Thin-film imaging: Past, present, prognosis

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As the limitations of conventional optical lithography approach, potential extensions of a current technology are examined more closely. One of these extensions is to limit the photoresist thickness that is needed for recording the imaging information. Because the low etch resistance of resist typically precludes the use solely of resists utilizing very thin film, a variety of alternatives have been explored. These range from elaborate trilayer schemes to relatively simple processes such as top-surface imaging (TSI) and a number of combinations thereof. In all of these systems, the aim is to limit the imaging resist thickness to a thin layer by confining the radiation near the surface of the resist. This improves process latitude (e.g., depth of focus, exposure latitude) and also reduces reflective notching and thin-film interference effects. The imaged pattern in the thin-film resist processed by TSI is then transferred by plasma etching into a thicker underlayer. This "stack" then serves as the resist mask for subsequent wafer processing. In this paper, we refer to all of these types of approaches as thin-film imaging (TFI) systems. We review TFI approaches from a historical perspective, examine a number of the schemes that have been proposed, and describe the various technical issues associated with the implementation of such systems. From this perspective, we suggest that TFI systems may find a role in manufacturing for lithographic applications at wavelengths at, or less than, 193 nm.

Introduction

Advances in conventional optical lithography have typically resulted from a series of modest improvements in tooling and processes. As the tooling becomes outdated, procedures to extend the life of a tool set are investigated. One such approach that has a number of advantages is to confine the radiation to a region near the surface of the resist, a process we refer to as thin-film imaging (TFI).

For instance, thin-film interference effects due to coating nonuniformities induced by the photoresist can cause large variations in the energy coupled into the photoresist, resulting in a linewidth dependence on resist thickness. This so-called swing curve effect, whether from a nonuniform resist application or the result of local variations in the chip topography, can translate into large linewidth variations. In addition, standing waves can be established in the resist that will cause resist profile deformation. Scattering from underlying topography can also be a cause of linewidth variations. A TFI system that is insensitive to variations in resist thickness and substrate reflectivity therefore has a decided advantage.

Also, TFI decreases the need for large depth of focus for two reasons. TFI approaches planarize topography on

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the substrate, resulting in a level planar surface on which to pattern. Furthermore, a smaller depth of focus is required to image a thin layer than to image a thick single-layer resist.

As with many unconventional "new" technologies, TFI approaches have waxed and waned in popularity. Typically, as one generation of exposure tools nears its limits, TFI approaches are studied, scrutinized, and sometimes implemented until the next generation of tooling becomes available. Recently, interest in these systems has paralleled the renewed interest in 193-nm lithography. At 193 nm, many conventional resist systems are relatively opaque and are therefore ideally suited for TFI approaches. For this reason, the majority of resist activity has been centered around these systems at this wavelength. For 193-nm lithography, TFI systems are mature compared to the status of single-level resist (SLR) systems.

In this paper, we review some of the common approaches to thin-film imaging that have been studied. We then outline from a historical perspective certain advantages and concerns, with selected examples of TFI systems. We begin by examining early TFI approaches that were investigated to extend the lifetime of G-line (436-nm)/I-line (365-nm) lithography. In this section, we discuss one of the most important issues for insertion of any new technology: manufacturability. The next two sections deal with process development for lithographic applications at wavelengths of 248 nm and 193 nm. Finally, we summarize some of the advantages and issues associated with TFI systems. Using this historical perspective, we attempt to assess the outlook for widespread use of such systems.

This paper is not intended to be a thorough review of all TFI approaches; it merely presents a representative sampling. Since most of the experience of the authors relates to top-surface imaging systems, much of the discussion is centered around this technique. It should be noted that the fundamental idea behind TFI (i.e., limiting radiation to a thin film that is optically isolated from the substrate) is common to all TFI systems; therefore, the results described are applicable, in large part, to all TFI approaches.

1. General description of TFI approaches

As stated above, TFI involves imaging only a very thin layer of resist. For this to be an effective means of pattern transfer to the substrate, the aspect ratio of this resist pattern must be increased by transferring the pattern into a thicker resist layer. This pattern transfer is typically accomplished with an oxygen plasma. The pattern is defined by use of a thin resist etch mask in either exposed or unexposed areas, depending upon the tone of the resist. This mask most commonly incorporates silicon or an oxide of silicon. If silicon is used, it reacts with the oxygen plasma, forming a silicon oxide. In both cases, the resultant silicon oxide is resistant to etching in the oxygen plasma. There are different approaches for forming this etch mask, ranging in complexity from trilayer to top-surface imaging (TSI) systems and combinations of the two.

Trilayer schemes involve the use of a thin imaging layer spun onto a thin oxygen dry-etch-resistant hard mask coated on top of a thick organic planarizing layer [**Figure 1(a)**] [1, 2]. The main advantage of this approach is the ability to separate the requirements of the various materials into separate layers, allowing the use of conventional photoresists for imaging; hard masks, such as plasma-deposited or spin-on silicon oxides; and planarizing layers that are tailored for optimal step coverage. The chief disadvantage is the complexity of a process in which three separate materials each require deposition and/or curing. The pattern developed in the thin top layer must be transferred to the hard mask layer and then into the planarizing layer.

Another approach, championed by Siemens, is known as Silicon Chemical Amplification of Resist Lines (Si-CARL) [3, 4]. An anhydride-containing thin imaging layer is spun onto a planarizing layer [**Figure 1(b)**]. Following exposure and development of the imaging layer, silicon is incorporated into the remaining resist, causing broadening of the resist lines (called the "amplification" step) by use of amino-containing siloxanes which react chemically with the anhydride. The top layer then acts as the etch-resistant mask for pattern transfer to the planarizing layer. This process requires spinning and baking of only two layers, but a silylation step is still needed.

In an approach used at AT&T [5], a thin imaging layer is spun onto a thick planarizing layer [see **Figure 1(c)**]. This thin layer is exposed and baked, causing cross-linking in the exposed areas. The resist is then treated with a silyating agent, which is preferentially incorporated in the unexposed (not cross-linked) region. Development of this system is carried out by oxygen plasma, resulting in a positive-tone image. This approach is similar in complexity to the Si-CARL system mentioned above, in that two separate deposition layers are needed as well as a silylation step. An advantage of this system, however, is that commercially available cross-linking negative resists can be used for the top layer.

