Bulk Specialty Gas Systems For Ammonia Gas Phase Delivery Vs. Liquid Phase Delivery

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Abstract. Three different Bulk Specialty Gas delivery Systems (BSGS) were designed and tested up to flow rates of 1000 slpm. Conventional gas delivery, conventional liquid delivery and a novel liquid delivery system featuring Total Vaporization (TV) were compared in terms of product consistency and the amount of available ammonia from a bulk container. The delivered gas was monitored for moisture fluctuations as a function of flow rate and time. Results from the TV design showed consistent moisture levels at all flow rates, while both the gas and the conventional liquid delivery systems exhibited dramatic fluctuations in moisture concentration. Additionally, liquid delivery systems supply continuous flow rates greater than 5000 slpm, while gas delivery systems can not sustain flow rates higher than 600 slpm due to heat transfer limitations. Furthermore, liquid delivery enables the consumption of nearly the entire product, while maintaining constant moisture levels. Empirical evidence has shown that 96% of the container's contents can be used if the liquid delivery system is employed. However, with a gas or conventional liquid delivery system the impurity levels are uncontrollable and increase throughout the consumption of the bulk container. As a result, it is uncommon for the product to be completely consumed and purifier lifetime can not be accurately assessed.

Introduction

The demand for Light Emitting Diodes (LEDs) and other compound semiconductor devices has increased dramatically in recent years. Commercial MOCVD manufacturing is rapidly transitioning to high volume production. Ammonia is one of the primary gases used in high volume for MOCVD growth of gallium nitride films in LEDs.

Until recently, cylinder delivery systems were used to deliver ammonia to MOCVD reactors. Due to the high flow rate requirement of the gallium nitride process, Bulk Specialty Gas Systems (BSGS) have begun to replace the conventional cylinder gas delivery systems. These systems comprise a Bulk Specialty Gas Unit (BSGU) such as a ton container, tube trailer or bulk tank filled by truck, and a gas piping system that can handle very high flows. BSGS are attractive due to their lower cost of ownership, increased safety, product quality, and consistency [1]. The use of a BSGU allows much longer run times with reduced source gas change outs. However, the method of the delivery of the ammonia from the BSGU is the main factor in determining the consistency and the quality of the product.

The most common BSGS is a gas phase delivery system. This system requires the ammonia to be vaporized within the 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 should be heated in order to maintain high flow rates. However, it is difficult to transfer the 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. A more serious problem is that the dissolved impurity levels increase in the ammonia as the BSGU is consumed. This is due to the higher relative volatility of ammonia to many of the dissolved impurities. 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.

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. We have studied two basic types of liquid delivery. The first is a conventional vaporizer where liquid ammonia is continuously evaporated in a partial vaporization mode similar to distillation, and a liquid fraction is periodically discarded. As will be shown in this paper, this vaporizer system has serious flaws. The second type of vaporizer system involves continuous Total Vaporization (TV) 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 TV BSGS concept and

apparatus. The information and data within this article will demonstrate that this new system delivers a consistent ammonia gas whose purity is not dependent on flow rate or gas usage. The TV design also allows the user to withdraw ≥96% of the product while maintaining consistent moisture levels during the delivery process.

Experimental

Gas Delivery Systems

Two similar high flow gas distribution systems were used for the experiments. Both systems were constructed with 3/8" and ½" 316L stainless steel tubing with ½" UHP valves and regulators. For the liquid delivery systems two different vaporizers were designed and used. The BSGU used in these experiments were 726 L gas containers filled with 800 lbs of anhydrous ammonia. Additional tests were performed on the liquid delivery system with 126 L and 44 L size ammonia cylinders. All of the ammonia containers were prepared to a known amount of water concentration for the moisture experiments. A relatively large moisture concentration was used in the BSGU since this helped to ascertain data trends more quickly and helped lower the equilibration time when changing parameters.

