Generic Scenario: Film Deposition in Integrated Circuit Fabrication

Introduction

The semiconductor industry is one of the fastest growing industries in the world, and integrated circuits (ICs) constitute a major segment of the industry. The U.S. integrated circuit manufacturers comprise a $15.8 billion industry which represents an approximately 100% increase since 1982 [1]. The industry size is based on factory shipments of ICs from U.S. manufacturers. A dramatic increase in mixed-signal IC demand is expected in late 1993 for use in communication components such as digital cellular phones, local-area networks (LANs), digital-signal processing (DSP), and data compression [2]. In conjunction with the increased IC production, the market for supplies to the industry is expected to rise sharply. For example, the ultrapure chemicals and gases market is expected to jump from $6 billion to $10 billion in 1997 [3].

The IC industry produces a variety of products, components, and devices [1]: (1) hybrid ICs (HICs) with thick-film composition by silk screen printing; (2) HICs with thin-film composition by vacuum deposition; (3) HICs with multichip circuits; and (4) monolithic bipolar ICs, e.g., diode transistor logic (DTL), transistor-transistor logic (TTL), current mode logic/emitter coupled logic (CML/ECL), linear bipolar, microprocessor, bipolar logic, random access memories (RAM), bipolar memories, and metal oxide semiconductors (MOS). These products all require several fabrication steps such as cleaning, photolithography, impurity doping, etching, and film deposition. Certain levels of environmental hazards are associated with each step [4]. This scenario examines the film deposition process generically to evaluate various IC products for human exposure to hazardous chemicals and chemical waste generated.

This report looks at a realistic scenario with both automated and manual process controls. However, most IC fabrication processes are automated and are performed in clean rooms, and the IC manufacturing industry is considered one of the safest industries in the United States. In fact, according to *Semiconductor International Magazine* [5], there has never been a fatal injury in a U.S. IC fabrication facility. This statistic is impressive considering the number of hazardous chemicals commonly used in the manufacture of ICs. However, questions on long-term effects still remain unanswered. The worst-case scenario of personnel exposure to hazardous gases or chemicals potentially will arise from equipment maintenance and accidents [6]. The chemicals used, the potential human exposure, and the waste generated during film deposition in the IC fabrication process are described below.

Film Deposition

Film deposition is an important step in IC fabrication. Thin films of various materials such as metals, dielectrics, and semiconductors are deposited on the surface of a silicon wafer several times during IC fabrication. These layers act as metal interconnects or leads, insulating layers, masking layers, or semiconductor layers of normally less than 5 μm thickness [7].

Prior to film deposition the wafer is **cleaned** by wet or dry cleaning methods, most often by wet cleaning. Standard IC cleaning involves a series of wet chemical etches called the "RCA" clean. Other solvent and acid cleaning steps sometimes are required [8]. The cleaning process removes contaminants such as particles, organics, native oxides, and metallics.

<u>Chemicals Used</u>: Sulfuric acid (H_2SO_4), methanol, hydrogen peroxide (H_2O_2), acetone, hydrochloric acid (HCl), methylene chloride, ammonium hydroxide (NH_4OH), isopropyl alcohol, ammonium fluoride (NH_4F), trichloroethane, and hydrofluoric acid (HF).

<u>Human Involvement</u>: Most cleaning cycles are conducted in automated, vented wet-chemical benches. There is minimal human involvement during the routine processes.
<u>Waste</u>: The cleaning processes result in extremely large quantities of chemical waste. The waste generally contains relatively high concentrations of each chemical.

The films are deposited on the cleaned wafer surfaces. The primary deposition processes are evaporation (e.g., chemical vapor deposition, CVD) and sputtering.

Thin-Film Deposition by Evaporative Techniques

Thin-film deposition by evaporative techniques involves heating the source materials at low pressure to vaporize them and subsequently condensing the source material on the desired surfaces. The deposition may occur on cooler surfaces within line of sight of the source, or in CVD the deposition may occur on hot surfaces where vapors of various source materials react and deposit after being transported through heated lines. In this technique, system pressures of 10^{-6} to 10^{-8} mmHg are achieved by using a diffusion pump backed by a mechanical force pump. The film thickness is monitored by a quartz crystal oscillator or by a control slide permitting the continuous measurement of the electrical resistance of the deposited film.

There are four approaches to evaporate precursor source materials: (1) solid source material is melted using a resistive coil, (2) powder source material is fed into a heated boat for flash evaporation, (3) the source material is directly heated by an electron beam, or (4) the liquid source material is boiled by inductive- or resistive-heating and the vapors are transported via insulated lines to the chamber (CVD).

