The Use of a Supercritical Carbon Dioxide-Based Solvent as a Cost Effective and Environmentally Sound Alternative to Current Photoresist Stripping Solvents

By

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ABSTRACT

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The semiconductor industry is facing challenges that involve the use of photoresist stripping solvents. This literature review compares the current solvents used, namely sulfuric acid and hydrogen peroxide and N-methylpyrrolidine, to an alternative supercritical carbon dioxide-based solvent. Currently used solvents have proven to be costly in terms of disposal, water usage and treatment, and replacement. These solvents have also been shown to have adverse affects on humans after short term and chronic exposures. The information gathered during this study shows that supercritical carbon dioxide-based solvents can reduce these costs immensely and may be a necessity for staying competitive in the future.

Acknowledgement

I would like to thank my family for the support they have offered during the pursuit of this degree and during the process of completing this research. I would also like to thank Kristy Hammons for the tremendous amount of patience she has had over the last year and a half. Next, I would like to thank the risk control staff and my advisor, Elbert Sorrell, for their guidance and for giving me the opportunity to further my education. Finally, I would like to thank my friends for the infinite amount of help they have offered me. I hope the relationships we have built will continue through our professional careers in the field of Risk Control.

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Chapter I

Statement of the Problem

Introduction

Semiconductor industries must use the best available technology to stay competitive and supply the demand for luxuries we have come to expect such as computers, television, and telecommunication (Moris, F., 1996). This technology usually involves using high volumes of chemicals and water as the fabrication process of wafers is primarily a series of chemical steps and processes. In fact, up to 20% of all process steps is wafer surface cleaning, requiring the consumption of large quantities of chemicals and purified water (Van Zant, P., 2000).

The removal of photoresist is one part of the cleaning process that consumes large amounts of water and chemical solvents. Although semiconductor industries have implemented stringent engineering and administrative controls such as gas detection systems and personal protective equipment to help reduce the risks associated with the chemicals in this process, employee exposure continues to be a problem (Van Zant, P., 2000). The need to reduce or eliminate toxic chemical use and waste has driven the industry to find better alternatives for the photoresist stripping process.

The two main photoresist-stripping methods used in the semiconductor industry today are dry stripping and wet stripping (Toy, 1990; Flamm, 1992). Downfalls of conventional dry stripping methods include incomplete removal of the photoresist and damage to the wafers by the deposition of metals onto the wafer (Flamm, 1992). In addition, this method often leaves a residue behind requiring a wet stripping method to be used as well.

Major downfalls to the wet stripping method are corrosive and toxic materials (i.e. sulfuric acid/hydrogen peroxide solution) that may incur high costs in handling and disposal (Livshits, et al, 1997). Also, the accumulation of contaminates (i.e. heavy metals and alkali metals) in the baths can reduce their effectiveness (Livshits, et al, 1997). Both of these methods have a potential of introducing hazardous chemicals to the environment and humans. Recently, highly pressurized gases known as supercritical fluids have been receiving attention as less toxic and even environmentally benign replacements for the currently used solvents.

Supercritical fluids are gasses that are subjected to high temperature and pressure. This gives them both liquid-like and gas-like properties, which allow them to dissolve and carry away materials like a liquid can but also enter very small spaces like a gas. Also, the density can easily manipulated by slightly increasing or decreasing the pressure that is applied. These properties are what make supercritical fluid technology so attractive for the photoresist stripping process.

Supercritical carbon dioxide-based solvents have been shown to be excellent alternatives for the photoresist stripping process, however many facilities are continuing to use the conventional wet or dry stripping methods. Facilities that continue the use of conventional photoresist stripping solvents instead of an environmentally sound alternative such as supercritical carbon dioxide are potentially causing environmental, human, and product loss.

Purpose

The purpose of this study was to compare and contrast traditional photoresist stripping solvents to a new supercritical carbon dioxide-based solvent for use in the photoresist removal process.

