Hazards of Dichlorosilane Exhaust Deposits from the High-Temperature Oxide Process as Determined by FT-ICR Mass Spectrometry

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Abstract—Gas samples from the exhaust system of tools employing dichlorosilane (DCS) in high temperature oxide (HTO) deposition that produced flammable solid deposits have been analyzed by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. Exact mass determinations by the high-resolution FT-ICR allowed the identification of various polysiloxane species present in such an exhaust flow. Ion-molecule reactions of dichlorosilyl cation with water and DCS indicate the preferred reaction pathway is disiloxane formation through HCl loss, a precursor to the highly flammable polysiloxanes that were identified in the gaseous exhaust and in exhaust deposits. Minimization of these hazardous deposits is discussed with respect to water contamination, dilution factor, and water scrubbing of the HTO exhaust.

Index Terms—Chemistry, ions, mass spectroscopy, occupational health and safety, pumps, safety.

I. INTRODUCTION

MANY chemical vapor deposition (CVD) process gases are often quite reactive and must be handled with appropriate caution. Particularly well known is silane, where the associated explosive nature of it has been well studied and reviewed [1]. Little consideration has been given directly to the combustion of dichlorosilane (DCS) or its reaction products [2], [3]. Conclusions by Sharp *et al.* [3] describe the DCS/air mixtures as "both very easily (and sometimes unpredictably) ignited, and that the explosive potential … is unusually high." Of interest here was their description of DCS exposure to water releasing HCl and that "the hydrolyzed silicon-containing residue was flammable, but not shock-sensitive." A general discussion by McKinley [4] mentions DCS and subatmospheric CVD "exhaust considerations" explicitly, but does not deal with solid exhaust deposits and is dated in that only oil pumps are considered. Another general CVD exhaust discussion by Hammond [5] includes a distribution of solids in vacuum processing where he estimates 80% ends up in the pump oil and pump exhaust. With today's oil-free pumps, this distribution of solids will undoubtedly shift further into the exhaust manifold, explaining the lack of previous investigation into this matter.

Current semiconductor manufacturing involving DCS for high-temperature oxide (HTO) deposition has revealed potential safety hazards in the exhaust tubing and ductwork due to solid deposit formation. This being especially true when they are disturbed by disassembly for cleaning or decommissioning [6]. Though mitigated by the use of nitrogen gas purging in the dry pumps and exhaust stream, there is buildup of combustible and occasionally pyrophoric deposits in this exhaust system. McKinley's review points out that exhaust gas mixtures are not well understood and concludes that extensive combustion and/or scrubbing is required for a safe and clean exhaust plume [4]. Aside from this, a large amount of the DCS is pumped out into the exhaust system unreacted and is here thought to be an exhaust precipitate precursor. To date, no detailed chemical reactions have been proposed to account for dichlorosilane's solid exhaust deposition or its extreme reactivity.

Comparatively, detailed studies have been performed with silane. Initial investigations by Mandich and Reents [7]–[9] on $Si(H/D)_{0-3}^{+}$ showed clustering reactions with silane and disilane. This was supported by theoretical mechanism details provided by Raghavachari [10], who confirmed a low transition barrier for sequential clustering. Further work lead Reents and Mandich to discover that, through a small addition of water, the cluster sizes were greatly increased [11], [12] and possibly responsible for micron-sized particulate formation. Around the same time, an extensive study of chlorosilane ion-molecule reactions by Murthy and Beauchamp [13] was performed and they determined the relative stabilities of the chlorosilyl ions. Though they observed no chlorosilane ion cluster formation, they did mention a "problem" with water creating side reactions that would then react further with either more water or chlorosilanes, but they did not investigate this fully. In a previous study on neutral DCS hydrolysis [14] it was determined that a stoichiometric amount of water slowly warmed will generate cyclic siloxanes, c-$[H_2SiO]_n$ ($n = 4$–23), evolving HCl when warmed from low temperature ($-30\,°C$).

