Analysis of Shipley Microposit Remover 1165 and AZ@ P4620 Photoresist Waste Disposal for Company XYZ

by

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A Research Paper

Submitted in Partial Fulfillment of the
Requirements for the
Master of Science Degree
With a Major in

Risk Control

Aproved: 3 Semester Credits

Investigation Advisor

The Graduate College
University of Wisconsin-Stout
May, 2001

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ABSTRACT

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Analysis of Shipley Microposit Remover 1165- AZ® P4620 Photoresist
Waste Disposal for Company XYZ
(Title)

Risk Control	John H. Olson, Ph.D	May, 2001	39
(Graduate Major)	**(Research Advisor)**	**(Month/Year)**	**(No. of Pages)**

Publication Manual of the American Psychological Association (Fourth Edition)
(Style Manual)

Company XYZ is a company that processes semiconductor wafers. In their process, AZ® P4620 photoresist, an organic compound, is removed by Shipley Microposit Remover 1165, an organic solvent. When this occurs they produce a waste that cannot be disposed into a city's water system. An analysis was conducted to determine the methods that could be used to treat the waste, recover the solvent and eliminate the use of organic solvents for photoresist stripping. Also the main components of Shipley Microposit Remover 1165 and AZ® P4620 Photoresist were analyzed for different health effects they might attribute for.

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Chapter 1

Statement of the Problem

I. Purpose of the Study

The purpose of this study is to evaluate and select the best method or process that Company XYZ should implement for the removal of Shipley Microposit Remover 1165-photoresist waste. In addition, it examines the health hazards associated with the main chemical components of Shipley Microposit Remover1165 (n-methyl-2-pyrrolidone) and of the AZ® P4620 photoresist (PGMEA).

Objectives

The goals of the study are as follows:

1.0 Identify and assess the health effects associated with n-methyl-2-pyrrolidone and propylene glycol monomethyl ether acetate.

2.0 Define the advantages and disadvantages of each waste removal method from a cost and risk control perspective and select the most appropriate one for Company XYZ.

II. Background and Significance

Company XYZ has a research and development lab that performs semiconductor manufacturing processes. Semiconductor manufacturing is a carefully controlled, multistage process. The process of manufacturing semiconductors uses a wide variety of organic solvents in processes such as cleaning, developing, stripping and degreasing. Two of the stages in semiconductor fabrication that are conducted in this facility are photolithography and electroplating. During the photolithography process, electronic circuits are patterned on semiconductor wafers using photoresist, a photosensitive material containing glycol ethers and ultraviolet exposure through a mask having transparent and opaque regions that define the circuit pattern. Photoresists contain polymeric ultraviolet sensitive materials in a mixed solvent carrier (Pinney and Lemasters, 1996). The type of glycol that is in the photoresist at Company XYZ is propylene glycol monomethyl ether acetate (PGMEA). A developer solution is then used to remove the exposed photoresist, leaving a positive image of the pattern on the wafer (Colcaser, 1980). However, there remains photoresist on the rest of the wafer.

After electroplating, the remaining AZ® P4620 photoresist is stripped off the wafer. A product called Shipley Microposit Remover 1165, an organic compound consisting of 95% n-methyl-2-pyrolidone, which is contained in a heated bath inside a wet bench, performs the stripping process. Stripping is the simple process of heating the Shipley Microposit Remover 1165 to 70° C and submerging the wafer into the heated bath for a specific amount of time. The time is dependent on how thick the AZ® P4620 photoresist was spun unto the wafer. Stripping is also conducted in the photolithography stage only if the wafer needs to be reworked. Rework is done if the original pattern had an error in it. Therefore, the original AZ® P4620 photoresist is stripped off and the photolithography step for that specific layer begins anew. After a wafer has been stripped, the bath now contains the AZ® P4620 photoresist along with the original Shipley Microposit Remover 1165. After a period of time the Shipley Microposit Remover 1165 loses its stripping ability due to the saturation of the bath with AZ® P4620 photoresist. Therefore, the "spent" batch must be removed and a fresh batch is poured into the wet bench bath.

Shipley Microposit Remover 1165 and the AZ® P4620 photoresist are flammable liquids that also pose as health hazards. These chemicals also cannot be disposed of by being poured down the city's water system. Currently, Company XYZ doesn't have a system in place for the removal of the Shipley Microposit Remover 1165- AZ® P4620 photoresist bath. Prior to implementing a system for Company XYZ, it is important to assess different waste systems and different processes of stripping wafers that may reduce or eliminate waste and/or the use of organic solvents.

Limitations of the Study

This study is limited to Company XYZ. The conclusions and recommendations are strictly for the disposal of the waste generated at Company XYZ that are specific to their process, the design of their equipment and the layout of their facility.

Definition of Terms

cutaneous: relating to or existing on or affecting the skin.

dermatitis: inflammation of the skin.

effluent: water mixed with waste matter.

epithelium: membranous tissue covering internal organs and other internal surfaces of the body.

exudate: a substance that is released through one's pores.

fab: (i.e. fabrication) the area in which integrated circuits are manufactured.

fetotoxicity: the toxic ability to interfere with the normal development and growth of the fetus.

implantation: the organic process whereby a fertilized egg becomes implanted in the lining of the uterus; pre-before implanting post-after implanting.

intraperitoneal: of or relating to or affecting within the peritoneum- a transparent membrane that lines the abdominal cavity.

lumen: an opening, space or cavity.

N-methyl-2-pyrrolidone (NMP): a solvent used for stripping photoresist.

organic: relating to or belonging to the class of chemical compounds having carbon basis.

ossification: the process of bone formation.

oxidation: the addition of oxygen to a compound with the loss of electrons.

ppm: parts per million.

permeation: the act of permeating, passing through or spreading throughout the pores, or interstices of any substance.

photoresist: a photosensitive material used for pattern imaging on wafers.

