DEPOSITION OF PATTERN TRANSFER MATERIALS BY THE MISTED CHEMICAL DEPOSITION PROCESS

A Thesis in

Electrical Engineering

by

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ABSTRACT

In semiconductor manufacturing, deposition of photoresist is commonly carried out by a spin-on process. This process is relatively simple to implement and has served well the semiconductor industry since the beginning of modern planar technology. However, it features some inherent shortcomings which in the light of ever increasing cost of materials, introduction of very large diameter wafers, and increasingly tighter tolerances regarding film thickness controllability and uniformity may limit its usefulness in future generations of IC manufacturing. In this investigation a method of mist deposition is introduced and studied as an alternative to the spin-on method of resist application in semiconductor device manufacturing. The results from this study suggest that mist deposition has no fundamental limitations regarding its use in photoresist processing and as such may be an attractive alternative to spin-on processes.
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Chapter 1

Introduction

Lithography was developed in Munich, Germany by Austrian actor and playwright Alois Senefelder in 1796. Looking for an inexpensive way to publish his own works, he experimented with etched stone slabs. This initial technique used an acid resistant ink as a resist on a smooth, fine grained, stone called Solnhofen limestone which occurs naturally in the German state of Barvaria. He discovered that this technique could be modified to allow printing from the flat surface of the stone, thus eliminating the stone etching portion of the process. With this refined technique in hand, he joined the Andre family of music publishers and developed the technique into a production quality process. He called the process “Stone Printing” or “Chemical Printing” but the French name “Lithography” became more widely adopted [1].

Photosensitive materials were first added to the lithography process around 1826 by Joseph Nicéphore Niépce, who created the first “permanent image from nature”, or in other words, the first photograph. This was accomplished by coating a polished plate of pewter with a thin coating containing of a type of tar called bitumen of Judea dissolved in lavender oil. After a long exposure to sunlight through a simple camera (his first exposure, an image of his courtyard, took 8 hours to expose) the bitumen of Judea was rendered less soluble in a developing solution of oil of lavender and white petroleum. Thus it created a relief structure in the remaining organic media on the surface of the
pewter. Thus, Niépce is not only credited with the invention of photography, but also with the invention of photolithography.

After the initial success of bitumen of Judea as a photosensitive material, the search began for more light sensitive materials so that exposure time could be reduced. The next major advancement came in 1839 when Mungo Ponton demonstrated the photosensitivity of paper soaked in ammonium dichromate. William H. Talbot refined the use of ammonium dichromate by adding it to a gelatin to create a resist material that could be cast into fine films, and could be dissolved in water after exposure. For this work, he was granted a British patent in 1852. It was this material that William Shockley and colleagues at Bell Laboratories used as resist materials when developing the first integrated circuits in the late 1940s [2].

1.1 Motivation

In modern microfabrication the lithography process is used to permanently alter a substrate through techniques such as etching and deposition. To accomplish this, stencils are created in thin films of resist, and the subsequent processing steps are performed in these masked off areas of the substrate. The resist materials then are more generally known as pattern transfer materials and their fundamental purpose is to accurately reproduce on the substrate the master pattern that has been transferred to the resist. However, due to the nonstop demand for smaller features to be created on larger
substrates with fewer failures, the evolution of pattern transfer tools and materials continues to become more sophisticated, and the techniques through which they are engaged are under continuous improvement and development. Within the photolithography process, the resist deposition step has multiple opportunities for improvement. The industry standard method for creating a resist film is the spin coating. This method has proven to be the only practical way to meet the performance demands of the resultant film and the manufacturing demands of the environment in which it is created.

There are, however limitations to its effectiveness. The sources of defects in a spin coated film can be grouped into two categories: Macro scale defects and micro scale defects. Macro scale defects include incomplete coverage, comets, pinholes, and striations. Incomplete coverage happens when not enough resist is initially deposited on the substrate. Comets occur when particulates on the surface get in the way of the resist during the spin process and prevent it from spreading any further, resulting in an area on the resist without resist that looks like a comet tail. Pinholes occur when the resist film separates and creates small voids in the film, and striations occur when the exhaust flow in the spin bowl is uneven and causes the resist’s solvent to evaporate in a non uniform manner. This can be identified as radial lines of resist which have a slightly different color, due to their differing thickness, than the rest of the film. Micro scale defects include surface roughness, non-uniformity, and spin shadowing. Surface roughness becomes increasingly important as feature sizes shrink and the depth of focus of the exposure tools needed to create them also shrinks. Non-uniformity of the resist thickness
from the center to the edge of the wafer is due to the continuous change in the angular velocity along the radius of the wafer. The result of this is that the resist is thicker in the center of the wafer and thinner near the edge, which can translate into variations in the exposed pattern across the entire wafer. Spin shadowing occurs when the substrate has features already on the surface. As the spun resist travels toward the edge of the wafer and encounters these features along the way, the resist flow will be obstructed by these features and the area around the far side of the feature will have a thinner film of resist than the side of initial impact.

Despite these issues, manufacturing facilities prefer the spin coating method. Lithography is the most frequently used technique of a fabrication facility. While some fabrication tools might encounter a specific wafer a few times in the course of its fabrication, every time that wafer needs a pattern, it has to go to through the lithography process. For very complicated products, this could mean multiple dozens of trips through the lithography process. Therefore, bottlenecks in the lithography area are a big concern and the rate of wafer throughput is an important fabrication metric. Forming a resist film with a spin coater is quick, usually taking only 30-60 seconds to create the film. Spin coaters are relatively simple machines as compared to other fabrication tools, and they can be combined with other tools needed in the resist deposition process to create efficient, automated wafer coating systems that perform every process needed to go from a bare wafer to a coated one as quickly as possible. In order to compensate for the film quality issues of spun on resist, manufacturers compensate by dispensing resist volumes large enough to avoid these issues.
This practice itself raises concerns as photoresist is one of the most expensive chemicals in the fabrication process. The cost of DUV photoresists currently available on the market is about $3000-$6000 per gallon [3]. The volume of photoresist dispensed on a 200 mm (8 in.) wafer is typically between 0.7 cc and 4.0 cc per coating. It is well known that the spin casting method of applying photoresist to substrates is a wasteful process. Depending on the source, it is reported that between 90% and 95% of photoresist is wasted [3], [4]. Additional costs are incurred in the process of disposing the waste photoresist. Because photoresists contain hazardous materials, the disposal cost can reach 60% of the original cost of the material [5] which further worsens the issue of material cost. Therefore, any step in the lithography process that can be adjusted to improve yield, reduce raw material consumption, increase throughput, or reduce waste, should be been studied. It is in this spirit that the process of depositing photodefineable materials via the liquid source mist deposition process is being studied.

1.2 Scope of Work and Thesis Overview

The breadth and depth of research on resist is extremely large, and can be divided into three main categories: resist chemistry, resist processing, and resist usage. This study falls under the resist processing category. Alternative approaches to all areas of the resist processing have been studied. Methods of reclaiming and regenerating waste resist and solvent have been explored, and there have been many studies that explore alternative methods of depositing resist to achieve resist layers specific qualities.
The work described here is a study of the feasibility of an alternative process for depositing photoresist onto a substrate. This work sets out to determine if resist can be deposited by the Liquid Source Misted Chemical Vapor Deposition (LSMCD) method, which has been used to successfully deposit other materials. Once it has been determined that the process can deposit resist, this work sets out to determine if the characteristics of the deposited films preferable in any way over the films created by the current methods.

Chapter 2 provides a background of the process photolithography. Chapter 3 provides a background of the LSMCD process. Chapter 4 describes the process of development and characterization of the LSMCD deposited photoresist and discusses the results. Chapter 5 provides a summary of the work and provides suggestions for future study.
Chapter 2

Overview of Photolithography

In this chapter the process of photolithography will be discussed. Since the goal of this work is to create a photodefined film with the LSMCD technique it is necessary to review the traditional lithography methods so that they can be compared to the results of the LSMCD generated materials.

First the basics of substrate patterning will be reviewed. After that, the individual steps in the photolithography process will be examined, and they will be addressed in the order that they are typically encountered in the course of lithography processing. Due to the wide variety of equipment, materials, and techniques, available for photolithography processing, the content of the following sections will be limited to those used in the course of the research experimentation done to support this work.

2.1 Wafer Patterning Basics

The purpose of lithography is to create a temporary masking stencil on the wafer or substrate, through which materials can be deposited or removed to form the features and structures of a device. Therefore, wafer patterning can be thought of simply as a two part process. The first part is creating the stencil layer on top of the substrate. The second
part is processing the stenciled wafer with any of the many additive, subtractive, or modifying fabrication processes available. Only then, after the pattern has been transferred to the substrate, is the process complete. This process of stenciling and pattern transfer is repeated until all components of the desired device are fabricated. For simple devices, this could be as few as two or three repetitions. For more complex structures the number of repetitions could be many more.

