

Review of Integrated Contamination Control for GaAs and InP MOCVD Process

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1. Introduction

The demand for Light Emitting Diodes (LEDs), Vertical Cavity Surface Emitting Laser (VCSEL) and other compound semiconductor devices such as Hetero Bipolar Junction Transistor (HBT), High Electron Mobility Transistor (HEMT) and Field Effect Transistor (FET) has increased dramatically in recent year. The purity of hydride gases such as arsine and phosphine at the point of use significantly influences the quality and the yield of these devices [1], [2].

There are many sources of trace impurities. Each element in a gas distribution system as illustrated in Figure 1 potentially can be a source of contamination at the tool. Due to the different nature of contaminants and the different physical and chemical properties of processes of each species, a detailed technical understanding of the governing processes facilitates the control of impurity levels in the MOCVD process [3].

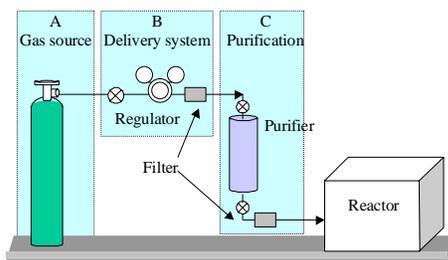


Figure 1. Source of contamination in gas distribution system

Point of use purification is vital to control the purity of gases at the point of tools since all the variance of impurity from cylinders and gas delivery system are minimized by the purifier. However, the lack of technical and operational understanding of process purifier sometimes leads poor performance of the purifier.

In this paper, we discuss the behavior of critical impurities in process gas cylinder, generation of contaminants from gas distribution system and point of use purification as solution for controlling those impurities.

2. Impurities in gas cylinder

Minimization of impurities in process gases is a key requirement for the growth of high quality III-V semiconductor devices. A detailed technical understanding of the source and nature of the most common contaminants as well as cylinder packages of process gases are essential to provide stable gas quality.

Since oxygen is not typically detected in arsine and phosphine cylinders, moisture is the contaminant of primary concern in arsine and phosphine gas cylinder. The degree of impact caused by moisture to crystal growth of III-V semiconductor depends on the concentration of impurities in process gases. According to previous studies by K. Matsumoto [2], 1 ppm of moisture caused defect in AlGaAs layer. Also H. Terao et al. [4], showed intentionally doped 0.1 ppm of oxygen caused low photoluminescence from AlGaAs.

As shown in Figure 2, our previous work [5] indicated that moisture in phosphine increased with the time of gas withdrawal. The moisture increases in phosphine is explained by the evaporation of the liquid phase of phosphine/water. The volatility of phosphine is several orders of magnitudes higher than that of water. The gas and liquid phase are expected to be in thermodynamic equilibrium during storage of the cylinder. When a cylinder valve is opened, a flow of true equilibrium gas is expected for some short time. Phosphine, however, evaporates at much higher rate than water based on its higher volatility. Therefore, water is

enriched at the surface. The moisture content of the evaporating phosphine depends on the liquid composition at the surface and therefore will increase if no effective mixing process with the bulk phase is present. Another possibility for causing the increase of moisture concentration is introduction of droplet into gas phase. Along with gas withdrawal temperature of gas cylinder becomes low due to the evaporation of liquefied gas. This cooling down of cylinder lowers the pressure inside cylinder and generates droplets. Introduction of the droplets that contains higher moisture increase the moisture concentration in gas. More detailed mechanism causing moisture increase in liquefied gas is discussed in Ref [6],[7],[8].

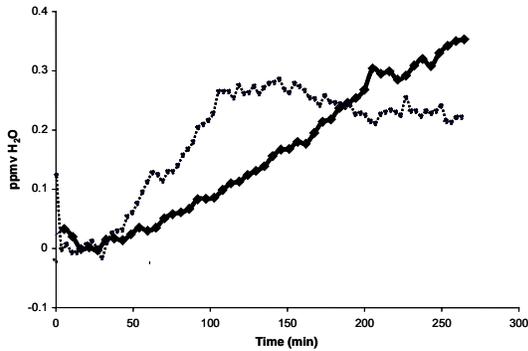


Figure 2. Time variation with of gas phase moisture concentration (FTIR) in two different phosphine cylinders sampled at the same flow rate of 1 slpm.

