Generic Scenario: Wet Cleaning Process in Integrated Circuit Fabrication

Introduction

The semiconductor industry is one of the fastest growing industries in the world. Manufacturing of integrated circuits (ICs) constitutes a major segment of the semiconductor industry. The U.S. IC manufacturers comprise a $15.8 billion industry [1] that represents approximately a 100% increase from the year 1982 [2,3]. The size of the industry is based on factory shipments of ICs from the manufacturers in the United States. A dramatic increase in mixed-signal IC demand is expected in mid to late 1993 for use in communication components such as digital cellular phones, local-area networks (LANs), digital-signal-processing (DSP), and data compression [4].

In conjunction with the increased IC production, the market for supplies to the IC industry is expected to rise sharply. For example, the global market for semiconductor cleaning equipment will grow from revenues of an estimated $284.3 million this year to $506.4 million in 1998 [5,6]. The U.S. percent share of the cleaning equipment market is approximately 41% and is expected to jump to 46% in 1998. In addition, the ultrapure chemicals and gases market also is expected to jump from $6 billion to $10 billion in 1997 [7].

All IC products involve several basic fabrication steps. These steps may include cleaning, photolithography, impurity doping, etching, and film deposition. Certain levels of environmental hazard are associated with each step [8]. All products, however, require cleaning steps at various levels of IC production. This scenario describes the wet cleaning process in the IC manufacturing process with both automated and manual process controls. Most IC fabrication processes are, however, automated and are performed in clean rooms. Personnel exposure to hazardous gases or chemicals potentially could arise from equipment maintenance and accidents [10]. The chemicals used, the potential for human exposure, and the waste generated during wafer cleaning in the IC fabrication process are described below.

Wet Cleaning Process

In the IC industry, the cleaning process is one of the most critical and important steps in IC fabrication. Uncleaned wafers and parts create defective devices and drastically lower the production yield. Wafer contamination originates from the particulates (dirt, grease, soil, aerosols, etc.) generated by the equipment in the work area and/or the residues from the process chemicals (resist, fluxes, metal oxides, etc.) that are used in the earlier steps.

There are several ways to minimize contamination of the wafers and parts, including the use of hoods and recirculating systems [11] in the clean rooms and cleaning the wafers or IC parts by wet or dry chemical methods [12]. Articles in *Semiconductor International* [5,6] indicated that the wet wafer cleaning method still led other cleaning technologies in 1993.

Cleaning and Defluxing Equipment

The techniques and materials used for cleaning are determined by the type of contamination to be removed, type of product being cleaned, speed, cost, and other such considerations. These methods may include solvent spray, pulsating spray, solvent dip, vapor degreasing, ultrasonic immersion, and scrubbing with brushes and wheels. In several production lines, two or more methods of cleaning are used together. Both completely automated and semiautomated cleaning equipment are used in the IC industry [12,13].

Brushing, spraying, scrubbing, and ultrasonic cleaning may be classified as *physical or dry cleaning* methods. *Chemical methods* may involve dissolving the contaminants in the solvent or reacting the contaminants with special solutions. The cleaning equipment, however, may combine both the wet and the dry types of cleaning methods.

Ultrasonic cleaning equipment consists of transducers that convert electrical energy into mechanical energy and a tank with cleaning liquid. High-frequency and high-intensity sound waves create cavitation or numerous tiny bubbles that simulate scrubbing at a very fine scale. This method removes contamination from small cavities that are difficult to clean otherwise. Automated systems with conveyor belts are used where parts are lifted from one tank and cleaned continuously. These processes are not performed in closed systems; however, they are conducted in a clean-hood recirculating environment.
Vapor degreasing involves *suspending* parts in a chamber where vapors of the heated solvents condense on the parts for repeated flushing or washing with fresh solvent. In some systems, parts are immersed in a boiling solvent, followed by *immersion* in a cool solvent, and then are suspended for final vapor rinsing. These steps are performed in self-contained units that use refrigeration to trap the solvent vapors.

Spraying also is used in certain production lines. Spraying avoids the contamination problems common in immersion systems.

Cleaning Solutions and Solvents

There are two categories of cleaning systems: one is termed *solvents* and the other is classified as *aqueous* detergents (saponifiers). The solvents are organic liquids of four types: (1) hydrocarbons, (2) chlorinated hydrocarbons, (3) fluorinated or fluorinated-chlorinated compounds, and (4) azeotropes. The solvents are selected based on their cleaning power, flammability, compatibility, stability, toxicity, and purity [12,14].

