

An ultra-uniform, ultra-thin resist deposition process

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Abstract

An ultra-uniform, ultra-thin resist deposition process is presented. Nanometrix applications development with Ultra Thin Polymer Films (UTPF) production process addresses several problems related to resist deposition for lithographic applications. The linear coating technology is a driven assembly process. Linear meter per minute coating rates are produced while providing an outstanding film quality at nano- to micro scale thinness. Therefore, this coating method provides a viable alternative for resist application. Our present developments on nano and micro ultra-thin polymer film coatings give substantial new solutions for improved, faster and less expensive coating production. Materials, writing and quality control costs may be substantially reduced with UTPF deposition technology. Results from three resists are presented in this paper. E-beam direct writing on 8 nm PMMA and photolithography on I-Line and DUV resists in the scale of 30 nm are presented. Thicker resist deposition has been performed as well in the range of 1-10 microns thick. Film edge bead in the order of film thickness are obtained (1000 x smaller than spin coating process). Substrates were all coated with uniform ultra-thin films at a rate of one square meter per minute with atomic smoothness. This technological breakthrough enables a valuable solution for resist deposition and lithography fabrication at the nano and micro scales and provides resist uniformity required for current and future critical dimension specifications.

Keywords: *Linear Coating, DMA process, nanotechnology, lithography, resist, ultra-thin film*

1 Introduction

Thin film resist quality control is one of the major challenges of current semiconductor production. Writing and transferring a desired pattern is based on the ability to uniformly deposit resist polymers on the surface of the substrates where the patterns have to be transferred.

Linear coating tools based on the Driven Assembly Process for ultra-uniform ultra-thin monolayer and polymer film deposition have been created for next generation industrial coating production [1]. This approach has provided impressive results in different sectors such as catalysis and fuel cells, optical devices and photonics, flat panel displays, Photo Voltaic cells, flexible electronics, micro- and nano-electronics and nanolithography. Thinness, uniformity and molecular orientation are all synonymous with performance, reliability and lower costs.

The semiconductor industry and lithography processes are rapidly approaching the ultimate limit, the atomic level. The SP method is a process that builds films one molecule at a time with the speed, reliability and quality required for current and future lithography specifications.

Reducing the size of patterned features for each technology node has enabled faster microprocessors and smaller, less costly integrated circuits on semiconductor wafers [2].

Advantages of ultra-thin films for microelectronics and microlithography have been reported and demonstrated for decades [3-4]. In 1983, monolayers were proof-tested and it became obvious from the point of view of specialists in monolayers that ultra-thin films (≤ 10 nm) could be tailored to any specific requirement down to one single molecular monolayer (≈ 1 nm).

In 1994, W. Lu et al. in "Superiority of Langmuir-Blodgett resist films in electron beam lithography as demonstrated by the backscattering yield" reported that for fabricating ultra-thin films the "bottom-up" approach remains the best choice [5].

Writing and quality control costs could be strongly reduced with UTPF technology. Slimming, backscattering, surface roughness and resist overheating due to high energy e-beam writing can be drastically reduced with ultra-thin resist coatings.

Resist costs continue to increase due to the high cost of research and development. The SP method significantly reduces the waste found with spin coating processes. Essentially, there is no waste with the SP process.

Additionally, current spin coating processes require edge bead removal and have high resist and solvent waste that require costly disposal.

Herein, we provide results showing that linearly coated deposited film edges are in the same range of the film thickness. For example, in the case of a micron thick resist film, our results are indicating a 1000 times smaller film edge than obtained with spin coating. This result eliminates the need for edge bead removal, hence, reducing coating and equipment costs.

Results for three resists are presented. PMMA, SP1813 and DUV-1400 were diluted to nanometric scale. E-beam lithography was done on the 8 nm PMMA resist film and DUV was done on 30 nm DUV-1400 and SP1813 films to demonstrate film performance and to verify that no loss in material functionality occurred. Substrates were all coated with uniform ultra-thin films at a rate of one linear meter per minute, with atomic smoothness. Defect density is quite low because the method works in high compression.

