

Abstract submitted for presentation at the 34th Annual Symposium of the New Mexico Chapter of the American Vacuum Society in Albuquerque, May 19-21, 1998.

Influence of Ammonia Reactions in the Surface Chemistry of GaN Chemical Vapor Deposition

Michael E. Bartram, Sandia National Laboratories, Albuquerque, NM

Engineering GaN films to have specific sets of properties requires a process model that can be applied over a wide range of deposition conditions. Within this type of robust process model, the chemistry model must utilize accurate rate constants for the GaN precursor reactions. To this end, the goal of this work is to identify the reaction pathways on the surface and measure the kinetics associated with reactions on GaN.

In this study, ultra-high vacuum thermal desorption mass spectroscopy studies of isotopically labeled ammonia ($N^{15}H_3$) chemisorbed on GaN(0001) demonstrate that ammonia can undergo both reversible and irreversible decomposition on the surface. Overall, $N^{15}H_n$ fragments and surface hydrogen from ammonia dissociation can either (I) recombine to liberate $N^{15}H_3$ or (II) decompose further to enrich the surface with N^{15} as judged by the desorption of N^{15}_2 , $N^{15}N^{14}$, N_2 , and H_2 at a temperature below that required for congruent GaN sublimation. In these key reactions can be found the "crossroads" for joining with the avenues of other reactions on the surface. Considering case I, production of surface hydrogen from ammonia decomposition suggests that this rate may be sensitive to hydrogen coverage and hence be dependent on the surface decomposition of the H_2 carrier gas used commonly in GaN CVD. Case II suggests that in addition to supplying the nitrogen for GaN growth, ammonia decomposition can also lead to the extraction of nitrogen from the surface when the nitrogen coverages are sufficiently high to allow the tremendous driving force of the nitrogen-nitrogen bond energy (226 kcal/mol) to result in N_2 formation. Therefore, while the nitrogen feed to the surface can compensate for congruent GaN sublimation and also contribute to GaN growth, it can also promote the removal of nitrogen from the surface. This suggests that the overall nitrogen incorporation rate must be well-matched to the Ga deposition rate to achieve the proper stoichiometry.

We have also shown with TMG and ammonia coadsorption experiments that ammonia can alter the surface chemistry sufficiently to raise the temperature of TMG desorption, producing an additional desorption state 100deg. higher than the first. This demonstrates that ammonia can extend the TMG lifetime on GaN significantly and that ammonia transients and perhaps NH_n surface species may well influence the TMG decomposition rate during GaN CVD. (Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.)