Recent developments in fluorine chemistry for microelectronic applications Some examples at Comurhex

A. Jourdan, B. Morel[*]

Comurhex BP No. 29, 26701 Pierrelatte, France

Abstract

High purity fluorides are very important for microelectronic applications. In this article, we have reviewed how to prepare, handle and analyse such products as WF_6 and ClF_3, respectively, a tungsten precursor for metal interconnects and an efficient cleaning agent. Material choice and passivation coupled with high performance analytical studies are the key factors to maintain the highest required purity. This methodology can be extended to other reactive fluorochemicals. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

One of the major trends of the 21st century is the growing need for fast and high capacity communication systems. Microelectronic devices must become more efficient and, as a consequence, smaller in size. The SIA road map shows an evolution of metal interconnects starting from 0.5 μm in 1992, evolving to less than 0.1 μm in 2006 [1]. These requirements cause stringent specifications for chemicals used in Fabs. For example, metals in ultra-pure water must go down from 25 ng/l each to less than 1 ng/l each [2]. In case of speciality gases, metals must go down from 100 ppb total to less than 10 ppb total. Additional parameters such as stability over time (shelf life), reliability (low variability in the production line) and cost are also becoming of growing importance.

This evolution is a major challenge for fluoride chemicals which are extremely corrosive, reactive and difficult to handle and analyse.

In this article, we review the recent developments at Comurhex for WF_6 and ClF_3 production for microelectronic applications.

2. Developments in WF₆

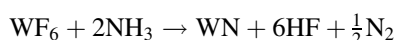WF_6 is produced by the direct exothermic fluorination of tungsten

$$W + 3F_2 \rightarrow WF_6, \quad \Delta H = -1721 \, \text{kJ/mol at } 298 \, \text{K}$$
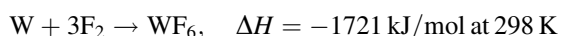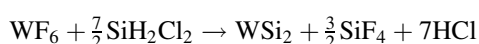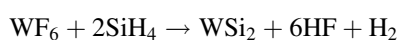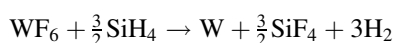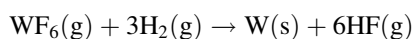
This crude product is purified from metal and gaseous impurities by several rigorous steps. Tungsten hexafluoride is then shipped as a liquid under its own vapour pressure in metal cylinders.

In Microelectronic Fabs, WF_6 is needed for metal deposition by CVD or PECVD

- W for contact and via [3,4].
- WSi_x or WN_x for gate electrode, local interconnect, bit line [5–7].
- WN_x, WSi_x, $W_xB_yN_z$, or $W_xSi_yN_z$ for barrier layer in the copper and metallization technology [8–13].

Many reactions can be involved

$$WF_6(g) + 3H_2(g) \rightarrow W(s) + 6HF(g)$$

$$WF_6 + \tfrac{3}{2}SiH_4 \rightarrow W + \tfrac{3}{2}SiF_4 + 3H_2$$

$$WF_6 + 2SiH_4 \rightarrow WSi_2 + 6HF + H_2$$

$$WF_6 + \tfrac{7}{2}SiH_2Cl_2 \rightarrow WSi_2 + \tfrac{3}{2}SiF_4 + 7HCl$$

$$WF_6 + 2NH_3 \rightarrow WN + 6HF + \tfrac{1}{2}N_2$$

* Corresponding author. Tel.: +33-4-75502930; fax: +33-4-75502882.
E-mail address: bmorel@comurhex.fr (B. Morel).

Fig. 1. Iron level in highest purified WF_6 at Comurhex.
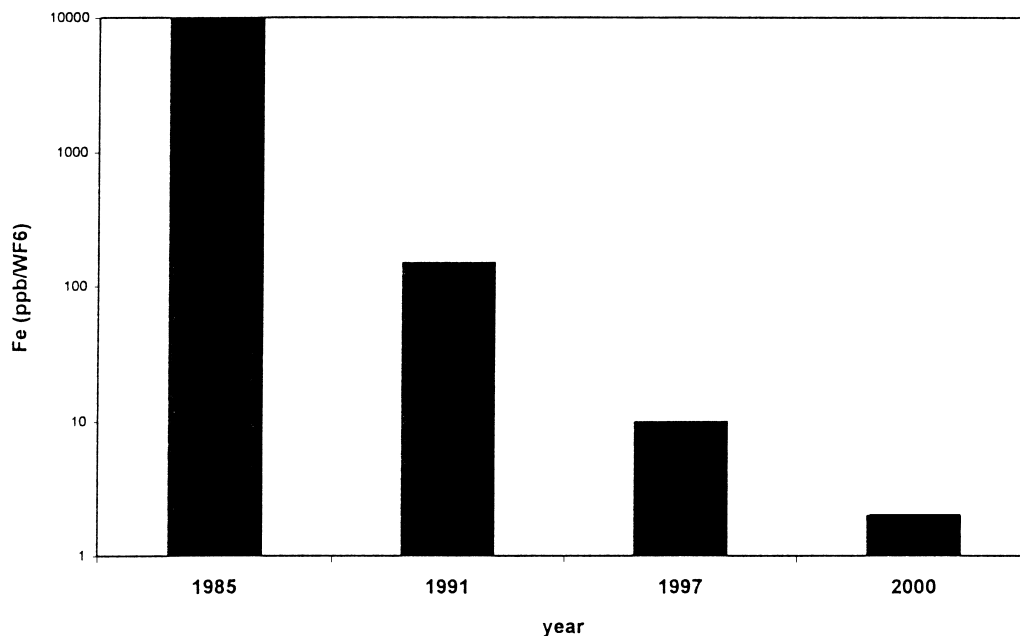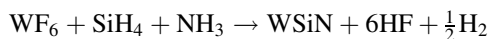
$$WF_6 + SiH_4 + NH_3 \rightarrow WSiN + 6HF + \tfrac{1}{2}H_2$$

$$WF_6 + \tfrac{1}{2}B_2H_6 + NH_3 \rightarrow WBN + 6HF$$

W thin films for gate applications can also be obtained by thermal conversion of WN_x films [14,15]. Fig. 1 shows the evolution of highest WF_6 purity produced at Comurhex in the last decade.

