James Kim
April 8, 2014

Assessing the Environmental, Safety, and Health Hazards of the Semiconductor Industry

Abstract

In 2013, the semiconductor industry reached $305.6 billion in worldwide sales, the industry's highest yearly total ever.[1] Despite advances in computer technology for the semiconductor industry, these manufacturing plants produce toxic waste that not only affects the environment, but also the safety and health of the workforce and community. Chemical vapor deposition (CVD), a process used to manufacture computer chips, emits perfluorocompounds (PFCs), greenhouse gases that accumulate in the atmosphere. Additionally, the chemicals used in the process, such as lead, arsenic, and benzene, have hazardous health problems upon exposure, ranging from irritation of the nose, throat, and eyes to lung and liver cancer. Pregnant women exposed to these chemicals can lead to spontaneous abortions and miscarriages. Significant improvements have been made to reduce the amount of exposure to the workers and the community by enforcing strict monitoring policies and routine maintenance of ventilation systems. In the manufacturing process, scrubbers are now installed directly after CVD to reduce greenhouse-gas emissions. Due to the rising costs of chemical waste disposal, many companies are conducting research into environmentally friendly alternatives to methods and materials.

Introduction

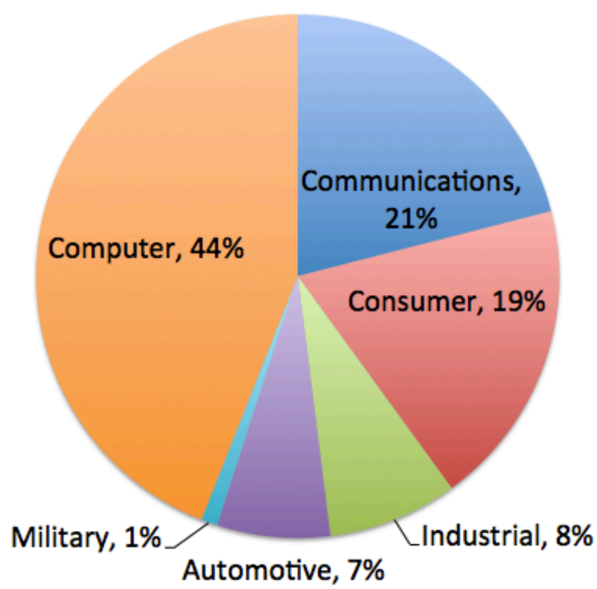
The semiconductor industry has contributed substantially to society's economic and technological growth [1]. Companies around the world, such as Intel, Samsung, Toshiba, and Qualcomm, compete to build innovative electronic devices that include cellphones, laptops, and

---

1 "Global Sales." *Semiconductor Industry Association*. <http://www.semiconductors.org/industry_statistics/global_sales_report/>

computers. Semiconductors are solid, crystalline materials that have higher electrical conductivity than insulators, but less than conductors [2]. Figure 1 shows the breakdown of the industry consumption of semiconductors [1]. Although semiconductors have come to be synonymous to computer chips, the industry's consumption of semiconductors for computers is only 44%. Other uses for semiconductors include communications, consumer, industrial, automotive, and military purposes. The process of manufacturing semiconductors is tedious and

Figure 1: Relative Consumption of Semiconductors by Industry



challenging. When making semiconductors, workers have to be extremely careful not to contaminate the wafers, which are thin slices of semiconductor material composed of silicon crystals. Clean rooms in fabrication facilities are used to produce semiconductors. These rooms are half a trillion times more filtered than the average hospital operating room. Workers are required to wear "bunny" suits to minimize the potential of any contaminants on the wafers.

The main concern in the semiconductor industry is the excess amount of toxic waste that is released into the environment. On average, 99.9% of the materials used to manufacture the chips are not contained in the final products. For a fabrication facility, around 2 million gallons of de-ionized water, 2.5 million cubic feet of high-purity nitrogen, and 240,000 kilowatt-hours of electrical power are used to produce roughly over 800 wafers per day. One 6-inch wafer requires 20 pounds of chemicals and more than 3,200 cubic feet of gases. Despite these staggering quantities of hazardous chemicals and harmful gases, significant efforts by manufacturing companies have been made to improve working conditions and develop environmentally friendly alternatives.

