Study of gallium nitride solubility in ammonothermal alkaline solution under various physicochemical conditions

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Gallium nitride (GaN) crystals of the best structural quality are grown by ammonothermal method in a supercritical ammonia solution inside high pressure autoclaves [1]. The idea of the ammonothermal process is the following: GaN, used as feedstock, is dissolved in supercritical ammonia (NH_3) in one zone of a high-pressure autoclave. The dissolved feedstock is transported to the second zone, where the solution is supersaturated and crystallization of GaN on native seeds takes place. An appropriate temperature gradient between dissolution and crystallization zones enables the convective mass transport. Some mineralizers are added to NH_3 in order to enhance the solubility of GaN. Thus, the ammonothermal growth can be proceeded under different environment: basic or acidic. The type of environment is, obviously, determined by the choice of mineralizers. Ammonobasic growth makes use of alkali metals or their amides as mineralizers, while in ammonoacidic growth halide compounds are present. The most frequently studied basic mineralizer is potassium amide (KNH_2) [2]. However, a few data on the solubility experiments with the basic mineralizer sodium amide ($NaNH_2$) can be found. The reason for this is the generally accepted opinion of the higher solubility of KNH_2 in NH_3 compared to $NaNH_2$. It is stated and commonly believed that in the case of $NaNH_2$ used as a mineralizer, a normal course of solubility is observed (it increases with increasing the temperature), the solubility of GaN does not dependent on the concentration of the mineralizer, $NaNH_2$ dissolves very poorly in supercritical ammonia and $NaNH_2$ does not contribute to the dissolution of GaN. On the other hand, the best, in terms of structural quality, and the largest, in terms of thickness and lateral size, crystals are grown by basic ammonothermal method with $NaNH_2$ as the mineralizer and with a reverse course of solubility (it decreases with increasing the temperature; this is called a retrograde solubility mode) [3]. This discrepancy is explained in this paper. The GaN solubility as a function of temperature, pressure, dissolution time, mineralizer concentration and surface area of GaN feedstock was investigated. The solubility of GaN in ammonobasic $NaNH_2$–GaN–NH_3 systems in the temperature range of 300–550°C was examined. In this work the methodology of the conducted research and the first results will be discussed. In particular, kinetics of the dissolution process, time to reach a saturated solution and solubility of GaN as a function of temperature will be presented.

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[2] Schwieger W., Baser H., in Ammonothermal Synthesis and Crystal Growth of Nitrides, E. Meissner and R. Niewa (eds.), Springer Series in Materials Science 304, (2021) 155
[3] Kucharski R., Sochacki T., Lucznik B., Bockowski M.,Growth of bulk GaN crystals, J. Appl. Phys., 128 (5), 2020, 050902