Figure 2.1 shows, with wafer cross sections, the flow of a basic wafer patterning process using photolithography to create the stencil and etching to transfer the resultant stencil pattern to a substrate. Photolithography is the most common and widely used of the lithography methods. As its name suggests, the process uses light waves, and optical apparatus to create stencils on the wafer. The light waves used are in the ultraviolet (UV) range (1 to 400 nm) and are used to expose a polymer material sensitive to light in the UV range. This material is called photoresist because it is photosensitive as well as being resistant breaking down during the subsequent processing. Often, for convenience, it is referred to as “resist” or “PR”. In Figure 2.1, image (a) shows the starting material. In this example it is a featureless wafer with a layer of silicon dioxide on the top, however, substrates with multiple existing patterns and layers can also be used. Image (b) shows the wafer with the deposited photoresist. Image (c) shows the exposure of the resist by a (UV) radiation source through a mask. The mask is made of glass with a chromium pattern. The chromium blocks the UV radiation from exposing the resist on the areas of the wafer where exposure is unwanted. Image (d) shows the resultant stencil pattern.
Image (e) shows the transfer of the pattern in the resist to the substrate by an etching process. Image (f) shows the resulting pattern after the resist has been removed [6].

Figure 2.1: Wafer patterning process flow using optical lithography for stenciling and etching for pattern transfer

2.2 Photolithography Process Steps

Successful creation of features on the substrate is a direct result of the quality of the lithography process. The interaction of materials, production tools, and processes, as shown in Figure 2.2, each need to be carefully controlled in order to achieve acceptable
results every time. Because of this, each step in the lithography process are subjects of continuous study and optimization. In this section we will discuss each step in the lithography process. Describing the Optical Lithography process as it is currently implemented is necessary so that the resulting samples from the experimental tool and process can be compared to it. From this comparison, the effectiveness of the experimental process can be evaluated. Inherently, within each process step we will discuss the equipment used in the processes. Following this, we will discuss in more detail the photosensitive materials used in the photolithography process.

Depending on the source referenced, the steps of the optical lithography process vary somewhat, [8,9,10]. All of the mentioned references start with a substrate preparation step. Later in the process, after the exposure step, the references vary as to the steps done and the point at which the process is considered complete. Notably, [8] and [10] both include the pattern transfer (in their example, etching) in the lithography process while [9] does not.

![Figure 2.2: Relationship between processes, equipment, and materials in lithography [7]](image)
The process developed and used in Penn State research facilities is a hybrid combination of these processes, the data sheets for the specific photoresist being used, and empirical trial and error. Figure 2.3 outlines this process. This process differs from the referenced processes in two ways. First, it recognizes the first step as a complete surface preparation step. This generally means a thorough substrate cleaning and then application of an adhesion promoter, but any operation that insures the subsequent photoresist application is successful should be included. Secondly, it introduces a preliminary stencil inspection in step 7, before the hard bake. Because the hard bake process makes the removal of the photoresist more difficult, this step provides an opportunity to remove a stencil if it does not turn out as expected without the need for harsh resist strip procedures. Each of these process steps contains numerous operations. The specifics of each operation, in terms of time, temperature, speed, etc. are dependent on the photoresist used and outcome desired, so the discussion will be limited to the procedures in general.

**Substrate Preparation**

In order to obtain the best results in the resist application step, it is necessary to condition and prepare the surface to accept the resist. The first operation is to clean the surface of the substrate so that it is free of contaminants and particulates. The second step is to dehydrate the wafer, so that it is free of as much moisture as possible. The last step is the application of a primer layer that promotes the adhesion of the resist to the wafer.
The type of cleaning method used depends on whether the substrate has been previously processed. In the case of a bare silicon wafer, the most common substrate, the surface can be cleaned with the chemically aggressive standard clean (SC1 and SC2) process as seen in Figure 2.4.
**Table 2.4:** Standard Clean 1 (SC1) & SC 2 cleaning processes

<table>
<thead>
<tr>
<th>SC 1 (Parts By Volume)</th>
<th>SC 2 (Parts By Volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5) DI Water</td>
<td>(6) DI Water</td>
</tr>
<tr>
<td>(1) 30% Hydrogen Peroxide</td>
<td>(1) 30% Hydrogen Peroxide</td>
</tr>
<tr>
<td>(1) 29% Ammonium Hydroxide</td>
<td>(1) 37% Hydrochloric Acid</td>
</tr>
<tr>
<td>5 minute soak at 70°C</td>
<td>5-10 minute soak at 70°C</td>
</tr>
</tbody>
</table>

In the case that there are materials on the surface, such as SiO₂ or metals, the surface cleaning must be limited to less aggressive chemicals that don’t etch or otherwise damage the sample.

A hydrophobic surface is preferred for the application of photoresist because it is also hydrophobic, and as such it will wet the surface. Unfortunately, even an initially hydrophobic surface won’t stay that way for long. Once the dry wafer is exposed to moisture, either through the air or an aqueous process, the surface condition begins to change to a hydrophilic (water attracting) state [10]. The existence of other materials and structures on the surface (which is predominantly the case throughout the manufacturing process) will also hinder the ability to achieve a hydrophobic state. The hydrophobic nature of the resist and the hydrophilic nature usually present on the substrate necessitate the use of additional steps to guarantee a hydrophobic surface is seen by the resist. Otherwise, the resist will not adhere properly to the surface. These steps are dehydration baking and priming.
Dehydration Bake

After the surface is clean, it is necessary to drive out any residual moisture that has been adsorbed during the cleaning processes. This is especially important if the surface has materials and features that are hydrophilic, such as SiO₂. Because hydrophilic surfaces easily attract moisture from the atmosphere, it is necessary to remove it before the application of the resist. Dehydration can be done on a hot plate or in an oven. Because an oven can be purged with a dry inert gas such as Nitrogen, this is the preferred method [9]. Dehydration baking can be done at various temperatures. Each temperature achieves different levels of dehydration. From 150-200°C surface water molecules are removed. At around 400°C loosely held water of hydration is released, and total dehydration is achieved at 750°C. Baking at 750°C is not always practical however, because temperatures that high will also affect other materials that may be on the wafer as well as dopant mobility within the wafer. The most common temperature range used is the low range because it is easy to implement and maintain the hot plate or oven equipment that can obtain these temperatures. However, regardless of how well the dehydration process is carried out as soon as the substrate is exposed to the ambient atmosphere, which inherently contains moisture, water will adsorb on the surface rendering it at least partially hydrophilic [8]. The best way to assure a compatible surface for the resist to is to deposit an intermediate priming layer that chemically modifies the surface to ensure good adhesion of the resist [10].
Wafer Priming

The most common primer used is Hexamethyldisilazane (HMDS), \((\text{CH}_3)_3\text{Si-NH-Si(\text{CH}_3)}_3\). As seen in Figure 2.5, HMDS chemically reacts with the surface water to create gaseous \(\text{NH}_3\), oxygen, and inert hexamethyldisiloxane which attaches to the surface oxide and creates an inert hydrophobic surface that is preferable surface for the resist to adhere to [8]. There are two main methods of applying the primer: spin priming, and vapor priming. Spin priming has the advantage of being integrated into lithography wafer track coating systems. With this method, the primer is applied in much the same way as resist is applied and is discussed in the next section. The vapor priming method has two advantages. The first is that because liquid is not being directly applied to the surface, contaminants are reduced. The second is that there is a reduction in waste with this method.

Figure 2.5: HMDS application to substrate surface to create a hydrophobic surface [8]
As was seen in Figure 2.5, primers are only meant to be one monolayer thick. The spin-on application results in most of the material being cast off the edge of the wafer and ending up as waste.

**Resist Application**

The goal of the resist application step is to reproducibly create a thin, uniform, defect free film of resist on the wafer surface [8, 11]. Typical resist layer thicknesses from 0.5 to 1.5 µm are common in microelectronic processing [10]. Although numerous methods have been investigated, spin coating has been the most effective method for achieving these results. With this technique, resist is spread across the wafer into a thin uniform film by the centrifugal force acting on it as the substrate rotates at high velocity (typically 2000-6000 rpm) [8].

There are three basic variances of the spin coating technique. All of which differ in the conditions under which the resist is dispensed onto the wafer surface. These methods are: static dispense, dynamic dispense, and moving arm dispense [10].

