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Photoresist removal using low molecular weight alcohol

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PHOTORESIST REMOVAL USING LOW MOLECULAR WEIGHT ALCOHOL

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By

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ABSTRACT

PHOTORESIST REMOVAL USING LOW MOLECULAR WEIGHT ALCOHOL

by Sheeja M. Krishnan

The most repeated step in the integrated circuit manufacturing is the photolithography step. Photoresist, an organic compound that absorbs light when radiated with ultraviolet or x-rays, undergoes chemical reaction in the exposed regions. The exposed regions after development can then be treated for further processing steps. Afterwards the photoresist, which remains on the surface, has to be stripped away. This report investigates the efficiency of isopropyl alcohol in stripping the photoresist after three different processing steps. The three different surfaces are post oxide surface which has the top layer as silicon oxide, post ion implanted surface which has the implanted surface and post metal surface which has the top layer as the metal. The use of isopropyl alcohol in an ultrasonic bath with the addition of ammonium fluoride and tetra methyl ammonium hydroxide is also investigated. The results show that for post oxide surfaces isopropyl alcohol in ultrasonic bath at 40 degree Celsius strips the photoresists at the rate of about 2600Å per minute and for post metal at about 9000Å per minute and for post ion implanted surface at about 764Å per minute.

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1. INTRODUCTION

1.1 INTEGRATED CIRCUIT MANUFACTURING

An IC (Integrated Circuit) is an essential component of electronic equipments in televisions, computers, and cars. ICs are built on a silicon wafer by integrating millions of transistors and other devices onto a single surface. An IC is sometimes referred to as a chip. These chips are smaller than a square centimeter but they contain millions of transistors. An integrated circuit is a three-dimensional structure that is made of different layers of material. An advanced IC can have up to 20 or more distinct layers [1].

Integrated circuits are built on silicon wafers because silicon is a natural semiconductor and it can conduct electricity. Common sand is purified to 99.9999% pure silicon for IC manufacturing. The other main reason that silicon is used for IC manufacturing is that the silicon dioxide, a passivation layer, which naturally forms onto the silicon, is very stable. This passive layer helps in covering the area that should be protected from doping or any pattern transfer. Semiconductor manufacturers produce many kinds of integrated circuits: Dynamic Random Access Memories, microprocessors, and Application Specific Integrated Circuits (ASICs) [1]. The precise process followed to make an IC varies according to purpose and the manufacturing company. Once wafer processing is complete, each chip (or die) on the wafer is tested for electrical performance, cut apart, and put into individual protective packages. Packaged chips are tested again to make sure they function properly before being shipped to distributors or placed in electronic products.

2. BACKGROUND

In IC manufacturing, copies of a microelectronic circuit are simultaneously fabricated on a thin semiconducting substrate, silicon, called a wafer. Silicon being a natural semiconductor, inexpensive, and abundant in nature, is used mainly in IC fabrication. Silicon wafers are typically 3 to 8 inches in diameter and 0.002 to 0.004 inch thick [1]. The manufacturing process is comprised of four major modules: wafer fabrication, wafer probe and sort, chip assembly, final chip test, and burn-in [2].

2.1 WAFER FABRICATION

Silicon wafers are cut from the large cylindrically shaped crystal silicon, which is grown by Czochralski method [1]. These wafers are used for the IC fabrication. The major steps involved in wafer fabrication are film deposition, photolithography, etching, and doping. The steps are repeatedly used to build a device onto a single surface. The following Figure 1 shows the wafer fabrication steps [1].

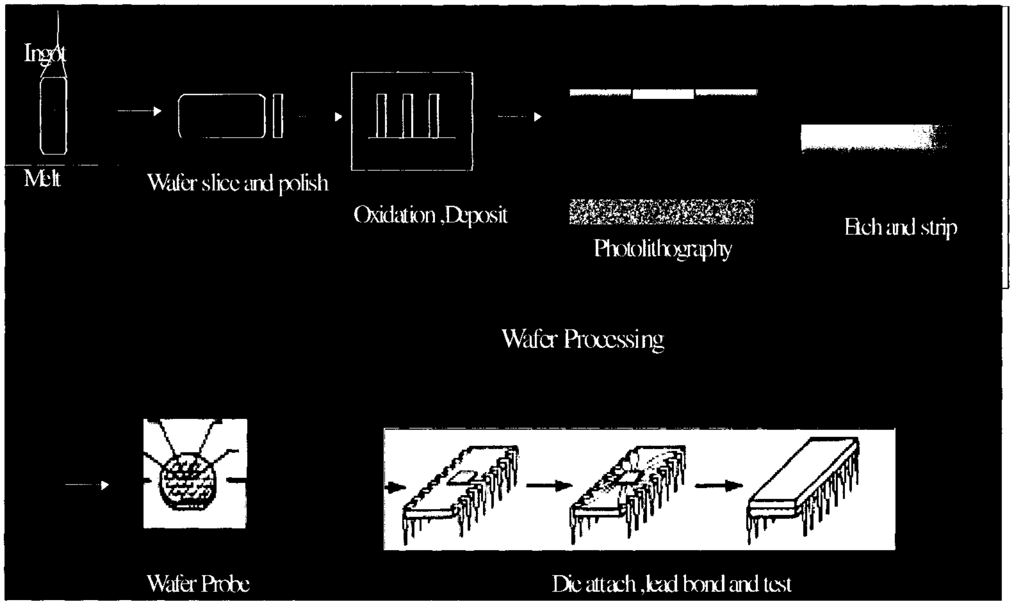


Figure 1 Fabrication Process [1]

2.1.1 FILM DEPOSITION

During wafer fabrication, thin films have to be deposited onto the wafer surface in order to make different electronic devices and also to connect the devices. Various layers are deposited onto the wafer surface, such as: silicon dioxide, aluminum, poly silicon, and silicon nitride. The main ways of depositing thin films are thermal oxidation, Chemical Vapor Deposition (CVD), and Physical Vapor Deposition (PVD). Silicon dioxide films are grown using the thermal oxidation in a furnace at elevated temperatures of 1000 degree Celsius (^{o} C). The oxide layer can be used as a mask during dopant diffusion, as a junction passivator, as an insulating field oxide, or as a gate dielectric in MOS (Metal Oxide Semiconductor) transistors [1].

Common PVD techniques are evaporation and sputtering. Both techniques can be used to deposit the metal. Evaporation, the method usually used for depositing metal such as aluminum, is done by heating the material to be evaporated in a vacuum by bombarding it with high-energy electrons and placing the wafers to be coated above the material [1]. In a method similar to evaporation, called sputtering, the wafers are placed below the material to be deposited. The material is then bombarded with ions that scatter the atoms, which deposit onto the wafers.

In chemical vapor deposition, the deposited material is a product of a chemical reaction on the surface of the wafer substrate. A key advantage of the CVD process lies in the fact that the reactants used are gases, thereby taking advantage of the many characteristics such as versatility and high purity. For example, polycrystalline silicon can be grown on the surface of a wafer by decomposing silane gas (SiH_4) in the presence of the wafer [1].

2.1.2 PHOTOLITHOGRAPHY

The photolithographic process was inspired by the physical lithographic engraving process used in printing businesses to transfer desired patterns onto surfaces [1]. In IC manufacturing, optical photolithography, electron-beam or X-ray lithography, is used to define patterns on a wafer. Once a layer is patterned, it can be etched into the underlying surface to create elements of a device. The lithographic process requires that the surface of a wafer to be initially covered with a thin film of photoresist. The photoresist is then exposed to an energy source through a photomask. It changes the solubility of photoresist exposed in a developing solution. This photoresist may remain there for some more processing steps like etching or ion implantation and then has to be removed.

2.1.2.1 *Photomasks*

A photomask is typically a glass plate that has a pattern of clear and opaque areas, repeated over its surface, which defines a single layer of a circuit. Between 15 and 20 masks are commonly used today to describe an entire circuit [1]. Photomasks are typically generated from circuit designs laid out with the aid of Computer Aided Design (CAD) tools. The transfer of the circuit design to the photomask is typically done by scanning a computer-controlled optical or electron beam across a photographic plate. The pattern, called a reticle, is then checked for accuracy. A reduced version of the reticle pattern is then reproduced and projected side by side on a final mask.

2.1.3 ETCHING

Etching refers to removal of the unwanted films. Etching can be physical, chemical, or a combination of both. Physical etching is done by bombarding the wafer with high-energy ions to physically remove the thin film. Chemical etching is done in either a liquid (wet) or gas (dry, or plasma) environment. In wet chemical etching, the wafer is placed in a highly selective but isotropic liquid chemical that dissolves an exposed surface material such as oxide. In the case of dry chemical etching, highly sensitive chemicals dissolve the unwanted film. Dry chemical etching combines the advantages of physical and wet chemical etching. The dry etching process makes use of different mechanisms such as physical sputtering, plasma etching, reactive ion etching, or ion-enhanced etching. Etching techniques are characterized by their selectivity and degree of anisotropy. In physical sputtering, the strongly directional nature of the incident energetic ions allows substrate material to be removed. The plasma etching process relies on the chemical nature of the ions. Reactive ion etching makes use of both techniques, thus overcoming the shortcomings of physical sputtering and chemical etching [1].

Dry etching techniques using the plasma systems have been used to strip the photoresist after the pattern transfer. The fluorine containing oxygen plasmas work well in the case of photoresist. Since the resist is organic, the fluorine atoms join with hydrogen to form HF. The hard masks such as silicon nitride are also stripped using dry techniques. Silicon nitride is a mask used for selective oxidation.

2. 2 WAFER PROBE AND SORT

In the second stage of wafer manufacturing, each die on a fabricated wafer is tested for functionality. Dice that fail are marked and the wafer is then sectioned into individual die by scribing lines between the dice and breaking the wafer along these lines. The defective dice are discarded, and the remaining dice are usually sent from the fabrication facility to a die bank inventory [3].

2.3 CHIP ASSEMBLY

In the third stage of wafer manufacturing, dice that have been fabricated and tested are assembled for product release. An inventory of tested die is usually maintained at the assembly plant to smooth out variations in productivity at the wafer fabrication stage. Individual integrated circuit die can be mounted in a wide variety of packages. A chip is generally assembled by placing it on a (commonly lead) frame, attaching electrical leads to it at contact points (for connections to the outside world), and sealing the assembly in a protective housing [1].

2.4 CHIP TEST AND BURN-IN

In the final stage, packaged chips are subjected to an extensive series of electrical tests to ensure that the circuit functions correctly and will continue to do so reliably. After final test, chips are sorted into different bins based on attributes like device speed and power consumption [3].

2.5 PHOTOLITHOGRAPHIC PROCESS

The investigation of an improved photoresist removal method is connected with the photolithographic process and the properties of photoresists. A detailed discussion of photoresist and lithographic process becomes necessary. Microcircuit fabrication requires precisely controlled quantities of impurities to be introduced into tiny regions of the silicon substrate. Subsequently these regions must be interconnected to create components and circuits. The main step is the patterning of the films without disturbing the underlying layers. The patterns that define those regions are created by lithographic processes. Photolithography is the process of transferring geometric shapes of a mask to the surface of a silicon wafer. Approximately one third of the total cost of the semiconductor manufacturing can be attributed to the micro lithographic processing [1].

2.5.1 PHOTORESISTS

Photoresist is an organic polymer, which changes its solubility in a developer solution when exposed to ultraviolet light. It contains a light-sensitive substance whose properties allow image transfer onto a silicon wafer. It is used in many applications within various industries such as semiconductor, biomedical engineering, holographic, electronics, and nanofabrication.

Conventional optical photoresists contain three major components: a matrix material (called resin), a photoactive component, and a solvent. The matrix is inert to the incoming radiation and it provides the resist film with adhesion and etch resistance properties. The matrix serves as the binder and establishes the mechanical properties of the film. The photoactive component is the active ingredient in the photoresist. The solvent keeps the photoresist in a liquid form until it is applied to the wafer. The photoactive component (PAC) undergoes a chemical reaction to the radiation.

There are two types of photoresists: positive and negative. After exposing to some kind of radiation such as UV or X-ray, the areas in the photoresist exposed to the light are made either soluble or insoluble in a specific solvent. The solvent is commonly called a developer. If the irradiated regions are soluble, a positive image of the mask is produced in the resist. Such material is called positive resist. If the non-irradiated regions are dissolved by the developer, a negative image is produced. The resist in this case is called a negative resist. The difference between the positive and negative photoresists is shown in Figure 2. Although both negative and positive photoresists are used in the IC industry, positive photoresists are widely used because of their higher resolution capabilities. In case of the positive resists, PAC acts as an inhibitor in unexposed regions. It slows down the rate at which the resist dissolves in the developer solution. The positive resists used commonly consists of diazonaphthoquinone PAC and novolac resin and are thus called DNQ/novolac resists [1].