In order to investigate the composition and possible chemical reaction pathways of the exhaust buildup, high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry was employed. The exhaust gas and solid samples were obtained both upstream and downstream of the vacuum pumps of a hot-wall HTO process. To understand the exhaust deposition cause(s) and to further elucidate reaction paths, controlled examination of some pertinent ion-molecule chemical reactions was performed. In particular, the ion-molecule reactions between dichlorosilyl cations ($SiHCl_2^{+}$) and molecules of O_2, H_2O, and N_2O were examined. Reaction products were only found in the water reactions within a reasonable time. As

a result of these studies, DCS/water reactions are the likely cause of the flammable solid buildup and are the focus of the discussion herein.

II. EXPERIMENTAL

FT-ICR mass spectrometric experiments were performed using a refurbished Finnigan FTMS-2000 that will be described here briefly. For a review of fundamental FT-ICR theory and application, see [15]. The superconducting magnet has been rewound to produce a 3.3 Tesla field, and much of the original control equipment was replaced by the MIDAS electronics and data acquisition software [16], [17]. A dual ion trap design was utilized, connection between the two traps provided by a centered 0.030-in differential pumping hole. Pumping on both sides was provided by oil diffusion pumps (Sanovac-5 oil in Edwards Diffstak 160, 750 l/s for air), where base pressures were typically 3×10^{-9} torr. An electron ionization beam traversed the dual trap to generate ions in either trap. Pairs of solenoid pulse valves allowed the controlled introduction of gas samples to either side of the ion trap. A typical ion-molecule experiment entailed pulsing of the DCS gas followed by the electron beam at $\sim$20 eV; this generated the $SiHCl_2^+$, where using the low electron energy reduces the SiH_2Cl^+ ion product. Resonance ion ejection techniques were used to isolate the $SiHCl_2^+$ species [18]. After a delay to allow the neutral DCS gas to be pump out, a second set of pulse valves introduced neutral gas to react with the trapped ions. DCS was obtained from United Chemical Technologies, Inc., and used directly after brief venting to expel excess HCl generated by DCS decomposition.

Process exhaust samples were collected from a reactor running the HTO process. The process gases mainly consisted of nitrous oxide (N_2O) with some DCS and a total flow of 200–700 sccm. Reactor temperatures were in the range of 700–900 °C, with pressures from 300 to 400 mtorr. The container used to collect a gas sample was a special silicon oxide coated, 1.8 L stainless steel bulb (SilcoCan, Restek Corp.). The coating prevented degradation of the sample. The exhaust gas was introduced into the bulb and evacuated several times to passivate its surface before the final collection. Mass analysis of the samples occurred over the next week with two experimental methods using the FT-ICR. The first method was direct introduction of the sample gas through pulsed valves, followed by ionization and detection on a short time scale ($\sim$0.2 s). This gave a relative profile of the gas concentrations to about 1%, scaled by the ionization efficiencies (cross sections). The second method was pulsed introduction and ionization of a high-pressure pulse of the exhaust gas, which was then allowed time to undergo electron transfer (predominantly from N_2^+) and proton/hydride transfers while the gas pulse was being pumped. This second "delayed" method allowed for the detection of many low concentration species that have low ionization potential and less hydride affinity, these typically being larger and more conjugated molecular species.

Solid samples were collected from three different HTO process exhaust systems. Samples were taken in the foreline and after the pumps. Foreline samples typically contained minimal buildup that was not very reactive and they are not further
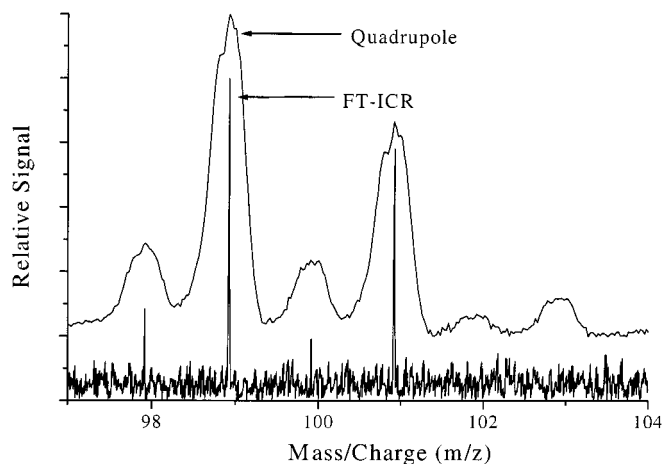

Fig. 1. Comparison of the resolution capability and dynamic range of the FT-ICR versus quadrupole mass spectrometry. Sample used was actual process pump exhaust, demonstrating significant amounts of unreacted DCS.

considered. The solid pump exhaust samples were examined by diffuse reflectance FTIR, direct- and cross-polarization NMR, and differential scanning calorimetry (DSC).