Cylinder package of arsine and phosphine is also an important factor for controlling moisture in arsine and phosphine. Conventional carbon steel cylinder used for hydride gases gradually generates moisture because of the reaction between hydrides and iron oxide of the internal carbon steel surface (1). Ikeda et.al.[7], showed that aluminum cylinder for arsine reduce the generation of moisture because aluminum does not react with arsine. Aluminum cylinder that was treated by new surface treatment method showed further reduction of moisture generation. Generally aluminum cylinder is used to high grade of arsine and phosphine and carbon steel cylinder is used to low grade or electronic grade of arsine and phosphine.



Impurities such as H₂S, SiH₄ and GeH₄ in arsine and phosphine are also critical [9], [10]. These hydride impurities are especially important for electronic device such as HEMT and FET. These impurities act as N-type dopant to lower the electron mobility and increases noise of HEMT and FET. As seen for the increase of moisture in phosphine cylinder, we also observed the increasing of H₂S measured by Gas Chromatograph with atomic emission detector (GC-AED). H₂S concentration in low grade of phosphine increased from single digit ppb to double digits ppb. This is probably because H₂S adsorbed on the internal surface of cylinder desorbed along with decrease of pressure of phosphine in the cylinder. Generally high grade of arsine and phosphine specify the level of hydride impurities but conventional electronic grade hydrides do not specify them.

Table 1 shows the comparison of electron mobility and carrier concentration for 9 μm thickness InP layer grown using high grade of phosphine and conventional electronic grade of phosphine (Matheson Trigas, Inc). High grade of phosphine was purified to remove moisture and hydride impurities by the state of art purification technique (Matheson Trigas, Inc) and was filled in aluminum cylinder. Conventional electronic grade phosphine filled in carbon steel cylinder contains higher moisture than high grade of phosphine and also does not specify hydride impurities. InP layer grown with high grade of phosphine achieved higher mobility and lower carrier concentration than those grown with conventional grade of phosphine.

Table 1. Electrical properties of 9 μm InP layers grown by low grade and high grade PH₃

Cylinder grade	Cylinder Package	Mobility (cm ² /V·s)		Carrier concentration (cm ⁻³)	
		77K	300K	77K	300K
Electronic -1	Carbon steel	143,000	4,700	3.9E14	3.0E14
Electronic -2	Carbon steel	138,000	5,500	4.6E14	3.9E14
High -3	Aluminum	173,000	4,950	2.9E14	2.4E14
High -4	Aluminum	205,000	5,600	1.7E14	1.2E14

Table 2 also shows the comparison of electron mobility and carrier concentration for 9 μm thickness GaAs layers grown using high grade of arsine and lower grade of arsine. High grade of arsine was purified to remove moisture and

hydride impurities by the state of art purification technique (Matheson Trigas, Inc) and was filled in aluminum cylinder. Lower grade of arsine was prepared for the purpose of comparison to high grade of arsine. It was only purified by the conventional purification technique without using the state of art purification technique and filled in Ni-lined cylinder. Therefore it contains higher moisture and presumably higher hydride impurities. GaAs layer grown using high grade of arsine demonstrated higher mobility than those grown using lower grade of arsine.