Propylene Glycol Monomethyl Ether Acetate (PGMEA): a solvent used to formulate photoresists used in semiconductor processing.

semiconductor: an element that has an electrical resistivity in the range between conductors and insulators. Integrated circuits are typically fabricated in semiconductor materials such as silicon or gallium arsenide.

solvent: a substance suitable for or employed in, solution, or in dissolving something.

supercritical fluid: a fluid (liquid or gas) which has been brought to conditions above its critical temperature and pressure.

teratogenicity: the ability of a toxin to cause a birth defect.

toxicity: the state of being toxic or poisonous.

wafer: the disc or substrate on which integrated circuits are manufactured.

Chapter 2

Review of Literature

Introduction

The stripping of photoresist is a necessary step for the production and reworking of wafers in the semiconductor industry. The main component of these photoresist strippers is N-methyl-pyrrolidone (NMP), while the main component of the AZ® P4620 photoresist that is stripped off is propylene glycol monomethyl ether acetate (PGMEA). Both components are organic solvents that can't be discharged into city water and treated at a municipal sewage treatment plant. The following literature review examines the chemical properties of NMP and PGMEA, studies on the health risks they pose, waste handling treatments and different processes that would reduce or eliminate the amount of waste.

N-methyl-pyrrolidone in Shipley Microposit Remover 1165

NMP is a slow evaporating solvent with low viscosity. Its excellent solvent power and low vapor pressure are two main reasons for its use in the chemical industry. In the semiconductor industry it is the solvent in a photoresist stripper called Shipley Microposit Remover 1165 that makes up 94-95% of the stripper (Shipley, 1999). Another advantage to using NMP is that it doesn't attack silicon, which is what most wafers are made of. Therefore, the AZ® P4620 photoresist is stripped off, but the substrate stays intact. Some of the physical and chemical properties of NMP's, which are analogous with Shipley 1165, are it is a natural colored liquid with a mild amine odor that is completely soluble in water. It is stable under normal conditions and should avoid conditions where there are high temperatures and static discharge because of its combustible properties. It is incompatible with oxidizing agents, acids and reducing agents. The electronic grades or ultra pure grades are the grades of NMP used in photoresist strippers (BASF, 1999).

Studies of NMP

The most common route of exposure to NMP in the workplace is by inhalation or by dermal contact. Studies have been conducted to see what toxic effects NMP has on rats and mice. In a study of mice, increased incidence of malformations and increased postimplantation loss were observed after intraperitoneal injection of NMP (100-170 mg/kg) on day 9 or on days 7-11 of pregnancy (Becci, Knickerbocker, Reagan, Parent and Brunette, 1992). However, since no information on maternal toxicity is given the results are difficult to interpret. Dermal application has shown to have a greater affect than inhalation exposures. For example, reduced fetal weights on day 21 of pregnancy and delayed ossification were seen previously in a teratology study with rats after dermal application of 750 mg NMP/kg on days 6-15 of pregnancy, but not after inhalation exposure to 90 ppm (Lee, Chromey, Culic, Barnes and Schneider, 1987). However, after inhalation exposure to 150 ppm on days 7-20 of pregnancy, a decrease in pup weight at birth and during the preweaning period was registered in a postnatal study (Hass, Lund and Elsner, 1994). Hass et al. also observed that impaired performance in behavioral tests coincided with lower fetal body weight after prenatal exposure to 150 ppm of NMP. In another study, Haas, Jakobsen and Lund (1995) have shown that prenatal exposure to 165 ppm of NMP caused increase preimplantation loss, lower fetal body weights and delayed ossification. All these studies have shown that if the NMP concentration is high enough through dermal contact or inhalation the potential for low birth weight can occur in rodents. In humans, learning problems are more common for children with low birth weight (Nelson, 1991). Therefore, low birth weight may be regarded as an indicator of increased risk of functional disturbances.

Studies of the teratogenicity of NMP generally found no effects at lower doses and fetotoxic effects at higher doses, often without any discernible effects on the mother. These studies involved mice and rats. There haven't been many studies conducted on humans. However, Solomon, Morse, Garbo and Milton (1996) reported a human case study of intrauterine growth retardation followed by fetal death at 31 weeks gestation. The mother was a laboratory worker with no apparent risk factors, who sustained occupational exposure to NMP throughout the first trimester of pregnancy. The lab workers responsibilities included operating two atomic absorption spectrophotometers, which solid samples were dissolved in NMP. Many of the samples were of negative photoresist used in the electronics industry. This is an example where NMP may have been the cause of or had some responsibility for the stillbirth of a human. The implications of the results from animal studies and the human case study show that NMP accompanied by chronic exposure may not be a harmless replacement for other organic solvents.

