



## REACTIVITY OF PHOSPHINE WITH POINT-OF-USE FILTERS OF DIFFERENT COMPOSITION

### Introduction

The reactivity of process gases with delivery system components can severely limit advances in semiconductor process capabilities. As the industry advances, an improved understanding of compatibility issues will be necessary. To that end, Entegris laboratories chose to investigate the reactivity of phosphine with various materials used in the construction of filters for the semiconductor industry. This investigation provided insight into material compatibility issues with phosphine and aided in the selection process of components for use in gas distribution systems.

The hydride gases—arsine, phosphine and silane—are widely used in the semiconductor industry and considered to be highly reactive. Phosphorous (P) is used as an n-type dopant in semiconductor processes with phosphine (PH<sub>3</sub>) traditionally used as a precursor for this deposition process. Single and polycrystalline silicon are doped in order to change the resistivity of the thin film. Silicon dioxide is doped to change the reflow temperature of the oxide film. PH<sub>3</sub> can react with various metals to decompose to P and H<sub>2</sub>.

Phosphine can decompose to phosphorous and hydrogen on the surface of nickel filter media. The decomposition rate is low at ambient temperatures, but nickel filters should not be used in low phosphine concentration applications, <1000 ppm, and they need to be sized properly.

Nickel filters rated for high flow rates may decompose a significant amount of phosphine if used at low flows. In addition to phosphine decomposition, nickel and phosphorous react to form solid nickelposphides. Over time a solid film growth of nickelposphides on filter membrane surfaces can increase the pressure drop across a filter and degrade filter performance.

This paper presents the results of our investigation and is intended to characterize the short-term performance of existing and upcoming filter media in phosphine service. Further investigations may be conducted to determine long-term compatibility and lifetime of filter media in phosphine service. The investigation may also be extended to include other hydride gases such as arsine and silane.

### Investigation

The compatibility of eight different filters with phosphine was investigated. Of the eight filters tested, two had nickel membranes, four were stainless steel, one was Teflon® and one had a chromium oxide membrane.

The goal of this investigation was twofold. First, to identify filter media that is nonreactive with phosphine. Secondly, to characterize and confirm a kinetic model for filter media found to be reactive.

In general, the decomposition of phosphine on the different filter media was monitored using a quadrupole mass spectrometer while the filters were slowly heated. Phosphine at mass 34 and 33 was easily detected by the mass spectrometer. The intensity of the mass 34 signal was referenced to helium mass 4 signal, the dominant peak, to compensate for instrumental drift. The flow rate through the filters was set at 150 sccm during the temperature ramp experiments. SEMI® grade phosphine was diluted to 250 ppm with helium using calibrated thermal mass flow controllers. The filters were heated and cooled during the temperature ramp experiments at 0.5°C/minute. Thermocouples were clamped directly to the filter housing of the filter under test so that the temperature of the filter could be monitored and that feedback to the temperature controller was provided. The filters and a section of the inlet tubing were heated and insulated for temperature control. The inlet tubing was heated to preheat the gas entering the filter and the insulation minimized hot spots. The temperature was either ramped to 185°C, the maximum temperature rating for the filter, or to where 100% of the phosphine decomposed. If no decomposition was observed at the maximum temperature, the flow rate was reduced to 50 sccm to increase the residence time in the filter. The test filter was then bypassed to check instrument calibration and verify phosphine concentrations.

Filters that demonstrated significant and stable phosphine decomposition at elevated temperatures were tested further to verify a zero order reaction rate model. To test the zero order reaction model, the temperature and concentration of phosphine

were kept constant while the flow rate was varied. Changing the flow rate caused a change in the residence time. When a steady state condition was achieved at a given flow rate, the amount of phosphine remaining after the decomposition reaction was measured. A schematic of the manifold used for the filter compatibility tests is shown in Figure 1.

