Developments in Abatement Technology for MOCVD Processing

Joseph Sweeney[1], Paul Marganski[1], Karl Olander[1], Tadaharu Watanabe[2], Nobuyasu Tomita[2], Gary Orlando[3], Robert Torres[3*]

ATMI[1]
7 Commerce Drive, Danbury, CT 06810

Nippon Sanso Corporation[2]
Electronics Business Division
1-16-7, Nishi-Shinbashi, Minato-Ku, Tokyo 105 Japan

Matheson Tri-Gas[3]

Advanced Technology Center
1861 Lefthand Circle, Longmont, CO, 80501, USA.

*denotes corresponding author. Contact information for corresponding author is listed below.

Robert Torres, Ph.D., R&D Manger of Gas Technology, Advanced Technology Center
1861 Lefthand Circle, Longmont, CO 80501 Office Phone: 303-678-0700 x315
rtorres@matheson-trigas.com

Abstract
A newly developed technical solution has been developed for hydride gas abatement that utilizes a new material. The ULTIMA-Sorb™ material provides high capacity but low heat of reaction with the hydride gases. The new technology results in a low cost of ownership (COO) with stable operation and also reduces the cost and quantity of waste disposal. This can be significant benefit for device manufacturers since it provides a viable and cost effective solution without any risk of arsenic leakage that is a primary concern with wet chemical scrubber systems. The contents of this paper will discuss the technical and economic benefits of the newly developed material in comparison to conventional abatement materials and systems. The capacity of the dry abatement materials significantly influence both COO relating to cash outflow and the cost of lost production. High capacity materials enable significant savings in cost of lost production in cases of low and high factory utilization conditions. Capacity of the abatement material appears to be the largest single factor to reduce COO of dry abatement systems.

KEYWORDS: A1. Abatement, B1. Arsenates, B1. Cuprates, B1. Phosphates

1. Introduction

Conventional abatement systems for MOCVD applications typically employ wet scrubbers due to their low cost. However, wet scrubber systems require many maintenance and service operations and also risk environmental contamination due to liquid leaks containing arsenic materials. Carbon based dry scrubbing materials have also been utilized and have offered the lowest cost solution in the dry scrubber abatement materials. However, carbon based materials also require many maintenance operations upon regeneration of the material. Carbon requires many regenerations due to the inherent low capacity of the material to remove hydride gases. Copper oxide based technology provides high capacity but is not cost effective due high raw material cost. Additionally, copper oxide based technology causes undesirable thermal runaway reactions and can influence the operation of the MOCVD manufacturing process.

2. New Abatement Solution

2-1. Advanced Layering Technology

The new gas adsorbent has been developed for use in dry scrubbing abatement systems. The adsorbent is specifically designed to remove toxic species, such as arsine and phosphine, from the effluent of MOCVD reactors, and combines the strengths of two different materials. One material provides high sorptive capacity with a low heat of reaction, while the other material is a high-efficiency polisher that serves to maintain the bed outlet concentration below threshold limit values (TLV's). The combination of the two materials has yielded an adsorbent with an overall sorptive capacity 2-5 times greater than commonly used materials such as impregnated carbon or copper oxide. The significant improvement in capacity enables longer uptime of the abatement system, reduces overall waste, and lowers cost-of-ownership relative to other adsorbents. Figure 1 shows the relationship of the inlet gas concentration of the hydride gas as it enters and traverses the length of the abatement bed. The top part of Figure 1 shows the expected trend for a material that has superior capacity but inferior efficiency compared to other materials used. The middle part of Figure 1 shows the expected trend for a material that has superior efficiency, but inferior capacity. By combining the two materials together, the overall result is that the abatement bed can be used with higher capacity while never exceeding the TLV threshold of the toxic hydride gases.

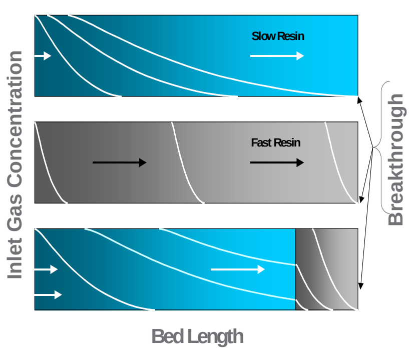

Figure 1. Depicts the different mechanisms of hydride abatement for different materials.