NMP is moderately toxic by all routes of exposure, however due to its low vapor pressure, dermal exposure represents the primary hazard in most settings. NMP has been reported to cause acute contact dermatitis involving swelling, itching and vesicular eruptions. Eye contact with NMP results in moderate eye irritation and may cause temporary corneal clouding. Skin contact results in mild irritation, redness and dermatitis if prolonged. Respiratory irritation may occur if vapors of NMP are inhaled. If accidentally ingested, NMP causes gastric disturbances and may result in nausea and vomiting (BASF, 2000). Although there are no current established limits for occupational NMP exposure in the United States, several European countries have adopted 8-hr time-weighted-average limits of 100 ppm (Cook, 1987). Shipley has limits of 25 ppm and 75 ppm for a 15-minute exposure. However, a study by Beaulieu and Schmerber (1991) indicated that severe eye irritation and headaches are expected at levels as low as 0.7 ppm in air for 30 minutes. A small electrotechnical company in Norway experienced irritant reactions to the skin after working a few days with NMP. After 2 days of work, 10 out of the 12 employees working with NMP displayed acute irritant contact dermatitis of the hands (Leira, Tiltnes, Svendsen and Vetlesen, 1992). Since dermal contact is the primary route of exposure for NMP, using proper gloves is vital in preventing NMP from contacting the skin. NMP has shown to penetrate latex gloves easily. The photoresist bath is heated and therefore the permeability of gloves in heated conditions is essential. Zellars and Sulewski (1993) conducted a permeation study between butyl-rubber gloves and natural-rubber gloves at different temperatures. Zellars and Sulewski concluded that butyl-rubber gloves provided excellent protection under all test conditions, suggesting that these gloves be used for protection from NMP in all cases where particulate contamination can be tolerated. Butyl-rubber gloves are more expensive, but the high cost is offset partially by its ability to be reused even after NMP exposure. The use of natural-rubber gloves may be adequate for certain situations, but the rapid permeation above room temperature and apparent persistence of NMP following exposure indicate that they should be replaced promptly if any exposure occurs.

Propylene Glycol Monomethyl Ether Acetate in AZ® P4620 Photoresist

AZ® P4620 photoresist is an amber-red liquid with a strong, characteristic odor. It partially dissolves in water leaving a floating viscous mass, i.e. two layers. It is classified as an OSHA combustible liquid and a DOT flammable liquid (Clariant, 2000). Although it is a stable chemical, thermal decomposition may generate carbon dioxide, carbon monoxide and oxides of nitrogen and sulfur. PGMEA has been used as a replacement solvent for ethylene glycol ethers and ether acetates in photoresist formulations used in semiconductor processing. PGMEA is a synonym for 1-Methoxy-2-propanol acetate, which accounts for 62% of the weight in AZ® P4620 photoresist (Clariant). The reasoning for this substitution is PGMEA has shown, through limited animal testing, no significant adverse reproductive health effects (Boggs, 1989). One of the tests was conducted by the U.S. Army (1989) on pregnant female rats that were exposed to 0, 500, 1980, or 4160 ppm propylene glycol monomethyl ether acetate for 6 hours/day on gestation days 6-15. The rats were examined grossly for structural abnormalities or pathological changes. PGMEA caused transient central nervous system effects, decreased food consumption and decreased weight gain in the rats at the higher two levels. Total weight gain was the only effect in the rats, which was significant at the end of the study. No other maternal effects were found. Fetuses exposed up to the highest concentration (4160 ppm) of PGMEA did not exhibit any teratological or other developmental effects. Although there appears to be no adverse reproductive effects, nasal and dermal irritation still remains. Miller, Hermann, Young, Calhoun and Kastl (1984) conducted a short-term vapor inhalation toxicity study. Miller et al. found degeneration of the olfactory epithelium in all mice that were exposed to PGMEA in concentrations of 300, 1,000 and

3,000 ppm. It was more severe in those that were exposed to 3,000 ppm. An acute inflammatory exudate was present in the lumen of the nasal cavities in some animals of the two higher doses. This study coincides with AZ® P4620 photoresist's MSDS that states high vapor concentration causes irritation to the nose, throat and lungs. Also PGMEA has the ability to readily permeate the intact skin. Due to this characteristic, as with NMP, glove selection is vital to prevent dermal contact. Zellars and Sulewski (1992) found that butyl-rubber gloves provided the best protection against PGMEA. However, these gloves are not suitable for cleanroom use because they are coated with a powder before packaging that could contaminate the work area. Nitrile rubber gloves also provided good resistance to PGMEA under continuous exposure conditions. While the permeation resistance decreased significantly with an increase in PGMEA temperature for the nitrile rubber gloves, the breakthrough of the solvent was observed long enough to provide adequate protection for most jobs. There is a concern of the persistent permeation of the PGMEA through the nitrile rubber gloves after a relatively short initial exposure and evidence of a change in the structure of the glove as a result of initial exposure (Zellars and Sulewski). This is a pertinent issue to consider when reusing these gloves for disposing of this material because the only exposure is a splash or spill, which is a relatively short initial exposure.

Solvent Recovery Process

Companies that use a process like Company XYZ's for stripping wafers have disposed of their waste by either sending it to a waste-recycling center or by having it destroyed. According to the MSDS's of the Shipley Microposit Remover1165, incineration is the recommended method of disposal. However, NMP is particularly suited to recycling and the manufacture of Shipley 1165 stated recovery/recycling is a viable option if there is on-site technology to perform the recovery/recycling. The process that can be used for this type of solvent recovery is distillation. The concept of distillation works by heating the solvent to its boiling point, causing the solvent to evaporate and separate from the contaminants. As solvent vapors pass through a water-cooled condenser, they are condensed into clean, reusable solvent. Solvent Kleene Inc. manufactures portable solvent recovery systems named the SK-6000 and the SR-2000. The SK-6000 design provides the ability to process waste solvents ranging from 20-gallon batches to 55-gallons in a continuous, closed-loop operation (Solvent Kleene Inc., 2001). This system is easy to operate and an employee can be trained in less than 15 minutes. To operate the system, a user selects the proper processing temperature and pushes the start button. Once the unit is initiated, no further operator attendance is necessary. Using a closed-loop continuous flow system, the SK-6000 is able to automatically feed waste solvent into the distillation tank, then into a 55-gallon clean solvent recovery tank. A pneumatic logic system is used to control the liquid level and the delivery of waste solvent to the processing tank. As liquid solvent is converted to vapor, the system automatically feeds additional solvent from the waste solvent drum into the processing tank. An auto pump-out allows automatic removal of any hot liquid contaminants i.e. AZ® P4620 photoresist left in the processing tank after solvent separation. With this option, it is possible to process 150 gallons of solvent every 36 hours without any contact or exposure to spent solvent or liquid contaminants (Solvent Kleene Inc.,). This recovery system can typically reclaim 95% of the solvent. The SK-6000 has a redundant automatic safety shut-off systems when: 1) if coolant temperature rises above 90° F 2) if vapor temperature exceeds differential margins 3) if temperature control fails 4) if temperature monitors fail. The SR-2000 is a smaller version of the SK-6000 and only does 6 gallon batch distillation. Both units have explosion proof electrical system that is UL approved. Both are designed to meet NFPA Class 1, Division 2, Group D standards for hazardous locations.