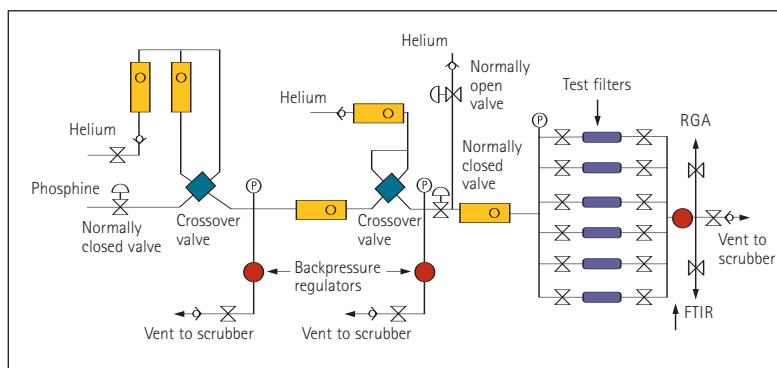


Figure 1: Compatibility manifold

### Data

Five of the filters tested exhibited no detectable reactivity with phosphine. Three of the nonreactive membranes were made of stainless steel, one was Teflon® and the other was a chromium oxide membrane. The temperature ramp data for these five filters is presented in Figure 2.

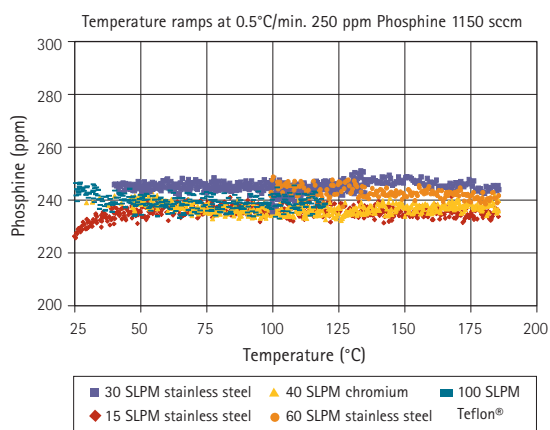


Figure 2: Data for nonreactive filter membranes

Maximum rated flow and membrane material differentiates the filters. The stainless steel membranes tested are representative of different membrane geometries and/or manufactures. All of the filters were tested with 250 ppm of phosphine at 150 sccm flow rate initially. When the maximum temperature was reached, the flow rate was reduced to 50 sccm to confirm the nonreactivity of the filter membrane with longer residence times. The stainless steel and

chromium oxide filters were heated to a maximum of 185°C. The Teflon® filter was heated to 120°C, its maximum temperature rating.

One stainless steel filter did decompose phosphine slightly with a flow rate of 150 sccm at the elevated temperatures. Heating and cooling curves were generated at a lower flow rate, 50 sccm. The results were inconsistent and the decomposition rate was not always stable when the temperature and flow rate were kept constant. Concentration versus temperature curves are plotted in Figure 3 for this filter.

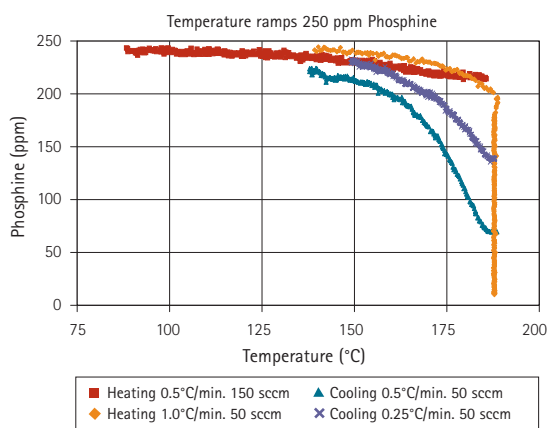


Figure 3: Data for 100 SLPM stainless steel filter membrane

The curves in Figure 3 are plotted in order of collection and “heating 0.5°C/min. 150 sccm” is the first set of data collected. Both before and after a temperature ramp, the phosphine concentration exiting the filter was allowed to stabilize. After the first temperature ramp was run, the phosphine concentration stabilized with about 10 ppm of phosphine decomposing at 150 sccm and 185°C. When the flow rate was reduced to 50 sccm, approximately 75 ppm of the phosphine decomposed at 185°C and the exit concentration was stable (not shown). The exit concentration did not stabilize when 185°C was reached during a second temperature ramp. Instead, the exit concentration continued to decline to near 100% decomposition (see Figure 3). Successive runs displayed less phosphine decomposition at 185°C. This may be indicative of a passivation process that takes place with the filter membrane from exposure to phosphine over time.