The next processes discussed are traditional bilayer approaches [see **Figure 1(d)**] [6]. Typically, an oxygen dry-etch-resistant resist is spun onto a thick planarizing layer. The imaging layer normally incorporates silicon or some other material forming an etch-resistant oxide during etching in an oxygen plasma. Following exposure, the resist is developed with conventional wet developers, forming the relief image. This pattern is then transferred

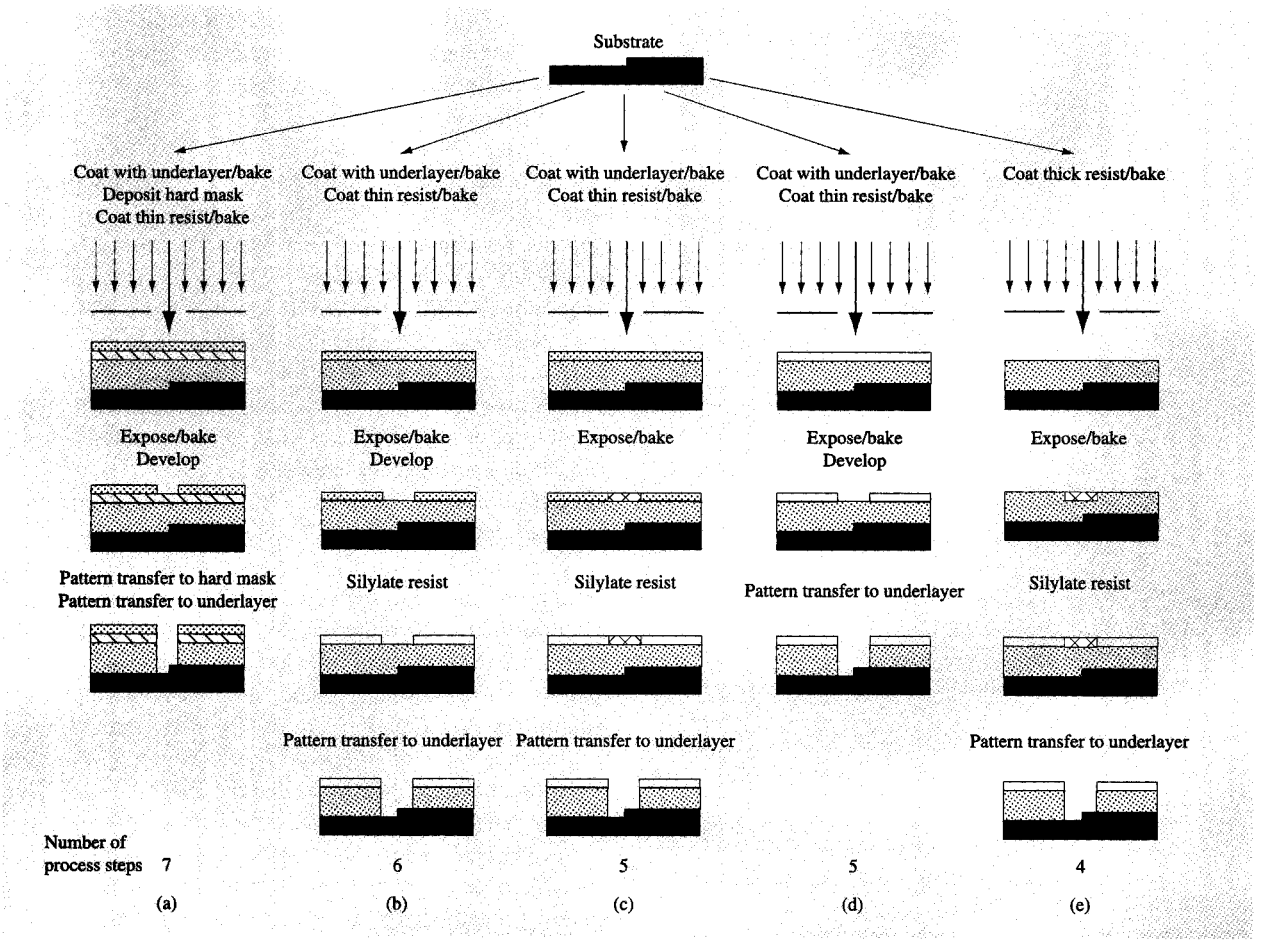


Figure 1

Schematic illustration of various thin-film imaging schemes: (a) Trilayer resist process; (b) Si-CARL process; (c) AT&T approach; (d) bilayer process; (e) TSI approach.

via dry etching to the planarizing layer. The advantage of this type of process is greater simplicity in comparison to the previously mentioned processes. However, the material challenges of making a high-resolution silicon-containing resist with wide process latitude are nontrivial. Typically, as one incorporates more silicon into the polymer, etch resistance increases but the T_g decreases, and finding the proper balance can be difficult.

Top-surface imaging (TSI) is an even simpler process than those mentioned above [**Figure 1(e)**] [7–9]. In this approach, a single layer of resist is used that is opaque to the exposing radiation. During exposure, only the top portion of the resist is exposed, resulting in differential diffusion rates in exposed and unexposed portions of the resist. A chemical agent, typically containing silicon, is then preferentially diffused into either the exposed or unexposed areas. Figure 1(e) outlines an example of a positive-tone process. As with the other systems, the silicon causes dry-etch resistance, and the pattern is dry-developed in an oxygen plasma. This is the simplest of all TFI systems, since it uses only a single layer of resist. However, one of the hindrances to implementing TSI is the need for a silylation step.

2. TFI in near-UV manufacturing: Texas Instruments perspective

Thin-film imaging lithography, in the form of a TSI process known as DESIRE [10], made the transition from research and development laboratories to manufacturing at Texas Instruments in the late 1980s. The application of this surface-imaging technique was for patterning top metal leads critical for DRAM memory chips [11]. The top metal level for a DRAM chip often has the most substantial topography as well as the highest reflectivity of

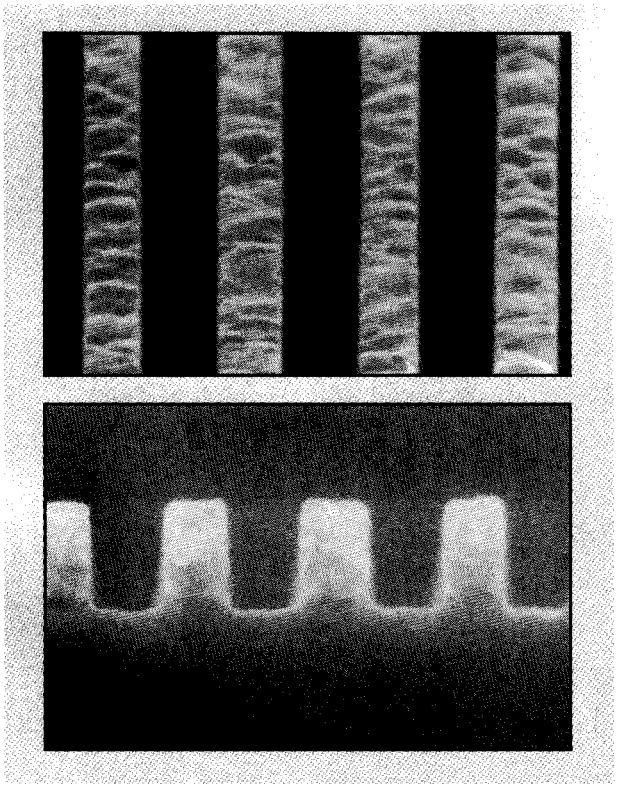


Figure 2

SEM micrography at 20,000× of metal lines patterned with the DESIRE process and etched.