Table 2. Electrical properties of 9 μm GaAs layers grown by low grade and high grade AsH_3

Cylinder grade	Cylinder Package	Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)		Carrier concentration (cm^{-3})	
		77K	300K	77K	Room temp
Electronic -1	Ni-lined	105,000		0.65E14	
		7,000		0.75E14	
Electronic -2	Ni-lined	101,000		0.65E14	
		6,950		0.85E14	
High -3	Aluminum	188,000		1.0E14	
		8,700		0.8E14	
High -4	Aluminum	131,000		2.8E14	
		8,000		2.5E14	

Ikeda et.al.[9], measured electrical properties of 5-10 μm of AsGas layer grown by conventional electronic grade and high grade of arsine (Nippon Sanso Corporation). High grade of arsine used in the experiments was purified to remove moisture and silane. Average electron mobility of GaAs layer using high grade of arsine cylinders and low grade of arsine cylinders were 119,000 $\text{cm}^2/\text{V}\cdot\text{s}$ at 77K and 80,400 $\text{cm}^2/\text{V}\cdot\text{s}$ at 77K, respectively. These independent results showed better control of both moisture and hydride impurity is very important for the controlling electrical properties of device.

The controlling of moisture at point of reactor is critical to contamination control of MOCVD gas delivery system since moisture concentration from gas cylinder drastically increases as demonstrated above and also moisture is generated from gas delivery system. In order to better control moisture at the point of reactor, point of use purification can be the most effective solution. On the other hand, although the hydride impurities are generally not emitted from gas delivery system, as we stated in the previous section, H_2S in phosphine was found to increase with the consumption of the cylinder. The strict control of these impurities at

manufacturing site is critical for controlling these hydride impurities.

3. Contamination from gas delivery system

Gas delivery systems comprise of stainless steel tubing, gas regulators, mass flow controllers, particle filters and so on. These components are all potential sources of contaminants such as moisture, oxy-acids, particles and volatile metals. Especially gas particle filters are the most concern as moisture sources because of their high surface area.

Particle filters

Figure 3 shows moisture generation from metal and Teflon[®] particle filters exposed to arsine. These particle filters are dried down with purified nitrogen prior to their exposure to the gases. Metal filters generated very high moistures during the exposure to arsine even after dried out with nitrogen. The metal particle filter pre-baked at 250 degree C in purified nitrogen prior to the exposure to arsine did not generate moisture. This result indicates that moisture is not generated by the reaction between the filter material and arsine but due to the desorption of moisture from the surface of metal particle filter material. Even though it is commonly assumed that polymer materials such as Teflon[®] emit more H_2O than metal surfaces, well dried hydrophobic polymer surfaces often retain significantly less H_2O than the more hydrophilic metal oxide surfaces [11]. Due to the polar nature of AsH_3 or PH_3 , the strongly adsorbed H_2O that could not be removed by inert purge is displaced.

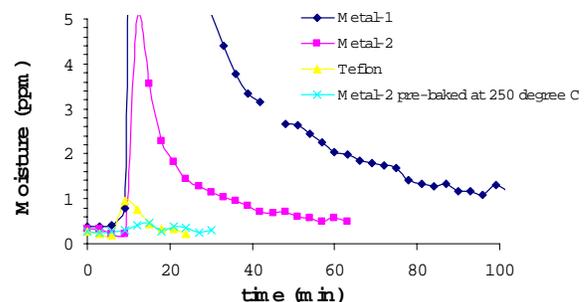


Figure 3. Moisture generation from metal particle filter and Teflon[®] particle filter exposed to AsH_3

This example illustrates that the choice of materials for the different components of the distribution system can strongly affect purge times and the ultimately achievable process gas purity levels at the point of reactor. Therefore metal particle filter should be avoided downstream of point of use purifier to prevent re-contaminate purified gases with moisture emission from particle filter unless metal filters are backed more than at least 250 degree C prior to their use.

Inline moisture analyzer

In line moisture analyzer based on high surface area device potentially becomes source of contamination in the gas distribution system. From our field experience, once the high surface device in moisture analyzer is contaminated with moisture, it takes for more than several days to be dried down even if the purified AsH₃ or PH₃ was used to dry down the device. Therefore, careful attention needs paying to use high surface area device in the system.