III. RESULTS

The high-resolution capability of the FT-ICR instrument routinely generates milli amu (atomic mass unit) measurements. This usually allows for exact molecular formula of the ions measured to be determined. Fig. 1 is a comparison of the FT-ICR and a quadrupole mass spectrometer (UTI, model 100C), from m/z (mass/charge) = 97–104, showing the unreacted dichlorosilane in the HTO pump exhaust line. These dichlorosilane signals result from the less than one percent DCS still contained in the actual process exhaust gas flow after pump ballast dilution. The majority of the sample was N_2 ($>$95%) from the introduction of pump ballast. For resolution and speed, the FT-ICR is superior, however, the dynamic range of the quadrupole mass spectrometer is better, resulting in its larger signal-to-noise ratio (SNL). There are ways around this limitation of dynamic range, the simplest being to eject the largest ion population(s), which leads to enhancement of the smaller ones. However, this was unnecessary to get the FT-ICR signal seen in Fig. 1.

The HTO process exhaust sample examined by quick direct pulse/ionization/detection led only to the detection of the major exhaust gas components: N_2, N_2O, and SiH_2Cl_2. However, with sufficient pressure and time, collisions of the dominant molecular nitrogen ion (which has a high ionization potential, $IP_{N_2} = 15.58$ eV) with a lower IP species, allows charge transfer to readily occur. The resulting FT-ICR mass spectra from the same process pump exhaust sample, for this "direct" and "delayed" detection, are compared in Fig. 2(a) and (b), respectively. The uncorrected relative intensities of the direct detection are skewed and favor the higher cross sections of N_2O and DCS. The "delayed" method resulted in ion signals for those species with the lowest ionization potential and lowest gas phase basicity, which are typically at too low a concentration to be directly observed. This experiment resulted in the detection
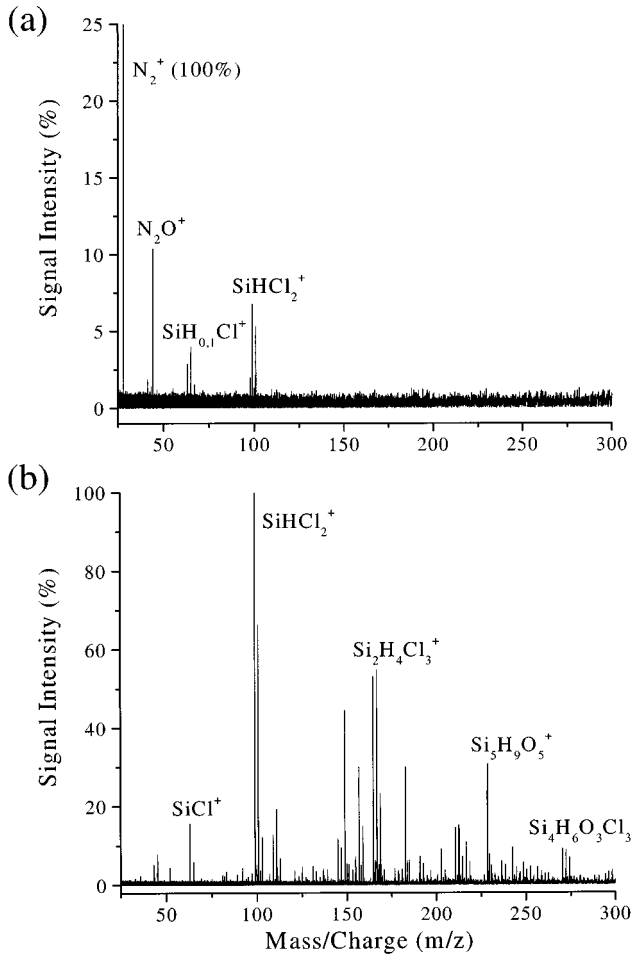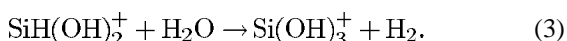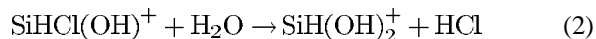
Fig. 2. FT-ICR/MS spectrum of same HTO process exhaust sample taken by: (a) direct and (b) delayed experiments. The direct experiment resembles actual gas concentrations, while the delayed experiment favors the trace species with low hydride affinity and ionization potential.
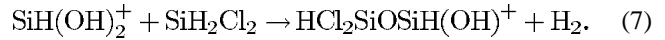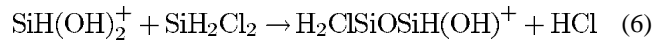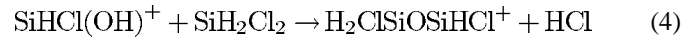
of many ions, a selection of which is summarized in Table I from a similar experiment as that shown in Fig. 2(b). The table identifies various chlorosilane, chlorosiloxane and siloxane ions by their exact masses. The mass scale was calibrated internally at four peaks: $SiCl^+$ ($m/z = 63$), $SiHCl^{37}Cl^+$ ($m/z = 101$), $Si_3O_2H_6Cl^+$ ($m/z = 157$), and $C_{19}H_{31}^+$ ($m/z = 259$). The standard deviation of the measured masses for the noncalibrated points in Table I is 0.0014 amu or 6.0 ppm.

