

技術報告

選択エッチングプロセス用無水フッ化水素に関する研究
-水分及び金属不純物の管理と測定-

**Anhydrous Hydrogen Fluoride for Selective Etch Processes
-Measurement and Control of Water and Metallic Impurities-**

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半導体製造のエッチングプロセスで用いられているフッ化水素 (HF) の純度は半導体デバイスの性能に多大な影響を与える。特に、HF エッチング処理後のシリコン表面上に残留した酸素含有化合物や金属不純物は、ゲート材料への影響が顕著である。

本研究では、HF 容器の気相および液相中の水分を FTIR にて測定し、液相中に数十 ppmv の水分が存在することが明らかとなった。二種の異なる容器において、HF を連続的に気相供給した時の水分濃度の変化を測定したところ、残存 HF が容器の底に近づくにつれて指数関数的に水分濃度が上昇する傾向が確認された。その水分濃度は初期使用開始時に数 ppm レベルであったが、容器中に残存する HF がなくなった時点では数十～数百 ppmv に達した。このような HF 供給時の不安定な水分濃度挙動から、水分を安定的に数 ppmv 以下に除去可能な精製器の開発を行った。また同時に金属不純物の除去についても検討した。

本報では HF 気相中の水分を定常的に 3ppmv 以下まで除去し、更に金属不純物 Ti, Cr, Ni, Cu, Co を分析機器の測定下限まで除去でき、また Fe やその他 10 種の金属分についても顕著な除去効果が認められた精製器を開発したので報告する。

The purity of hydrogen fluoride (HF) used in semiconductor etch processes can critically affect device performance, as any oxygenated or metallic impurities retained on the virgin silicon surface after cleaning will be in close proximity to the gate materials. In this work, water in the vapor and liquid phases of HF cylinders is measured by FTIR spectroscopy and found at tens of ppmv in the liquid phase. Cylinder depletion tests are performed on two cylinders to track the water concentration as vapor phase HF is progressively removed from the cylinder and reveal that the water concentration increases exponentially as the heel of the cylinder is approached, rising from low ppmv levels at the start to tens-hundreds of ppmv when fully depleted. Due to the inconsistent H₂O concentration in the delivered HF gas, purifier materials are evaluated with the aim of removing water to low ppmv levels while also minimizing metals contaminants. One material consistently removes water to 3 ppmv in vapor phase HF, while also removing Ti, Cr, Ni, Cu and Co to below their detection limits and significantly reducing the concentration of Fe and 10 other elements.

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1. Introduction

As the demands of semiconductor manufacturing increase, technologies and processes must adapt to changing needs. Cleaning, etching or deposition processes that achieve 60 nm node specifications may not be viable at the 32 or 22 nm nodes. One example is the RCA cleaning process which includes a dilute wet HF etch to remove the low quality SiO_2 formed by the previous chemically oxidizing steps^{1,2)}. This has been a universal semiconductor work-horse process due to its high through-put and low cost. Yet when exposed to ambient air, the virgin silicon surface of these newly-cleaned wafers forms a self-passivating oxide layer. To avoid the formation of this uncontrolled oxide layer, the initial HF cleaning etch can be performed inside the tool using anhydrous HF gas, just prior to deposition.

Additionally, advanced semiconductor technologies are requiring higher source/drain mobilities which can be achieved by strained silicon. A future alternative solution is to utilize pure germanium at lower deposition temperatures to increase mobility. However, since germanium forms no stable oxide it is incompatible with deposition on SiO_x , which would need to be removed in a process similar to that noted above. The use of HF gas has the advantage of selectively etching only silicon oxide, while leaving SiN and SiGe untouched. Thus future advancements, along with the needs described above, call for higher quality anhydrous HF to be used in front-end process etching to produce increasingly oxide-free wafers.

