



# Ion Implanter Cross Contamination And Maintenance Safety Considerations With High Dose Phosphorus

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**Abstract.** The contamination on previously implanted Phosphorus into other species, known as “implant memory” has been previously reported with emphasis on diffusivity of the P in As (or Sb) [1,2,3]. This study continues some of the investigations done earlier but with some additional focus on some safety considerations. The residual Phosphorus or Arsenic in beamlines, target chambers and on implant disks has resulted in emissions of PH<sub>3</sub> or AsH<sub>3</sub> exceeding the TLV locally for extended periods during maintenance. Measurements taken during the cleaning of P contaminated ion source chambers in situ or on a bench top show that the maintenance technician can be exposed to PH<sub>3</sub> levels in excess of several hundred ppb or more. Freshly created PH<sub>3</sub> is available during maintenance due to the reaction of water vapor and AIP and AIs in quantities that need attention. Certainly self-contained breathing apparatus is used for gas bottle changes but that use is not always dictated for cleaning of major subassemblies whether in place (on the implanter) or under a designated, remote work area – and it should be in these circumstances.

**Keywords:** Cross Contamination, Autodoping, Toxic Gas, Phosphorus, Hydrides, Aluminum Phosphide

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## INTRODUCTION

The safety protocols for proper handling of Phosphine and Arsine gas bottles are well documented [4,5]. These protocols have remained essentially unchanged with the introduction in late 1992 of sub-atmospheric gas delivery systems [5,6]. Many fabs use solid materials (elemental Arsenic, elemental Antimony and other solids) in a vaporizer to make a gaseous state available in the ion source, due often to company or local regulations. This study is a result of data and information collected at many locations and from results at an implant foundry where a higher than normal % of Phosphorus is run. A reluctance to running Phosphorus in some fabs, especially high dose Phosphorus is due to the cost of implanter dedication in order to avoid cross contamination [3] at their own location or to simply reduce the long, high dose implants.

Hydride emissions from two types of high current implanters were assessed – Axcelis GSD and Varian VIISion. Both of these implanters use full wheel disk/platens. Care was taken to assure that a minimum of exposure to the local atmosphere (with a general relative humidity/RH = 50%) was maintained during measurements.

## CONTAMINATED IMPLANTER ASSEMBLIES

There have been many discussions in the implant industry of the so-called “implant odor” when opening a beamline or a target chamber after prolonged use with As or P operation. This odor is present even in cases where no hydride precursors have been used [8]. Maintenance routines that expose Phosphorus or Arsenic coated implanter assemblies to the water-laden atmosphere can create potentially hazardous levels of PH<sub>3</sub> and AsH<sub>3</sub> if proper precautions are not taken. Two very enlightening reports [7,8] show how the hydrides of Arsenic and Phosphorus can be created from deposited P and As - additional mechanisms for the creation of PH<sub>3</sub> and AsH<sub>3</sub> are shown later. Given a further understanding of the various mechanisms for hydride formation, proper safety guidelines can be incorporated into maintenance procedures. One product group at the authors’ Sunnyvale facility refurbishes implanter disk/wheels for fabs worldwide. When the disks are cleaned, using a wet-slurry cleaner, there are often noticeable odors during the early stages of the cleaning. Extensive tests have been done using a

portable gas detection system (MST-Satellite) bearing in mind the LDL of 0.05 ppm for PH<sub>3</sub> and a LDL of 0.005 ppm of AsH<sub>3</sub>. During these times when heavily implanted (with P and/or As) disks were cleaned different reports of odor were acknowledged, and measurements were taken. There has been no detectable PH<sub>3</sub> or AsH<sub>3</sub> using the appropriate gas detector sensor (for MST-Satellite). The odor threshold of PH<sub>3</sub> is often reported to be 0.14 ppm and the odor threshold of AsH<sub>3</sub> is often reported as 0.5 ppm. No detectable PH<sub>3</sub> or AsH<sub>3</sub> during disk decontamination is consistent with a previous study [8]. Several people have been questioned during times when odors are present and they odors are characterized as “fishy”, “garlic”, “metallic” or “carbide”. The fishy and carbide are indicated as characteristic odors in selected AIP MSDS (11). Selected agencies have indicated the odor threshold of Phosphine in a range from as low as 0.01 PPM up to 5.0 ppm depending on various conditions, i.e., relative humidity. See Table 1 for selected agency or organization reports.

Agency	Odor Threshold (ppm)
NIOSH (Traditional)	0.14
CHRIS; Chemical Hazard Response Information System (US Coast Guard)	0.14
AAR; American Association of Railroads. Bureau of Explosives.	0.02
AIHA; American Institute of Industrial Hygienists	0.01 - 5.0

The strength of the odor gives no indication of the PH<sub>3</sub> concentration [13].