Waste Treatment Processes

There are two possible processes to treat wastewater containing Shipley Microposit Remover 1165 and AZ® P4620 photoresist to make it acceptable for dumping down a city's water system. The two methods are UV/Ozone/Peroxide treatment and the CerOx process.

UV/Ozone/Peroxide treatment is an ultraviolet radiation and oxidation technology. As the name implies UV/Ozone/Peroxide treatment is comprised of three individual components: ultraviolet radiation, ozone gas and hydrogen peroxide solution. The components together use radiation and chemical oxidation to disinfect and destroy a wide range of contaminants. Chemical oxidation is a process by which compounds, such as waste products are oxidized to a more environmentally benign state. Ozone is commonly used in wastewater treatment applications as a disinfectant because it is a powerful oxidant and reacts with most toxic organics. Hydrogen peroxide is used to treat liquid and solid hazardous wastes because it readily reacts with organic chemicals to form carbon dioxide and water. Radiation is a process by which energy is transferred from one location to another. Ultraviolet (UV) light is a form of radiation. UV light is often used as a disinfectant in water and wastewater treatment. It is also powerful enough to break many covalent bonds. In combining these three processes, the limitations of the individual components are reduced. A full scale UV/Ozone/Peroxide treatment system consists of a UV/Oxidation reactor, and air compressor with an ozone generator module and a hydrogen peroxide feed system (Clarin, Fletcher and Reichardt, 1998).

There advantages for using an UV/Ozone/Peroxide treatment system. The first involves the actual treatment technology. An UV/Ozone/Peroxide treatment system is a destruction process, so the final products are carbon dioxide, water and inert salts (Chin, Foughy and Kamiya, 1997). These end products do not need any additional treatment. Secondly, ozone is used as an oxidant instead of chlorine. Ozone is a better disinfectant than chlorine and is not known to produce toxic or mutagenic substances. The final advantage is that a wide variety of contaminants and concentrations can be treated.

There are also disadvantages to this system. The equipment needed can be expensive and require a large amount of space. The energy required to run this system is high, which results in a larger cost. The production of ozone is expensive because it must be generated on-site and immediately applied to the system. Each of the three constituents of the process need risk controls. Ozone is explosive, toxic and an irritant to the skin, eyes, respiratory tract and mucous membrane. It is also an air pollutant. Hydrogen peroxide is an irritant, can cause chemical burns and is an explosive. UV light can burn unprotected skin and the mercury in the lamps can damage the central nervous system along with inflaming the nose and throat area. Finally, the UV/Ozone/Peroxide process mechanisms are still not fully understood (Clarin et al.).

The other treatment process is called the CerOx process. The CerOx process is based on the oxidation of organic compounds with the use of a catalyst or mediator. The catalyst used in the CerOx process is a lanthanide metal called cerium. Cerium will dissolve into ions when placed in a strong acid such as nitric acid. In its ion form, cerium will maintain a stable Ce^{3+}. To run the process, cerium is oxidized to one higher valent state, then placed into a container to regain its lost electron from any organic compound placed in contact with it. After the cerium is reduced to Ce^{3+} by taking an electron from an organic compound, the cerium is recirculated through the electrochemical cell and reoxidized to Ce^{4+} to repeat the operation (CerOx Corp., 2001). The electrochemical cell, called T-CELL, is proprietary and was designed and patented by CerOx Corporation. The T-Cell plus external modules for electrolyte circulation and storage, hazardous waste injection, mixing and holding, off-gas handling and processing, electrolyte regeneration are balanced into a single system. Systems are self-contained, fully automated plants that, for smaller applications, and are built into small steel cabinets complete with containment. Because the waste generated at Company XYZ is a miscible compound that boils at greater than 100° C, it will be processed in the liquid phase reactor. Wastes are pumped into a bleed stream of anolyte. This mixture flows through a sonicator, where intense sound waves bombard and emulsify any immiscible compounds allowing for quicker contact with the Ce^{4+}. The emulsion then flows into the liquid phase reactor where the cerium to waste ration is maintained at a high level allowing the cerium solution to overwhelm the organic compounds (CerOx Corp.). The organics are oxidized at 90-95° C and reform as carbon dioxide and water. The carbon dioxide is vented and the water is removed and sent down the drain.

Process to Eliminate the use of Organic Solvents

The use of organic solvents has brought up risk control considerations such as environment, safety and health. Organic solvents produce a waste stream, consume large amounts of water for rinsing, are flammable and can be toxic or an irritant to employees. The elimination of organic solvents is the best risk control technique that can be utilized. An emerging technology for conventional solvent replacement is the use of supercritical fluids based on carbon dioxide. Supercritical fluids based on CO_2 are viable options to industrial processes for several reasons. CO_2 is non-toxic, non-flammable, doesn't produce a waste stream and is relatively inexpensive. The unique combination of physical, chemical and economic properties of supercritical CO_2 ($SCCO_2$) has prompted an evaluation into its use as a replacement for organic solvents used in photoresist stripping.