Oxygen impurity: Analysis

Our recent study indicated that small amounts of oxygen immediately react with arsine and phosphine to form oxy-acids. Improper purging of gas system while cylinder changes or slight leaks of VCR connections that are not detected by leak check procedure are possible oxygen sources. We measured oxygen concentration diluted in helium by gas chromatograph with pulse discharge ionization detector (GC-PDID) before and after the exposure of the system to arsine and phosphine. 100 ppb of oxygen from a standard gas cylinder was introduced into the system of gas chromatograph.

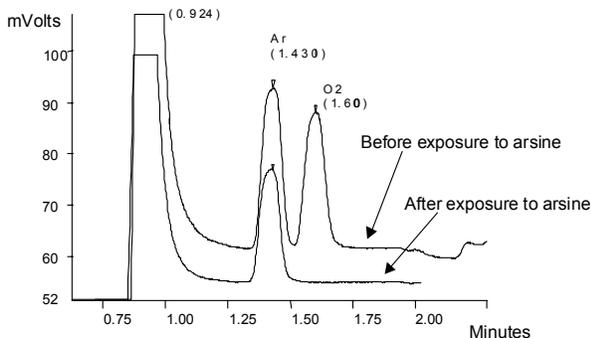
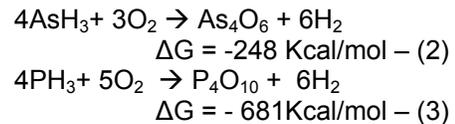


Figure 4. Oxygen peak measured by GC-PDID through piping system before and after exposure to AsH₃

As shown in figure 4, clear oxygen peak in helium observed for before the exposure of the system to arsine disappeared for after the exposure of the system to arsine. This indicates that oxygen reacted with residual arsine in the gas system. Similar results were observed with phosphine. The reactions of arsine and phosphine with oxygen to stoichiometric or unstoichiometric oxy-acid such as As_xO_y and P_xO_y are thermodynamically favorable as shown in (1) and (2). This result agrees with our empirical data that we did not observe the oxygen in arsine and phosphine.



Although there are no reports for the effective way to remove oxy-acids impurities, the use of point of use purifier is expected to minimize the influence of oxy-acids impurities.

4. Point of use purification

As we discussed in previous section, moisture impurity in process gas increase with the depletion of process gas cylinder. Moisture and oxy-acid impurities can be generated from the gas delivery system. Even though the highest grade of process gases are employed, the quality of process gases at the inlet of MOCVD reactor may not be as high as that at source of process gases. The point of use purification minimizes the influence of increase and generation of impurities from process gas cylinder and gas delivery system and provides the highest quality of process gases at the inlet of MOCVD reactor.

4-1. Quick dry down of system using arsine purifier

Figure 5 shows the dry down of the gas analytical system after the installation of arsine purifiers with different particle filter. Before the moisture drydown was measured proper start up procedure of the purifiers was performed. Although the arsine used to this test contained 3.5 ppm of moisture, both of the arsine purifiers with Teflon filter and 250 degree C -backed metal filter dried down the system to less than 100 ppb (the detection limit of the moisture analyzer) within 20 min. The results

demonstrated that proper selection of purifier component and proper start up procedure for the purifier can reduce the moisture in arsine in very short time.

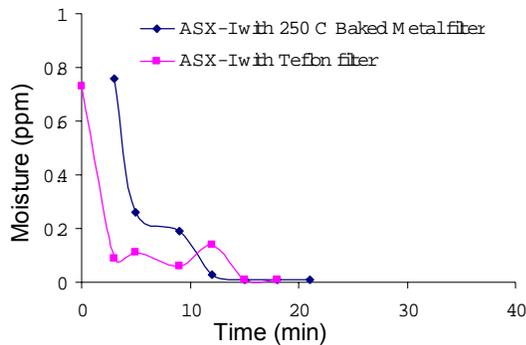


Figure 5. Dry down of the system using arsine purifier with different type of particle filters

4-2. Efficiency of Organometallic and inorganic purifier for phosphine service

Organometallic based purifier and inorganic based purifier materials are available for point of use purifiers for hydride gases. Generally organometallic purifiers are considered to have higher efficiency for the removal of impurities because of their very strong reactivity to oxygenated species. However, organometallic purifier requires very strict control of on site chemical conditioning with arsine and phosphine when it is employed in the system at the first time. On the other hand, inorganic base purifier does not require chemical conditioning in its start up procedure but is considered to be less efficient than organometallic purifier.

