

SEMI F79-0710

GUIDE FOR GAS COMPATIBILITY WITH SILICON USED IN GAS DISTRIBUTION COMPONENTS

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NOTICE: This document was completely rewritten in 2010.

1 Purpose

1.1 The purpose of this guide is to identify resource information on compatibility of gases in contact with silicon in the wetted path of a gas delivery system operating at typical gas distribution system conditions.

2 Scope

2.1 The information and conclusions provided are taken from published literature. References are cited. Recommendations are made based on the cited literature, although no opinion is made as to the validity of the cited literature.

2.2 The suggestions are specific to high purity silicon, single or poly crystal, covered by native oxide.

NOTICE: This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the users of this standard to establish appropriate safety and health practices and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 This guideline applies to the gas distribution system for a typical semiconductor process tool. It is assumed that silicon is in the wetted path as a coating or a silicon-based component (e.g., a valve, orifice, sensor, mass flow controller) in the gas distribution system. The ambient temperature and operating temperature limits are typical for gas distribution systems in the semiconductor fabrication industry. No additional energy source, thermal, radiative or ionizing, is present. The moisture content of the gas is not specified for the purpose of this guideline.

4 Referenced Standards and Documents

4.1 SEMI Standard

SEMI E52 — Practice for Referencing Gases, Gases Mixtures and Vaporizable Materials Used in Digital Mass Flow Controllers

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Abbreviations and Acronyms

5.1.1 T — Temperature

5.2 Definitions

5.2.1 E_{etch} — energy of etching.

5.2.2 K — boltzman constant.

5.2.3 n_x — atomic concentration of element x.

5.2.4 $R(x)$ — etching rate of species x.

5.2.5 $Si(111)$ — 111 crystallographic plane of silicon.

5.3 Symbols

5.3.1 B — boron

- 5.3.2 *Br* — bromine
- 5.3.3 *C* — carbon
- 5.3.4 *Cl* — chlorine
- 5.3.5 *F* — fluorine
- 5.3.6 *H* — hydrogen
- 5.3.7 *I* — iodine
- 5.3.8 *N* — nitrogen
- 5.3.9 *P* — phosphorous
- 5.3.10 *S* — sulfur
- 5.3.11 *Si* — silicon
- 5.3.12 *W* — tungsten
- 5.3.13 *Xe* — xenon

6 Classification of Gases

6.1 The classification of gases in this document follows that of SEMI E52 with the exception of the addition of bases. The user is referred to SEMI E52 for lists of specific gases assignments to classes:

- 6.1.1 Inerts,
- 6.1.2 Hydrogen,
- 6.1.3 Hydrocarbons,
- 6.1.4 Halogenated Hydrocarbons,
- 6.1.5 Hydrides,
- 6.1.6 Halogens; other than Fluorine,
- 6.1.7 Halides; other than Fluorides,
- 6.1.8 Fluorine and Fluorides,
- 6.1.9 Organo-metallic and Siloxanes,
- 6.1.10 Oxygen and Oxides and Sulfides,
- 6.1.11 Nitrogen and Nitrogen Compounds,
- 6.1.12 Acids,
- 6.1.13 Bases.

7 Review of the literature

7.1 *Inert Gases* — References ^{1,2,3,4,5} indicate these gases do not react with silicon under the conditions typical for gas distribution systems.

7.2 *Hydrogen Gas* — References ¹⁻⁵ indicate these gases do not react with silicon under the conditions typical for gas distribution systems.

7.2.1 Hydrogen has been reported to react with silicon⁶ and silicon carbide⁷ at temperatures above 1100°C.

1 Williams, K., and Muller, R., "Etch Rates for Micromachining Processing" *IEEE J. Microelectromech. Sys.*, Vol. 5, No. 4 (1996): pp. 256-269.

2 Jansen, H., *et al.* "A Survey on the Reactive Ion Etching of Silicon in Microtechnology" *J. Micromech. Microeng.*, Vol. 6 (1996): pp. 14-28.

3 Eriksen G., and Dyrbye, K., "Protective Coatings in Harsh Environments" *J. Micromech. Microeng.*, Vol.6 (1996): pp. 55-57.

4 Pogge, H. B., eds. "Electronic Materials Chemistry" Marcel Dekker, 1996.

5 Walker, P., and Tarn, W., eds. "CRC Handbook of Metal Etchants" CRC Press, 1991.

7.3 *Hydrocarbon Gases* — References ^{1-5,8,9} indicate these gases do not react with silicon under the conditions typical for gas distribution systems.

7.4 *Halogenated Hydrocarbon Gases* — References ^{1-5,8,9,10,11,12,13,14,15} indicate these gases do not react with silicon under the conditions typical for gas distribution systems.

7.4.1 Extensive review papers by Flamm⁸ and Coburn⁹ cite numerous references on the etching of silicon and other materials using halogenated hydrocarbons. The critical requirement for etching of silicon, or any material using a halogenated hydrocarbon, is the presence of a radical species of fluorine, chlorine or other halogen such as generated by a low pressure plasma. In addition, Winters¹⁶ points out that for an unassisted etching reaction to take place adsorption onto the silicon surface must be followed by four well defined steps. Should any of the steps not occur, or be interrupted, etching will not proceed.