**Static Dispense**

With this method, the resist is first deposited in a small puddle in the center of the substrate while it is stationary. Once the appropriate amount of resist has been dispensed,
the wafer is accelerated quickly to the necessary spin speed and this speed is maintained until the desired thickness has been reached. This method, depicted in Figure 2.6, produces the least uniform film.

![Figure 2.6: Static dispense resist application method](image)

**Dynamic Dispense**

In this approach, depicted in Figure 2.7 the wafer initially rotates at a slow speed (approximately 500 rpm) during the dispense of the resist. This initial rotation helps to spread the resist evenly over a larger area of the wafer. After the resist is deposited the spin speed is ramped up quickly to the final speed necessary to achieve the desired film thickness. This approach requires less resist and improves the thickness uniformity across the wafer as compared to the static dispense method.

![Figure 2.7: Dynamic dispense application method](image)
Moving Arm Dispense

The Moving arm method takes the approach of dynamic dispense one step further and moves the nozzle across the radius of the wafer while spinning it slowly during dispense of the resist. This is depicted in Figure 2.8. Because this method provides the most uniform initial resist layer, it also provides the most uniform final layer of the three methods.

![Figure 2.8: Moving arm dispense application method][10]

Film Thickness

The thickness and uniformity of the final film is a function of many variables, as shown in Figure 2.9. The two dominant variables are the spin speed (ω) and the viscosity of the fluid, which is a component of the flow rate (Q).
Figure 2.9: Fluid dynamics of photoresist during spin coating [8]

Figure 2.10, a graph of spin curves from the Shipley S1800 series photoresist data sheet [12], illustrates this. The S1822 formulation has the highest viscosity of the group, and as such, results in the largest thickness value. The S1805 formulation has the lowest viscosity and the film thickness achieved by spinning it is the lowest. It can also be seen by this figure that slower spin speeds produce thicker films than faster spin speeds. The relationship between resist thickness and spin speed is obviously nonlinear. Films of specific thickness can be estimated with manufacturer’s data such as this, and then refined by adjusting the resist type, spin speed, and spin duration.
Soft Bake

After wafers are coated, they are subjected to a heating step to drive out solvents left in the film. Since the only function of resist solvents is to keep the resist fluid enough to spin out to a thin layer on the substrate, they are no longer necessary, and in fact become a liability in the success of the lithography process.

Because the solvents are very volatile, much of the solvents in dispensed resists evaporate during the deposition. However, the film remains sticky due to the remaining solvents and as such the solvent content of the film needs to be brought down to about 5% so that airborne particulates don’t get caught in this sticky film [8]. The most common method of soft baking is with a hot plate. Convections ovens have also been used for soft baking; however because of the uniform temperature of an oven, a resist “crust” tends for form on the surface which restricts solvent...
evaporation [10]. Infrared and microwave methods have also been used, however they are much harder to control [13]. Hot plate soft baking is effective because it creates a temperature gradient from the bottom of the wafer, where the hot plate makes contact, to the top of the resist, which prevents this crust formation and allows effective evaporation of the solvent.

Soft baking is also important for other aspects of the lithography process. First, the soft bake process improves the adhesion of the resist to the substrate by thermally relieving the shear stresses in the film that are created during the spinning process [8]. Secondly, it prevents contamination of the optics in the exposure tools in the subsequent exposure step. As the wafer is exposed the resist film heats up as it absorbs the light energy. If there is excess solvent in the film, it will outgas and coat the exposure optics [9]. Thirdly, driving out the solvent and creating a solid film before exposure will prevent the mixing of the exposed products with the unexposed zone after exposure [13]. Lastly, forcing out the excess solvents will slow down the dissolution of the unexposed resist during the development process. Figure 2.11 shows an example of this [13]. It can be seen that the dissolution rate \( R_0 \) of unexposed resist is faster for the lower soft bake temperature than the higher temperature.

![Figure 2.11: Dissolution rates of unexposed \( R_0 \) of DQN resist after soft baking at different temperatures [13]](image)
Alignment and Exposure

After the solvents have been evaporated away with the soft bake step, a stencil image can be transferred from the mask to the resist coated substrate. There are two main steps to this process: Alignment and Exposure. The alignment step is only necessary if there are pre-existing features on the substrate. This will be the case more often than not, because most devices are created with multiple mask steps. Successful pattern to pattern alignment is achieved with the use of alignment marks (also called targets, or registration marks). Figure 2.12 shows an example of some typical alignment mark structures. The substrate is moved in the x, y, and θ directions so that the alignment marks on the substrate fit either inside, or around the alignment marks on the next layer to be imaged.

Figure 2.12: Alignment mark structures [14]

If the alignment procedure is not done correctly, the layer to be imaged will not be positioned correctly with respect to the features already on the surface. Examples of
common types of misalignment can be seen in Figure 2.13: (a) is an example of misalignment in the x-direction, (b) is rotationally misaligned, and (c) is increasingly misaligned with the center of each die. This is called run-out, and is seen in alignment performed by steppers.

Figure 2.13: Common misalignments: (a) x-direction, (b) rotational, (c) run-out [10]

Once alignment has been achieved the exposure process can be performed. In general, regardless of the exposure system used, the process has one basic requirement: pass enough energy of the proper type (in our case, radiation is provided by light waves, but for other types of resists could need to be ions or electrons) through the mask’s transparent areas so that the photochemical transformations needed for the exposure process can occur throughout the entire thickness of the resist. Specifically, for positive acting resist, the energy delivered to the resist causes the exposed material to polymerize, and for negative acting resist, the exposed material is de-polymerized. The duration of the exposure is dependent on the type of resist, the thickness of that resist, and the intensity of the light used to expose the resist. For a given resist, a clearing dose, or
exposure dose, profile is given as a part of that resist’s data sheet. An example of this, from the Shipley S1800 series photoresist is shown in Figure 2.14. As can be seen, the exposure dose varies periodically with the thickness of the resist layer. Because the light intensity of exposure systems, which is defined by power per unit area (mW/cm²), is calibrated and kept constant, it is usually well known. Therefore, knowing the exposure dose, and the light intensity, the exposure time can be calculated for a given film thickness.

![Figure 2.14: Exposure dose vs. photoresist thickness for Shipley S1813 resists](image)

Figure 2.14: Exposure dose vs. photoresist thickness for Shipley S1813 resists [12]

Two types of alignment and exposure systems were used during this project, a contact aligner, and a step and repeat aligner (stepper). Although there are other types of optical aligners, they were not used and therefore will not be discussed.
Contact/Proximity Aligner

Until about the mid 1970’s the contact/proximity aligner was the workhorse for the semiconductor industry. On a system such as the one in 2.15, the resist coated wafer is placed on a stage that has a vacuum chuck to hold the wafer in place from the back side, as well as X, Y, Z, and θ movement capabilities. In contact mode, the wafer is placed in direct physical contact with the mask plate. In one way, this is beneficial, as the mask and wafer cannot get any closer, which can produce good image resolution [15]. The drawbacks of this mode are the physical stresses placed on both the resist and the mask. Contact mode can damage the resist, the mask, or both if either of them is contaminated with particulates. Any dirt that adheres to the clear portions of the mask will block light during exposure. Because of this, production contact masks require frequent cleaning and replacement [10].

Figure 2.15: Contact/proximity aligner system [15]
To alleviate the problem that contact and contamination bring to this type of system, the proximity mode can be used. Using the Z direction motion control, a very small gap can be created between the mask and the wafer. This eliminates some of the physical contact concerns while maintaining good resolution.

This type of system has a number of inherent drawbacks. First is that it is a very manual system, and as such there are always going to be operator associated defects. Secondly, because the entire wafer is exposed at the same time, any non-uniformity in the light intensity across the wafer will cause non-uniformities in the resultant exposure [15]. Lastly, contact/proximity alignment systems are typically only good for making very large features. Submicron resolution is possible with the proper resist and a well tuned and controlled process.

**Step and Repeat Aligner**

The step and repeat aligner (commonly referred to as a stepper) alleviates the problems associated with contact/proximity aligner systems. As its name suggests, the exposure operation is repeated across the wafer, exposing only small areas of the substrate at any one time. This methodology can be seen in Figure 2.16. The UV light source passes through a mask of a single die, called a reticle, whose features are up to 10 times larger than the pattern on the wafer [15]. The light that passes through the reticle gets reduced
through a reducing lens. Once an area of the wafer has been exposed with the reticle pattern, the wafer is moved and the next image is exposed adjacent to the previous image.

Steppers correct for the disadvantages of contact/proximity aligners in a number of ways. First, because the exposure area is only a small portion of the wafer (4 mm x 3 mm in Figure 2.16), the problem of light intensity uniformity across the entire wafer is eliminated.