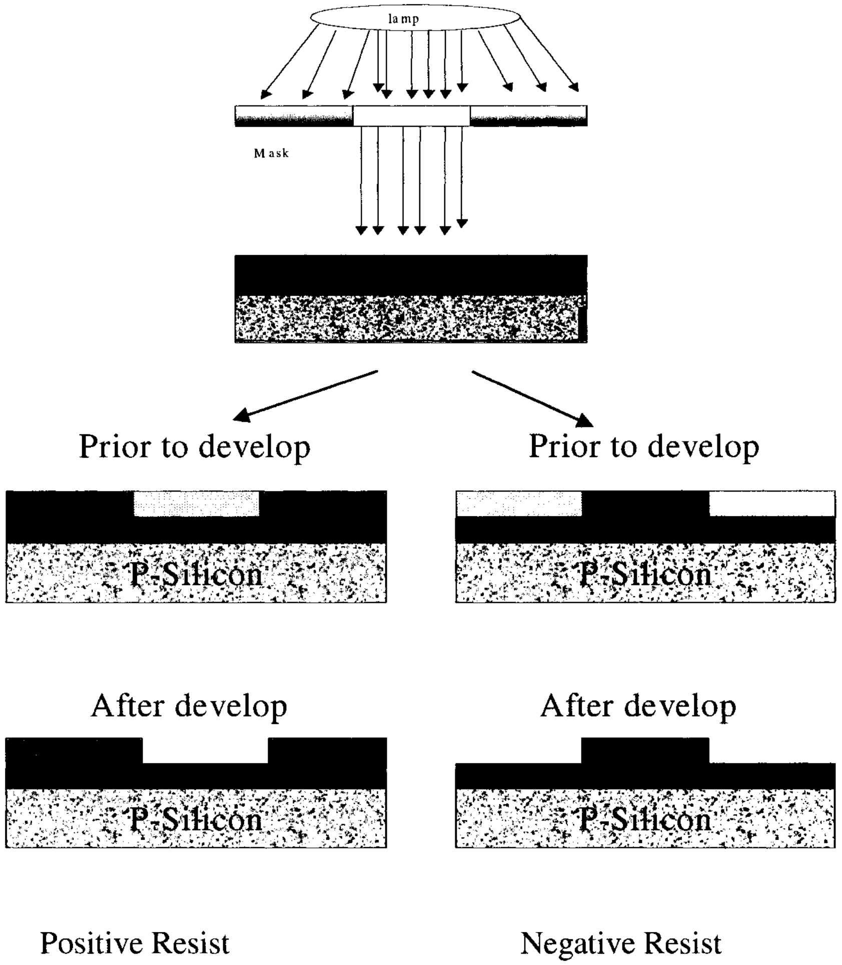


Figure 2 Positive and Negative Photoresists After Exposure and Development

2.5.2 RESIST PROCESSING

Initially, the photoresist is deposited onto a clean wafer by spin coating. The deposited resist film must be uniform, adherent, and contaminant free. An excess amount of photoresist is placed on the substrate. The substrate is then rotated at high speed in order to spread the fluid by centrifugal force. Rotation is continued for some time, with fluid being spun off the edges of the substrate, until the desired film thickness is achieved. The film thickness after spin coating depends only on the spinning parameters such as: rotational speed, ambient temperature, spin time, and spin ramp recipe. After the resist is deposited, the wafers are subjected to a low temperature-baking step (soft bake). The soft baking helps in removing the solvent from the wafer and improves the adhesion of the resist by relieving the stresses that arise from shear forces encountered during the spinning process [1]. The time and temperature of the soft bake depend on the particular photoresist.

Once the wafer is spin coated and soft baked it is ready for the exposure step. A photomask is placed on top of the wafer. Energy of a specific wavelength is directed through the openings in the photomask. The pattern of the photomask is transferred to the wafer. The degree of exposure is adjusted by the energy impinging the photoresist. A photochemical reaction occurs within the resist during the exposure. Following exposure, the resist film undergoes a development step. If the process is making use of positive photoresist, the developer should not attack the unexposed photoresist. There are three different methods of development. They are immersion, spray, and puddle single wafer developing [1]. In the case of positive photoresists, the developer solutions are alkaline while for negative photoresists the developer solutions are organic solvents. A common developer for positive resists is tetramethyl ammonium hydroxide (TMAH). In the case of positive photoresists, a carboxylic acid photoproduct is neutralized by the alkaline developing solution. Figure 3 shows a common reaction for a positive photoresist [4].

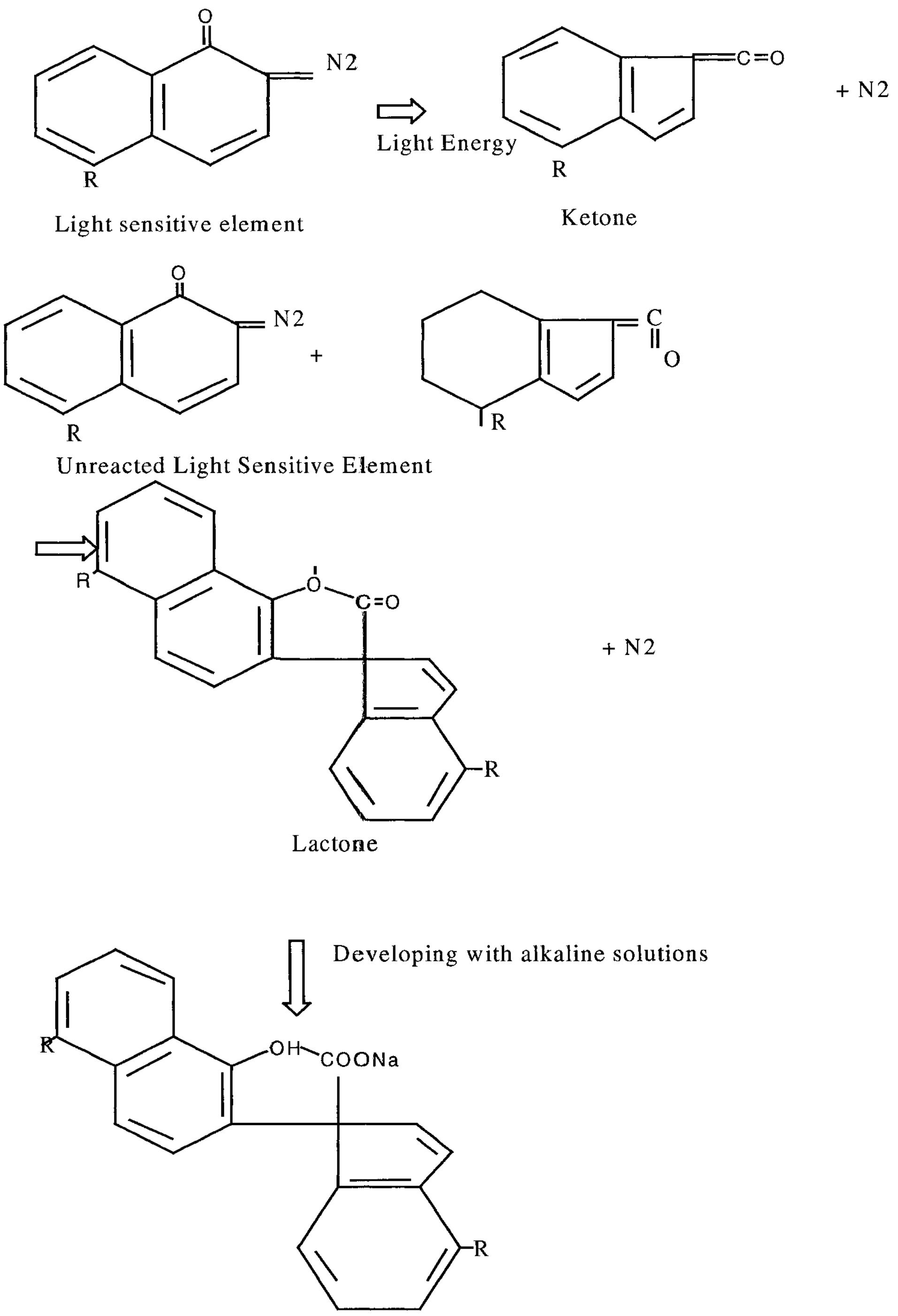


Figure 3 General Reactions Occurring During Resist Exposure and Development [4]

After development, the wafer undergoes a high temperature bake. The post exposure bake (PEB) improves the adhesion and etch resistance of the resist film. The temperature and time of the PEB process depends on the particular photoresist and the subsequent etch or implant processing that may occur. After the pattern transfer and post exposure bake, the exposed regions (in the case of positive photoresists) are subjected to a variety of subtractive (e.g., etching) or additive (e.g., ion implantation) processes that transfer the pattern to the substrate surface. The photoresist remaining can also be a part of the subsequent processes. Figure 4 shows the flow chart of typical resist process [1].

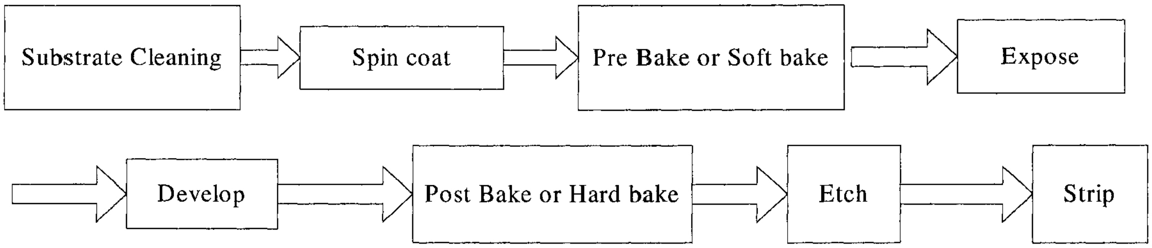


Figure 4 Typical Resist Process [1]

Removal of photoresist remaining after the pattern transfer is termed as photoresist stripping and there have been various technologies to be used in the removal from wet stripping to plasma and laser stripping.

2.6 METHODS FOR PHOTORESIST STRIPPPING

Before additional layers can be deposited on the wafer, the remaining photoresist must be removed from the wafer. The processes, like etching and ion implantation, change the property of the photoresist on the wafer. The changes that the etching process makes are different according to whether it is dry etching involving plasma or wet chemical etching. Ion implantation is done with high-energized plasma. So this high-energy bombardment makes the photoresist harder and gives it more adhesion to the wafer surface thus making it difficult to strip [5]. There are some other situations also where photoresist has to be removed such as simple removal of misaligned patterns. The common procedures used in the IC industry for the photoresist removal are dry or plasma stripping and liquid stripping [1]. Dry systems mainly consist of downstream RF and microwave plasmas. The method of stripping the resist using plasma is called ashing. Using a plasma source, a monatomic reactive species is generated. The commonly used reactive species are oxygen and fluorine. The reactive species combines with the photoresist to form an ash, which is removed with a vacuum pump. Typically, it creates monatomic oxygen plasma by exposing oxygen gas (O_2) to ionizing radiation, and this monatomic oxygen becomes the high-energized species. Oxygen is used as the reactive species since it doesn't attack the underlying layers such as silicon, silicon dioxide, or aluminum. These dry stripping methods vary according to the density of plasma, its relative position with the chamber, and the plasma source.

There are two main types of wet strippers: organic solvents and oxidizing solutions. Wet strippers remove the photoresist by breaking the structure of the photoresist. Early organic strippers were phenol based where now phenol free strippers are widely used [6]. Organic strippers are used even after dry stripping to complete the removal process efficiently. Oxidizing type strippers are solutions of sulfuric acid and an oxidant. The most commonly used oxidant is hydrogen peroxide. These strippers oxidize the carbon in the photoresist film into carbon dioxide, which exits as gas rapidly.

3. LITERATURE REVIEW

3.1 A HISTORY OF PHOTORESIST STRIPPING

The earliest trend in the photoresist stripping was for the wet strippers that use either the organic or oxidizing strippers [6]. The problem with the wet strippers was the contamination from the wet chemicals to the wafer surface. As the technology improved, the improvements in plasma systems made dry stripping viable. The initial dry plasma strippers were configured for wafers as a batch in a "barrel", which used 13.56MHz frequency as the excitation plasma frequency. This barrel stripper had problems with excessive wafer handling and poor uniformity. Modifications in the design and the introduction of single wafer downstream processing led to more uniformity and damage free photoresist removal. By 1990s, the 13.56MHz plasma excitation led to damage due to the relatively high-energy ions. It has been reported that by using high pressures and inductively coupled plasma, the damage can be further reduced [6].

As the technology improved the plasma systems also changed. The low energy neutrals at microwave downstream plasma has been used which resulted in less damage. The main problem for the design of these types of reactors and systems is the temperature and the pressure. Microwave technology generates high active species and therefore the design highly depends on the surface temperatures. So it has been reported that the high throughput is nevertheless achievable [6]. The industry is making use of both wet and dry techniques and a combination of the two for effective stripping. The research has made improvements to the stripping methods, which range from the ozonated systems to solventless carbon dioxide systems. The choice over wet or dry depends on several factors such as the specific process requirements, device sensitivity, and throughput.

3.2 COMPARISON OF WET AND DRY STRIPPING SYSTEMS

Both wet stripping and dry stripping have advantages and disadvantages. It is reported that the most effective way to strip the photoresist is the use of both stripping techniques [7]. The reports show that when the wet stripping follows dry stripping, the surface carbon levels can be reduced [7]. Wet stripping is good for situations where the devices are easily damaged.

In a wet process, there is no problem of equipment calibration. As in the case of dry systems there is no need for controlling the gas flow. In the wet stripping, wet chemicals oxidizes the carbon to form CO_2 and decomposes itself with one of the by products being water. However, this makes it difficult to maintain the composition of wet baths. The stripping solutions are often toxic and corrosive. The oxidizing type strippers can't be used for resist stripping after metalization since the stripper will attack the metal. The contamination that occurs in the stripping process accumulates in the bath itself, which drastically affects the yield. The toxic and corrosive chemicals used, make it difficult for handling and disposing which makes the process expensive. There are certain rules and regulations to be followed when disposing the corrosive or toxic chemicals. Other problems are due to mass transport and surface tension associated with solutions. For deep sub micron technologies, solutions can't circulate and tend to accumulate in the patterned structure.

The advantages of using the dry system are its high selectivity, high pattern transfer, and high etching rate. There is no waste handling problems like the wet stripping techniques. It is helpful when removing the hardened resists after implantation and UV exposure, where wet chemical treatment fails. The dry stripping method is also useful when stripping photoresist after the metalization.

Plasma ashing is associated with several types of damages. These damages are due to UV radiation, currents, charges, and elevated temperatures [8]. Resist removal is often incomplete. Charge damage occurs when the charged species from the plasma accumulate on the wafer surface. Again, when using the dry system the metallic impurities on the photoresist film remain on the wafer surface even after stripping and migrate to the silicon oxide layer. In barrel ashers, though the wafer is placed within a shield, the mobile metals cause contamination by the charged bombardment.

After the plasma resist stripping, a liquid processing step is required using acids to remove the implant residue. This post plasma treatment may require several steps after resist stripping. For the complete removal, it has to be treated with de-ionized (DI) water and then dried. These approaches raise the issues of using DI water and the chemical waste disposal. It has been reported that approximately 2000 gallons of DI water are used to process a single 8 in. wafer [9]. Plasma ashing may result in resist popping and incomplete removal [9]. This is highly expensive and can incorporate the contaminant such as Fe, Cu, and Na, which cause severe damage to the circuits.