It is advantageous to both reduce and control the water concentration in the anhydrous HF vapor. Water contamination inherent in the HF will lead to corrosion of stainless steel delivery lines which can generate particles entrained in the gas stream. We have found previously that, in liquid source cylinders, water partitions into the condensed phase which produces variable and increasing water concentrations from the heel of the cylinder³⁾. It is probable that this effect is common to other condensed gases, especially highly polar or hydrogen-bonding gases such as HF.

Other impurities in the HF gas, such as metals, are likewise detrimental to wafer processing. HF used to remove the native oxide layer is critical since any residual contaminants are juxtaposed with the gate components. Mobile ions such as Ca^{2+} can change the gate voltage when present at concentrations as low as ppb levels^{4,5,6)}. At concentrations in the ppm range, the majority of transition metals will reduce carrier lifetimes. Iron is an especially damaging contaminant in that it may be both soluble in silicon and a major gate-oxide-integrity killer⁷⁾.

One plausible solution to reduce and control both water and metals impurities in HF, is to develop a point-of-use purifier to be placed in the gas stream. This paper presents the results of an investigation on how water partitions between the vapor and liquid phases and how this delays and concentrates its presence in the heel of the cylinder. Data are also presented on the evaluation of a purifier material for removal of both water and metals contaminants from an HF gas stream.

2. Experimental

2.1 Materials

N_2 gas purified with a Nanochem[®] OMX purifier, was used for purging during all experiments. For partition, cylinder depletion and metals analysis studies, hydrogen fluoride (4N5 purity) packaged in a nickel cylinder was used. Materials evaluated for removal of water vapor were tested with HF sources that contained water at appreciable levels (75-150 ppm). Purifiers were assembled with 316 L stainless steel parts and were assembled with 60 μm fritted Ni gasket VCR[®] connections to APTEch 3625 valves.

2.2 Water Impurity Analysis in HF

The experimental equipment used for analyzing water in HF is shown in Fig. 1. The HF gas sample was introduced into a Nicolet 550 FTIR spectrometer equipped with a solid Ni 15 cm path-length cell. Heat tracing on the cell was maintained at 100 °C to prevent gas-phase hydrogen bonding of HF in the cell,⁸⁾ and the cell pressure was measured using a 0-1000 torr Baratron pressure gauge and manually maintained at 760 torr \pm 10 torr via the use of needle valves. All HF-wetted components were heat traced and temperature controlled to prevent HF condensation. Flow was maintained at ~500 ml/min.

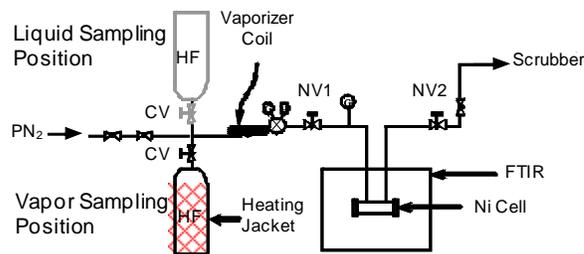


Fig. 1 Schematic of sampling manifold to introduce purified N_2 , vapor phase HF or vaporized liquid phase HF into the FTIR spectrometer for analysis of water.

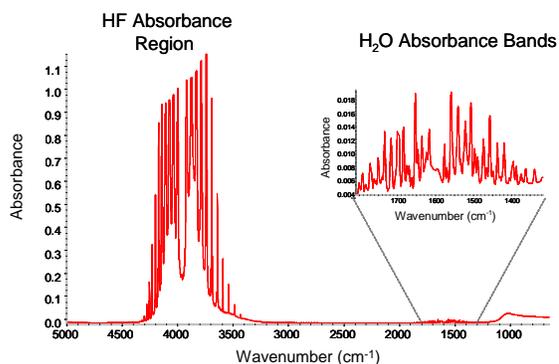


Fig. 2 Infrared spectrum showing absorption peaks of HF from 3000-4300 cm^{-1} and an expanded view of the water absorption region that was used for detection.

The cylinder position was varied according to the diagram in Fig. 1 to switch between vapor and liquid phase withdrawal. A vaporizer coil was heated and independently controlled at 100°C to ensure complete vaporization of the liquid phase HF.