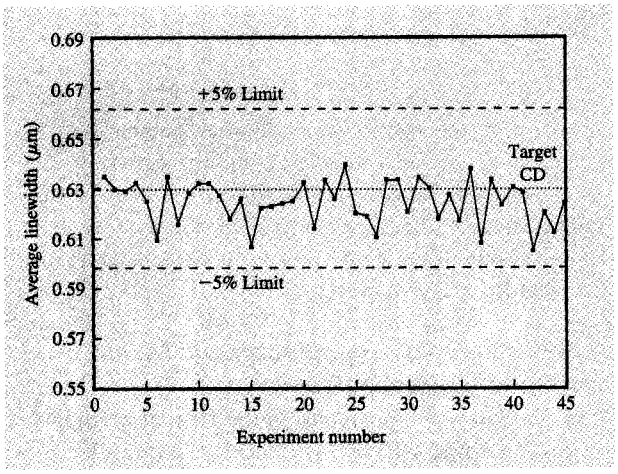


Figure 3

Average linewidth measurements for nominal 0.63-μm lines patterned by the DESIRE process.

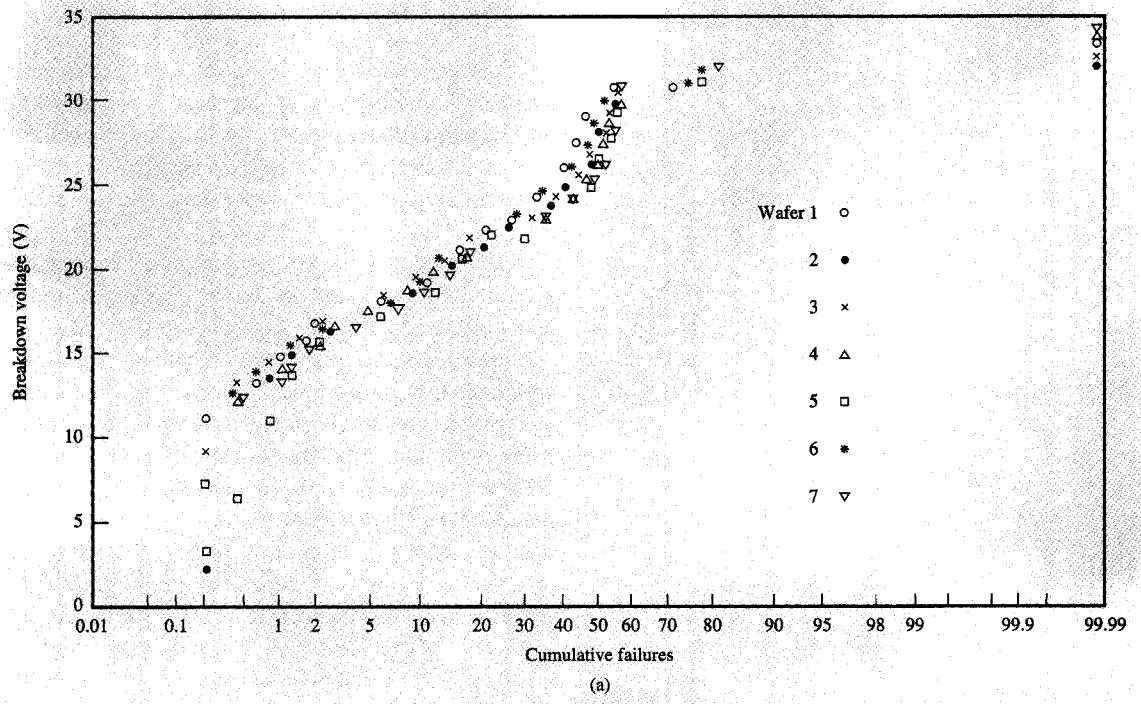
any level, and it is therefore a very difficult level to pattern. The high reflectivity exaggerates thin-film interference effects and dramatically affects control of critical dimensions [12].

In the pilot plant, a G-line exposure tool (436 nm, 0.54 NA) was used to expose Plasmask® 200-g photoresist supplied by Japan Synthetic Rubber (JSR). The silylation step was performed with a single-wafer reactor, Plasmaster®-Si, manufactured by Tokyo Electronics Laboratories (TEL). Dry development of the silylated photoresist was performed in a Materials Research Corporation (MRC) Aries etcher. Using the DESIRE process, nominal 0.6-μm lines were patterned on the top metal level of a DRAM chip with vertical profiles (**Figure 2**) and excellent linewidth control.

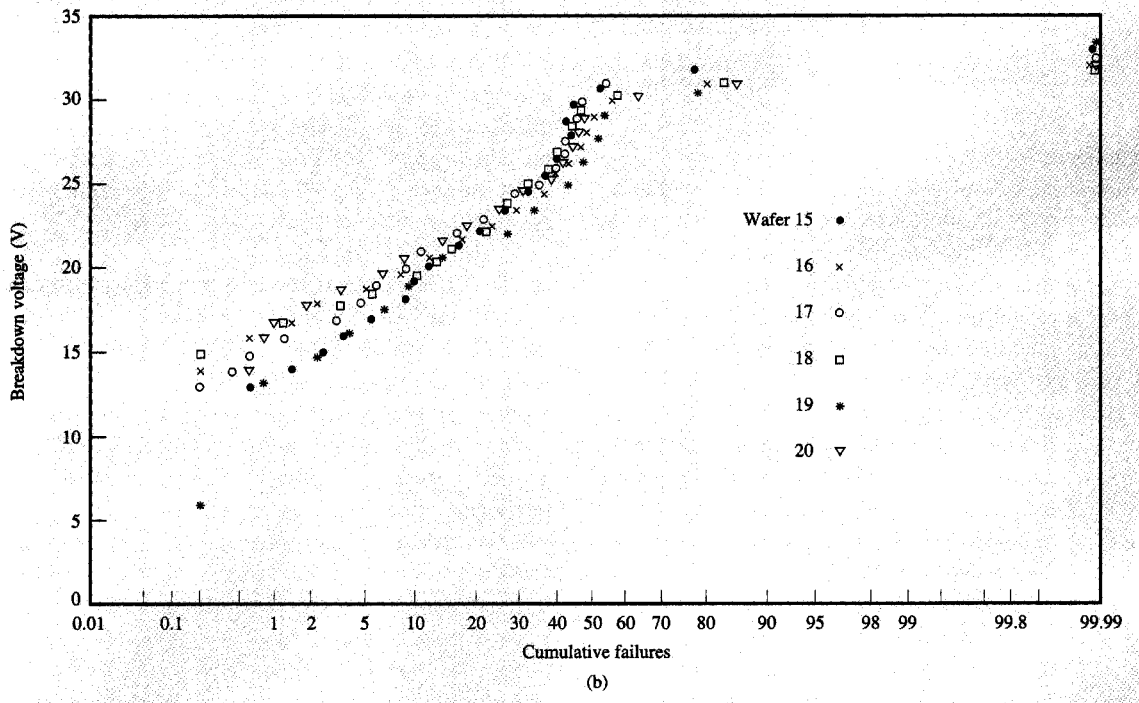
Control of linewidth for the DESIRE process required very uniform incorporation of silicon into the resist, and good uniformity at the dry development step. After optimization of these steps, the DESIRE process was demonstrated to be reproducible [13]. In a production environment, the critical linewidth was monitored by measuring five sites per die and five places on sample wafers. The measurements are displayed in **Figure 3**. Over a three-month period, the run-to-run variation (3σ variation of the averages) was determined to be 0.034 μm. The 3σ variation wafer-to-wafer was within $\pm 5\%$ of the average critical dimension. The insensitivity of the surface-imaging process to variations in wafer reflectivity and coating nonuniformity provided an advantage for controlling linewidth. In addition, the large depth of focus, 1.8 μm for printing the 0.6-μm lines, established a large process window which also aided process stability.