Plasma systems have disadvantages of the tendency for isotropic etching, poor pattern transfer, relatively expensive equipment, and small sample throughput. In the case of Ar- O_2 plasma afterglow systems, high flow rate of extra pure oxygen is needed to avoid loading effects. For RF systems there is a problem of increased oxide charges and increased trap densities [10]. Again, UV radiation hits the wafer surface, and the charged particle bombardment causes the significant contamination by mobile metals. For the microwave plasma also this can happen though the wafer is located well upstream from the plasma [11].

3.3 DRY STRIPPING

The two basic mechanisms in plasma etching are chemical and physical. In a physical mechanism the strip is due to the sputter effect of the gaseous charged species. The chemical mechanism is performed by the reactive species generated in the gas phase that diffuse into the surface where they adsorbed [12]. A chemical reaction occurs between the active species and the photoresist.

Another method of stripping is to employ the use of low energy neutrals to reduce the damage. It is reported that the neutral stream processing can be well suited to photoresist removal [13]. Again this requires a plasma source. Most of the research done in the dry stripping systems is for oxygen and argon afterglow microwave plasma

[10,11,14]. Spencer et al [14] have suggested by using a plasma stripper in the afterglow of a microwave discharge of O_2, the productivity is increased without any wafer damage. This is a single wafer chamber. In this the oxygen, the atom source, doesn't make any energetic bombardment with the wafer. Separation of the discharge processes from the wafer processes characterizes an afterglow. Microwave excitation provides efficient excitation to the bulk gas for process requiring high flux of gaseous atoms.

Metselaar [11] has investigated introducing argon in the oxygen afterglow plasmas. Argon helps to reduce the loading effect and plasma stabilization. Oxygen is particularly sensitive to the loading effect. The loading effect is caused by the reduction in the rate of process due to the consumption of the species reacting. They also suggested that the reduction in the pressure would help increase the etching rate. This is usually done at high temperatures like 200°C and needs extra high pure oxygen. The removal rate is high as 3μm/min.

It has been shown that by using an inductively coupled plasma (ICP) source the production rates of the reactive species could be increased so as to meet the requirements like the high rate of removal [8]. The ICP source has been developed to reduce the amount of the ionization while increasing the dissociation of oxygen molecules for high photoresist removal rates. Their result shows that the gate oxide integrity and contamination control were either equal or better than the microwave plasma systems. Advantages of this system are low power, low damage, high anisotropy, and high selectivity.

Boris Livshits et al have suggested a method for photoresist removal using a laser [15]. The process is dry and plasmaless. This process requires laser ablation with reactive chemistry. The authors reported that it provides high stripping rate at low temperatures. This removal eliminates the alkaline and heavy metal contamination. No carbon content was detected after the removal. The absence of carbon content indicates the complete removal of the photoresist. A wet cleaning is not required after the laser stripping method as in the case of dry systems.

3.4 WET STRIPPING

Wet stripping technology makes use of either oxidizing solutions or organic solvents. They alter the structure of the resist layer and solvating residues. The traditional wet photoresist cleaning makes use of sulfuric acid and hydrogen peroxide (SPM) or sulfuric acid with ozone. A vast amount of DI water is required after the removal to clean off the residues. In 1978, research showed that the photoresist could be removed by using aldehyde or a ketone [16]. It consists of a solution that includes an activated compound of ammonium hydroxides or carbonates and an aldehyde or ketone. A stripping solution comprising about 80% H_2SO_4 and 0.5% HClO and 4%CrO was also found to be a good stripping solution [17]. The solutions, which contain 30% weight aryl or alkyl sulfonic acid, have found to be efficient in stripping the photoresist [18]. The reports show that the photoresist can be removed when a hot solution of tetramethyl ammonium hydroxide is used with a surfactant and then dipped in the trichloroethane [19]. This stripping has to be done around 80°C.

Strippers containing N-methyl-pyrrolidone (NMP) replaced the glycol ether based strippers because of their biodegradable nature and high solubility in water. These solvents are often used after the dry oxygen plasma to complete the dry removal [15].

Researchers have made use of ozonated DI water for photoresist removal [20,21]. Steve Nelson has reported a new technique, which employs the ozonated water, a strong oxidizer, as the active liquid. It has been reported that a spray tool system, which issues ozonated deionized water, can remove the resist effectively. In this technique, ozone is the active species and OH^- radicals from water is the initiator for the reactions. It has been reported that the rate of stripping is 1190Å per minute. The research also has been done on the stripping efficiency of the ozonated water for the ion implanted surfaces. Only the wafers that were implanted with less doping have undergone the stripping. But this stripping technique didn't strip the highly implanted resist. Ozonated chemistry couldn't attack the resist on the post metal wafers, but the improved technique, which involves NH_4HCO_3 in ozonated water, stripped the resist at a rate of 1010 Å per minute.

The addition of nucleophilic catalysts to the solvent systems such as NMP has been also a topic for research. IBM Technical Bulletin discloses that nucleophilic agents like dimehtyl amino pyridine, when added to the NMP system, showed greater stripping efficiency [22]. This system even can remove the resist that is hard baked over 200^{o} C, where the conventional methods cannot.

The stripping technologies have improved even further. The solventless CO_2 system has been able to strip the photoresist off effectively [23]. The lithographic process can be integrated to use the CO_2 technology. New CO_2 processed fluoropolymer photoresist systems allow CO_2 to be a casting solvent, developer, and stripper.

Photoresist stripping can be also be done using the low molecular weight alcohols. The research has been done mainly on isopropyl alcohol (IPA) systems. The other alcohols like acetone have been included in the research. Acetone, ethyl alcohol, and methyl alcohol are toxic and bear a risk of ignition even when they are diluted to 10% with deionized water [24].

3.4.1 LITERATURE ON IPA STRIPPING SYSTEMS

Ojima and coauthors have reported that photoresist removal could be done using isopropyl alcohol (IPA) [24]. They also tested the rate of removal with addition of alkali halides and ammonium fluoride. They have employed the help of megasonic excitation to strip the photoresist. They found it optimum to use IPA with potassium fluoride (KF). IPA and KF don't react with each other and hence they can be reused after filtration. The mechanism removing photoresist was found to be physically stripping off rather than dissolving it. The stripping mechanism is considered to have the following three steps: i) due to high wettability of IPA/KF on the surface, IPA penetrates deeply into the photoresist, ii) photoresist is swollen by the IPA and silyl groups are removed by F- and iii) photoresist is physically stripped off by means of megasonic excitation.

Kamal and Hess [5] also studied the IPA stripping system. The investigation led them to use the IPA rather than any other low molecular weight alcohol since IPA leaves less residual carbon on the wafer surface and its similar to that of standard RCA cleaning process. They found that high pressures are needed to remove the photoresist after ion implantation. The advantages of using low molecular weight alcohols are the reduction in the use of deionized water, reduction in cost due to the absence of plasma, and no waste disposal due to volatile alcohols. Kamal and Hess investigated the removal rates of photoresist on ion-implanted wafers. They found out that it is more difficult for the IPA to attack the patterned edges than non-patterned edges. They also found that the increase in temperature increases the rate of removal. Through AFM images they concluded that IPA does not roughen the silicon dioxide or aluminum surfaces.

Kamal and Hess [9] reported that by the addition of an alkaline solution such as ammonium hydroxide to the IPA, the rate of removal of photoresist could be enhanced. They concluded that by adding ammonium hydroxide solution in water into IPA solution, photoresist removal rate is enhanced due to the release of the OH- ions present in the system due to water. The higher temperature helps the dissociation of the ammonium hydroxide additive. All these researches on the IPA stripping system have been conducted on the post implant surface.

4. REASEARCH HYPOTHESIS AND OBJECTIVE

4.1 HYPOTHESIS

The new stripping process should efficiently remove the photoresist after various processing steps such as: ion implantation and post metal and oxide etch. This process should be an improvement over the current stripping processes utilized in the IC lab at San Jose State University. The current stripping technique varies according to the preceding process steps. Table 1 shows the current stripping techniques after different process steps.

Process	Stripping Method
After Oxide Etch	H_2SO_4/H_2O_2 Etch
After Implantation	Plasma Ashing
After Metalization	Microposit Stripper

Table 1 Stripping Methods After Different Process Steps.

The improved process should be able to remove the resist from all three different surfaces. Previous research has shown that IPA can successfully remove resist [5]. Utilizing ultrasonic energy in conjunction with IPA may improve resist removal. The addition of TMAH or ammonium fluoride into the IPA will make the stripping faster.

The increase in the temperature for the stripping solution also will make the resist stripping faster.

4.2 JUSTIFICATION

When treating the wafers with IPA or low molecular weight alcohols, there will be no need for DI water rinsing or drying, since they are usually volatile, which in turn reduces cost and space. IPA is one of the most commonly used solvents in drying. IPA can replace water and has a low boiling point compared to water. TMAH developer solutions are most often used in the semiconductor industry and they are inexpensive [9]. TMAH is used for photoresist development after the exposure step. So the addition of TMAH into IPA in the stripping solution will enhance the stripping rate. The advantages of using this technique are: 1) no chemical vapor generation, 2) no chemical waste treatment, and 3) no residual metallic impurity. It is reported that IPA is already used in for drying in the semiconductor industry for the maximum efficiency and better financial control [25,26].

The current researchers have not discussed the issue of photoresist removal after metal etch. Though Ojima [24] deals with the effect of mega sonic excitation it didn't deal with ultrasonic excitation. Ojima and coworkers have already proved the efficiency of IPA with ammonium fluoride with megasonic excitation in photoresist stripping. There is no literature that reports how IPA stripping will affect the underlying layers such as oxide or metal. It has been reported that the addition of potassium fluoride into IPA accelerates the rate of removal [24]. The incorporation of metallic salts might not be suitable for the stripping due to the possibility of metallic contamination on the surfaces. There is no data which shows that the potassium (an alkali metal) is not diffusing into the underlying thin films. Since TMAH is already being used as a developer solution at 0.25 to 1% by weight in the semiconductor industry, it might be better to use a low concentration in IPA and to investigate the combined efficiency of IPA and TMAH with ultrasonic excitation. The TMAH at about 2% in IPA doesn't attack the oxide layer or metal layer underneath.

IPA and TMAH are used in the IC industry. TMAH at 2.5wt% is able to etch the silicon. The reports show that during etching when IPA is added to the TMAH, the undercutting can be reduced [27]. TMAH is already being used in the IC industry and is compatible with the CMOS technology [27].

4.3 OBJECTIVE

The objective of the thesis was to investigate how successful a low molecular weight organic solvent such as IPA would be in stripping PR. The effectiveness of using IPA as a photoresist stripper was investigated as a function of temperature, ultrasonic energy, and ionic additives. Initial screening experiments were used to identify the effect of temperature and ultrasonic energy. The effect of additives was studied at the best conditions of temperature and use of ultrasonic energy. The investigation for the surface from which the resist can be removed easily, was also done. Using the best conditions, the rates of removal for various surfaces also were determined.

5. EXPERIMENTAL APPROACH

5.1 SURFACE DEFINITION AND PREPARATION

The experiments were done in San Jose State University's Integrated Circuits laboratory. Table 2 lists the surfaces prepared for the experiments. The samples prepared were soft baked, post exposure baked (PEB), post oxide etched, post implanted and post metal etched. The experiments were divided into three phases: screening, additives effect, and optimization. In the screening phase the surfaces used were soft baked and PEB. The additive effect phase used only the soft baked surface. In the optimization phase, post metal etched, post ion implanted, and post oxide etched samples were used.

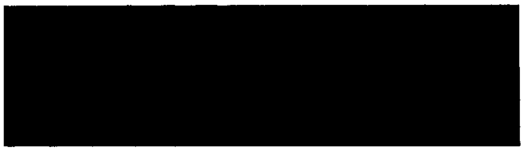
Surface Prepared	The different layers
Soft Baked	
Post Exposure Baked	
Post Oxide	
Post Implant	
Post Metal	

Table 2 Structure of Different Samples Used in the Experiments

5.1.1 GENERAL WAFER PREPARATION

The cleaning and PR application for all wafer surfaces were identical. The exposure and development times for the post oxide, post implanted, and post metal surfaces were identical. The wafers were cleaned using the standard industry process [1]. The photoresist was spun on the wafer surface according to the parameters listed in Table 3.

Spin Ramp Up Speed	Spin Ramp Up Time	Spin Speed	Spin Time
1500 RPM	5 seconds	20 seconds	20 seconds

Table 3 Process Conditions for the PR Spin Coating

OCG 934 photoresist was used in all experiments. The vendor recommended process conditions for the softbake and PEB are listed in Table 4.

Process	Temperature (^{o} C)	Time (minutes)
Pre Exposure Bake (Soft Bake)	110	15
Post Exposure Bake (Hard Bake)	130	30

Table 4 Process Conditions for the Soft Bake and Post Exposure Bake for OCG

Exposure was done using the Quintel Mask Alignment System Q4000 series™ aligner system in the lab. A g-line source of 107mJ/cm^2 was used to expose the wafers. Development of the exposed photoresist was done using a bath of room temperature the OCG 3:2™ developer.

5.1.2 SPECIFIC WAFER PREPARATION

The post oxide, post implant, and post-metal surfaces were prepared according to the standard process conditions used in San Jose State IC lab. For the soft baked samples, after cleaning the silicon wafers, a layer of photoresist was spun on the wafers. The wafers were soft baked according to the vendor recommended procedure. The following Figure 5 gives the flow chart of the surface preparation. For the PEB samples the procedure was same as soft baked samples except after the soft baking there was an additional high temperature treatment, which was the hard bake. The soft baked and the post exposure baked samples didn't undergo any exposure step to the light source. They only have undergone the photoresist application and the high temperature treatments. The following figures Figure 5 and Figure 6 show the flow chart of soft baked and post exposure baked sample preparation.