Additional activity in underway to determine defectivity of these films.

2 Spinning Artifacts

Spin coating is essentially a pulling process where the photoresist is spread out and thinned down due to the high rotational speed of the substrate. Complex hydrodynamic environment, disjoining pressure, surface tension and evaporation are common physical and chemical variables contributing simultaneously to the quality of the film during spin coating. Striations, edge bead, streaks, material loss and environmental impact are some of the most important problems associated with spin coating [6-8].

Spin coating becomes extremely challenging below 100 nm. Thinning down polymers to less than 100 nm in thickness implies supersonic speed at the edge of a 6-inch blank. Surface tension and disjoining pressure start becoming extremely important because at few nanometers thick, the solution surface starts collapsing with a force that is inversely proportional to the 6th exponential.

In the end, spin coating is a complex process that faces tremendous challenges with respect to surface roughness and thickness control due to its intrinsic concept. On the contrary, the linear coating process is gentle, works by compression and it is a “bottom-up” process.

3 Linear-Assembly Process

3.1 The Method

Linear coating technology was created to provide significant improvements for the deposition of monolayers and building of films at the molecular scale. Depositing monolayers is not a novel process. However, making

monolayers and ultra-thin films in a continuous, well-packed, uniform way is a novel approach.

The construction of ultra-thin films by the SP method is performed by sliding elements on the surface of a liquid until they meet the ultra-thin film formation line. In this process, the natural flatness of liquid surface is used, and its flow is the driving force that packs the elements (particles or molecules) one against the other in an orderly and continuous manner. At the same rate the elements are being deposited onto the interface and packed at the formation line, the monolayer is transferred from the liquid surface onto a solid substrate. The whole process works in a dynamic and continuous equilibrium.

A linear meter per minute, typically means, for a molecular scale element, one billion elements per second that are integrated in the monolayer matrix with our present linear coating tools.

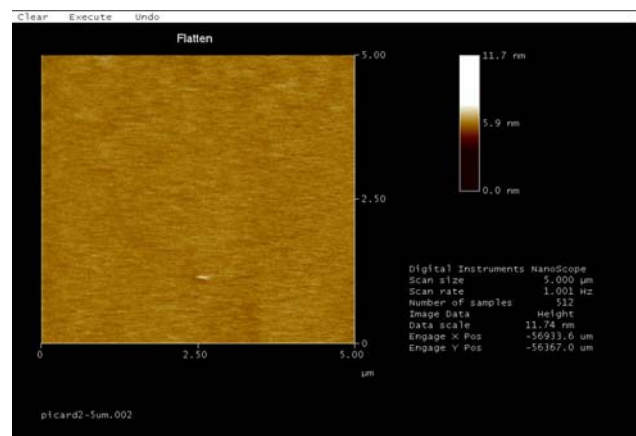


Figure 1. AFM image of PMMA ultra-thin film. The appearance is featureless, except an airborne dust. The thickness is 1.2 nm, which fits perfectly the expected value. AFM analysis shows 0.1 nm surface roughness.

To date, monolayers of many kinds and types of elements have been produced and displayed. Ultra-thin films are made in the same way and at the same production rate. Polymer film thickness can be tailored to have different values starting at 1 nm thick with a mean roughness at the atomic scale (0.1 nm) (see Figure 1). Thicker polymer films can be engineered with typically a surface roughness under 1 nm.