A water quantification method having a minimum detection limit of 1.9 ppmv and a calibration range of 2-50 ppmv was developed for this system using the water absorbance region shown in Fig. 2. The FTIR was calibrated with a certified permeation-based water generator at 6 different known water concentrations to create a linear regression curve having an average error of $\pm 1.78\%$.

2.3 Cylinder Depletion Studies

To explore the causes of moisture fluctuations in HF vapor, a full cylinder of HF was wrapped in a heating blanket and temperature controlled by PID at 35 °C. The cylinder (Fig. 3) was placed on a cylinder scale to track the weight as HF was withdrawn from the cylinder. Heat tracing was applied to the ancillary plumbing to maintain it at 40 °C.

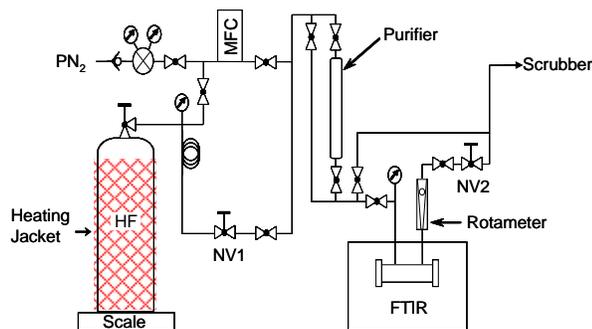


Fig. 3 Schematic of the manifold used to explore H₂O concentration during HF cylinder depletion, and to test purifier material performance in removing H₂O from HF gas.

The cylinder was attached to the manifold by a 1.2 m x 3.175 mm o.d. stainless steel pigtail to decouple the effect of tubing tension on the scale reading. The tubing was allowed to relax, and the proper scale performance was verified by adding and removing a 862 g weight at the top of the HF cylinder.

The HF vapor flow rate from the cylinder was monitored using a combination of MFCs and needle valves. Although MFCs from several different manufacturers were tried, simple tests revealed that none gave trustworthy values for the flow rates⁹⁾. Thus the MFCs and needle valves were used only for their flow control capabilities. The actual HF flow rate at an appropriate setting was experimentally determined to be 1.2 L/min by tracking weight loss from the cylinder over time.

2.4 Water Removal

A 316 stainless steel purifier body was filled with purifier material, purged with purified N₂ and installed into the testing system shown in Fig. 3. For verification, the water content in the unpurified HF gas was periodically measured throughout the experiments.

Testing began by checking for atmospheric impurities under 1-2 L/min N₂ purge using the FTIR. Once the system was known to be free of contaminants, HF was introduced into the FTIR cell via the bypass to establish the inherent water concentration in the HF challenge gas. Then the HF was diverted through the purifier for several hours at a time while the IR spectrum of the effluent was monitored for water concentration. Between each day of testing, the purifier was valved off and the system was purged overnight with 1-2 L/min N₂ via the bypass.

2.5 Metals Removal

A new purifier was prepared and installed in the system shown in Fig. 4. An identical but empty blank purifier body was installed alongside the new purifier to provide a baseline for any metals contamination that might originate from the purifier body and valve materials. The gas handling system consisted of a 316L SS manifold for delivering either HF gas or purified, filtered N₂ to the purifiers.

The stainless steel portions of the manifold were heat-traced to 40 °C and the manifold was dried down overnight with purified N₂. The entire system (except purifiers) was then passivated with HF flow for 45 minutes prior to sampling. The effluent from the purifiers was filtered and handled in a perfluoroalkoxy (PFA) manifold to reduce the degree of contamination from large metal particles generated while actuating valves^{10,11)}. The HF from the purifiers was bubbled through the sample collection vessel at a slow rate such that the entire gas flow was dissolved in the water.