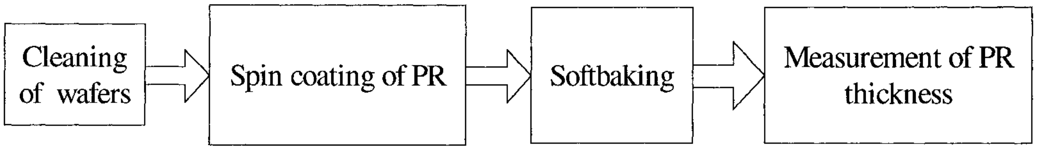


Figure 5 Flow Chart for the Soft Bake Sample Preparation

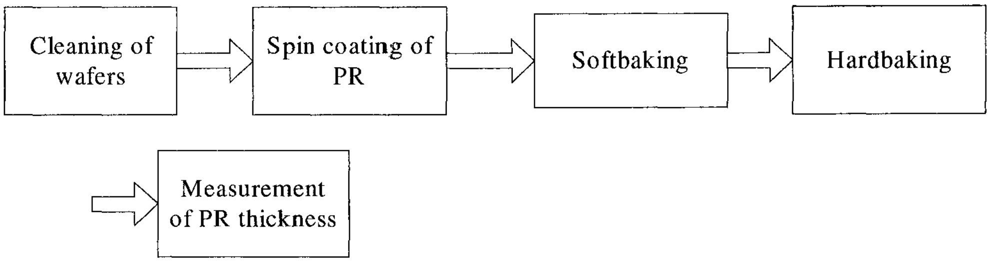


Figure 6 Flow Chart for the Post Exposure Bake Sample Preparation

Post oxide samples had an oxide layer that was approximately 800 Å thick. These were exposed and patterned. After the development, some wafers were then etched using dry etch for oxide (plasma etch). For the remaining wafers the oxide was etched using the wet etch process (in Hydrofluoric acid). Figure 7 shows the flow chart of the post oxide sample preparation.

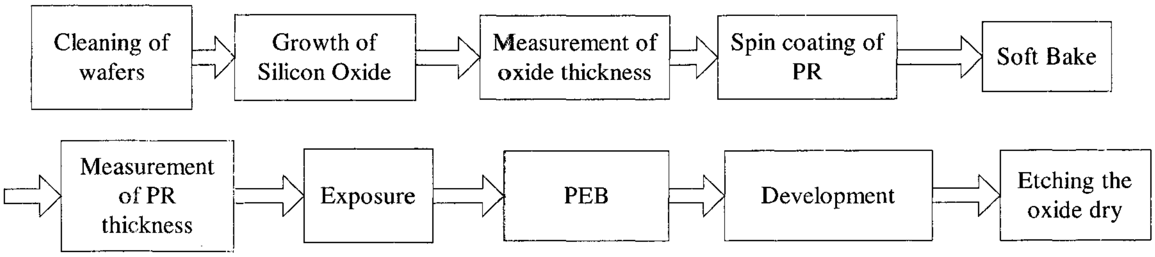


Figure 7 Flow Chart of the Post Oxide Sample Preparation

The post metal sample was prepared by evaporating 1000 Å of aluminum on an oxidized wafer. Then the metal layer was patterned using photolithography and the opened metal was etched using the metal etching solution, which is a mixture of phosphoric acid, acetic acid, nitric acid, and water.

The implanted wafers were prepared by implanting with high-energy Arsenic atoms into a patterned oxidized wafer of oxide thickness 800Å. The dose of the implantation was 10^{15} atoms with 50 KeV. Figures 8 and 9 give the flow chart for the preparation of post metal and post implanted wafers. After all these surfaces were done PR was removed using the IPA using different additives and at different process conditions.

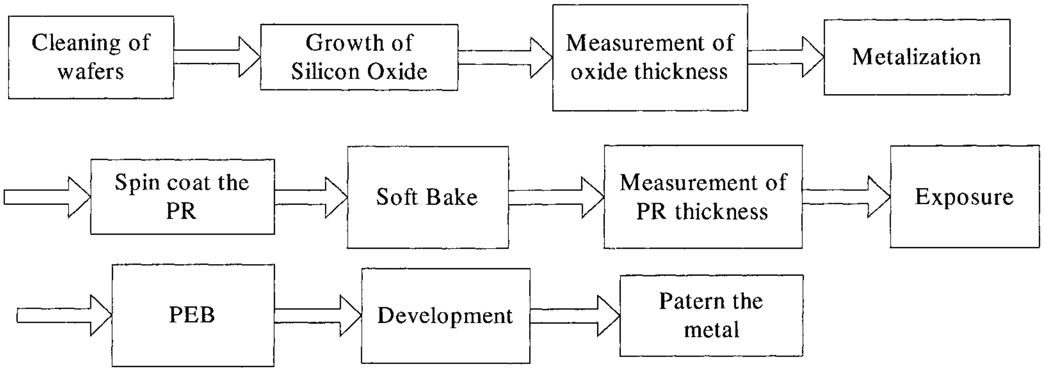


Figure 8 Flow Chart of the Post Metal Sample Preparation

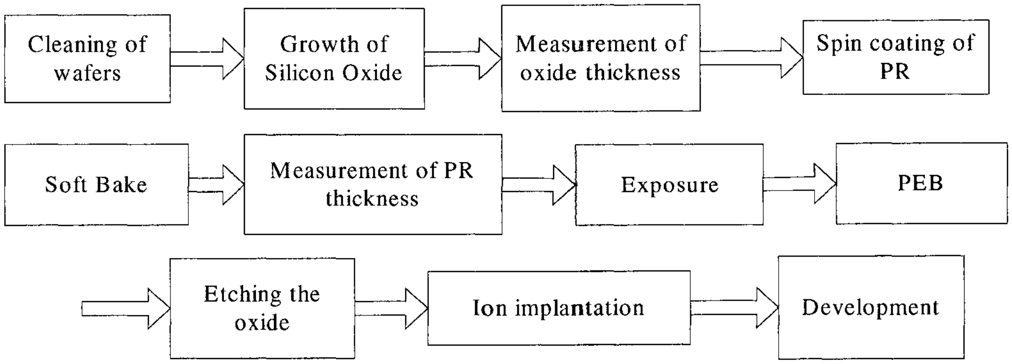


Figure 9 Flow Chart of the Post Implant Sample Preparation

5.2 EQUIPMENTS USED

The application of IPA for the resist removal has to be tested after different stages of the process in IC fabrication, so almost all the equipment needed for the basic IC fabrication are required for the experimentation. For each testing, three more duplicate wafers are needed. Table 5 gives the list of equipment used.

1) Oxidation Furnace
2) Filmetrics
3) MTR Photoresist Spinner
4) Contact Aligner
5) KLA-TENCOR P1 Long Scan Profiler
6) Aluminum Evaporator
7) Applied Materials AME 8100 Plasma Etcher
8) Ultrasonic tank

Table 5 Equipment

5.3 CHEMICALS USED

The following Table 6 shows the chemicals used for the experiment.

Chemicals used	Brand and Concentration
Isopropyl Alcohol	Ashland Chemicals, 100% Liquid
Ammonium Fluoride	Fischer Scientific, Solid
Tetramethyl Ammonium Hydroxide	Across Organics, 25% wt in water, Liquid

Table 6 Chemicals Used

5.4 EXPERIMENTAL PLAN

The experiments are discussed in the following sub sections as screening phase, effect of additives phase and optimization phase. The experiments were repeated three times for the repeatability.

5.4.1 SCREENING PHASE

The screening phase was designed to discover the parameters affecting the stripping. The experiments were designed in such a way that after they were done, a general trend of the parameters affecting the stripping rate, like temperature, IPA, and the ultrasonic energy should be known. Photoresist layer in the soft baked sample is having the least adhesion with the surface because of the lack of high temperature curing and implantation. The two surfaces used for the experiments were soft baked and PEB samples.

In the screening phase, the softbaked and PEB samples were stripped in IPA at different temperatures and with and without ultrasonic (US) excitation (Table 7). Each sample was placed in the stripping solution for 40 seconds. Forty seconds is a sufficiently short time to allow for a meaningful comparison between experimental conditions.

Parameters	Range
IPA concentration	30%, 100% by volume
Temperature	30° C, 40 °C
Ultrasonic energy	Yes, No

Table 7 Parameters for the Screening Experiment

To investigate the ease of removal for different surfaces, the optimal condition from the screening experiment was chosen and applied to the PEB sample, post oxide sample, post implant, and post-metal samples.

5.4.2 EFFECT OF ADDITIVES PHASE

In this phase, the effect of additives such as Ammonium Fluoride (NH_4F) and TMAH in the IPA stripping system was investigated. NH_4F and TMAH were introduced separately into the IPA stripping solution according to Table 8. Since Ammonium fluoride (NH_4F) is not soluble in pure IPA, a 30% aqueous solution of IPA was used to investigate the effect of NH_4F additive [24]. A soft baked sample was treated with

30%IPA and 5% NH_4F solution so that after treatment it could be compared with the wafer that was treated with 30%IPA alone. The temperature and whether we need US excitation or not, depend on the optimal condition from screening experiment.

Parameters	Range for NH_4F addition	Range for TMAH addition
IPA concentration	30% by volume	30%, 90% by volume
Temperature	Optimal from screening experiment	Optimal from screening experiment
Ultrasonic energy	Optimal from screening experiment	Optimal from screening experiment
Additive Composition	5%by wt	1.25% by wt

Table 8 Parameters for the Effect of Additives Phase

TMAH at 1.25% by weight was added to the 30%IPA and 90% IPA solution. The temperature and ultrasonic excitation depend on the optimal condition found from the screening experiments.

5.4.3 OPTIMIZATION PHASE

The optimization phase was designed to optimize the results from the screening phase and the effect of additives phase. The rates of removal of PR for the three different surfaces were found for different concentrations of additives. Then the best condition was used to get the optimum rates.

5.4.3.1 *Part 1*

In this part 1 of optimization phase, only post oxide samples were used. The concentration of NH_4F was varied while the others kept constant. The time taken to completely remove the PR layer was determined. Again the temperature and US excitation depends on the optimal condition from the screening phase. The ammonium fluoride concentration was changed from 0 to 15% by weight. Parameters used are given in Table 9.

Parameters	Range for NH_4F addition	Range for TMAH addition
IPA concentration	30%	30%, 90%
Temperature	Optimal from screening experiment	Optimal from screening experiment
Ultrasonic energy	Optimal from screening experiment	Optimal from screening experiment
Additive Composition	0,5,7,10,15%by wt	0,1.25,2.5% by wt

Table 9 Parameters for the Optimization Phase Part 1

Using the 30%IPA and by changing the concentration of TMAH, time taken to completely remove the PR layer was found out. Again the temperature and US excitation depends on the optimal condition. The TMAH concentration was changed from 0 to 2.5% by weight.

5.4.3.2 *Part 2*

From optimization phase Part 1, the optimal condition for the photoresist removal was known and this was employed in the removal of photoresist from the post-implanted surface and post metal surface. The table of the parameters is given below as Table 10. After each experiment the profile was carefully examined through the KLA-TENCOR P1 long scan profiler and the measurements were done for the trenches and vias.

Parameters	Range for NH_4F addition	Range for TMAH addition
IPA concentration	30%	30%, 90%
Composition of additive	Optimal from optimization Part 1	Optimal from optimization Part 1

Table 10 Parameters for the Optimization Phase Part 2

5.5 METHOD OF DATA ANALYSIS

The measurement of PR thickness was done using an optical spectrophotometric tool. In this project, surface profiling was done using the Tencor P-1 long scan profilometer. The Tencor P-1 Long Scan Profiler is capable of measuring surface roughness, waviness, and step height. This instrument is ideal for measuring/verifying the thickness of vapor deposited films. For this application, fabrication of a well-defined step is very important. Films under 100Å can readily be measured as long as the step height is well defined. Other capabilities include scan averaging where the profiler performs multiple scans for averaging of data and 3-D. The sample is loaded on the stage and a stylus is lowered with a set pressure (force). The stylus scans the surface of the sample literally "feeling" the surface to determine the surface morphology.

6. RESULTS AND DISCUSSION

6.1 RESULTS

6.1.1. SCREENING PHASE

From the screening experiments, the effect of temperature and ultrasonic excitation on the stripping process was observed. Figures 10 to 17 show the results of the screening experiments. These are pictures of the wafers after the treatment produced by the digital camera. The wafers shown by Figures 10 to13 were treated with 100%IPA. All these wafers are soft baked samples. In all these four wafers, the photoresist is completely removed after 40 seconds of treatment. There is some residual film on all four wafers. The residual 'white' film is more in the sample shown in Figure 10. The residual film is very reduced when there is an elevated temperature treatment and ultrasonic excitation as seen in Figure 13. When comparison is made between Figure 10 and 12 the run involving high temperature (Figure 12) has less white film on the surface. The Figure 13 shows a clean sample, which is treated with 100%IPA with ultrasonic excitation at 40 ° C. This is found to be the optimal condition.

The samples shown by Figures 14 to 17 are treated with 30% IPA and they all have PR remaining on them. The wafers, which have undergone 30%IPA treatment, are not rid of photoresist. The circles on the Figures 14 to 17 shows the area where the photoresist still remains. Figure 17 shows the soft baked wafer sample after treatment with 30%IPA at 40 ° C with US excitation. The difference between the wafer shown in

Figure 13 and the Figure 17 is only in the change in IPA concentration. As shown in the figures, the wafer in Figure 17 has photoresist, while that in Figure 13 has no resist.