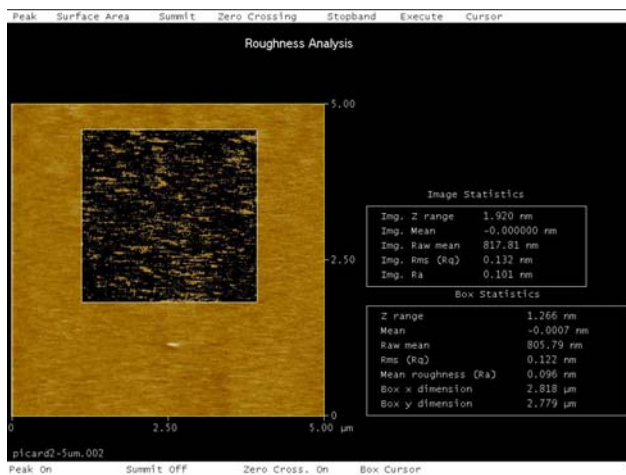


Figure 2. Typical results with PMMA film deposited by our Linear Coating Tool. The AFM analysis confirms a 0.1 nm surface roughness.

3.2 Polymer Deposition

During the SP method of ultra-thin film deposition, polymer solutions are applied at the gas-liquid interface. The receiving phase or the sub-phase is a moving flat liquid. After injection, the polymer solution thins down in different ways depending on the physico-chemical characteristics of the solvents and liquids. Evaporation and immersion are the main ways in which the solvent concentration, after spreading the polymer, fades down from the gas-liquid inter-phase. This dynamic continuous process transforms the polymer solution from liquid to solid as shown in Figure 3. The solution starts in the liquid phase, moves toward a gel phase and ends at the formation line in the solid phase being deposited simultaneously on the substrate; wafer or photomask blank.

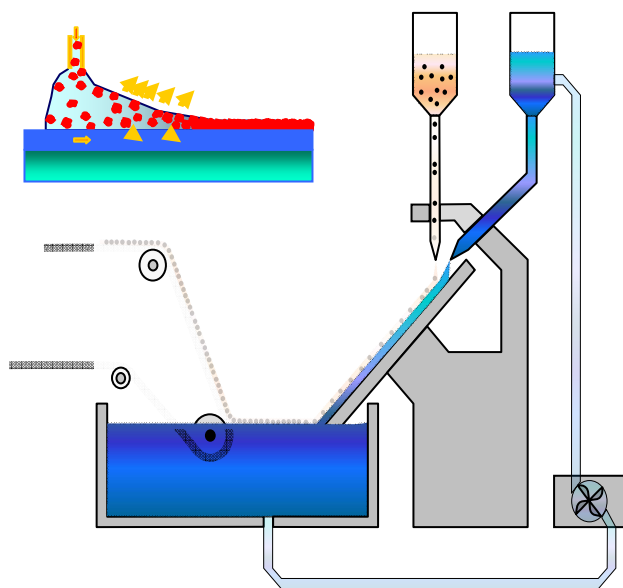


Figure 3. UTPF and monolayer deposition diagram.

The gas-liquid interface natural properties like flatness, mobility and tension, together with other natural forces such as gravity are elegantly used with the proprietary process. The material attached at the interface is hydrodynamically driven one after the other toward and onto a film formation line. The pressure applied onto the film's long axis is kept constant while the film is transferred from the liquid surface toward the solid substrate.

The pressure inside a monolayer is about 300 atmospheres for a 1 nm layer. Such a compression level means that no lateral forces on the solid surface are likely to rupture the thin film. In fact, thinness as small as one nanometer with PMMA has been achieved, with no pin holes and defects. To date, detected defects are caused primarily from environmental particles and not from surface or resist particles.

The process was invented to resolve a basic problem with quasi-static monolayer methods: self-organization [3]. High speed hydrodynamics for mass production also cures defects in monolayers and ultra-thin films. Because of the speed, molecules and polymer chains are driven at the interface with preferential direction preventing self-organization by random motion. This linear method is a driven-assembly process.

3.3 Main Characteristics of the SP Method for Ultra Thin Polymers Deposition

3.3.1 Substrate Size: Independent of size of the surface, namely all wafer sizes currently used by the semiconductor industry and blanks for the photomask sector.

3.3.2 Compression Instead of Tension: The polymer is assembled in a compression mode, up to 300 atmospheres for a film with few nanometers thick. No stress and forces pulling apart the polymer are implicated in the process.