The purifier was tested according to the following procedure. HF was flowed through the blank and 3 nm particle filter to the scrubber for 30 minutes. A blank HF sample was collected by dissolving a sample of HF into deionized water in the sample vessel. HF was then flowed through the HF purifier and 3 nm particle filter to the scrubber for 30 minutes and a sample from the HF purifier was collected in a separate sample vessel as above. Finally a follow-up blank HF sample was collected to confirm no residual metals contamination. All samples were analyzed by inductively coupled plasma mass spectrometry (except P by ion exchange chromatography, and Si by graphite furnace atomic absorption spectroscopy) and back-calculated to determine the concentrations in the HF gas stream.

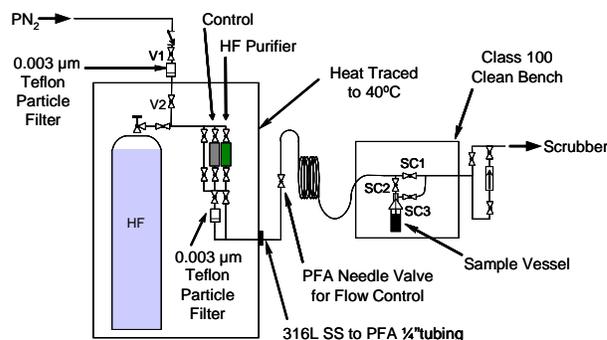


Fig. 4 Schematic of the manifold used to test purifier material performance in removing volatile metals from HF gas.

3. Results and Discussion

3.1 Water Concentration during Cylinder Depletion

During several HF cylinder evaluation experiments various water concentrations in the HF vapor were documented and attributed potentially to temperature fluctuations in the laboratory. The HF cylinders were then wrapped in heating blankets, and the manifold was heat traced to maintain constant temperature; but this did not completely solve the problem. As this variability could have a direct bearing on degrading the performance of a semiconductor fabrication tool, we investigated the change in water concentration over the course of depleting an HF cylinder.

A full HF cylinder was placed on a scale in the system (3) to track the water concentration as a function of HF remaining in the cylinder. This test consisted of simply flowing the HF vapor via the bypass line to the IR cell. The initial water concentration from the full HF cylinder was between 2.5 and 3 ppmv (near the minimum detection level of the H₂O quantification method). The cylinder was depleted over 5 days, with the highest measured water concentration being about 160 ppmv.

As shown in Fig. 5, the trend each day and over the whole cylinder depletion is an exponential rise in water concentration following weight of HF depleted. The water concentration at the beginning of each day, however, was slightly less than the final concentration from the previous day. This may be due to purging the system overnight with N₂, and the resulting ‘reconditioning’ of the wetted manifold surfaces with HF at the start of the next day. The weight fluctuation is thought to have been due to temperature affects in the laboratory. While the cylinder ran out early in Day 5, Day 4 suggests that the highest water concentration would have been over 200 ppmv had the cylinder run dry at the end of a full day of testing.

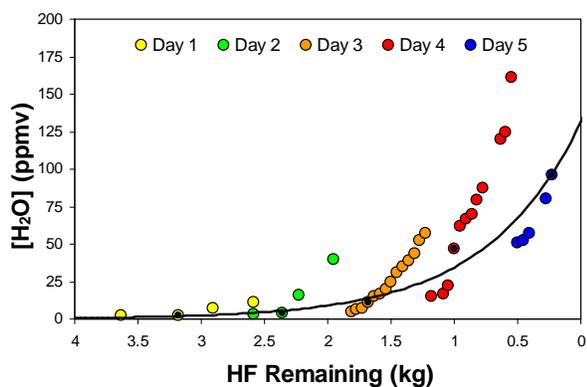


Fig. 5 Concentration of water in HF vapor versus the weight of HF remaining in the cylinder over 5 days. The overall and daily trends are an exponential increase in water concentration, with each day starting at a lower concentration than at the end of the previous day. The conservative exponential trend line is based on the (black) data point taken between the first and second hour of each day.