![Figure 2.16: Stepper exposure method [15]](image)

Secondly, because the master pattern on the reticle is many times larger than the resulting image on the wafer, the effect of any dust or particulates that happen to be on the reticle are minimized as their image is shrunk in the reduction lens. Thirdly, because each exposure area must be aligned individually, the alignment must be done by machine. Die-by-die alignment by hand is not possible at a production rate [10]. Due to this is the
benefit that alignment is much more accurate. In addition to this, the alignment can be more accurate within the small exposure area of a stepper than it can be across an entire wafer, which is the situation in the case of contact aligners.

**Post Exposure Bake**

After the wafer has completed the exposure step, it enters the post exposure bake (PEB) step. This step is a necessity in order for chemically amplified DUV resists to catalyze critical resist chemical reactions. Resist manufacturers include recommended time and temperature specifications for PEB in their product data sheets [16].

The PEB step is utilized for different reasons in the case of conventional UV resists. Unlike DUV resists, which require the PEB to finish the creation of soluble resist regions, the PEB step is used to improve adhesion and reduce standing waves in UV resist. Standing waves are produced when the wafer exposed has a reflective surface under the resist layer. This surface reflects the UV light back up through the resist, and depending on the thickness of the resist, constructive and destructive interference is created with the reflected light and the incident light. This phenomenon is shown in Figure 2.17.
An example of the resultant resist features are shown in Figure 2.18. The constructive and destructive interference pattern is distinctly visible in this resist, which was not subjected to the PEB process before developing.

The standing wave effect is reduced by the PEB process by providing thermal energy so that the photoactive compounds in the unexposed regions of the resist can diffuse into the exposed region, reducing the amplitude of the standing waves through what is essentially an averaging effect on the standing wave boundary.
Develop

Both exposed and unexposed areas of the resist are soluble in developer solutions. However, the exposed areas dissolve much faster. The objective of the development step is to completely remove the exposed resist regions (for positive tone resists) while minimizing the dissolution of unexposed regions and doing this in a reproducible, controlled manner [18]. The goals of an effective development process include: a) the original film thickness of unexposed resist should not be measurably reduced during development; b) the development time should be as short as possible; c) development should cause minimum pattern distortion or swelling; and d) specified pattern dimensions should be precisely reproduced [8].

In the case of both positive and negative resists, the develop process consists of three main steps: washing the substrate with a developer solution; rinsing the substrate; and drying the substrate. The first step dissolves the uncrosslinked resist in the developer. The second step is used to stop the first process. This step is necessary because even the crosslinked resist is soluble in the developer, but it dissolves away at a much slower rate than the uncrosslinked areas. In order to achieve the desired feature sizes, stopping the dissolution process immediately after the uncrosslinked areas have been removed is warranted. The rinse step also ensures that the now open areas of the resist are free of any partially polymerized pieces of resist debris. The last step is to dry the wafer so that it is ready for further processing.
Developing and rinsing are usually done in one of three ways: immersion, spray, or puddle processes. Immersion processes are the oldest, simplest, and require the least complicated equipment. In this process, shown in Figure 2.19, a wafer (or cassette of wafers) is completely submerged in a solution of the developer chemical. Once the wafer has been in the developer long enough for it to dissolve the unexposed resist, it is moved to the rinse tank where it is submerged in the rinsing agent. After the wafer has been sufficiently rinsed, the wafer is then dried.

![Figure 2.19: Immersion development [19]](image)

There are many disadvantages to immersion development. Contamination can occur and process control is difficult [19]. This method of development has been largely replaced because of these issues. Instead, single wafer based spray and puddle development are used. In single wafer spray development systems, the developer is sprayed onto a spinning wafer, and each wafer is treated with fresh solution. In puddle development systems, as can be seen in Figure 2.20, a fixed amount of developer is dispensed onto the surface of the wafer. This amount is carefully measured so that a meniscus of developer forms on the wafer surface immersing all of the resist while minimizing wetting the
backside of the wafer. After the required dwell time the develop action is stopped by rinsing the wafer with a stream of deionized water. A spin dry step follows the rinse [8].

Regardless of the equipment used, the process needs to be carefully controlled in all aspects. The developer temperature is monitored and maintained because temperature variations in the solution will affect the reaction rate of the develop process.

![Figure 2.20: Puddle development [16]](image)

The develop time is monitored so that underdevelopment or overdevelopment is avoided. The developer volume is monitored so that enough is dispensed, but not too much. If too little is dispensed, there will not be enough fresh product to completely develop the wafer. If too much is applied, the unused developer is discarded as costly waste.
The chemicals used to perform the development depend on whether the resist used is a positive acting resist or a negative acting one. Positive resists are most commonly developed using tetramethyl-ammonium hydroxide (TMAH). A 0.26 N solution is a standard normality for this developer for its high selectivity to the exposed resist. Another benefit of TMAH is that the rinse chemical for it is deionized water. The developer for negative resists is typically an organic solvent such as xylene. After the development, the rinse is done in another organic solvent. For the case of xylene, the solvent is n-Butylacetate. In terms of development, the most significant drawback to negative resists is resist swelling due to the absorption of the developer during the wash. Because of this, negative resists aren’t suitable for geometries below about 2 microns [16].

**Post Develop Inspection**

The purpose of this step is to insure that the steps of the lithography process up to this point have been performed correctly. This is one of the few processes where the rework of rejected wafers is possible. At this point, if a wafer is rejected, the photoresist can be easily removed and the wafer can be reinserted into the lithography process. Some of the aspects of the resist process that are monitored are a) correct mask has been used; b) resist is free from contamination, scratches, bubbles, striations, etc.; c) image quality is adequate (i.e. good edge definition, linewidth uniformity, indications of bridging); d) critical dimensions are within the specified tolerances; e) defect types and densities are recorded; f) registration is within specified limits [8].
Hard Bake

After a wafer has undergone and passed the post development inspection process, it can now be hard baked (also referred to as a post-development bake). This is done to evaporate any remaining solvent, developer, and water that remain in the photoresist. Once the resist has had all of its liquids driven out by the hard bake, it is at its most dense. This resulting film will have the best etch resistance at this point. Better adhesion can also be achieved during the hard bake, however, the opposite might happen if the hard bake temperature is too high, and the heat ruptures the resist bond to the wafer. For this step, the hard baking temperature can be raised higher than the soft bake temperature. The upper limit of the hard bake temperature is dependent on the specific resist being used. In addition to avoiding the temperatures that will result in decreased adhesion, a temperature characteristic of the resist, called the glass transition temperature must also be avoided. This is the temperature at which the resist polymer material begins to soften and can begin to flow and deform the pattern. Although the time and temperature of a hard bake process should be determined experimentally, guidelines may be given as a part of the data sheet for the resist being used, as shown in Figure 2.21, which is from the Shipley UV5 resist data sheet.
The equipment used for soft baking can also be used for hard baking. As with the soft bake step, the preferred method is a hot plate, as it can be easily incorporated into existing automated systems.

**Final Inspection**

Final inspection occurs after the hard bake process to assure that the patterns on the wafer have not changed due to the hard bake process. This step is necessary to assure that the wafers leaving the lithography area for permanent physical changes, through processes such as etching, deposition, or doping, are patterned correctly. Although the resist has been hardened and is more difficult to remove, it is still possible to take it off and repeat the lithography. This is the last opportunity to make this decision.
2.3 Photoresist Components and Properties

Negative and positive photoresists designed for the semiconductor industry were first introduced in the late 1950’s. Initially by Eastman Kodak, then later by the Shipley Company [10]. In the semiconductor industry the resist is seen to perform two roles in the lithography process. First it must respond to the exposing radiation in such a way that the mask image can be replicated in the resist. Second, the remaining areas of resist must protect the underlying substrate during subsequent processes. Therefore, it is easy to see how photoresist got its name: “photo” for its ability to be changed by radiation or light, and “resist” for its ability to withstand the processing steps it will encounter [8].

Resists are classified by two broad categories: positive resists, and negative resists. Positive resists are insoluble in their intended developers until they have been exposed. Oppositely negative resists are soluble in their intended developer until they are exposed, after which they become soluble [21]. Resists can also be categorized by the type of radiation needed to expose them. These groupings are: a) Ultraviolet (UV) resists; b) Deep ultraviolet (DUV) resists; c) X-ray resists; and d) e-beam resists. Ultraviolet resists are sensitive to wavelengths in the 300 to 450 nm range. Deep ultraviolet resists are sensitive to wavelengths in the 193 to 248 nm range, as can be seen in Figure 2.22. X-ray resists are sensitive to wavelengths less than 100 nm. E-beam resists are sensitive to focused beams of electrons. These categories can also be looked at from the point of view of feature size, since the size of the wavelength of the radiation used will be around
the same size as the smallest features being created [9]. For our purposes, since only UV and DUV resists were used in this work, those will be the only resists discussed.

