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Sapphire-based pressure transducers with stable long-term operation in concentrated hydrofluoric acid

Abstract

As device dimensions shrink and etch tolerances become tighter, controlling the dispense rate of hydrofluoric acid (HF) in semiconductor manufacturing processes is becoming more important since it directly affects etch rates in most applications. We discuss the long-term performance of a sapphire-based pressure transducer designed for use in pressurized fluid dispensing systems where aggressive chemicals such as HF may be used. Transducers were fitted in an application using 49% HF. The transducers were removed after five, nine and 24 months use and their measurement characteristics determined. The performance change of all units was found to be less than +/- 0.06 PSIG (<0.2% of their 0-30 PSIG measurement span). The sapphire sensing element was also found to be stable in HF, contributing less than eight nanograms (ng) of aluminum per sensor per day when immersed in 49% HF at room temperature.

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Introduction

Liquid pressure sensors have found numerous applications in semiconductor fabs including: installation after a pump to ensure the pump is working within specification; installation to ensure valves, nozzles and other system subcomponents are functioning properly; liquid level measurement; and overall system diagnostics and use in pressurized fluid dispensing systems to make certain that the correct flow is dispensed.

Controlling the dispense rate of hydrofluoric acid (HF) in semiconductor manufacturing processes is extremely important since it directly affects etch rates in most applications. Inadvertent over- or under-use of HF can cause too much or too little etching, and increase wafer defects and processing costs. The effect on yield becomes even more pronounced as manufacturers move to smaller line width processes where lower tolerances of variations in etch depths require tighter process control. The instrumentation and methods for controlling HF volume dispense have therefore become critical to production control. Although a very common chemical in semiconductor processing, HF is also one of the most aggressive. Maintaining tight control over HF volume dispense requires pressure sensors that are able to withstand long periods in contact with high concentrations of HF. As semiconductor device technology has progressed, the requirements on contamination control have also become more stringent. Parts in contact with process chemicals must not introduce contamination downstream. Pressure sensors for use with HF are most commonly constructed with metal or ceramic coated with TEFLON® material. However, these are known to degrade over time and may introduce contaminants to the liquid, which can damage critical material integrity.

This paper presents the performance results of a sapphire pressure sensor, with no moving parts that can be used in direct contact with HF for extended periods of time with little or no effect on its performance, or introduction of contaminants [1].

Methodology

To test the pressure sensors ability to withstand long-term exposure to HF, six model 4150 single port sapphire NT® Pressure Transducers manufactured by Entegris (numbered 1-6 for reference) were installed in an actual fab application using room temperature 49% HF. This level of HF concentration is well above that typically used for wafer contact and so provides a particularly stringent test. The 4150 units are designed to measure 0-30 PSIG with an accuracy of +/-1% full scale (+/- 0.3 PSI). A cutaway diagram of a 4150 unit is shown in Figure 1.

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A Mensor Model PCS 400 pressure calibration system, accurate to +/- 0.025% full scale, was used to test the sensors for accuracy before installation. The test was carried out several times to make sure the measurements were repeatable. Two units each were removed from the 49% HF application after 5, 9 and 24 months to determine if their performance had been affected by prolonged contact with HF. The Mensor pressure calibration system was used to test the units after use, and the readings were compared with the pre-installation data. Again, several measurements were taken to ensure that the data was repeatable.

Hydrofluoric acid (HF) is a particularly aggressive etchant, and as sapphire is highly pure single crystal Al_2O_3, it was reasonable to predict that some aluminum may become dissolved in the HF during use and possibly come into contact with downstream processes. Testing was therefore conducted to determine if any metal was extracted during contact with 49% HF.

Square samples of sapphire with 2 cm per edge giving a total of 8 cm^2 of surface area were tested for extraction in 49% HF. The test was conducted using two sapphire sensor material samples. Each sample was cleaned with isopropyl alcohol, 49% HF and deionized (DI) water prior to the test. The samples were placed in separate vessels containing 49% HF for a total of 168 hours (7 days). A sample of 49% HF not in contact with sapphire material was used as a control.

After 24 hours, 10 g of liquid HF was removed for sample preparation of trace metals analysis. Ca, K and Fe levels were determined by graphite furnace atomic absorption spectrometry (GFAAS) or cold plasma ICP-MS, and all other elements were measured by hot plasma ICP-MS. The same procedure was repeated after 48 and 168 hours.

Results and discussion

A representative sample of the accuracy results from pressure testing before installation and after removal are reported in Figures 2-7 with the applied pressure on the X-axis, and the error expressed as a percentage of the full 30 PSIG span on the Y-axis.

