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Top-Surface Resists for Lithography with Strongly Attenuated Radiation

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Top-Surface Imaging Resists for Lithography with Strongly Attenuated Radiation

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ABSTRACT

Strong resist photoabsorption at wavelengths below 248 nm necessitates the use of a thin layer imaging (TLI) scheme for microlithography using 193 nm, 157 nm, or 13.4 nm radiation. Previous to this work, a TLI process commonly known as silylated top surface imaging (TSI) was developed by a Sandia/AT&T team for use in extreme ultraviolet lithography (EUVL) at 13.4 nm. Using this bilayer process, 0.13 μm resolution with 87° sidewalls in 0.7 μm of resist was achieved for EUV exposures. New imaging layer polymers, silylation reagents and crosslinkers, and process conditions were screened for improvement in this TSI process with the ultimate goal of demonstrating a resist technology capable of 0.10 μm critical dimension (CD). The results of these attempted improvements to the TSI process are described in this report.

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TOP-SURFACE IMAGING RESISTS FOR LITHOGRAPHY WITH STRONGLY ATTENUATED RADIATION

I. INTRODUCTION

The work described in this report was conducted from April 1996 through September 1996 as part of the Laboratory Directed Research and Development (LDRD) program in the area of microelectronics and photonics sponsored by the Department of Energy under contract DE-AC04-94AL85000. The goal of the work was to screen new resist formulations, silylation reagents, and TSI processing conditions for improvements that would lead to the demonstration of 0.10 μm resolution for EUV lithography.

Resist Requirements for EUV Lithography

Specific demands on the photoresist arise in EUVL due to the unique nature of an imaging system using 13.4 nm radiation — the relatively low photon flux achievable at the wafer plane, the use of a vacuum to prevent photon absorption by gases, and the strong attenuation of the radiation in virtually all organic resist materials. (1) Because radiation with wavelengths below 248 nm is so strongly attenuated in organic resists, a thin layer imaging (TLI) process is necessary for EUVL, as well as other candidate technologies such as 157 and possibly 193 nm lithography. For EUVL throughput considerations, it is estimated that the required dose for this TLI process will be about 10 mJ/cm^2 , suggesting that only chemically amplified resists can be used. A limit on the line edge roughness is estimated to be about 5-10 nm to control CD variation at less than 10% of the linewidth at the desired resolution of 0.10 μm . The thickness of the pattern resist must be greater than 0.3 μm to cover existing topology, but probably less than 0.6 μm , and the sidewall angles are expected to be at least 88°. Finally, both positive and negative tone TLI processes are desired, but the positive tone process would be preferred if only one tone proves to be manufacturable.

TLI Processes for EUV Lithography

Several TLI processes have been identified for potential use for EUVL, and the common theme in these approaches is the transfer of the aerial image to a thin layer of refractory-containing material, which is then used as a dry O_2 etch mask during a subsequent pattern transfer to the device layer. (2) The refractory material is almost always silicon, which provides a SiO_2 etch mask in the O_2 etch process. One TLI process that has been extensively examined for EUVL is the silylated top-surface imaging technology (TSI) shown in Figure 1.

The bilayer shown in Figure 1 consists of an organic planarizing layer spun over an existing device topology, followed by a thin, top layer of imaging resist. The bottom layer is generally a crosslinked novolac resist (4000-5000 Å), while the top layer is 1500-2000 Å of a chemically amplified negative tone resist. The bilayer is patterned by exposure of the top layer using EUV radiation followed by a post-exposure bake step in which photogenerated acid catalyzes a crosslinking reaction. The bilayer is subsequently exposed to a gaseous silylation reagent, usually an aminosilane, that will ideally diffuse only into the unexposed,

uncrosslinked areas, where incorporation of the silicon-containing reagent induces a volume swelling (Figure 2). However, because the crosslinking is partially incomplete at the surface due to environmental effects, a very thin layer of silylated resist is formed across the exposed regions as well (Figure 1). This layer of adventitious silylation is removed in a short, non-selective plasma etch called a breakthrough etch, which is followed by a longer anisotropic O_2 etch to transfer the pattern down to the device level. During the O_2 etch process, a thin SiO_2 etch mask is formed from the silylated material. Greater silicon content in this mask means greater resistance to the oxygen etch and better pattern transfer.

Figure 1: TSI silylated bilayer process for thin layer imaging with strongly attenuated radiation.

The characteristics of this silylated layer largely determine the ultimate lithographic performance of the TSI process. Low silicon content, low etch resistance, large pattern distortion upon swelling, or large amount of silylated resist flow all lead to loss of resolution and poor lithographic performance. Previous work by Wheeler and Taylor (3) showed that low silicon content and etch resistance can be improved by switching from a monosilane to a disilane silylating reagent. However, unacceptable amounts of pattern distortion and resist flow was observed if pure disilane was used as the silylation reagent. Wheeler and Taylor (4) demonstrated that silylation with disilanes reduced the glass transition temperature (T_g) of the resist from above $70^\circ C$ to below room temperature which accounted for the large amount of silylated resist flow seen in cross sectional experiments. The solution to this problem was the use of a few weight percent of bis(amino)disilane to act as a crosslinker to control flow.