The resist proved to be quite robust during subsequent etch processes, in which the vertical profiles were transferred into the etched metal. To alleviate concern over the possibility of etch-induced damage to the gate dielectric during the dry development step, tests for gate oxide integrity (GOI) were conducted. Groups of wafers were processed identically up to the patterning step, where they were then split between the DESIRE process and conventional resist. The dielectric breakdown voltage characteristics were similar for the two groups of wafers (**Figure 4**). A defect monitor which used flat pilot wafers showed comparable yield for conventional resist processing and the surface-imaging process. However, when topography was present, the surface-imaging technique demonstrated enhanced yield and linewidth control.

Yield reduction for the metal level occurs either in the form of lines that are unintentionally connected electrically (shorts) or have unintended breaks (opens) in the metal leads. These types of yield problems can be caused by incomplete resolution of the pattern feature or by particles which block the patterning or etch process. In



(a)



(b)

Figure 4

Breakdown voltage behavior for wafers patterned (a) by the DESIRE process and (b) by conventional photoresist processing.

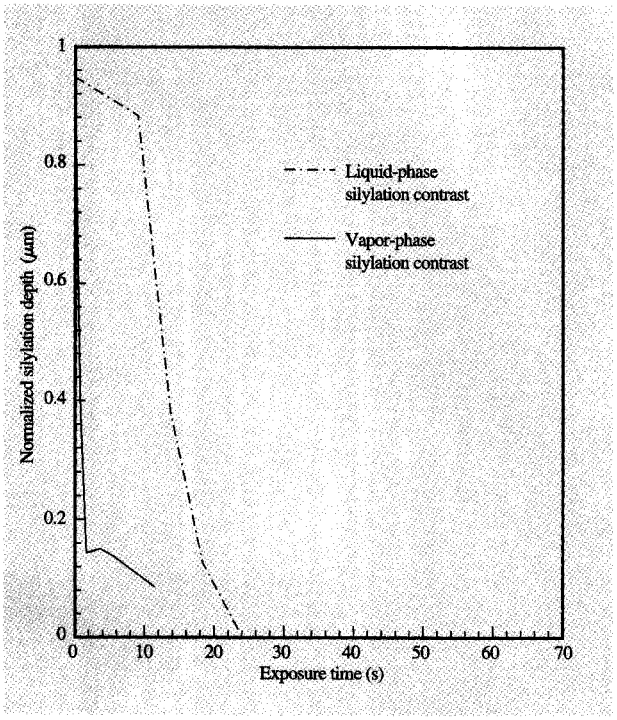


Figure 5

Silylation contrast of AZ5214 liquid-phase silylation (dashed curve) versus early vapor-phase silylation (solid curve).

our manufacturing line, a defect monitor level (no topography, metal level only) was routinely processed to detect any problems with the electrical connectivity of the pattern. Particles in the resist, lithography equipment, silylation machine, or dry developer are detected using this method. No difference was observed in a side-by-side comparison between wafers processed using DESIRE and wafers processed with wet-developed resist. On wafers with actual topography, a comparison of DESIRE wafers with those patterned with conventional I-line resist and an antireflective coating showed a factor of 3 greater yield for the DESIRE wafers. Additionally, the focus budget for the DESIRE process was 50% better than that for I-line resist with an antireflective coating (ARC).

In the DESIRE manufacturing process, the photoresist is applied using a standard coater. Two additional machines, a silylation tool and a dry-develop etcher, are required for this surface-imaging process. While the dry-develop etcher had throughput comparable to that for a wet-development process, there is no parallel to the silylation machine in standard resist processing. Thus, surface imaging carries additional costs in added machinery. When introduced, the silylation and the dry-develop tools were new designs and required modifications for the manufacturing environment. More problematic, however, was the occasional arcing which occurred in the dry-develop etcher, causing destruction of all of the devices on a wafer [14]. As with any new technology, there were additional problems to be solved. Cleanup and stripping of the photoresist, for example, required development of new methods because the standard approach was ineffective. New sensors for an etching endpoint and for silylation were required to control these processes [15].

Fully functional DRAM memory chips were qualified using the DESIRE surface-imaging process for top metal leads. At the point in the flow where the DESIRE process was used, the reflectivity of the metal and the large variations in surface topography precluded the use of conventional resists. Eventually the use of a wet-developed I-line resist and antireflective coating replaced the DESIRE top-surface-imaging process in the manufacturing line. However, much optimization of the standard process was necessary, e.g., to improve planarity at the top metal level before yields and critical dimension (CD) performance could equal that of the DESIRE process.

The use of the surface-imaging technique allowed the qualification of a fully functional DRAM device with challenging design dimensions and topography requirements. In a manufacturing setting, the process was shown to be reproducible with good control of linewidth. Eventually I-line steppers, improved planarity, and antireflective coatings could be used with photoresist developed for the standard process, replacing the surface-imaging process. However, the use of a surface-imaging resist did provide a manufacturing process that offered advanced production capability.

3. TFI development for 248-nm lithography at IBM

At IBM, the need for TFI lithography has been driven by the need to realize higher-resolution imaging and increased lithographic process latitudes from an existing tool set rather than from concerns over wafer topography. In early studies on both positive and negative TSI imaging, resists silylated using vapor-phase silylation techniques were slowed by comparatively low silylation contrast because of the status of TSI resist chemistries, vapor silylation hardware, and plasma development technologies [16–19]. For this reason, a number of papers reporting on the use of liquid silylation have been published [20–22]. Liquid silylation, as first practiced by Hatzakis and co-workers at the IBM Thomas J. Watson Research Center [23], was attractive primarily because a vast improvement in silylation contrast (**Figure 5**) between exposed and unexposed areas of resist was thought to be due to the differences in the diffusion kinetics between the two silylation processes, i.e., chemically driven as opposed to heat driven.

We have used commercially available AZ® 5214 novolak-based, acid-catalyzed photoresist which has an optical density (OD) of 1/μm at 248 nm, making it suitable for a TSI application. After exposure, the resist is baked to induce acid-catalyzed cross-linking in the exposed regions. The resist is then treated with a solution of an organosilicon-containing compound, which silylates non-cross-linked areas preferentially at hydroxyl (-OH) sites along the novolak polymer chain. Silylation in cross-linked regions of resist is inhibited by large molecular weight changes in the resin and the absence of hydroxyl sites for bonding. Dry development in an oxygen plasma produces a positive image [24, 25]. The liquid silylation technique employs a mixture of an active solvent, in this case propylene glycol monomethylether acetate (PGMEA), in combination with a polyfunctional silylating agent, hexamethyl cyclotrisilazane (HMCTS), and an inert carrier solvent (xylene).