The two nickel filter membranes tested both decomposed 100% of the 250 ppm of phosphine at elevated temperatures. Exit phosphine concentration versus temperature curves are presented in Figures 4 and

5 for the two nickel filters, respectively. The filter membranes are geometrically different. The 120 SLPM filter membrane is a high unit surface area tubular construction device and the 75 SLPM filter membrane has a lower unit surface area and is shaped as a flat disk. There is some hysteresis in the data and the temperature where 100% decomposition occurs varies between heating and cooling curves and between the different filters. The differences can be explained by heat transfer phenomena, instrument response time and the physical differences of the membranes.

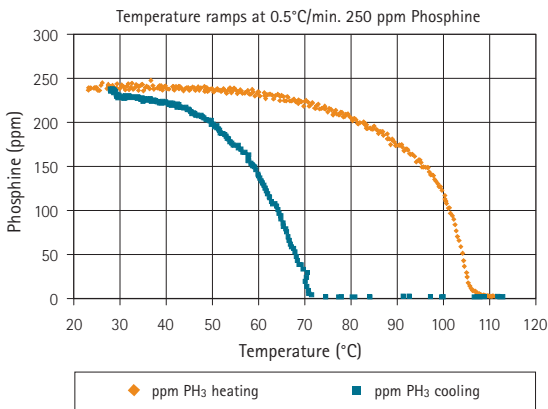


Figure 4: Data for 120 SLPM nickel filter membrane

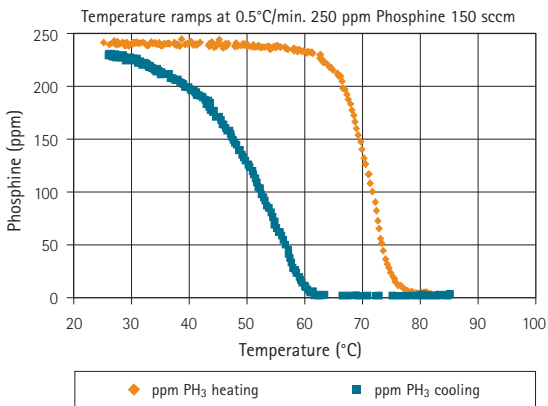


Figure 5: Data for 75 SLPM nickel filter membrane

### The Kinetic Model

Chemical kinetics is the study of reaction rates and can be used to predict how much of something reacts, or how long it takes to react, or at what temperature it reacts. Reaction rate theory defines a rate constant  $k$  as a measure of the speed of a chemical reaction. For our case, it will be how much phosphine decomposes per unit time. The rate equation is expressed below for a zero order reaction.

$$C = C_0 - kt$$

$C_0$  is the phosphine concentration entering the filter,  $C$  is the concentration exiting the filter and  $t$  is the residence time. Residence times are calculated by dividing the void volume of the filter membrane by the flow rate. Chemical reactions can take other forms, making it necessary to verify the reaction order for a chemical reaction. Zero order reactions are typical of heterogeneous or surface reactions. Also, based on previous studies in our laboratory, a zero order reaction model was assumed to describe the reaction between nickel and phosphine. Verification of the zero order reaction model for these two filters was accomplished by collecting data at various residence times and plotting the amount of phosphine decomposed versus the residence time,  $t$ . The resulting graph will be a straight line if the reaction order is zero. Figures 6 and 7 below verify this relationship for the 120 and 75 SLPM nickel filters, respectively.