In order to make proficient use of a supercritical fluid as a solvent, it is desirable to use a closed-loop system (Rubin, Davenhall, Taylor, Sivils and Pierce). The closed-loop system begins with a liquid-CO_2 storage reservoir. The liquid is brought to above its critical pressure during a pumping operation that sends the pressurized liquid to a heating unit. The heating unit warms the pressurized CO_2 to above its critical temperature, so that the supercritical fluid is formed. The supercritical fluid enters the treatment vessel and is brought into contact with the substrate. It is during this time the photoresist is solubilized in the CO_2. On exiting the treatment vessel, the $SCCO_2$, containing the photoresist is sent to a separation vessel. Here, the $SCCO_2$ is depressurized to a gas, reducing the CO_2 density to a gas-like value. The photoresist's solubility is greatly reduced in the low density CO_2 gas and therefore is deposited in the bottom of the separator. The CO_2 gas exits the top of the separator where it is chilled back to a liquid and re-enters the liquid-CO_2 storage reservoir (Rubin et al.). The photoresist on the bottom of the separator is collected and then either disposed of or recycled. The closed-loop system means there are no waste streams exiting the system.

Shipley Microposit Remover 1165 and AZ® P4620 photoresist have components, such as, NMP and PGMEA, that are flammable and can cause irritation of the skin and respiratory tract when acutely exposed. However, people are predisposed to different sensitivities and may have irritations at various concentrations. Everyone will react differently to different concentrations of the chemicals. Acute exposure is what most employees would have when disposing waste, due to the short period of time around the waste and the potential for spills. Certain types of gloves are permeable to both chemicals and the permeability of gloves can change with temperature. The “spent” bath mixture is heated to 70° C, therefore, the permeability characteristic of gloves is important to know when disposing of the bath.

An alternative to disposing of the waste would be solvent recovery. The process that reclaims solvents is distillation. Two sytems: SK-6000 and SR-2000 are solvent recovery units that can perform such process at individual companies. These systems can typically reclaim 95% of the solvent. The recovery of the reusable solvent can reduce hazardous waste disposal by up to 95%, while reducing the purchase of new solvents.

Waste treatment processes like UV/Ozone/Peroxide and CerOX process can be used as a precursor to dispose of the “spent” bath. These processes allow the waste to be broken down to water and CO_2 and no secondary treatments are necessary. For the UV/Ozone/Peroxide system, large amounts of waste must be generated for these systems to be cost-effective because the initial costs and operating costs of this system are expensive. High energy is required to operate this process, which increases the probability of risk. The CerOx also requires high energy and it takes multiple units if there is high volume of waste to be treated because it isn't as efficient. Both processes need large amount of space for installation of the system as well.

Using supercritical CO_2 to strip photoresist is becoming an emerging technology. By using this process, organic solvent use in photoresist stripping could be eliminated. Supercritical CO_2 use can eliminate waste streams, reduce the volume of waste, lessen the flammability exposure that exists when using an organic solvent, reduce water consumption and reduce adverse health effects to employees.

A cost/benefit analysis might be conducted before implementing any of the processes that have been reviewed. Cost/benefit analysis can be of assistance to the decision-maker when uncertainties as to a course of action exist; particularly uncertainties related to priorities, or to the efficiencies or the economic aspects of alternatives (Biancardi, 1978). First, it should be determined if the problem is substantial enough to warrant a detailed analysis. One should recognize the drawbacks associated with a cost/benefit analysis. Biancardi states that this process isn't precise in spite of its quantitative quality. Also people might disagree which factor, social or economic, is more important when considering the objective of a project. Currently, Company XYZ has not considered a cost/benefit analysis for the disposal of Shipley Microposit Remover 1165 and AZ® P4620 photoresist waste.

Chapter 3

Methodology

The methodology used for this field problem consisted of a literature review to learn the chemical properties and health risks associated with NMP and PGMEA. The literature review also entailed researching processes that treat organic solvents for disposal down city water systems or recovering the solvent all together. The last part of the review analyzes a process that can eliminate the use of organic solvents as a photoresist stripper. In addition, informal interviews were conducted with various professionals in the semiconductor industry. Finally, a system, using a cost/benefit analysis, was recommended to Company XYZ.

I. Literature Review

- 1.0 Chemical properties of NMP and PGMEA
- 2.0 Health effects of NMP and PGMEA
- 3.0 Treatment processes of organic solvents
  - 3.1 UV/Ozone/Peroxide treatment
  - 3.2 CerOx process
- 4.0 Solvent recovery process
  - 4.1 SK-6000 and SR-2000 systems
- 5.0 Elimination of organic solvents
  - 5.1 Supercritical CO_2

II. Informal interviews

- 1.0 Manufacturer of Shipley Microposit Remover1165
  - 1.1 Disposal methods

2.0 BASF

2.1 NMP's biodegradability, storage and handling

3.0 Waste professionals in the semiconductor industry

3.1 Disposal methods

4.0 Salesman for the solvent recovery systems

4.1 Cost, efficiency and effectiveness of systems

5.0 Maintenance and facilities personnel

5.1 Design of wet bench

5.2 Input on parts and placement of system

III. Data collection

1.0 Quantity of Shipley Microposit Remover 1165 used

2.0 Wafer production schedule-present and future

3.0 Dimensions and parts needed to install system

IV. Data Analysis

1.0 Analyze data and compare disposal options

2.0 Develop a recommendation for waste disposal

3.0 Present findings to the director of NTL for Company XYZ

Chapter 4

The Study

Introduction

Company XYZ strips AZ® P4620 photoresist off wafers by immersing the wafer in a heated bath of Shipley Microposit Remover 1165 that is contained in a SCP wet bench. This process produces a "spent" bath, which is classified as a hazardous waste and cannot be disposed of into the city's water system. However, Company XYZ has been dumping the waste into the city's water stream because they didn't know that procedure was incorrect. There is a drain at the bottom of the bath in the wet bench that leads to the city's water system. This is how they have been disposing the "spent" bath. The purpose of this study is to evaluate and select the best method or process that Company XYZ should implement for the removal of Shipley Microposit Remover 1165-photoresist waste. In addition, it examines the health hazards associated with the main chemical components of Shipley Microposit Remover1165 (n-methyl-2-pyrrolidone) and of the AZ® P4620 photoresist (PGMEA).

