

## Measurement and Control of Trace Carbon Dioxide in Ultra-High Purity Ammonia for the Semiconductor Industry

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### Abstract

The absence of trace oxygenated impurities such as carbon dioxide, in ultra-high purity ammonia is important for the growth of defect-free epitaxial nitride films. As CO<sub>2</sub> and NH<sub>3</sub> gases react spontaneously and exist in heterogeneous equilibrium with the reaction product, solid ammonium carbamate (NH<sub>4</sub>COONH<sub>2</sub>), both free and complexed carbon dioxide impurities may be present within an ammonia cylinder or the gas distribution system depending on the conditions. This reaction equilibrium complicates analysis and control of CO<sub>2</sub> in NH<sub>3</sub>.

The development of an analysis system based on gas chromatography with pulsed helium discharge ionization detection (GC-PDID) is described for the measurement of CO<sub>2</sub> in NH<sub>3</sub> at trace levels. A heated sampling manifold optimized at 110°C is used to decompose the ammonium carbamate so that free CO<sub>2</sub> is measured. The analysis system is used to evaluate (i) the CO<sub>2</sub> levels in the gas and liquid phases of various ammonia cylinders and (ii) the efficiency of a new purification medium (NHX-Plus) for the removal of both free and complexed CO<sub>2</sub> in gaseous ammonia. The removal of 50 ppm CO<sub>2</sub> in NH<sub>3</sub> in either free or complexed form to below the detection limit of the instrument is demonstrated.

### Introduction

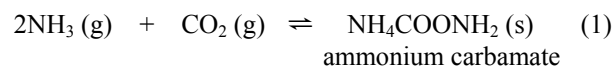
Electronic specialty gases such as ammonia must be free of trace levels of contaminants that may be potentially incorporated into semiconductor devices during film growth [1]. For example, carbon and oxygen-containing impurities in the ammonia used to deposit silicon nitride layers for masking and passivation processes may weaken the deposited layers. Further, in the metal-organic chemical vapor (MOCVD) deposition of GaN and other III-V compound semiconductors, spurious contamination of the ammonia and organometallic precursors by trace oxygenated impurities can cause unintentional doping, lattice defects and undesirable oxide formation in deposited layers. These defects can considerably reduce the photoluminescent properties of optoelectronic products such as light emitting diodes and lasers [2,3].

Traditionally, process gas purity has been determined by measuring the concentration of the free gaseous impurities in the gas phase using gas chromatography (GC), Fourier transform infrared spectroscopy (FTIR) or mass spectrometry (MS) techniques. However, several studies

have shown that gas phase concentrations of certain impurities (such as moisture) are often not consistent due to partitioning between the gas and liquid phases within the cylinder [4]. In addition, it is also important to consider that some impurities may form reaction products or reservoir species with the matrix gas that can significantly complicate analysis. In this work we discuss some of the challenges associated with measuring trace CO<sub>2</sub> in NH<sub>3</sub> and present CO<sub>2</sub> capacity and efficiency data obtained with a new purifier medium (NHX-Plus) developed for this application.

### Reaction Equilibrium

As shown in reaction 1 below, CO<sub>2</sub> reacts reversibly with NH<sub>3</sub> to form ammonium carbamate, a white crystalline solid. The reaction is exothermic and occurs under mild conditions merely on mixing the two gases.



The equilibrium properties of ammonium carbamate have been characterized by Bennett and coworkers [5] and Janjic [6]. Their data show that ammonium carbamate is stable to 59°C at atmospheric pressure, but decomposes back to the reactants above this temperature. Further, as this is a heterogeneous equilibrium, the ammonium carbamate also coexists with its decomposition products, NH<sub>3</sub> and CO<sub>2</sub>. Even at ambient temperature, the equilibrium partial pressures of CO<sub>2</sub> and NH<sub>3</sub> are appreciable. For example, the equilibrium dissociation pressure above solid ammonium carbamate is 85 torr at 25°C, and increases over five times to 453 torr at 50°C. Consequently, any CO<sub>2</sub> impurity in ammonia within the cylinder or gas delivery system may be present in “free” and/or “carbamate” forms. Therefore, analysis of only the “free” CO<sub>2</sub> at room temperature will be unrepresentative of the actual levels in the gas.

