented along with seeded growth of single crystal GaN. Applicability of TZM as a 'universal', liner-free autoclave material suitable for both acidic and basic chemistries will be discussed based on basic ammonothermal growth experiments performed in a molybdenum capsule.

2. Autoclave Material and Design

2.1 Material Property Considerations for Robust Autoclave Design

TZM is a molybdenum alloy (ASTM B-387, 0.5 wt% Ti, 0.08 wt% Zr, 0.01-0.04 wt% C, Bal. Mo) with high creep resistance ($<10^{-6} \text{ h}^{-1}$ at 1100°C and ~350 MPa) and a high recrystallization temperature of 1400°C.[18] However, it has a relatively high ductile-to-brittle transition temperature of 100-150°C, with the transition temperature depending on the sample orientation in testing. TZM can elongate in tension yet cracks under bending stresses.[19,20]

While TZM has many potential uses as a high temperature structural material, much of the prior work related to TZM autoclaves has been performed in geological research. Williams suggested a TZM autoclave for geological research with an operating range of up to 100 MPa at 1200°C using copper gaskets and an argon jacket in 1966.[21] Since then, experimental vessels have been used to study mineralogical thermodynamics and crystallization as well as gas evolution at temperatures and pressures of up to 1030°C at 100 MPa, 1050°C at 120 MPa, 1000°C at 180 MPa, and 1025°C at 150 MPa with runs lasting up to 72 hours.[22–25] Work by Shi et al. on thermomechanical fatigue behavior indicates a fatigue limit of around 200 MPa at 500°C (comparable to the stress on the inner wall of a typical autoclave with an outer to inner diameter ratio of 2.25 and an internal gas pressure of 130 MPa).[26] However, data for fatigue at higher temperatures does not appear to be available.

At elevated temperatures molybdenum reacts with oxygen to form relatively volatile molybdenum trioxide (MoO_3). Smolik, Petti, and Schuetz calculated a linear thickness loss of 6.24 $\mu\text{m/h}$ at 599°C in air from mass loss measurements performed on 22 mm diameter disks of TZM that were 1.75 or 3.5 mm thick.[27] With ammonothermal growth times of 100-1000 hours, this would represent a substantial material loss leading to potential autoclave failure. Additionally, Liu and Inouye performed oxidation experiments indicating that oxygen embrittlement can occur due to internal oxidation of titanium and zirconium in TZM.[28] Thus, protection of the material through use of coatings, such as titanium nitride

(TiN), or by operating the autoclave in a strictly oxygen free environment is required for autoclave longevity and safety.

2.2 Autoclave Design Considerations for a Resealable Autoclave

Gasket Material Considerations: Williams' design for a high pressure autoclave provides some guidance but the copper gasket Williams used would corrode in ammonothermal environments.[7,17] Nickel is often used as a gasket material and can be found in high temperature antiseize lubricants. However, it cannot be used in contact with TZM and molybdenum at high temperatures because it can form brittle intermetallics.[29] Gold, palladium, platinum, vanadium, niobium, molybdenum, and titanium have been identified as suitable materials in acidic ammonothermal conditions by a previous study from our group.[7] An ideal gasket would be chemically inert and have a yield stress sufficiently high to contain the internal pressure but sufficiently low relative to the autoclave body to preferentially deform. Gold, palladium, and platinum satisfy these requirements but are cost prohibitive. Niobium has a very low yield stress and titanium may form hydrides and subsequently expand.[30,31] Niobium, titanium, and vanadium all have a significant thermal expansion mismatch to TZM.[18,32,33] Molybdenum has a fairly high yield strength and will require a higher load to attain a high quality seal. Thus, the choice of gasket material depends on the specific seal design yet niobium, vanadium, and molybdenum appear to be the most promising candidates. Niobium and molybdenum have both been successfully tested at >100 MPa and 600°C in the autoclave design indicated below (see Figure 1).

