Background on Thin Layer imaging

(Excerpts from PhD Thesis of Mark Somervell)

1.1 Introduction to Thin Layer Imaging

Thin layer imaging (TLI) techniques have long been considered as alternatives to single layer resist technology. Schematically, they may all be represented as shown in Figure 1.1 below.

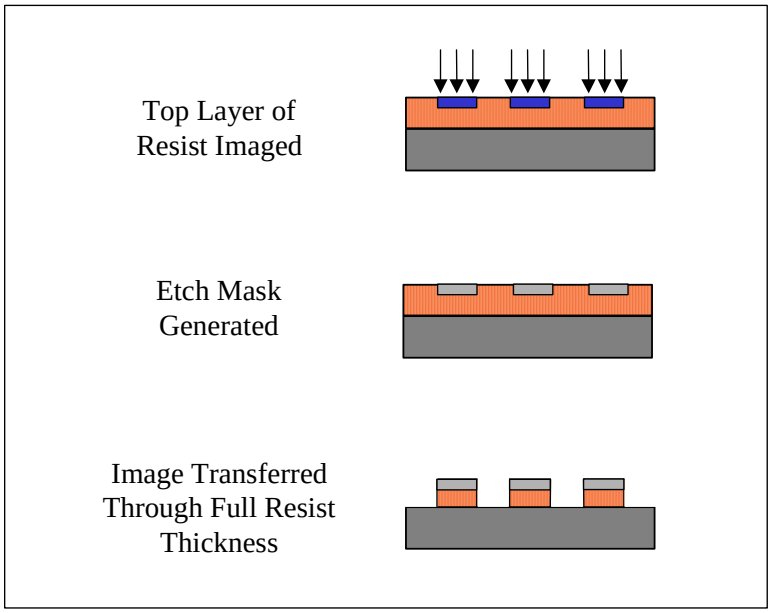

Figure 1.1: Conceptual design of thin layer imaging systems

In these systems, the uppermost layer of the resist is imaged and this image is used to create an etch mask. Finally, the images are developed using an anisotropic reactive ion etching (RIE) process.

This type of imaging scheme has several benefits. Because only the top portion of the resist is imaged, the resist may be relatively opaque at the wavelength of the exposure tool, and a larger variety of materials may therefore be used as photoresists. Additionally, no light is reflected off the silicon substrate or existing topography on the wafer. Normally, this reflected light interferes with light that is propagating through the resist to form standing wave patterns. It is undesirable to have standing waves in the resist because they make controlling the dimensions of the features difficult.[i] By eliminating the aberrations that result from reflected light, the top surface imaging lithography system theoretically allows for better linewidth control.

The next benefit of TLI processes concerns the "depth of focus." Microelectronic devices are made through the use of repeated lithography steps. As devices are built on the wafer, the wafer loses its planarization. Because of this non-planarity, the exposure

light must be focused over a range of depths in order to maintain consistent imaging. The Rayleigh criterion for depth of focus is given by the following expression:

$$Depth of\ Focus = \frac{\lambda}{2NA^2} \qquad 1.1$$

where λ is the exposure wavelength and NA is the numerical aperture of the lens. This equation shows that as the wavelength of exposure decreases, the depth of focus also decreases. Exposure at 248 nm with a 0.6 NA lens provides a depth of focus of only 0.35 μm. Clearly, even very shallow topographic features can create a focus problem. A TLI resist, however, requires only a very small depth of focus, and so it is ideal for use at lower wavelengths.

The final benefit of the TLI system lies in its ability to produce high aspect ratio images. With wet developed systems, the developer dissolves the photoresist in both the vertical and lateral directions. Even though the exposure of the resist creates a condition in which the lateral development rate is much lower than the vertical development rate, the finite lateral development rate limits the aspect ratio of the images. With a reactive ion etch, the ion etchants may be directed by an electric field so that they etch in only one direction. This characteristic leads to high anisotropy in the etch process and ultimately allows for production of very high aspect ratio images. In addition, as feature size and pitch continue to shrink, feature collapse due to capillary forces from the developer is becoming a more and more significant problem.