2-2. Capacity comparison

Figure 2 shows the capacity range obtained for the Ultima-Sorb material in comparison to the commonly used materials of copper oxide and carbon. The results show that the Ultima-Sorb material has significantly higher capacity than the other materials tested. All three materials were tested under identical conditions. Additionally, the Ultima-Sorb was tested under two different space velocities in an attempt to correlate the effect of higher flow rates on capacity to remove the hydride gases.

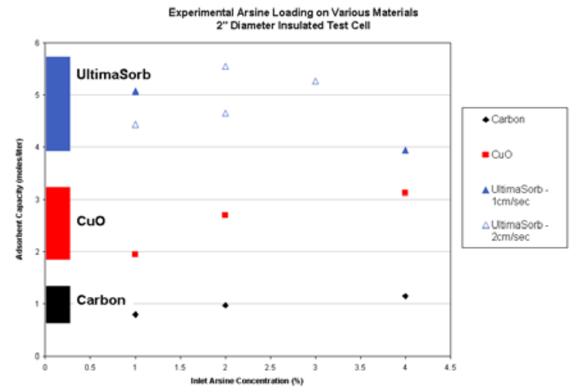

Figure 2. Capacity comparison of Ultima-Sorb, copper oxide, and carbon tested under identical experimental conditions.

2-3. Comparison of heat of generation

In addition to capacity and cost considerations, there has been significant concerns raised over the excessive heat observed while using dry scrubbing abatement systems. Figure 3 shows the results obtained from measuring the internal temperature for 3 different materials tested in identical hardware and experimental conditions. The hydride gas concentration was increased at a constant flow rate and the internal temperature of the bed was measured. The results show that copper oxide generates the highest temperature followed by Ultima-Sorb and then carbon. It is believed that carbon generates the smallest amount of heat upon exposure to hydride gases since the mechanism of removal of the hydride gas for carbon is based on physisorption and not a chemical reaction. Alternatively, the copper oxide and Ultima-Sorb undergo chemical reactions with the hydride gas and generate more heat than the carbon material. In addition, the results shown in Figure 4 show that at a temperature less than 80 °C, copper oxide undergoes reduction by hydrogen. Once this event occurs then a run-away reaction can take place within the abatement canister where elevated temperatures can cause a dangerous situation to occur. Figure 4 also shows that the Ultima-Sorb materials appear to be stable to hydrogen reduction when tested against copper oxide under identical conditions. No significant temperature increase was measured for the Ultima-Sorb material.

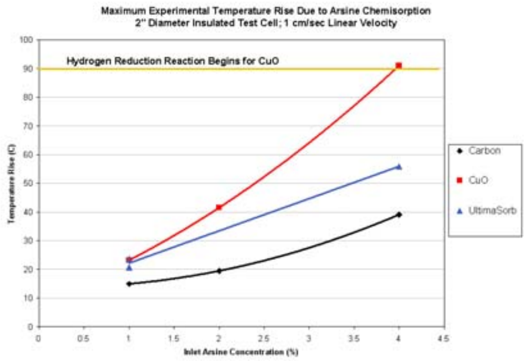

Figure 3. Comparison of internal temperatures for carbon, copper oxide, and Ultima-Sorb as a function of increasing hydride gas concentration.

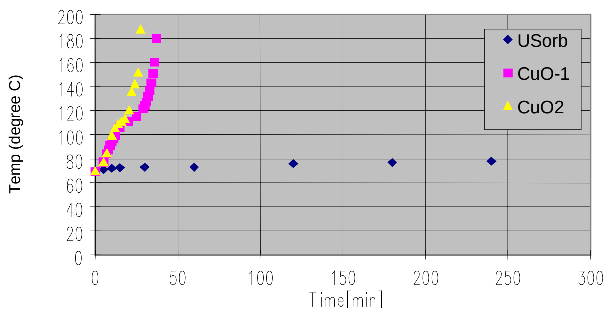

Figure 4. Comparison of internal temperatures for two samples of copper oxide (CuO-1 and CuO-2), and Ultima-Sorb.

In addition to the laboratory experiments conducted to measure the temperature excursions of the carbon, copper oxide and Ultima-Sorb, several field trials of the Ultima-Sorb materials were conducted to measure temperature profiles of the Ultima-Sorb material under actual field conditions. Figure 5 shows the temperature profiles of four different thermocouples imbedded internally into the commercial abatement canister. The results show the temperatures within the Ultima-Sorb material as the MOCVD reactor is running and producing actual devices.