TSI Process using a Two-component Disilane Reagent

Based on the work of Wheeler and Taylor, a TSI process was developed by Sandia for EUVL that produced images with $0.13 \mu m$ resolution with 87° sidewalls in $0.7 \mu m$ of resist (Figure 3). The silylation reagent used for this demonstration was a 95/5 wt.% mixture of dimethylaminopentamethyldisilane (PMDS) and a crosslinker, bis(dimethylamino) tetramethyldisilane (BDMATMDS). The use of this two component reagent, however, presented process control problems because the volatility of the crosslinker was significantly less than that of the

major component. The result was fractional distillation from the mixture which made reproducibility impossible. Acceptable results were obtained only when fresh reagent mixture was charged in the heated delivery vessel of the commercial silylation tool.

Figure 2: Chemistry of chemically amplified crosslinking and resist silylation.

Another undesirable aspect of this particular TSI process was the considerably long breakthrough etch required to remove all of the adventitious silylation prior to pattern transfer. New resist material and silylation reagents that greatly reduce the amount of unwanted silylation will be needed before the TSI process can be used in microelectronic fabrication.

(a)

(b)

Figure 3a: 0.3, 0.25 (foreground), 0.2 and 0.15 μm (background) lines and spaces printed with silylation reagent PMDS/BDMATMDS. Figure 3b: close up of 0.15 μm lines and spaces.

II. EXPERIMENTAL

Equipment

The resist coated wafers were prepared by spin coating and soft baking the wafers with an SVG-90 wafer track. Thickness of resists were determined using a Nanospec 4000 with parameters for negative tone resists on silicon.

Exposures using 193 nm radiation were done at Intel Corporation on a ISI ArF 193 nm high NA stepper with an internal dose monitor. EUV exposures were performed on the 10xII microstepper at Sandia/CA.

Silylations were performed on a Genesis Microstar 200c silylation tool at Intel Corporation and an experimental tool built by Yield Engineering Services under contract to Sandia National Labs. Incorporation of silicon was estimated in most cases by measuring the amount of swelling in the resist with the Nanospec.

Breakthrough etching and final pattern transfers using an oxygen plasma etch were done in a Lam TCP 9400 etcher at Intel Corporation.

Materials

Resist formulations were provided by the Shipley Company. XP-9472 is a novolac based resist containing a proprietary photoacid generator (PAG) and a crosslinking agent. The silylation reagent PMDS was obtained from Silar, and the crosslinking agents, BDMATMDS and bis(dimethylamino)ethylmethyilsilane (BDMAEMS) were provided by D. R. Wheeler at Sandia/NM. The synthesis of these materials will be reported in a subsequent SAND report.

III. RESULTS AND DISCUSSION

Stable Two-Component Silylation Reagents for the TSI Process

For a two-component silylation reagent to be useful in a robust manufacturing process the volatilities of the components must be matched to prevent fractional distillation. Therefore, a primary goal of this work was to identify a bifunctional aminosilane with a volatility close to the volatility of PMDS (b.p. 149 °C). There was no obvious choice among potential disilane crosslinkers (Table I), so the monosilane, bis(dimethylamino)ethylmethyilsilane was synthesized and chosen for evaluation with PMDS. Mixtures of BDMAEMS and PMDS could not be separated on a Carbowax capillary column of a gas chromatograph, which was strong evidence that the two components had volatilities close enough to use together in TSI silylation.

Silylation reagent	Boiling point (760 torr)
BDMATMDS	196°C
(Et ₂ N) ₂ SiMe ₂	81°C
(Me ₂ N) ₂ SiMe ₂	128°C
(Et ₂ N)SiMe ₂ H	109°C
(Me ₂ N) ₂ SiMeH	112°C
(Me ₂ N) ₂ SiMeEt	146°C

Table 1: Boiling points of commonly used silylations agents and crosslinkers

A procedure for the BDMAEMS/PMDS silylation of single layers of XP-9472, the same novolac-based resist used for the exposure in Figure 3, was established. A series of formulations were tested in the silylation tool to determine the percentage of crosslinker required to allow for reasonable amounts of Si incorporation while minimizing flow. The hot block of the Genesis silylation tool was typically charged with 50 mL of reagent and heated to 110 °C *in vacuo* to generate approximately 230 torr of gas pressure. Typical silylation times were 30-120 seconds. A formulation of 10% crosslinker was found to be the optimal formulation for novolac-based resist which typically produced 1200Å of swelling. To understand wafer-to-wafer stability, a lot of six wafers was silylated at 90 °C, 100 torr chamber pressure, and 120 seconds reaction time. The silicon uptake results are shown in Table 2.

Wafer Number	Initial Thickness (Å)	Final Thickness (Å)	Change (Å)
1	1694	2959	1265
2	1644	2971	1327
3	1625	2927	1302
4	1624	2950	1326
5	1616	2923	1307
6	1608	2933	1325

Table 2: Silicon uptake (swelling) for BDMAEMS/PMDS silylation of XP-9472 resist

The uniform data in Table 2 indicates that the BDMAEMS/PMDS silylation mixture is stable and not fractionally distilling. The pressure in the hot block remained around 230 torr for days and several sets of experiments. This type of wafer-to-wafer consistency and stable hot block pressure was not seen for even small lots of wafers silylated with the original BDMATMDS/PMDS reagent mixture.

CONCLUSIONS

During the six months of this LDRD we have synthesized a matched volatility cross-linker (BDMAEMS) for PMDS and tested this new mixture with silylation experiments. The percentage of crosslinker by wt. was established for a novolac-based resist. As expected, the formulation improved wafer-to-wafer process stability.

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