Background

Walter Brattain, John Bardeen, and William Shockley developed the first microchip, the transistor, in December 1947 at the Bell Laboratories in New Jersey. 50 years later, microchips made up 74% of the global semiconductor market. There have been many lawsuits filed against semiconductor manufacturing companies because of poor monitoring and maintenance [3]. Many employees have suffered adverse health effects, including cancer, reproductive problems, and miscarriages due to prolonged exposure of cancer-causing chemicals. [2,3]

Semiconductors - General Process

Manufacturing semiconductors is very complex and can require up to 2-3 months to complete [4]. First, silicon crystals are melted and purified to almost 99.99% purity. The melted silicon is molded into long cylindrical ingots, where they are cut into thin slices called wafers. Only one side of the wafer must be polished to be absolutely smooth, a process called chemical-mechanical polishing. The polished wafers are then placed into a bath of hazardous chemicals for cleaning; the resulting product is sent into a reactor to undergo chemical vapor deposition (CVD). In CVD, alternating layers of insulation and conduction are sprayed directly onto the

---

[2] "I.B.M. Toxic-Chemical Suit Heads to Court." *New York Times*. <www.nytimes.com/2003/10/13/business/ibm-toxic-chemical-suit-heads-to-court.html?pagewanted=all&src=pm>

[3] "Scottish workers sue National Semi." *Silicon Valley Business Journal.* <www.bizjournals.com/sanjose/stories/1999/05/24/daily5.html>

surface. Following deposition, a layer of photoresist, a mixture of chemicals sensitive to light, is sprayed for the purposes of etching. Next, photoelectrochemical etching occurs in a machine called a stepper. The stepper is calibrated to project an extremely fine image of transmitted light onto the photoresist such that the parts exposed to this light harden to a tough crust while the other parts remain soft, resulting in a chip. Figure 2 shows a stepper. Depending on the diameter of the silicon wafer, copies of the chip are printed until the entire surface is exposed. After this step, the wafer is submerged into another bath, removing the "soft" layer of photoresist as well as the alternating conduction and insulation layers beneath; however, the photoresist that was exposed to the light remain and protect the underlying layers. The series of steps, CVD, photoresist, photoelectrochemical etching, and etching bath, is repeated more than a dozen times. The resulting product is then coated with another insulator, but this time the wafer becomes plated with a thin layer of metal, usually aluminum or copper. Another photoresist layer is formed on top and is sent to the stepper for photoelectrochemical etching. After several layers of metal and photoresist, a final wash step is performed and the semiconductor is finally complete.

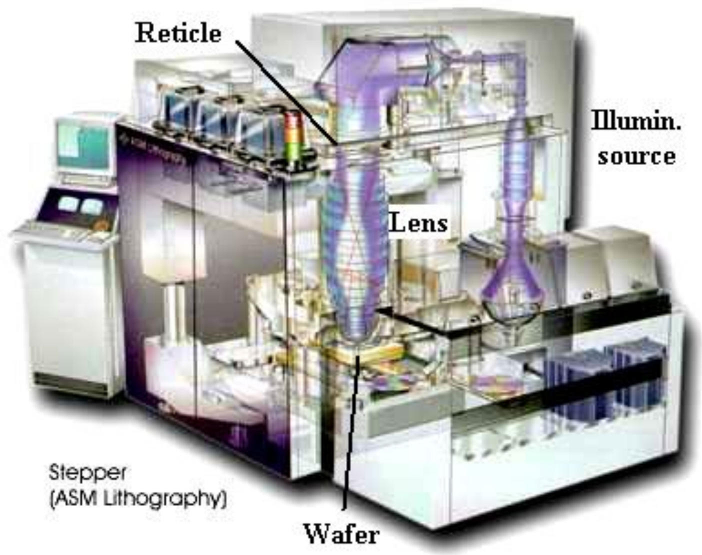


Figure 2: Illustration of a stepper (image from Solid State Electronics).

Semiconductors are produced in fabrication facilities called "clean" rooms. Most of the surfaces in these rooms are stainless steel. The air is filtered through the ceiling and the floor constantly, removing unwanted tiny particles that may be 1/100 the width of human hair. Bright yellowish light in these facilities prevents mold and mildew behind the equipment. Before the workers enter the "clean" room, they go through a series of closed "air showers" to remove unwanted particulates from their clothes. Additionally, workers walk across a sticky floor mat to remove particulates from the bottom of their shoes. Once the workers are thoroughly clean, they suit up into the "bunny" suits, which are composed of a bulky suit, helmet, battery pack, gloves and boots.

