Detection and Control of Oxy-Impurities in Group V Hydride Gases and Gas Delivery Systems

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Abstract. Trace oxygenated impurities are responsible for many undesirable effects in epi layers. Hydride gases are a significant source of oxygenated impurities. Some of these impurities concentrate within the cylinder as "iceberg" species in the liquid phase, either due to solubility effects, adduct formation or irreversible reaction. This complicates both analysis and control of gas phase impurities, as measured concentrations are unrepresentative and can change in gas phase over time. Moisture concentrations depend on gas-phase withdrawal conditions such as flow rate and increase over time as the cylinder empties. Other oxygenated impurities such as carbon dioxide may form adducts or other reaction products in the hydride gas. Efficient control of free and complexed oxy-impurities is key to the delivery of high purity Group V hydride gases. This work explores the identification of "iceberg" species in hydride gases and demonstrates their removal to detection limit by point-of-use purifiers specially developed to operate in hydride gas service.

Introduction

The control of defects in epi layers is critical to the performance of III-V compound semiconductor devices. Spurious contamination by trace impurities can cause unintentional doping, lattice defects, and undesirable oxide formation, particularly at interfaces between layers. Critical contaminant atoms include O, C, S, Se, Si, and Ge, as well as Group III and Group V heteroatoms.

There are many potential sources of trace impurities. They can be present in the process gases and organometallic precursors, in the carrier and purge gases, on the substrate, or they can be environmental contaminants such as trace atmospheric gases, oil and grease, cleaning solvents, etc. Unfortunately the killer defect level of trace impurities in epi layers is often below the detection limit of best available detection technology, and researchers are only just now beginning to uncover quantitative relationships between epi quality, atomic impurity levels, and source gas quality [1].

For this reason, process engineers have focused on contamination control using all available technology. Controls include use of the best quality source gases available, meticulous preparation of wafers prior to epi growth, thorough cleaning/passivation of wetted surfaces within the reactor and gas delivery system, and by vigilant exclusion of atmospheric contaminants at all stages of growth. Point-of-use (POU) purifiers can also play a valuable role in control of unintentional contamination in gas streams at the point of entry into the reactor.

In this paper, we will describe the identification of trace oxygen-containing impurities in hydride gases. These impurities are often difficult to detect due to their solubility in the liquid phase of the hydride gas, and/or their tendency to form adducts with the hydride gas during vapor transport. The removal of oxy-impurities from hydride gases by a new series of POU purifiers recently developed by us at Matheson Tri-Gas will be demonstrated. In particular, the successful removal of oxy-adducts will be demonstrated.

Experimental

Sampling of trace impurities in hydride gases was done either by conventional withdrawal of gas from the headspace of a cylinder, or by liquid phase withdrawal. For liquid phase sampling, the cylinder was inverted and a liquid sample was drawn off. The liquid sample was then vaporized completely by expansion at a controlled temperature. Samples were analyzed for impurity species by FTIR, GC-AED, or GC-DID.

The experimental details of FTIR [2] and GC-AED [3] measurements are described in detail elsewhere. GC analyses were performed on a Finnigan Model 9001 GC-DID with a Porapak PS column (10' x 1/8", 80/100 mesh) and a Porapak Q column (1.8m x 2mm; 80/100 mesh) at 55ºC. Samples and standards were

injected at 20 psig at 55ºC. The detector temperature was set to 150ºC, and the valve oven was set to 120ºC. Data were acquired and analyzed with EZ-Chrom software.

The quantitative behavior of trace oxy-impurities in a hydride gas stream was studied by preparing deliberately doped gas streams using a gas dilution manifold that mixes a calibrated amount of trace gas impurity into the matrix gas stream. This system has been described in detail elsewhere [2]. All instruments were calibrated for impurities *in the actual matrix gas* using this method.

To test for the presence of adducts of CO_2 with gases, the lines from the cylinder to the analytical instrument were selectively heated. A two-zone heating system allowed doped CO_2/matrix gas streams to be heated either upstream of a gas purifier, downstream of the purifier, both, or neither. Heating serves to break up any CO_2 adduct into free gases (vide infra) so that the amount of adduct could be detected as free CO_2.