A decoration procedure was used to gain an understanding of each of the steps in this process [21]. Aqueous tetramethyl ammonium hydroxide-based (TMAH) photoresist developer decorates cleaved cross sections of cross-linked and silylated resist regions so that they may be characterized by SEM, as shown in **Figure 6**. Changes in post-exposure bake temperature, silylation bath chemistry, and silylation time were measured using this technique to determine their effect on silylation depth and linewidth, as shown in **Figure 7**.

Finally, the dry-develop process was evaluated using an optimized post-exposure bake (PEB) temperature and silylation conditions. Development of the silylated resist layers was carried out in a Sumitomo electron cyclotron resonance (ECR) system. Exposure and focus windows were measured. Exposure and focus latitude here are defined respectively as the dose and focus range that can be tolerated while maintaining ±10% CD control. A total exposure latitude of 24% was obtained for both nested and isolated 0.4-μm lines, with a total depth of focus of 1.8 μm for nested lines and 2.4 μm for isolated lines. An optimum exposure dose of 18–22 mJ/cm^2 on a Nikon 0.42-NA DUV stepper was determined for all measured linewidths.

Liquid silylation was then compared with other TFI approaches, which included several internally developed bilayer and vapor-silylatable TSI systems. We concentrated on AXT-248, a resist developed at IBM which uses a dyed polyvinylphenol (PHOST) resin and acid-induced cross-linking to provide silylation contrast and which is specifically tuned for a vapor-silylation TSI process [26]. The process was developed using Micrascan® I 0.35-NA 248-nm and Micrascan II 0.5-NA steppers. A Genesis Microstar 200 silylation system was used for silylation, and an etch process development was done using several LAM 9400 TCP etch tools from LAM Research, Fremont, CA.

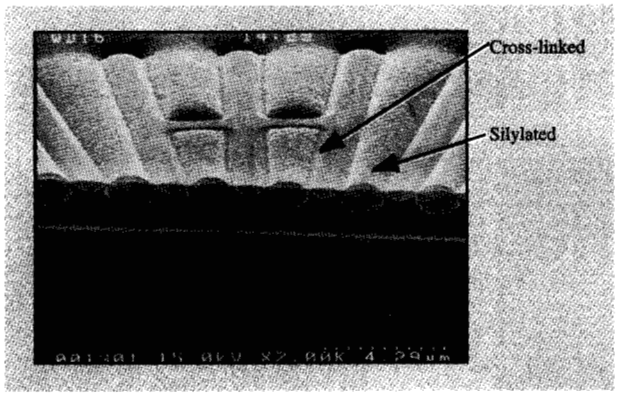


Figure 6

Silylated resist cross section decorated using TMAH developer.

During the development and optimization of a TSI process for this resist, we discovered that better control of the vapor-silylation step was required. Early vapor-silylation systems had poor temperature uniformity, which resulted in poor across-wafer silylation uniformity. The Genesis silylation tool is the first of a generation of tools specifically designed for vapor silylation. The system demonstrated better than ±0.5°C temperature uniformity across a 200-mm wafer and was capable of delivering silylating agent to a wafer surface in a highly reproducible manner. The system demonstrated the performance necessary to achieve the critical dimension control for IBM's advanced device programs.

This study also highlighted the importance of high-plasma-density etch systems for TSI approaches. In more conventional etch systems, formation of residues in open areas, often referred to as "grass," is a major problem. One source of grass is micromasking of areas to be etched by residual silicon which can be present as a result of the sputtering of silicon from silylated areas. Our results indicate that the process window for elimination of grass is much wider for high-plasma-density systems, presumably because ions of much lower energy are attacking the resist surface, thereby decreasing the sputtering of silicon.

Another source of grass formation is the incorporation of a thin layer of silicon in unwanted areas during the silylation step. One approach to solving this problem is to remove this thin layer of silicon by using a halogen-containing plasma etch chemistry before dry development in an oxygen plasma. With this approach there is concern that small amounts of fluorine can act as a catalyst, increasing the etch rate of photoresist and possibly affecting profile control [27]. Since the residence time of fluorine in a vacuum chamber may be quite long, these

