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Environmental Management of Wastes in the Semiconductor and Electronics Industries

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ABSTRACT

The management of wastes in the semiconductor and electronics industries requires a multidisciplinary approach that considers the health and safety of employees as well as the treatment and recycling of waste materials. The manufacturing of semiconductor devices requires the use of many toxic chemicals and gases. Air emissions from manufacturing tools must be carefully monitored both inside and outside of the fabrication facility. Liquid effluents must be collected and pretreated before discharge to local wastewater systems. The subsequent use and eventual discard of electronic devices such as television sets and personal computers by consumers has created a new set of recycling and reuse problems. This paper will discuss approaches to the manufacturing and post-consumer disposal of electronic components and devices.

THE SEMICONDUCTOR MANUFACTURING PROCESS

The manufacture of semiconductor devices such as microprocessor and integrated circuit chips has become one of the leading industries of the 21st century. Although the manufacturing process is complex, it can be broken down into several smaller steps including: circuit design, photolithography, layering and doping, removal of layers, and final testing and packaging. These steps are briefly described below. The Intel website has an animated description of the complete process (Intel, 2000).

Circuit Design

The fundamental building block of modern electronic devices is the transistor. Developed by Bell Laboratories of the United States in 1948 and perfected for commercial application by Texas Instruments of the United States and SONY of Japan and others, the transistor soon replaced the older vacuum tube technology. Small, lightweight, and requiring low power consumption, transistors were ideal for a wide variety of applications in both industry (main frame computers) and the home (radios, televisions, and high fidelity sound systems).

In early designs in the 1950's and 1960's, transistors were used as a direct replacement for vacuum tubes; for example, older radio receiver circuits that used 4 or 5 vacuum tubes were replaced by newer designs using 4 or 5 transistors. This approach was radically changed by the development of the integrated circuit in the late '60s which placed hundreds or thousands of transistors and other components on a single chip of silicon to form an entire computer, or microprocessor chip. The 4004 microprocessor chip developed by Intel in 1971 was the first circuit of this type. It contained 2,300 transistors. By comparison, Intel's Pentium II microprocessor chip, developed in 1997, contains 7.5 million transistors.

The design of microprocessors and other integrated circuits has become so complex that they are designed by computer aided design systems themselves. First, the processing specifications of the chip are set by the chip "architect". Then, a team of engineers designs the integrated circuit to produce the desired characteristics. Since a modern computer chip such as an Intel Pentium II, may contain the equivalent of millions of individual transistors and connecting wires, the complexity of the final design is staggering.

Photolithography

The end product of the design is a series of drawings which represent the physical shape of the circuits. These drawings are transferred to the surface of a silicon wafer (the raw material of a computer chip) by a photographic process called photolithography. The drawings are photographically reduced in size to match the actual size of the chip to form a mask (similar to a photographic negative). The silicon wafer surface is coated with a photosensitive resin called photoresist. Then the wafer is exposed to ultraviolet (UV) light that passes through the mask, producing an image of the desired circuit. The ultraviolet light changes the hardness of the resist, and permits it to be selectively removed by solvents. Both positive and negative resists, which react differently to UV light, can be used.

After the circuit layout has been "printed" on the surface of the silicon wafer, unwanted parts are etched away using either a wet chemical process (hydrofluoric acid is most commonly used) or a dry process, plasma etching. After etching, another wet chemical process, stripping, removes the unwanted photoresist.

Deposition of Layers

After the circuit pattern has been laid down by photolithography, a controlled amount of impurities, or "dopants" are added to the surface of the etched chip. Commonly this is accomplished under a vacuum in a high temperature diffusion furnace. Finally additional layers of material are added to form insulating regions (silicon dioxide) or conducting paths (aluminum or copper in newer designs). This is accomplished by chemical vapor deposition (CVP).

Removal of Layers

Since the final chip design may have over 10 layers, excess material is removed by precision mechanical polishing machines (similar to lens grinding equipment). Then the cycle of photolithography, doping, deposition, and grinding is repeated as often as necessary for the design. It may take over 2 weeks for a chip to progress through the fabrication line.

Final Testing and Packaging

The final step is testing of the circuits. Hundreds of individual chips are produced on a single wafer. The chips are electrically tested by an automated testing machine. Substandard chips are marked for disposal. The wafer is sliced into individual chips which are mounted in plastic or ceramic carriers. The final step is connecting fine gold wires to connection pads on the chip. The wires are then connected to larger pins, which connect the chips to external circuits.

HAZARDOUS MATERIALS USED IN SEMICONDUCTOR MANUFACTURING

A number of hazardous materials are used in the manufacture of semiconductor devices. They can be classified as gases, solvents, acids, bases.