Despite all of these advantages, thin layer imaging techniques are used only when single layer technologies fail. Each of the TLI systems has added process complexity that increases the cost of the manufactured devices. Additionally, the TLI techniques require processing which is not traditionally associated with lithography, and consequently, companies must invest in the research and development of these technologies so that they can implement them. Nevertheless, research continues on TLI and in some specialized cases, these methods have been used industrially.

Many different approaches to implementation of thin layer imaging have been explored. Both the photochemistry and the mechanism of image transferal differ in these systems, and so a brief overview of thin layer imaging techniques is given in sections 1.2 through 1.5 below.

1.2 BILAYER LITHOGRAPHIC PROCESSES

The earliest approach to thin layer imaging was proposed by Havas and coworkers at IBM and utilized a trilayer structure to generate three-dimensional images.[ii, iii] Later, Lin developed a different TLI system termed the portable, conformable mask (PCM) process.[iv, v] These two systems were the first to use thin layer imaging concepts, and although complex in implementation, they laid the groundwork for other simpler systems. The next development in TLI processing was the discovery of bilayer resists. The functional principle of these systems is schematically depicted in Figure 1.2.

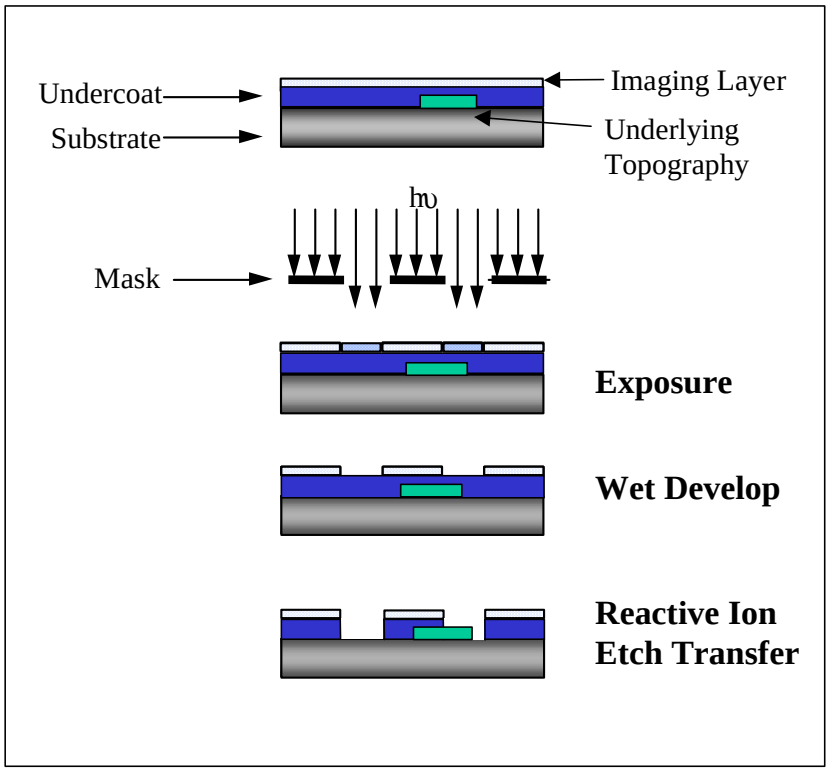

Figure 1.2: Bilayer resist schematic

In this system, a thin, silicon-containing imaging layer is coated on top of a cross-linked underlayer. During the exposure step, the imaging layer undergoes traditional single layer resist photochemistry (either chemically amplified or nonchemically amplified). For a positive resist the exposed portion of the resist becomes soluble in an aqueous basic developer. The image is then transferred through the underlayer using an oxygen RIE. The undissolved organosilicon resist oxidizes in the plasma to form a refractory oxide.[vi, vii] This oxide then acts as an etch barrier that protects the underlying material while the unmasked underlayer is etched away. By tuning the parameters on the etch tool, an etch process may be obtained that etches only in the vertical direction. Such anisotropic etching is required to transfer the image through the underlayer.