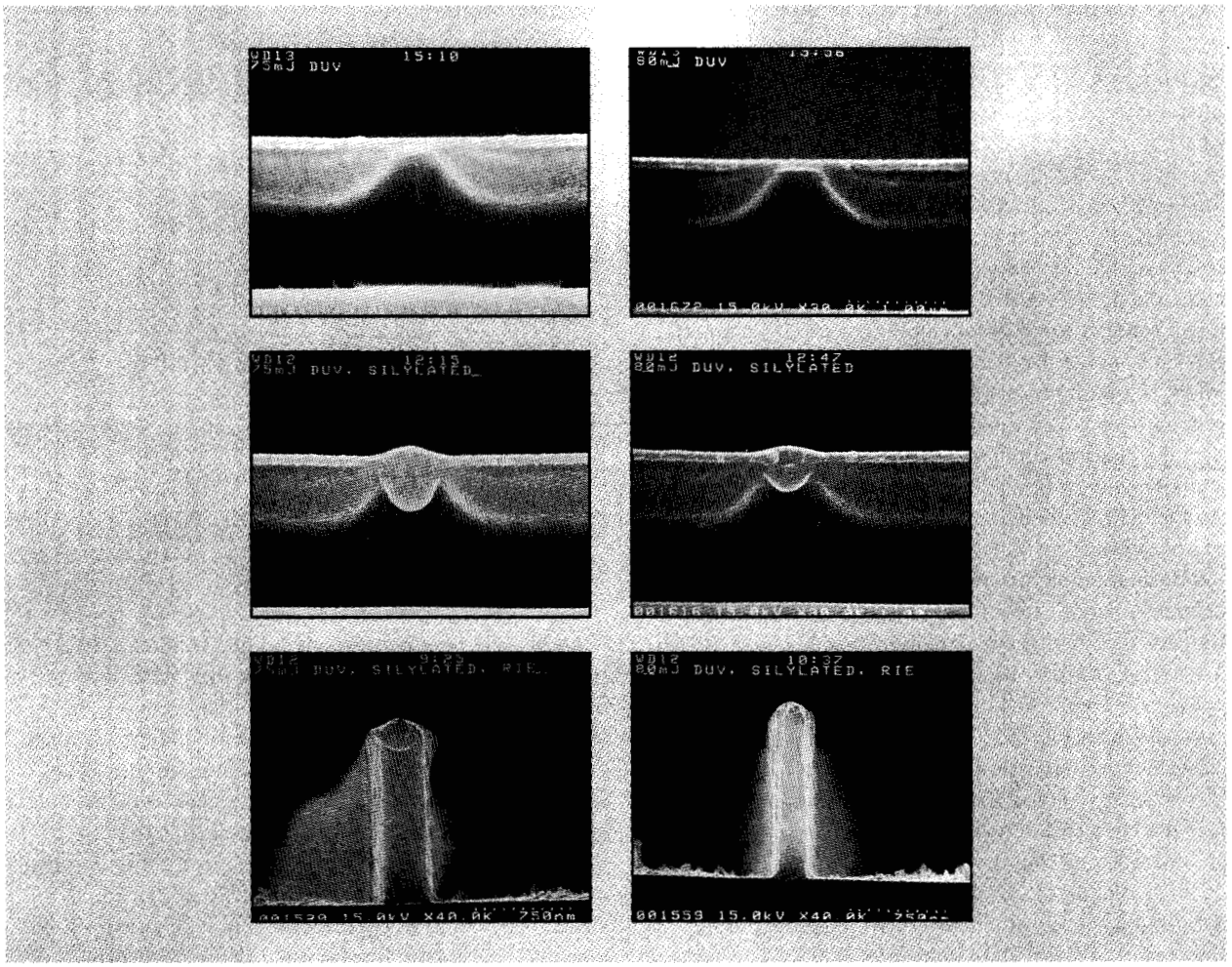


Figure 7

Resist cross sections decorated for process development studies. Top photographs show cross-linked resist profile; middle photographs show silylation profile; bottom photographs show etched, isolated line structure. Exposure dose: Left column–75 mJ/cm^2; right column–80 mJ/cm^2.

effects could be cumulative and not easily controlled. We therefore developed an all-oxygen etching process based on previous work at Texas Instruments.[1] This process has proven to be quite robust, exhibiting greater than 20% latitude for all process variables, and has been transferred easily among several LAM 9400 tools during the process development cycle.

With both silylation and etch conditions well optimized, the lithographic properties of the resist system could be characterized. Post-apply and post-exposure baking conditions were optimized using the central composite statistical approach. Optimum values of 128°C for 60 seconds and 125°C for 120 seconds were found to yield the best combination of photo-speed, resolution, and exposure/focus latitudes. Linewidth variation due to PEB temperature was measured at 10 nm/°C, while delay times of up to 30 minutes between exposure and PEB in unfiltered air had no effect on lithographic performance [28].

The following data were obtained by a combination of SEM and electrical linewidth measurements to characterize a CMOS gate-conductor-level process. As a result, the majority of the data pertain to isolated lines, with less emphasis on line/space (L/S) pairs and contact holes. The ultimate resolution for the optimized AXT-248 TSI process was found to be 0.15-μm isolated lines (**Figure 8**) on the Micrascan II (0.5-NA) at an exposure dose of 11.5 mJ/cm^2. At 0.5-NA imaging, linearity has been

[1] M. Hanratty and C. Garza, Texas Instruments Corporation, Dallas, TX, 1994, unpublished results.

Table 1 Dependence of polymer structure on sensitivity for TSI system exposed at 193 nm.

Resin	*Molecular weight*	T_g	*Dose*
m-/p-cresol	8600	105	135
m-/p-cresol	4600	99	120
m-cresol	1900	75	225
m-cresol	2750	—	116
m-cresol	13400	100	65
m-cresol	38000	130	45
m-cresol	~50000	150	70
PHOST	2800	152	70
PHOST	14500	158	55
PHOST	38000	180	45
PHOST	79800	190	45

measured at 0.25-μm L/S and 0.175 μm for isolated lines (**Figure 9**). On the Micrascan II, exposure and focus latitudes were measured electrically for isolated 0.25-μm line structures at 20% total exposure latitude and 1.2-μm total depth of focus.

4. Renewed emphasis on TFI: 193-nm lithography at Lincoln Laboratory

The extremely high absorbance of phenolic polymers limits 193-nm radiation to penetration of only 30–40 nm below the surface. This high opacity makes 193 nm a wavelength ideally suited for application of top-surface-imaged resists. The development of TSI resists for 193 nm began at Lincoln Laboratory in 1989, and in the following years a number of both novolak and chemically amplified 4-hydroxystyrene-based formulations were evaluated. The most important observation from this original work was that of a relatively efficient direct photochemical cross-linking induced in phenolic polymers by 193-nm radiation [29]. This direct cross-linking, presumed to be free-radical-mediated, occurs roughly ten times more efficiently at 193 nm (50–100 mJ) than at 248 nm (~1 J/cm^2) for neat novolak resin. Further studies [30] revealed both a molecular weight and resin composition dependence on the minimum dose required to inhibit silylation. For a given resin, required doses scale inversely with molecular weight, as is common for negative-tone wet-developed resists. **Table 1** summarizes these results. In addition to the molecular weight effects, the polymer structure plays a role as well, but it is unclear whether these structural effects are important as a result of changes in cross-linking quantum efficiency or as a result of changes in glass transition temperature, which in turn can affect the silylating reagent diffusion mechanism. In fact, these variations in diffusion mechanism and rate between polymers can make direct sensitivity comparisons difficult. The data in Table 1 were obtained by measuring the dose

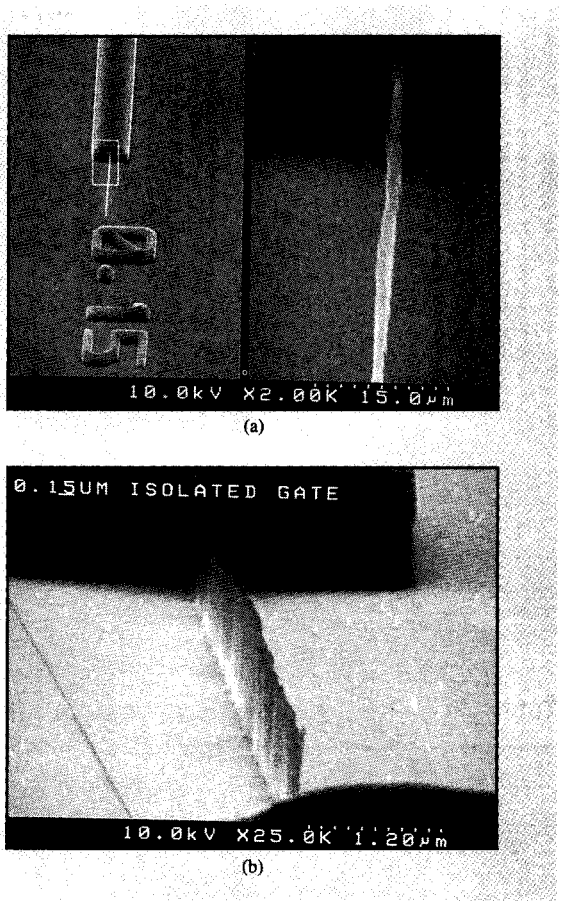


Figure 8

Best resolution for AXT-248 TSI process for isolated 0.15-μm line using Micrascan II: (a) Top views: Left–low magnification; right–high magnification. (b) Oblique view.