Health Hazards Associated with NMP and PGMEA

There are different health effects associated with acute exposure to NMP. NMP is moderately toxic by all routes of exposure, however due to its low vapor pressure, dermal exposure represents the primary hazard in most settings. Contact by the eye with the liquid can result in moderate eye irritation and may cause temporary corneal clouding. Contact with the skin results in mild irritation, however repeated or prolonged contact may produce defatting of the skin leading to irritation and dermatitis. Exposure by inhalation may cause irritation of the nose, throat and respiratory tract. However, studies have shown that some people are more susceptible to respiratory irritation than others. Ingestion exposure, usually done accidentally, causes irritation of the mouth and throat and gastric disturbances. This may result in nausea and vomiting. Studies have shown toxic effects of embryos if the mother is exposed to high doses by oral, dermal or intraperitoneal routes.

PGMEA has shown no adverse health effects. This is the main reason why it has replaced the ethylene glycols as the solvent for photoresists. However, it can be an eye and skin irritant if come in contact. Inhaled at high vapor concentrations it will cause irritation to the nose, throat and lungs. In animal studies, rats that were exposed to PGMEA for along term at high levels showed adverse effects to the livers and kidneys. Overall, NMP and PGMEA are not toxic chemicals that produce life-threatening health effects. However, they can be nuisance irritants causing burns to the employee if splashed on the skin or eye. They also can burn the nose, throat and respiratory tract if inhaled. These are all possible health effects that can be posed upon an employee when disposing of the waste.

Storage and Handling of Waste

The Shipley Microposit Remover 1165-AZ® P4620 photoresist waste is considered a combustible liquid. Waste should be stored in approved safety-type disposal cans that are properly labeled as to their contents and hazard. According to manufactures of Shipley Microposit Remover 1165 and AZ® P4620 photoresist, the waste cans are to be stored at the proper temperature, approximately 55°F. The cans also will be stored away from sources of heat or ignition. Storage area should be cool, dry, well ventilated and out of direct sunlight. BASF (2000) recommends secondary containment is needed for 110% of each cans volume. When handling the waste wear proper protective eyewear, butyl-rubber gloves, apron and chemical vapor cartridge respirator if exposure exceeds 100 ppm.

Waste and Process Systems to Recover, Reduce or Eliminate Shipley Microposit Remover 1165

There are different processes Company XYZ can choose to how they can handle their waste. The UV/Ozone/Peroxide treatment and CerOx process are systems that treat the waste stream and give byproducts of CO_2 and water. After treatment the waste stream is environmentally benign and can go into the city's water system. The UV/Ozone/Peroxide treatment system requires a large amount of space for installation and a large flow of waste stream to operate. It is expensive to operate this system because huge amounts of energy are required. This large amount of energy can cause hazardous conditions. Also from a risk control perspective, each one of the components in this system has hazards associated with it. UV can burn skin and the mercury in the lamps can cause damage to the central nervous system. Ozone is an air pollutant. Hydrogen peroxide can cause chemical burns and is an explosive. The last problem associated with UV/Ozone/Peroxide treatment is the chemistry between the three is not fully understood.

The CerOx process dissolves cerium into ions when placed in a strong acid. Nitric acid is an acid that will dissolve cerium into ions. In this state, Ce^{3+}, the ion is stable. But when it is oxidized, Ce^{4+}, it will attack organic compounds. The oxidizing is done by a T-Cell. This chemistry is how the CerOx process makes waste manageable. However, nitric acid has potential risks associated with it. It is extremely hazardous; it is corrosive, reactive, an oxidizer and a poison.

Both processes treat waste streams to be disposed of into city water. But for them to operate effectively and efficiently certain situations need to apply. The CerOx needs the waste to be collected and then transferred to the T-Cell, where it would be connected and discharged into the drain. This requires space, which Company XYZ doesn't have. The UV/Ozone/Peroxide system needs a large quantity of waste stream generated in a short period of time because ozone production is expensive and needs to be used immediately when produced. Company XYZ doesn't generate enough waste to justify the cost of the treatment.

Solvent recovery is usually done at large reclamation facilities. They have distillers capable of recovering massive amounts of solvents. Solvent Kleene Inc. has manufactured two solvent recovery systems that are smaller and are for use on-site. The SR-2000 is the smaller unit and can only distill 6 gallons at a time. The SK-6000 has the capability to distill a batch of 20 gallons. However, with the continuous feed operation it can distill 55 gallons and it is possible to process 150 gallons of solvent every 36 hours. The disadvantages to these systems are they can only distill certain solvents, the solvents must have a boiling point between 100-400° F, the waste must be collected and tests must ran to see if the waste generated at Company XYZ can be recovered.

The last system eliminates the use of organic solvents as a photoresist stripper. This system uses supercritical CO_2 as the stripper. The wafer is transferred into a chamber and is exposed to the supercritical CO_2, where it lifts the photoresist off. This process eliminates waste streams and reduces water consumption because the wafers don't need to be rinsed. The use of this system would eliminate flammability exposures to the fab and the irritant effects of acute exposure to Shipley Microposit Remover 1165. However, this is still a new technology and tools are still being developed for processing wafers.