Objectives

1) Examine the toxicity and effectiveness of photoresist removal solvents that are currently used in the semiconductor industry.
2) Determine the toxicity and effectiveness of supercritical carbon dioxide-based solvents that would be used for photoresist removal.
3) Compare startup and long-term costs of supercritical carbon dioxide-based and currently used photoresist stripping solvents.

Background and Significance

There is a continuous push to make the architecture on wafers smaller, which is not only limited by the physics involved but also by the ability to clean within such small areas. Although the current solvents used for photoresist removal are excellent cleaning agents, they are limited in effectiveness by their physical properties. Since the most common solvents are water based, they have physical properties close to water such as surface tension. It is this surface tension that does not allow the solution to enter small pores on the wafer (Goldfarb, dePablo, Nealey, et al. 2000).

The ability to clean the wafers between photoresist applications in a cost effective and low risk manner is imperative to the quality of the product since the slightest impurity may render the entire product useless. Alternative solvents with little to no surface tension that are environmentally benign are needed to remove and clean particles from such small areas safely and effectively. In this study, information on a supercritical carbon dioxide-based solvent will be gathered to determine if it is feasible alternative for future use in the semiconductor industry.

Limitations of the Study

Losses in the semiconductor industry are considered proprietary information therefore actual loss data is not available and can only be estimated. Supercritical carbon dioxide-based solvents for photoresist stripping are a new to the photoresist stripping process and not currently used extensively. This limits the data on effectiveness and costs of running such a system.

Definition of Terms

Edema*	An excessive accumulation of serous fluid in tissue spaces or a body cavity.
Photoresist**	A chemical that changes properties when exposed to light. This change allows the exposed chemical to resist the development process.
Plasma*	An electrically neutral, highly ionized gas composed of ions, electrons, and neutral particles. It is a phase of matter distinct from solids, liquids, and normal gases.
Pulmonary*	Of, relating to, or affecting the lungs.
Supercritical***	Above a certain temperature where a vapor can no longer be liquefied, regardless of pressure.
Surface Tension*	A property of liquids arising from unbalanced molecular cohesive forces at or near the surface, as a result the surface tends to contract with properties resembling those of a stretched elastic.

* Source: The American Heritage Dictionary of the English Language, 4th edition
** Source: http://courses.nus.edu.sg/course/phyweets/projects99/xrl/photoresist.htm
*** Source: http://ull.chemistry.uakron.edu/chemsep/super/

Chapter II

Review of Literature

Introduction

The purpose of this study was to compare and contrast traditional photoresist stripping solvents with a new supercritical carbon dioxide based solvent. The literature review will explain the photoresist stripping process and the toxicity of current solvents. Information regarding the current use of supercritical carbon dioxide and a background on supercritical fluids is presented as well. This review will also provide comparisons and contrasts in order to establish a basis for the objectives of this study.

Overview of Wafer Production Process

Layering, patterning, doping, and heating are four basic operations in the production of a wafer. In the layering operation, thin layers of a conductor, semiconductor, or non-conductor are added to the surface of the wafer (Van Zant, 2000). Patterning involves a series of steps, which ultimately result in the selective removal of the preciously deposited layers (Van Zant, 2000). Doping is a process that adds dopants to the wafer surface to change the conductivity of the semiconductor (Van Zant 2000). The heating portion of the production process is a heating and cooling of the wafer to ensure good electrical conductivity (Van Zant, 2000).

Each of these steps may be performed multiple times on a single wafer. Within each basic operation, there are several procedures performed and with most of the procedures, there are many options to choose. The options that are chosen are based on the type of circuit and its composition (Van Zant, 2000). For the purposes of this research, the focus is on the patterning step in the process since photoresist stripping is a procedure within this step.

