

# An Integrated Solution Approach for the Use of Ammonia in Growth of GaN Based Semiconductors

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Ultra-high purity ammonia delivered to the point of use is critical for growth of gallium nitride semiconductors. Recent studies have demonstrated that the origin, properties, and fluctuations of impurities are related to starting impurity levels within the cylinder, cylinder usage conditions, type of ammonia withdrawal systems, microcontamination from gas distribution components, and proper use of ammonia purifiers. In order to deliver ultra-high purity ammonia to the POU, all of these factors must be considered, understood and controlled. An Integrated approach that considers all sources of contamination from the cylinder to the POU has been developed and tested. Results from cylinder tests, conventional vs. non-conventional delivery systems, and regenerable purification will be presented.

## 1 Control of Impurities From Cylinders and Bulk Containers

The chemical and physical properties of impurities in a condensed liquefied gas cylinder cause concentration fluctuations that are complex and convoluted. The impurities emitted from a cylinder or bulk container can be influenced by many factors such as solubility of the impurity in the liquid phase, and vapor pressure of the impurity and matrix gas. Furthermore, usage conditions of the cylinder or bulk container can also have a large impact on the variability and absolute concentrations of impurities emitted from a cylinder. For example, H<sub>2</sub>O as an impurity in hydride gases is highly soluble in the liquid phase and during initial use of the cylinders, when sampled from the gas phase, H<sub>2</sub>O concentrations might be at low and acceptable levels. As the source is consumed, however, concentrations can rapidly increase since the liquid phase is enriched with H<sub>2</sub>O due to selective vaporization of the high vapor pressure matrix gas. Liquefied gases are usually sampled for volatile impurities by gas phase analysis, a procedure in which the gas in the headspace of the cylinder is drawn off under natural pressure (114 psig at room temperature for ammonia). Figure 1 shows a typical measurement of moisture concentration variations in ammonia by gas phase sampling at 2 and 6 slpm. Usually, the observed moisture level dropped rapidly to a minimum and rose again. The time required to observe increasing moisture after an initial drop ranged anywhere from a few minutes to several hours. Moreover, the shape of the moisture curve was highly variable, so that neither the time nor the moisture level of the minimum was reproducible from sample to sample.

In addition to variability over time, the gas phase measurements showed marked sensitivity to flow rate. Figure 2 shows changes in gas phase moisture as a function of flow rate from a cylinder containing 127 ppm moisture in the liquid phase, which is equivalent to < 3 ppm in the gas phase. The increase in moisture over time during gas phase sampling was generally more rapid at higher flow rates. The effect of stirring by agitation of the cylinder can also be seen in Figure 2. Agitation of the cylinder temporarily caused the moisture levels to drop significantly.

The instability of the moisture level in the gas phase of an ammonia cylinder over time is a phenomenon that is qualitatively reproducible, although highly variable from sample to sample. Clearly, evaporation of the liquid phase of the ammonia/water system inside the cylinder is a non-equilibrium process. The dependence of moisture level upon flow rate and the sudden drop in moisture produced by mixing also point to non-equilibrium gas flow. No quantitative model for the observed behaviour is currently available. However, a qualitative model based on transport limitations at the gas/liquid interface has been previously proposed[1].

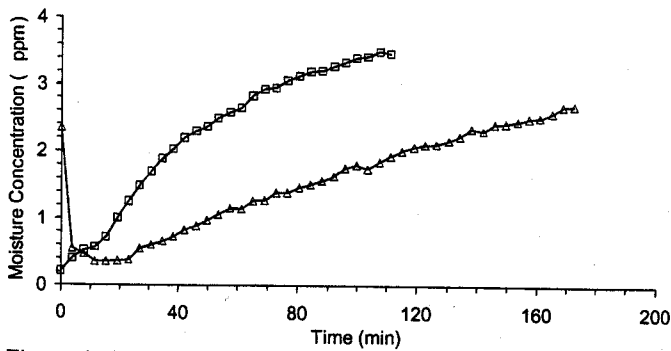


Figure 1. Typical profiles of gas phase sampling of an ammonia cylinder at constant flow rates of 2 SLPM (-Δ-) and 6 SLPM (- -).