The *hydrocarbon solvents* include alcohols, ketones, and some other aliphatic and polar solvents. The cleaning power of these solvents is low and they have medium compatibility and toxicity; however, they are highly flammable. Hydrocarbons are not recommended for vapor degreasing. The *chlorinated solvents* include methylene chloride, tetrachloroethylene, perchloroethylene, trichloroethylene, and methyl chloroform (1,1,1-trichloroethane). These solvents generally are nonpolar, nonflammable, strong cleaning agents with high toxicity. The *fluorinated solvents* include trichlorotrifluoroethane, trichloromonofluoromethane, and tetrachlorodifluoroethane. They are compatible with most products and have relatively low toxicity, but they have low cleaning power. The *azeotropic solvents* are a mixture of the above solvents with constant boiling systems. Azeotropes can be used in vapor degreasers.

The *aqueous detergents* can have a pH ranging from 0 to 14. The solutions vary from acidic (low pH), to non-ionic neutral (pH of 7), to alkaline (high pH). Aqueous detergents are targeted to remove scales, oxides, atmospheric dust, oils, and/or rust. Some of these chemicals include sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), ammonium hydroxide (NH_4OH), ammonium fluoride (NH_4F), several surfactants, and hydrofluoric acid (HF).

The wafer or IC parts are cleaned with either a solvent or an aqueous cleaner. Following the wet cleaning process, the wafer or IC parts typically are dried in a closed drying chamber.

<u>Human Involvement</u>: Most cleaning cycles are conducted in automated, vented wet chemical benches. Some of the completely automated systems are presented in *Semiconductor International* [5,6]. These types of wet cleaning systems require only one operator who sometimes runs three machines at a time. Hence, the latest state-of-the-art wet cleaning equipment requires minimal human involvement during routine cleaning processes.

<u>Waste</u>: The cleaning processes result in extremely large quantities of chemical waste. The waste generally contains relatively high concentrations of each cleaning chemical. Much of the solvent and precious metal waste is being recycled by today's IC industry to minimize waste.

An Example of a Wet Cleaning System and Operation

A generic, fully automated wet cleaning system may consist of as many as 10 stations [15]. The operations are all controlled by a multitask robotic computer system. All the operations are programmed into the systems, and the operation continues round-the-clock with a 2-axis transfer robot. As an example, for an 8" wafer system, 12-gallon tanks with recirculation capabilities filled with liquids are used at each station. At the first station, warm H_2SO_4, H_2O_2, or O_3 mixture in water is used to remove the inorganics and photoresist residues at temperatures up to 70°C. The second station would rinse the wafers with recirculating hot deionized water. The third station would contain dilute HF (in 1:10 ratio or less) to remove oxide contaminations at above or below the ambient temperatures. The fourth station would involve a constant cascading rinse with deionized water. In the fifth station, either RCA (Radio Corporation of America) or SC1 (Summo Clean) mixture would be applied. The latter consists of H_2O:H_2O_2:NH_4OH in the ratio of 5:1:0.5. This process normally is conducted at 73°C to remove organic contaminants. The sixth step is a rinse in deionized water, followed by an SE2 treatment (HCl+H_2O_2+H_2O) to remove metal contamination at the seventh station. The eighth and ninth stations perform post rinsing and the final rinse with deionized water. The tenth station is used to dry the wafers or IC parts by either a vapor drying or a spin rinsing process. Some of the rinsing steps may involve megasonic cleaning, which provides mechanical energy to physically remove residual contamination. The PMN chemical might be used as a solvent or a detergent specially in station #1, #3, #5, #7, and #10 as described above.

For an 8" wafer assembly line, 200 wafers are cleaned per hour (4 lots/hr and 50 wafers per lot). The treatment tanks are approximately 12 gallons in capacity. This system is completely enclosed and requires minimum supervision, with the possibility that one operator can run three wet cleaning systems at a time. In the recirculating baths, parallel filters are used to trap most of the particulates, and part of the stream is regenerated constantly. In contrast, older systems have tanks with 8 to 12 hours of life and have to be regenerated at the end of that period. The waste generated containing precious metals is collected and the metals are regenerated in separate equipment [15].