Fig. 3 shows the mass spectra resulting from the controlled reaction of dichlorosilyl cation with H_2O and DCS at two different stages of reaction, (a) midway and (b) nearly complete. Numbered mass peaks correspond to the ion products of the numbered reactions, where initially water proceeds to hydrolyze $SiHCl_2^+$, as follows:

$$SiHCl_2^+ + H_2O \rightarrow SiHCl(OH)^+ + HCl \qquad (1)$$

$$SiHCl(OH)^+ + H_2O \rightarrow SiH(OH)_2^+ + HCl \qquad (2)$$

$$SiH(OH)_2^+ + H_2O \rightarrow Si(OH)_3^+ + H_2. \qquad (3)$$

Reaction (3) was relatively slow and was only observed when the relative water pressure is much greater than the dichlorosi-

lane pressure. Products from (1) and (2) were then observed to undergo further elimination reactions with DCS:

$$SiHCl(OH)^+ + SiH_2Cl_2 \rightarrow H_2ClSiOSiHCl^+ + HCl \qquad (4)$$

$$SiHCl(OH)^+ + SiH_2Cl_2 \rightarrow HCl_2SiOSiHCl^+ + H_2 \qquad (5)$$

$$SiH(OH)_2^+ + SiH_2Cl_2 \rightarrow H_2ClSiOSiH(OH)^+ + HCl \qquad (6)$$

$$SiH(OH)_2^+ + SiH_2Cl_2 \rightarrow HCl_2SiOSiH(OH)^+ + H_2. \qquad (7)$$

The early channels resulting in the loss of HCl were at least 5 times faster than their competing H_2 loss channels, seen by the greater product intensities of reactions (4) and (6) versus (5) and (7), respectively, in Fig. 3. The resulting disiloxane species underwent complete hydrolysis when there was sufficient water and/or reaction time. Thus, the complete reaction equation is

$$SiHCl_2^+ + SiH_2Cl_2 + 6\,H_2O$$
$$\rightarrow (OH)_3SiOSi(OH)_2^+ + 4\,HCl + 3\,H_2. \qquad (8)$$
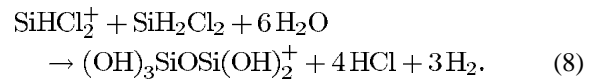
Further polymerization past disiloxane was not observed, probably due to the low pressure of DCS in the reaction cell of the ICR.