Ductile-Brittle Design Considerations: To achieve the desired growth conditions, ammonia is condensed into an autoclave cooled using liquid nitrogen. Once filled, the vapor pressure of ammonia increases as it warms back to room temperature, pressurizing the autoclave. Generally, the pressure is <10 MPa before reaching 150°C, the beginning of the ductile regime, but the TZM is still in the brittle regime and so special consideration and attention must be given to adhere to safe engineering design to avoid stress concentrations in any autoclave component. However, pressurization of the system at low temperatures could be avoided by use of a compressor which would allow autoclave filling at higher temperatures.

Thermal Considerations: In general, the ammonothermal technique drives growth by establishing a temperature gradient and thus thermal management must be considered. Traditional autoclave designs use nickel superalloys [8–10,12–14,17] which generally have thermal conductivities of ~20 W/m*K while TZM has a thermal conductivity of nearly 120 W/m*K at RT.[18,34] Therefore, when engineering the

heating profile for externally heated vessels, the spacing between heaters must be considered to prevent thermal leakage between zones through the autoclave wall. Thermal losses through lower temperature components (such as the head assembly here) must also be considered. Higher thermal conductivity may also be advantageous, as it should reduce the difference in temperature between the autoclave fluid and the outer autoclave wall.

While it is tempting to use ductile materials, such as stainless steel, for components that are not in contact with the internal chemistry, consideration must be given to the differing thermal expansion coefficients (TZM: 5.2 ppm/°C, 316 stainless steel: 14.7 ppm/°C at RT)[18,35] as thermal expansion mismatches may lead to plastic deformation at high temperature causing degradation of a seal. The result is uncontrolled leakage of the contained gases upon cooldown.

2.3 Designed Autoclave

Given all of these design considerations, a tube-based autoclave was designed and built (see Figure 1 for schematic). A bead is used to load the gasket against a flat polished surface to provide a high pressure seal. In this design, all parts are fabricated from TZM except the closure nuts, valve, pressure transducer, and the two tubes that lead to the valve and pressure transducer. Corrosion of the stainless steel and contamination of the growth environment is reduced by cooling the steel to around 200°C during growth via forced convection and spatial separation from the heated zones.

Using this autoclave design, a TZM autoclave body was manufactured with a 1 inch outer diameter, 7/16 inch inner diameter, and an inner bore length of 15.5 inches (Plansee Corporation). For oxygen resistance, the external surface of the body was coated with TiN. The body was capped and connected to the gas management system (valve, pressure transducer) using custom designed TZM parts (Eagle Alloys Corp.) The pressure transducer was rated to 30,000 psig with a 17-4 PH stainless steel internal surface (Omegadyne, PX02S1-30KG10T). The valve body was 316 stainless steel with a 17-4 PH stainless steel stem (High Pressure Corporation, 30-12HF4). The head assembly and base assembly both consisted of an adapter that interfaces with a closure nut and a cross (head assembly) or a tee (base assembly) with all parts being made of TZM. The flat sealing surfaces of the head and base assembly were polished using 600 grit silicon carbide sandpaper and the bead of the autoclave body was polished using 2000 grit silicon carbide sandpaper.

Two independent resistive heater sets were used to define temperature zones (see Figure 1 for details). Within the autoclave, baffles were used to separate these zones and a basket was used to

contain polycrystalline GaN (poly-GaN) as feedstock. Stands were used to hang crystals in the desired temperature zone.

3. Experimental Methods

A hole was drilled in the center of the m-plane GaN seed grown using hydride vapor phase epitaxy (HVPE) (Mitsubishi Chemical Corporation) with a diamond drill bit to allow the seed to hang in the growth zone. The seed was cleaned in acetone and isopropyl alcohol for 3 minutes each in an ultrasonic bath. The seed was weighed, its thickness measured (± 0.001 mm, Mitutoyo, No. 293-765-30), and optical images were recorded (Canon Powershot SD780 IS) before it was suspended from the crystal stand using 0.01 inch diameter molybdenum wire (99.95%, Alfa Aesar). Poly-GaN (Mitsubishi Chemical Corporation) was loaded into the basket and weighed (± 0.01 mg, Mettler Toledo, AB135-S/FACT) and then the basket was attached to the crystal stand. The stand, poly-GaN, and seed assembly were passed into a nitrogen filled glovebox (MBraun Labmaster 130).