Ultraviolet resists are engineered to respond to one of three distinct wavelengths of UV light. These wavelengths are identified in Figure 2.22 as g-line, h-line, and i-line as being 436nm, 405nm, and 365nm, respectively. Why these particular wavelengths were chosen can be seen in Figure 2.23, as they are the wavelengths of highest intensity that can be generated with a mercury vapor arc lamp, a common UV light source.

Figure 2.23 also shows the DUV wavelength of 248 nm, and it can be seen that the relative intensity of the 248 nm peak is 80% less than that of the g, h, and i-line resists. In order to expose a resist with 248 nm light, the exposure time would have to be much longer than an equivalent exposure with, say, an i-line resist.
Because of this, DUV light sources are laser systems, which produce high intensity light over a very narrow spectrum, as shown in Figure 2.24.

Photoresists have four main ingredients: polymers, solvents, sensitizers, and additives. The polymers are large, hydrocarbon molecules. These are the materials that are intended to provide the process resistance of the resist. The solvents are used to thin out
the resist so that it can be easily applied. The sensitizers provide the photosensitivity of
the resist material. The specific material chosen as the sensitizer is based on what
wavelengths will be used to expose it. The additives category is a catch-all category that
includes chemicals to fine tune the properties of the resist. The materials in this category
can be surfactants, dyes, leveling agents, or any other material needed to achieve the
desired process results [10]. Although resist additives are usually proprietary chemicals,
much is known about the basic composition of the polymers solvents and sensitizers.
These materials differ for UV and DUV resists, and will be discussed individually. Since
positive tone resist is by far the most common, and the only tone resist used in this work,
it will be the only category discussed.

**UV Positive Resist Chemistry**

The polymer utilized in almost all UV resists is a phenol-formaldehyde polymer
commonly called novolak, an example of which can be seen in Figure 2.25.

![Novolak resin (ortho-ortho coupling arrangement) [22]](image)

Novolak is soluble in aqueous basic solutions such as NaOH, KOH, or tetramethyl
ammonium hydroxide (TMAH) in water.
Diazide napthaquinone (DNQ) is an insoluble material in these same solutions. DNQ, however, is photosensitive and converts to indenecarboxylic acid, which is soluble in the aqueous basic solutions through the process shown in Figure 2.26.

When sufficient quantities of novolak resin and DNQ are mixed, the resultant compound dissolves at a very slow rate in basic solutions. Once the compound has been exposed to UV light and the DNQ converted to indenecarboxylic acid, both the novolak and indenecarboxylic acid are soluble in basic solutions [21].

![Diagram of the photo induction rearrangement of DNQ to indenecarboxylic acid](image)

Figure 2.26: Photo induced rearrangement of DNQ to indenecarboxylic acid [21]
DUV Positive Resist Chemistry

The use of novolak resins and DNQ sensitizers in the DUV (193-248 nm wavelength) range was found to be problematic. The reason for this is that the absorbance of those materials in the DUV range is out of proportion. This can be seen in Figure 2.27 where, in the 200-300 nm wavelength region, the absorbance of the novolak (denoted by N), is higher than the DNQ (denoted DQ) in some areas and in all areas the novolak will end up absorbing some of the light energy delivered to the film. In contrast to the i-line and g-line spectrums where these resist were meant to operate, they are not very efficient in the DUV regime. In addition to that, as was seen in Figure 2.23, the intensity of the light in that region of the mercury lamp’s spectrum is much less than in the UV range. Because of these factors, different materials had to be developed.

Figure 2.27: Absorbance spectrum for novolak and DNQ [22]
This problem was solved with the invention of chemical amplification. In this strategy, which can be seen in Figure 2.28 the resin polymer, which is soluble in its intended solvent, is surrounded by a protecting group. The photoactive compound in the resist is a material called a photoacid generator (PAG). Upon exposure to the appropriate wavelength of light, the PAG produces an acid that, with the addition of the heat from a post exposure bake process can cleave the protecting group from the polymer backbone, rendering it soluble [21].

Figure 2.28: a) Cleaving of protecting group by PAG and, b) examples of PAGs [21]
Chapter 3

Overview of Liquid Source Misted Chemical Vapor Deposition

The LSMCD process was developed by McMillan et al. and patents for it were granted in 1992 [23] [24]. The original name given to the process in these patents was Liquid Source Chemical Vapor Deposition (LSCVD). This was not an accurate description as the materials used in the process are not gas phase chemical vapors. Therefore, the name Liquid Source Mist Deposition (LSMCD) was adopted and has been in use ever since [25].

LSMCD was initially developed by McMillan, et. al. as an alternative deposition method for compound materials such as ferroelectrics and high dielectric constant (high-k) materials. The motivation behind the development of this process was the need for a method of depositing these types of materials that produced better films than the conventional spin-on (or sol-gel) method. The spin-on method of applying thin films of high-k materials is well known and widely used. It is similar to the spin-on application of photoresist discussed in Chapter 2. This method is easy to implement due to its similarity to photoresist spin coating, the accessibility of spin coating equipment, and the ease of integration of spin coating equipment into the manufacturing process.
The need for high-k materials is fueled by the demand for ever smaller transistors for integrated circuits. Of particular interest in the miniaturization of transistors is the Metal/Oxide/Semiconductor (MOS) gate stack of MOS Field Effect Transistors (MOSFETs). The gate stack, regulates the current flowing from the source to the drain of a MOSFET. The gate stack as seen in Figure 3.1 is essentially a capacitor.

![Figure 3.1: MOS capacitor [26]](image)

The top electrode of the capacitor is a conductive film such as a metal or doped polysilicon. The insulator has traditionally been made of silicon dioxide, and the bottom electrode of the capacitor is the doped silicon wafer. The value of this capacitance is calculated with the equation.

\[ C = \frac{k\varepsilon_0 A}{t} \]

Where:

- \( C \) = Capacitance
- \( k \) = dielectric constant of the insulator
- \( \varepsilon_0 \) = Permittivity of free space
- \( A \) = Area of the insulator
- \( t \) = Thickness of the insulator
When the lateral dimensions of the device decreases, the area of the insulator will decrease and therefore, the value of the capacitance of the gate stack will also decrease. When this happens, the value of voltage that must be applied to the gate stack to turn the transistor on and off will change. In order to keep this from happening, so that the external supply requirements do not need to change with every reduction in device size, the capacitance value is kept constant by also reducing the thickness ($t$) of the silicon dioxide layer.

As devices continue to shrink, the silicon dioxide insulator in the gate stack has become so thin that both performance and manufacturing problems have arisen. According to the International Technological Roadmap for Semiconductors (ITRS), the thickness of oxide layers used was into the 1.0-1.2 nm range [27] in 2007. From the standpoint of manufacturing, it has become difficult to grow thin uniform layers of silicon dioxide on the wafers. According to The ITRS, this has been one of the most challenging areas for future device scaling, and the ITRS reports and updates have been anticipating the need for substitute gate materials for many years. This is because we are approaching the lower limits of growing effective silicon dioxide. A monolayer of silicon dioxide is only 25 Å thick, and it is necessary to have at least 5 monolayers (a 1.25 nm film thickness) for a functional oxide: one monolayer each on the metal and semiconductor interfaces and three monolayers are needed for the thin oxide film. From the point of view of electrical performance, tunneling of electrons through the gate stack is much more prevalent in thin oxide layers.
In order to resolve these problems, the use of high-k dielectrics (materials with $k$ values larger than that of silicon dioxide) is a favorable alternative to silicon dioxide. Since the decrease in the area of the dielectric will be offset by the increase in $k$ value of the new materials, we can avoid the physical constraints that are becoming a reality in the ability to grow thin enough gate oxide.

The materials looked at to fill this role have mainly been compound metal oxides. Because of the complexity of these films, they are difficult to deposit with traditional thin film techniques such as magnetron sputtering, low pressure chemical vapor deposition (LPCVD), or Plasma Enhanced CVD (PECVD). The only viable option has been the spin on process. The source material is a fluid mixture that contains the compound of interest in a solvent. Once it has been spun on, the solvent is evaporated out, and if the desired thickness has not been attained, the process is repeated. Once the thickness has been reached, the film is annealed to create a continuous film from the multiple layers.

The spin on method, although the most easily implemented of the deposition options, has drawbacks. Namely, greater defect density, poor step coverage, and poor thickness uniformity. The reason behind the development of the LSMCD process was to take advantage of the already existing liquid precursors available and deposit them in a way that produces a more suitable thin film than the spin-on method provides [25].
Figure 3.2 shows the LSMCD process equipment developed by McMillan et al., and used for the deposition of high-k dielectric materials.