Another cylinder of higher purity HF was similarly depleted while monitoring water concentration in the HF vapor over several days. The overall exponential rise and daily “restarting” of the water concentration was duplicated in this cylinder and is shown in Fig. 6. It is significant to note that, although the initial moisture content of this cylinder was also 2.5 – 3 ppmv, the heel produced only 31 ppmv water, far less than the first cylinder. For these cylinder sizes and 35 °C, both the ideal gas law and van der Waals equations predict phase break to occur with 9 g remaining in the cylinder. As HF is far from an ideal gas, phase break was not detected.

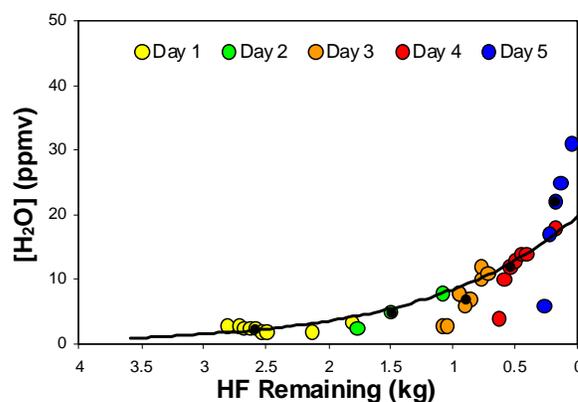


Fig. 6 Concentration of water in HF gas versus the weight of HF remaining in the cylinder over 5 days of analysis. The overall trend is an exponential increase in water concentration, with each day starting at a lower concentration than the end of the previous day. The exponential trend line is based on the data point taken between the first and second hour of each day (black).

The data in Fig. 5 and 6 show that the water in the HF cylinder partitions into the liquid phase as vapor is withdrawn from the headspace, leading to higher water concentrations from the heel of the cylinder. In contrast, HF can be withdrawn from the cylinder directly from the liquid phase. It would be expected that the water concentration in the liquid HF should be initially higher than that in the vapor phase, yet more constant throughout the cylinder life. Other cylinders analyzed for both liquid and vapor phase initial water concentrations show this to be true (Table 1).

Additionally, the total amount of water in the HF cylinders from Fig. 5 and 6 (approximated by integrating under the trend line), when spread evenly over the weight of HF withdrawn, give concentrations of 35 and 7.5 ppmv respectively.

Table 1: Initial moisture concentrations (ppmv) in both the vapor and liquid phases of HF cylinders

Phase	Cylinder 1		Cylinder 2		Cylinder 3	
	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
H ₂ O (ppmv)	4.9	15.4	2.3	10.7	4.3	34.6

3.2 Water Removal

After discovering that the initial water content in HF vapor belies the inherent increase during cylinder use, we set out to develop a purifier to eliminate this variance in the system. The chosen purifier material was tested over a period of about 20 hours (spanning 5 days) to determine both its efficiency at removing water from HF gas, and its method of saturation. Fig. 7 illustrates the second day of testing. The initial concentration of water in the HF challenge was about 80 ppmv and rising. The purifier reduced this to 3 ppmv and maintained that efficiency for over 5 hours of testing on this day.

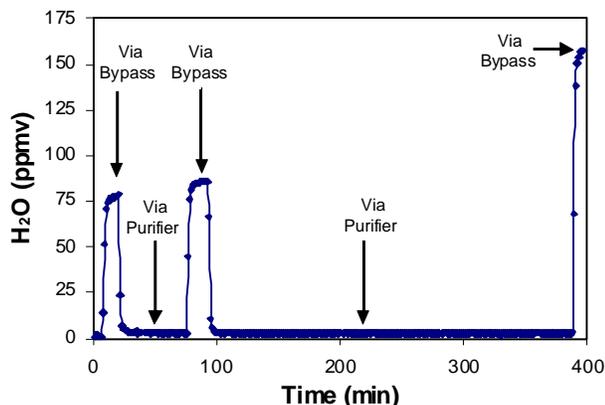


Fig. 7 Water concentration in HF during purifier efficiency testing. The purifier reduced H₂O impurity in HF from 80 – 160 ppmv in the challenge, down to 3 ppmv.