Data/Assumptions for Human Exposure and Waste Generated During the Cleaning Process in IC Fabrication

1. There are more than 200 IC production sites in the United States. These are located primarily on the West Coast (50% in California and Oregon), in the Northeast (25% in Massachusetts, New York, and Connecticut), and in the Southwest (15% in Texas, New Mexico, and Arizona) [16,17]. More than 35 companies market cleaning equipment and solutions for the IC industry.

2. The facilities typically operate 345 days/year.

3. Most facilities run 3 shifts/day.

4. For a completely automated cleaning system, a throughput of 200 wafers (8") per hour rate is possible with only 1 operator for 2 to 3 wet cleaning systems. Depending on the type of IC process and product, the wet cleaning system can be customized. However, several organizations still use semiautomatic systems where one or two operators are required to run each system. Normally, both semiautomatic and automatic systems operate with about 80 to 85% up time. The treatment tanks are approximately 12 gallons in capacity. Older systems would regenerate the tanks every 8 to 12 hours. Therefore in a given 8-hour workday, 10 to 12 gallons of material would be spent. The trend recently has been to move to recirculating systems which are more closed loop; therefore the quantity of spent cleaning solution is decreased.

Waste Generation, Environmental Releases, and Exposure-Level Calculations

PMN chemicals are most likely to be used as additives to aqueous cleaning solutions in the IC manufacturing process. Although organic solvents currently are used in IC cleaning, there is increasing focus on the use of water-based cleaning processes for minimizing environmental

impacts from the manufacturing process. In addition, hydrocarbon cleaners typically are pure solvents and hence are unlikely to contain PMN chemicals as minor components, as typically considered in these generic scenarios.

Assuming that the PMN chemical is a nonvolatile (or low-volatility) additive to an aqueous cleaning solution, we can consider the potential for environmental releases and worker exposure to the PMN chemical as a result of its use in IC cleaning. We assume that the cleaning solution containing the PMN chemical is provided ready for use to the IC cleaning facility. The wafer cleaning process also is assumed to be conducted using an automated system in a clean-room environment.

Assumptions

%PMN: weight percent of PMN chemical in the aqueous cleaning solvent; estimate for concentration 5%; 12 gallons tank size, 100 lb water, therefore 5 lb of PMN chemical used per day

W: weight in pounds of PMN chemical used per day of IC cleaning

D: number of days per year of operation of the IC processing facility

Environmental Releases (total lb/yr at a single IC processing facility)

Solid Wastes: Solid wastes from IC cleaning operations could include residues or sludge from equipment cleaning, reprocessing of aqueous cleaning solvent photoresist, and solid waste deposits in the filtration systems associated with the cleaning modules. Information collected from manufacturers of IC cleaning equipment (e.g., SSI, 1993 [15]) indicates that the modular cleaning tanks have built-in filtration systems for maintaining the requisite solution purity specifications. PMN additive that is contained in the filter cake in the filtration system would then have to be disposed of as solid waste. Spent aqueous solution containing the PMN chemical is likely to be treated prior to disposal; we assume here that the PMN additive can be removed as solid waste following treatment of the spent cleaning solution. In addition to these factors, the PMN additive may be recycled at the cleaning facility as part of the cleaning module maintenance activities.

The maximum amount of PMN chemical that would be released as solid waste from a single IC cleaning facility can be estimated roughly as:

$$W * D * (1- RF) = ? \text{ lb/yr}$$

where RF is a factor between 0 and 1 that describes the degree to which the PMN chemical is reacted, is otherwise removed from the aqueous solution during its use, or is recycled at the cleaning facility. As a default, assume that RF = 0 (that is, 100% release).

Air Emissions: Air emissions of the PMN chemical are expected to be negligible. Because the PMN additive to the aqueous cleaning solution is likely to be nonvolatile and because all cleaning operations are conducted inside sealed cleaning tanks, air emissions may be considered to be insignificant.

In the case of a volatile PMN, air emissions will have to be estimated from empirical relationships [19] or from analogy with known air emissions of a volatile PMN currently used in the cleaning process.