This apparatus consisted of a deposition chamber, a nitrogen inlet for chamber venting and purging, and an inlet for the deposition material. The deposition chamber is made to hold high vacuum so that it could be evacuated and backfilled with a known pure gas (such as N₂), and contains a rotating wafer stage, a semicircular inlet and outlet for the deposition material each with equally spaced holes to promote a laminar flow of material across the wafer. The chamber also contains a top plate to direct the material to the wafer surface and prevent it from filling the entire chamber. Lastly, the chamber contains a UV lamp which aids in water desorption from the chamber before the deposition, and can improve the deposition of some UV sensitive precursors [23]. The material inlet is
connected to an argon source, which is the carrier gas for the mist particles, and an ultrasonic nebulizer which turns the liquid material into a mist. The nebulizer for this system operates at 1.65 MHz and creates droplet sizes of less than 1µm. Because of the higher frequency of operation of this transducer, the system can achieve smaller particle sizes and therefore differentiate itself from spray techniques which use transducer frequencies of 100-150kHz, to create droplets of several tens of microns in size. This apparatus was used for the deposition of many types of ferroelectric and high-k dielectric films [29] [30], [31].

The second type of LSMCD system, shown in Figure 3.3, is a variant of the original design and has a number of differences in both the chamber and the material delivery subsystems. This is the type of system configuration used for the experimental work presented in chapter 4.

In the process chamber, the delivery of material is done from the top, perpendicular to the wafer surface. This is different from the side entry of the earlier system that necessitated flow of the material parallel to the surface. This perpendicular arrangement allows for a more uniform material flow to the surface. This system also utilizes a shower head to evenly distribute the material across the diameter of the wafer. Instead of a UV lamp for chamber and substrate heating, this system uses resistive heaters attached to the exterior of the chamber. Lastly, the system places a bias on the wafer through a power supply connected to the pedestal, and grounds the chamber with a field screen to attract the material to the wafer.
This is needed because the mist droplets are so small that gravitational effects on the droplets are negligible, and the electric field is necessary to attract the misted source material to the surface. The mist generation and delivery method is also different than its predecessor. This system does not use argon as the delivery gas. Instead, it uses high purity nitrogen for all process related gas needs. Low pressure nitrogen is used to force the liquid precursor into the atomizer. The atomizer, which is fundamentally different from the nebulizer of the previous model, uses high pressure jet of nitrogen to initially break apart the precursor, and subsequent impactors to break the droplets down further before reaching the delivery tube to the chamber. Mist droplets that are too large are filtered out of the mist by gravity, and collect at the bottom of the atomizer.
Chapter 4

Process Development and Characterization

This chapter discusses the results of developing the process for LSMCD deposition of photoresist and the characterization of the resultant deposition process. The goal of this work was to create a useable photoresist film on a substrate. A number of technical challenges presented themselves along the way as roadblocks to achieving this goal. Each of them had to be resolved in succession in order to continue. The first roadblock was that of the quality of the deposited film itself. It is known that the LSMCD process works when depositing metal oxides, but photoresist materials are much different. The question to be answered then, was could this method repeatedly and reliably deposit a photoresist film. Once that issue had been resolved, it would be necessary to determine if these films were still photodefineable. If it is possible to consistently create photodefined films, the next issue to resolve is if the deposition process is controllable with the available physical variables such as flow rate, voltage, temperature, etc. If it is possible to control the process, the last issue to be resolved is whether or not it can be done with other photodefinable materials. The experiments and results presented in this chapter will illustrate how these challenges were addressed.

The substrates used in this study were prime grade, 150 mm (6 in.) dia., <100> orientation, p-type silicon wafers. Prior to use, wafers were cleaned using an SC1/SC2
silicon cleaning sequence as described in Figure 2.4. After the cleaning process, approximately 1100 Å of oxide was grown on the wafer surface. This was done to protect the wafer surface from further contamination until it was used. Oxide protection was a procedurally necessary step. The SC1/SC2 process lends itself to batch processing, so it was more efficient to clean a batch of wafers instead of one at a time as needed. Because the deposition process is a single wafer process, the time between cleaning and use could be lengthy, thus growing an oxide layer on the surface prevents the clean surface from coming in contact with contaminants while it is waiting to be used.

Immediately before use, wafers were stripped of their oxide in a 10:1 buffered oxide etch (BOE) solution, then rinsed with DI water, and baked on a hot plate at 150°C for 5 minutes in ambient air to remove surface moisture.

Two types of photoresist were used in this study: 1805, and UV-5, both from Shipley Microelectronics. For a majority of the experiments, 1805 was used. This resist is relatively inexpensive and widely used in the university community for common lithography processes, so its behavior is well known. UV-5 was chosen as a second resist to test after acceptable results were achieved with 1805. It was chosen because it is functionally different. This resist is used in stepper lithography to create smaller features than can be made with the 1805 resist.
4.1 Process Development

Before beginning the work of developing a mist deposited resist film, the Shipley 1805 resist was deposited using the traditional spin on method and patterned. This was done so comparisons could be made when patterned mist deposited resist was created. Starting with a clean and dry wafer, the process for depositing and patterning this resist is as follows:

- Apply HMDS and spin on at 4,000 rpm for 40 seconds
- Apply 1805 resist and spin on at 4,000 rpm for 40 seconds
- Soft bake at 115°C for 60 seconds
- Expose resist for 1 second using Karl Suss MA-6 Contact aligner
- Developed in 1:1 solution of DI Water: MF312 Developer for 45 seconds
- Hard baked for 5 minutes at 125°C

Figures 4.1 and 4.2 show the resultant film. Figure 4.1 shows that the resultant pattern is clean and defect free; however the higher magnification image shows that it has been slightly overdeveloped, as can be seen at the undercut edges around the feature. The profilometer scan in Figure 4.2 shows that the edge of the feature is closer to 0.4 µm thick and increases towards 0.5 µm the further the scan progresses in towards the bulk of the photoresist.
Figure 4.1: Optical microscope images of patterned 1805 photoresist at 10x (left) and 50x (right) resolutions

Figure 4.2: Profilometer scan of patterned 1805 resist

**Development of Mist Deposited Resist Films**

As a starting point, the first misted resist deposition was performed using process conditions similar to those used in the deposition of metal oxide films. Shipley 1805 was
used as the source material. The pressure of the nitrogen gas used in the atomizer was 70 psi, the chamber pressure was set at 730 torr, the bias voltage of the wafer was set to 3 kV. After depositing for 3 minutes the sample was removed and it was observed that the resultant film was powdery in nature, and an opaque hazy green color.

Although this film looked very different than a spun on film, a film was deposited, so the decision was made to attempt to pattern it. The wafer was soft baked for 90 seconds at 90°C, and exposed to a pattern for 1 second with a Karl Suss MA-6 contact aligner. After exposure, the film was developed in a 1:1 solution of Shipley MF312 developer solution and DI water. During development, it could be seen that the exposed regions of the resist started to develop, but the unexposed regions dissolved away in the solution soon after, and the sample was not able to be taken out of the develop process quickly enough for measurable results to be left behind.

Additional trials were attempted and similar films were attained. These films were exposed and developed using various exposure times, develop times, and developer concentrations with the hopes of retrieving the sample out of the immersion development bath before the unexposed resist washed away so that measurements could be taken and characteristics such as thickness and roughness could be determined. In all cases, this proved to be unsuccessful. However, due to the development of the exposed areas first, there was indication that the resultant film was photosensitive, so process development continued in an effort to improve the film.
There are six main physical variables that can be manipulated to create different deposition conditions:

- Source material composition
- Pressure of source material supply to the atomizer
- Deposition chamber pressure
- Deposition chamber temperature
- Electrical bias on the wafer
- Deposition time

The first variable adjusted was the source material composition. It was thought that the viscosity of undiluted 1805 was too great to allow for adequate flow through the small feed tube that delivers the liquid resist to the atomizer and as a result, the mist was not being formed effectively, resulting in the powdery opaque film. Therefore, in an attempt to provide better material flow to the atomizer, and thus a better mist to the chamber, the source material was thinned. The 1805 resist was thinned using propylene glycol monomethyl ether acetate (PGMEA). The thinning agent was not expected to cause any detrimental change to the resultant mist deposited resist since it is the solvent already used to thin the Shipley 1800 series resists. The 1805 resist contains the same components as other resists in its product family: 1827, 1813, and 1811. The difference between the 1827 and the 1805 is the amount of solvent in the resist formulation. The 1805 contains more solvent per unit volume than any of the others in the family. As a result it has the lowest viscosity of the group and when spun on, the resultant film is not
as thick (0.5 µm vs. 2.7µm). Specifically, 1805 contains 83% solvent, 1811 contains 75% solvent, and 1827 contains 63% solvent.