In order to certify this purity to the end user at the Fab, it has become necessary to address the following items:

- mastering the behaviour of materials in contact with WF_6 (cylinder, pipes, gaskets and valves);
- predicting the evolution and distribution of impurities in liquid and gas phases, when the cylinders are emptied at the end point user;
- developing the capability to sample and analyse this product at the sub-ppb level.

2.1. Choice and preparation of materials

It is well known that passivation of materials is a critical step when dealing with fluoride gases. To avoid corrosion, pollution and particle generation, it is necessary to passivate metallic parts with high purity (low oxygen and low HF) fluorine or fluorine mixtures (e.g. F_2/N_2). This treatment, at first use or when exposed to air, removes unwanted residual organic or moisture and forms a fluoride metallic barrier. For example, in stainless steel, it is necessary to obtain a continuous well defined stoichiometric structure film. CrF_2 has a better corrosion resistance than FeF_2 and may be obtained by thermal treatment following passivation [14]. Low oxygen content is required because of CrO_2F_2

evolution. For nickel, it is important to remove the volatile phosphorus compound that may be formed (such as PF_5) in order to maintain a continuous NiF_2 film [16,17]. If fluorine is not available, WF_6 self passivation is possible but will be less efficient [18].

When choosing the material for the cylinder, several metals are possible: nickel, Monel, aluminium and alloys, stainless steel, carbon steel, depending on requested purity for the product.

Shelf life studies are necessary to certify that WF_6 remains at specification in the cylinder during use. At first sight, it could be assumed that critical impurities would be SiF_4 or CF_4, because they could be formed if the metal used for the cylinder contains traces of silicon (nickel, stainless steel, carbon steel cylinders) or carbon (carbon steel cylinders). In fact, we have never observed such an evolution for CF_4 but it is certainly the case for SiF_4. SiF_4 evolution will depend on material and passivation. Maximum difference in behaviour is obtained with non passivated low grade carbon cylinder and passivated high grade nickel cylinder (Fig. 2).

Other gas impurities can also evolve. Significant increase in hydrogen is always observed in nickel based cylinders. More generally, HF evolution is also detected.

During a shelf life study, metals such as Fe, Cr, Mn must be also monitored (Fig. 3). In the sub ppm range, they can be dissolved in liquid WF_6. However, they are less prone to cause problems to the end user because they are generally non-volatile (the end user empties the cylinder from the gas phase).

The initial point ($t = 0$) corresponds to WF_6 in the mother container prior to cylinder filling. In this experiment, Fe and Cr levels increase at the beginning of the shelf life study and
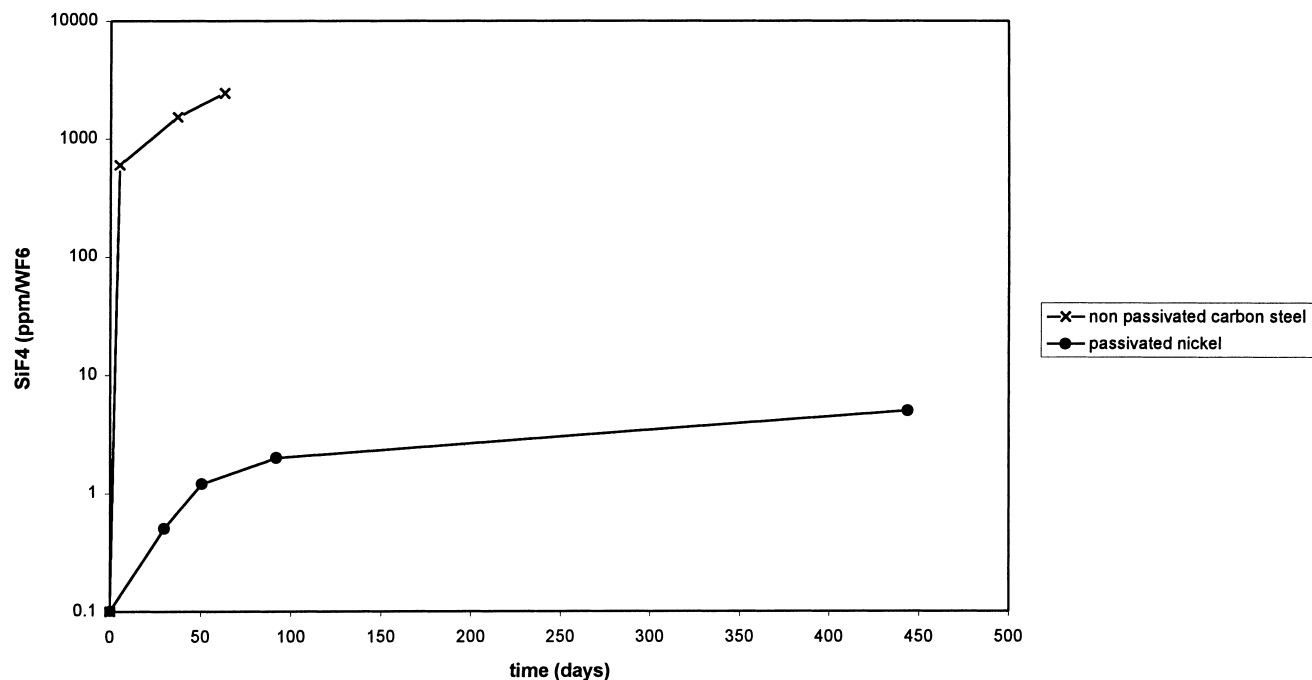
Fig. 2. Evolution of SiF$_4$ in WF$_6$ in two cylinders.

then stabilise during storage when an equilibrium is reached with cylinder walls. A second increase is observed after 400 days storage. This has been correlated to the rise of HF content in the cylinder.

Plastics are also used for pipes and valves. Resistance to HF corrosion and WF$_6$ swelling must be tested in clean rooms, for example, by dipping samples in the corrosive media and analysing the metal evolution in the liquid.

Fig. 4 shows a typical evolution of iron in an acidic media (HF/HCl) for PTFE, PFA, FEP and PVDF samples over 7 and 14 days. In this experiment, FEP exhibits minimum pollution. Iron is expressed in μg/cm^2 of exposed plastic. BR is the reagent blank: the acidic media is kept in a same beaker for the same amount of time but without sample exposure.

Again performance depends on the surface history and preparation of these materials.