Analytical Instrumentation

The FTIR spectroscopic method used in this work has been described in detail elsewhere [3]. A Nicolet Magna 550 FTIR bench with an MCTA detector was equipped with additional internal purge lines and an external purge box to ensure low and constant background moisture levels in the beam path. Nanochem-purified nitrogen (<1 ppb moisture) was used as purge gas. Lines and valves were heated with heating tapes to avoid adsorption-desorption of moisture. A 10-m path length cell was used for gas sampling. A MKS pressure controller was placed on the outlet of the FTIR to monitor and control the pressure in the cell to 820 torr. An 1/8" 316L line was connected to the high flow manifold to deliver a continuous ammonia sample (2 slpm gas phase) to the FTIR. A valve was installed at the liquid outlet of the ton container for periodic direct liquid sampling. Spectra were collected at a resolution of 4 cm^{-1} and the signal was analyzed with Happ-Genzel apodization.

Calibration and Data Analysis

Calibrations were performed in an ammonia matrix with a moisture-generation source and a two-stage dilution manifold. The moisture source was maintained under nitrogen flow at constant pressure, temperature and flow rate. A small fraction of the wet nitrogen stream from the moisture source was introduced into a purified ammonia stream. The concentration of nitrogen in ammonia did not exceed 10% for all of the moisture calibration points obtained.

A Classical least square (CLS) method implemented in Nicolet's OMNIC QuantPad software was used for data analysis. The CLS method mathematically combines calibration spectra for moisture and ammonia to match the sample spectra and calculates the actual concentration from the individual contributions of the calibration spectra. This method potentially can analyze several components simultaneously and the residual spectra yield information of additional impurities. The algorithm requires choice of a spectral region where the matrix gas absorption causes the least interference. Several spectral windows in the region 3682-3988 cm^{-1} were used for this work, and in each window the spectrum of free water vapor (as measured in inert gas) was deconvoluted from the spectrum of the ammonia matrix. Method detection limits were calculated using linear regression analysis at 99.87% confidence. This method takes variances of the calibration system as well as changes in the bench moisture background and reproducibility of blanks into account. The LOD for the experiments reported here was ≤ 100 ppb at a dynamic range between 0 and 400 ppm.

Results

Gas Phase Delivery

We have previously shown [3] that the moisture content in gas phase ammonia from a cylinder is unstable and unreproducible with respect to time, flow rate, and temperature. This work also clearly demonstrated how the moisture level in the gas phase increases exponentially as the cylinder is consumed. We therefore expected to observe similar phenomena when testing BSGU containers.

The moisture in gas phase ammonia from the BSGU was measured at flow rates up to 1000 slpm. Figure 1 shows the gas phase moisture concentration in ammonia as a function of flow rate. The data demonstrate that the free

water concentration in the ammonia gas stream has a strong dependence on flow rate. The water concentration initially increases as the flow rate increases, reaches a maximum, and then declines as the flow rate continues to increase. This behavior was observed in two independent experiments. A detailed analysis of this phenomenon will be published elsewhere [5]. Briefly, it is a result of the combined effects of thermodynamics, fluid dynamics, and heat transfer within the BSGU. As the temperature of the liquid phase inside the BSGU decreases due to evaporative cooling, the temperature difference between the container wall and the liquid ammonia increases. The change in temperature profile causes the ammonia boiling mechanism to change within the BSGU, thus changing the moisture concentration in the gas phase with flow rate.

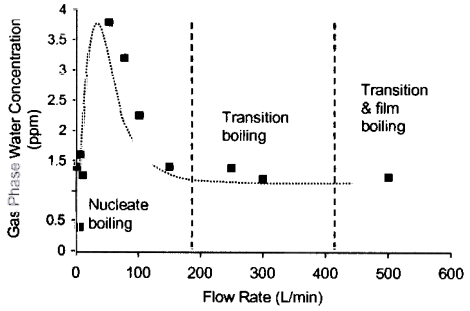

Figure 1. Change in the gas phase water concentration in ammonia as a function of flow rate from a gas phase delivery system.