The next experimental deposition was performed under the following conditions:

- Deposited Material: Shipley 1805 diluted in PGMEA in a 1:3 ratio of Shipley 1805 to PGMEA (which results in a solution that is 94.3% solvent and 5.7% solids by volume)
- 70 psi nitrogen gas in the atomizer
- 730 torr chamber pressure
- 3 kV substrate bias
- 3 minute deposition time

Depositions performed under these conditions still produced powdery opaque films. However it was noticed that there were areas of the film around the edge of the substrates that looked like what we would expect a spun on resist film to look like. In these small areas, the film looked smooth and coherent. It was unknown why this only occurred around the edges, or why it only occurred in small areas, but it was considered positive progress as it showed that diluting the resist made some improvement in the film.

The next variable chosen for examination was chamber pressure. The results from diluting the resist led to hypothesizing that in previous experiments, the powdery nature of the resist might be due to the solvent content completely evaporating out of the mist
before it gets to the wafer surface, which prevented the droplets from combining on the surface into a continuous film. Since the exhaust is on the side of the chamber near the sample’s edge rather than in another location, for example the bottom of the chamber, the mist must flow past the edge of the wafer to get to the exhaust. The mist that has the shortest distance to travel from chamber input to exhaust has the best chance of creating a coherent film because its solvent might not completely dry up in transport to the sample surface. In the small areas around the edge of the sample where the resist film looked better, the excess solvent used to dilute the resist was thought to be preventing the mist droplets from drying out before they reach the substrate surface.

The previous experiments were done under the slightly negative pressure of 730 torr. This was done because it was similar to the operating conditions for the deposition of metal oxides. It was decided to increase the pressure to 760 torr and keep the rest of the deposition conditions unchanged for this next experimental trial. The pressure increase is expected to increase the time it takes for the solvent to evaporate from around the solids in the mist as well as slow down the flow from input to exhaust in the chamber which will create a more solvent rich ambient environment and also slow the rate of solvent evaporation.

The film that resulted from increasing the pressure inside the deposition chamber was much improved over previous runs. Instead of the hazy, powdery film that had been produced, this one was smooth and specularly reflective in appearance and looked much more like a spun on film.
An attempt was made to pattern this film so that the thickness could be measured. Although a thickness reading could be taken with a spectroscopic reflectometer, it was decided to attempt to perform lithography on this sample instead. Because the actual composition of the film is unknown and characteristics such as index of refraction are needed to compute the film thickness, it would not have been possible to know if the resultant measurement was accurate until a collaborating profilometry measurement could be taken and the data gathered from the two measurement methods compared.

The sample was soft baked for 90 seconds at 115°C, then exposed for 1 second with the Karl Suss MA-6 contact aligner. The exposed sample was placed in a weak 1:2 (MF312:Water) developer solution so that the develop process would progress slower than normal and be controlled easier. The development process took 10 seconds, after which the sample was rinsed and dried. Figures 4.3 and 4.4 show optical microscope and profilometry pictures of the resultant film.
Figure 4.3: Optical microscope image of first LSMCD deposited resist after chamber pressure increase

Figure 4.4: Profilometer scan of first LSMCD deposited resist after chamber pressure increase
A number of conclusions can be drawn from the results shown in Figures 4.3 and 4.4. First, it is clear that in the most basic sense lithography was performed. The profilometry shows that the film was smooth but extremely thin at about 700-750 angstroms. Second, it can be seen that the resolution of the resultant lithography is poor. This could be due to a number of reasons associated with the manual nature of the processing of this sample or it could be due to the composition of the film itself. After measuring the thickness of the film, it is apparent that the exposure time was much too long, and the resist was so thin that the fine features were unable to survive the development process. As a reference, the same patterns were created using traditional lithography methods and are shown in figures 4.5 and 4.6.

Figure 4.5: Optical microscope image of the same mask used in figure 4.6, made using traditional lithography methods and Shipley 1805 photoresist
Figure 4.6: Profilometer scan of the pattern in Figure 4.5, made using traditional lithography methods and Shipley 1805 photoresist

With the previous experiment being mostly successful in creating a lithographically definable film, the deposition time was doubled for the next sample in an attempt to make a thicker film. It is anticipated that this thicker film will hold up to lithography processing better than the previous sample.

Upon visual inspection, the resultant film looked similar to the previous film. The sample was treated to the same lithography process as the previous sample. It was soft baked for 90 seconds at 115°C, exposed using a Karl Suss MA-6 contact aligner for 1 second, and then developed in a 1:2 solution of MF312 in Deionized water for 10 seconds. The resultant patterns are much improved compared to the previous sample, and the results can be seen in Figures 4.7, 4.8, 4.9, and 4.10.
Figure 4.7: Optical microscope image of LSMCD deposited resist pattern after increasing deposition time.

Figure 4.8: Profilometer scan showing film thickness of LSMCD deposited resist pattern after increasing deposition time.
Figure 4.9: Profilometer scan showing feature resolution of LSMCD deposited resist pattern after increasing deposition time

Figure 4.10: Profilometer scan showing roughness of LSMCD deposited resist pattern after increasing deposition time
Figure 4.7 shows that the patterns came out similar to what would be expected from a spin on deposited film, and the profilometry data in Figures 4.8-4.10 show that the film is approximately 1700 angstroms thick, the features patterned were about 10 µm in size, the resist roughness is in the 2 nm range and the uniformity over an 80 micron scan is about ±5nm.

4.2 Process Characterization

With deposition conditions now sufficiently tuned to create films that can be lithographically patterned, the focus of the experimentation turned to characterizing the deposition characteristics themselves. It is of particular interest to find out how the deposition rate changes as factors such as deposition time, substrate bias, and source material concentration are changed. It is also of interest to determine if materials other than bare silicon can be deposited on and if other source materials can be used. The following data is a result of 40 sample depositions under these varying conditions.

For all of the samples, the post deposition treatment was the same: They were first hard baked at 150°C for 5 minutes then their thickness was analyzed using a nanometrics nanospec AFT 200. The AFT 200 is a spectroscopic reflectometry tool that can measure the thickness of various types of films including silicon dioxide, silicon nitride, and both positive and negative tone photoresist. The accuracy of the measurement data generated by the nanospec was verified by comparing profilometry scans and nanospec measurements of patterned samples. It was determined that the nanospec measurements
correlated sufficiently. This allowed the deposited film thicknesses to be measured without the need for the lithography step. Hard baking the unpatterned films was done so that all of the solvents content was driven out of the deposited films and the only material left was the photoresist solids, regardless of the amount of solvent used in the delivery system. The thickness of the film on each sample was measured in 9 places as shown in Figure 4.11.

Figure 4.11: Position of measurement points taken on each sample

The first variable investigated was deposition time. The remaining deposition parameters for these films were:
• Deposited Material: Shipley 1805 diluted in PGMEA in a 1:4 ratio of Shipley 1805 to PGMEA (which results in a solution that is 95.75% solvent and 4.25% solids by volume)
• 70 psi nitrogen gas in the atomizer
• 760 torr chamber pressure
• 4 kV substrate bias

As shown in Figure 4.12, the thickness of the film varied linearly with deposition time. Using the linear relationship shown here, the thickness of resist mist deposited under constant conditions can be reliably and accurately predicted. It was determined that photoresist films in the thickness regime below < 50 nm can be readily formed by mist deposition in a controlled and reproducible manner. Thickness variation of less than 2% across the wafer was achievable for wafers with a resist thickness of about 100 nm. However, to achieve this level of uniformity in a reproducible fashion it was important to maintain the shower head assembly inside the deposition chamber free from the residue of resist. This was accomplished by cleaning parts of the chamber interior after every ten to twelve deposition runs.
The next characteristic examined was the deposition rate dependence on resist dilution. The minimum amount of dilution required is of interest because it has already been determined that undiluted Shipley 1805 photoresist will not produce an acceptable film. Performing depositions with various dilutions will aid in determining both the extent to which the resist needs to be diluted and still creates a good film, and the impact those dilution levels have on deposition rate. For these samples, the ratio of Shipley 1805 resist to PGMEA was varied and the remaining deposition parameters were kept the same as the previous time dependency experiment. The deposition time was held constant at 6 minutes for each sample. The trend line in Figure 4.13 shows that deposition rate decreases slightly as the ratio of thinner to resist increases, but relative to the deposition and measurement error of each series of runs, the effect of dilution on the deposition rate is considered to be minor.
The next characteristic investigated was the deposition rate as a function of DC bias on the sample. As indicated earlier, the mist deposition process allows for control of the deposition rate by an electric field applied between the wafer and field screen. As shown in Figure 4.14, the deposition rate of 1:4 diluted 1805 resist can be varied from about 10 nm/min to about 50 nm/min depending on the DC bias. Figures 4.15-4.17 show similar results for other levels of source material dilution.
Figure 4.15: Photoresist deposition rate vs. wafer DC bias for 1:3 diluted Shipley 1805 Photoresist

Figure 4.16: Photoresist deposition rate vs. wafer DC bias for 1:2 diluted Shipley 1805 Photoresist
Figures 4.15-4.17 show that although slight differences exist in the resist deposition rate at each level of dilution, it is not as significant a factor as the DC bias effect on the rate. This is due to the large amount of solvent in the mist. The solvent is a polar molecule and because it is already over 90% of the volume of fluid being misted, regardless of dilution rate, it will be the main component in the rate vs. DC bias characteristic.