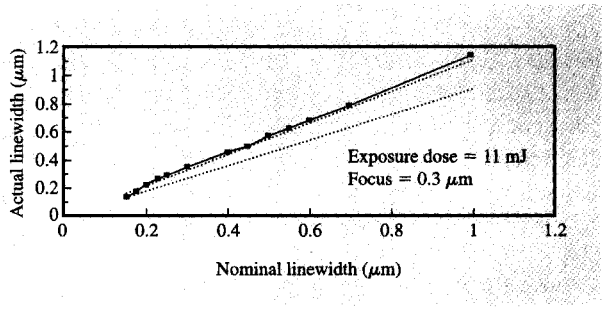


Figure 9

Linearity to 0.175 μm of AXT-248 isolated resist line on Micrascan II at 0.5 NA.

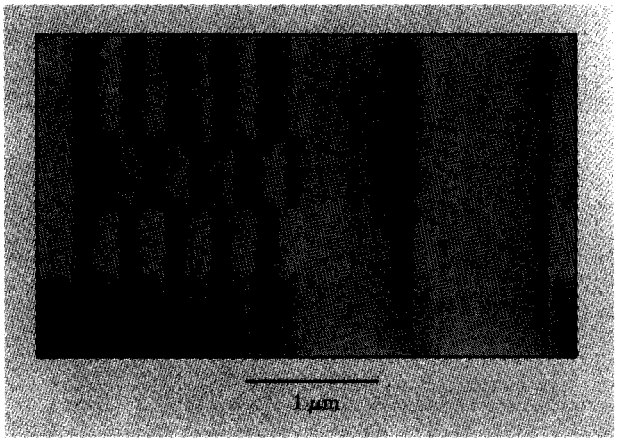


Figure 10

Test silylation resist structures (0.2 μm) using single-component TSI process exposed at 193 nm.

Table 2 Sensitivity of TSI systems exposed at 193 nm.

Resist	*Sensitivity* (mJ/cm^2)	*PEB*
PHOST	22	none
Shipley SNR® 248 6	6	none
IBM AXT 248	~5	none
Shipley SAL® 601 12	12	none

(Note that the doses differ from those of Table 1 because of differences in silylation conditions.)

required to inhibit silylation in exposed areas when the unexposed regions have been silylated to a fixed depth. When the resist exposure doses are compared after silylation to 200 nm using dimethylsilyl dimethylamine (DMSDMA), the only phenolic polymers not falling into the 40–100-mJ/cm^2 range are those having a T_g lower than or near to the silylation temperature (100°C for Table 1). For these cases, the silylation mechanism shifts from Case II to Fickian [30], resulting in significant changes in diffusion rate. Other factors can also play a role in determining the sensitivity of these one-component TSI systems, e.g., residual polymerization initiators, which may act either as cross-linking agents or as free-radical traps [31].

These simple, high-T_g, one-component TSI resists designed for 193 nm are resins [e.g., novolak, poly(hydroxystyrene)] commonly used in photoresists today. They represent the most mature 193-nm TSI resists developed to date. One such resist based on high-molecular-weight poly(4-hydroxystyrene) is currently in use at Lincoln Laboratory to fabricate 0.2-μm-gate-length CMOS devices using a 0.5-NA 193-nm Micrascan. **Figure 10** shows 0.2-μm test structures for this resist process [32]. Despite these advances, the required exposure doses (~50 mJ/cm^2) are not sufficiently low for large-volume production with current exposure tooling.

The use of chemical amplification (CA) for 193-nm TSI resists was first evaluated by Lincoln Laboratory in 1992 [33]. In a CA system, a photon causes generation of an acid from a photo-acid generator (PAG). This acid then catalyzes a chemical reaction in the resist during a bake step following exposure (PEB). These chemical changes are important in differentiating between exposed and unexposed areas. In this way, one photon can initiate many chemical reactions, and these systems are typically faster than conventional approaches. Several important differences were observed for CA TSI systems as compared to neat resin-based systems:

1. Photospeed was greatly enhanced by addition of both a cross-linker and a photo-acid generator, even in the absence of a PEB to activate the CA reaction. Apparently, both the generation of acid and activation of the cross-linking reaction can be accomplished via direct photochemical means at 193 nm. This effect can be quite dramatic, as shown in **Table 2**. The implication is for greater process control due to lack of a PEB step (although the thermal cycling that occurs during silylation will further activate cross-linking reactions and must be considered). In many cases, photospeed exposure doses are less than 1–2 mJ/cm^2 when the resists are used with a PEB.
2. As with positive-tone, wet-developed CA resists, surface contamination can poison the CA reaction at the surface of the exposed regions. This poisoning allows the silylating reagent to be incorporated in areas that should be cross-linked, thereby forming a thin masking layer, or "skin," in areas that should etch. The result is a requirement for a two-step etch: a "de-scum" step followed by the usual etch. This requirement complicates the pattern transfer step to a level not necessary for non-CA formulations.
3. Since most CA resist formulations are multicomponent, the glass transition temperatures of such formulations are often lower than those of the neat host resins. This reduction in T_g is due to plasticization of the resin by the PAG and/or cross-linker. Experience has shown that this effect can be dramatic enough to severely compromise the thermal stability of the silylated resin [34]. One solution proposed for this is to incorporate multifunctional silylating agents, which act to cross-link the resin as they silylate, thereby providing increased thermal stability. The other method is to employ very high-T_g (>180°C) host polymers. From this, it becomes apparent that the two-step dry-develop process and the

increased attention paid to the resist thermal budget make 193-nm CA systems more complex to process than the slower single-component systems.

A potential alternative would be a high-quantum-efficiency non-CA process that possesses high thermal stability (>130°C). Because of the high photon energy at 193 nm (6.4 eV), very high-quantum-efficiency processes are within reach. One such resist system[2] already tested at 193 nm, consisting largely of highly monodisperse, high-molecular-weight novolac blended with a polymer containing chloromethylstyrene, exhibited a twofold increase in photospeed, corresponding to a decrease in exposure dose from ~50 mJ/cm^2 to ~20 mJ/cm^2. This work suggests that alternative high-photospeed resists can be developed that have the simplicity of the neat resin resists already in use at Lincoln Laboratory, but without the inherent process complexities associated with CA systems.

In addition to requirements for resolution and photospeed, a full understanding of a resist process is necessary in order to determine the ultimate utility of a given process under a wide range of conditions. For conventional resist processes, this is usually aided by process modeling. However, understanding of the silylation resist process on a level equivalent to that for single-layer resists does not yet exist. In addition to the diffusion/reaction kinetics that must be understood to accurately model CA resist systems, silylation resists have the added requirement to model the diffusion/reaction mechanisms for the silylation step. Current understanding of this process is not at the level needed for first-principles model development, where phenomena such as concentration-dependent diffusion, diffusion as a function of temperature (through the glass transition), and detailed reaction kinetics must be thoroughly understood. Several authors have attempted empirical modeling based on numerous experimental observations [35–37]. Although all of these models have shortcomings, the compilation of a more advanced empirical diffusion model, such as that presented in Reference [37], with thorough CA diffusion/reaction and etching algorithms, such as exists in SAMPLE [38], would provide the most advanced silylation model at the present time.