The presence of larger polysiloxanes, similar to those found in the exhaust gas sample, was detected in solid samples from the exhaust tubing analyzed by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopies. NMR study of the flammable samples indicated the presence of siloxane species $Si-(O-Si)_{3-4}$ (at -100 and -110 ppm versus TMS), this was supported by IR spectra indicating a strong $Si-O-Si$ absorbance at 1110 cm^{-1}. The flammable samples were typically orange/brown in color, becoming less reactive as the color lightened to tan, and finally unreactive when white. The $Si-O-Si$ signals in both NMR and IR spectra decreased as the sample color lightened and their reactivity decreased. The trends in reactivity were also confirmed by differential scanning calorimetry (DSC). DSC shows the reactive samples need little extra energy in order to decompose (<300 J/g), as compared to semireactive (900–1600 J/g) and nonreactive (1600–2000 J/g) samples.

IV. DISCUSSION AND CONCLUSION

The use of high-resolution FT-ICR mass spectroscopy has provided the identification of many products in the MTO exhaust flow besides the process components, and has emulated their formation process. The exhaust gases detected are consistent with the solid flammable buildup determined to be mostly composed of various siloxane/chlorosiloxane species. Table I indicates cation species ranging from various linear siloxanes ($Si_4H_8O_3Cl^+$, $Si_4H_7O_3Cl_2^+$, and $Si_4H_6O_3Cl_3^+$) to the cyclic polysiloxanes ($Si_5H_9O_5^+$ and $Si_6H_{11}O_6^+$) demonstrated from the controlled hydrolysis of dichlorosilane [14]. Of course, some of the compounds here may be either impurities or generated in the hot reactor. Reactor generated products should be relatively small in size and quantity due to the short residence times ($\sim$25 ms/liter of chamber) at average reactor conditions. The protonated trichlorodisilane in Table I is a common impurity in the DCS, and some of the smaller oxygen containing species could be generated from the hot reactions with nitrous

TABLE I
SILICON SPECIES IDENTIFIED FROM HTO EXHAUST STREAM

Ion formula	Ion exact mass (amu)	Relative Intensity[a]	Measured mass (amu)	Mass error (milli-amu)
HSi=O	44.97967	2.1	44.97947	-0.20
SiCl	62.94578[b]	10.8	62.94581	0.03
$Si^{37}Cl$	64.94283	3.7	64.94269	-0.14
$SiHCl_2$	98.92246	100.	98.92189	-0.57
$SiHCl^{37}Cl$	100.91951[b]	71.4[c]	100.91924	-0.27
Si_2H_2OCl	108.93327	9.3	108.93352	0.25
Si_2H_4OCl	110.94892	16.4	110.94878	-0.14
$Si_2H_5Cl_2$	130.93069	4.3	130.93151	0.82
$Si_2H_5Cl^{37}Cl$	132.92774	3.8[c]	132.92690	-0.84
$Si_3H_5O_3$	136.95465	5.2	136.95442	-0.23
$Si_2H_3OCl_2$	144.90995	13.0	144.91066	0.71
$Si_2H_3OCl^{37}Cl$	146.90700	8.8[c]	146.90628	-0.72
$Si_3H_6O_2Cl$	156.93642[b]	37.0	156.93720	0.78
$Si_3H_6O_2^{37}Cl$	158.93347	14.6[c]	158.93329	-0.18
$Si_2H_4Cl_3$	164.89172	62.9	164.89048	-1.24
$Si_2H_4Cl_2^{37}Cl$	166.88876	63.2[c]	166.88721	-1.55
Si_4H_7O	182.94212	60.8	182.94118	-0.94
$Si_3H_5O_2Cl_2$	190.89744	11.5	190.89759	0.15
$Si_3H_5O_2Cl^{37}Cl$	192.89450	8.5[c]	192.89531	0.81
$Si_4H_8O_3Cl$	202.92391	17.5	202.92358	-0.33
$Si_4H_8O_3^{37}Cl$	204.92096	7.9[c]	204.92265	1.69
$Si_3H_6OCl_3$	210.87921	18.5	210.87925	0.04
$Si_3H_6OCl_2^{37}Cl$	212.87626	19.2[c]	212.87629	0.03
$Si_4H_6O_4Cl$	216.90318	21.1	216.90444	1.26
$Si_4H_6O_4^{37}Cl$	218.90023	12.3[c]	218.90097	0.74
$Si_5H_9O_5$	228.92964	67.6	228.92812	-1.52
$Si_4H_7O_3Cl_2$	236.88494	18.2	236.88474	-0.20
$Si_4H_7O_3Cl^{37}Cl$	238.88199	13.8[c]	238.87836	-3.63
$Si_5H_7O_6$	242.90891	24.3	242.90800	-0.91
$Si_5H_{10}O_4Cl$	248.91140	11.5	248.91148	0.08
$Si_4H_6O_3Cl_3$	270.84597	27.3	270.84603	0.06
$Si_4H_6O_3Cl_2^{37}Cl$	272.84301	29.1[c]	272.83897	-4.04
$Si_6H_{11}O_6$	274.91713	18.3	274.92084	3.71
$Si_5H_7O_5Cl_2$	296.85170	13.1	296.85051	-1.19
$Si_5H_7O_5Cl^{37}Cl$	298.84874	11.1[c]	298.84675	-1.99