**Alternative Source and Substrate Materials**

The experiments discussed above were all carried out using Shipley 1805 resist. This choice was made because the Shipley 1800 family of resists is a relatively low cost material, its process conditions are well known, and performance criteria are well established. The results of these experiments show that the material can be deposited in a controllable manner and that the resultant film can be patterned. For this deposition
technique to be truly useful, it is necessary to confirm the performance of mist deposition using other types of photoresist and different types of substrates.

For an alternative source material, a deep UV resist was chosen to be deposited so that it could also be determined if the resultant film could produce submicron features. Shipley UV-5 diluted 4:1 with its solvent, Ethyl lactate, was mist deposited to form a mechanically coherent, uniform film just like in the case of the 1805 material. A Nikon NSR Stepper outfitted with a Lambda Physik KrF (248 nm wavelength) eximer laser was used to expose the film.

Figure 4.18 shows a the test pattern defined in mist deposited UV-5 resist. It clearly demonstrates adequate photochemical characteristics of the resist film. In Figure 4.19 the view is magnified to show that patterns in the half micron range were resolved, and Figure 4.20 is a higher magnification optical microscope image showing that the 250 nm features were resolved. It can be seen in those previous three images that the color of the deposited resist is not as uniform as it was with the 1805. Figure 4.21 shows a FESEM image of the 250 nm resist features showing the resist feature, the line spacing and the line edge roughness of the sample.
Figure 4.18: Test Pattern created in Mist Deposited in Shipley UV-5

Figure 4.19: Higher magnification of test pattern showing resolution performance area of test pattern
Figure 4.20: Image of pattern in Shipley UV-5 showing 250 nm features resolved

Figure 4.21: Line Width and Line Edge Roughness of 250 nm pattern in UV-5
Figure 4.22 is a profilometry scan of the patterned UV-5. From this scan it can be seen that the resist is approximately 125 nm thick, and has a surface roughness of ±5 nm. Therefore, the color variation does not seem to have an effect on surface roughness as compared to mist deposited 1805. Although the cause of the non uniform coloration is not known, as seen in this figure high quality patterns can be delineated in this mist deposited resist.

The results shown in Figures 4.20-4.22 are significant because past experiences with this particular exposure tool were such that the standard UV-5 process has produced at best 350 nm resolution features in the resist when applied in the standard spin on process, which produces a film with a thickness of 700 nm. This re-enforces the earlier observation that as the thickness of mist deposited resist is decreases, finer features are possible due to the reduction in light dispersion through the resist. This is consistent with [21] where it is stated that the best resolution is often obtained with thin resists.
Depositions were performed on three other types of surfaces: silicon dioxide and silicon nitride, and silicon with a layer of HMDS spun on it. The silicon dioxide was the same thermally grown oxide that was being used as a surface protecting layer. It was an 1100 Å thermally grown oxide. The silicon nitride was a 2000 Å layer deposited by low pressure chemical vapor deposition (LPCVD). Depositing on an HMDS layer was a necessary verification step as none of the silicon wafers in the previous experiments had an HMDS layer on them. The first alternative surface examined was the thermally grown silicon dioxide surface. Deposition was performed under the following conditions:

- Deposited Material: Shipley 1805 diluted in PGMEA in a 1:4 ratio of Resist to PGMEA
- 70 psi nitrogen gas in the atomizer
- 730 torr chamber pressure
- 4 kV substrate bias
- 6 minute deposition time

The initial deposition run resulted in a powdery and opaque film, similar to the films formed in the early process development stage. It was noticed that the entire substrate was coated with a layer of oxide. A wafer with a thermally grown oxide will have the entire surface coated in an oxide layer. The oxide layer on the back side of the wafer could be preventing the DC bias placed on the sample by the stage from providing enough of an attractive force at the sample surface for the mist to create a film.
The second deposition run was performed on a wafer whose back side oxide had been removed. This deposition was performed under the same conditions mentioned above. The resultant film was also powdery and opaque. For the final deposition run on an oxide surface the substrate had its backside oxide removed, and the front side oxide was etched away until only 350 Å was left on the surface in order to further improve the DC bias seen by the mist at the surface of the sample. The deposition conditions were kept the same as in the previous two runs. The resultant film, although improved over the previous two runs was not a coherent film, and did not compare favorably to the quality of films seen on the deposition of a bare silicon surface.

The second alternative surface examined was LPCVD grown silicon nitride. The film of silicon nitride was 2000 Å thick. For the first deposition, the process conditions were the same as those for the depositions on silicon dioxide. The resultant film was as good as the films produced on bare silicon surfaces. A second deposition was done under the same conditions to verify the results, and this run also produced a good quality film. The results obtained here further support the DC bias dependence seen on the bare silicon and oxide surface results. Since the dielectric constant of silicon nitride is almost twice that of silicon dioxide (7.5 vs. 3.9 respectively) the surface is more attractive than the silicon dioxide surfaces tested.

The final alternative surface investigated was HMDS. As stated in Chapter 2, HMDS is an adhesion promoter that is necessary to bind photoresist to substrates. For this investigation, HMDS was applied to bare silicon wafers, and then mist deposited resist
was applied under the same conditions as the oxide and nitride samples. Two depositions were performed and both resulted in good films. Film thickness were measured to be 210 nm and the deposition rate was 35 nm/min, which correlates well to similar results on bare silicon for the same deposition parameters.
Chapter 5

Summary

The goal of this work was to determine if photoresist could be deposited by the liquid source misted chemical deposition method in such a way that the resultant film was comparable in performance to a photoresist that had been spun on by traditional methods. It has been shown here that under the correct process conditions, Shipley 1800 series UV resist, and UV-5 DUV photoresist are both able to be deposited. Furthermore, it has been demonstrated that the deposition rate can be controlled through various parameters such as substrate bias, source material dilution, and deposition time. The relationship between deposited thickness and deposition time is linear and can be a means to provide a fine level of control over the final film thickness. This is in contrast to the controllability of a spun on film whose thickness must be estimated from a non linear relationship. The rate of deposition can be controlled with both the bias applied to the substrate and the dilution level of the resist. It has been shown in experiments with Shipley 1800 series resist that it can be deposited at rates from as low as 6 nm/min to as high as 58 nm/min with a roughness of around 2 nm and a uniformity of 2% of the deposited resists thickness.

It was also shown that these films are adequately photodefineable using standard lithography equipment. Films created with 1800 series resist were patterned using a Karl Suss MA-6 mask aligner. The resulting pattern was comparable to patterns created in spun on film of similar thickness. The Shipley UV-5 resist was patterned with a Nikon stepper using a KrF eximer laser. Resist features of less than 250 nm were able to be
created with this process and which is significant since the particular exposure tool had not been able to create features smaller than 350 nm before that time.

Results were also obtained when depositing on surfaces other than bare silicon. While it was not possible to deposit an acceptable film on a silicon dioxide surface, it was possible to deposit an acceptable film on a silicon nitride surface and a silicon surface coated with HMDS.

There are many options available for future work in the area of depositing photoresist materials and more generally, materials used in the pattern transfer process. There are many other types of patternable resist materials to attempt to deposit such as negative tone resists, resists that respond to other wavelengths of radiation, and electron beam resists. There are other films such as adhesion promoters, anti-reflection coatings, and dual layer resist materials that may also benefit from the LSMCD deposition process. The types substrate material that can be pattern transfer material can be deposited on can also be studied. It was shown that depositions on silicon dioxide surfaces were not successful. Developing method that can successfully deposit onto silicon dioxide will allow this technique to be useful in a number of traditional silicon manufacturing processes, and manufacturing on various types of glass substrates, which could areas such as medical device processing and display manufacturing.
References