The imaging layer must have both acceptable imaging capabilities and sufficient silicon content to provide the etch contrast required for image transfer. Polysiloxane materials were the first used in this application,[viii] but since then, silicon has been incorporated into a vast array of materials including poly(methyl methacrylate) polymers,[ix, x] novolacs,[xi, xii] and sulfone polymers.[xiii] The underlayer generally possesses superb etch resistance and is chosen so that it does not hinder the imaging of the top layer. Cross-linked novolacs are commonly used for this purpose, but quite often, underlayer materials must be customized for use with the imaging material. Currently, bilayer materials for 193 nm lithography are available from resist suppliers, but 193 nm bilayer processes have not yet been implemented in a manufacturing environment, as far as we know.

1.3 THE SI-CARL PROCESS

Another two-layer scheme that has been implemented in industry is the "Silicon Chemical Amplification of Resist Lines" or Si-CARL process. A schematic of this technology is shown below in Figure 1.3.

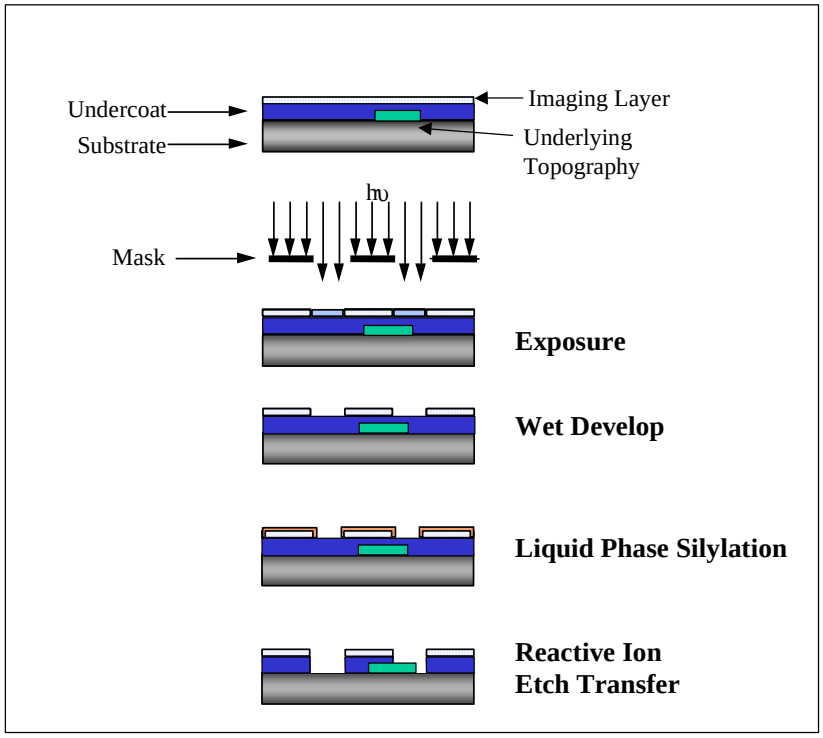

Figure 1.3: Process schematic for Si-CARL process

In this system, a thin imaging layer is again coated on top of a cross-linked underlayer. In this instance, however, the imaging layer does not contain silicon. The imaging layer is exposed and developed using traditional aqueous basic developers. The resist is then submerged in a solution of a bifunctional, oligomeric aminosiloxane.[xiv] This "CARL reagent" reacts with anhydride functionalities in the imaging layer to create a cross-linked, silicon-rich etch barrier. The image is then transferred down through the underlayer using oxygen RIE.

Although the process flow for the Si-CARL process appears to be terribly complex, it has several distinct advantages. The liquid phase silylation agent yields a silylated material with high silicon content thus improving the quality of the etch barrier. Additionally, the swelling that occurs during the silylation can be used to balance any line-width shrinkage that often occurs in the dry development step.[xv] Workers at Siemens have been able to optimize this process effectively, and it has been used extensively in the manufacturing of memory chips. This technology has proven to be flexible and has been customized for use at a variety of wavelengths. Finally, the depth of focus in this process is extremely large.