[a] Noise level across spectrum is ~0.2. Note: These intensities are from a similar spectrum to that shown in Fig 2.
[b] These ion masses (as well as $C_{19}H_{31}$ measured at 259.24178) used as internal mass calibration points for whole spectrum.
[c] Contribution to ^{37}Cl identified species from ^{30}Si (3.12% abundance) is not insignificant nor resolvable ($\Delta\Delta mass[^{35,37}Cl - ^{28,30}Si] = 0.0002$ amu).

oxide. No simple homogeneous polymerization mechanism can be created by DCS/N_2O gas phase reactions alone and no ambient temperature reaction was observed between the DCS cations and nitrous oxide. The ion reactions observed (Fig. 3) indicate the formation of the polysiloxanes occurs when trace water is present along with DCS in the exhaust tubing. This has parallels to the reactions seen in the silane/water system [11], [12] but is even more prolific because of the more easily generated HCl product. The corresponding initial neutral gas reaction results mostly in chlorosiloxanol (similar to reaction 1) that will react with DCS to form dichlorodisiloxane (similar to reaction (4), again with preferential loss of HCl). Apparently, the process of reaction with water and DCS can continue in the exhaust gas, creating larger polysiloxanes, until the polysiloxane molecule precipitates or reacts onto a surface or is finally exhausted. Heterogeneous reactions will undoubtedly occur on the surface, continuing the polymerization with DCS and water until layered over by more precipitates and growth then becoming blocked from further reaction at this point.

The resulting layers of trapped polysiloxane precipitate now creates the main hazard of the DCS exhaust buildup because it is still potentially reactive when disturbed and upon exposure to air/water. This hazard is exacerbated by the preferential loss of HCl in the DCS reactions with water seen by the ion reactions and the cyclization experiments [14]. The chlorine depletion is also evidenced by the types of polysiloxanes detected in the exhaust gas, where at most there are three chlorine atoms identified in the Table I species containing three and four Si atoms. The resulting chlorine depleted polysiloxanes will be more flammable due to their evolution of hydrogen gas upon reaction with air/water than those containing more chlorine. The presence of only small amounts of water vapor allows for this preferential elimination of HCl and formation of longer polymers that do not have the chance to be completely hydroxylated.