Water: Liquid waste containing the PMN chemical will arise from rinsing of cleaning tanks and disposal of spent cleaning solution. If the process liquids are processed to remove the constituent solid chemicals from the cleaning solution for recycling or disposal as solid wastes, releases of PMN additive as a liquid waste are expected to be small or negligible. Liquid wastes may contain a small fraction of PMN releases if incompletely or not removed from the cleaning solution by the recycling/treatment process. If substantial residues of the PMN chemical remain in the treated solution, the significance of this release route would have to be estimated. Tanks would most likely

be rinsed out at the end of a production run or if there would happen to be a problem with the cleaning solution during the process. The frequency of rinsing would be highly production dependent.

Worker Exposure

Worker exposure to the PMN additive used in the aqueous cleaning solution is likely to be small due to the minimal level of operator involvement in the cleaning process and the enclosed work environment. Typically, as discussed previously, the cleaning process is automated with a minimal number of workers present in what is primarily an oversight role. In addition, the process is conducted in a clean-room environment in enclosed cleaning tanks. All of these factors minimize the likelihood of worker contact with the PMN additive during the course of the cleaning process. If the cleaning solution is prepared on site by mixing individual chemical constituents, however, exposure to the PMN chemical could arise. In addition, exposure to the PMN chemical may also arise from handling solid wastes containing the PMN chemical. Accurate quantification of the various routes for potential worker exposure is difficult with the limited information currently available. For the purpose of this generic scenario, the various potential routes of worker exposure are discussed qualitatively. The concentration of the PMN in solution is probably in the 3 to 5 (wt)% range based on weight of water in the cleaning solution.

Inhalation: If the cleaning solution is provided to the IC cleaning facility ready for use, this route of exposure would not need to be considered. Inhalation of the PMN chemical may occur if the cleaning solution must be prepared on site. Estimating the inhalation exposure from preparing the cleaning solution will require additional information not available in preparing this generic scenario. As a default, assume PMN is transferred as a liquid from a drum [19].

Dermal Exposure (mg/day): Dermal exposure to the PMN additive is expected to be minimal, and is expected primarily from handling solid wastes containing the PMN chemical. Dermal exposure to the PMN will be *very low* (CEB, 1991 dermal exposure category system), particularly if the workers are wearing protective clothing such as gloves and eyewear typical of IC fabrication facilities.

Disposal Concerns

The containers used to transport the PMN-containing aqueous cleaning solution to the IC processing facility are assumed to be reused or disposed of appropriately. Solid wastes containing the PMN chemical are disposed of according to government regulations.

References

[1] *Ceramic Industry*, July 1993, p. 39.
[2] *1992 Electronic Market Data Book*, Electronic Industries Association, p. 2.
[3] Farwell, J., "Economic Indicator," *Semiconductor International*, April, 1992, p. 40.
[4] Hutcheson, G.D., "Return of Profitability Anticipated in 1993," *Solid State Technology*, March, 1993, p. 45.
[5] *Semiconductor International*, July, 1993, p. 61.
[6] Singer, P., "Trends in Wafer Cleaning," *Semiconductor International*, Vol. 15, No. 13, December, 1992, pp. 36-39.
[7] "Industry News," *Semiconductor International*, April, 1993, p. 24.
[8] Wolf, S. and Tauber, R.N., *Silicon Processing for the VLSI Era*, Lattice Press, 1986.
[9] Iscoff, Ron, "Fab Safety: High Marks, But Some Questions Linger," *Semiconductor International*, Vol. 13, No. 11, October 1990, p. 74-79.
[10] Baldwin, David and Stuart, James, "An Overview of Health Hazards in Semiconductor Manufacturing," *Solid State Technology*, Vol. 32, No. 7, July, 1989, pp. 73-75.
[11] Literature from Armos-tech Industries, 1108 Polluck Avenue, Ocean, NJ 07712.
[12] *Electronic Manufacturing*, March, 1988, pp. 12-23.

[13] *Electronic Manufacturing*, July, 1988, p. 58.
[14] *Electronic Manufacturing*, July, 1988, p. 59.
[15] Conversations with John Hamma and literature from Submicron Systems, Inc.
[16] Barney, C., "Winds of Change," *Electronics*, April 2, 1987, p. 62.
[17] *Thomas Register*, 5109/CIR.
[18] U.S. Department of Health and Human Services, *NIOSH Pocket Guide to Chemical Hazards*, June 1990, No. 90-117.
[19] CEB, 1991. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessments*, Volume 1, Contract No. 68-D8-0112, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C., February 1991.