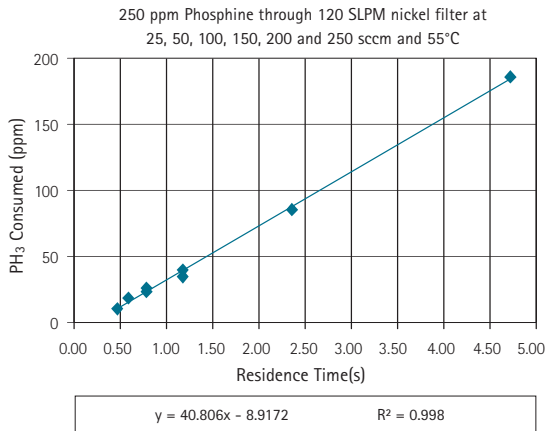


Figure 6: Linear plot for zero order reaction

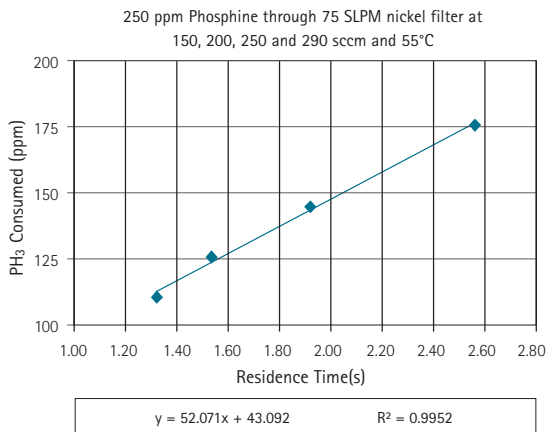


Figure 7: Linear plot for zero order reaction

Reaction rate constants are temperature dependent. The rate constant  $k$  can be expressed as a function of temperature by the Arrhenius equation presented below.

$$k = A e^{-E_a/RT}$$

$A$  is a constant called the frequency factor,  $E_a$  is the activation energy,  $R$  is the ideal gas constant and  $T$  is the absolute temperature. Experimental data is used to calculate the frequency factor and the activation energy defining the dependence of the rate constant on temperature. A plot of  $\ln k$  versus  $1/T$  should be a straight line with the slope of  $-E_a/R$  and intercept of  $\ln A$ . Choosing consistent units to manipulate the experimental data yields the Arrhenius equation plots in Figures 8 and 9 below for the 120 and 75 SLPM nickel filters, respectively. The slope of the curves generated multiplied by the ideal gas constant equals the activation energy.

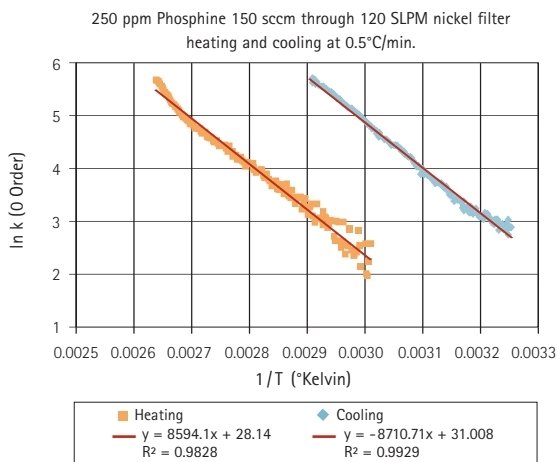


Figure 8: Zero order rate constant

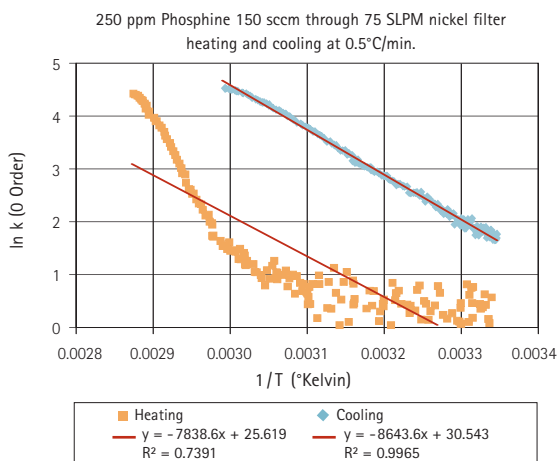


Figure 9: Zero order rate constant

Table 1 presents the activation energies and frequency factors calculated from this experimental data. The ideal gas constant used to calculate the activation energy was 1.987 cal/°K mole. The calculated values are consistent with earlier studies conducted in our laboratory. Data obtained at 55°C and at various flow rates are compared to the rate model for the cooling curve data from Figures 8 and 9, respectively. The results are tabulated in Tables 2 and 3. The theoretical rate constants at 55°C for the 120 and 75 SLPM nickel filters are 87 and 67 s<sup>-1</sup>, respectively.

By comparing the experimental data with the theoretical data in Tables 2 and 3, one can observe that the experimental data for the 120 SLPM filter is <1/2 of the theoretical prediction. While the experimental data for the 75 SLPM filter matched the theoretical prediction very well, a possible explanation for the difference in behavior between the filters may be due to the geometric differences of the filter elements, which would contribute to heat transfer and flow effects. It is interesting to note that the calculated rate constants for the two nickel filters become nearly identical when normalized for surface area and void volume as presented in Table 4.