### Optimization of Sampling Conditions

One of the objectives of this work was to develop an analysis method to quantify trace CO<sub>2</sub> in NH<sub>3</sub>. A Shimadzu GC-14A gas chromatograph was set up with a pulsed helium discharge ionization detector, a heated switching valve oven and packed columns. The GC was plumbed using a standard back-flush plumbing configuration to backflush the ammonia matrix off the column (Figure 1).

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Early experiments quickly showed evidence of a reaction when low levels (~100 ppbv) of CO<sub>2</sub> spiked into NH<sub>3</sub> could not be distinguished from background levels in the neat ammonia using unheated lines. In order to detect the CO<sub>2</sub> in NH<sub>3</sub>, the sampling manifold had to be heated above 60°C to force the equilibrium in reaction 1 towards the reactants. A sampling manifold with temperature controlled zones was therefore set up as shown in Figure 2 to calibrate the instrument, optimize the CO<sub>2</sub> response and perform purifier investigations.

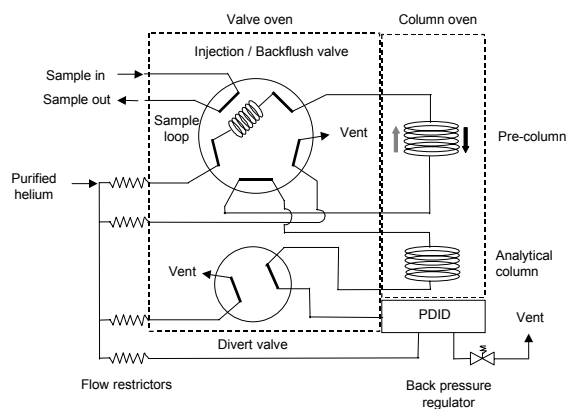


Figure 1. Schematic diagram of GC-PDID system

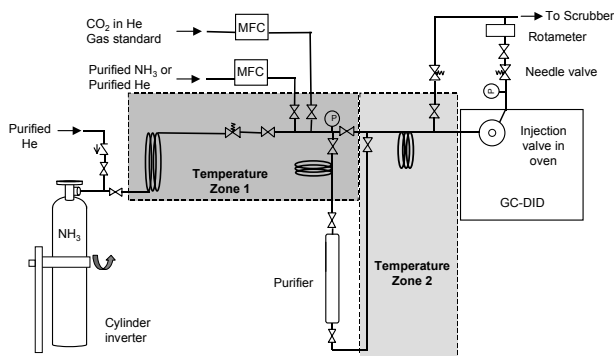


Figure 2. Sampling manifold with two independently heated zones for calibration, liquid and vapor phase sampling of ammonia cylinders and purifier evaluations.

Figure 3 shows the peak area of free CO<sub>2</sub> measured in ammonia by the GC-PDID using heated and unheated manifold/sampling lines respectively. When the manifold and lines (zones 1 and 2 in Figure 2) were heated to 145°C, the measured CO<sub>2</sub> peak area was about twice that measured when the lines in zone 1 and 2 were unheated (22°C). This indicates that the CO<sub>2</sub> impurity exists simultaneously in both free and complexed forms in ammonia. Further, in order to accurately quantify the CO<sub>2</sub> impurity, it is necessary

to dissociate the ammonium carbamate back to its gaseous reactants and analyze the total “free” CO<sub>2</sub> in the ammonia.

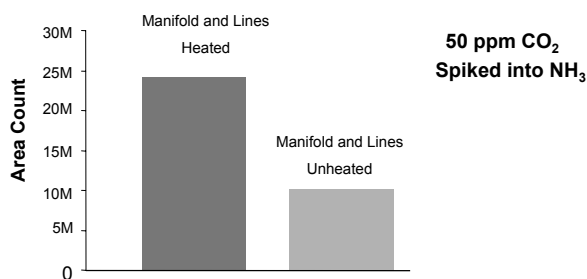
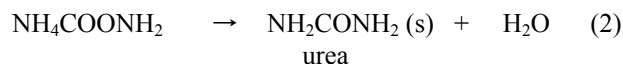


Figure 3: Free CO<sub>2</sub> in NH<sub>3</sub> measured with heated (145°C) and unheated manifold and lines.

The effect of sampling manifold temperature on free CO<sub>2</sub> response was investigated by heating both zones 1 and 2 in Figure 2 in the range 30 - 250°C and analyzing ammonia spiked with 90 ppm CO<sub>2</sub>. The results of the experiment in Figure 4 show that the CO<sub>2</sub> response increased with increasing line temperature and that the response reached a maximum near 110°C. Further increases in the manifold temperature up to 250°C resulted in reduced response. This is likely to be due to side reactions such as the irreversible formation of urea, shown in reaction 2 that occur at elevated temperatures (>127°C) [7].