Gases

Typical gases used in semiconductor processing include:

Ammonia (NH_3) - Used in chemical vapor deposition. Flammable, toxic, and corrosive. TLV = 25 ppmV (Threshold Limit Value from Williams and Baldwin, 1995)

Arsine (AsH_3) - Used in thermal oxidation, thermal diffusion, chemical vapor deposition, and etching. Flammable and toxic. TLV = 0.05 ppmV

Chlorine (Cl_2) - Used in etching and water treatment. Toxic and corrosive. TLV = 0.5 ppmV

Fluorine (F_2) - Toxic, corrosive, and flammable. Especially hazardous to workers because it can penetrate the skin, binding to bone calcium. TLV = 1 ppmV

Phosphine (PH_3) - Used in thermal diffusion and chemical vapor deposition. Flammable, pyrophoric, and toxic. TLV = 0.3 ppmV
Note: Pyrophoric gases spontaneously combust when exposed to air.

Silane (SiH4) - Used in chemical vapor deposition. Flammable and pyrophoric. Silane explosions have caused several deaths in the semiconductor industry.

Liquids

Several categories of hazardous liquids are use in semiconductor manufacturing including acids, bases, and organic solvents:

Hydrofluoric Acid (HF) Corrosive. Especially hazardous for workers because it can penetrate the skin and bind with bone calcium.

Hydrochloric Acid (HCl) Corrosive.

Sulfuric Acid – (H_2SO_4) Corrosive

Hydrogen Peroxide (H_2O_2) Reactive

RCA Cleaning Sequence Four step process used for cleaning silicon wafers:

1. $H_2SO_4 + H_2O_2$
2. Ultrapure Water
3. $HF + H_2O$
4. Ultrapure Water

Photoresist Organic liquids. Possible mutagens.

Xylene Organic solvent used to dissolve negative photoresist.

Potassium Hydroxide Base used to dissolve positive photoresist.

HEALTH AND SAFETY ISSUES FOR EMPLOYEES

Worker health and safety is a prime concern of the semiconductor industry. Workers can be potentially exposed to a wide variety of hazards including:

- Poisons and toxics.
- Physical hazards such as noise and ionizing (gamma rays) and non-ionizing radiation (RF energy, laser light).
- Ergonomic issues such as lifting, bending, and stooping.

Codes and Standards

In the United States, these issues are addressed by a number of codes and standards issued by both governmental agencies and non-governmental associations including:

- ANSI - American National Standards Institute (www.ansi.org)
- OSHA - Occupational Health and Safety Administration (www.osha.gov)
- NIOSH - National Institute of Occupational Health and Safety (www.cdc.gov/niosh/homepage.html)
- SEMI - Semiconductor Equipment and Manufacturing International (www.semi.org/web/winitiatives.nsf/url/ehshome)
- SSA - Semiconductor Safety Association (www.semiconductorsafety.org)
- State and Local Fire Codes
- Insurance Company Fire Standards

Control Strategies

Employee health and safety is protected by a three part strategy:

- Administrative Controls - Limit employee exposure to hazardous environments by health monitoring and screening. Monitor working environment with real time gas monitoring equipment.

- Engineering Controls - Design manufacturing tools to eliminate or greatly reduce potential worker contact with hazardous materials. Design manufacturing tools and processes that eliminate the use of hazardous materials.

- Personal Protective Equipment - Provide workers with Personal Protective Equipment to prevent body contact with hazardous materials. Examples include eye protection, hearing protective devices, gloves, protective clothing, respirators, and in extreme case, self contained breathing equipment. Personal Protective Equipment is considered the last line of defense and should be used after all possible Administrative and Engineering controls have been implemented.

Management of Health and Safety Programs

All semiconductor manufacturing facilities have Environmental, Health, and Safety (EHS) organizations which plan an execute EHS programs. Effective EHS programs are an essential part of an effective management system. To assist manufacturing industries in managing EHS programs, the International Standards Organization has developed a voluntary auditing and certification program known a ISO 14000. The program does not regulate industries, but rather assists them in structuring an EHS program. ISO 14000 Certification has become a hallmark of a well run manufacturing organization (www.tc207.org).

WASTE TREATMENT STRATEGIES FOR SEMICONDUCTOR MANUFACTURING

The semiconductor industry must not only protect its employees but must also protect the general public at large outside of the plant. In most semiconductor manufacturing facilities there is a combined management organization responsible for both worker health an safety and protection of the environment.

The hierarchy of waste management for the semiconductor industry is:

- Waste Elimination - Change manufacturing techniques to eliminate hazardous materials.
- Waste Reduction - Modify manufacturing techniques to reduce environmental emissions.
- Waste Treatment - Treat waste emissions to meet or exceed local and national environmental standards.