2.2. Predicting WF$_6$ purity when emptying the cylinder

WF$_6$ is present in two phases in the cylinder: a liquid phase and a gas phase. As it is used as a gas at CVD Fabs, it is necessary to fully determine the distribution of impurities between the phases [19]. Indeed, impurities more volatile than WF$_6$ (e.g. CO$_2$, SiF$_4$) will decrease when emptying the cylinder, whereas impurities less volatile (e.g. MoF$_6$, UF$_6$) will increase.

To empty completely the WF$_6$ cylinder at the Fab or to neglect an initial purging of the gas phase will imply the same following drawback: a major variation of WF$_6$ quality during use. Therefore, prediction of WF$_6$ quality will enable to optimise the residual heel and the initial gas phase purging.

To predict the behaviour of volatile impurities, a calculation is required and involves the measurement of the Henry
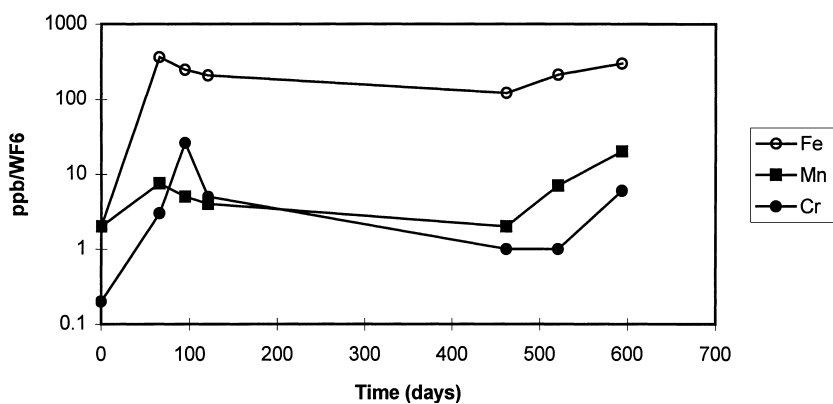

Fig. 3. Evolution of metal impurities in cylinder during a shelf life study.
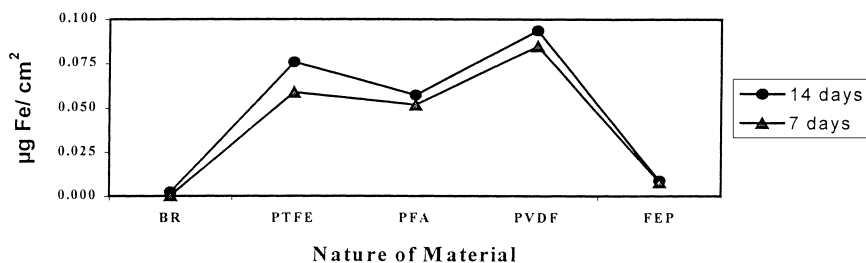
Fig. 4. Fe contamination from various fluorinated plastics.

coefficient in the WF_6 media (i.e. the repartition of the impurities between the two phases). Henry's law shows that the partial pressure of an impurity remains proportional to its concentration in the liquid phase.

Fig. 5 shows the dramatic drop of CO_2 concentration when emptying a cylinder with an initial concentration of 1 ppm.

2.3. Optimising WF_6 analysis

In order to prevent bias, liquid phase sampling is necessary for metal impurities, whereas gas phase sampling is needed for gas impurities. In order to reach the sub ppb level for metals (e.g. 0.1 ppb for thorium), the tungsten must be removed.

Tungsten removal can be performed by hydrolysis and selective liquid/liquid extraction [20]. This technique is reliable but does not apply to all elements (Mo or U are generally co-extracted with W) and does not provide very low detection limits because of the use of chemicals such as amines. Mo and U must then be determined in the W hydrolysate.

Another technique for W removal is called the "residue method": WF_6 is simply evaporated under a slow helium flow and the residual impurities are dissolved in $HF + HNO_3$ mix and dosed by ICP-MS or GFAAS [21]. Mastering the speed of evaporation

- prevents unwanted loss of residue particles or clusters;
- favours the fixation of select volatile impurities (e.g. MoF_6 or UF_6) which react more readily with trace residual water than WF_6 itself. Good recovery rates can then be obtained for traditional volatile species (MoF_6, UF_6).

Controlling the evaporation speed can be performed through on-line FTIR measurement of WF_6 peaks at 1386 and $712 \, cm^{-1}$, as shown in Fig. 6. Monitoring the WF_6 signal also helps to optimise the duration of the evaporation. W concentration in the "residue" $HF + HNO_3$ solution is important because it impairs the analytical detection limits (e.g. WO_3 isobaric interference on Th when using ICP-MS).