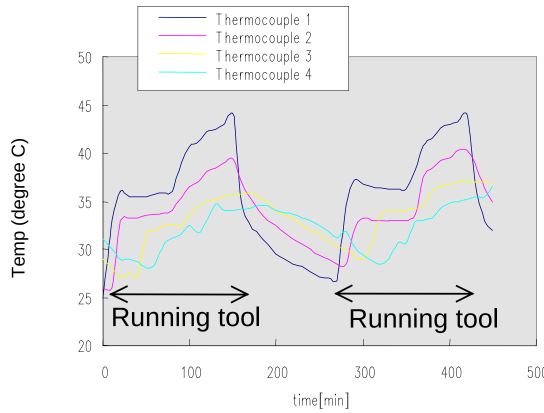

Figure 5. Internal temperature measurements from a commercial abatement canister filled with Ultima-Sorb material during actual production of MOCVD devices.

In an additional actual field trial, Ultima-Sorb was installed into a commercial abatement canister and challenged with approximately 0.9% Arsine, balance hydrogen, at a linear space velocity of 1.2 cm/sec. The results, shown in Figure 6, demonstrate the maximum temperature observed with the Ultima-Sorb material was less than 45 °C. The test was conducted over a long period of time that lasted well over 150 hours of MOCVD processing time.

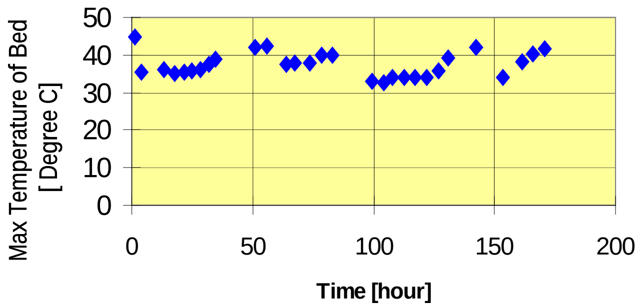

Figure 6. Internal temperature measurements from a commercial abatement canister filled with Ultima-Sorb material during actual production of MOCVD devices.

3. Cost of Ownership Comparison

The cost of ownership is still the most important factor for manufacturers of III-V devices. Based on ATMI's knowledge and experience in abatement business, the capital cost required for installing the dry abatement system and wet chemical system has been estimated and has been considered to be equivalent. The cost of ownership has been compared for ULTIMA-Sorb to conventional dry abatement materials such as copper oxide, copper oxide impregnated carbon and pure carbon from a cash outflow point view and over all cost of ownership. This also included lost production due to production down time for the maintenance of abatement system. For comparison purposes, the capital required for installing the abatement systems have been excluded. The following section involves the comparison of cash outflow for the various dry abatement materials under the circumstances when facility utilization is low. This case was selected to simulate business conditions when the semiconductor industry is relatively stagnant due to economic conditions. In addition, the comparison of over all cost of ownership including lost production has been made for the various dry abatement materials under the circumstances when facility utilization is high. This case was selected to simulate business conditions when the semiconductor industry is relatively active due to economic conditions. Finally, the cost of ownership for the ULTIMA-Sorb material was compared to that of a wet chemical scrubber.

3-1. Comparison of COO relating direct cash outflow (low utilization at facility)

In this COO comparison, the focus was on the operational cost of abatement that does not include initial capital requirements for installing abatement system. As previously described, the estimated capital cost required for installing the dry abatement system and wet chemical system was considered to be equivalent. During periods of low utilization of the manufacturing facility, the manufacturer's primary concern involves the amount of cash spent on the abatement of hydrides. The maintenance time for bed replacement is not a primary factor since the MOCVD tool is not used 100 percent of the time under these business conditions.

Basic factors to formulate a cost of ownership for dry abatement scrubbers directly relating to cash outflow is shown below.

- A: Capacity (mol/L)
- B: Material cost ($/L)
- C: Disposal Cost ($/L)

The COO equation is:

COO ($/mol-hydride) =(B+C)/A   Eqn.(1)

The COO equation expresses the cost required to abate one mole of hydride gas. Capacity is defined as a number of hydride moles abated with one liter of a material. Material cost is the actual cost paid for a liter of material by a user of abatement scrubber. Disposal cost is the required cost for disposing a liter of spent material. This cost is estimated for the cost of disposing spent material through incineration or landfill and also the cost of cleaning a canister for refilling with the new material.
It is obvious that the capacity of dry abatement material is very sensitive to COO and proportionally contributes to lowering the COO. The higher capacity of material also contributes indirectly to lowering the COO by reducing the amount of disposed spent material. It also significantly influences the "up" time of facility during high facility utilization conditions. A direct comparison of the capacity of four different dry abatement materials is shown in Figure 7.