Photoresist Application

Photoresist is a chemical that is sensitive to light energy (i.e. UV, Infrared) and undergoes a change in chemical properties after being exposed to that energy (Van Zant, 2000). Photoresist is applied, and must be removed, every time a new layer is applied to the wafer. The pattern is "printed" on the wafer by exposing the photoresist to light energy through a negative, or mask, of the pattern (see figure 1), changing the chemical properties of the portion that was exposed (Van Zant, 2000). This process is similar to the photograph developing process.

The altered photoresist can then be removed chemically (developed) to leave the pattern on the wafer (see figure 2). The purpose of the remaining photoresist is to leave a pattern of material on the surface of the wafer that is resistant to the process used to etch out the unwanted areas of that layer (Van Zant, 2000).

Figure 1

Exposure of Photoresist

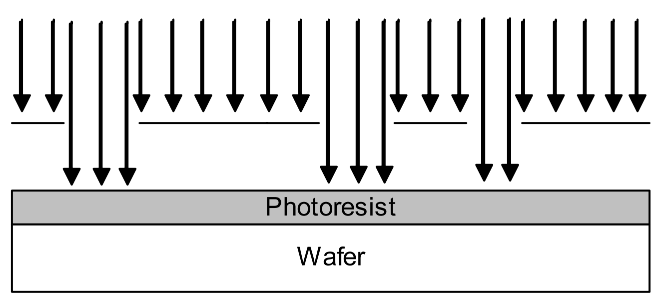
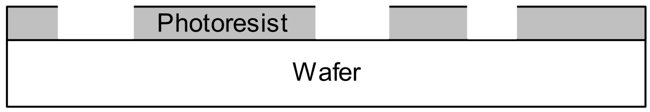


Figure 2

Wafer Surface after Developing



Photoresist Stripping

The photoresist that was a barrier for the etching process is no longer needed after the etching process is completed. Therefore, it must be removed by solvents or by a dry plasma method (Van Zant, 2000). This process is repeated every time a layer is added to the wafer and etched and could take place up to thirty times for each wafer. This repetition adds to the concern for reducing the cost and increasing the effectiveness of the process.

There are two main methods of photoresist stripping. One method utilizes solvents and is referred to as wet stripping while the other is called dry stripping and uses plasma. Wet stripping is the favored method because of its history, cost effectiveness, and removal of metal ions (Van Zant, 2000). However, the stripping method used on the wafer is dependent on several factors including surface type of the wafer and the polarity of the photoresist (Van Zant, 2000).

There are several types of solvents used in wet stripping and the one used is dependant upon the type of resist being removed. The solutions used can be grouped into acids and organic solvents. Figure 3 shows the most common photoresist chemicals used in the industry. These chemicals all have hazards inherent to their use and need special attention when handling and disposing the solvents.

Figure 3

Common Wet Stripping Chemicals

Stripper Chemistry	Strip Temperature (Centigrade)	Surface Oxide	Metallized	Resist Polarity
Acids:				
Sulfuric Acid + Oxidant	125	X		+/-
Organic Acids	90-110	X	X	+/-
Chromic/Sulfuric	20	X		+/-
Solvents:				
NMP/Alkanolamine	95		X	+
DMSO/Monothanolamine	95		X	+
DMAC/Diethanolamine	100		X	+
Hydroxylamine (HAD)	65		X	+

Microchip Fabrication: A Practical Guide to Semiconductor Processing, p. 271, Peter Van Zant, 2000. Permission requested.

The other photoresist stripping method is called dry stripping. This method utilizes a dry plasma process that oxidizes the photoresist into gases that are removed via ventilation of the plasma chamber (Van Zant, 2000). The advantage to utilizing a dry stripping process is the elimination of the chemical hoods and solvents needed for wet stripping. However, the dry etching process does not produce enough energy to remove, or vaporize, metal ions.

The inability to be able to remove the metallic residues requires an additional wet stripping process (Van Zant, 2000). This not only adds another step to the process, but also brings back the need for the chemical hoods and hazardous chemicals. Another downfall to the dry stripping process is that it has the ability to deplete the integrity of the wafer because of the radiation required to generate the plasma field (Van Zant, 2000).