3.3.3 Surface Roughness: Surface roughness of the polymer is in the order of an Angstrom.

3.3.4 Polymer Thickness: Can be tailored with ease to have different values starting at 1 nm thick. The uniformity is constant across the whole substrate.

3.3.5 Linear Production: Production rate is in the order of the square meter per minute.

3.3.5 Edge Bead: There is practically no edge bead. At the very edge of the film, a tiny meniscus is observed. Its size is less than 1000X smaller than current spin coating edge bead. For ultra-thin films, the edge is negligible.

3.3.6 Conformal: Films as thick as several microns have essentially perfect conformality to topographic surfaces.

4 Results

4.1 Surface Topography

AFM, SEM and ellipsometry are used to control and characterize the polymer and resist films. Substrates with different shape, size, and surface affinity were coated with no distinction.

PMMA is a classical polymer for spin coating. Large surfaces such as 300 mm wafers or 6-inch photomasks are difficult to coat uniformly. Using a PMMA/chloroform solution, ultra-thin films were produced. Layers down to of 1.2 nm with a surface roughness of only 0.1 nm, i.e. an atom thick were obtained with ease. The production rate of such films is in the order of a linear meter per minute. Higher deposition rates are achievable.

Ellipsometry data of various polymers have been obtained as well. Figure 3 shows the topography of a typical resist coated wafer with 70 nm UV-1400, ultra-thin DUV resist obtained with the Linear Coating Tools. Differences in colour show a full thickness variation lower than 1 nm, across the entire 8-inch silicon wafer. Data was obtained generously from Horiba Jobin Yvon Team with their new fast mapping spectroscopic ellipsometer, the MM-16.

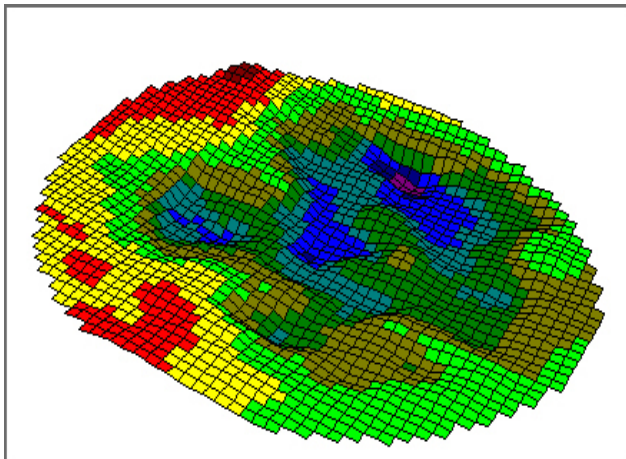


Figure 3. Ellipsometry image of a 70 nm UV-1400 Nanometrix ultra-thin DUV resist. Full thickness variation obtained is lower than 1 nm, across the entire 8-inch silicon wafer.

4.2 E-Beam and Photolithography

Polymers were bench tested to see the potential impact of this deposition method in nano- to microelectronics. PMMA, DUV-1400 and Shipley 1813 resist have been used for lithography demonstration. All of them have shown our ability to perform ultra-thin film lithography at 360 nm, 245 nm and e-beam. All polymers were

transferred to rigid substrates such as silicon wafers, glass and quartz substrates with ease.

4.2.1 E-Beam Lithography

PMMA is a common e-beam resist. It has been suggested in literature that a 5 to 7 nm PMMA coating would be the best target to avoid backscattering artifacts from e-beam pattern generation. In this case, 2, 4 and 8-inch silicon wafers were coated successfully with PMMA. Figure 4 shows a sectional analysis of patterns obtained with an 8.3 nm PMMA thin resist. E-beam direct writing was performed from few microns down to 25 nm line width patterns. These features were obtained with 1070 down to 240 $\mu\text{C}/\text{cm}^2$ doses, showing our ability to obtain nanometer size features with operational conditions with a broad exposure dose range.