Informal Interviews

A waste treatment engineer for the Shipley Company informed Company XYZ that Shipley Microposit Remover 1165 is a mixture of organic solvents; a “spent” bath cannot be treated by conventional waste treatment process. Therefore, they do not have a recommended treatment procedure. The formerly recommended procedure simply states that organic solvents should be sent off-site for reclaim or destruction, usually incineration. Shipley recommended recycling or shipment of the “spent” bath off-site for incineration if the consumer doesn’t have the technology for on-site solvent recovery/recycling. The engineer informed Company XYZ about Solvent Kleene Inc. Company XYZ does not have a recovery/recycling system on-site.

Very few semiconductor companies had the set up like Company XYZ. The ones that did have a photoresist stripper bath in a wet bench, had the bath plumbed to drain in a solvent collection tank. The stripper was drained by gravity to the collection tank, which were located in the basement or underground. The collection tank was pumped out once or twice a year and the solvents were hauled off to be either recovered or destroyed. Unfortunately, the fab (NTL) were photoresist stripping is done is located in the basement of Company XYZ and the sub-fab underneath NTL’s floor is only 30 inches high and filled with ductwork and wiring. Therefore, no collection tank or 55-gallon drum could fit underneath the fab floor so a gravity feed system would not work to drain the “spent” bath.

System to Drain the “spent” Bath

Maintenance personnel and the risk control department brainstormed on how to design a system to drain the bath. There were two wet benches that had baths in them. The photolithography area had one bath for rework while the electroplating area had two baths. A drain was on the bottom of each bath, as was tubing that was connected to the water system. That was how the bath was being disposed of in the past. It was determined to use the existing drain and tubing and plumb a pipe system behind the wet bench in the plating area and to use the existing drain and tubing and plumb a pipe system to the side of the photolithography wet bench because there was no room behind it. Table 1.0 breaks down the parts and cost for plumbing each wet bench.

Table 1.0 Parts and cost for drain system in each wet bench.

Wet Bench	Part	Cost
Electroplating & Photo	(1) ½” Bulk head/bench	$14.13
Electroplating & Photo	(1) ½” Ball valve/bench	$36.94
Electroplating & Photo	(1) ½” Flex spout/bench	$6.00
Electroplating	(4) ½” Hex nipple fittings	$11.49 each
Photo	(2) ½” Hex nipple fitting	$11.49 each
Photo	(1) 90° ½” Elbow	$25.27
Photo	(1) 16” ½” Pipe	$10.25
Electroplating	(1) ½” Tee	$28.50
Electroplating	(2) ½” Socket Union	$17.50 each
Photo	(1) ½” Socket Union	$17.50

Note: Prices from McMaster-Carr and Parker Fittings catalogs.

Table 2.0 Total cost of system for each wet bench

Cost units	Electroplating	Photolithography
Parts	$166.53	$133.07
Labor (8hrsx2)	$400.00	$400.00
Total	$566.53	$533.07

The total price to affix a drain system to each bench was $1,099.60. The systems were similar except the electroplating bench needed a tee because it had two lines leading to it. The photolithography bench needed an elbow and a 16" pipe so the workers could drain the bath at the front of the bench because there was no room to the side or in back of it. Maintenance personnel of Company XYZ installed the system. The similarity of each bench and having Company XYZ's personnel do the work saved on labor time and cost. After the drain system was completed, the waste needed to go somewhere. An exhaust ventilation system was already functional in the chemical storage room. 55-gallon drums were placed under the exhaust system. They will be used as storage units. WRR in Eau Claire was sent a sample of the waste to see if it could be disposed of or recycled at their facilities. The results showed it was a recyclable waste. The cost would be $185/55-gallon drum to be recycled.

The next step was to train employees on how to drain the bath and pour it into the storage drum. First step was to put on the proper PPE (butyl-rubber gloves, apron and goggles. Place 5 gallon transfer container into secondary containment unit so the spout is inside the container's opening. Go to the control panel of the wet bench and press the drain button. The baths' volume ranges from 3-4 gallons so there will not be any overflow into the collecting container. Once the bath and drain pipe are empty, the ball valve is closed and the drain button is pressed again to close it. The collecting container's cap is put back on. The facilities personnel are notified and the employee inside the fab transfer the container in a chemical spill cart to facilities person outside the fab area. The cart is then wheeled to the storage are and the container is poured through a funnel into the drum. While pouring the employee is wearing butyl-rubber gloves, faceshield and an apron. The employees still have exposures with this method. The employees also have to manually refill the baths with fresh Shipley Microposit Remover 1165 by pouring it from one gallon bottles.

Data Collection

A cost benefit analysis was conducted to see if buying a solvent recovery system was beneficial to Company XYZ. History use of Shipley Microposit Remover 1165 was analyzed as well as future wafer production schedules. From 9/6/00 to 4/19/01 70 gallons of Shipley Microposit Remover 1165 was used. Starting on 10/1/01 single-layer wafer production will be 1,000 wafers per month. The electroplating wet bench has 2 baths: one 3 gallon and one 4 gallon. The 4-gallon bath can strip approximately 100 single-layer wafers before it becomes spent. The 3-gallon bath can strip between 50-75 single-layer wafers before it is spent. The electroplating technicians only use one bath until it is spent and then transfer over to the other bath. Therefore, a clean bath is ready at all times. Approximately 250 wafers need to be stripped starting 10/1/01. That equates to 11 gallons of Shipley Microposit Remover 1165 used per week. Shipley Microposit Remover 1165 costs $42/gallon and there is no price breaks if it is bought in bulk. Table

3.0 gives the cost of purchasing and disposing of Shipley Microposit Remover 1165 every 5 weeks when future production starts.