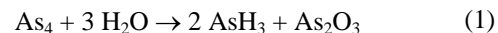
## HYDRIDE PRODUCTION MODELS

One report [7] related to MBE chambers showed that relatively high amounts of AsH<sub>3</sub> were detected

Disk Type	Disks Tested (#)	With Disk in Place	Chamber Walls (Disk Removed)	Notes
GSD	2	a) 30 - 50 (coated) b) 80 - 100 (uncoated)	a) 20 - 30 b) 30	Measurement < 10 sec after door open (High P dose run just prior to test)
VIISion	1	40	20 - 40	Disk pulled out of chamber. Chamber with N2 bleed. Phosphorus was ~ 40% of use.

Several series of tests were done on implanters or implanter assemblies at several locations in the US and Asia. Some of the maintenance activities showed some

when no AsH<sub>3</sub> was used – only solid Arsenic. Two tentative reactions (1,2) were subsequently proposed:



The same types of reactions are expected with P<sub>4</sub> or 2P<sub>2</sub> respectively [9]. Another well documented hydride release is from the formation of Aluminum Arsenide (AlAs) or Aluminum Phosphide (AlP) [10]. The majority of the implanter vacuum system (including the disk in the case of many high current, batch implanters) is made of 6061 T6 Aluminum. The AlP (or AlAs) in the implanter may react with water vapor - generally a fixed, repeatable % in fabs, and create measurable amounts of PH<sub>3</sub> (or AsH<sub>3</sub>). These reactions can be represented (3,4) as:

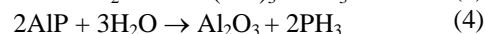
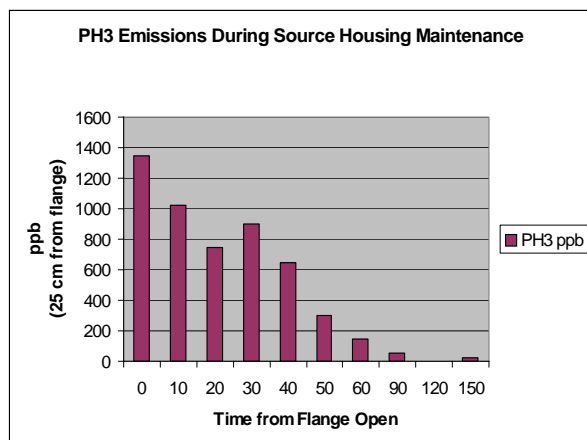


Table 2 shows emissions from two disks (GSD) in separate implanters in the same fab. One was a silicon coated disk and the other a non-coated disk that were run with a high dose of P (~1.2E17 cm<sup>-2</sup>) just before opening the target chamber. There is a measurable difference in PH<sub>3</sub> levels between the two disks immediately after door opening whereas the empty bare Aluminum chambers show little difference. The silicon-coated disk does not have the AlP levels that the uncoated disk has. Note also that most users of the silicon-coated disks notice a reduction in overall Phosphorus cross contamination compared to bare Aluminum disks [3]. There are many reports of AlP releasing PH<sub>3</sub> in agricultural applications where AlP pellets are used for fumigation of certain food commodities for human or livestock consumption as well as tobacco [12]. These and other agricultural reports provide a very large world-wide human toxicology database.

serious shortcomings on personnel protection. Some of these were a result of poor training, even today, with 3rd party or even 4th party personnel. Many fabs may

employ a 3rd party “full maintenance contractor” (not employed by the fab or by the OEM). In many instances, that 3rd party, after establishing maintenance protocols with the fab personnel – production and maintenance management, hires a sub-contractor (“4th party”) or temporary employees to do many of the lower skilled tasks, i.e, pump changes, maintenance activities and so forth.

Figure 1 shows PH<sub>3</sub> measurements from a freshly opened source housing of a high current, batch implanter that had seen a total of > 1.2E18 P cm<sup>-2</sup> over a 3 – 4 day period. The implanter is used almost exclusively for high dose P (60keV, 1.2E16) Maintenance activities consisting of scraping and periodic vacuuming began within minutes of source removal. PH<sub>3</sub> levels were recorded using an Analytical Technology PortaSense II at several intervals over 2.5 hours.



**FIGURE 1.** PH<sub>3</sub> Levels Measured 25 cm from an Open Source Chamber/Housing During Maintenance (High Current Implanter with dedicated P)

There were unexpected bursts up to 1200 ppb in the measurement possibly due to PH<sub>3</sub> in the newly generated, air-borne flakes during the scraping exercise. It is suggested that since the implanter vacuum system had been purged with clean, dry N<sub>2</sub> it is unlikely to see any AIP from water reaction until some of the high volume of AIP or P particles became airborne as a result of local high volume exhausting and aggressive scraping. The graph shows the level of PH<sub>3</sub> over time with the probe fixed at a point 25 cm from the flange face. This shows the need for appropriate (per local, regional, national codes) particle masks and aggressive air exhaust or SCBA during the entire cleaning process. This becomes especially important if the source housing is removed for a modular PM and is cleaned offline at a later time