Without water vapor entering the exhaust flow, most of these polysiloxanes should not be formed to any extent. Since this is a long-term buildup (usually months or years of process time between disassembly and cleaning of exhaust tubing) it takes a
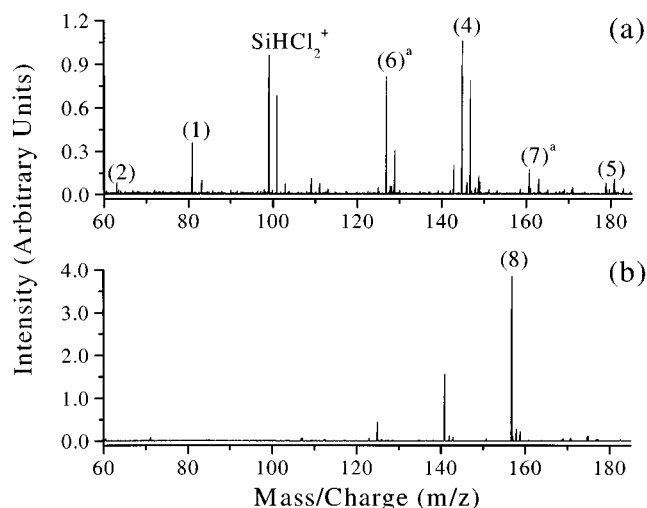
Fig. 3. Reaction FT-ICR spectra of $SiHCl_2^+$ with H_2O and DCS at two times: (a) middle of reaction course and (b) very near the end of reaction. Numeric labels correspond to the product ions from reactions given in the text. Noted products, $(n)^a$, also have other possible routes of formation.

very small concentration of water to continue surface growth onto any previous precipitates. The water could come from the venting of the process chamber to atmosphere too often or small leaks in the chamber or pump connections. Berman extensively discusses water vapor problems in vacuum process systems opened to atmosphere [19]. Alternatively, the nitrogen purge for the pumps might contain water as a contaminant. The largest buildups, however, were seen when the exhaust tubing itself was not made with airtight connections. Sleeved tubes that were riveted together showed the worst clogging and most hazardous flammable buildup that ignited upon attempted disassembly [6]. Exposure to significant water vapor should consume any DCS by complete hydroxylation, as exemplified by the long time-delayed high-pressure water reaction (8). Similarly, the protonated form of $(OD)_3Si–O–Si(OD)_3$ was also proposed to be the possible terminal species in similar silane/water ion reactions [11]. This species cannot have further reactions with water and so should be quite stable upon exposure to air. A water bath is in fact the initial reactive quenching and cleaning solvent for HTO ducting removed from service [6]. These hazardous deposits should be of concern to any semiconductor manufacturer that utilizes DCS as a process gas and exhausts it into ducting at significant concentrations (about 0.1% or greater). Dilution to well below this should effectively reduce any amount of solid buildup due to the corresponding reduction in the polymerization rate. Also, the facts of the DCS reactivity lead us to conclude that a proper water scrubber on the exhaust tubing, located close to the pump exhaust, will eliminate any polysiloxane buildup further downstream.

Extrapolation of this information to more chlorinated chlorosilanes seems plausible. The general trends would be that more chlorine results in faster polymerization but less flammability. Therefore, tetrachlorosilane may readily generate extensively branched chloropolysiloxanes but the resulting products would only release HCl upon water reaction. Trichlorosilane should also readily polymerize to form chloropolysiloxanes, and these should release about half the

amount of hydrogen gas as those polysiloxanes from DCS, reducing the flammable content. Just as the pyrophoric nature of silane is reduced by chlorine substitution, so should the flammability of the water-formed chloropolysiloxanes decrease with further chlorination.

Mass spectral examination of the ion-molecule reactions of dichlorosilyl cation with H_2O in the ICR ion trap found the precursor species of the (chloro)polysiloxanes detected in an HTO process exhaust sample. Similar polysiloxanes were then found in the exhaust tubing as a flammable solid precipitate, thereby confirming that the ion-determined reactions are also occurring in the exhaust DCS upon contact with trace water. Therefore, the diligent minimization of all possible water/air contamination sources should be undertaken in similar HTO process systems to avoid the creation of this exhaust buildup hazard at any point in the exhaust system prior to scrubbing or heavy dilution.