Toxicity of Current Photoresist Stripping Solvents

The most commonly used solvent for photoresist stripping is called piranha and rightfully so since this solvent is a mixture of sulfuric acid and hydrogen peroxide and is usually heated to a temperature of 125ºC (Van Zant, 2000). Both of these substances alone can cause immense damage to almost anything they encounter at room temperature and when heated, they become even more damaging (Weast, 1984).

Sulfuric acid is very corrosive and is an irritant to mucous membranes and skin as well as a possible carcinogen (ATSDR, 1999; ACGIH, 2001). This acid emits highly toxic vapors when heated and has the potential of catching fire when exposed to a variety of substances including acetone and finely ground metals (ATSDR, 1999). When released into the environment, sulfuric acid causes acid rain.

As the oxidant portion of the solution, hydrogen peroxide reacts violently to a number of organic and inorganic compounds such as ethanol and sulfuric acid (NTP, 2001). Hydrogen peroxide is also an irritant to the skin and mucous membranes causing blistering of the skin and eye injury at high concentrations. The main concerns facing industries employing the sulfuric acid/hydrogen peroxide solution in their procedures are chronic exposure due to low-level concentrations of sulfuric acid droplets and/or gas in the air of the workplace, acute exposure to high concentrations of sulfuric acid in the air or on the skin, and the effects on the environment from ventilation exhaust and/or spills.

Other acids that are used in the photoresist stripping process include chromic sulfuric acid. Chromic sulfuric acid has been found to cause pulmonary edema upon inhalation, deep ulcers and dermatitis upon skin exposure, and coma (University of

Akron 2002). The U.S. National Toxicology Program (NTP) has also identified chromium and certain chromium compounds as being known carcinogens.

The organic solvents sometimes used to remove photoresist with a positive polarity pose health risks as well. N-methylpyrrolidine is the most widely used organic solvent for photoresist removal (Van Zant, 2000). Chronic exposure to N-methylpyrrolidine has been found to cause allergic respiratory sensitization. Sensitized people can experience symptoms of bronchial asthma such as wheezing, difficult breathing, sneezing and runny or blocked nose at low airborne concentrations that have no effect on non-sensitized individuals (ATSDR, 2002). Repeated or prolonged skin contact with some amines can cause allergic skin sensitization. Once a person is sensitized to a material, contact with even a small amount causes outbreaks of dermatitis with symptoms such as skin redness, itching, rash, and swelling.

Many of the chemicals being used in the photoresist stripping process have been found to be harmful to humans. This is especially true after chronic exposure to the chemicals. The removal of these chemicals from the photoresist stripping process should be a priority in the semiconductor industry because of the risk they impose on the employees. The use of supercritical fluids in this process may be the key ingredient for the complete removal of these highly hazardous chemicals.

Background on Supercritical Fluids

The study of gasses under high pressures was a major topic one hundred and twenty-five years ago and grabbed the interests of famous chemists from that period (Mendelejeff, 1870). In 1879, it was found that highly compressed gasses were good solvents and that their ability to dissolve substances was dependent on pressure (Hannay and Hogarth 1879). The density of gasses under pressure can be greatly influenced by slight changes in pressure. This is important to understand since the solubility power of a substance is dependent on its density.

Supercritical fluid technology has been used widely in industry for extraction, purification, and chromatography processes (King, Johnson, Friedrich 1989; McHugh, Krukonis, Pratt 1994). In addition, the use of supercritical carbon dioxide has been receiving attention lately as a possible alternative to the use of chlorofluorocarbons in areas that have very few environmentally benign alternatives available (Pirrota, Pava 1994; Spall 1993).

Substances have a critical temperature (T_C) and pressure (P_C) and if a graph of temperature versus pressure is constructed, the point at which the critical temperature and pressure intersect is called the critical point (CO_2's critical point is 31ºC and 72.8 atm). Substances that have exceeded this point are considered supercritical. Gasses near their critical point exhibit properties that are both gas-like and liquid-like (Poliakoff 2001).