In order to compare the efficiencies of organometallic purifier and inorganic purifier in pure process gas, we measured moisture efficiencies of organometallic purifier (Nanochem OMX) and inorganic purifier (Nanochem PHX) in pure phosphine using FTIR. Phosphine cylinder that contains 5.2 ppm of moisture was used for the moisture efficiency test. 1 slpm of phosphine gas was introduced into Nanochem PHX and consequently the same gas was introduced into Nanochem OMX to compare the efficiency of two purifiers side by side. Figure 6 shows that both inorganic Nanochem PHX purifier and organometallic Nanochem OMX purifier removed moisture in phosphine below 33 ppb that is the detection limit of FTIR for the moisture in phosphine. It was found that the efficiency of inorganic Nanochem PHX purifier is the same as

that of organometallic Nanochem OMX purifier under the detection limit of 33 ppb.

Ultimately organometallic based purifiers can have better efficiency than inorganic based purifiers, inorganic based purifiers are recommended for a point of use purification because of their easier startup conditioning procedure.

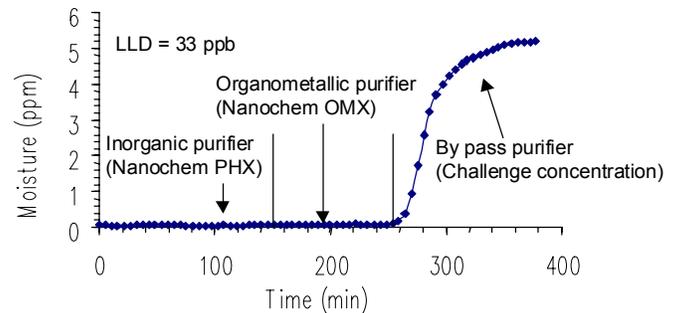
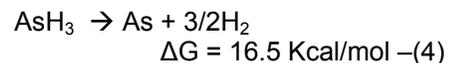


Figure 6. Efficiency of organometallic purifier (Nanochem OMX) and inorganic purifier (Nanochem PHX) for moisture in PH₃ measured by FTIR

4-3. Pressure-build-up for arsine purifier

Since arsine has positive Gibbs free energy of formation (4), the decomposition of arsine into arsenic and hydrogen is thermodynamically favorable and can be triggered by the contact of arsine with high surface area of purifier material.



The decomposition of arsine into hydrogen and arsenic can cause the build up of pressure in the purifier when the purifier is isolated. Figure 7 shows a typical pressure-build-up curve of newly installed Nanochem ASX-I purifier. The rate of pressure increase decreases with the exposure time of purifier to arsine. Arsenic formed by the arsine decomposition gradually covers the catalytically active site of purifier material. When the sites are completely covered with arsenic, the arsine decomposition ends.

The decomposition of arsine on purifier material has been reported by another purifier manufacture. For example, Scoggins et.al.[12], reported that MgH₂ base purifier increases the pressure in the purifier by 2 – 3 times of initial pressure in 6 - 12 hours.