To prepare the autoclave, the TZM autoclave body was weighed (± 0.01 g, Sartorius MSA14202S) and then the base assembly was attached to the autoclave body with the closure nut using a high temperature antiseize to lubricate all threads. Loading of the autoclave occurred in a nitrogen filled glovebox where the ammonium chloride (99.999% by metals basis, Alfa Aesar) was weighed and the molybdenum stands (material from Alfa Aesar, 99.95%), GaN seed, poly-GaN, and ammonium chloride were loaded. The head assembly was attached using the closure nut and pre-sealed at a low torque to prevent oxygen contamination.

After removal from the glovebox, a final torque was applied to the head assembly closure nut to seal the system at high pressure and the autoclave was enclosed between two $\frac{1}{4}$ inch thick aluminum plates to protect the autoclave body from accidental damage. The autoclave was then weighed and connected to a gas manifold. The autoclave was pumped down to vacuum and cooled with liquid nitrogen. Ammonia was condensed in the autoclave until the specified volume of ammonia was reached (details of the setup used to fill the autoclave are provided in [13]). The autoclave was then allowed to warm up to room temperature and weighed. The protective aluminum plates were removed and the autoclave was loaded into a secondary enclosure which was evacuated and back filled with nitrogen gas. The secondary enclosure served both to provide an oxygen-free atmosphere for the autoclave as well as a hermetic barrier between the lab and the autoclave in the event of a leak.

The autoclave was heated with resistive radiant heaters over a 5 hour period to the predefined operating temperatures. After growth, the heater power was abruptly terminated and the autoclave was cooled down by convection over a period of about 6 hours. It should be noted that the closure nuts were stainless steel in the hot zone and autoclave leaks were observed during cooling. The secondary enclosure was allowed to purge to remove residual ammonia and the autoclave was attached to an exhaust line via the valve to ensure no pressure remained. The autoclave was then removed from the containment vessel and opened in a fumehood. The stands and crystal were then removed from the autoclave. All autoclave components were cleaned with de-ionized water and isopropyl alcohol for 3 minutes each in an ultrasonic bath. The seed was cleaned with de-ionized water, acetone, and isopropyl alcohol for 3 minutes each in an ultrasonic bath. TZM and molybdenum parts were then stored in a vacuum oven at 80°C.

The growth of GaN under basic ammonothermal conditions in molybdenum-containing growth environments was also explored. A pure molybdenum capsule (99.95%, Thermo Shield) was manufactured with identical specifications to that of a pure silver capsule which was successfully used to demonstrate transition metal free growth of GaN crystals.[13] Short (5 days) and long (60 days) growth runs were performed using pure sodium (99.95%, Alfa Aesar) as a mineralizer at source temperatures ranging between 515°C and 550°C and growth temperatures between 560°C and 600°C. Further details on the executed experimental methods and GaN crystal growth results will be published in a separate publication.[36]

The seed grown in the acidic system was characterized using x-ray diffraction (XRD) using a Panalytical MRD Pro with an open detector with a 4-bounce (220) Ge monochromator and Cu K α radiation. A skew-symmetric ω -rocking curve was taken with a rotation in Psi to account for the surface miscut. Secondary ion mass spectrometry (SIMS) was performed with a Cameca IMS 7f-Auto Secondary Ion Mass Spectrometry system using a cesium gun for C, O, and Cl while an oxygen gun was used for Nb, Fe, Cr, and Ti. SIMS and XRD were performed on as-grown crystal without polishing or other surface preparation. Energy dispersive x-ray analysis (EDX) was performed using an FEI XL30 Sirion FEG scanning electron microscope.