Supercritical fluids are liquid-like in that they have transport and dissolving properties like a liquid and are much more dense than a gas. This gives the fluid the ability, much like that of a light hydrocarbon (i.e. pentane), to dissolve most solutes (Poliakoff 2001). Supercritical fluids are gas-like in respect to their very low viscosity and little to no surface tension allowing them to enter the smallest pores or spaces on a wafer. These properties are what make supercritical fluids so appealing for cleaning, extraction, and chromatography.

The relative inertness of carbon dioxide compared to the hazardous effects of the solvents currently being used for photoresist stripping makes supercritical carbon dioxide very attractive as an alternative. The major downfall to this new technology is that it is not yet proven in an industry setting. This causes industries to remain unconvinced of its potential.

Summary

This literature review presented information regarding the hazards associated with the most common solvents being used in the photoresist stripping process. Background information on the properties of supercritical fluids was also presented to show why they are so attractive for use in the photoresist stripping process. This data is essential in providing a basis for further comparison in Chapter IV.

Chapter III

Methodology

Introduction

The purpose of this study, as stated in Chapter I, was to compare and contrast traditional photoresist stripping solvents to a new supercritical carbon dioxide-based solvent for use in the photoresist removal process. A review of professional literature was used to gather information on: (a) current photoresist stripping solvents and (b) supercritical carbon dioxide-based solvents.

Current Photoresist Stripping Solvents

The information on the types of solvents used in the photoresist stripping procedures was gathered from *Microchip Fabrication: A practical Guide to Semiconductor Manufacturing*, by Peter Van Zant. In his book, Van Zant details the types of solvents used for each type of photoresist and the most common types used in the industry today. As stated in Chapter II, the two most common photoresist strippers are sulfuric acid/hydrogen peroxide solution and N-methylpyrrolidine. The Agency for Toxic Substances and Disease Registry (ATSDR) was then used to determine the major health effects of these two chemicals. Other effects such as environmental and fire hazards were also obtained from ATSDR. Information on the effectiveness of sulfuric acid/hydrogen peroxide and N-methylpyrrolidine was then gathered from professional literature sources.

Supercritical Carbon Dioxide-Based Solvents

Background information such as the properties and discovery of supercritical fluids was obtained through a literature search and review. Professional literature was then used to determine the effectiveness and cost of supercritical carbon dioxide-based solvents for photoresist removal. In addition, a toxicological study on propylene carbonate was used for determination of possible health effects of this component of the solvent.

Summary

Using the information gathered for current solvents and supercritical carbon dioxide-based solvents, a comparison was made and the viability of supercritical carbon dioxide as a photoresist stripping solvent was assessed.

Chapter IV

The Study

Introduction

The purpose of this study was to compare and contrast traditional photoresist stripping solvents to a new supercritical carbon dioxide-based solvent for use in the photoresist removal process. The objectives of this study, as stated in chapter I, will be fulfilled in this chapter by presenting information on the effectiveness, hazards, and cost of supercritical carbon dioxide-based solvents to provide a comparison to currently used solvents.

Objective 1: Toxicity and Effectiveness of Current Photoresist Removal Solvents

Information that is available on the hazards and toxicity of the solvents used for the photoresist stripping process is very extensive. The most commonly used solvent for this process is a solution of sulfuric acid and hydrogen peroxide that is heated to around 100°F. At this temperature, the solution is very corrosive and becomes a fire hazard. In addition, many of the chemicals used as solvents are shown to have toxic effects on humans. Some of the effects that are common among many of the solvents are irritation to mucous membranes, severe burns of the skin and eyes, pulmonary edema, and sensitization of the respiratory system. There have been engineering controls, such as ventilation hoods, implemented to reduce the exposure and hazardous effects of the chemicals, however the potential threat of employee exposure or property damage is still an issue. The use of personal protective equipment by the employees can also control exposure to the chemicals, but it does not remove the hazard from the workplace.