The recovery rate of the residue method can be checked using spikes. However, such spikes may not always be fully representative of the behaviour of the real impurities in WF_6. For example, to spike molybdenum with a standard solution
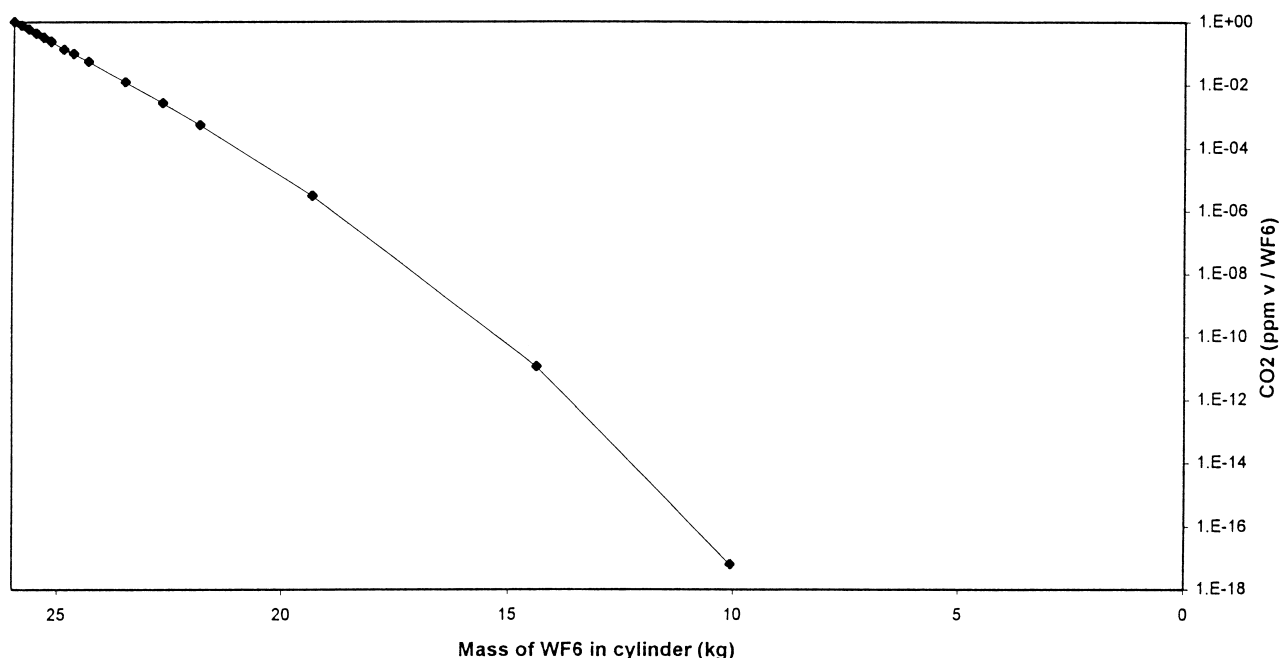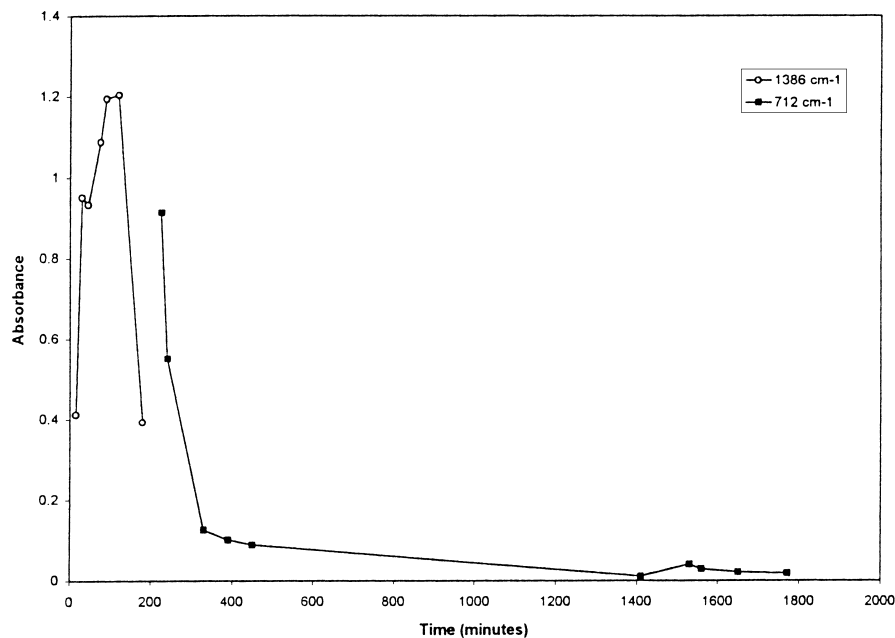

Fig. 5. Calculated CO_2 level in WF_6 when emptying cylinder.

Fig. 6. FTIR absorbance during WF_6 evaporation.

will yield, depending on conditions, a salt, oxide or oxy-fluoride. These species may not readily form MoF_6 upon addition of WF_6 and, therefore, the volatile properties of molybdenum, as expected for MoF_6, may be biased by such spike.

For other elements (such as calcium), to spike as representative chemical species (such as CaF_2) is feasible. However, one must keep in mind that below the sub-ppm level, most fluorides will be soluble in WF_6. Therefore, it must be made certain that during the experiment the spike has time to dissolve. During the evaporation process, the impurity will precipitate in a very disperse form. Such fine

powder is expected to be very sensitive to the speed of the helium flow (due to potential loss by the gas flow). If the spike does not dissolve, then the final granulometry may not be representative.

When implementing this residue technique, it is, therefore, highly recommended to compare results with the hydrolysis method (when applicable), or with a direct determination in the W matrix. In Table 1, we have compared the hydrolysis and the residue techniques. It was concluded that they were in fair agreement.

All these considerations have permitted to obtain a very pure WF_6 as requested by customers for ULSI applications.

Table 1
Comparison of two analytical techniques for WF_6 (hydrolysis and residue)[a]

| Impurity	Batch 1		Batch 2		Batch 3		Batch 4		Batch 5	
	Residue	Hydrolysis	Residue	Hydrolysis	Residue	Hydrolysis	Residue	Hydrolysis	Residue	Hydrolysis
Al	2	<50	2	<50	15	<50	4	<50	2	<50
Ca	2	7	2	24	9	7	5	8	3	11
Co	0.4	0	0.3	0	2	0	0	0	<1	<1
Cr	10	9	12	1.2	10	13	2.5	0	1.3	1
Cu	2	2	17	2	3.5	2	3	7	–	<1
Fe	44	50	–	18	47	37	5	6	7	14
K	4	2	3	5	6	1	1	13	1.1	6
Mg	2	16	2	6	17	17	3	4	0.4	18
Mn	10	5	4	2	20	3	2.5	0	0.4	<1
Mo	3	<10	2	<10	–	<10	<0.1	<10	–	–
Na	4	10	20	17	9	3	8	7	0.9	1
Ni	17	12	–	6	10	7	0.5	0	–	7
Pb	0	0	0	0	–	4	0.4	0	0.1	<1
Th	0.06	<10	0.05	<10	–	<10	–	<10	–	–
U	0.1	<10	0.1	<10	0.08	<10	0.02	<10	–	–
Zn	1	18	0.5	16	10	19	13	9	1.6	11

[a] All results in ppb/WF_6.

However, it must also not be forgotten that lower purity WF_6 can be also used for certain applications (e.g. LSI circuits).