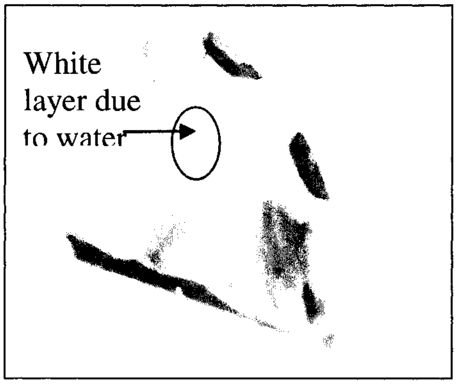


Figure 10 100%IPA at 30^0 C

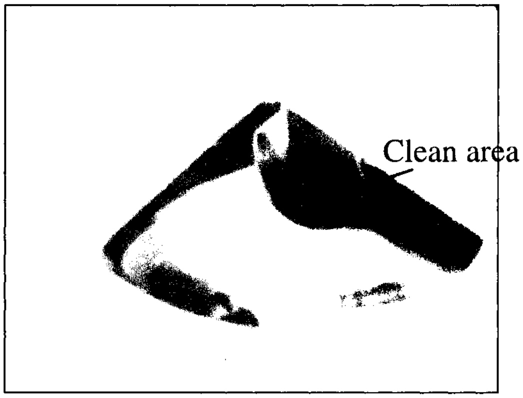


Figure 11 100%IPA at 30^0 C with US

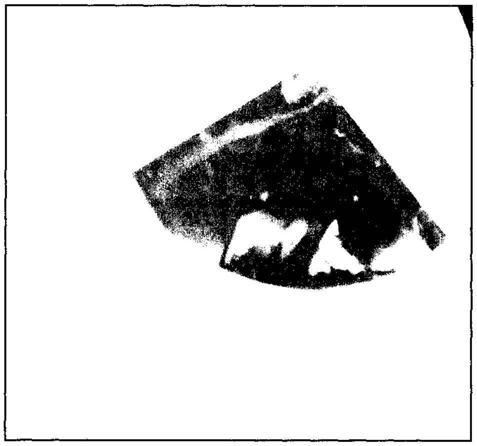


Figure 12 100%IPA at 40^0 C

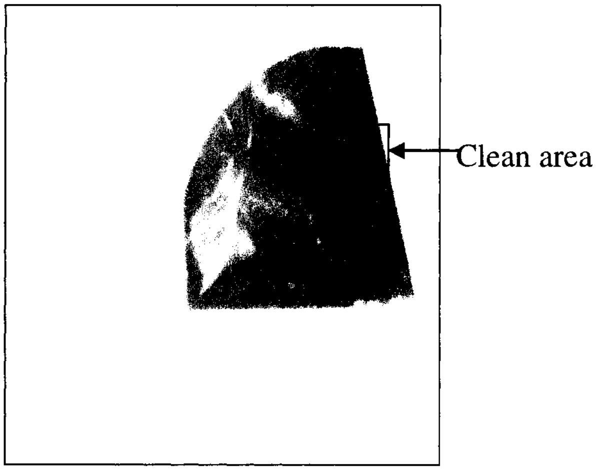


Figure 13 100%IPA at 40^0 C with US

So the optimal condition from the screening tests was set as 100%IPA at 40 °C with US excitation.

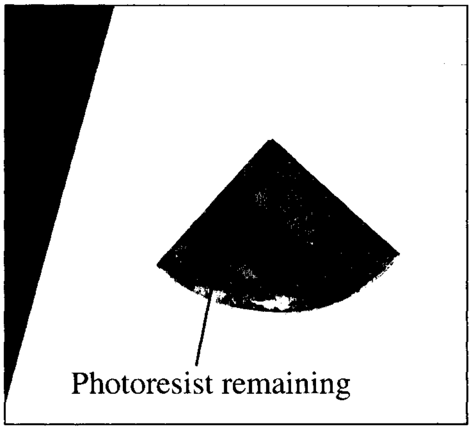


Figure 14 30%IPA at 30^0 C

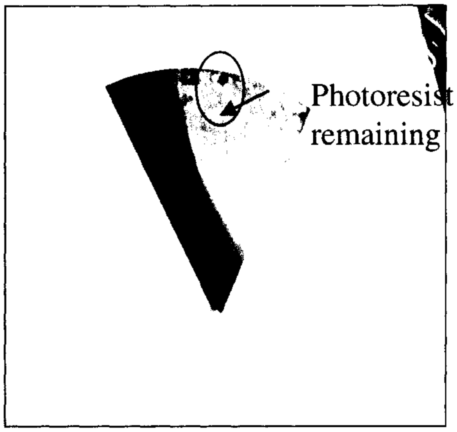


Figure 15 30%IPA at 30^0 C with US

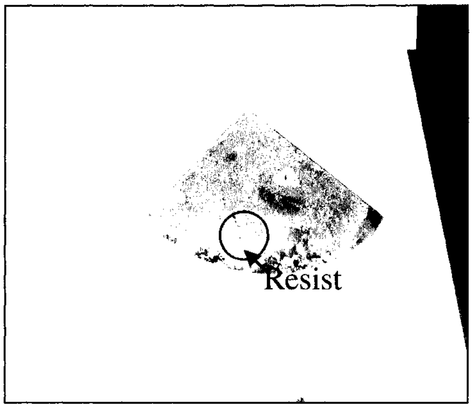


Figure 16 30%IPA at 40^0 C

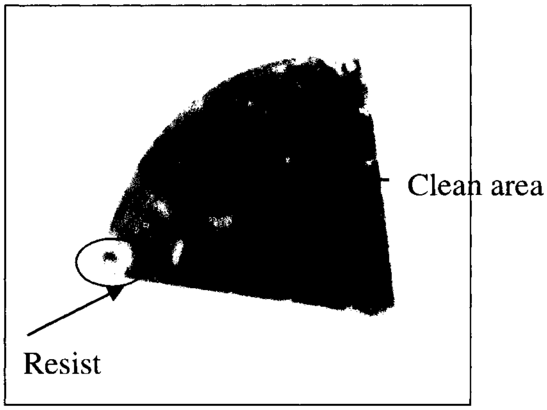


Figure 17 30%IPA at 40^0 C with US

To check the ease of removal from different surfaces, the optimal condition from the screening phase was chosen and treated the PEB sample, post- oxide sample, post implant, and post-metal samples. These four surfaces were treated with 100%IPA at 40 ^{o} C and with US excitation. After treatment for 30 minutes the wafers are given in Figures from Figure 18 to 21. The photoresist is almost removed from the PEB sample (Figure

18) except the light colored areas. There is some residual film on the surface of the wafer shown by Figure 18. For the post oxide sample, the photoresist layer has just started to peel off.

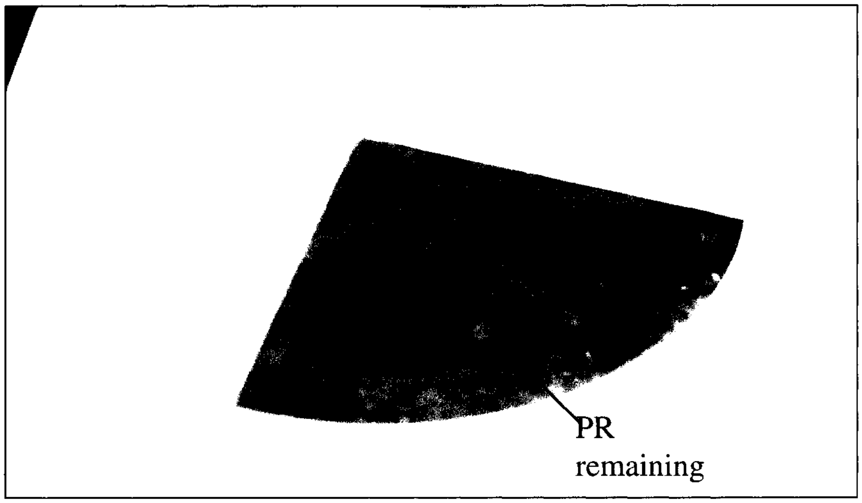


Figure 18 PEB Wafer after Treatment with 100%IPA at 40 °C with US for 30 minutes

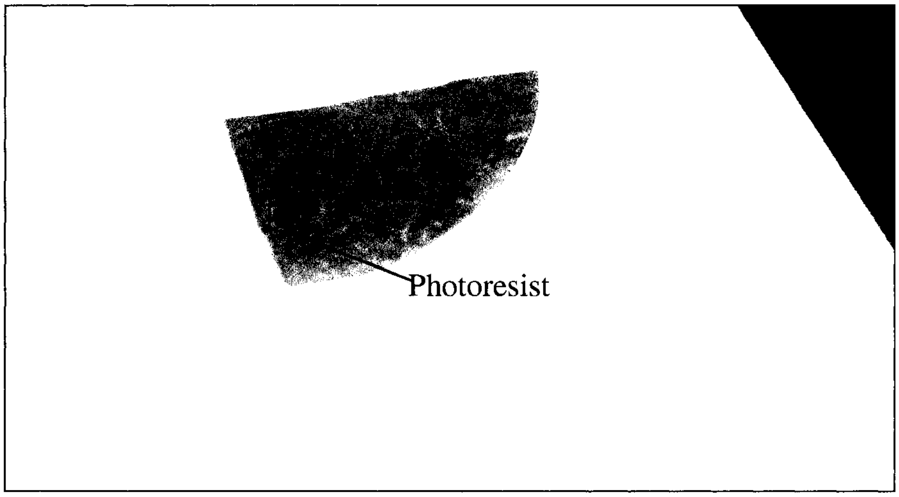


Figure 19 Post Oxide Wafer After Treatment with 100%IPA at 40 °C with US for 30 minutes

The implant sample after treatment with 100%IPA at 40°C with US excitation for 30 minutes is shown in Figure 20. The photoresist was not at all removed from the surface. The circled area shown in Figure 20 has no photoresist and due to exposure to the stripping system, resist layer has started to peel off. Figure 21 shows the post metal samples after the same treatment same as that for implanted sample. The photoresist is almost removed though there is little remaining.

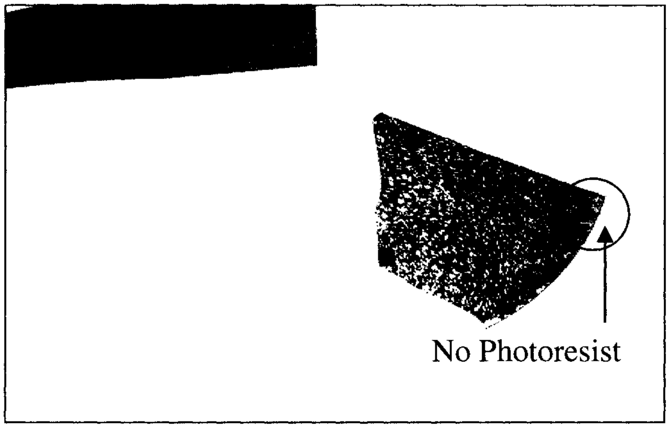


Figure 20 Post Implanted Wafer After Treatment with 100%IPA at 40 °C with US for 30 Minutes

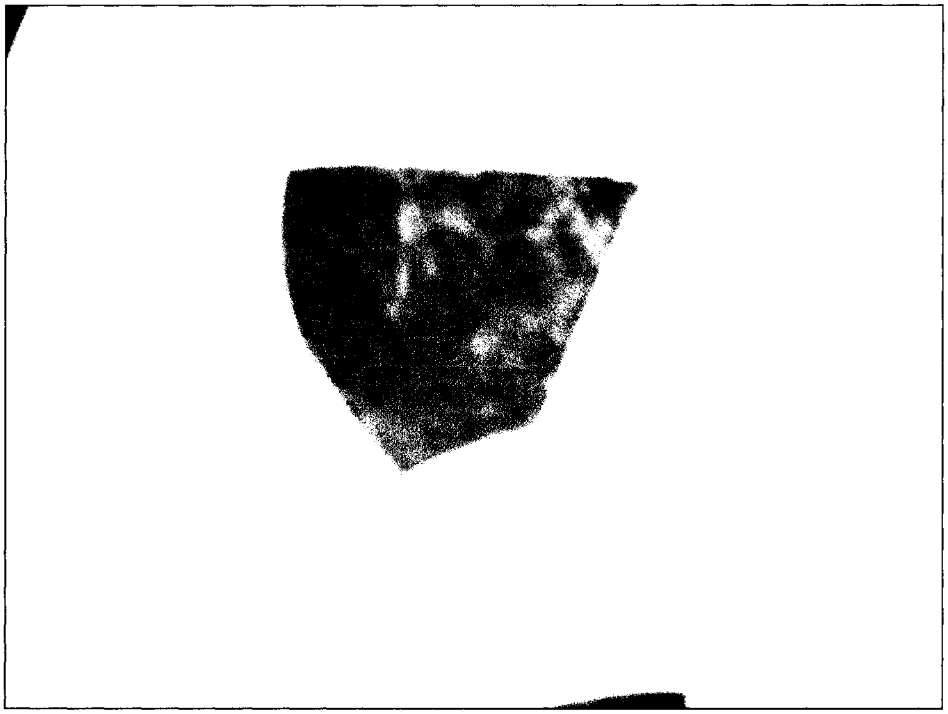


Figure 21 Post Metal Wafer After Treatment with 100%IPA at 40 ° C with US for 30 Minutes

As seen from the above figures, the most difficult surface to strip the photoresist is the post-implanted surface.

6.1.2. EFFECT OF ADDITIVES PHASE

The addition of ammonium fluoride and TMAH to IPA is found to aid the stripping of photoresist from the soft baked wafer samples. The Figures 22 and 23 show the result when soft baked samples were treated with IPA and NH_4F and IPA and TMAH with the aid of US excitation and at 40 ° C respectively.

The comparison can be made between the Figure 22 and 17 where NH_4F is varied while the temperature and time are held constant. The sample shown by Figure 22 has less photoresist remaining (shown by the circles) than that by Figure 17. But the wafer has some spotting marks on it. The wafer shown by Figure 23 is an improvement over the wafer shown by Figure 17. The wafer in Figure 23 has some residual film but no photoresist remaining on it. This is by the additive TMAH and here the wafer smoothness has not changed like the wafer in Figure 22.