Thin-Film Deposition by Sputtering

Cathode sputtering is a process where the source material is bombarded by ions causing evaporation of the material. This process is referred to as a "cold" technique because it does not require heating to high temperatures for activating the source material. The system normally contains low-pressure argon (5 to 50 mmHg) gas and the heavy inert ions strike the high- voltage cathode (source material) and vaporize atoms or molecules that are deposited on the grounded substrate.

There are three types of sputtering processes:

1. In <u>d-c sputtering</u>, a plasma of cations is formed in the voltage drop of ~4000 V between the target and the substrate. The pressure is approximately 40 mmHg and the deposition rate is lower than the rate when using evaporative techniques. This technique is limited to good conductors (metals) only.

2. In <u>RF sputtering</u>, radiofrequency waves activate the source material and the chamber pressure is maintained at ~5 mmHg. This technique can be used to deposit both conducting and insulating films (ceramic).

3. In <u>reactive sputtering</u>, another reactive gas is added to the chamber containing argon to form multicomponent films. For example, aluminum oxide films are deposited when aluminum metal atoms react with oxygen gas in the reactive plasma.

Human Exposure During Film Deposition

Human exposure to the chemicals during the evaporation or sputtering vacuum processes is negligible. Both sputtering and evaporative film deposition processes are conducted and operated in a closed environment, inside the clean room; however, several toxic gases are used in CVD processes [3,8].

<u>Gases Used in the CVD Process</u>: Ammonia (NH_3), arsine (AsH_3), carbon dioxide (CO_2), diborane (B_2H_6), dichlorosilane (SiH_2Cl_2), germane (GeH_4), helium (He), nitrous oxide (NO_2), oxygen (O_2), phosgene ($COCl_2$), phosphine (PH_3), silane (SiH_4), silicon tetrachloride ($SiCl_4$), and tungsten hexafluoride (WF_6).

<u>Human Involvement</u>: Exposure to CVD gases during operations usually is negligible because the equipment operates in a closed system. The greatest risk with the toxic gases is during a cylinder change operation and maintenance [6,8]. Film deposition is a batch process (one wafer at a time) conducted in

closed systems with one (1) operator normally required to run each CVD or sputtering machine. These machines commonly deposit films on 8 to 12" wafers.

Waste: There is very little hazardous waste in the CVD process.

Data/Assumptions for Human Exposure and Waste Generated During Film Deposition in IC Fabrication

1. Of more than 200 IC production sites in the United States, most are located on the west coast (50%; CA, OR), in the northeast (25%; MA, NY, CT), and in the southwest (15%; TX, NM, AZ) [9].

2. The facilities normally operate 345 days/year.

3. Most facilities run 3 shifts/day.

4. For a completely automated film deposition production line with a film deposition of 54 wafers per hour, 1 operator is required for each machine [10]. There are multiple film deposition steps and, depending on the number of layers, the number of operators increases linearly. A normal system operates with about 85% up-time.

Waste Generation, Environmental Releases, and Exposure-Level Calculations

PMN chemicals may be used as source materials (solid or liquid) or reactive gases in the film deposition processes (note: chemicals used as part of the wafer cleaning process are not being considered in this generic scenario). For the environmental releases and worker exposure calculations conducted in this generic scenario, it is assumed that the PMN chemical is used as a reactive gas in chemical vapor deposition (CVD)-based film deposition processes. Although CVD is only one of the many techniques used for film deposition, it is popular and has a high potential for worker exposure and environmental release. By comparison, other film deposition techniques such as evaporation or sputtering are conducted within closed systems with minimal chemical transport within the fabrication facility. For example, solid source materials may be used as sputtering targets in a vacuum system for film deposition by evaporative or sputtering processes. The transport and use of the source material in such a system presents minimal opportunities for worker exposure and environmental release.

Reactive gases used in CVD film deposition therefore have been selected as the point of introduction of the PMN chemical because their transport to the point of use and their subsequent use in the CVD process and release following use in the process can all potentially result in exposure and releases. For this scenario, it is assumed that the PMN chemical used as a reactive gas is provided to the IC processing facility in pressurized containers, such as a cylinder or a tank. In a facility processing 1,000 cm^2 surface area per hour and using gas at a rate of 20 L/minute, annual gas usage in the worst case could be about 7.9 $\times 10^6$ L/year. There are about 200 sites in the United States using this technology.