3. Developments in ClF$_3$

ClF_3 is produced by the direct exothermic fluorination of chlorine

$$Cl_2(g) + 3F_2(g) \rightarrow 2ClF_3(g), \quad \Delta H = -159 \, kJ/mol \, at \, 298 \, K$$
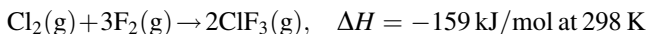
Other compounds ClF and ClF$_5$ can be obtained following the conditions of the process.

$$Cl_2(g) + F_2(g) \rightarrow 2ClF(g)$$

$$Cl_2(g) + 5F_2(g) \rightarrow 2ClF_5(g)$$
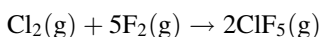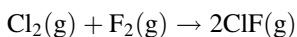
ClF_3 is a reactive fluorinating agent used in large scale since several years for nuclear applications. It is used as an in situ cleaning and passivation agent for gas diffusion barriers in uranium enrichment plants [22–25].

Since 1993, most Japanese companies have integrated this molecule for cleaning the LP CVD and PE CVD reactors used by semiconductor manufacturers [26].

There are many examples of applications (semiconductors, micro-machines and solar cell technology) [27–39]. Indeed, ClF_3 presents the following advantages:

- capacity to etch a wide range of coatings;
- increase of tool productivity because of high etching rate and no loss of time between deposition and cleaning steps;
- low temperature process without plasma, furthermore ClF_3 will clean all the parts of the machine including inner and outer lines.

As a consequence, maintenance is reduced and operating costs are lowered. This gas has been widely demonstrated as safe to handle. It is even considered safer than wet cleaning. Furthermore, it does not yield any release of GWP gases such as CF_4, C_2F_6 and NF_3 [40] and, therefore, has less impact on the environment. Technologies for controlled abatement have been extensively studied [41].

Despite all these advantages, the use of ClF_3 remains limited for the moment outside of Japan.

3.1. Choice and preparation of materials

As already presented for WF_6, the use of a corrosive fluoride gas such as ClF_3 is possible if some conditions are well taken care of as described below. The right choice of materials will guarantee safety and purity consistency of the product.

Several studies focus on the design of supply and exhaust gas systems and also on the design of packages [42,43]. In order to prevent corrosion in ClF_3 supply and exhaust pipes, it is, for example, necessary to avoid not only leaks but also ClF_3 condensation. An application of this approach is perfectly described in a recent paper [44].

For the cylinder body, mechanical and chemical resistant materials must be chosen. Stainless steel and nickel have proven good materials at ambient temperature. For the seat of the valve, metal to metal contact must be used.

Indeed for each new material or new conditions, it is necessary to run specific tests with ClF_3. In Fig. 7, we have selected three examples. Stainless steel, PTFE high and low grade samples have been exposed to liquid ClF_3 for 40 h at room temperature.

SEM pictures and EDX spectra were collected before and after the test.

The EDX spectrum show no evolution for stainless steel, whereas for PTFE an increase of the fluorine to carbon ratio is noticed for the composition of the film.

No major evolution is detected for the micro-structure of stainless steel, except perhaps a reduction of surface microporosity. For PTFE, the effect is more important for the low grade material where significant swelling or degradation is observed. It shows that careful attention must be taken when choosing a polymer for ClF_3 use. Such polymeric tape is used to screw the valve on the cylinder body.

Our great experience in ClF_3 manufacturing and our testing program of materials in gaseous and liquid ClF_3 permit a right selection of materials.

These materials must be absolutely passivated before use. This process is done with gaseous ClF_3, following precise experimental conditions. It must be performed on initially cleaned surfaces, free of residual grease, oil or organics. For stainless steel, an alternative treatment is possible by strong ozone passivation [45].

3.2. Optimising ClF$_3$ analysis

Since ClF_3 is just used as a cleaning agent, 99.9% purity is only required. Gas impurities are easily detected in the 5–10 ppm range by FTIR (HF, CO_2) or GC (ClF, Cl_2, N_2, O_2, ClO_2F, ClO_3F). GC can even be performed without back-purging and using conventional catharometers (whereas in the case of WF_6, back-purging is required and tritium detectors or helium discharge detectors must be used in order to detect sub ppm level of impurities). The largest difficulty here for ClF_3 is really to obtain standard calibration mixtures for such gases as ClF, ClO_2F, etc.