Table 3.0 Shipley 1165 purchasing and disposal costs for future production

Shipley 1165	Disposal	Total
$2,310.00	$185.00	$2,495

The future project is contracted for 4,000 wafers. The projected cost for the purchasing and disposal of Shipley Microposit Remover 1165 for this contract would be $24,950.00. The cost of the photo bath is substantially less. Around only 10% of the wafers are reworked in this area. This means approximately 100 wafers are stripped per month in this area compared to 1,000 wafers in electroplating. The annual cost of the project in the photo area would be $689.00. The overall cost of Shipley 1165 use and disposal for a year starting on 10/1/01 would be $25,639.

The cost of a SK-6000 recovery system is $13,500. The cost of a SR-2000 recovery system is $6,488. Both systems have a 95% solvent recovery rate. Table 4.0 shows the amount of solvent that may be recovered annually by using one of the systems the cost-savings associated with it by not having to purchase new Shipley 1165.

Table 4.0 Solvent recovery and savings per year.

Shipley 1165 used	Shipley 1165 recovered	Savings
584 gallons	555 gallons	555 x $42= $23,310

Note: Assuming 95% solvent recovery.

By implementing a solvent recovery system, the SR-2000 will pay for itself after 3.3 months, while the SK-6000 will break even with initial investment after 7 months. Additional costs would be a one drum spill-deck with bladder from Lab Safety for 66-gallon secondary containment. The cost is $205.50 for this unit. Further analysis is needed to know if the SR-2000 or SK-6000 can recover Shipley Microposit Remover 1165.

Chapter 5

Conclusions and Recommendations

The purpose of this study is to evaluate and select the best method or process that Company XYZ should implement for the removal of Shipley Microposit Remover 1165-photoresist waste. In addition, it examines the health hazards associated with the main chemical components of Shipley Microposit Remover1165 (n-methyl-2-pyrrolidone) and of the AZ® P4620 photoresist (PGMEA).

Objectives

The goals of the study are as follows:

1.0 Identify and assess the health effects associated with n-methyl-2-pyrrolidone and propylene glycol monomethyl ether acetate.

2.0 Define the advantages and disadvantages of each waste removal method from a cost and risk control perspective and select the most appropriate one for Company XYZ.

Conclusions

Overall, NMP and PGMEA are not toxic chemicals that produce life-threatening health effects. However, they can be nuisance irritants causing burns to the employee if splashed on the skin or eye. They also can burn the nose, throat and respiratory tract if inhaled. These are all possible health effects that can be posed upon an employee when disposing of the waste.

An alternative to disposing of the waste would be solvent recovery. The process that reclaims solvents is distillation. Two sytems: SK-6000 and SR-2000 are solvent recovery units that can perform such process at individual companies. These systems can typically reclaim 95% of the solvent. The recovery of the reusable solvent can reduce hazardous waste disposal by up to 95%, while reducing the purchase of new solvents. Shipley Microposit Remover 1165 may be a recoverable solvent. The recovery of this chemical can save Company XYZ money on an annual basis.

Waste treatment processes like UV/Ozone/Peroxide and CerOX process can be used as a precursor to dispose of the "spent" bath. These processes allow the waste to be broken down to water and CO_2 and no secondary treatments are necessary. For the UV/Ozone/Peroxide system, large amounts of waste must be generated for these systems to be cost-effective because the initial costs and operating costs of this system are expensive. High energy is required to operate this process, which increases the probability of risk. The CerOx also requires high energy and it takes multiple units if there is high volume of waste to be treated because it isn't as efficient. Both processes need large amount of space for installation of the system as well. At this time Company XYZ doesn't generate enough waste or have space allocated to install these systems. Also the high energy factor and the unknown chemistries of both processes increase the probability for an unwanted event to occur.

Using supercritical CO_2 to strip photoresist is becoming an emerging technology. By using this process, organic solvent use in photoresist stripping could be eliminated. Supercritical CO_2 use can eliminate waste streams, reduce the volume of waste, lessen the flammability exposure that exists when using an organic solvent, reduce water consumption and reduce adverse health effects to employees. Currently tools are in development for this process. Therefore it cannot be applicable to Company XYZ at this time.

Recommendations

Company XYZ has proceeded with the first recommendation of this study. That was to have the wet benches plumbed so the “spent” bath can be drained to a waste collection container. A system, as described in chapter 4, is in place for the storage and disposal of the waste. The recommended PPE for handling the waste is butyl-rubber gloves, face and eye protection in the form of goggles and/or face shield and a chemical resistant apron. The waste is profiled and should be recycled when a 55-gallon drum is full.

The following recommendation is from a risk control perspective. The study shows that that $23,310.00 can be saved potentially by incorporating a solvent recovery system into Company XYZ’s normal operation. Solvent Kleene Inc., manufacturers of the SK-6000 and SR-2000, will conduct a profile of the waste to analyze if the waste solvent can be recovered. The price is only $100 for the profile plus the cost of shipping and handling of 5 gallons of waste to be sent to their labs. Company XYZ should send a waste sample to Solvent Kleene Inc for profiling. The risk/reward ratio is huge; spend a little over $100 for a possible $23,000.00 return. If the waste can be recovered a closed loop system should be designed from the electroplating wet bench to the solvent recovery system. This system would allow the spent bath to be pumped into a 55-gallon drum that is connected to the solvent recovery system. In turn, the recovered solvent can be pumped back into the wet bench bath. The system would require two pumps, tubing or chemical pipe and the SK-6000 solvent recovery system. The bath in the photo wet bench would be too far away and therefore not feasible to pump at such a distance. However, there is a batch unit in the SK-6000 so the waste collected by procedures described previously can be poured in the system and recovered. The bath in the photo area is drained once a month compared to 12 times for the electroplating area. Therefore, it has a greater probability for exposure to employees and is the priority area for designing a closed-loop system. The closed-system would reduce employee exposure, while concurrently increases the amount of time that could be spent on production.

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