5. Issues that limit widespread use of TFI systems

From the above discussion, it is apparent that TFI systems hold substantial appeal from the point of view of lithographic performance. These systems have demonstrated improved performance over topography resulting in elimination of reflective notching. An improvement of 2× in exposure latitude relative to SLR systems has also been realized, primarily as the result of imaging only a thin resist layer (see Section 3). Similar improvement in depth of focus of these systems has also been demonstrated (see Section 2). Imaging at aspect ratios unachievable with SLR systems has been realized. Finally, we have demonstrated not only that TFI systems are manufacturable but that they can provide greater yield than more conventional SLR systems. This improvement in yield is primarily the result of the demonstrated improvement in the lithographic process window.

We have also seen that many of the concerns that arose in the early process development of TFI have largely been overcome. These include control of silylation conditions for TFI processes requiring silylation and dry-etch issues such as residue (grass) formation. Given the advantages and the apparent resolution of many of the issues, one might ask why these systems are not in widespread use today. In the following discussion, we examine this question in more detail.

First, all TFI approaches are perceived as being more complicated than conventional single-layer resists. An increase in complexity translates into increased cost. Therefore, use of a simpler SLR system that maintains the specification required for a given technology is preferred. However, if one closely examines the process flow of SLR systems and TFI systems, there is little difference in the number of process steps. This is because many "SLR" systems actually require an antireflection layer, and in some cases may involve the use of a top layer to protect the resist from environmental contamination. In fact, if one compares the number of process steps in an SLR + ARC process with that of a TSI process, the TSI process is actually simpler [compare **Figure 11** with Figure 1(e)].

More fundamentally, since TFI approaches use only a thin etch mask, any loss of integrity of this film will lead to pinhole defects. There is then a trade-off in the thickness of the etch mask. The thicker the mask, the less chance for pinholes, but the higher aspect ratio that is needed and the more difficult it becomes to form the image. However, given the evidence cited above regarding manufacturing yields, this is an issue that has been demonstrated to be controllable. It would seem that a reasonable operating point can be achieved, where the layer used is thin enough to gain lithographic performance yet thick enough to maintain yields (see Section 2).

For these and other reasons, there is reluctance to implement TFI approaches. To prompt serious consideration of these systems, there must be a fundamental failure of the current technology.

6. TFI approaches: Prognosis for the future

TFI systems have served niche advanced development needs when next-generation lithography tooling/processes are not available, or are at the early stages of

[2] R. R. Kunz and R. D. Allen, unpublished results.

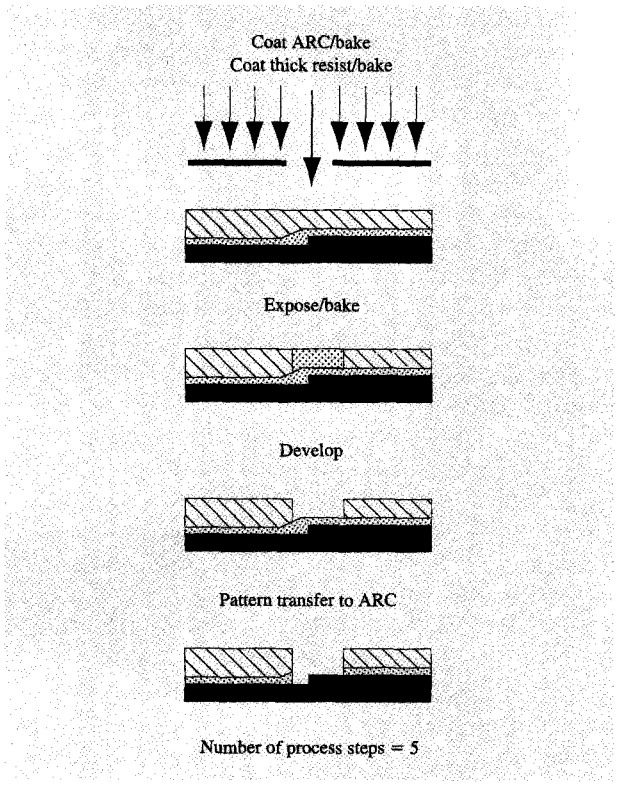


Figure 11

Process scheme for SLR system with antireflection coating.

development. For this reason, TFI systems are an attractive alternative for early product learning on existing tool sets.

As ground rules continued to shrink (early 1990s), the industry migrated from I-line (365-nm) exposure tools to DUV (248-nm) tooling. Many products with aggressive ground rules have now made this switch to the DUV/SLR approach. The level of interest in TFI systems declined during this period.

Today, ground rules continue to shrink further; as a result, there is interest in shifting mask exposure wavelengths to 193 nm. Because of the optical opacity of conventional resist materials at this wavelength, most resist studies have centered on TFI systems (see Section 4). TFI systems have been more thoroughly studied than single-layer systems for 193-nm lithography. Nonetheless, recent activity in designing SLR systems for 193-nm lithography will affect widespread use of TFI systems. At present, the lithographic performance of TFI systems for 193-nm lithography is superior to that of SLR systems, but it is still early in the 193-nm SLR development. Even if SLR approaches are improved, there are substantial concerns over aspect ratio limits for wet-developed SLR systems. Surface tension effects can degrade the structural integrity of wet-developed resist features, causing them to collapse. TFI systems, where the high aspect ratio is formed during the dry plasma development step, do not suffer from this limitation.

As ground rules and wavelengths continue to shrink, the resist material choices become increasingly limited for SLR lithography. In the G-line/I-line era, a vast array of organic polymers was available for use, including a whole host of aromatic-based materials. As the industry moved to 248-nm lithography, the aromatic material set shrank to poly-hydroxystyrenes because of the relative opacity of conventional aromatic (novolak) resins. As we move from 248 nm to 193 nm, the materials set for SLR will be further limited to non-aromatic polymers, again because of optical transparency constraints. These acrylates may be adequate for some 193-nm applications, but will be too opaque for the next wavelength being considered for optical lithography, 157 nm. Almost all organic materials may be too opaque at this wavelength for SLR approaches. The following generation will shift the wavelength to the realm of extended ultraviolet (EUV) lithography. At these very short wavelengths, the optical opacity of materials will necessitate the utilization of TFI approaches. In summary, the ultimate widespread use of TFI systems is directly coupled with the continued advance of optical lithography to shorter wavelengths.

Conclusions

The probability of using TFI lithography increases as we move to ground rules smaller than those being studied today. Currently, the use of TFI systems at I-line or 248-nm wavelengths is limited and will decrease as more advanced SLR systems displace TFI systems. The first extensive application of TFI systems is expected for 193-nm lithography. As of this writing, it is unclear whether SLR approaches will advance to the appropriate level of performance to partially or completely displace TFI systems. For wavelengths at or below 157 nm, only TFI systems are envisioned at this time. The widespread use of TFI systems then depends on the continued development of optical lithography and its migration to shorter wavelengths.

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