Results and Discussion

From the perspective of both the gas vendor and grower, a key goal is to identify and remove critical impurities from process gases to a level where they no longer have an influence on device quality. Unfortunately, it is extremely difficult to measure or even detect many micro-contaminants, as contamination levels are not always above state-of-the-art detection limits of the best available analytical technology. Materials characterization techniques such as SIMS, PL, MPL, TEM, or GDMS can routinely measure killer impurities in epi materials at the level of 1E16 atoms-cc^{-1} and more rarely down to levels as low as 1E14 atoms-cc^{-1}. Direct analysis of the process gases by techniques such as GC, FTIR, AED, MS, APIMS can usually measure molecular impurities at the ppb-ppm level, and more rarely down the level of 10-100 ppt.

Recent work on the correlation of impurity levels in epi layers with electron mobility [1] has begun to identify hydride gases as the likely source of impurities such as silicon. However, there is mounting evidence that the killer defect levels of many impurities in epi material do not correspond to measurable impurities in the gases themselves [4].

The "Iceberg" Issue - Impurities in the Liquid Phase of Process Gases

Recent work by our group has focused on detection [2,3] and control [5] of trace impurities in the Group V hydride gases ammonia, arsine, and phosphine. Our results have begun to identify an important issue surrounding detection of impurities in condensed gases such as Group V hydrides. Because impurity measurements are traditionally made on the headspace gas of condensed gases, highly soluble impurities are often not accurately detected by conventional techniques. In effect, they are "iceberg" species, since the majority of their concentration lies unseen below the surface of the liquid.

One of our most significant discoveries has been the existence of trace moisture in the liquid phase of ammonia at concentrations up to 200 times that measured in the gas phase [2]. Figure 1 shows the partition of moisture between the gas and liquid phase of a cylinder of ammonia at near zero flow.
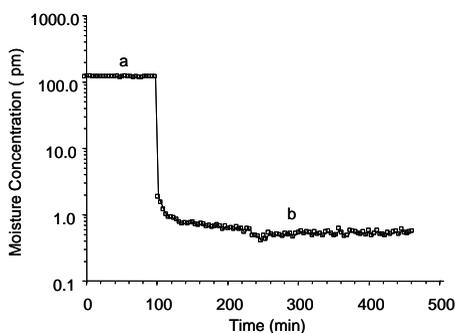

Figure 1. Moisture concentration in an ammonia cylinder sampled by FTIR from a) the liquid phase and b) the gas phase at near-zero flow.

Such measurements are made difficult by the fact that the gas phase moisture level is a strong function of gas flow rate, temperature, pressure and mixing, so that a stable value is nearly impossible to achieve except at zero flow. Figure 2 shows the variation of moisture from a cylinder of ammonia sampled gas phase.
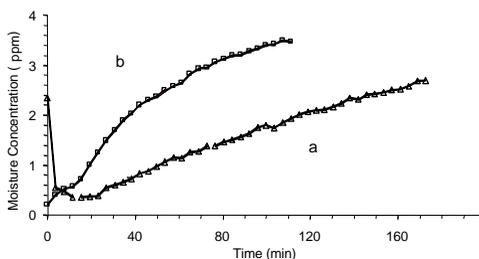

Figure 2. Time variation of gas phase moisture concentration (FTIR) from an ammonia cylinder sampled at two different flow rates: a) 2 slpm and b) 6 slpm.

Figure 3 shows similar results of sampling of two cylinders of phosphine. Thus a moisture spec for a hydride gas measured in the gas phase of a full cylinder does not give an accurate picture of the true amount of moisture in the cylinder.
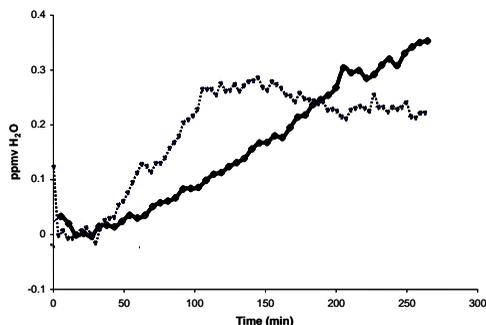

Figure 3. Time variation with of gas phase moisture concentration (FTIR) in two different phosphine cylinders sampled at the same flow rate of 1 slpm.