At very low flow rates, the temperature difference between the liquid-vapor interface and the container wall is low and a smooth evaporation occurs with minimal convection of the liquid. With increasing flow rate (10-50 slpm in this BSGU), a nucleate boiling regime becomes predominant, where bubbles are formed on the container surface. At higher flow rates (50-200 slpm in this BSGU), the temperature difference increases, causing the bubble generation rate and heat flux to become very high. There is significant amount of mixing inside the container. Between 200 and 500 slpm the number of nucleation sites becomes very high and a vapor film with a lower thermal conductivity covers the surface of the walls. At this point, film boiling is established, which causes a reduction in the heat flux from the container walls to the liquid phase and restricts liquid flow to the surface [4].

We propose that these different boiling regimes cause different moisture levels in the gas phase by affecting the liquid-vapor interface. As smooth evaporation occurs, an enrichment of moisture develops at the liquid-vapor interface. Surface enrichment increases with an increased flow rate and therefore the moisture concentration increases. At a certain flow rate, ~40 slpm in our BSGU, the nucleate boiling becomes vigorous enough to disrupt and mix the liquid-vapor interface which starts to lower the surface enrichment of moisture. At 200 slpm a film boiling regime develops and heavy mixing is found within the BSGU. As a result the surface enrichment is not capable of developing and a lower, more consistent, moisture level is observed.

As expected, the moisture level in ammonia delivered from the gas phase is also dependent on the extent of depletion of the BSGU. The moisture level in the BSGU increases as the ammonia is consumed, as seen in Figure 2. Figure 2 shows the increase in the moisture content in both the gas phase and liquid phase of the BSGU. The gas phase results showed an increase of 116 ppb moisture for every 1% of ammonia consumed (every 8 lbs.). Although empirical measurements were not conducted over the entire life of the BSGU, an extrapolation of the moisture content can be made based on the trend observed in Figure 2. When the BSGU is filled to capacity (100%) the moisture level in the gas phase was 0.5 ppm. At 50% consumed the moisture content was observed to be 6.3 ppm. Extrapolation of this data suggests that at 90% consumed, the moisture content from the gas phase will be ≥ 11.0 ppm. Additionally, since the moisture level increases exponentially towards the end of the BSGU usage, the actual moisture level could be significantly higher than expected. This dramatic increase in moisture content at the end of the container will have a significant impact on purifier efficiency and process stability. Due to this effect, it is typical for a MOCVD grower to stop using an ammonia cylinder when up to 30% of the liquid phase still remains.

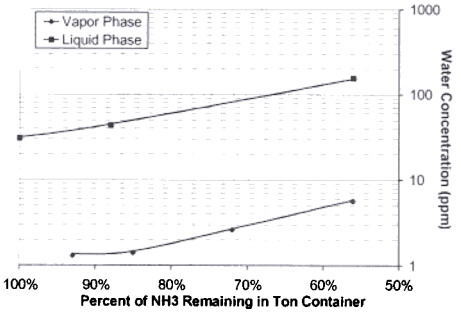

Figure 2. Change in the concentration of moisture in gas and liquid phase ammonia as a function of ammonia remaining in the BSGU during gas phase withdrawal.

We have shown [3] that the distribution of moisture between the liquid phase and gas phase of ammonia is approximately 200:1 under quasi-equilibrium conditions. However, from Figure 2 it can be seen that this ratio is approximately 30 for flow rates of 250-300 slpm from our BSGU. Unstable gas phase measurements prevented us from measuring the ratio at lower flow rates.

Liquid Phase Delivery- Conventional Design

Liquid phase delivery consists of withdrawal of liquid phase ammonia from the BSGU and using an external vaporizer to convert the liquid ammonia to gas phase ammonia. Conventional liquid phase delivery typically uses an electric or water heated vaporizer as the external heating source. A reservoir of liquid is maintained in the vaporizer and is replenished periodically by filling from the BSGU. Because of this partial vaporization design, the vaporizer acts as a single plate distillation vessel, and liquid phase impurities build up in the vaporizer reservoir in the same way they build up within the BSGU in a gas phase delivery system.

To evaluate this conventional vaporizer design, a commercially available electric vaporizer was used to collect empirical data on the moisture variations as a function of time and flow rate. The results in Figure 3 show that the moisture level fluctuates periodically, corresponding to depletion and refill of the liquid reservoir in the vaporizer. Figure 4 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.