REFERENCES

[1] V. M. Fthenakis and P. D. Moskowitz, "An assessment of silane hazards," Solid State Technol., vol. 33, pp. 81–85, Jan. 1990.
[2] R. G. Aivazyan, V. V. Azatyan, V. I. Kalachev, and T. A. Sinel'nikova, "Stable products and some kinetic features of dichlorosilane-air combustion," Kinetics and Catalysis, vol. 36, pp. 168–173, 1995.
[3] K. G. Sharp, A. Arvidson, and T. C. Elvey, "Hazard potential of dichlorosilane," J. Electrochem. Soc., vol. 129, pp. 2346–2349, Oct. 1982.
[4] R. J. B. McKinley, "Vacuum equipment exhaust considerations for subatmospheric pressure CVD applications," Solid State Technol., vol. 30, pp. 119–122, Aug. 1987.
[5] M. L. Hammond, "CVD exhaust—Safety and environmental sanity," J. Phys. IV, vol. 1, no. C2, pp. 449–457, Sept. 1991.
[6] Private communications with Intel Corporation, Nov. 1999.
[7] W. D. Reents, Jr. and M. L. Mandich, "Sequential reactions of SiD_{0-3}^+ and $Si_2D_{0-6}^+$ with disilane," J. Chem. Phys., vol. 97, no. 10, pp. 7226–7233, Nov. 1992.
[8] M. L. Mandich and W. D. Reents Jr., "Sequential clustering reactions of SiD^+ with SiD_4: Rapid growth to kinetic dead-end structures," J. Chem. Phys., vol. 95, no. 10, pp. 7360–7372, Nov. 1991.
[9] M. L. Mandich, W. D. Reents, Jr., and K. D. Kolenbrander, "Sequential clustering reactions of SiD_3^+ with SiD_4 and SiH_3^+ with SiH_4: Another case of arrested growth of hydrogenated silicon particles," J. Chem. Phys., vol. 92, no. 1, pp. 437–451, Jan. 1990.
[10] K. Raghavachari, "Theoretical studies of clustering reactions. Sequential reactions of SiH_3^+ with silane," J. Chem. Phys., vol. 92, no. 1, pp. 452–465, Jan. 1990.
[11] M. L. Mandich and W. D. Reents, Jr., "How to grow large clusters from $Si_xD_y^+$ ions in silane or disilane: Water them!," J. Chem. Phys., vol. 96, no. 6, pp. 4233–4245, Mar. 1992.
[12] W. D. Reents, Jr. and M. L. Mandich, "Water induced particle formation in the ion chemistry of silane," Plasma Sources Sci. Technol., vol. 3, no. 3, pp. 373–380, Aug. 1994.
[13] S. Murthy and J. L. Beauchamp, "Examination of ion-molecule reactions in chlorosilanes by Fourier transform ion cyclotron resonance spectrometry and determination of the relative stabilities of chlorosilyl ions," J. Phys. Chem., vol. 96, no. 3, pp. 1247–1257, Feb. 1992.
[14] D. Seyferth, C. Prud'hommen, and G. H. Wiseman, "Cyclic polysiloxanes from the hydrolysis of dichlorosilane," Inorg. Chem., vol. 22, pp. 2163–2167, 1983.
[15] A. G. Marshall, C. L. Hendrickson, and G. S. Jackson, "Fourier-transform ion-cyclotron resonance mass-spectrometry: A primer," Mass Spectrom. Rev., vol. 17, pp. 1–35, Jan.–Feb. 1998.

[16] "MIDAS (Modular FT-ICR Data Acquisition and Analysis System)," is a product of FT-ICR/MS group at the National High Magnetic Field Laboratory, Florida State University, available HTTP: http://magnet.fsu.edu/~midas/, July 1999.

[17] M. W. Senko, J. D. Canterbury, S. Guan, and A. G. Marshall, "A high-performance modular data system for Fourier transform ion cyclotron resonance mass spectrometry," *Rapid Commun. Mass Spectrom.*, vol. 10, pp. 1839–1844, Nov. 1996.

[18] J. L. Beauchamp and J. L. Armstrong, "An ion ejection technique for the study of ion-molecule reactions with ion cyclotron resonance spectroscopy," *Rev. Sci. Instr.*, vol. 40, pp. 123–128, 1969.

[19] A. Berman, "Water vapor in vacuum systems," *Vacuum*, vol. 47, no. 4, pp. 327–332, Apr. 1996.

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