A consequence of the solubility of moisture in the liquid phase of hydride gases is that moisture builds up in the cylinder as the more volatile matrix gas is removed and the less volatile moisture is left behind. Figure 4 shows the rise in moisture level that results from this concentration effect. The spike of moisture observed at the end of the measurement indicates the point at which the liquid phase of the cylinder is used up and the remaining moisture if flash-evaporated into the gas phase.
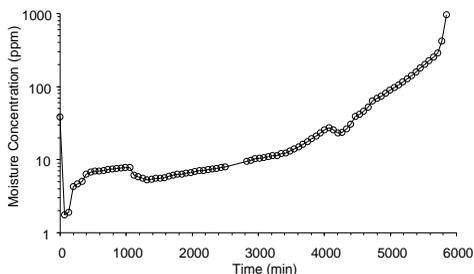

Figure 4. Moisture measured by FTIR in a standard cylinder of ammonia as the cylinder was emptied to dryness.

Mechanisms of Impurity Incorporation in Hydride Gases - Adduct Formation

The presence of liquid phase "iceberg" impurities is a particular problem for hydride gases, as they are excellent solvents, particularly for oxy-impurities. They are highly polar, can form hydrogen bonds, and are amphoteric, meaning they can act as either an acid or base to dissolve species of the opposite character.

In addition to dissolving, oxy-impurities can associate and also react with Group V hydrides. Figure 5 shows several ways that oxy-impurities are known to incorporate into the liquid phase of hydride gases. Acidic species such as CO_2 react readily with hydride gases to form reversible adducts that can in some cases react further. Hydride gases are also reducing agents and will react irreversibly with oxidizers. For example, arsine and phosphine are known to react instantly with molecular oxygen to form oxy-acids. Figure 5 includes the well-known reaction of O_2 with phosphine to yield a soluble orange substance commonly called LOOP - Lower Oxides of Phosphorous.
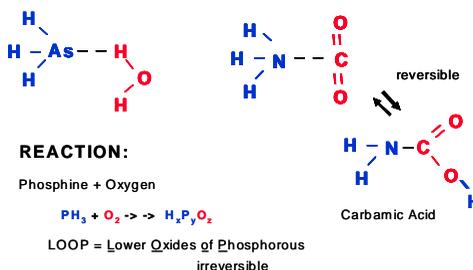

Figure 5. Illustration of the species formed by association and reaction of oxy-impurities with hydride gases.

Evidence of an adduct formation between CO_2 and hydride gas was observed by us for ammonia. To create the adduct, a known concentration of CO_2 was doped into an ammonia gas stream and analyzed by GC-DID for free CO_2.

The lines to the GC could either be heated or left unheated. Figure 6 shows the results of sampling ammonia doped with 50 ppm of CO_2 with and without heating the lines. Without heating, over half the free CO_2 is undetected in the gas that reaches the GC-DID analyzer. With heating, the CO_2 complex is readily broken up and the signal level of free CO_2 is close to that expected in an inert gas matrix.
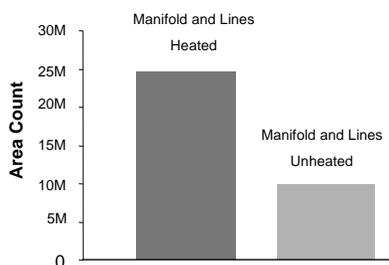
Figure 6. Free CO_2 detected in a gas stream of ammonia doped with 50 ppm of CO_2 and passed to the GC through heated vs. unheated gas lines. Flow rate was 0.5 slpm and line length was 3.5 m. Lines were heated to 145°C.

Control of Oxy-Impurities - Free Species and Adducts

Recently Matheson Tri-Gas has developed a series of purifier materials targeted for use in POU hydride gas purifiers for III-V epi growth [5]. These media are inert inorganic solids that remove moisture and oxy-impurities from arsine (ASX™), phosphine (PHX™), and ammonia (NHX™). More recently, NHX™ has been improved (NHX-Plus™) to give it the additional capability to remove molecular oxygen, a species that is stable in ammonia although not in arsine or phosphine.