7.4.2 Two of the most widely used halogenated hydrocarbons are CF₄ and C₄F₈. The Matheson Gas Book¹⁷ states CF₄ is extremely stable, reacting only slightly even at the temperature of a carbon arc, and C₄F₈ is extremely stable, unreactive with other materials under ordinary conditions.

7.5 *Hydride Gases* — References ^{1-5,18,19,20} indicate these gases do not react with silicon under the conditions typical for gas distribution systems.

7.6 *Halogen Gases, other than Fluorine* — The halogens represent a special class of materials. Molecular or atomic chlorine, iodine or bromine have been reported not to etch silicon at temperatures below 200°C or without the assistance of a plasma ^{8,9,21,22,23,24}.

7.6.1 Schwartz ²⁵ makes the comment “Although Cl₂ chemisorbs spontaneously on silicon, (in a plasma) at low temperatures the reaction between Si and Cl does not proceed to the formation of SiCl₄. That is, silicon does not etch in Cl₂ except at elevated temperature.” He goes on to note: “...except in the case of highly doped silicon, etching occurs at low temperatures in the reactive ion etching system not because of the ease of Cl attachment but because partially reacted silicon can be sputtered readily.” Schwartz then reports the observation that there was no perceptible etching after thirty minutes in a Cl₂ plasma when there was no cathode bias on the wafer; in contrast to 4.5 micrometers of removal when the bias was applied.

6 Lange, G. A., *et al.*, “RCA Review.” 24 (1963): p. 488.

7 Harris, J. M., *et al.*, “Etching Characteristics of Silicon Carbide in Hydrogen.” *J.E.C.S.* 116 (3) (1969): p. 380.

8 Flamm, D. L., *et al.*, “The Design of Plasma Etchants.” *Plasma Chemistry and Plasma Processing* 1 (4) (1981): p. 317.

9 Coburn, J. W., “Plasma-Assisted Etching.” *Plasma Chemistry and Plasma Processing* 2 (1) (1982): p. 1.

10 Gugliemini, C. J., *et al.*, “Properties and Reactivity of Chlorine Trifluoride.” *Semiconductor International* (1999).

11 Ephrath, L. M., *et al.*, “Parameter and Reactor Dependence of Selective Oxide RIE in CF₄ + H₂.” *J.E.C.S.* 129 (10) (1982): p. 2282.

12 Wolf, S., *et al.*, “Silicon Processing for The VLSI Era.” Lattice Press, 1986; ISBN 0-961672-3-7.

13 d'Agostino, R., *et al.*, “Diagnostics and Decomposition Mechanism in RF Discharges of Fluorocarbons Utilized for Plasma Etching or Polymerization.” *Plasma Chemistry and Plasma Processing* 2 (3), (1981): p. 213.

14 du Pont, E. I., de Nemours and Company, “Zyron Electronic Gases.” *Application Guide: Dry Etching of Silicon Dioxide* www.dupont.com/zyron/appguide/app2.html.

15 Schilling, U., *et al.*, “Evaluation of c-C₄F₈ as Cleaning Gas in an Applied Materials Lamp Heated Universal Chamber for 200 mm Wafers.” International SEMATECH, technology Transfer #01084152A-TR (2001).

16 Winters, H. F., *et al.*, “The Role of Chemisorption in Plasma Etching.” *J. Appl. Phys.* Vol. 49 (10) (1978): p. 5165.

17 Braker, W., *et al.*, “Matheson Gas Data Book.” Sixth Edition, L of C 80-83159, 1980.

18 Cotton, F. A., *et al.*, “Advanced Inorganic Chemistry.” 5th Edition; John Wiley and Sons, 1988.

19 Douglas, B., *et al.*, “Concepts and Models of Inorganic Chemistry.” 2nd Edition; John Wiley and Sons, 1983.

20 Huheey, J. E., *et al.*, “Inorganic Chemistry: Principles of Structure and Reactivity.” 4th Edition; HarperCollins, 1993.

21 Ibbotson, D. E., *et al.*, “Plasmaless Dry Etching of Silicon with Fluorine-Containing Compounds,” *J. Appl. Phys.* Vol. 56 (10) (1984): pp. 2939–2942.

22 Tian, W. C., *et al.*, “Comparison of Cl₂ and F-Based Dry Etching for High Aspect Ratio Si Microstructures Etched With an Inductively Coupled Plasma Source.” *J. Vac. Sci. Technol. B* 18(4) (2000): p. 1890.

23 Walker, Z. H., *et al.*, “Kinetics of the Reaction of Molecular Bromine with Doped Polycrystalline Silicon.” *J.E.C.S.*, 138 (10) (1991): p. 3050.

24 Choe, J. Y., *et al.*, “Analysis of the Etching of Silicon in an Inductively Coupled Chlorine Plasma Using Laser Thermal Desorption.” *J. Vac. Sci. Tech.*, A15(6) (1997): p. 3024.

25 Schwartz, G. C., *et al.*, “Reactive Ion Etching of Silicon.” *J. Vac. Sci. Tech.*, 16 (2) (1979): p. 410.