Besides the potential for employee exposure, these solvents are limited in their effectiveness of removing materials from very small areas on the wafer. This may limit the efficiency of production as the industry moves towards higher definition on the wafer surface. The solvents also have to be cleaned from the surface of the wafer before continuing to the next step of fabrication. This requires the use of highly purified water, which can become expensive after many years of operation. Also, the solvents that are currently used have a very short lifecycle. This requires disposing and replacing the solvents many times per month.

Objective 2: Effectiveness and Toxicity of Supercritical CO_2 as a Photoresist Stripping Solvent

There has been a lot of attention given to supercritical carbon dioxide as a resist dryer to be used after the etching process (Namatsu, Yamazaki, Kurihara 2000; Goldfarb, et al. 2000). This was due to photoresist collapse caused by the surface tension created from drying the solvents used to clean the wafers. Namatsu, et al. developed a supercritical resist dryer, which effectively cleans the wafer with no collapse of the photoresist. However, it was shown that at higher pressures water contaminated the inside of the chamber. This resulted in a collapse of the photoresist due to surface tension.

The problem was solved by reducing the pressure inside the chamber to just above the critical pressure of carbon dioxide, which still allowed for the attractive qualities of carbon dioxide in its supercritical state. Although this process was shown to work effectively, it must be noted that water is not readily miscible in carbon dioxide therefore a water removal process prior to the drying stage was required. It was found that dipping the wafer into a bath of *n*-hexane would remove the water, resulting in additional chemicals other than carbon dioxide needed for the process (Goldfarb, et al. 2000).

The use of supercritical carbon dioxide as a photoresist stripper has also been researched and compared to ozonated water as replacements for the acidic solvents currently used in the process (Rubin, et al. 1998). Although ozonated water is an alternative already in practice, supercritical carbon dioxide was shown to reduce water use and increase speed of removal. Rubin, et al. observed that carbon dioxide alone did not affect the photoresist. This was solved by the introduction of propylene carbonate (4-methyl-1,3-dioxolan-2-one) as a co-solvent.

Propylene carbonate was first discovered as an alternative photoresist remover because of environmental concerns surrounding methylene chloride and methyl chloroform (Papathomas, Bhatt 1996). Papathtomas, et al. found that propylene carbonate was only slightly less effective than methylene chloride at removing photoresist from printed circuit boards when the temperature was over 60ºC. One of the main attractions to propylene carbonate is its low toxicity to humans and the environment as shown by an extensive toxicological review (Beyer, Bergfeld, Berndt, et al. 1987). However, it was found that propylene carbonate alone would not affect the photoresist (Rubin, et al 1998). In an earlier study involving a carbon dioxide and propylene carbonate solution under supercritical conditions, it was found that a mixture of the two compounds made materials much more soluble than in either carbon dioxide or propylene carbonate alone (Page, Raynie, Goates, et al. 1991).

Through their research, Rubin, et al developed a closed-loop system utilizing a mixture of 5% (v/v) propylene carbonate and supercritical carbon dioxide. This system was “effective in removing photoresists” and “fully compatible with commonly used metallization systems”. Los Alamos refers to this process as Supercritical Carbon Dioxide Resist Remover, or SCORR. This system has been shown to be effective at removing both negative and positive photoresist that is either hard baked or ion implanted to the wafer.

Supercritical carbon dioxide has been termed an environmentally benign alternative to current photoresist solvents. This is true in that its reactivity and toxicity to humans is low relative to the acidic solvents being used. However, other threats are introduced into the process such as highly compressed gas and the ability carbon dioxide has to displace oxygen. If a large leak or spill of carbon dioxide were to occur in an area, there is a chance of asphyxiation of nearby workers. Carbon dioxide is also a greenhouse gas that may contribute to the warming of the atmosphere. This may be a concern of facilities using this technology in the future however, in a closed-loop system the only carbon dioxide that enters the atmosphere is the gas left in the chamber when it is opened (McHugh and Krukonis 1986).