4. Results and Discussion

4.1 Autoclave Behavior

The TZM autoclave has successfully operated under ammonothermal acidic conditions for over 2,500 hours with no significant corrosion at temperatures of up to 650°C. Any leaks that occurred during growth were attributed to gasket failures but leakage of the autoclave from the gasket upon cooling, due to thermal mismatch of components, is typical. Initially, small amounts of black residue were observed on the pure molybdenum stands (but not on the TZM) and after several runs the residue was no longer present. The black residue was a non-spalling surface coating but could be removed by mild abrasion.

Comparable black powder was consistently found on the surface of the pure molybdenum parts after exposure to basic ammonothermal conditions and temperatures of $T_{\text{wall}} > 560^{\circ}\text{C}$. Powder XRD of the collected, loosely adhering, black powder suggests the presence of two molybdenum nitride materials: hexagonal $\delta\text{-MoN}$ (Powder Diffraction File (PDF) card 98-006-0168) with smaller amounts of cubic Mo_3N_2 (PDF card 01-089-3712). Continuous formation of powder was only observed under basic conditions ($\sim 10\text{--}20$ mg/day loss of Mo from Mo parts). TZM parts experienced reduced areal density formation of molybdenum nitrides ($\sim 4\times$ less when normalized to comparable areas vs. pure Mo parts) suggesting they are better suited to exposure under basic conditions. EDX of the surfaces of pure Mo and TZM parts exposed to Ga containing basic ammonothermal conditions for more than 80 days did not reveal the presence of any Ga, nor did the powder XRD reveal the presence of any Ga containing Mo compounds. EDX of pure Mo and TZM parts exposed to >30 days of acidic ammonothermal conditions with Ga also revealed no Ga, suggesting Ga-Mo compounds do not readily form under ammonothermal conditions.

Pressure profiles for three runs in the TZM autoclave with NH_4Cl mineralizer targeting 100 MPa are shown in Figure 2. A continuous rise is observed and is likely due to decomposition of ammonia, as seen in basic ammonothermal systems.[37,38] Ehrentraut et al. did not report any data with respect to ammonia decomposition but did mention having little concern over it in the acidic system[39], which is consistent with our observations. Runs 1 and 2 have the same temperature profile (500°C cold zone, 600°C hot zone) while Run 3 has a small portion of the reactor that is hotter (650°C).

Under basic ammonothermal conditions in Ni-Cr superalloy autoclaves, significant pressure drops are observed, presumably due to diffusional hydrogen loss.[13,38] The permeability of hydrogen through TZM ($\sim 2\times 10^{-12}$ [40][41] $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1/2}$) is lower than through Ni-Cr superalloys ($\sim 7\times 10^{-11}$ $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1/2}$)[42]. Assuming initially pure NH_3 and no H_2 loss as decomposition occurs, the runs performed in the TZM autoclave should achieve a total system pressure of ~ 135 MPa under operating

conditions[37] (using an average temperature based on the initial pressure before significant decomposition occurred). The observed peak pressures are considerably below this value, suggesting negligible decomposition, and the lack of pressure decay suggests minimal hydrogen formation. Assuming zeroth order kinetics for ammonia decomposition on molybdenum[43], ~26 days are needed to reach equilibrium which suggests growth occurs under non-equilibrium conditions for the solvent in our case.

4.2 Growth Results

In the acidic system, the autoclave body mass was measured before and after each run with no measurable mass change within error of the balance (0.01 g) when no GaN was present in the run. GaN deposition on the autoclave walls of up to 0.05 g was observed and verified to be GaN using EDX for runs containing GaN source materials. The poly-GaN deposition was yellow or green in color with significant hexagonal faceting and crystallite sizes in the range of 10-100 μm . An SEM image of crystallites removed from the autoclave wall is shown in Figure 3. The deposition of the crystallites implies that both dissolution and recrystallization of GaN is possible in this system.

