SEMI F79-0914 (Reapproved 0922)
GUIDE FOR GAS COMPATIBILITY WITH SILICON USED IN GAS DISTRIBUTION COMPONENTS

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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: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 This Guide 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 Guide.

4 Referenced Standards and Documents

4.1 *SEMI Auxiliary Documents*

SEMI AUX030 — Codes for Referencing Gases, Gas 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

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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 Guide follows that of SEMI AUX030 with the exception of the addition of bases. The user is referred to SEMI AUX030 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.

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[1] Williams, K., and Muller, R., "Etch Rates for Micromachining Processing." *J. Microelectromech. Sys.* vol. 5 (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.

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7.2.1 Hydrogen has been reported to react with silicon[6] and silicon carbide[7] at temperatures above 1100°C.

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 Flamm[8] and Coburn[9] 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, Winters[16] 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 CF_4 and C_4F_8. The Matheson Gas Book[17] states CF_4 is extremely stable, reacting only slightly even at the temperature of a carbon arc, and C_4F_8 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 Cl_2 chemisorbs spontaneously on silicon, (in a plasma) at low temperatures the reaction between Si and Cl does not proceed to the formation of $SiCl_4$. That is, silicon does not etch in Cl_2 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 Cl_2 plasma when there was no cathode bias on the wafer; in contrast to 4.5 micrometers of removal when the bias was applied.

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[6] Lange, G. A., *et al.* "RCA Review." (1963): p. 488.

[7] Harris, J. M., *et al.* "Etching Characteristics of Silicon Carbide in Hydrogen." *J. Electrochem Soc.* vol. 116 No, 3 (1969): p. 380.

[8] Flamm, D. L., *et al.* "The Design of Plasma Etchants." *Plasma Chem Plasma Process*. vol. 1 (1981): p. 317.

[9] Coburn, J. W. "Plasma-Assisted Etching." *Plasma Chem Plasma Process*. vol. 2 (1982): p. 1.

[10] Gugliemini, C. J., *et al.* "Properties and Reactivity of Chlorine Trifluoride." *Semiconductor International II*, 1999.

[11] Ephrath, L. M., *et al.* "Parameter and Reactor Dependence of Selective Oxide RIE in CF4 + H2." *J. Electrochem Soc*. vol. 129 (1982): p. 2282.

[12] Wolf, S., *et al.* 'Silicon Processing for The VLSI Era.' Lattice Press, 1986.

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[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.

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[17] Braker, W., et al. 'Matheson Gas Data Book.' Sixth Edition, L of C 80-83159, 1980.

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[25] Schwartz, G. C., *et al.* 'Reactive Ion Etching of Silicon.' *J. Vac. Sci. Technol.* vol. 16 (1979): p. 410.

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