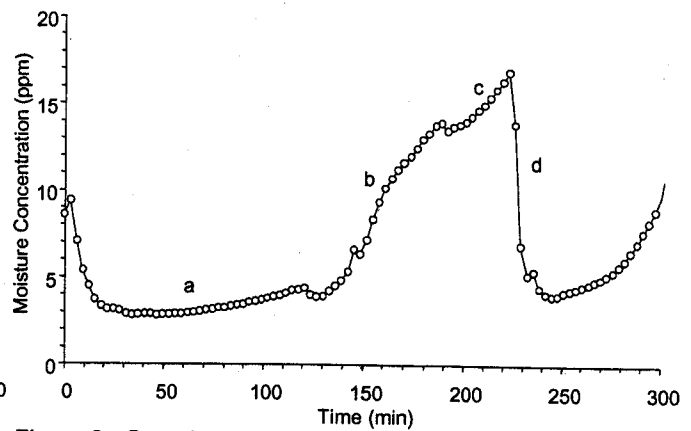


Figure 2. Gas phase sampling of an ammonia cylinder at different flow rates: a) 0.8 SLPM, b) 2 SLPM, c) 0.8 SLPM, d) effect of agitation of the cylinder at 0.8 SLPM.

## 2 Control of Impurities Within Delivery Systems

### *Conventional Gas Phase Delivery vs. Liquid Extraction Total Vaporization (LETV)*

The most common Bulk Specialty Gas System (BSGS) is a gas phase delivery system. This system requires the ammonia to be vaporized within the Bulk Specialty Gas Unit (BSGU) and run through the BSGS as a gas. Our studies [2] have identified several problems associated with gas phase BSGS delivery of ammonia. First, the BSGU must be heated in order to maintain high flow rates. However, it is difficult to transfer the heat efficiently into the contents of the unit. The amount of heat must be constantly adjusted as the tank is emptied in order to maintain the delivered gas at a constant temperature. We also found that the moisture concentration in the gas phase ammonia coming from the BSGU is flow rate dependent. Moisture spikes are observed whenever the flow rate is changed over the typical range of an ammonia BSGS, see Figure 3. A more serious problem is that the dissolved impurity levels increase in the ammonia as the BSGU is consumed, see Figure 4. This is due to the higher relative volatility of ammonia to many of the dissolved impurities.

In order to solve these problems, we have investigated liquid delivery BSGS, where the ammonia is withdrawn from the BSGU in the liquid phase and evaporated in a vaporizer that is specifically designed for controlled vaporization. The vaporizer system involves continuous Liquid Extraction Total Vaporization (LETV) of the ammonia with no liquid residue. This newly designed system draws liquid ammonia from the source vessel and vaporizes it 100%. A patent has been filed and is currently pending on the LETV BSGS concept and apparatus. The results demonstrated that this new system delivers a consistent ammonia gas whose purity is not dependent on flow rate or gas usage. The LETV design also allows the user to withdraw  $\geq 96\%$  of the product while maintaining consistent moisture levels during the delivery process. Results from experiments conducted with LETV technology are shown in Figure 5. For comparison purposes, typical results obtained from conventional liquid vaporization experiments were obtained. Figure 6 shows that severe fluctuations in the water emission occur as the flow rate is changed. It is believed that most of the fluctuations are due to temperature and pressure fluctuations within the vaporizer that influence the distribution of moisture between the liquid and gas phase ammonia. Additionally, it is apparent that the vaporizer is accumulating water in the liquid phase and periodically, the accumulated moisture is flash evaporated and sent into the gas stream. Essentially, all the problems associated with moisture fluctuations when delivering from the gas phase are now transferred to the external vaporizer when utilizing conventional liquid delivery systems. However, LETV technology allows consistent impurity levels and more product usage. A more detailed description of bulk specialty gas systems used for ammonia delivery has been previously published [3].

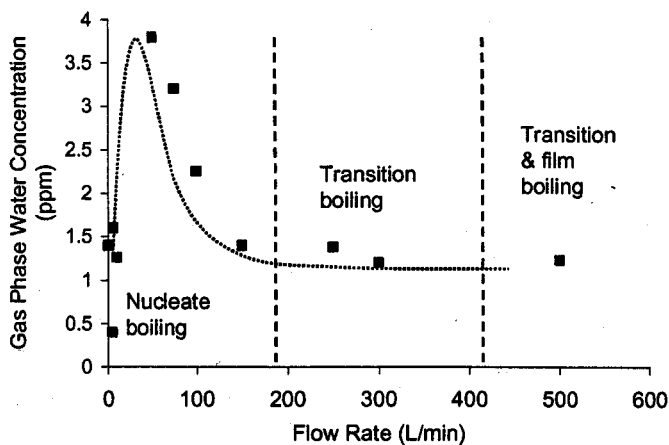


Figure 3. Change in the gas phase water concentration in ammonia as a function of flow rate from a gas phase delivery system.