1.4 TOP SURFACE IMAGING THROUGH VAPOR PHASE SILYLATION

Unlike the TLI techniques described in section 1.2 and 1.3 above, the next type of TLI scheme utilizes only a single resist layer. Many imaging systems have been proposed that utilize this technology.[xvi-xxiv] These processes were inspired by the early work of Taylor[xvi, xvii] and are reviewed in a book chapter by B.J Lin.[v] Past TSI schemes have been described by a creative set of acronyms including DESIRE,[xx, xxi] PRIME,[xxii] SUPER,[xxiii] and SAHR.[xxiv] Most of these processes have been tailored for 365 nm or 248 nm exposure, and some have been modified to work at shorter wavelengths.[xxv, xxvi] TSI systems based on vapor phase silylation fall into two categories, and the first type is best illustrated with the DESIRE (Diffusion Enhanced SIlylated REsist) process. This scheme, depicted below, was first introduced by workers at the UCB Chemical Company in Belgium.[xx, xxi]

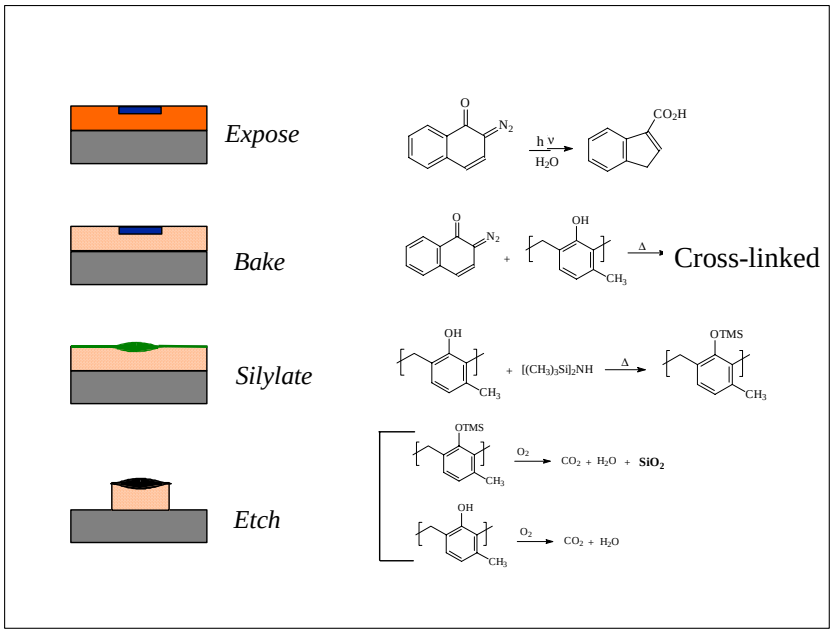

Figure 1.4: The DESIRE process

A traditional novolac/DNQ photoresist (see Section 1.3) is coated on a wafer. Upon exposure to light, the DNQ undergoes photodecomposition to yield an indene carboxylic acid. The resist is then baked *in vacuo* at high temperatures so that essentially no water is present. Under these conditions, the DNQ undergoes thermal decomposition to form an unstable ketene. In the absence of water, the ketene reacts with the nucleophilic phenol functionality on the novolac resin. Most PAC molecules contain multiple DNQ groups; so, the unexposed resin is cross-linked by the high temperature bake process. As a result of the cross-linking, the permeance of the unexposed region to gaseous molecules is drastically diminished. The resist is then exposed to the vapor of a reactive aminosilane compound (also called a silylating agent). This compound

permeates into the exposed regions of the photoresist, reacts with the free phenolic sites, and incorporates silicon into these regions (see Figure 1.5).