On the contrary, analysing metals in liquid ClF_3 presents a real challenge. The hydrolysis of the liquid is not practical due to the extreme reactivity of ClF_3 with water. The hydrolysis of gaseous ClF_3 has been tested [46]. However, because all specified impurities do not form volatile fluorides (Fe, Cr, K, Na, Ca, Cu, etc.), this technique may not be representative of cylinder content (mostly liquid ClF_3). Besides, large F + Cl concentration (which might result from ClF_3 hydrolysis in water) will yield high isobaric interference for ICP-MS even when using cold plasma conditions. Fig. 8 shows the effect of 4 g/l of F + Cl on the reagent blank for masses from 50 to 58 (RF power: 600 W, flow rate: 1.2 ml/min, total integration time per
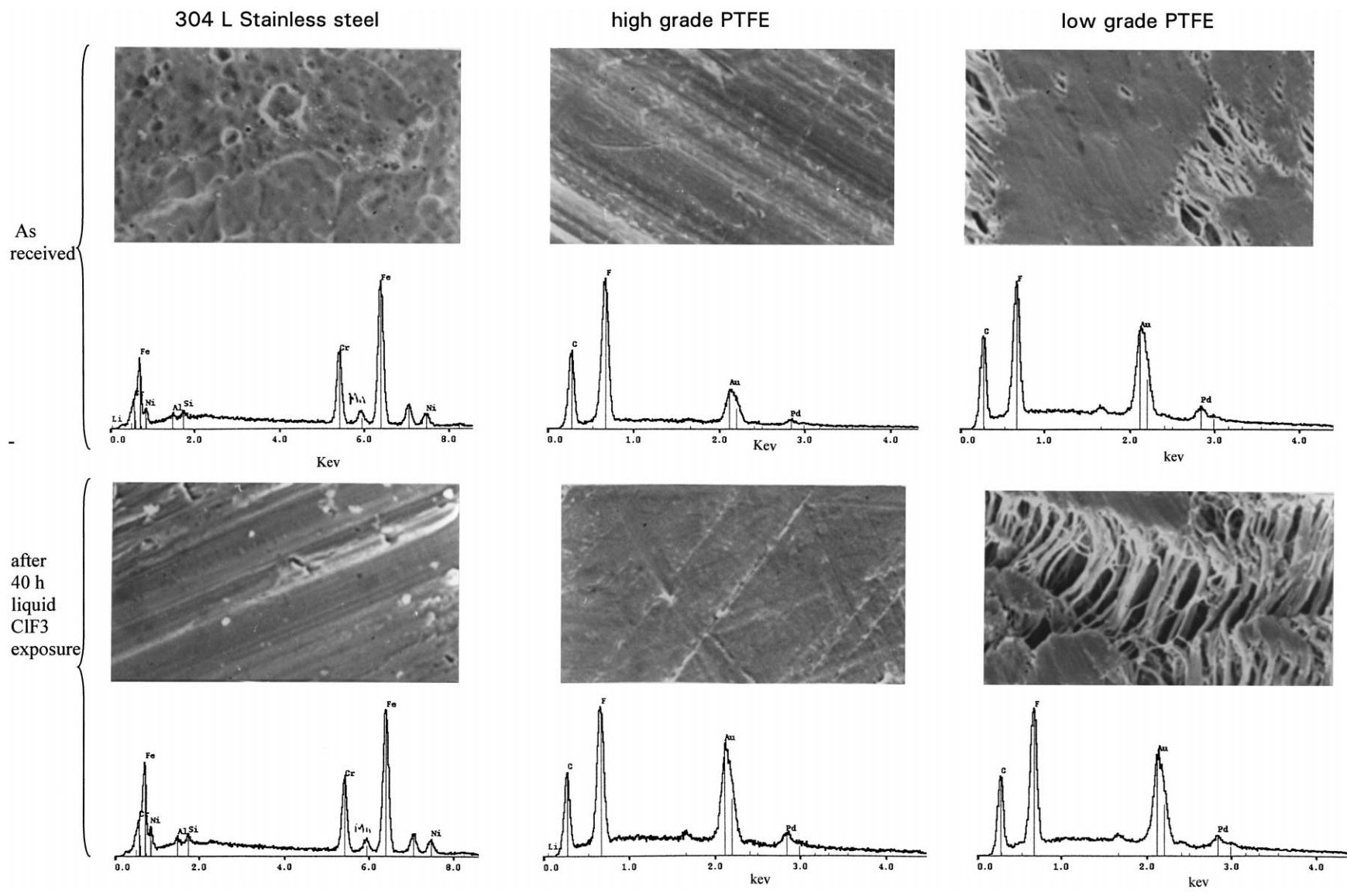
304 L Stainless steel

high grade PTFE

low grade PTFE

As received

after 40 h liquid ClF3 exposure

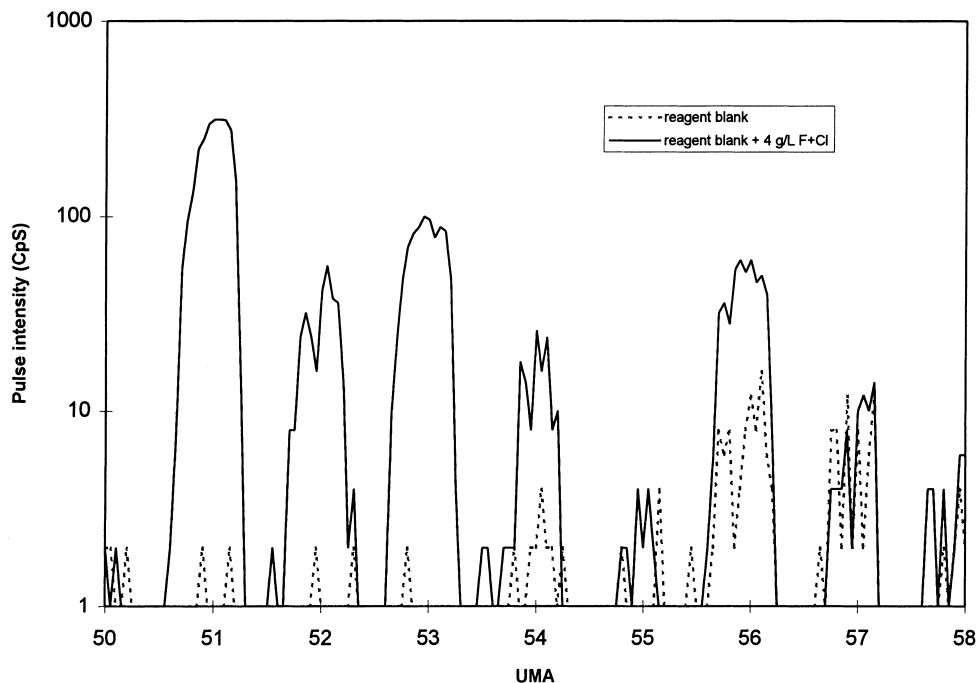Fig. 7. Testing several materials in liquid ClF$_3$ (X 2000) SEM pictures of exposed surface with EDX spectra.

Fig. 8. ICP-MS mass scanning of two solutions.

mass: 10 s). The large increase is due to ^{35}ClO (mass 51), $^{35}ClOH$ (mass 52), ^{37}ClO (mass 53), ^{35}ClF (mass 54), ^{37}ClF (mass 56). They impair the determination of ^{51}V, ^{52}Cr, ^{53}Cr, ^{54}Fe and ^{56}Fe.

When developing ClF_3 for microelectronic application, we have chosen the residue technique. 500 g to 1 kg liquid ClF_3 is sampled in a nickel or aluminium 1 litre pot (see Fig. 9). ClF_3 is then evaporated under a 5 l/h helium flow and
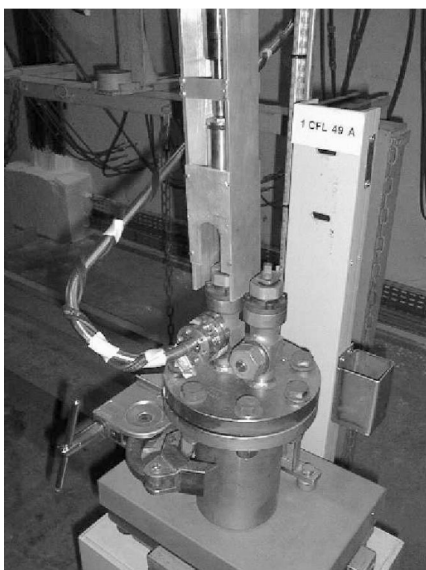
Table 2
Detection limit for Fe, Ca, K in ClF_3

Impurity	Detection limit (3σ basis) ppb/ClF_3
Fe	0.01
Ca	0.2
K	0.02

the residue is dissolved in 100 ml H_2O and 100 ml 2% volume HNO_3 after opening in a clean room. The pot is systematically spiked with Re and Rh prior to sampling with ClF_3 and a recovery rate is calculated when dosing the residue. Recovery rates vary from 85 to 105%.