Objective 3: Cost Comparison

Cost is another driving force in the search for alternative solvents in the semiconductor industry. In 1992, it was estimated that a 55-gallon drum of organic solvent, from purchase to disposal, cost about $5,000 (Purtell, Rothman, Eldridge, et al. 1993). Since solvents have only a limited lifespan and need to be changed frequently, the cost can add up quick. Include with that the need to rinse the wafers after resist removal with deionized water, treatment of contaminated water after the rinse, and hazardous waste disposal fees and one can see the cost rising to great proportions. The operation cost of a deionized water system was estimated to be $130,000 per year in 1997 (Smith and Huse 1998).

When comparing this to a supercritical carbon dioxide system, Smith and Huse showed that the cash flow needed to sustain the system after seven years of operation would be less than half of a system utilizing deionized water. These cost reductions can be attributed to the availability and low cost of carbon dioxide and propylene carbonate, less frequent purchasing of solvents, and the elimination of deionized water needed for the process. Also, the amount of hazardous waste that is generated is much less reducing the cost of treating and/or disposing of wastes.

Summary

The information gathered on the current photoresist stripping solvents and supercritical carbon dioxide-based is presented in figure 4 to assist in the comparison of the types of solvents.

Figure 4

Comparison of Current Photoresist Solvents and Supercritical Carbon Dioxide

	Sulfuric Acid/Hydrogen Peroxide	**N-methylpyrrolidine**	**Supercritical Carbon Dioxide**
Effectiveness	Currently, the most effective at removing all types of photoresist. Limited by size of architecture on the wafer.	Very effective at removing photoresists with a positive polarity. Limited by size of architecture on the wafer.	Very effective based on lab results. Will not be hindered as architecture becomes smaller on the wafer due to no surface tension.
Cost	Low startup cost. High cost in water treatment, solvent replacement and disposal, and employee injury.	Low startup cost. High cost in water treatment, solvent replacement and solvent disposal.	High startup cost. Low cost of running sine there is little solvent replacement needed and water use is eliminated.
Toxicity	Very corrosive. Possible carcinogen. Fire hazard.	A sensitizer that may cause dermatitis and asthma.	Asphyxiant at high dosage.

After compiling this data, it can be seen that supercritical carbon dioxide-based solvents would be a viable alternative to current solvents for the photoresist stripping procedure based on risk and effectiveness. It seems that the limiting factor in the development of procedures utilizing supercritical carbon dioxide is the cost of engineering the tools needed to achieve fast and effective photoresist removal. Since this technology is not currently used in the industry, tooling is not yet developed to run the process on a large scale. It seems that the high startup costs are deterring companies from implementing a procedure that could save millions of dollars in the long run.

Chapter V

Summary, Conclusions, and Recommendations

Summary

Photoresist stripping solvents that are currently used in the semiconductor industry have the potential to cause human and property loss due to their inherent hazards and toxicity. Facilities that continue the use of conventional photoresist stripping solvents instead of an environmentally sound alternative such as supercritical carbon dioxide are potentially causing environmental, human, and product loss. This study used professional literature and chemical databases to compare and contrast traditional photoresist stripping solvents to a new supercritical carbon dioxide-based solvent for use in the photoresist removal process. To fulfill the purpose of this study, objectives were set and achieved.

Specific objectives of the study were to:

1) Examine the toxicity and effectiveness of photoresist removal solvents that are currently used in the semiconductor industry.
2) Determine the toxicity and effectiveness of supercritical carbon dioxide-based solvents that would be used for photoresist removal.
3) Compare startup and long-term costs of supercritical carbon dioxide-based and currently used photoresist stripping solvents.