Summary of capacity for various materials

Material	Capacity for hydrides (mol/L)
ULTIMA Sorb	4.4-5.5
CuO	1.9-3.1
CuO/Carbon	0.8-1.1
Carbon	0.2-0.4

Figure 7. Comparison of capacity for different dry abatement materials.

The capacity of dry abatement materials vary depending on the superficial liner velocity and hydride concentration as shown in previous sections, however the capacity values reported herein were obtained under similar conditions. Figure 7 summarizes the capacity ranges of the various materials since experimental error prevents obtaining identical values upon measurement of replicate samples. The results show ULTIMA-Sorb has a significant advantage for lowering the COO because of the demonstrated higher capacity compared to other material candidates.

The range of material cost for those materials is $6/L-$60/L depending on materials. Carbon based material tends to be priced relatively low in the market. Disposal cost is estimated to be \$4.5/L for all the materials.

Based on above information, the range of the COO has been estimated for the discussed materials. Figure 8 shows the results of calculations. ULTIMA-Sorb shows the lowest COO followed by CuO/Carbon, CuO and Carbon. This is primarily due to ULTIMA-Sorb's high capacity.

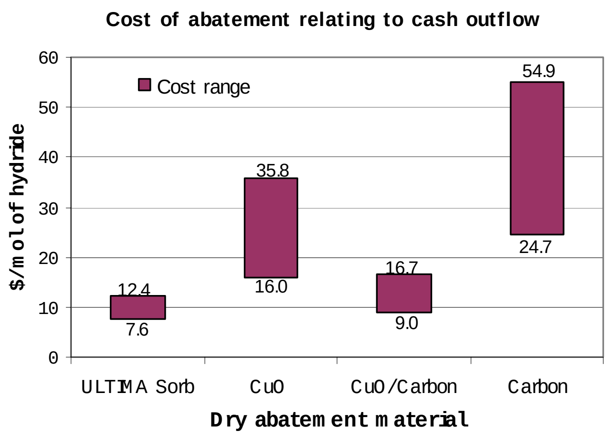

Figure 8. Cost comparison of the different dry abatement materials for conditions of low facility utilization.

3-2. Comparison of COO including lost production (high utilization at facility)

During conditions of high facility utilization, the cost of lost production becomes important as well as the cost directly relating to cash outflow from abatement operations. In most cases, the cost of lost production is much larger than the direct cash costs relating to cost of abatement.

As shown below, additional factors have been introduced into the COO model to incorporate the aspects of high facility utilization. The COO model and formulated equation is shown by equation (2).

- D: Labor cost (\$/h)
- E: Change out time (h)
- F: Tool down time per change out (h)
- G: Lost production cost (\$/h)

COO equation is:

COO=((B+C)+D*E+F*G)/A Eqn.(2)

Equation 2 includes labor cost and lost production cost in addition to material and disposal costs. Labor cost is hourly charge for changing out a canister when the material is completely spent and replacing with a canister containing new abatement material. The labor cost was estimated it to be \$20/h. Change out time is defined as the time required to remove the spend canister, eliminate the contents of the spent canister, insert new abatement material, and install the new canister. The change out time was estimated it to be 6 hours per change out. The wafer tool down time per change out was estimated to be 8 hours. Lost production cost was considered to be monetary loss from potential products that could have been produced during tool down time due to canister change out. Lost production cost was estimated to be from \$300/h to \$700/h. Based on the above estimations, the overall COO of each material was estimated using the same values for D, E, F, and G.

Figure 9 shows the results of the calculations. During conditions of high factory utilization, the advantage of ULTIMA-Sorb was much more significant compared to CuO/Carbon, CuO, and Carbon.

The primary advantage of the ULTIMA-Sorb material is derived from the demonstrated high capacity. The high capacity performance of the ULTIMA-Sorb minimizes the cost of lost production by reducing down time attributed to canister change outs.