It can be seen that the curves have slightly different shapes for each unit, but importantly, the units hold their characteristic curve shapes after prolonged exposure. Also, the curve shifts after exposure are small, with each of the units changing in performance by less than 0.2% of span, which for 0-30 PSIG equates to a performance change of less than +/- 0.0 6 PSIG.

The mass spectrometry measurements for metals in the HF exposed to the sapphire samples showed that aluminum was the only leachable trace metal detected

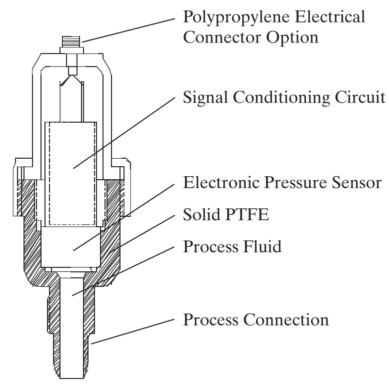

Figure 1. A cutaway view of a model 4150 single port sapphire NT® Pressure Transducer.

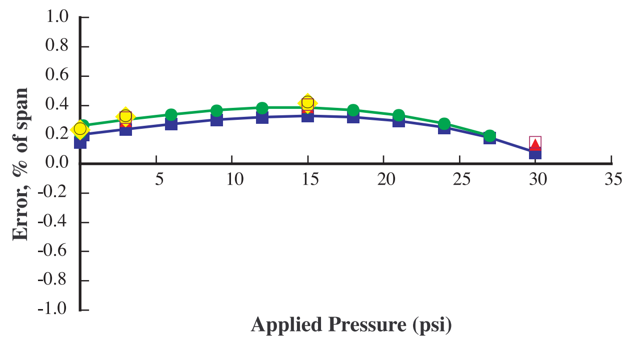

Figure 2. Accuracy for sensor 1, a new and unused unit.

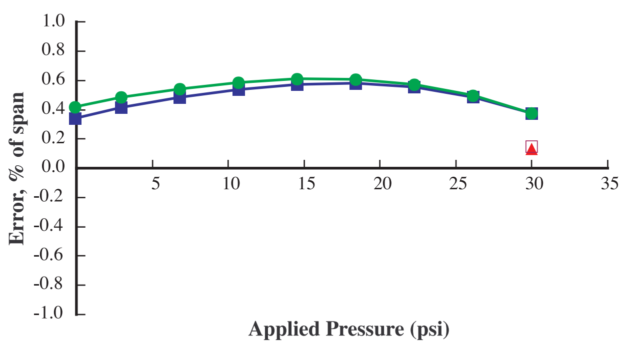

Figure 3. Accuracy for sensor 1 after installation for 5 months in a 49% HF application.

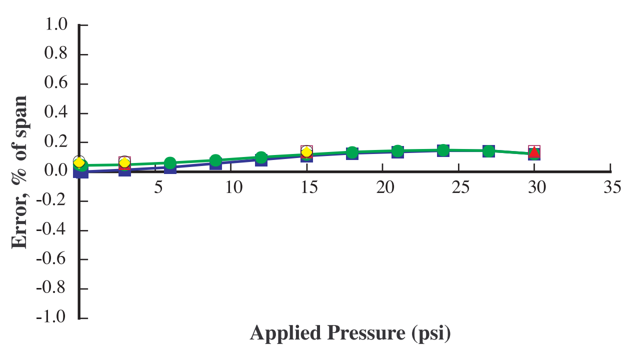

Figure 4. Accuracy for sensor 4, a new and unused unit.

$$(13\mu gAl/L/8cm^2/week)(\frac{1000ng}{\mu g})(0.04L)(\frac{8cm^2}{10.4\ sensors})(\frac{1\ week}{7\ days}) = 7.1ng\ extracted\ per\ day$$

Equation 1. Formula used to determine the amount of aluminum extracted per day from the sensor.

in a quantity significantly above the detection limit (Table 1). Ni, Ti and Zr were measured at levels slightly over their detection limits. The amounts of all other metals were below the detection limits (mostly 0.01 ppb) for the two analysis techniques.

The amount of aluminum extracted from the sapphire sample of 8 cm^2 surface area after 168 hours (7 days) from a 40 ml sample of 49% HF was 13 ppb. If 1 ppb = 1µg/L and each sensor has a sapphire surface area of 0.77 cm^2 (the equivalent of 10.4 sensors per 8 cm^2 sapphire sample), then each sensor would extract 7.1 ng per day using the formula in Equation 1.

The amount of aluminum measured after 168 hours was the equivalent of less than 8 ng extracted per sensor per day in 49% room temperature HF. SEMI has published a specification for trace metals in high purity liquids, F57-0301 "Provisional specification for polymer components used in ultrapure water and liquid chemical distribution systems". The detected metals are well below the specified limits in the standard. This standard states that polymer products, such as PFA tubing, in contact with semiconductor liquids should extract less than 10 µg of aluminum per m^2 of material per 7 days of exposure.