Assumptions

W : weight in pounds of PMN chemical used per hour of film deposition process operation
N : number of hours of operations per day that involve use of the PMN chemical
D : number of days per year of operation of the IC processing facility

Environmental Releases (total lb/year at a single film deposition facility)

Solid Wastes: Solid wastes containing the PMN chemical are not expected to arise from CVD film deposition. The reactive gas PMN chemical used in the process is converted to a form suitable for

deposition as a film on the wafer substrate. No solid wastes containing the PMN chemical therefore are anticipated.

Air Emissions: Air emissions of the gaseous PMN chemical could arise from venting of gas left unreacted after the CVD process or from purging of the reactor and transport lines after the process is completed. CVD film deposition typically is conducted in a closed system and gases exhausted from the reactor are passed through a control device prior to be being vented to the ambient environment. Control devices used typically consist of adsorption columns or incinerators. Potential air releases of a gaseous PMN chemical from the process can be estimated as:

W * %Reacted/100 * (100%Removal Efficiency)/100 * N * D = ? lb/year

where %Reacted is the percentage of PMN that is reacted in the CVD reactor, and %Removal Efficiency is the PMN removal efficiency of the control equipment employed at the facility.

PMN may be 5% to 100% of the reactant gas. To estimate the weight of PMN used per facility or potentially vented in a time period, assume that the PMN is 100% of the reactive gas which is at standard temperature and pressure. Gas in these conditions is 22.4 L per mole.

If density of the gas is known:

(flow rate) × (unit time) × (density) = W

If density is known, calculate the formula weight in grams per mole:

$$\frac{\text{(flow rate)} \times \text{(unit time)} \times \text{(formula weight)}}{\text{(22.4 L/mole)}} = W$$

Water: Liquid wastes containing the PMN chemical are expected to be small or negligible. Liquid wastes may become a significant release route if the gaseous exhaust control device used in the process involves sorption or neutralization of the gaseous PMN into a liquid medium. If the PMN gas is unreacted when sorbed in the liquid medium, the potential for waterborne release exists. The maximum amount of PMN that could be released through such a route is:

W * %Reacted/100 * %Removal Efficiency/100 * N * D = ? lb/year

where %Reacted and %Removal Efficiency are as defined earlier.

Worker Exposure

Worker exposure to the PMN gas in CVD film deposition could occur at several points within the process. Reactive gases used in the process typically are stored in compressed cylinders or tanks at some distance from the closed reactor within which film deposition is conducted. Exposure to a gaseous PMN could arise from leaks during cylinder changing operations and maintenance of the transport lines and film deposition reactors. Other possibilities for exposure include leaks during process operations from the reactor, transport lines, and control equipment. Exposure from wafer handling and transfer operations to unpurged gaseous PMN remaining in the reactor also is possible, though unlikely. Accurate quantification of the various routes for potential worker exposure is difficult with the limited information currently available. For this generic scenario, the various potential routes of worker exposure are discussed qualitatively.

Inhalation: Inhalation is expected to be the primary route of worker exposure from CVD operations. As discussed above, exposure to PMN gases may result from cylinder changing operations, and from leaks in transport lines, reactors, or control equipment. Inhalation exposure also may occur during wafer loading and unloading operations from incomplete purging of the reactive gas from the reactor. The extent of

these exposures is impossible to predict in this generic scenario. The extent of leakage of gaseous PMN from various components in the CVD process will need to be experimentally measured to estimate worker exposure from these types of releases. The potential for the presence of unpurged PMN gas in the reactor needs to be determined experimentally. The impact of an accidental release of gaseous PMN at an IC fabrication facility also must be considered. The latter may be derived from worst-case estimates of the release of the entire compressed gas volume into the facility and the duration of potential exposure before an emergency evacuation can be conducted.

Inhalation exposure for a gaseous PMN used in CVD film deposition should be estimated from personnel monitoring data. If data for the PMN gas are unavailable, data for an analogous/surrogate reactive gas could be applied with appropriate scaling to estimate worker exposure to the PMN gas.

Dermal Exposure (mg/day) Dermal exposure to gaseous PMN used in CVD film deposition is expected to be minimal. Except for catastrophic accidental releases, dermal exposure to the PMN gas will be very low dermal exposure category system [13]), particularly if the workers are wearing protective clothing such as gloves and eyewear.

Disposal Concerns

The cylinders used to transport the PMN gas to the IC processing facility are assumed to be reused when empty or purged through a control device.

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