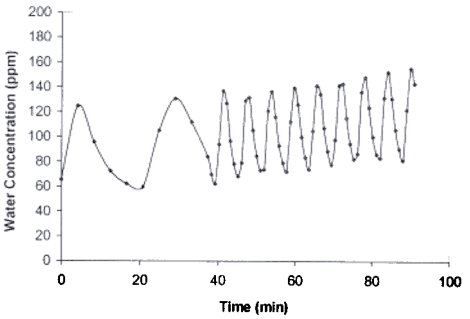

Figure 3. Moisture variation from a conventional ammonia vaporizer at a constant flow rate of 50 slpm.

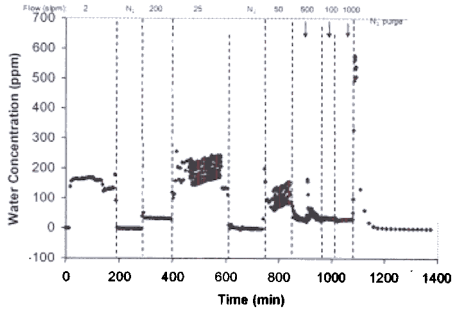

Figure 4. Fluctuations in moisture concentration from conventional ammonia vaporizer as a function of changing flow rates.

Liquid Phase Delivery - Total Vaporization

Matheson's Total Vaporization (TV) design for liquid delivery of ammonia was developed specifically to circumvent the problems observed with gas phase delivery and conventional liquid phase delivery. The basic design concept involves a proprietary vaporizer (patent pending) that achieves total vaporization of the ammonia while maintaining constant temperature and pressure within the vaporizer. The flow rate from the vaporizer is easily increased, up to 5000 slpm, by adjusting the heat flux. Thus it appears the flow rate limitation for this type of liquid delivery system will not be due to heat flux limitations, as observed in gas phase delivery systems, but more likely due to restricting orifice sizes on gas distribution components.

To demonstrate the stability of moisture levels in ammonia delivered by the TV system, tests were conducted on a BSGU containing 161 ppm liquid phase moisture for a period of 7 hrs at 250 slpm. Results are shown in Figure 5. The water concentration of 161 ppm was constant throughout the course of the experiment and the standard deviation in the data was 1.6 ppm.

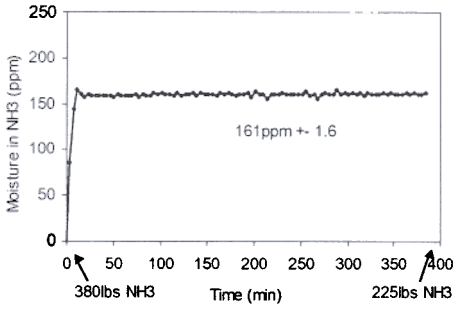

Figure 5. Moisture concentration from Matheson liquid delivery system and ammonia vaporizer at a constant flow rate.

Results for this BSGU of variation in flow rate from 2 to 250 slpm are shown in Figure 6. The data were collected continuously throughout the experiment, including the stabilization points when the flow rate was changed. Throughout the test, the standard deviation was only 3.0 ppm when the flow rate was changed. Since data points were taken every 4 minutes, it took only 4 minutes for the system to be stabilized when the flow rate was increased to 250 and also when decreased to 50 slpm. The 2 slpm data were taken in order to simulate the real processes where the gas delivery is totally stopped for a certain amount of time.

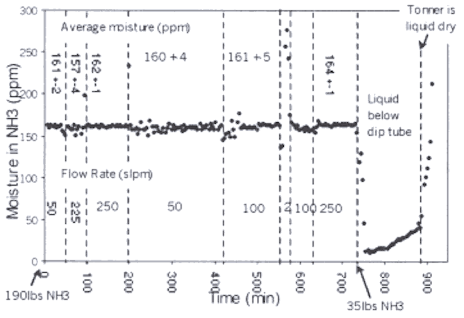

Figure 6. Moisture concentration from Matheson liquid delivery system and ammonia vaporizer while changing flow rates.