Although this specification relates to polymer components, it is interesting to see how the extraction from sapphire equates with that specified for polymer parts. The less than 8 ng/day of aluminum extracted from the sapphire samples is the equivalent of the allowable amount of aluminum extraction allowed by the SEMI specification for a 2.7 inch length of 1 inch internal diameter PFA tubing.

Taking an example application which uses a sapphire pressure sensor in a process flow of 100 ml/min (144 L/day) of 49% HF, the extraction rate of 8 ng (0.008 µg) of aluminum per day per sensor, gives a contamination level from the sensor in this application of only 0.000056 µg/L, or 0.000056 ppb.

Conclusions

We have developed sapphire-based pressure transducers that are resistant to long-term HF exposure making them suitable for use in HF dispensing systems. Test data confirms a performance change of less than +/- 0.06 PSIG after two years in 49% HF. The amount of aluminum leached from the sapphire on exposure to HF is 8 ng/day and in a flow of 100 ml/min this equates to 0.000056 ppb of aluminum contamination. No measurements have been carried out using HF at higher temperatures, these will take place in the future. These results

Metal	Detection Limits (ppb)	HF Control 24-hour (ppb)	Sapphire Sample 24-hour (ppb)	Sapphire Sample 48-hour (ppb)	Sapphire Sample 168-hour (ppb)
Aluminum	0.01	0.28	3.7	5.6	13
Nickel	0.01	0.12	0.013	0.014	0.055
Titanium	0.01	0.035	0.057	0.094	0.098
Zirconium	0.01	<0.01	<0.01	<0.01	0.013

Table 1. Concentrations of the four metals found to be present above the detection limits of the mass spectrometers out of the 34 that were tested for.

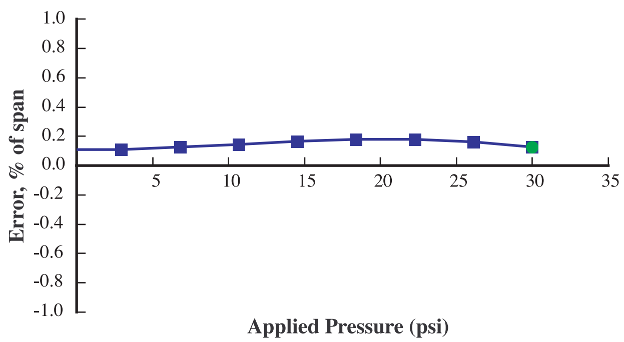

Figure 5. Accuracy for sensor 4 after installation for 9 months in a 49% HF application.

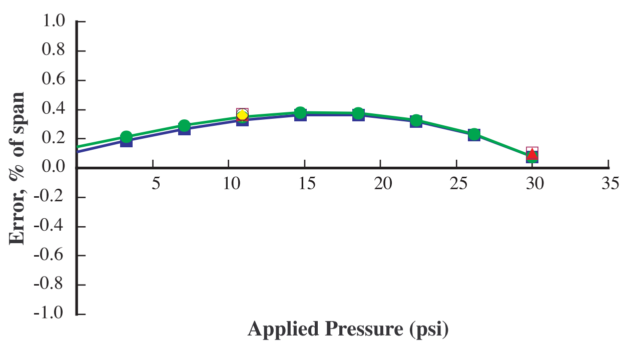

Figure 6. Accuracy for sensor 6, a new and unused unit.

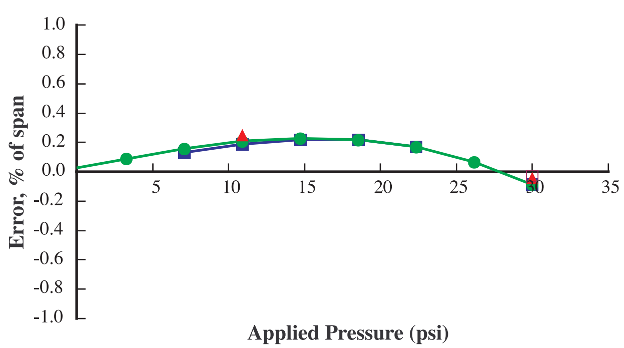

Figure 7. Accuracy for sensor 6 after installation for 24 months in a 49% HF application.

demonstrate the suitability of sapphire-based pressure measurement systems in the accurate dispensing of concentrated HF for etch applications, without the contamination or reliability concerns typically encountered with instrumentation in such aggressive chemical environments.

References

[1] US Patent 6,612,175

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