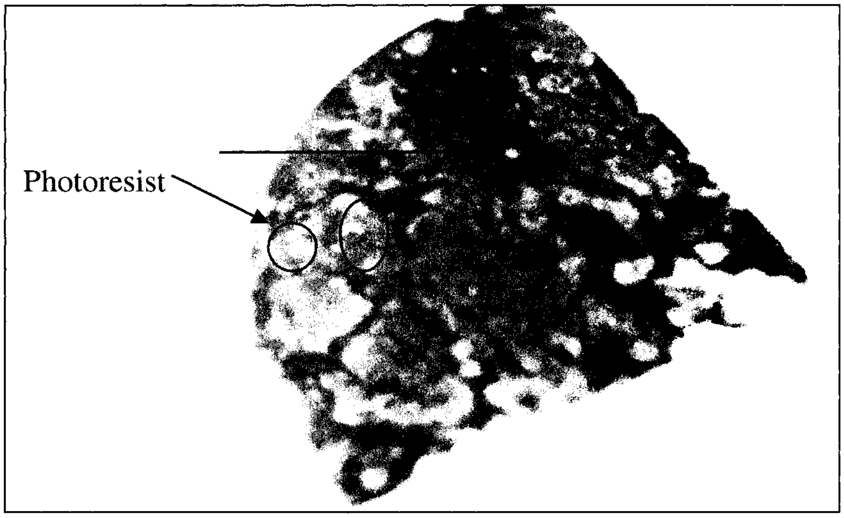


Figure 22 Softbaked Wafer after Treatment with 30%IPA at 40^0 C for 40sec with US and 5% NH_4F

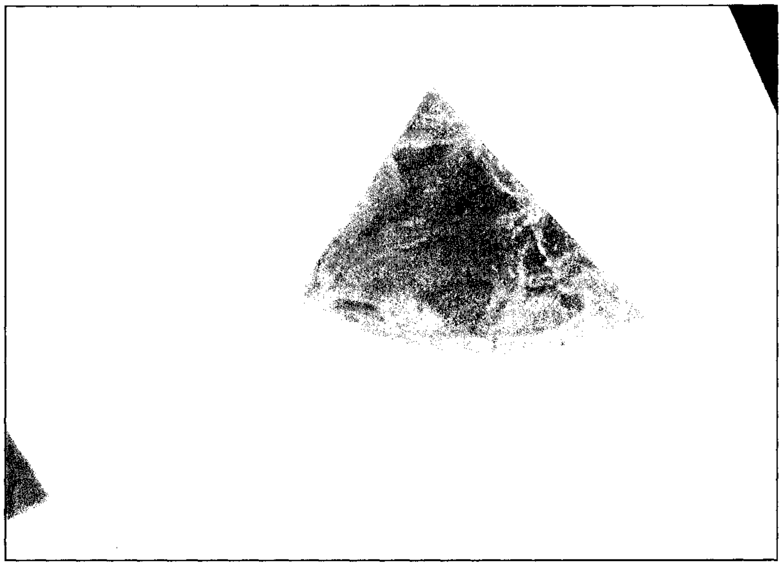


Figure 23 Softbaked Wafer after Treatment with 30%IPA at 40^0 C for 40sec with US and 1.25% TMAH

6.1.3 OPTIMIZATION PHASE

Part 1

The following chart shows the rate of PR removal from the post oxide sample with differing ammonium fluoride concentration.

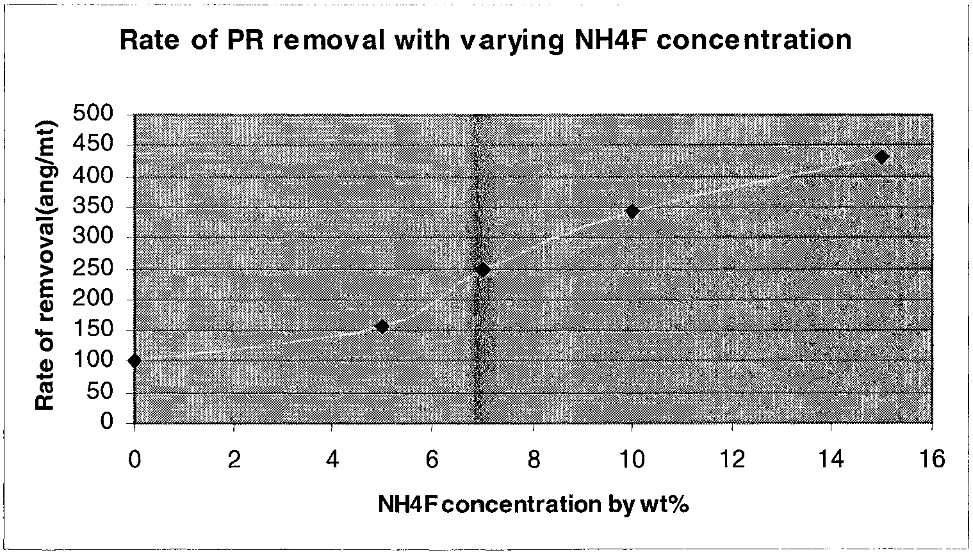


Chart 1 Rate of PR Removal with NH_4F Concentration for Post Oxide Sample

The post oxide samples were treated with IPA and ammonium fluoride at 40 °C with the excitation of the ultrasonic energy, until the resist is completely removed. These were done with varying ammonium fluoride composition. The following Table 11 gives the average time and the standard deviation for each run.

Composition	30%IPA + 0% NH_4F + 40 °C + US	30%IPA + 5% NH_4F + 40 °C+ US	30%IPA + 7% NH_4F + 40 °C+ US	30%IPA + 10% NH_4F + 40 °C+ US	30%IPA + 15% NH_4F + 40 °C+ US
No of Runs	3	3	3	3	3
Average Time Taken	130 minutes	82 minutes	52 minutes	38 minutes	30 minutes
Standard Deviation	1.73	1.73	2.8	2.08	2.51

Table 11 Average Time Taken to Completely Remove the Resist From the Post Oxide Wafer with Varying NH_4F Concentration

By increasing the amount of ammonium fluoride, the rate of PR removal can be increased. Figure 24 shows a wafer after treatment with 30%IPA and 15%TMAH at 40° C with ultrasonic energy. The wafer is not clean and there is some residual film on the wafer.

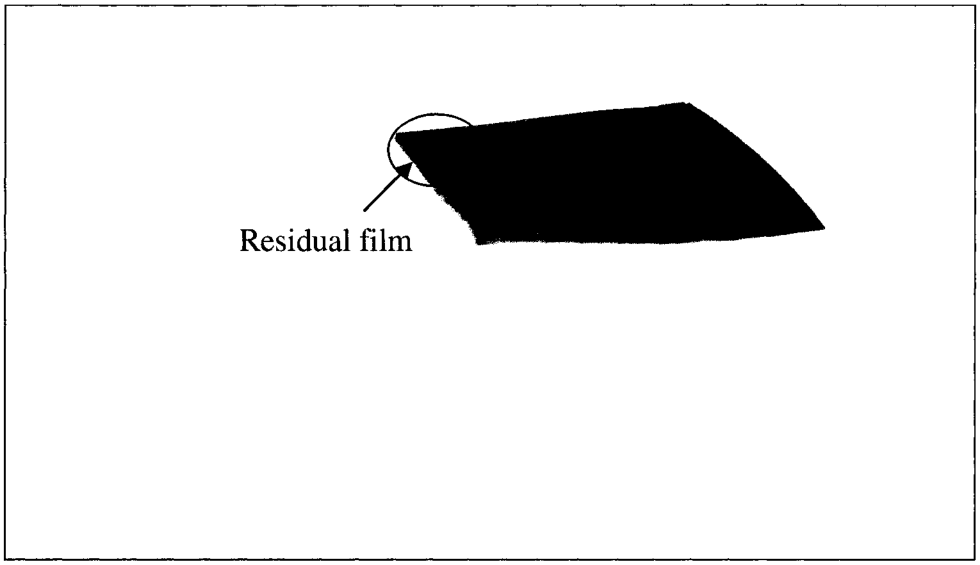


Figure 24 Post Oxide Wafer After Treatment with 30%IPA+15% NH_4F for 30 minutes at 40^0 C with US

The following Chart 2 shows the rate of PR removal from the post oxide sample with differing TMAH concentration. The following table (Table 12) gives the time taken for complete removal from post oxide samples, for the different combinations of IPA and TMAH.

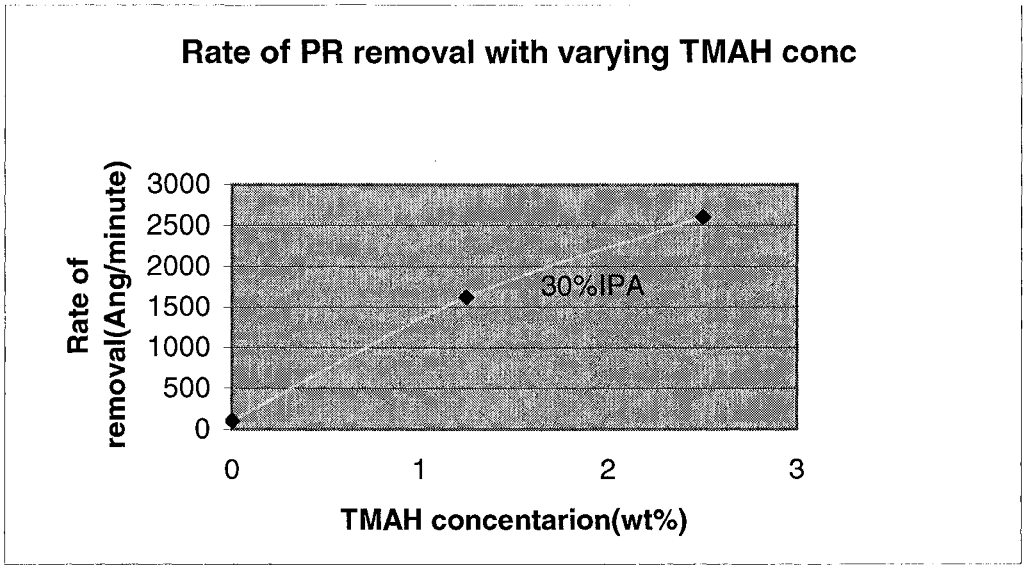


Chart 2 Rate of PR Removal from the Post Oxide Sample with Varying TMAH

30 % IPA+ 0%TMAH+ 40deg+US	30 % IPA +1.25%TMAH +40deg+US	30 % IPA+ 2.5 %TMAH+ 40deg+US	90% IPA +1.25%wt TMAH+ 40deg+US	90% IPA +2.5%wt TMAH+ 40deg+US
No of Runs	5	5	5	5
Average Time	8minutes	5minutes	12 minutes	10minutes
Standard Deviation	0.51	0.469	0.56	0.49

Table 12 Average Time Taken to Completely Remove the Resist From the Post Oxide Wafer with Varying TMAH Concentration

The following Figure 25 shows the post oxide wafer after the treatment with 30%IPA and 2.5%TMAH at 40°C and with ultrasonic energy. This is after the complete removal of photoresist on the wafers.

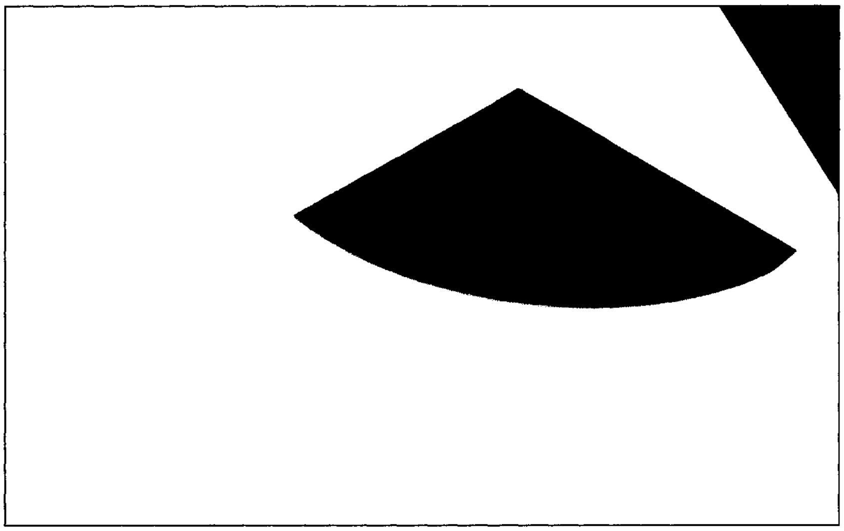


Figure 25 Post Oxide Sample After Treatment with 30%IPA+2.5%TMAH at 40 ° C with US Excitation

The Figure 25 shows a clean picture of wafers after the treatment with the IPA stripping system with TMAH as additive. The fastest stripping rate was observed when 30%IPA and 2.5% TMAH are used.

The rate of resist removal for wafers that have gone though the wet chemical oxide etch is much greater than that have gone through the dry plasma process. After treatment with 30%IPA and 2.5%TMAH at 40 ° C with US excitation, the rate was found to be 6500 Å per minute for the post oxide wafers that has undergone a wet chemical oxide etch.

Part 2

From the optimization phase Part 1 the optimal condition is 30%IPA and 2.5% TMAH with 40 ° C and with the Ultrasonic excitation. Since the TMAH when exceeding 2% would attack the metal, only 1.25% is added when treating with the post metal surface. Table 13 shows the rate of PR removal.

Surface/Condition	30%IPA+ 2.5% TMAH+40deg+US	30%IPA +1.25%TMAH+40deg+US
Post implant	764 Å per minute	
Post metal		9000 Å per minute

Table 13 Rate of Removal From the Post Metal and Post Implant Samples.

Figure 26 shows the post-metal wafer after the treatment with 30%IPA and 1.25% TMAH with ultrasonic excitation at 40 ° C. This figure depicts the fact that the TMAH/IPA stripping system strips photoresist from the metal surface. The stripping rate of PR from the metal surface is even higher than any of the other surfaces like post oxide and post implant. There is no PR remaining.

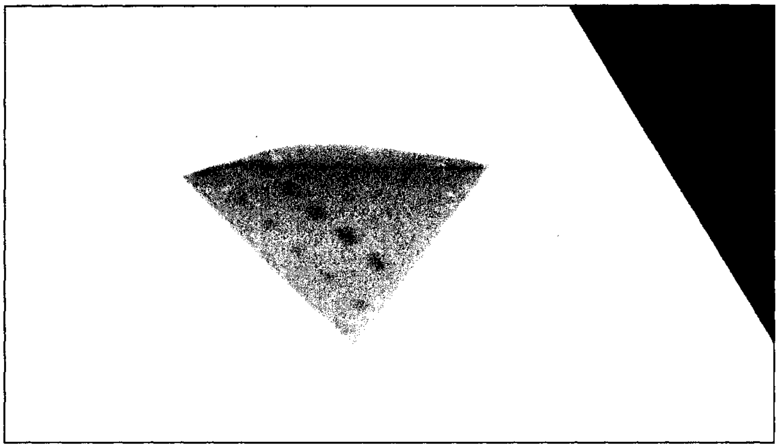


Figure 26 Post Metal Wafer After Treatment with 0%IPA+1.25%TMAH at 40°C with US

The following Figure 27 gives the post ion implanted wafer after the treatment with 30%IPA and 1.25% TMAH with ultrasonic excitation at 40 ° C. The photoresist has been completely removed from the surface. For the post-implanted surface, the rate of PR removal is very less. Figure 26 below shows that the IPA/TMAH system can completely remove the PR off the implanted surface. All the experiments were repeated for a 4-inch wafer and the results were same as that of the broken wafers.

