

Bulk Single Crystal Gallium Nitride Growth

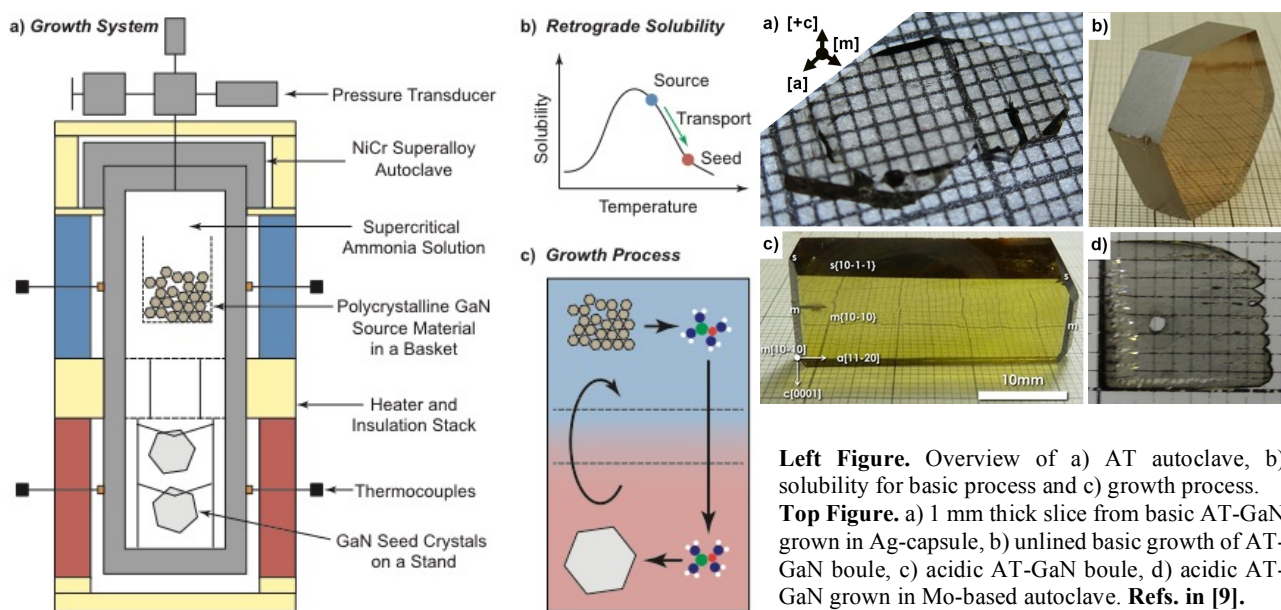
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Gallium nitride (GaN) is a wide bandgap semiconductor which has received widespread attention as it has enabled the development of short wavelength (UV, blue) optical emitters and promises highly efficient, high power electronics. Common to these fields is the need for a high quality, single crystal bulk GaN substrate to minimize efficiency losses caused by dislocations, permit growth of GaN epitaxial layers in arbitrary crystallographic orientations and enable vertical device structures to further increase the operating breakdown voltages for GaN power electronics.

Bulk GaN growth is challenging due to the inability to readily melt the material ($T_{\text{melt}} > 2200 \text{ K}$, $P_{\text{melt}} > 6 \text{ GPa}$).¹ The ammonothermal (AT) method² circumvents this challenge by dissolving GaN into a supercritical ammonia solution under elevated temperatures ($\sim 600 \text{ }^\circ\text{C}$) and pressures ($\sim 2000\text{--}3000 \text{ atm}$). Mineralizers, such as alkali metals or halides, are added to the solution to increase GaN solubility leading to basic or acidic solutions, respectively. Basic solutions are less corrosive than acidic solutions permitting use of unlined Ni-Cr superalloy autoclaves, whereas acidic autoclaves typically require precious metal lined autoclaves. Recently, molybdenum-based autoclaves have for the first time demonstrated their suitability as an unlined autoclave for use in both acidic and basic growth environments.³ Non-hermetically sealed capsules have been developed enabling higher purity growths of GaN in basic environments.

Important advances in the field which will be highlighted include improvement of growth rates leading to demonstrated peak growth rates of $60\text{--}340 \mu\text{m/day}$ for basic systems⁴ and $250\text{--}960 \mu\text{m/day}$ for acidic systems⁵, development of an equation of state to thermodynamically describe the decomposition of ammonia at typical operating conditions⁶, and a reinvestigation of the observed retrograde behavior of GaN solubility in basic ammonothermal systems⁷. Properties of ammonothermally grown GaN crystals will be presented, including improvements in crystal purity, explanations for their observed sub-bandgap optical absorption⁸ and coloration due to the presence of point defects⁹, including most notably hydrogenated gallium vacancies.



Left Figure. Overview of a) AT autoclave, b) solubility for basic process and c) growth process. **Top Figure.** a) 1 mm thick slice from basic AT-GaN grown in Ag-capsule, b) unlined basic growth of AT-GaN boule, c) acidic AT-GaN boule, d) acidic AT-GaN grown in Mo-based autoclave. **Refs. in [9].**

¹ S. Porowski, et al., *J. Phys. Chem. Solids*. **85** (2015) 138–143. doi:10.1016/j.jpcs.2015.05.006.

² D. Ehretraut, E. Meissner, M. Bockowski, eds., “Technology of Gallium Nitride Crystal Growth”, Springer, 2010.

³ S. Pimputkar, et al., *J. of Supercritical Fluids*. **110** (2016) 193–229. doi:10.1016/j.supflu.2015.10.020.; T.F. Malkowski, et al., *J. Cryst. Growth*. **456** (2016) 21–26. doi:10.1016/j.jcrysgr.2016.07.045.; S. Pimputkar, et al., *J. Cryst. Growth*. **456** (2016) 15–20. doi:10.1016/j.jcrysgr.2016.07.034.

⁴ S. Pimputkar, et al., *J. Cryst. Growth*. **403** (2014) 7–17. doi:10.1016/j.jcrysgr.2014.06.017.; E.R. Letts, et al., *J. Cryst. Growth*. **350** (2012) 66–68. doi:10.1016/j.jcrysgr.2011.12.024.

⁵ Y. Mikawa, et al., *SPIE Opto*, 2015: p. 936302. doi:10.1117/12.2078137.; D. Ehretraut, et al., *Jpn. J. Appl. Phys.* **52** (2013) 08JA01. doi:10.7567/JJAP.52.08JA01.

⁶ S. Pimputkar and S. Nakamura, *J. of Supercritical Fluids*. **107** (2016) 17–30. doi:10.1016/j.supflu.2015.07.032.

⁷ S. Griffiths, et al., *J. Cryst. Growth*. **456** (2016) 5–14. doi:10.1016/j.jcrysgr.2016.08.041.

⁸ S. Pimputkar, et al., *J. Cryst. Growth*. **432** (2015) 49–53. doi:10.1016/j.jcrysgr.2015.09.016.

⁹ S. Suihkonen, et al., *Adv. Electron. Mater.* **3** (2017) 1600496. doi:10.1002/aelm.201600496.