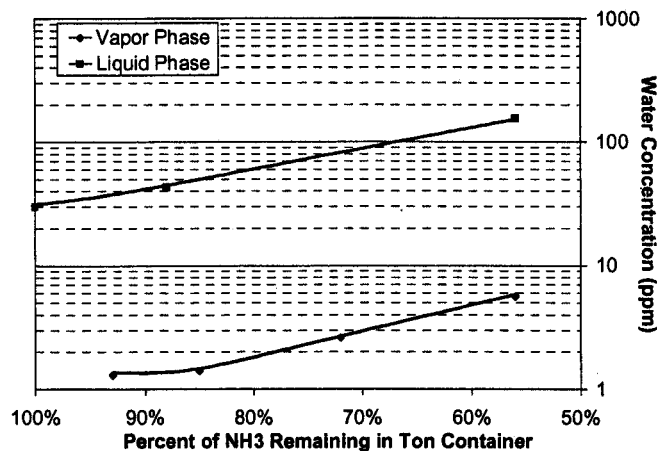


Figure 4. Change in moisture concentration as a function of ammonia remaining in the container during gas phase delivery.

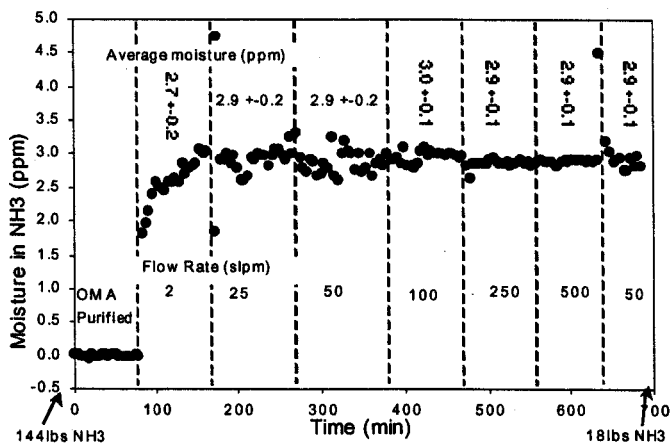


Figure 5. Moisture concentration from Matheson's LETV system as a function of flow rate.

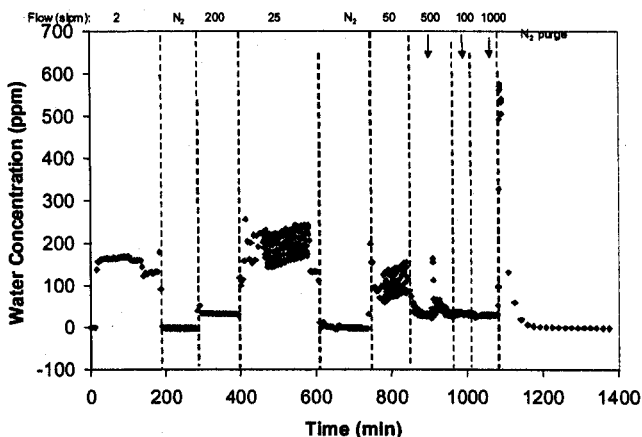


Figure 6. Moisture concentration fluctuations from a conventional ammonia vaporizer as a function of flow rate.

### 3 Control of Impurities by Implementing Source Gas and POU Purification

The Phoenix™ Regenerable purifier was developed to remove all critical impurities from ammonia for the manufacture of GaN based semiconductor devices. The results showed that even when the purifier is challenged with extraordinary impurity concentrations, the purifier has the ability to remove the impurities to detection limits of the instrumentation. This demonstrates that the purifier can withstand impurity fluctuations much greater than will be experienced in actual process use. In addition to demonstrating the efficacy of the purifier to remove critical impurities, such as oxygenated species and dopants, the purifier was tested and showed no deleterious metals emission. Finally, the purifier was tested for regenerability and demonstrated that the material is fully regenerable and encountered no deterioration of the physical characteristics and no degradation of performance.

### 4 References

- [1] H. Funke, M. Raynor, B. Yucelen, V. Houlding, J. Electronic Materials, Vol. 30, 2001, 1438-1447.
- [2] B. Yucelen, J. Vininski, R. Torres, and V. Houlding, Semicon West, July 2000, San Francisco, California.
- [3] J. Vininski, B. Yucelen, R. Torres, and V. Houlding, CS-Max 2001, Boston, MA.