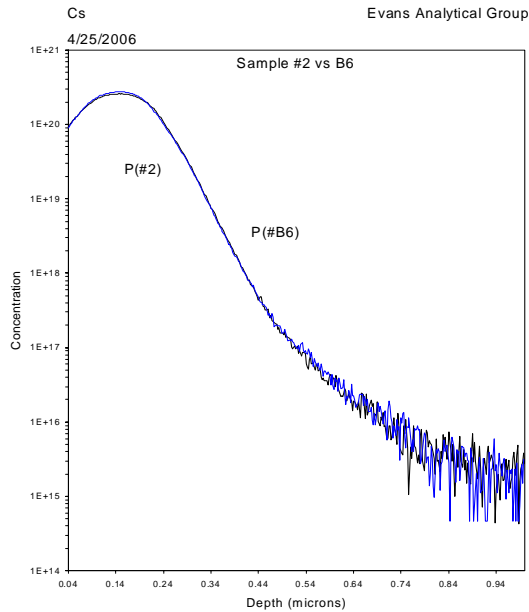
Note that the levels stay high for a long time period during aggressive cleaning. There are burst levels during the early part of the cleaning and these bursts tended to remain >800 ppb for up to 10 to 20 seconds, approximately - even after scraping was stopped. The possibility of delays in measurement response was evaluated three times by removing the probe away from the source flange and the decay in the reading was almost immediate (< 3 sec). At the 50-minute interval, a continuous DI water mist was used on the deposited residue as an attempt to reduce any PH<sub>3</sub> from entering the general area beyond the source flange.

### Contamination – P in P

Another aspect of Phosphorus is the insidious nature of even low levels (500ppm and lower) of P cross contaminating a high concentration of As and Sb and the disproportionate change in Rs due to a compromise of the junction. [1,2,3]. Implant disks contribute heavily (up to 80%) to the overall sputter of previous dopants [2]. The trend of Rs for a B implants following runs of high dose P are well known where the P simply counter dopes the B for up to 30 – 60 minutes of implants following the P operation – but without any diffusion anomaly. Beyond the As, Sb and B – could P “self-contaminate” or autodope?

A “P in P” test was conducted with a number of wafers (p-type, <100>, 10 – 50 Ω-cm). Half of the wafers were bare and the other half coated with a screen oxide of 200Å. These wafers were all implanted together with P, 120 keV, 5E15 cm<sup>-2</sup> in one run on a high current, batch implanter which is dedicated to all high dose P implants (and selected B implants) and which also had a series of P implants run (accumulation 8E16) so there was likely to be a saturation [2] of Phosphorus present. These wafers were evaluated for discernible surface contamination on the bare and oxide coated wafers. SIMS using a high precision protocol with better than 2% precision against a NIST standard was performed. The SIMS was done on annealed (oxide-on and oxide-stripped) and on unannealed wafers to determine if any added surface concentration affected the junction due to any possible high dose damage enhancement. We also wanted to see if there was any profile effect. In Table 2, notice that there is a small difference shown in the near surface (<200 and <300 Å) whereas the total SIMS dose is within 2.4% (1σ) for all wafers. No discernible different in P SIMS dose was seen on the profile or the surface/near surface using HPIC SIMS (See Table 2). See Fig 2 for an overlay of annealed P wafers profiled with SIMS on wafers with and without

the implanted oxide layer. There is also no profile anomaly observed.



**FIGURE 2.** SIMS overlay of two wafers run with P, 120 keV, 5E15. Wafers were coated with 200 Å oxide through anneal. Sample B6 had oxide stripped prior to SIMS, Sample 2 did not.

Depth Measurement	Bare (Not Annealed)	Oxide & Stripped (Annealed)	Oxide (Annealed)
<300 Ang	3.53E+13	1.34E+14	1.93E+14
>200 Ang	4.95E+15	4.71E+15	4.67E+15
<300 Ang	3.5E+15	1.34E+15	1.93E+14
Total SIMS Dose	4.95E+15	4.77E+15	4.73E+15

## SUMMARY

Hydrides of Phosphorus and Arsenic (and we expect Antimony although that was not studied here) can be generated long after the parts were exposed to Phosphorus or Arsenic beams. Although the odor threshold of these emissions is often well below the TLV proper monitoring and safety guidelines are required. Heavily implanted Aluminum parts are especially prone to releases of PH<sub>3</sub> or AsH<sub>3</sub>. Fabs should ensure that all levels of contractors – and their subcontractors follow the fab or local/regional safety guidelines for implanter and parts cleaning and that they have full access to training and support equipment. Local/direct monitoring at or near the

part(s) is strongly recommended. Phosphorus self-contamination was investigated using a high dose “P dirty-up implant”. More investigation is needed using lower energy P with a corresponding higher concentration but at this point, the SIMS results show very little or no effects of P self contamination in high dose applications.

## ACKNOWLEDGMENTS

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