Growth has also been demonstrated on a GaN seed with a total thickness increase of 10 μm (2.5 $\mu\text{m}/\text{day}$). The actual growth thickness may be larger, as etching of the crystal may have occurred at the start of the run. The low growth rate may be due to a lack of optimization of important growth parameters including seed position, temperature gradient between zones, as well as baffle geometry. As this was one of our first growths, these parameters will be varied and optimized in future work. Images of the seed before and after growth are shown in Figure 4. SIMS indicates bulk concentrations of $1 \times 10^{19} \text{ cm}^{-3}$ for O, $4 \times 10^{17} \text{ cm}^{-3}$ for C, $1 \times 10^{16} \text{ cm}^{-3}$ for Fe, $<10^{15} \text{ cm}^{-3}$ for Cr, and $1 \times 10^{15} \text{ cm}^{-3}$ for Ti. No molybdenum was detected in the sample (detection limit: 10^{17} cm^{-3}). Although no Zr calibration was available for SIMS, the Zr was close to the detection limit. Assuming Zr sensitivity is similar to Ti sensitivity in GaN indicates $<10^{16} \text{ cm}^{-3}$ for Zr. Similarly, no SIMS calibration was available for Nb or Cl, yet assuming similar detection sensitivity for these elements in GaAs a concentration of near 10^{16} cm^{-3} can be estimated for both Nb and Cl. The growth had similar coloration to that observed in high temperature growth in a platinum lined nickel-based superalloy vessel by Yoshida et al.[12] The origin of this coloration is not yet understood. An XRD ω -rocking curve of the sample indicates relatively high crystal quality with a FWHM of 216 arcseconds for the (10 $\bar{1}$ 0) peak. More recent (0002) oriented growths essentially replicated the seed crystal quality. The ω -rocking curve FWHM of the (0002) peak of the (0002) oriented seeds showed only minor differences before and after growth. In one case the

seed and growth had FWHM of 99 and 107 arcseconds, respectively, while the second seed and growth had FWHM of 142 and 140 arcseconds, respectively.

5. Conclusion

A TZM autoclave was designed and fabricated for use in ammonothermal growth. With over 2,500 hours of operating time at pressures of up to 150 MPa and temperatures up to 650°C in the presence of chloride chemistry, no significant degradation was observed. Growth of polycrystalline wurtzite GaN crystallites on the TZM walls has been observed and high quality growth of GaN on a GaN seed has been demonstrated with [O] concentration of $\sim 10^{19} \text{ cm}^{-3}$ and negligible transition metal impurities ($< 10^{17} \text{ cm}^{-3}$). It has also been demonstrated that TZM is compatible with sodium chemistry leading to the possibility of using TZM as a universal autoclave wall material for use with acidic or basic mineralizers or both simultaneously.

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Figure Captions

Figure 1: single column

Figure 2: two column

Figure 3: single column

Figure 4: single column

Figure 1. a) Schematic of TZM autoclave. Dashed lines represent regions where thermal insulation is in place outside the autoclave. The autoclave is only operated at high temperature in a secondary containment vessel with a N_2 gas purge flowing to prevent oxidation of the TZM components. Black lines indicate 316 stainless steel parts. Orange, blue, and maroon indicate the autoclave body, head assembly, and base assembly, all of which are TZM parts. The head and base assemblies consist of the adapter that interfaces with the closure nut as well as the cross (head assembly) or the tee (base assembly). The thick green indicates gaskets which can be niobium or molybdenum. b) Zoomed-in image of the head assembly. The inset shows the bead that is used to form the seal on the TZM autoclave body.

Figure 2. Pressure vs time for three ammonothermal runs with NH_4Cl mineralizer. Run 1 and Run 2 have the same temperature profile (500°C cold zone, 600°C hot zone) while Run 3 has an extra heated zone (650°C) below the 600°C zone.

Figure 3. SEM image of GaN crystallites removed from the hot zone autoclave wall. The hexagonal faceting of the crystal indicates wurtzite GaN. The crystallites were removed by abrasion, likely causing the observed fracture.

Figure 4. Seed crystal grown on in a TZM autoclave using NH_4Cl mineralizer before (left) and after (right) growth. The seed was $(10\bar{1}0)$ with a 4.92° miscut towards (0001) . The dark line down the center is a face where the seed fractured through the hole used to hang the seed (2 pieces are shown here, placed together). Divisions are 1 mm.

Figure 1

Figure 2

Figure 3

Figure 4