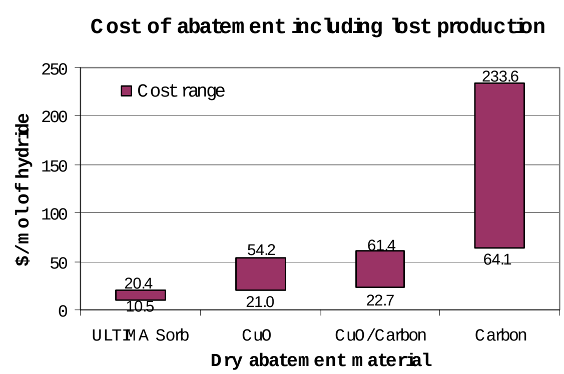

Figure 9. Cost comparison of the different dry abatement materials for conditions of low facility utilization.

3-3. Comparison of ULTIMA-Sorb to a Wet Scrubber System and Combustive Scrubber System

The COO relating to direct cash outflow of ULTIMA-Sorb was compared to a wet scrubbing system. The COO of a wet chemical scrubber system was estimated by assuming a 75,000 gallon per year aqueous discharge containing 3600 lbs./yr of NaOCl and 2000 ppm of the abated hydride species. Based on the aforementioned assumptions, the COO of a wet chemical scrubber was estimated to be $6.4/mol -$7.6/mol. Therefore the COO of a wet chemical scrubber system is nearly equivalent to the COO of the ULTIMA-Sorb. This cost estimation indicates that the ULTIMA-Sorb dry abatement material can potentially be used to abate hydrides at nearly the same cost as wet chemical scrubber without the detriments of the wet chemical scrubber.

Combustive or thermal oxidation has been used as an abatement method. The combustive type abatement system is a simple burner or "burnbox". These units use natural gas or hydrogen as a fuel to create a very hot reaction chamber. Effluent gases from the MOCVD reactor are oxidized in the flame to form the respective products As_2O_3, P_2O_5, and water vapor. The arsenic and phosphorus oxides are solids at room temperature and have the potential to accumulate in the exhaust lines of the scrubber. Particulate that remains entrained in the exhaust stream must be filtered.

In commercial applications the combustive part of the system is often combined with a wet scrubber. Effluent gases from the MOCVD reactor are first oxidized in the thermal unit. The majority of the solid by-products are then removed in the absorption tower. Very small particulate (e.g. submicron in size) may require additional separation means. The main advantage afforded by combustive or thermal and thermal-wet treatment systems is the relatively low cost of required consumables – namely fuel, electricity, and filters.

Disadvantages include: a) potentially hazardous maintenance operations due to pipes and ducts clogging with arsenic-containing compounds, b) relatively high capital cost, c) significant cooling requirements due to the presence of high concentrations of hydrogen in the effluent stream, and d) the requirement to handle and treat aqueous arsenic waste in the case of thermal-wet systems.

3-4. Summary

The capacity of the dry abatement materials significantly influence both COO relating to cash outflow and the cost of lost production. High capacity materials enable significant savings in cost of lost production in cases of low and high factory utilization conditions. Capacity of the abatement material appears to be the largest single factor to reduce COO of dry abatement systems.

As shown in Figure 10, ULTIMA-Sorb achieves the lowest COO among other materials and has the closest COO to that of wet chemical scrubber. Since the installation cost of dry abatement scrubbers and wet chemical scrubbers are essentially equivalent, the dry abatement materials can be significant benefit for MOCVD device manufacturers.

Range of COO for various technologies

	COO relating to cash out flow ($/mol)	COO including Non-cash relating cost ($/mol)
ULTIMA Sorb	7.6-12.4	10.5-20.4
Copper	16.0-35.8	21.0-54.2
Copper/Carbon	9.0-16.7	22.7-61.4
Carbon	24.7-54.9	64.1-233.6
Wet Chemical	6.4-7.6	-

Figure 10. Cost of ownership comparison relating to cash and non-cash costs for all hydride gas abatement systems.

4. Conclusion

Matheson Trigas and ATMI have developed advanced materials and layering technology to provide the highest capacity material for the abatement of hydride gases. The ULTIMA-Sorb material demonstrated the lowest COO among other competitive materials due to its high capacity. The ULTIMA-Sorb material also showed the greatest benefit under high factory utilization conditions. ULTIMA-Sorb also achieves the closest COO to that of wet chemical scrubber system. This can be significant benefit for device manufacturers since it provides viable and cost effective solution without any risk of arsenic leakage that is a primary concern with wet chemical scrubber systems.