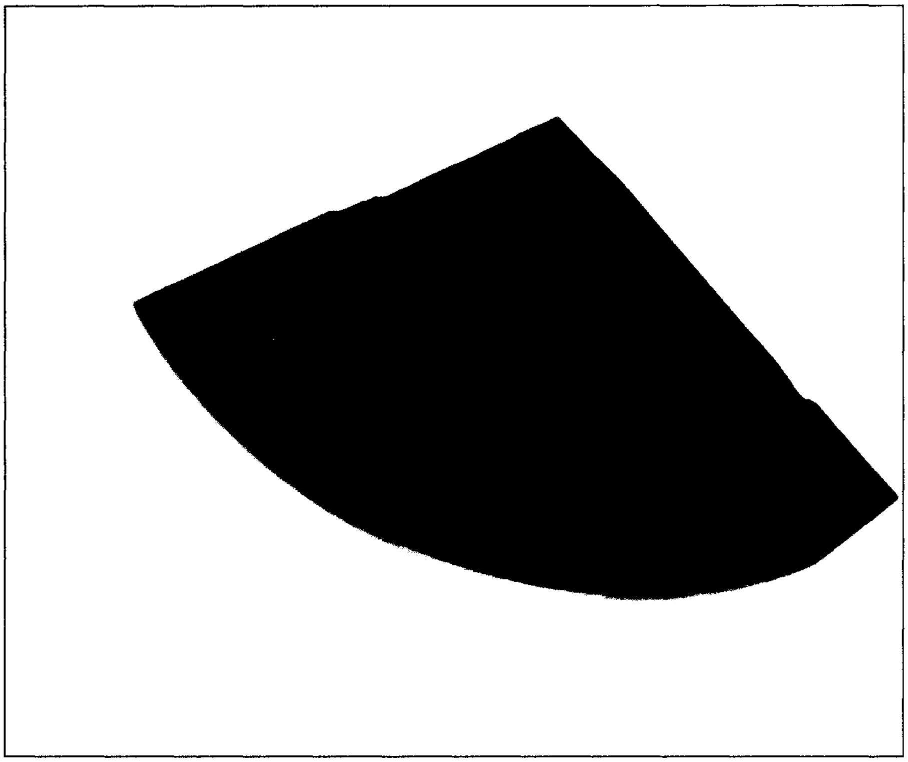


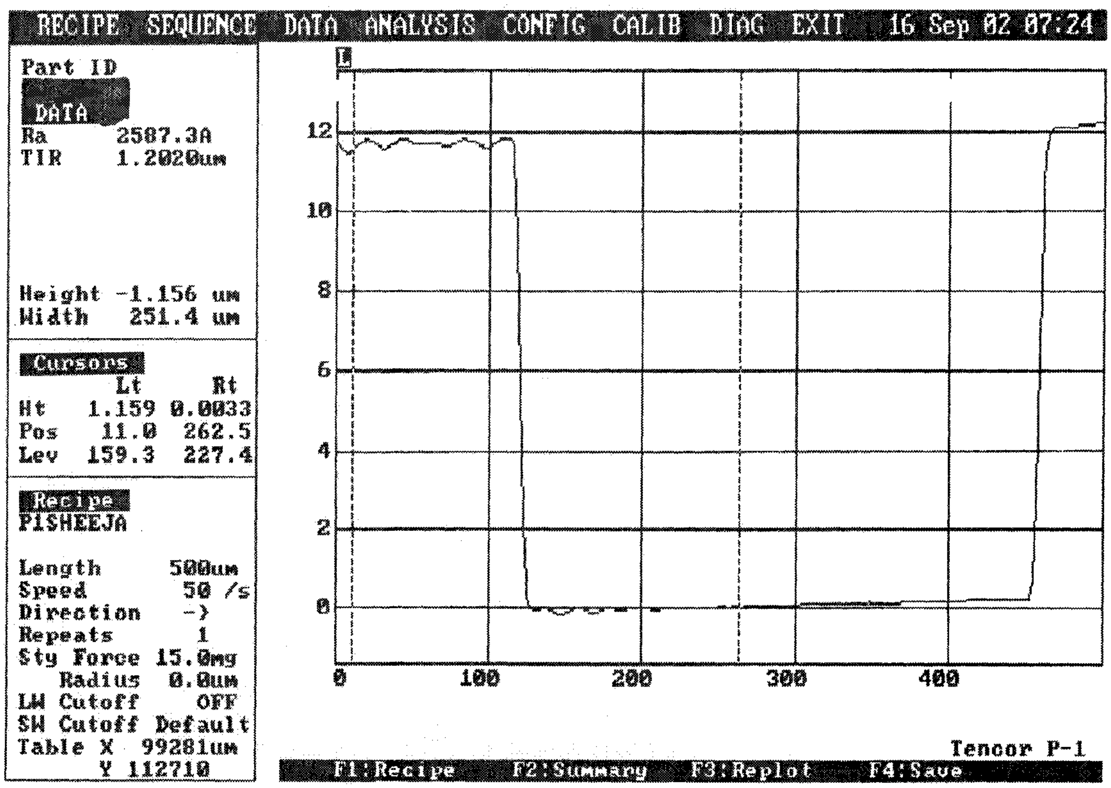
Figure 27 Post Implanted Wafer After Treatment with 30%IPA+2.5%TMAH at 40°C with US

6.2 DISCUSSION

From the results, the easiest surface is the softbaked surface where the adhesion of the photoresist with the surface is less due to the absence of hard baking step. 100% IPA at 40 °C was able to remove the photoresist at a rate of 19500 Å per minute from the soft baked sample. When the ultrasonic excitation is used, there is no change in the smoothness of the wafer. From the screening experiments, it is concluded that higher temperature and ultrasonic excitation improve stripping. The screening experiments show the general trend of the IPA stripping system.

It can be said that the difficulty of removing the photoresist is highest for the ion-implanted wafer, since the high-energy ions used during the implantation makes the photoresist layer hard and difficult to strip. PEB sample is the easiest among post metal, post oxide, and post implant samples. The addition of ammonium fluoride also helps, even though after treatment the surface is rough. The Chart 1 clearly says that increasing the ammonium fluoride concentration increases the rate of removal. From the Chart 2, by increasing the TMAH from 1.25% to 2.5%, the rate of stripping has almost doubled.

Charts 3 and 4 show the post implant wafers before and after PR stripping using IPA and TMAH at 40 °C and with ultrasonic energy. The step height in the Chart 3 shows the height of PR layer. In Chart 4 it shows the height of oxide layer. The oxide thickness was measured to be in the range of 800 to 900 Å before the stripping and the Chart 4 shows the oxide thickness as 872 Å. It shows there has been a complete removal of PR from the wafer including the pattern. The trench in Chart 3, which is before treatment, shows a flat profile while the same in Chart 4 shows a wavy profile. It can be said that the thickness is varying in the trench. The variation is about 20 Å. This means the surface is little rough by an amount 20Å.



Part ID
DATA
Ra 2587.3A
TIR 1.2020um

Height -1.156 um
Width 251.4 um

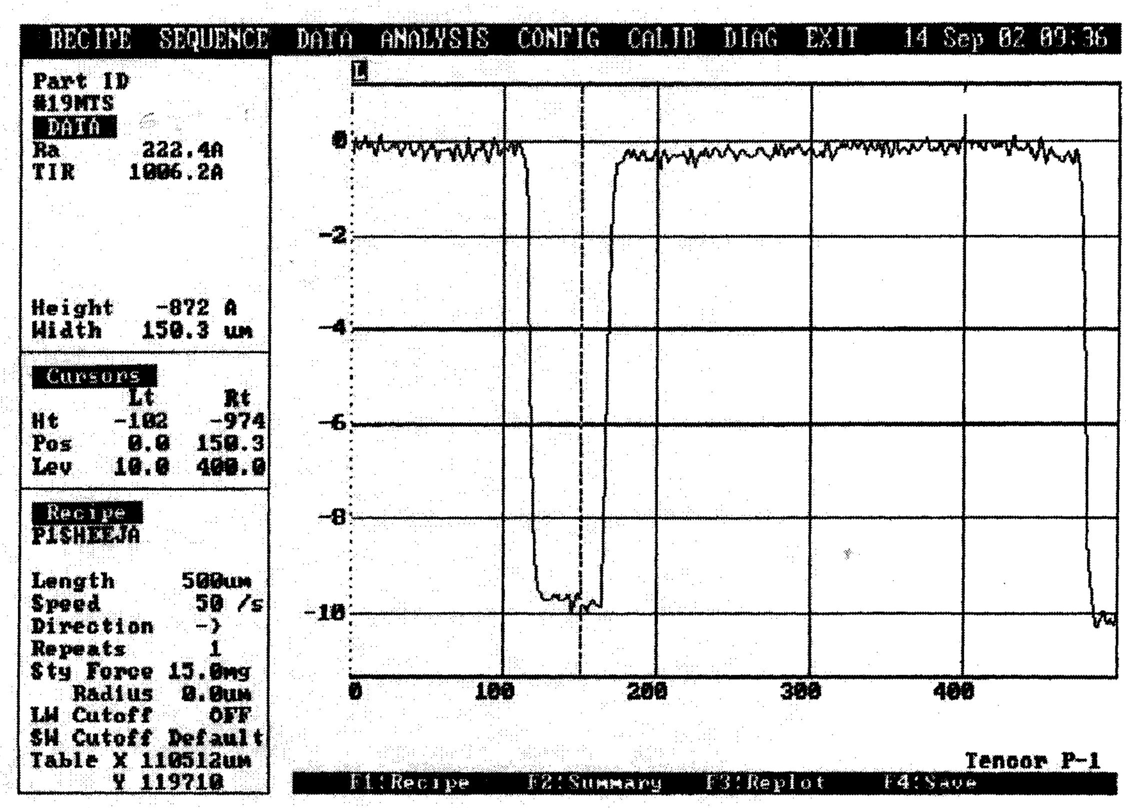
Cursors

	Lt	Rt
Ht	1.159	0.0033
Pos	11.0	262.5
Lev	159.3	227.4

Recipe
P1SHEEJA

Length	500um
Speed	50 /s
Direction	->
Repeats	1
Sty Force	15.0mg
Radius	0.0um
LW Cutoff	OFF
SW Cutoff	Default
Table X	99281um
Y	112710

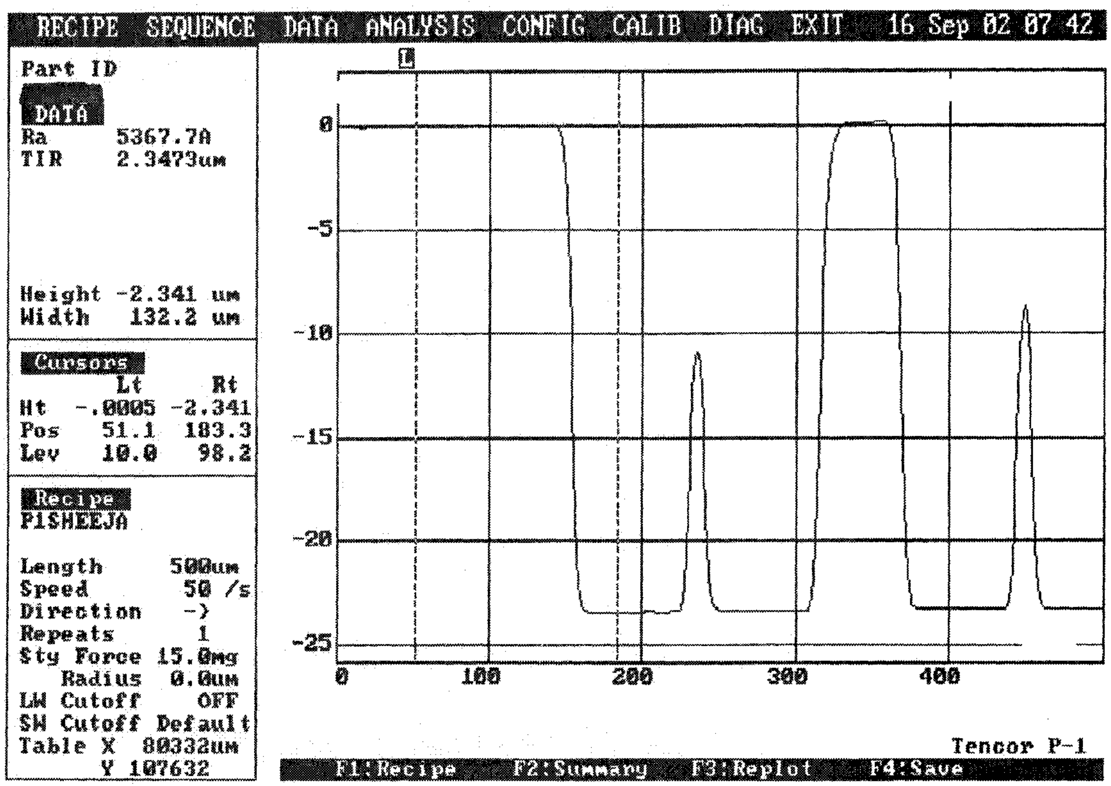
Chart 3 Profile of Post Implant Wafer Before PR Stripping



```
Part ID
#19MTS
DATA
Ra        222.4A
TIR      1006.2A

Height     -872 A
Width     150.3 um

Cursors
           Lt      Rt
Ht       -102    -974
Pos       0.0   150.3
Lev      10.0   400.0

Recipe
PISHEEJA

Length       500um
Speed         50 /s
Direction     ->
Repeats        1
Sty Force 15.0mg
    Radius  0.0um
LW Cutoff     OFF
SW Cutoff Default
Table X 110512um
      Y 119710
```