It is clear that high acceleration voltage gives better resolution (low blur) and low acceleration voltage implies higher throughput (more blur). To be able to reach finer nodes, extremely thin resist processes are needed for low acceleration voltage in order to make forward scattering in resist smaller, hence increasing line resolution and yield [6]. Moreover, thin resist processes are suited and necessary for finer nodes in order to avoid pattern collapse. To maintain and improve throughput, low acceleration voltage is viable with ultra-thin resists such as the ones obtained with this process.

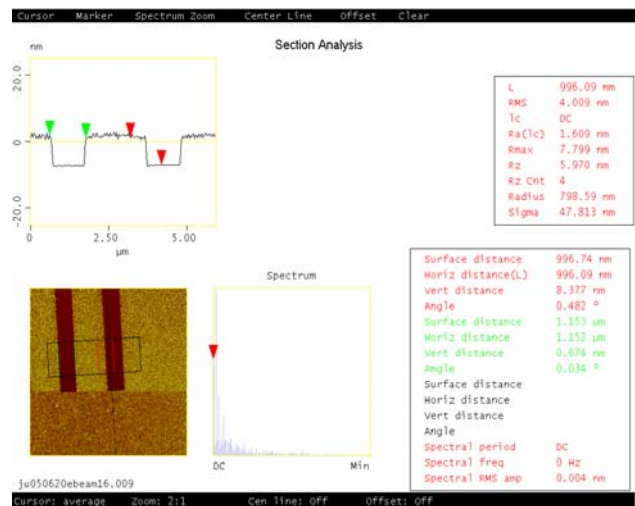


Figure 4. AFM section analysis image showing an 8.3 nm PMMA resist. Lithography was performed with direct e-beam writing.

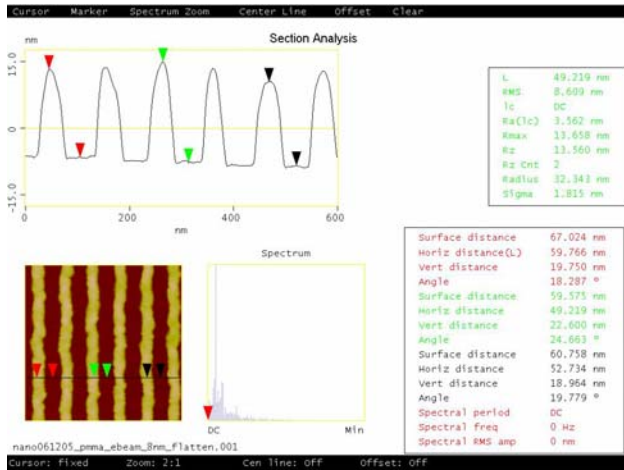


Figure 5. AFM section analysis image showing a 20 nm PMMA resist 25 nm half pitch. Lithography was performed with direct EB writing.

4.2.2 Photolithography: DUV resist

Mask fabrication is accomplished with both e-beam and optical pattern generation. UV, DUV and e-beam resists are common materials used in both e-beam and optical mask pattern generation. UV-1400 resist from Rohm and Haas was used for lithographic demonstration.

Figure 6 shows an optical image of a 30 nm resist pattern, transferred successfully after 248 nm DUV exposure and development.

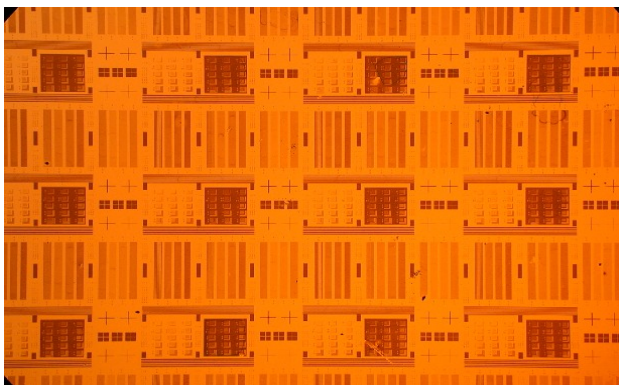


Figure 6. 30 nm DUV resist patterns obtained after exposure and development on a silicon wafer.