The data indicate that the sampling manifold should be heated high enough to dissociate as much of the ammonium carbamate as possible, but low enough to prevent conversion to urea and water. Since the maximum CO<sub>2</sub> peak area was measured with the manifold lines in zones 1 and 2 heated at 110°C, instrument calibration and cylinder analyses were performed at this temperature.

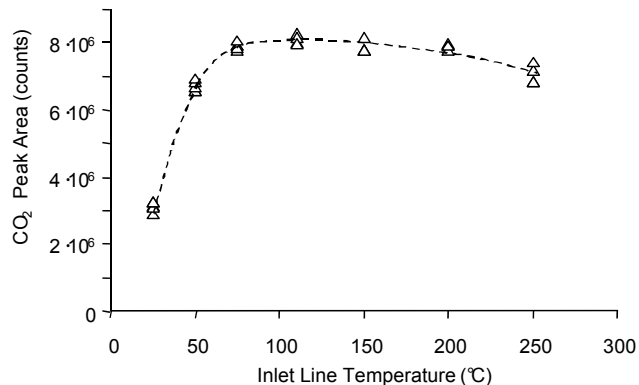


Figure 4. Effect of manifold temperature on free CO<sub>2</sub> response in ammonia

Calibrations were performed in helium and ammonia matrix gases to investigate the influence of the matrix gas on the CO<sub>2</sub> response. CO<sub>2</sub> was spiked at different concentrations into each matrix gas using the dilution manifold (Figure 2). The results graphed in Figure 5 show that the CO<sub>2</sub> response in helium was approximately double that in ammonia matrix, indicating that only half the CO<sub>2</sub> spiked into the ammonia was detected as free CO<sub>2</sub>, even with heated lines. This may be due to (i) incomplete decomposition of the ammonium carbamate in the heated lines and manifold, (ii) the occurrence of other side reactions or (iii) reduced instrument sensitivity caused by the ammonia matrix. For this reason, calibration in ammonia matrix was always carried out prior to cylinder analysis. The limit of detection for CO<sub>2</sub> in NH<sub>3</sub> calculated using the 3s/n definition [8] was 11 ppbv. Using a 3σ/m definition [9], the limit of detection was 30 ppbv.

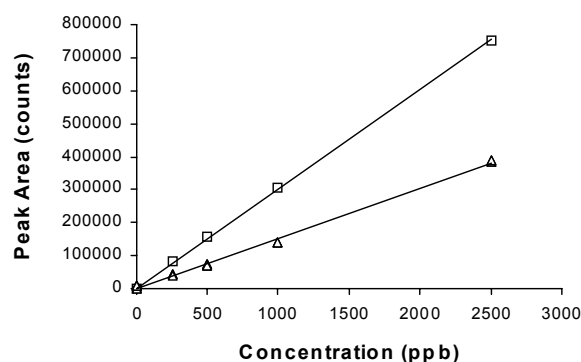


Figure 5. Calibration curves for CO<sub>2</sub> in He (□) and NH<sub>3</sub> (Δ) matrices.

### Cylinder Analysis

Several ammonia cylinders from different sources were analyzed to evaluate the level of CO<sub>2</sub> in the gas and liquid phases, and to determine where and in what form the CO<sub>2</sub> predominantly exists within the cylinder.

The isothermal dissociation constant for reaction 1 given by:

$$K_P = p_{\text{NH}_3}^2 p_{\text{CO}_2}$$

where  $p_{\text{NH}_3}$  and  $p_{\text{CO}_2}$  are the partial pressures of ammonia and carbon dioxide respectively and  $P$  is the dissociation pressure of ammonium carbamate at a given temperature indicates that the addition of excess ammonia will decrease the dissociation of ammonium carbamate. Thus, in an ammonia cylinder at room temperature (21°C) and cylinder pressure (129 psia), the equilibrium will favor the product and the carbon dioxide impurity is expected to exist more in the carbamate form within the liquid phase than in the free form in gas phase.