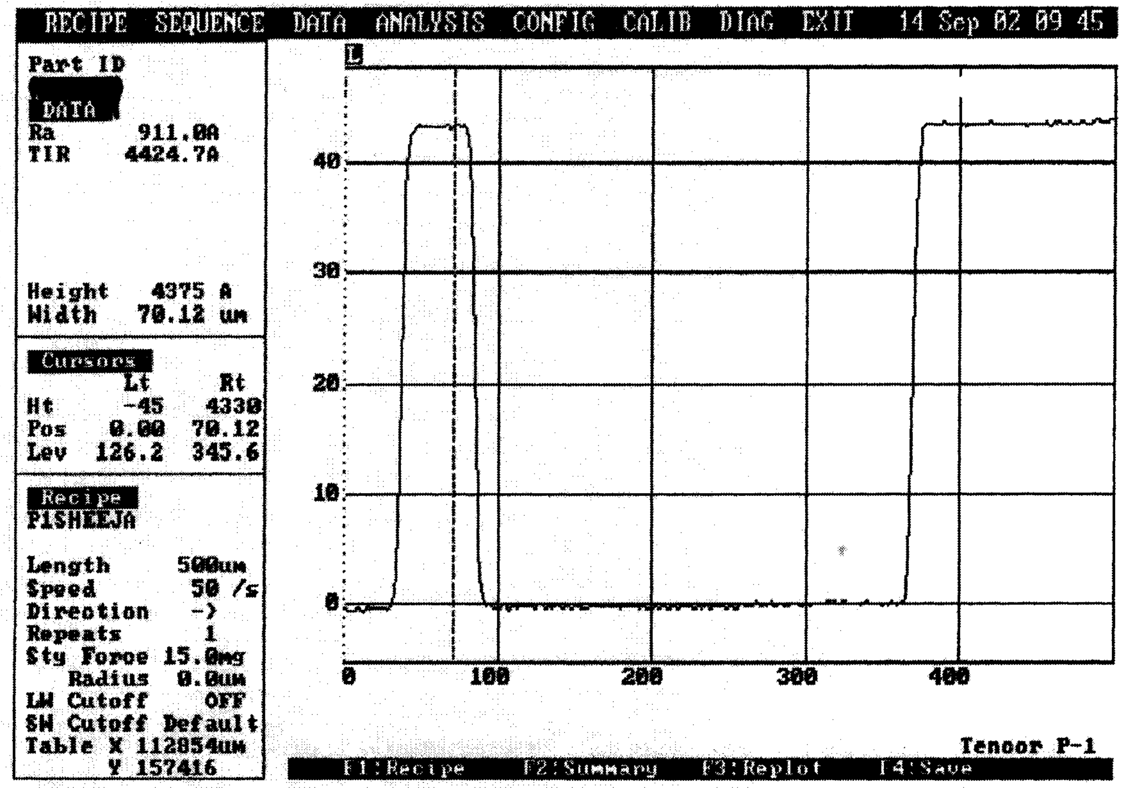
Chart 4 Profile of Post Implant Wafer After PR Stripping

Charts 5 and 6 give the profile of post metal wafers before and after PR stripping. In the case of post-metal surfaces, the roughness is increased about 10 Å. In Chart 5, the profile of the wafer surface shows a flat profile while the wafer after treatment shows a difference in thickness on the surface of about 10 Å· The post oxide wafers before and after stripping is given as Charts 7 and 8. The oxide wafers show that the surface after stripping is rough in the range of 100 Å. The depth of the trench in the Chart 8 can be read as 696 Å in one place and in another it is about 800 Å· So there is an increase in roughness.



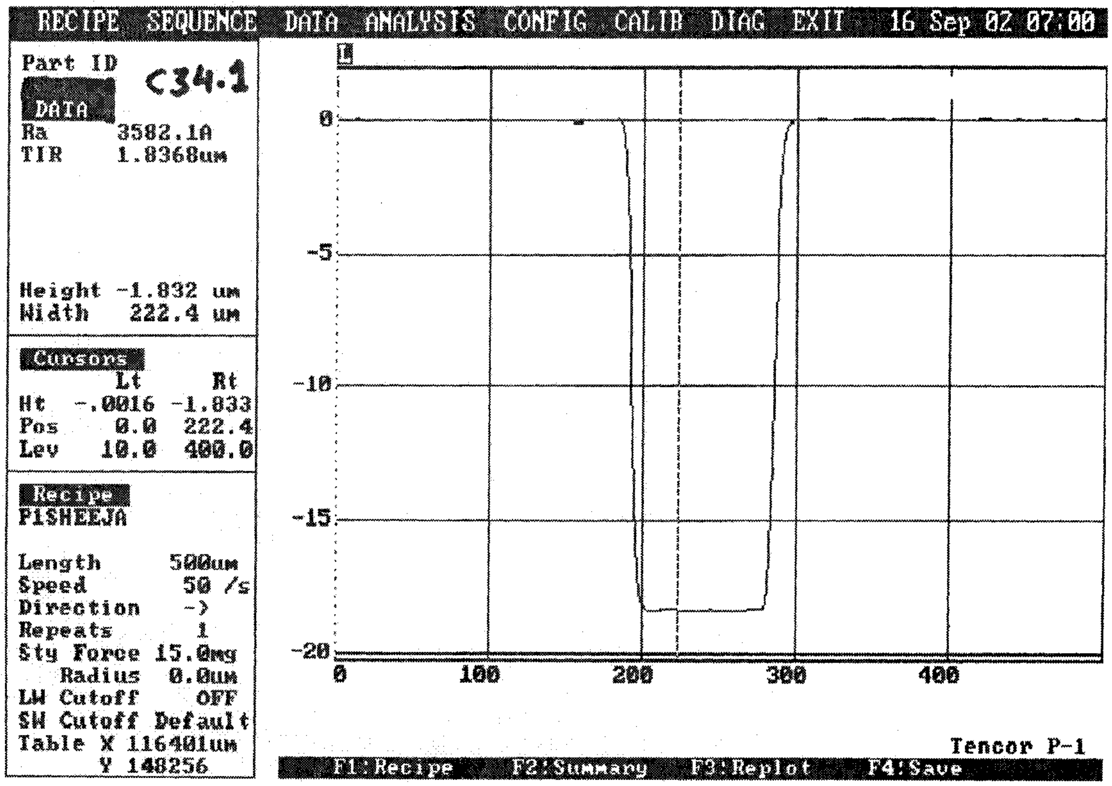
```
Part ID
DATA
Ra      5367.7A
TIR     2.3473um

Height -2.341 um
Width   132.2 um

Cursors
         Lt      Rt
Ht  -.0005 -2.341
Pos   51.1  183.3
Lev   10.0   98.2

Recipe
P1SHEEJA

Length      500um
Speed       50 /s
Direction    ->
Repeats      1
Sty Force 15.0mg
   Radius  0.0um
LW Cutoff    OFF
SW Cutoff Default
Table X  80332um
      Y 107632
```

Chart 5 Profile of Post Metal Wafer Before PR Stripping



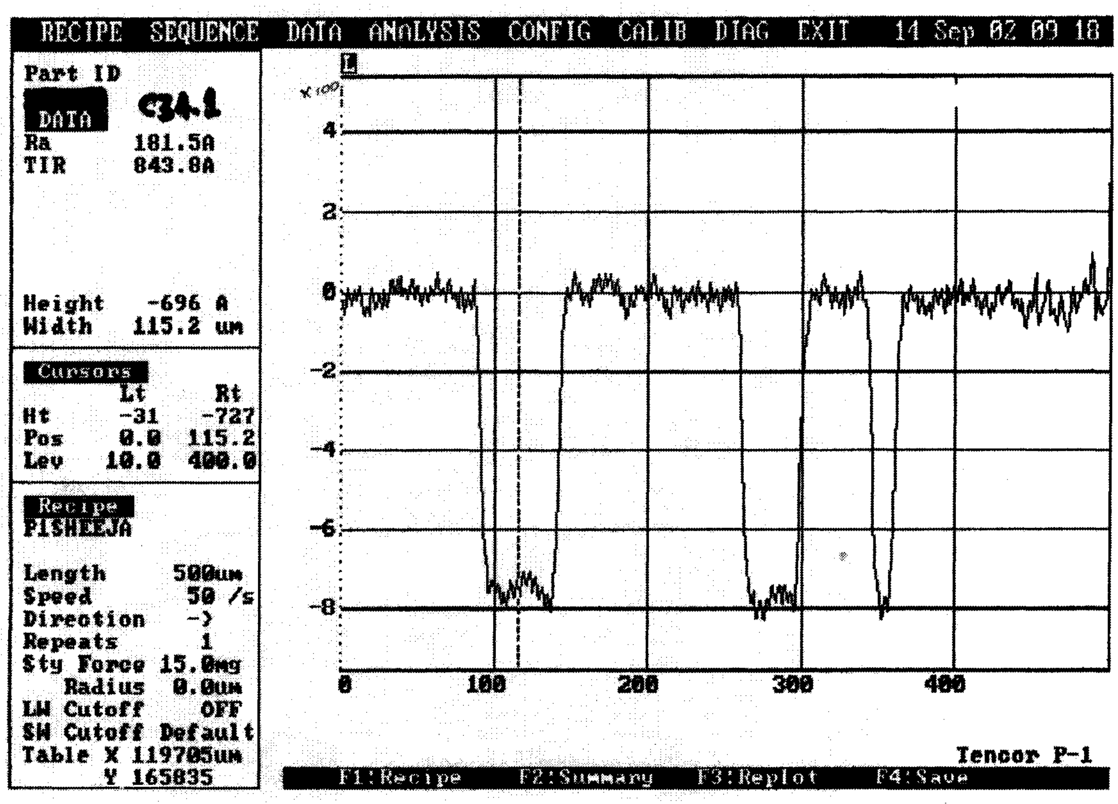
```
Part ID
[redacted]
DATA
Ra        911.0A
TIR      4424.7A

Height    4375 A
Width    70.12 um

Cursors
          Lt      Rt
Ht       -45    4330
Pos     0.00   70.12
Lev    126.2   345.6

Recipe
P1SHEEJA

Length       500um
Speed         50 /s
Direction      ->
Repeats        1
Sty Force 15.0mg
    Radius   0.0um
LW Cutoff      OFF
SW Cutoff Default
Table X 112854um
      Y 157416
```

Chart 6 Profile of Post Metal Wafer After PR Stripping



```
Part ID   C34.1
DATA
Ra        3582.1A
TIR       1.8368um

Height -1.832 um
Width   222.4 um

Cursors
         Lt      Rt
Ht   -.0016  -1.833
Pos     0.0   222.4
Lev    10.0   400.0

Recipe
P1SHEEJA

Length       500um
Speed        50 /s
Direction    ->
Repeats      1
Sty Force 15.0mg
   Radius  0.0um
LW Cutoff      OFF
SW Cutoff Default
Table X 116401um
      Y 148256
```

Chart 7 Profile of Post Oxide Wafer Before PR Stripping



```
Part ID
 DATA     C34.1
Ra        181.5A
TIR       843.0A

Height    -696 A
Width    115.2 um

Cursors
          Lt     Rt
Ht       -31   -727
Pos      0.0  115.2
Lev     10.0  400.0

Recipe
PISHEEJA

Length       500um
Speed         50 /s
Direction    ->
Repeats        1
Sty Force 15.0mg
   Radius  0.0um
LW Cutoff     OFF
SW Cutoff Default
Table X 119705um
      Y 165035
```

Chart 8 Profile of Post Oxide Wafer After PR Stripping

The rate of removal of photoresist is greater for the post metal surface then for the post oxide surface. The post metal samples have undergone the wet chemical etch for the oxide etch and the metal etch. The photoresist has also undergone these wet chemical actions. So the resist will be much easier to remove. The post oxide samples, which have undergone the wet chemical oxide etch also has the rate of removal close to post metal samples. The minimum rate is found with the post-implanted surface with the IPA/TMAH stripper at 40°C with the ultrasonic excitation. The conclusion can be drawn that the ultrasonic excitation is helpful in removing the peeled photoresist from the wafer surface where IPA/TMAH system helps in penetrating into the photoresist film and makes it loosen from the surface. So the mechanism of removal is considered to be partly dissolution of PR film with the chemical capabilities of IPA and TMAH and then partly peeling it due to ultrasonic excitation. The elevated temperature helps the process to complete faster. So the IPA/TMAH stripping system is an environmentally friendly, cheap, easier to maintain, highly successful stripping system for various process surfaces such as metal and ion implanted oxide.

7. CONCLUSIONS

Photoresists can be removed using low molecular weight alcohol, IPA. When IPA is alone used for stripping, the rate of removal is low. The rate of removal is enhanced by the addition of additives such as ammonium fluoride and tetramethyl ammonium hydroxide. The rate is maximum for the post metal surface and minimum for the implanted surfaces. The maximum rate is about 9000 Å per minute when TMAH is added with ultrasonic excitation and elevated temperature. Since this method doesn't use much DI water and doesn't cause harmful by products as other wet chemical stripping methods, this can be employed as a solution to stripping problems like the hazardous waste management. IPA is a volatile alcohol and there is no problem of waste management. TMAH is a commonly used chemical in the electronic industry. IPA/TMAH system is a success over the current problematic stripping methods. It is inexpensive and easy to maintain also. Again this is suitable for samples after various processing steps such as ion implantation and metalization.

8. FUTURE WORK

The future work related to this project includes the AFM observation of the surfaces to investigate the roughness and the changes in electrical properties. The question of whether the surface after the IPA treatment is contaminant free can also be investigated. Though the proposed stripper works for various process samples, the investigation of whether this will attack any of the underlying films is still a question. Again before absorbing this stripper as a regular standard, the investigation has to be done for surface roughness and contamination. It is also necessary to study the bath life of the IPA/TMAH system before absorbing as a regular stripping standard.

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Appendix

	30 % IPA+ 0% NH_4F +40°C + US	30 % IPA +5% NH_4F +40°C + US	30 % IPA +7% NH_4F +40°C +US	30 % IPA +10% NH_4F +40°C + US	30 % IPA +15% NH_4F +40°C +US
Rate of Removal	<100 Å per minute	158 Å per minute	250 Å per minute	342 Å per minute	433 Å per minute

Table 14 Raw data used to generate Chart1

	30 % IPA+ 0%TMAH+ 40°C +US	30 % IPA +1.25%TMAH +40°C +US	30 % IPA+ 2.5 %TMAH+ 40°C +US
Rate of Removal	<100 Å per minute	1625 Å per minute	2600 Å per minute

Table 15 Raw data used to generate Chart 2