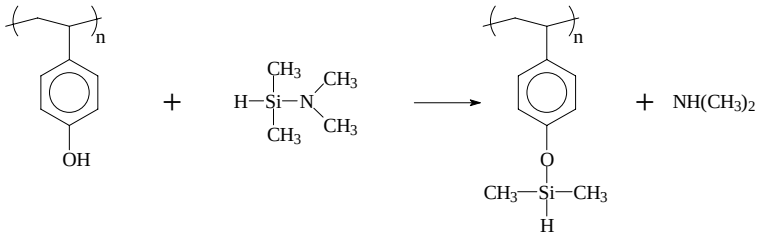

Figure 1.5: Reaction of silylation agent with poly(*p*-hydroxystyrene)

Since the unexposed region is cross-linked, the silylating agent diffuses very slowly into these areas. Therefore the high permeance of the silylating agent into the exposed regions of the film provides a method of selectively incorporating silicon atoms into the resist. The silylated film may then be placed into an oxygen RIE and developed as in the other systems.

Since DESIRE requires only one film to be coated, it is considerably simpler than the two layer schemes presented earlier. The vapor phase silylation used in this system offers both advantages and disadvantages. Since the reagent is a vapor, less of it is required than for the liquid phase silylation used in the Si-CARL process. However, the vapor phase silylation step requires a new equipment module, and an entirely new process must be optimized in order to use this technology. Nevertheless, this process was implemented successfully by Texas Instruments in the production of memory devices.

DESIRE results in negative tone images. Many similar systems have been developed that lead to positive tone images. These systems still use the permeance of the resist film to provide contrast in the silylation process, but the photochemistry that causes the selective incorporation is much different. In the simplest of these systems, the exposure radiation itself causes the resist to cross-link.[xxiv] The silylating agent then diffuses into the unexposed regions of the resist while the exposed, cross-linked materials remain relatively unsilylated. After dry development, positive tone images are obtained.

1.5 Digital Top Surface Imaging Using Vapor Phase Silylation

In the previous systems that utilize vapor phase silylation, the uptake of silicon is controlled by the permeance of the film to the silylating agent. The silicon uptake may also be controlled by modulating the *reactivity* of the polymer with the silylating agent. This technology was first developed by workers at IBM in 1985 [xviii, xix] and is depicted in Figure 1.6 below using a *t*-BOC-styrene resin and a generic photoacid generator. In this system, exposure of the photoresist causes the generation of acid. This acid can then deprotect the *t*-BOC-styrene resin at elevated temperatures. In this process, a phenolic moiety is generated, and carbon dioxide and isobutylene are liberated to the atmosphere. Additionally, another mole of acid is generated so that the deprotection occurs via chemical amplification. As in the DESIRE process described above, the wafer is exposed to a silylating agent, and the phenolic sites that were generated during the exposure and

post-exposure bake step react with the silylating agent. The protected sites, however, are chemically inert to the silylating agent and therefore cannot react with it. The final step in the process is to place the wafer into an oxygen RIE to develop the images.