Results of the cylinder analyses shown in Table 1 support the theory. The CO<sub>2</sub> concentrations reported are based on an average of five GC analyses and were calculated after instrument calibration in ammonia matrix. In full cylinders, CO<sub>2</sub> concentrations in the gas phase were <100 ppb and remained in this range as gaseous ammonia continued to be withdrawn from the cylinder. Liquid phase CO<sub>2</sub> levels were up to 2 times higher than the gas phase concentrations. The higher CO<sub>2</sub> levels measured in the liquid phase indicate that the CO<sub>2</sub> is present there in the complexed form and will likely be concentrated as gaseous ammonia is withdrawn from the cylinder. However, as ammonium carbamate is reported to be virtually insoluble in liquid ammonia [10], it is unclear whether it is dissolved, dispersed in the liquid phase and/or deposited on the cylinder walls at these concentrations.

Table 1. CO<sub>2</sub> concentration in the gas- and liquid-phases of ammonia cylinders

Cylinder	Gas Phase CO <sub>2</sub> (ppbv)	Liquid Phase CO <sub>2</sub> (ppbv)
1	22 ± 4	48 ± 2
2	18 ± 6	23 ± 14
3	27 ± 4	58 ± 10
4	58 ± 7	59 ± 7
5	47 ± 4	NA
6	NA	207 ± 40
7	61 ± 4	91 ± 9
8	30 ± 4	40 ± 3

Evidence that ammonium carbamate is concentrated in a cylinder during gas withdrawal was found when analyzing the gaseous ammonia from a liquid-dry NH<sub>3</sub> cylinder (cylinder 3 in Table 1). This cylinder, which originally contained 27 ppbv CO<sub>2</sub> in the gas phase and 58 ppbv CO<sub>2</sub> in the liquid phase when full, was later found to contain 0.5 ppmv CO<sub>2</sub> when liquid dry (cylinder conditions: 45 psig and 22°C). The higher CO<sub>2</sub> concentration measured from the cylinder in liquid dry condition is likely to be due to the lower cylinder pressure, which shifted the equilibrium in reaction 1 towards the reactants and resulted in increased dissociation of the ammonium carbamate reservoir species.

To confirm this result, the cylinder was heated to decompose as much of any remaining ammonium carbamate as possible. As shown in Table 2, the CO<sub>2</sub> concentration increased significantly as the cylinder temperature increased. A concentration of 9.8 ppmv CO<sub>2</sub> was measured in the ammonia at a cylinder temperature of 100°C.

Table 2: CO<sub>2</sub> concentrations measured in gaseous ammonia from a liquid dry cylinder (cylinder 3 in Table 1).

Cylinder Temperature (°C)	CO <sub>2</sub> Concentration (ppmv)
22	0.5
60	2.1
88	5.7
100	9.8

Based on our findings, ammonia gas delivered from cylinder sources may contain CO<sub>2</sub> in both free and complexed forms at levels up to ~100 ppbv. Higher levels can be expected if vaporized liquid sources are used or if the cylinder becomes liquid dry. As CO<sub>2</sub> is of potential concern in a number of microelectronic fabrication processes, a new purifier material has been developed and characterized for removal of both free and complexed CO<sub>2</sub> (ammonium carbamate) from an ammonia gas stream.

### Control of Free and Complexed CO<sub>2</sub> in NH<sub>3</sub>

The inorganic based NHX-Plus (Matheson Tri-Gas) purification medium was prepared and installed in the manifold as shown in Figure 2. To evaluate the purifier efficiency for removal of free CO<sub>2</sub>, the lines to and from the purifier (zones 1 and 2) were heated to 110°C. To evaluate the purifier efficiency for removal of complexed CO<sub>2</sub>, only the purifier outlet line to the GC instrument (zone 2) was heated (110°C). Heated lines in zone 2 were used so that any CO<sub>2</sub> present in the purified stream was decomposed and analyzed as free CO<sub>2</sub>. The results of the two experiments are summarized in Figure 6.