Health Risks in the Semiconductor Industry

Despite the dust-free environment in the "clean" rooms, the purpose of the "bunny" suits and filtered air is to prevent the wafers from being contaminated, not protecting the workers from the harmful chemicals. Industrial hygiene has always been an issue in the semiconductor industry. Table 1 lists 10 of the most commonly used chemicals in the semiconductor industry. The Health and Safety Executive (HSE), a national independent regulator for work-related health, safety, and illness, conducted a groundbreaking study to investigate the lawsuits filed against semiconductor industries. Due to the advancement of technology, fabrication facilities constantly change their chemicals and equipment to create better semiconductors. In terms of these lawsuits, there is not enough evidence to pinpoint one of over 300 chemicals used as the leading cause of the health problems experienced by the workers. Additionally, visible signs of cancer don't develop until many years after exposure. A counterargument to these lawsuits by the semiconductor industry is that the cancer may have developed due to other reasons, such as drinking, smoking, family history, and eating habits.

Environmental Risks

The semiconductor industry uses greenhouse gases (GHGs) to clean CVD chambers. Perfluorocompounds (PFCs), such as tetrafluoromethane (CF_4), hexafluoroethane (C_2F_6), octafluoropropane (C_3F_8), nitrogen trifluoride (NF_3), and sulfur hexafluoride (SF_6), are extremely hazardous to the environment and cause climate change. In 1981, trichloroethane and Freon, chemicals used in the semiconductor industry, were found in drinking water [5]. I.B.M. and Fairchild Semiconductor were responsible for the chemical spill because the companies' underground storage tanks leaked tens of thousands of gallons of toxic solvents into the groundwater. Another issue is the buildup of old electronic devices and systems discarded in landfills.

Chemical Name	Role in manufacturing process	Health problems linked to exposure
Acetone	Chemical-mechanical polishing of silicon wafers	Nose, throat, lung, and eye irritation, damage to the skin, confusion, unconsciousness, possible coma
Arsenic	Increases conductivity of semiconductor material	Nausea, delirium, vomiting, dyspepsia, diarrhea, decrease in erythrocyte and leukocyte production, abnormal heart, rhythm, blood vessel damage, extensive tissue damage to nerves, stomach, intestine, and skin, known human carcinogen for lung cancer
Arsine	Chemical vapor deposition	Headache, malaise, weakness, vertigo, dyspnea, nausea, abdominal and back pain, jaundice, peripheral neuropathy, anemia
Benzene	Photoelectrochemical etching	Damage to bone marrow, anemia, excessive bleeding, immune system effects, increased chance of infection, reproductive effects, known human carcinogen for leukemia
Cadmium	Creates "holes" in silicon lattice to create effect of positive charge	Damage to lungs, renal dysfunction, immediate hepatic injury, bone defects, hypertension, reproductive toxicity, teratogenicity, known human carcinogen for lung and prostate cancer
Hydrochloric acid	Photoelectrochemical etching	Highly corrosive, severe eye and skin burns, conjunctivitis, dermatitis, respiratory irritation
Lead	Electroplated soldering	Damage to renal, reproductive, and immune systems, spontaneous abortion, premature birth, low birth weight, learning deficits in children, anemia, memory effects, dementia, decreased reaction time, decreased mental ability
Methyl chloroform	Washing	Headache, central nervous system depression, poor equilibrium, eye, nose, throat, and skin irritation, cardiac arrhythmia
Toluene	Chemical vapor deposition	Weakness, confusion, memory loss, nausea, permanent damage to brain, speech, vision, and hearing problems, loss of muscle control, poor balance, neurological problems and retardation of growth in children, suspected human carcinogen for lung and liver cancer
Trichloroethylene	Washing	Irritation of skin, eyes, and respiratory tract, dizziness, drowsiness, speech and hearing impairment, kidney disease, blood disorders, stroke, diabetes, suspected human carcinogen for renal cancer

Table 1: Chemicals of concern in the semiconductor industry [3].

Halogen Fluorides - An Alternative to Perfluorocompounds

One alternative is the use chlorine trifluoride (ClF_3) as a substitute cleaning agent rather than PFCs. Because halogen fluorides have powerful oxidizing potentials, they are useful for cleaning CVD equipment. Chlorine trifluoride was chosen because ClF_3 is the most reactive halogen fluoride. The main advantage of ClF_3 is that the high reactivity allows the maintenance process to be executed at normal temperatures, unlike PFCs that require plasma or high temperatures to dissociate the film residue. Other advantages include high etching rate, higher effectiveness, relatively easy storage, and no global warming potential. Although these pros seem very appealing, the high reactivity results with toxic hydrolysis products, which include hydrogen fluoride (HF), chlorine (Cl_2), and chlorine dioxide (ClO_2).