Figure 7 shows a higher magnification image of the same substrate, obtained with SEM. Some defects can be seen. In fact, this lithography demonstration was performed outside of the clean room. Some particles were deposited during the process showing our ability to perform the resist coating without major artifacts from particles and without “comets” normally found in spin coating.

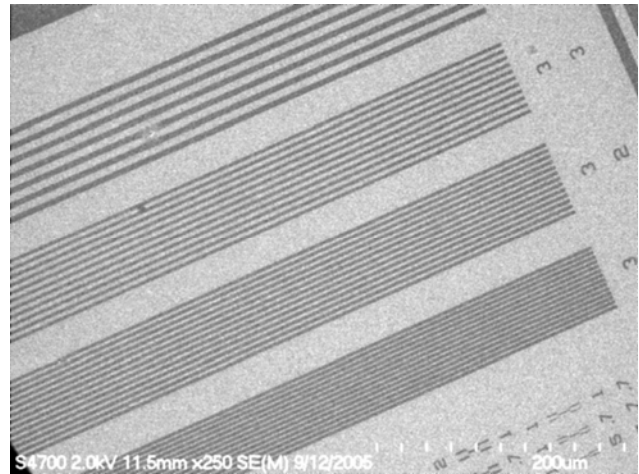


Figure 6. SEM image of 30 nm UV-1400 DUV resist. Coating was performed outside our clean room. Dark regions are the remaining resist after development.

4.2.3 Photolithography: I-Line resist

I-Line resists such as Shipley 1813 were used for demonstration. Patterning was transferred and created successfully by photomask direct contact as well as by interferential approach.

Figures 7 and Figure 8 show AFM analysis of 30 nm Shipley 1813 resist coatings on silicon wafers. Figure 7 shows resist lines in the range of 30 nm separated by 20 nm grooves obtained after exposure and development. We clearly see that our coating process is able to perform at the limits of this particular resist capabilities. Shipley 1813 is composed of polymeric units in the range of 20 nm diameter on average.

The right side of Figure 7 clearly shows edge roughness due to the size of the polymeric material used to formulate the resist. Line roughness best case limit will be, in average, in the 10 nm range (half the average diameters of the polymer).

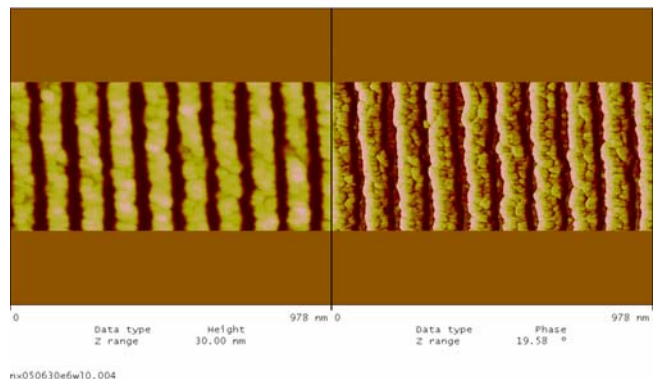


Figure 7. Interferential patterns obtained with Shipley 1813 resist for lithographic demonstration.

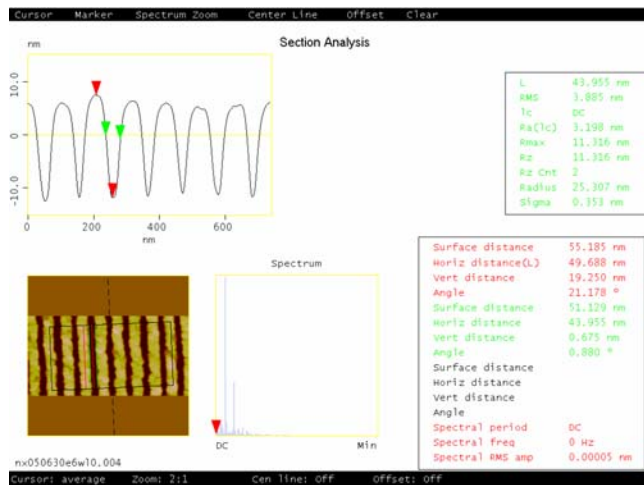


Figure 8. Results of AFM analysis on interferential patterns obtained on SP1813 for lithographic demonstration. Results obtained are in agreement with expected values.