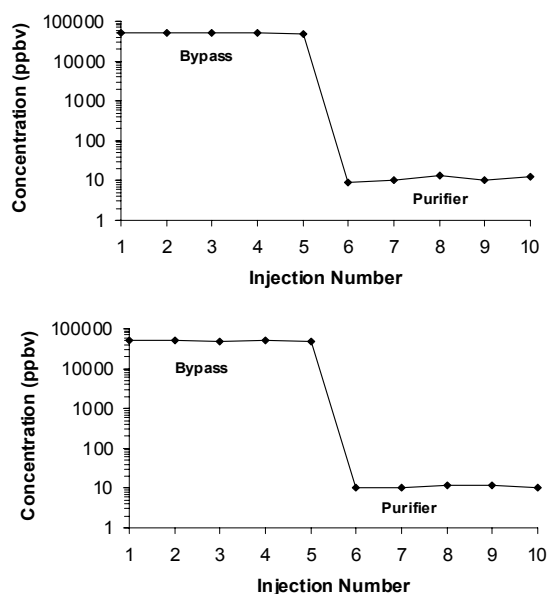


Figure 6. Efficiency experiment showing removal of 50 ppmv CO<sub>2</sub> in ammonia by NHX-Plus, Upper graph: removal of free CO<sub>2</sub> (zones 1 and 2 heated to 110°C). Lower graph: removal of complexed CO<sub>2</sub> (zone 1 unheated and zone 2 heated to 110°C).

Using a 50 ppm CO<sub>2</sub> challenge, the purifier demonstrated efficient removal of both free and complexed CO<sub>2</sub> in NH<sub>3</sub>, to below the detection limit of the GC-PDID.

An experiment was also carried out to determine the capacity of NHX-Plus material for CO<sub>2</sub> removal. The capacity was determined using a 500 ppmv CO<sub>2</sub> in He challenge at 1 slpm and by monitoring the CO<sub>2</sub> concentration in the purified stream at five minute intervals with the GC-PDID. A concentration of 1 ppmv in the purified gas stream was used as the cut-off criteria for determining breakthrough. The capacity test was performed in helium, rather than ammonia, to prevent formation of ammonium carbamate that otherwise blocked the purifier inlet and restricted the gas flow. The graph of CO<sub>2</sub> concentration in the purified gas stream with time in Figure 7 shows breakthrough of CO<sub>2</sub> occurring at 665 minutes. This corresponds to a capacity of 5.5 L CO<sub>2</sub> /L purifier material.

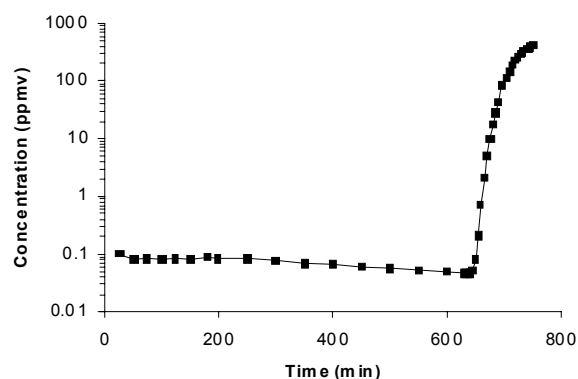


Figure 7. NHX-Plus purifier capacity experiment showing CO<sub>2</sub> removal to <50 ppb and breakthrough at 660-665 minutes. Challenge: 500 ppmv CO<sub>2</sub> in helium at 1 slpm.

### Conclusions

Due to the reversible reaction of CO<sub>2</sub> with NH<sub>3</sub> to form ammonium carbamate, any CO<sub>2</sub> impurity in ammonia will be present in the gas in free and/or complexed (ammonium carbamate) forms depending on the temperature and pressure conditions. Therefore, GC analysis of only the free CO<sub>2</sub> at ambient temperature is not representative of the actual levels in the ammonia gas. Accurate measurement of the CO<sub>2</sub> level is possible using heated manifold lines (110°C) to dissociate the ammonium carbamate back to the reactant gases, so that all the CO<sub>2</sub> is detected in the free form. The analysis of ammonia cylinders from various sources has shown that gas phase CO<sub>2</sub> levels are typically <100 ppb and liquid phase CO<sub>2</sub> levels are up to 2 times higher than the gas phase concentrations. This indicates that within the cylinder, the reaction equilibrium favors the ammonium carbamate product, which becomes concentrated in the cylinder heel as gas ammonia is withdrawn from the cylinder.

As the presence of ppb levels of carbon and oxygen-containing impurities in electronic grade NH<sub>3</sub> may cause

defects during the growth epitaxial nitride films, a new inorganic based purifier material has been evaluated for removal of CO<sub>2</sub> in NH<sub>3</sub>. Our results show that the purifier has a high capacity for CO<sub>2</sub> and is capable of removing both free and complexed CO<sub>2</sub> in NH<sub>3</sub> to below the detection limit of the GC-PDID.

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