Semiconductor Equipment and Manufacturing International has recently published a comprehensive guideline on these topics, SEMI S2-0200. It is available on the SEMI website (www.semi.org/web/winitiatives.nsf/url/ehshome).

Waste Elimination

This is the most promising area for research in the waste management hierarchy. Advances in the materials sciences can have a great benefit in this area. Sometimes a relatively simple modification can have a profound effect on the environment. For example, the use of citric acid water based solvents for surface cleaning of silicon wafers instead of strong acids or organic solvent based rinses has both environmental and cost benefits. Other recent innovations include the use of "dry" plasma cleaning schemes for the interiors of chemical vapor deposition reactors. This has eliminated the use of strong acid washing, a practice which was both hazardous to workers and the environment.

Waste Reduction

Water is the most commonly used liquid in semiconductor manufacturing. In some locations, availability of water has become a limiting factor for the siting of new fabrication facilities. Reduction of water use saves both money and protects the environment. Some waste reduction techniques are relatively simple such as the use of counter current flow rinsing which minimizes water use and actually produces a better quality silicon wafer.

Waste Treatment

The final step in the hierarchy is waste treatment. Both gaseous emissions and liquid effluents must be treated. Since this is an expensive process, all possible steps for waste elimination and reduction must be taken first.

- Gaseous Emissions - The most commonly controlled emissions are from semiconductor tools using organic solvents. Small, point of source incinerators (commonly referred to as "burn boxes") are typically used. One of the most critical control problem is emission of silane, a pyrophoric gas that ignites upon contact with air. Liquid scrubbers are also used when acid or basic mists need to be controlled.

- Liquid Effluents - Every effort must be made to reduce liquid effluents. Most semiconductor manufacturing sites use separate waste lines for acidic, basic, and organic based liquid wastes. Acid and organic wastes are neutralized before discharge into local wastewater treatment systems. Organic waste streams may also require pretreatment before discharge.

POST-CONSUMER RECYCLING AND REUSE OF ELECTRONIC DEVICES

The manufacture and distribution of electronic devices such as personal computers (PCs), TV sets, video tape recorders, stereo equipment, and portable radios is one of the largest industries in the world. Most electronic consumer goods tend to be fairly long lived, with useful lives exceeding 10 years. The major exception to this rule is the personal computer. With advances in software and hardware occurring at a breakneck pace, the useful life of a personal computer is probably 3 years or less. This has created a massive worldwide disposal problem. In the United States alone, 21 million PCs were disposed of in 1998 (Los Angeles Times, 2000). Of that total, less than 11% were recycled or reused. Several disposal options are available: landfill or incineration, reuse, recycling.

Landfill or Incineration

This is the least desirable alternative for PC disposal. It is in fact becoming illegal in many U.S. states. The major concern is groundwater or air pollution from the many hazardous materials found in typical PCs. The element of most concern is lead, as up to 4 kg of lead are in a typical cathode ray tube (CRT). Other elements of concern include mercury, cadmium, and beryllium, which are found in much smaller amounts in batteries, capacitors, and other small components used in PC circuit boards.

Reuse

The reuse of PCs as working computers is the most desirable and cost effective solution. It is however a limited solution in many cases as older computers may not run current software. For Windows compatible PCs, an 80486 machine is probably the minimum acceptable PC for most current software. For Macintosh PCs, a Power PC equipped machine is the minimum configuration for modern Macintosh software. Older Windows and Macintosh PCs may still be useful to elementary schools and other entry level training activities. High school and colleges require current up to date equipment.

Recycling

Obsolete PCs will increasingly be recycled. A worldwide infrastructure of firms specializing in PC disassembly and recycling is being developed. This trend will accelerate as more U.S. states and other countries mandate landfill and incineration bans on PCs and electronic devices.

Recycling of PCs and other electronic devices is a multi-step process. First the PCs are disassembled and major components are stripped off. Then the parts and components are sorted into recyclable categories:

- Monitors – CRTs are removed and leaded glass sold for recovery, plastic cases are sorted for possible recycling, circuit boards retained for further processing.
- Copper Wiring – recovered and sold.
- Steel – Recovered and sold
- Plastics – Ideally recovered and sold, however there is no standardization in the computer industry, and many plastics cannot be easily identified, resulting in a greatly reduced resale value.
- Circuit Boards – Require considerable processing including grinding and separation processes such as screening and flotation. It may be possible to recover a copper rich fraction and even a small amount of gold. The boards themselves are made from plastics and fiberglass resins and essentially have no value.

It is unlikely that PC and electronic recycling operations can be made profitable without a subsidy or "tipping fee". As this is common practice in other forms of waste disposal and processing, it should not be a detriment to the development of a larger PC and electronics recycling industry.

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