It is also important to note that throughout the consumption of 96% of the total ammonia in the container, the water concentration stayed constant at a value of 161 ppm. This allows the BSGS to deliver ≥96% of the product before the liquid level in the BSGU drops below the dip tube. The effect of going "liquid-dry" in the system can be seen in Figure 6 at the end of the experiment. When the liquid level decreased to levels below the dip tube, the water concentration started to decrease as the ammonia was being delivered in the gas phase. Then the moisture rises sharply as the last of the liquid ammonia, containing concentrated moisture, is evaporated from the bottom of the BSGU.

Experiments were also conducted on ammonia containing lower moisture levels to understand how the TV system works at lower water concentrations. A container was filled with ammonia having a moisture concentration of ~3.0 ppm in the liquid phase. The moisture level was monitored at flow rates from 25 to 500 slpm and observed to be relatively constant at 2.9 ± 0.1 ppm throughout the entire usage of container, as seen in Figure 7. Again, the data presented were collected continuously throughout the experiment, and no data points were omitted from the figure.

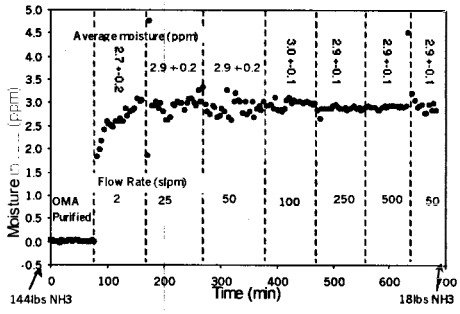

Figure 7. Moisture concentration from Matheson liquid delivery system and ammonia vaporizer while changing flow rates. Ammonia source contained considerably less moisture than previous experiments.

Matheson's Best-of-Breed ammonia was also tested. The liquid phase water concentration in this container was below the FTIR detection limit of ≤100 ppb. At these concentrations, the effect of the drying down of the tubing was significant. Therefore, the average concentration decreased with time. The results are given in Figure 8 for flow rates of 2, 50, and 250 slpm.

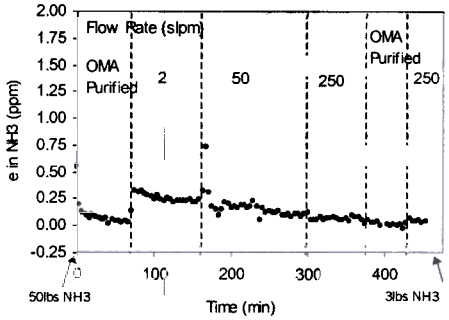

Figure 8. Moisture concentration from Matheson liquid delivery system and ammonia vaporizer while changing flow rates. Ammonia source moisture concentration was less than the detection limit of the calibrated FTIR.

Conclusions

The data show that the newly developed, 100% Total Vaporization liquid delivery system has distinct advantages over gas phase delivery systems and conventional liquid phase delivery systems. We have demonstrated that the Matheson TV liquid delivery system delivers ammonia at variable flow rates while maintaining a constant moisture concentration that is equal to the liquid phase concentration of the source. This was demonstrated for three different grades of ammonia. Even during abrupt changes in ammonia flow rate, only minimal fluctuations in the moisture concentration were observed. Furthermore, we have demonstrated that these consistent moisture concentrations can be maintained from beginning to end of an 800 lb BSGU.

This type of TV delivery system will simplify the issues surrounding BSGS ammonia for GaN epi growth. By delivering the ammonia in a consistent manner, a stable moisture level is obtained in the delivery system that is independent of the end user's operating parameters. One key advantage of a constant moisture level is that point-of-use purification can be accurately controlled. Knowing the inlet moisture concentration for a BSGS purifier allows the end user to easily calculate the lifetime of the purifier and make provision for periodic maintenance. Additionally, it allows the end users to eliminate the source gas as a variable over the lifetime of a BSGU when diagnosing poor wafer performance, since the impurity levels in the process gas will remain constant during the entire life of the container.

References

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