As a result, low detection limits have been obtained even for difficult elements when using ICP-MS (see Table 2). The use of a semi-quantitative panoramic program was successful for determining all metals. No bias, due to potential residual F or Cl was found even for Cr, Mn, Co, Ga, V, As and Se [47].

4. Conclusions

Comurhex has shown with WF_6 and ClF_3 a reliable capacity to offer new fluorinated products for microelectronic applications. This was made possible because of a long experience in UF_6 and F_2 fabrication. Material studies and analytical developments were also necessary.

Fig. 9. Evaporation test installation for ClF_3.

With a F_2 production of more than 2000 t per year in its Pierrelatte Plant, Comurhex can satisfy current and future market needs for new fluorinated molecules.

Acknowledgements

References

[1] Peter Von Zant, Microchip Fabrication, McGraw-Hill, 1997, p. 15.

[2] C. Esteban, M. Druges, Future Fab International, Issue No. 6, p. 195.

[3] L. Ulmer, L. Georges, J.C. Veler, Y. Morand, M. Bakli, V. Ferrier, M. Lerme, L. Perroud, T. Morel, Effect of tungsten chemical vapor deposition nucleation step on via performance (CEA LETI Grenoble), Microelectron. Eng. 33 (1–4) (1997) 121.

[4] J. Wu, Y.L. Wang, J. Dun, Y.L. Wu, Integration methodology of chemical vapor deposition TiN, chemical vapor deposition W and W chemical mechanical planarization for sub-quarter micron process application, in: Proceedings of the First International Conference on Advanced Materials and Processes for Microelectronics, San Jose, CA, USA, 15–19 March 1999, J. Vac. Sci. Technol. B, Microelectronic Nanometer Struct. (USA) 17 (5) (1999) 2300.

[5] Ozkan, S. Cengiz, Moinpour, Mansour, M. Sarikaya (University of Standford), Characterization of dichlorosilane based tungsten silicide films for local interconnects, Symposium on Advanced Metallization for Future ULSI, San Francisco, 1996, pp. 297–302.

[6] C.J. Galewski, C.A. Sans, P.N. Gadgil, L.D. Matthysse, N. Zetterquist, W/WN_x as a low-resistance gate material and local interconnect (Genus, Div. Thin Film), Microelectron. Eng. 37/38 (4) (1997) 365.

[7] J.S. Byun, D.K. Sohn, S.J. Choi, B.H. Lee, J.S. Park, J.J. Kim, Formation of high conductivity WSi_x layer and its characterization as a gate electrode (Novellus Systems/LG Semicon. Co. Ltd.), J. Electrochem. 145 (1998) 3228.

[8] P.M. Smith, J.S. Custer, J.G. Fleming, E. Roherty-Osmun, M. Cohn, R.V. Jones, (Sandia National Labs.) Chemical vapor deposition of ternary refractory nitrides for diffusion barrier applications, Interconnection Conference, Santa Clara, USA, June 1996.

[9] M.T. Wang, L.J. Chen, M-C Chen, Barrier capabilities of selective chemical vapor deposited W films and $WSiN/WSi_x/W$ stacked layers against Cu diffusion, J. Electrochem. 146 (1999) 728.

[10] Sandia Corp., US Patent 5916634 A, Tungsten silicon nitride or tungsten boron nitride thin films for micro-machining and diffusion barriers in semiconductor manufacture.

[11] J.P. Lu, W.Y. Hsu, Q.Z. Hong, G.A. Dixit, V.T. Cordasco, S.W. Russel, J.D. Luttmer, R.H. Havemann, L.K. Magel, L.H. Tsai, (Texas Instruments, Dallas) An ammonia-free PECVD process for depositing tungsten nitride films and its application in copper metallization,

[12] Park Byung lyul, Ko Dae Hong, Kim Young Sun, Ha Jung Min, Park Young Wook, Lee Sang In, Lee Myoung Bum, Chung U. In, Koh Young Bum, Lee Moon Yong, (Samsung Electronics Co. Ltd.) Characteristics of PECVD grown tungsten nitride films as diffusion-barrier layers for ULSI DRAM applications, J. Electron. Mater. 26 (2) (1997) 1.

[13] K.K. Lai, A.W. Mak, T.P.H.F. Wendling, P. Jian, B. Hathcock, (Applied Materials, Santa Clara, CA) Characterization of a PECVD W_xN process using N-2, H-2 and WF_6, Thin Solid Films 332 (1/2) (1998) 329.

[14] C.J. Galewski et al. (Genus, Steag, Accurel), European semiconductor, February 2000, 28.

[15] N. Miki, M. Maeno, K. Maruhashi, Y. Nakagawa, T. Ohmi, Fluorine passivation of stainless steel (Hashimoto Chem. Corp.), Corrosion Science 31 (1990) 69.

[16] M. Maeno, R. Hirayama, H. Izumi (Hashimoto Chem. Corp.), N. Miki, K. Chiba, Y. Mikasa, H. Matsushita (Mitsubishi Aluminium Company), Fluorine passivation of metal alloy surface with volatile reaction enhanced mechanism, J. Electrochem. Soc. Corrosion Sci. 139 (7) (1992) 1865.

[17] M. Maeno, R. Hirayama, H. Izumi (Hashimoto Chem. Corp.), H.R. Takahashi, K. Chiba (Mitsubishi Aluminium Company), R.N. Vrtis, T. Ohmi, Fluorine passivated electroless Ni–P films, Journal of Electrochem. Soc. Corrosion Sci. 141 (1994) 2649.

[18] D.A. Bohling, M.A. George (Air Products), Controlling contamination in WF_6 applications, J. Semiconductor Int., 1991.

[19] C. Allgood, Solid State Technology, September 1999, p. 63.

[20] W. Saab, A. Sarda, Anal. Chim. Acta (Comurhex) 248 (1991) 235.