These purifier materials have excellent efficiency for removal of moisture from hydride gases. Table 1 below shows a summary of data we have collected to date on performance of these materials in inert and hydride gases.

Impurity Tested	Capacity (L/L)	Efficiency (ppb)	Challenge (ppm)	Method
ASX™				
H_2O in Ar	31	<0.3 (D/L)	35	API-MS
H_2O in AsH_3	*	<75 (D/L)	3.5	MAH-2
$H_xAs_yO_z$	-	*	-	GC-MS
PHX™				
H_2O in Ar	35	<0.3	9	API-MS
H_2O in PH_3	*	<45	5	FTIR
$H_xP_yO_z$	-	*	-	GC-MS
CO_2 in He	6	<75	500	GC-DID
NHX-Plus™				
H_2O in Ar	31	<0.3	35	API-MS
H_2O in NH_3	22-25	<75	3.5	FTIR
CO_2 in NH_3	-	<11	25	GC-DID
O_2 in NH_3	1	<50	100	GC-DID
GeH_4 in NH_3	-	<1	0.5	GC-AED
SiH_4 in NH_3	-	<3	0.5	GC-AED
TEOS in NH_3	-	<40	640	GC-DID

* - Work in progress

Whether the purifiers are also active in removing adducts and reaction products of oxy-impurities, is an important question. Recently researchers at Nippon Sanso Corporation have seen evidence by GC-MS that PHX is capable of removing $H_xP_yO_z$ from phosphine [6]. We are currently working to investigate this phenomenon. We have also investigated the capability of NHX-Plus to remove adducts of CO_2 from an ammonia gas stream.

To study adduct removal, 50 ppm of CO_2 was doped into ammonia as in Figure 6. The gas stream was passed through a heated/unheated line, into a purifier/bypass circuit, and then through a heated line into the GC-DID for analysis. If the first line was heated, the CO_2 in the gas stream passed into the purifier/bypass circuit as free CO_2; if unheated, the majority of CO_2 passed into the circuit in adduct form. Thus the performance of the purifier for removing the adduct could be directly compared to its performance in removing free CO_2. The final gas line from the purifier to the GC was heated in order to break up all adduct so that it could be quantitatively analyzed as free CO_2 by the GC-DID. Results of the two experiments are shown in Figure 7.
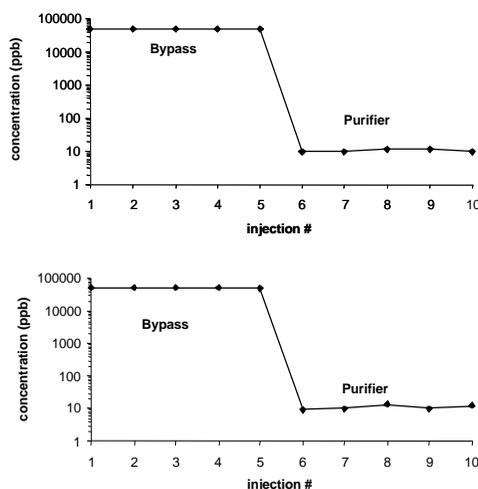

Figure 7. Removal of 50 ppm CO_2 from ammonia by NHX-Plus™ purifier. Top graph: free CO_2 (heated lines). Bottom graph: adduct (unheated lines).

Conclusion

Control of oxygenated impurities in Group V hydride gases is difficult to achieve, especially as impurities may be in the free or complexed form and may also concentrate in the liquid phase. Increasing moisture levels in

hydride gases such as ammonia and phosphine are observed during gas phase withdrawal from cylinder sources because such impurities concentrate in the liquid phase and are emitted at progressively higher concentration as the cylinder empties. However, other impurities such as carbon dioxide may react reversibly or irreversibly with the hydride matrix to form complexes, adducts or reaction products. Removal of all killer impurities including the "iceberg" species is essential to prevent contaminated gas from entering the reactor. A new series of point-of-use purifiers has been demonstrated and shown to be particularly effective for removal of these oxygenated species.

References

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