During the CVD process, the film material accumulates on the walls in the exhaust handling system. Without proper cleaning, film material will further accumulate and can potentially cause wafer contamination and malfunction. The traditional method of cleaning involves the dry method by plasma etching using a halogen-containing compound as the etching gas. The cleaning gas reacts with the accumulated deposit using free radicals to ionize and remove the film material. In this case, PFCs are the ideal cleaning gases in this process; however, for ClF_3, plasmaless dry cleaning has been used successfully since 1993 for low-pressure chemical vapor deposition (LPCVD) and plasma-enhanced chemical vapor deposition (PECVD). Tables 2 and 3 list the issues of PFCs as cleaning gases and the advantages of using ClF_3, respectively.

Table 2: Environmental issues using PFCs as cleaning gases
Significant values of global warming potential (GWP) and long atmospheric lifetimes
Cleaning process is low-yield reactions, thus most of the gases are released into the atmosphere
Not suitable to clean thermal CVD systems because plasma generation is necessary
May cause serious damage to CVD components due to induction effects by plasma
Cannot clean the backside of the radio frequency power (RF) and the inside walls of the exhaust pipes

Table 3: Advantages of using ClF_3 as a cleaning gas
Able to etch a wide range of deposits and coatings
Increase CVD tool productivity because of high etch rate and *in situ* chamber cleaning
Low temperature process
No release of PFCs

Point-of-use (POU) Abatement System

POU abatement system is often used to minimize the overall environmental, health, and safety impacts of the semiconductor processes. Wet scrubbing, oxidation, cold bed, hot bed, and recycle system are some of the many techniques researchers of the semiconductor industry have discovered that can reduce the emission of toxic gases. POU devices are designed to remove the toxic contaminants before they enter the exhaust system in order to increase production and protect fabrication equipment and personnel.

One research paper focused on the destruction or removal efficiency (DRE) of the local scrubbers on five PFCs: SF_6, NF_3, CF_4, C_2F_6, and C_3F_8 [6]. Two types of scrubbers were assessed: combustion (CB) and electric-thermal (ET). Air samples were taken at the inlet and outlet streams of local scrubbers and were analyzed using a multi-column gas chromatography system equipped with thermal conductivity detection (TCD). The three columns used to assess the DRE were two Porapak Q columns and one Molecular Sieve (MS)-5A column. Each column separates different PFCs in the gas mixture; Porapak Q separates C_2F_6, C_3F_8, and SF_6 while MS-

5A separates CF_4, C_3F_8, and NF_3. He or H_2 is used as a tracer for the experiments. Based on the results, the CB scrubbers received higher values than ET in DRE for C_3F_8 and CF_4, the two most harmful GHGs.

Conclusion

Although the semiconductor industry has made significant advances in technology and has contributed to global economic growth for the past 60 years, environmental, health, and safety issues have become extremely important due to recent lawsuits and climate change. Semiconductor fabrication facilities are known to consume substantial amounts of both electricity and water, while using hazardous chemicals can cause health risks to workers, ranging from eye and skin irritation to lung and liver cancer. By the 1990s, alternative and environmentally friendly methods have been introduced to reduce greenhouse-gas emissions. One involves using ClF_3 as the cleaning agent versus PFCs. Although ClF_3 is highly reactive and produces dangerous hydrolysis products, HF, Cl_2, and ClO_2, this compound has no global warming potential unlike PFCs. Another approach to reducing greenhouse-gas emissions is the POU abatement system that involves installing scrubbers and other efficient reactors around the CVD system.

References

[1] J. Mazurek, Making Microchips: Policy, Globalization, and Economic Restructuring in the Semiconductor Industry. Cambridge, Massachusetts: MIT Press, 1999.

[2] J. Turley, The Essential Guide to Semiconductors. Upper Saddle River, New Jersey: Prentice Hall Professional Technical Reference, 2003.

[3] R. Chepesiuk, "Where the Chips Fall: Environmental Health in the Semiconductor Industry." Environmental Health Perspectives 107 (1999): 452-457.

[4] Holden, J.; Kelty, C. The Environmental Impact of the Manufacturing of Semiconductors, Connexions Web site. http://cnx.org/content/m14503/1.3/, Jun 2, 2009.

[5] B. Pimentel, "The Valley's Toxic History." San Francisco Chronicle 30 Jan. 2004, final ed.: B_1.

[6] C.F.O. Yang, S.H. Kam, C.H. Liu, J. Tzou, J.L. Wang, Assessment of removal efficiency of perfluorocompounds (PFCs) in a semiconductor fabrication plant by gas chromatography, Chemosphere 76 (2009) 1273-1277.