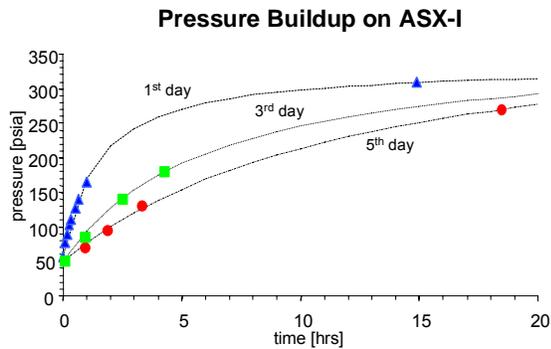


Figure 7. Typical pressure-build-up curve of newly installed Nanochem ASX-I purifier isolated with pure AsH_3

To address safety concern of arsine purifier, Nanochem ASX-II purifier that do not build pressure was developed by Matheson Trigas Inc. Figure 8 shows the comparison in pressure build of Nanochem ASX-I purifier and ASX-II purifier. Nanochem ASX-II purifier demonstrated stable pressure for more than 50 hours. Also, the moisture efficiency test for Nanochem ASX-II purifier demonstrated the purifier removed 9 ppm of moisture in arsine to less than 100 ppb (the detection limit of moisture analyzer). Generally the employment of arsine purifier requires awareness of purifier characteristics for the safe operation.

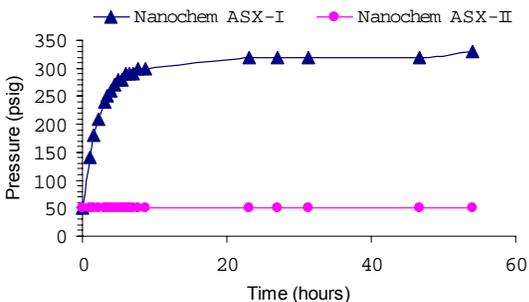


Figure 8. Comparison of pressure-build-up between Nanochem ASX-I purifier and newly developed Nanochem ASX-II purifier for AsH_3

5. Summary

Integrated contamination control for efficient operation of GaAs and InP MOCVD process requires detailed technical understanding of the governing process from process gas source to at the point of reactor. For the controlling of hydride impurities in arsine and phosphine can

be only managed by gas manufacturing site. For oxygenated contaminants such as moisture and oxy-acid, impurity partitioning in liquefied sources between gas and liquid phase, chemical reactions of the impurities with matrix and dry-down of delivery system such as particle filter and valves have to be considered. Point of use purifier minimizes contaminants but requires better understanding of its employment into the process. Integrated management for contamination control including gas source, appropriate component selections and use of point of use purification are recommended for optimized process control.

Reference

- [1] J.Newey, Compound Semiconductor 12 (2001) 51-54
- [2] K.Matsumoto and K.Uchida, Denki-Gakkai research report, EFM-90-34 (1990), 9p
- [3] T.Watanabe, H.Funke, R.Torres, M.W.Raynor, J.Vininski, V.Houlding, ICMOVPE 2002, TueP26
- [4] H.Terao and H.Sunakawa, J.Crystal Growth, 68, (1894) 157-162
- [5] M.W.Raynor, D.Sims, H.H.Funke, T.Watanabe, D.Fraenkel, J.Vininski, R.Torres and V.Houlding, Proceedings of CS-MAX (2001)
- [6] H.H.Funke, M.W.Raynor, B.Yücelen and V.Houlding, J.Electronic Materials, Vol.30, No.11, 2001
- [7] B.Jurcik, R.Udischas and H.C.Wang, Proceeding of Institute of Environmental Sciences, 1997, p73
- [8] H.C.Wang, R.Udischas and B.Jurcik, Proceeding of Institute of Environmental Sciences, 1997, p6
- [9] T.Ikeda, H.Noda, K.Matsumoto, J.Crystal Growth, 124, (1992) 272-277
- [10] T.Watanabe, D.Fraenkel, R.Torres, M.W.Raynor and V.Houlding, R.Kirk, Proceedings of ICMOVPE, 2000 We-B11
- [11] H.H.Funke, M.W.Raynor and V.H.Houlding, Solid State Technology, May Supplement: Contamination Control (2000) S1-S3
- [12] T.Scoggins and J.Snow, Mykrolis application notes "Purification of arsine and phosphine", www.mykrolis.com