It was found that many of the most commonly used solvents for photoresist stripping in the semiconductor industry are toxic to humans, have a high potential for causing property loss, and will become inefficient in the near future as the microchips become smaller and more defined. It was also found that supercritical carbon dioxide-based solvents would be an excellent alternative for companies that are willing to invest time and resources into the development of the new process.

Conclusion

The conclusions of this study are based on the information gathered from professional literature and chemical databases. They are drawn from comparisons made in chapter IV and are organized according to the corresponding goals of the study. The first objective was to examine the toxicity and effectiveness of photoresist stripping solvents currently in use in the semiconductor industry. Although current photoresist stripping solvents are effective at removing most photoresists, it was found in chapter 2 that they are a limiting factor in the reduction of microchip size due to their physical properties. There is also great potential for property and human loss due to the oxidizing and corrosive effects of the chemicals used for photoresist stripping. Although there are controls in place to reduce the hazards posed by the solvents, it would be most beneficial to remove the solvents from use entirely. This would reduce or eliminate much of the water use in the photoresist stripping step of the process and potentially lower the cost of wafer production considerably.

The second objective of this study was to determine the effectiveness and toxicity of supercritical carbon dioxide-based solvents in the removal of photoresists. The move to discover environmentally benign alternatives to chemicals and to reduce the size of the architecture on the wafers has driven researchers in the semiconductor to find new solvents for the photoresist stripping process. Current research on supercritical carbon dioxide-based solvents shows that there is high potential for the effective use of the solvent for the process. However, the technology has not been used extensively in the manufacturing setting. The threat that carbon dioxide and the co-solvent, propylene carbonate, have on human life and property damage is minimal when compared to the chemicals that are now used. If the semiconductor industry is truly looking to reduce the affects that their processes have on the environment and the health of their workers, it should be looking at supercritical carbon dioxide-based solvents for the future of photoresist removal. In addition, the implementation of this alternative photoresist stripper could completely eliminate the use of water and drastically reduce the chemical consumption within this step of the process.

The third objective was to compare the startup and long-term costs of the currently used system of photoresist stripping and the new system of using supercritical carbon dioxide-based solvents. It was found that because supercritical carbon dioxide technology is new, startup costs would be much higher than if a company were to use the older system. This higher startup cost is due to the engineering and implementation of tooling that has never been developed yet. In addition to those costs, making the new system of photoresist stripping work effectively and efficiently would take a lot of effort and time. However, in the end those initial costs would be beneficial to the company.

It is estimated that after seven years of being implemented into a process, supercritical carbon dioxide technology would be less than half the cost of the conventional system. This is due to the need to continually purchase and replace the solvents since they have a short time of effectiveness. Also, the cost of treating the water needed to rinse the wafers makes the current system much more costly. After the inconsistencies of the newly designed carbon dioxide process are eliminated, the system would work effectively and at a very low cost compared to the current system of photoresist removal.

Recommendations

Although the current photoresist stripping solvents have a long history of use in the semiconductor industry, they have proven to be high risk in terms of cost, property loss, and human loss. Other indirect costs of the current process are water treatment, both before and after use, and high volumes of solvent disposal. Based on this, it is recommended that the semiconductor industry further examine alternatives and eventually implement them into the process in order to eliminate or drastically reduce the risks and costs of the currently used solvents.

To become leaders in the use of much smaller, higher definition microchips, fabrication companies must find a way to remove contaminates from very small areas on the wafer in an efficient manner. Liquid solvents do not have this ability due to physical properties such as surface tension and capillary force. However, supercritical fluids do not possess these properties and are able to penetrate spaces that liquids cannot enter. One alternative that has been getting some research is supercritical carbon dioxide. Research on this solvent has been done within the laboratory setting, however it has not been through any trials within an industrial setting.

Cost may be one contributing factor to this, but it is recommended that companies in the semiconductor industry investigate this new solvent and process more in-depth. Areas that companies should look into are the type of tooling needed for the process and other co-solvents that may be more efficient at removing their specific types of photoresists.

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