4.3 Film Edge and Conformality

Resist film edge bead is an unwanted artifact of current spin coating processes. This artifact requires the need for edge bead removal which is a costly process in terms of yield, solvent waste and time. The advantage of the SP method is that the need for edge bead removal is obviated.

Additionally, resist film conformality is required in many lithography levels to uniformly coat surface topography. The SP method provides for uniformly conformal films.

Figures 9 through 13 provide the results for edge bead and conformality.

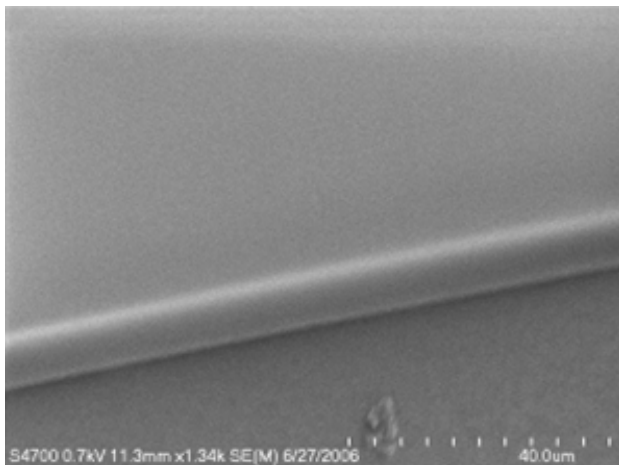


Figure 9. SEM of AZ 9060 film edge. Film thickness is in the order of 5 microns. A rounded edge is obtained in the same size range.

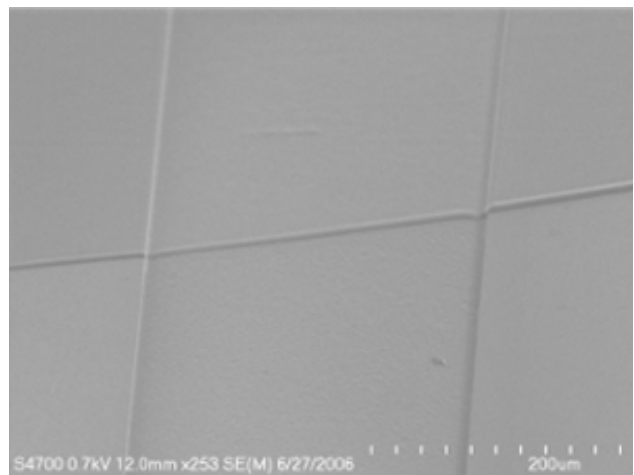


Figure 10. SEM of AZ9060 film edge. Film thickness is in the order of 5 microns. An arbitrary deposition region on top of a substrate with previous topography is shown. Film edge is not affected by topography.

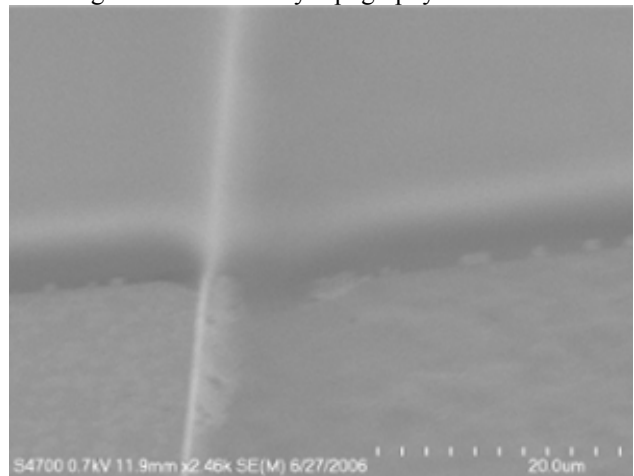


Figure 11. Higher magnification of SEM in Figure 10 showing how the polymer follows the topography.