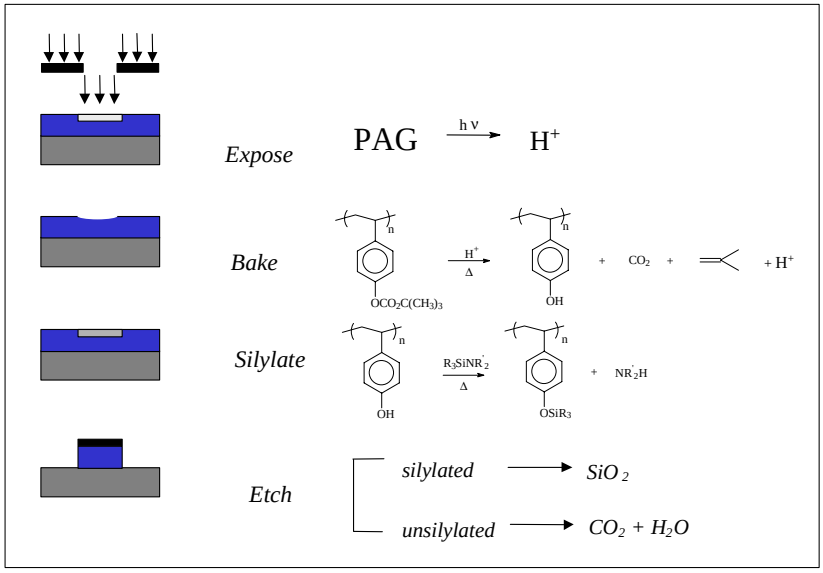

Figure 1.6: Digital TSI using vapor phase silylation

Any of the systems detailed in this chapter could be used for 193 nm or 157 nm lithography (and other researchers have in fact explored them), but the digital silylation scheme was selected because it offers advantages over all of them. Since it requires only a single resist film, its requires fewer processing steps than bilayer resist processes. The digital silylation scheme also holds two distinct advantages over the DESIRE process and similar technologies. The first of these two advantages involves the nature of the silylation. The silylation in the digital silylation scheme is in fact digital; the silylation can only react with the deprotected phenolic sites. In the other schemes, the silylation agent has low permeance into the cross-linked regions of the resist, but it still slowly penetrates the film and finds reactive sites there. Hence, there is always a thin layer of silylated material in the regions where there should be none, and the dry development of the images is considerably more complex. Usually, a brief descum etch step that uses fluorinated etch gases is used to strip off the top portion (~20 nm) of the film.[xxvii, xxviii] This descum step removes the undesired parasitic silylation, but it also erodes the silylated portions of the film that serve to transfer the image. The shape of the silylated hardmask (i.e. the portion of the resist that allows image transferal) is critical to the development of acceptable final images, and the use of this nonselective descum process introduces process complexity and unreliability to these systems.

A second disadvantage of the diffusion-based schemes involves the swelling of these materials during the silylation step. By its very nature, the silylation reaction adds mass to the resist. In order to accommodate the additional mass, the resist film itself

must swell. This swelling leads to distortion of the image and is highly undesirable. The problem is actually exacerbated by the very nature of diffusion. After the silylation agent dissolves into the resist film, it must then diffuse to find reactive sites. Of course, nothing prevents the silylation agent from moving laterally as well as vertically, and silylation then begins to occur underneath the cross-linked regions. These phenomena acting together result in the well-documented "bird's beak" profile:[xxix]

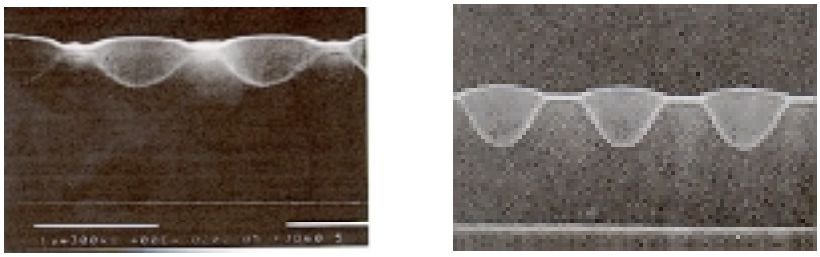

Figure 1.7: Examples of "bird's beak" silylation profiles

Using such silylation profiles as masks for image transferal ultimately leads to faulty imaging.

In principle, the digital silylation scheme does not suffer from these issues. During resist processing, there are two steps that lead to changes in the resist film thickness. First, in the post-exposure bake (PEB), volatile products are liberated from the resist film causing it to shrink. The silylation reaction subsequently adds some percentage of this mass back to the resist film. The thickness changes that occur in the PEB and silylation steps may be tailored to cancel one another and eliminate undesired image distortion. Additionally, since the system does not rely upon the permeance of the resist film to the silylation agent, it is not important that the diffusion is two-dimensional. The silylation agent may diffuse throughout the entire film, but it will only react with deprotected sites. This system therefore seems to have many attractive features for use at 193 nm and 157 nm.

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