[21] R.L. Sutton, J. Anal. Atomic Spectrometry (Airco) 9 (1994) 1079.

[22] L.M. Vincent et J. Gillardeau (Centre d' Etudes Nucléaires de Saclay), Le Trifluorure de Chlore, Rapport CEA No. 2360.

[23] D.F. Williams, J.C. Rudolph, G.D. Del Cul, S.L. Loghry, D.W.Simmons (Oak Ridge Nat. Lab.), Laboratory tests using Chlorine Trifluoride in support of Deposit Removal at MSRE, ORNL/TM-13403 Sponsored by DOE, April 97.

[24] L.D. Trowbridge ((Oak Ridge Nat. Lab.).), Technical bases for the use of ClF_3 in the MSRE reactive gas removal project at Oak Ridge National Laboratory, ORNL/ER-402-Sponsored by DOE, June 97.

[25] K.J. Wills (Batelle Mem. Inst., Oak Ridge), The reaction of chlorine trifluoride and uranyl fluoride: a critical literature review and kinetics analysis, in: Proceedings of the Topical Meeting on Decommissioning, Decontamination and Reutilization of Commercial and Government Facilities, September 97.

[26] SEMI, SIA, SSA, NCFCA, SEMATECH, Hazards versus Benefits of ClF_3, August 1998.

[27] TOSHIBA, Cleaning process for film forming chamber involves removing treated substrate from chamber after finishing selective CVD process for forming tungsten film, Patent JP 7094418 A (1995).

[28] FUJITSU LTD, Thin film forming appts. for cleaning reaction furnace of low pressure CVD furnace, dilutes density of ClF_3 gas by supplying inert gas and is introduced inside reaction furnace to clean it, Patent JP 8088177 A (1996).

[29] CENTRAL GLASS, Cleaning gas for film forming unit comprises tetrafluoromethane or hexafluoroethane contg. specified amts. of fluorine, chlorine trifluoride, and bromine tri or pentafluoride, Patent JP 8060368 A (1996).

[30] H. Habuka, T. Otsuka, Qu. Wei-Feng, Dominant overall chemical reaction in a chlorine trifluoride–silicon–nitrogen system at atmospheric pressure (Isobe R&D Center Shin-Etsu/Handotai Co.), Jap. J. Appl. Phys. 38 (1) (1999) 6466.

[31] SEMICONDUCTOR ENERGY LAB, Etching appts., e.g. for semiconductor IC mfr. has light source which irradiates light beams on outline of substrate installed in reaction receptacle, along vertical direction, Patent JP 8167597 A (1996).

[32] TOSHIBA KK, Surface treating appts. For high speed and uniform etching has reaction chamber contg. Rotating sample holder which rotates at high speed, Patent JP 8274072 A (1996).

[33] J.P. Chang, Z. Zhang, H. Xu, H.H. Sawin, J.W. Butterbaugh, Metal removal with a ClF/sub 3/beam at room temperature, in: Proceedings of the Fourth International Symposium on Cleaning Technology in Semiconductor Device Manufacturing, MIT Press, Cambridge, October 1995.

[34] A.M. Pierce, M. Taylor, J. Sauer, D. Ruppert, Safe usage of ClF$_3$: supply, vacuum service and exhaust gas management (Edwards High Vacuum Int. CA), Solid State Technology, CP–USA, Vol. 40, No. 9, pages 107, 110, 112, 114, September 1997.

[35] CENTRAL GLASS, Cleaning tantalum oxide production apparatus comprises removing piled decomposed tantalum oxide by reacting with e.g. fluorine or chlorine trifluoride, Patent JP 9301718 A.

[36] H.M. Kim, M. Shibuya, A. Yoshida, M. Kitagawa, Gas-phase etching with ClF$_3$ gas at atmospheric pressure and at room temperature anisotropic etching (Matsushita Elec. Ind. KK), Appl. Surf. Sci. 133 (1998) 1.

[37] TOKYO ELECTRON, Cleaning method of reaction tube used during formation of silicon layer by epitaxial growth, CVD process involves using chlorine trifluoride for cleaning interior of chamber after taking out processed substance from it, Patent JP 10156172 A.

[38] APPLIED MATERIALS, Removing unwanted deposits especially metals by applying a high temperature plasma of a chlorine containing gas, Patent EP 855453 A.

[39] MATSUSHITA ELEC IND. KK, Semiconductor based solar battery manufacturing method involves sending ClF$_3$ gas into quartz furnace at temperature of 400°C under atmospheric pressure, Patent JP 10178194 A.

[40] F. Fracassi, R. d' Agostino, F. Illuzi, Evaluation and reduction of the contribution of SiO$_2$ dry etching to global warning (ST Microelectronics Central R&D), Le VIDE 292 (1999) 245.

[41] A.M. Pierce, M. Taylor (Edwards high Vacuum International), J. Sauer, D. Ruppert (BOC Gases) Safe usage of ClF$_3$: supply, vacuum service, and exhaust gas management, Solid State Technology September 1997, p. 107.

[42] C.J. Gugliemini, A.D. Johnson (Air Products and Chemicals Inc.), Properties and reactivity of chlorine trifluoride, Semiconductor International, June 1999, p. 162.

[43] A.P. Taylor, R. Hogle (BOC) B. Fruhberger (Sensor Research & Development Corp.), Interaction of ClF$_3$ with metal alloys and polymer gaskets, Semiconductor International, July 1999, pp. 201–211.

[44] D. Ruppert et al. (BOC Group), ClF$_3$ and other low vapor pressure gas system, Semiconductor International, July 1997, 253.

[45] K. Koike, G. Inoue, T. Takata, T. Fukuda, Ozone passivation technique for corrosive gas distribution system (Iwatani), Jap. J. Appl. Phys. 36 (1) (1997) 7437.

[46] S.N. Ketkar, K.L. Marhefka, M.D. Wagner (Air Products & Chemicals Inc. Allentown), Analysis of trace metals in chlorine trifluoride (ClF$_3$), in: Proceedings of the Annual Technical Meeting 1998.

[47] P. Costamagna, D. Jacques, B. Morel, A. Jourdan (Comurhex), ICP-MS determination of metals in ultra-pure ClF$_3$, poster presented at the ICP-MS winter conference, Pau, France, January 1999.