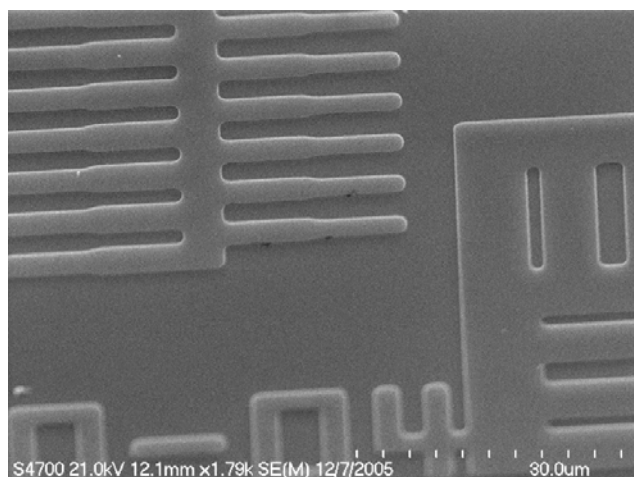


Figure 12. SEM of 10 nanometer thick DUV resist over a silicon substrate with previous topography.

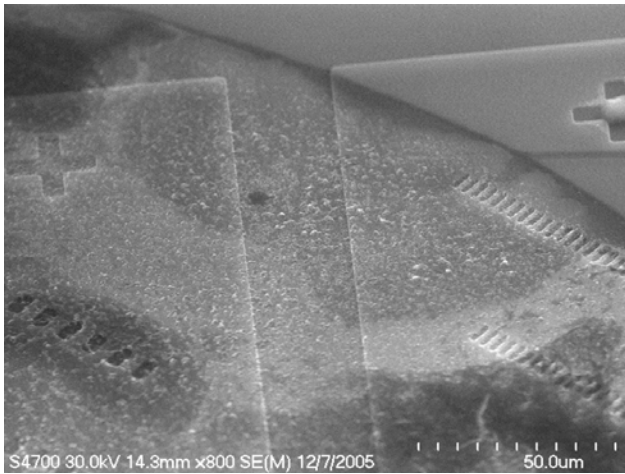


Figure 13. SEM of 10 nanometer thick DUV resist over a silicon substrate with previous topography after acetone drop deposition revealing the presence of the resist over the silicon substrate.

5 Discussions and Future Work

In this paper, we have demonstrated that the Linear Coating Technology is a breakthrough process capable of atomic resist thin films smoothness deposition suitable for next generation mask making and lithography processes. Instabilities responsible for the formation of dewetting and pin holes can be avoided with this process to ensure stable, smooth, continuous, uniform and pinhole-free films.

We have demonstrated the ability for e-beam and optical lithography at nanometer scale thicknesses independent of the substrate size. Slimming, backscattering, surface roughness and resist topography modification due to overheating could be reduced significantly with our coatings, with great potential for yield improvement and costs reduction.

Conformal behavior up to micron micrometer thick resist has been demonstrated and film edge in the range of the thickness of the resist are commonly obtained with the linear coating tools eliminating edge bead artifacts present in standard spin coating methodologies.

Resist consumption with the Linear Coating Process has been demonstrated to be highly efficient. Less than 20 % of resist material is wasted with linear coating compared to an average 80% using current spin coating technology. Therefore, a 4X improvement efficiency and huge waste reduction is obtained, meaning an important economy.

Lithography options for the coming technology nodes such as 1X masks, 4X reticles with sub-resolution features or the nano-imprint lithography (NIL) require features finer than those on current 4X reticles [9]. Ultra-uniform SP resist films made with the Linear Coating Tools could

reduce risk and smooth out the next technology transition in the mask and lithography industry.

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