## Conclusion

Teflon® chromium oxide and most of the stainless steel filters demonstrated no detectable phosphine decomposition within the range of experimentation. This work would suggest that any of these filters could be used with phosphine and likely the other hydride gases. The one stainless steel filter that did show some reactivity was only slightly reactive. The reaction may have been the result of surface iron oxides on the stainless steel membrane for this filter. The reactivity of phosphine with Fe<sub>2</sub>O<sub>3</sub> has been previously established. The filter will need to be cut open and analyzed for surface composition to further identify the nature of this reactivity. This filter appeared to be passivated with prolonged exposure to the phosphine.

Nickel filters did decompose phosphine in these tests. The decomposition rate was slight at ambient temperatures and reasonable flow rates. The calculated decomposition rate was in the single digit ppm range under normal conditions. Nickel filters should be avoided in critical low concentration and or low flow applications were the impact of even slight decomposition would have a dramatic impact on process performance. The filters used in this study were grossly oversized. The flow ratings were significantly

greater than the actual flow used during the testing to exaggerate the reaction kinetics were well beyond what would be observed in recommend use. The results do point out the necessity of sizing filters appropriately for the particular application. Bigger filters do not always translate to better operational performance. The rate constants for the two filters tested when corrected for membrane surface area and void volume as listed in Table 4 are remarkable in their agreement. For these two products, the fundamental reactivity between phosphine and the filter membrane is the same. Notice, through a comparison of Figures 2 and 3, that this was not the case for the stainless steel filters tested.

Results obtained in this study are specific to the particular filter types tested. Geometric and surface chemistry differences impact chemical reaction dynamics. It may not be acceptable to merely assume a filter membrane material is nonreactive because it is made from a material that has been previously tested. The reactivity of one of the stainless steel filters with phosphine does highlight the potential for surface differences which may react with gases. It is speculated in this case, an increase in  $Fe_2O_3$  on the surface of the membrane is responsible for the increased reactivity. As the reaction of phosphine with these iron oxides takes place, the surface of the membrane becomes passivated and the reactivity of the filter decreases. There may be a long-term impact to these filters from this reaction which could increase the pressure drop or create particles that could potentially shed from the filter.

The ever-increasing demands that are placed on process systems will require increased awareness and understanding of system components. It will be imperative to perform compatibility tests with system components and the gases or liquids that they are used for. The results of this study do provide insight into materials for construction of phosphine gas delivery systems. Teflon,<sup>®</sup> chromium oxide and some stainless steel filters are compatible under normal and elevated operating conditions as demonstrated by this investigation. Nickel does show signs of some incompatibility; however, the reaction rate at normal ambient conditions is slight, indicating that using nickel filters for certain phosphine operations is not necessarily precluded. This usage depends on the requirements for flow and on the concentration of phosphine gas that might be used for a process. Critical operations should use one of the alternatives highlighted in this investigation. New gases will need to be thoroughly investigated for any potential compatibility issues before they are used in semiconductor process operations.

Filter and Curve	Activation Energy (Calories/Mole)	Frequency Factor
120 SLPM filter (heating)	17076	$1.66 \times 10^{12}$
120 SLPM filter (cooling)	17308	$2.93 \times 10^{13}$
75 SLPM filter (heating)	16015	$8.77 \times 10^{14}$
75 SLPM filter (cooling)	17175	$1.84 \times 10^{13}$

Table 1: Experimental activation energy and frequency factors

Flow Rate (SCCM)	Amount Decomposed (PPM) Measured	Amount Decomposed (PPM) Theory
25	186	410
50	85	205
100	35	103
100	40	103
150	23	68
150	26	68
200	18	51
250	10	41

Table 2: 120 SLPM nickel filter theory and experimental comparison at 55°C

Flow Rate (SCCM)	Amount Decomposed (PPM) Measured	Amount Decomposed (PPM) Theory
150	176	171
200	144	129
250	125	103
290	110	89

Table 3: 75 SLPM nickel filter theory and experimental comparison at 55°C

Filter (Maximum Rated Flow)	Rate Constant 55°C (s <sup>-1</sup> )	Surface Area to Void Volume Ratio (cm <sup>-1</sup> )	Rate Constant per Unit of Surface to Volume Ratio (cm/s)
120 SLPM	86.76	15997	$5.4 \times 10^{-3}$
75 SLPM	66.86	11290	$5.9 \times 10^{-3}$

Table 4

*This application note is based on a paper originally presented at the Symposium on Contamination Free Manufacturing for Semiconductor Processing, SEMICON West 2000.*

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