The challenge water concentration was verified during the experiment and at the end of the day. While the purifier was still purifying the HF to 3 ppmv water, the concentration of water in the challenge had climbed to about 160 ppmv, representing a minimum 99.98% efficiency. On the following day (not shown) the purifier maintained 3 ppmv water while the challenge concentration exceeded 200 ppmv.

3.3 Metals Removal

Following the effective removal of water from HF, it was proposed that the purifier might also remove other volatile contaminants from the gas stream. To determine the performance of the purifier material, the metal contaminants present in the effluent from the purifier material were quantified for comparison with those inherent in the HF source. Since the resident moisture in the HF leads to corrosion of stainless steel components, a blank purifier was also tested to evaluate the contribution of just the purifier body to the metals contamination.

The hydrolysis metal analyses results in Table 2 show that the HF gas via blank purifier body contained elevated levels of Na, Al, Ca, K, Fe, As and P and detectable levels of elements such as Mg, Ni, Pb, Cu, Ti, Cr and Zn. Potential sources of these contaminants include the manufacturing of HF by the action of H₂SO₄ on fluorite (CaF₂),¹²⁾ and the presence of contaminants in the raw materials^{13,14)} as well as potential corrosion products from delivery components. The results obtained for the purified HF gas stream shows

significantly reduced concentrations of all metal impurities over those detected in the blank.

Table 2: Concentrations (ppbw) of metals in the HF gas flowing from the Blank and HF Purifiers. Values with less than symbol indicate the concentration was below the limit of detection.

Element	Via Blank (Average) (ppbw)	Via HF Purifier (ppbw)
Na	22.0	1.7
Mg	4.9	0.6
Al	25.9	1.4
P	490	150
K	11.1	1.6
Ca	64.5	5.3
Ti	2.8	<0.1
V	0.045	<0.02
Cr	0.585	<0.05
Mn	0.25	<0.05
Fe	18.6	1.3
Co	0.18	<0.05
Ni	0.82	<0.1
Cu	0.38	<0.05
Zn	8.15	0.24
As	2440	1980
Si	<1 ppmw	<1 ppmw
Pb	0.08	<0.02

Na, Al, K, Ca and Fe were reduced from tens of ppbs to low single digit ppb levels. Other elements such as Ni, Cu, Pb, Ti, Cr, Mn and Co were removed from single digit ppb levels to below their detection limits. Although the purifier lowered the concentrations of P and As, it was not fully effective in removing them. This indicates that these species are likely stable and volatile molecules such as PF₃ and AsF₃ which did not interact strongly with the purifier material.

4. Conclusion

The concentration of water during vapor phase HF delivery is not a controlled system and changing levels may be detrimental to sensitive semiconductor processes. Water was found to partition into the condensed phase, and be emitted most prevalently from the heel of the cylinder. Thus the quality of the HF as judged from the initial vapor phase water concentration is misleading. Two cylinders of anhydrous HF both started with 2.5 – 3 ppmv moisture in the vapor phase, but ended with either 31 or >160 ppmv upon depletion.

A purifier has been designed to remove water from HF gas. When challenged with 80 to 200 ppmv water in HF, the purifier maintained a 3 ppmv effluent moisture concentration over a period of many hours at a flow rate of 1.2 L/min HF.

The purifier was also successful at removing other contaminants from the gas stream. The purifier eliminated elements such as Ti, Cr, Ni, Cu and Co to below their detection limits, while significantly reducing the amount of Fe and 10 other elements. Neither arsenic nor phosphorous was

significantly removed from the HF gas, but this may be due to their presence as stable and volatile fluorides.

For current and future applications where very low water and metals concentrations are critical to process control, such as silicon wafer native oxide etch, a high purity HF source and a point-of-use purifier offers a viable solution for control of water and metals in HF gas.

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