



Chemically Amplified Molecular Resists for E-Beam Lithography

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Computers get more powerful every year. Powering this improvement has been our ability to cram ever more transistors in to ever smaller spaces. This has been possible because of improvements in photolithography (PL), which is used to print the transistors onto a silicon wafer using light. The smallest feature that PL can produce is limited by the wavelength of light used because of diffraction, and over the last forty years increasingly short wavelengths have been needed to continue the improvements. In order to continue the evolution of computers we need a new type of lithography. One alternative is electron beam lithography (EBL). EBL can already be used to create transistors much smaller than in current chips. However, it is very slow. A PL system can make more than 50 wafers of computer chips every hour, whilst EBL systems can make less than 10. One way to improve the speed is to make the resist more sensitive to electrons. A more sensitive resist needs fewer electrons to record an image and the machine can therefore run faster. Currently resists are available that are either fast but can't record very small features or that are slow but capable of recording fine patterns. Fast resists often rely on a process called chemical amplification (CA), where one electron is used to create an acid in the resist that reacts with several resist molecules – amplifying the effects of each electron. However, the acid moves about within the film and this diffusion reduces the resolution of fast resists. We are investigating chemically amplified resists where the typical polymeric material is replaced with small molecular material. Small molecules mean that the acid does not have to diffuse as far before it reacts, and chemically amplified molecular resists have demonstrated a promising combination of resolution, line width roughness (LWR), and sensitivity.



Feasibility Project

Here we present the characterization of a molecular resist system based on a fullerene derivative. The chemically amplified fullerene resist was composed of (a) the fullerene derivative MF07-01, (b) a photoacid generator, (c) an epoxy novolac crosslinker and (d) an optional base additive (see Fig 1), which has previously demonstrated sparse feature resolution of 12 nm, a half pitch resolution of 20 nm, sub 5 nm LWR, sub 10 $\mu\text{C}/\text{cm}^2$ sensitivity, and high etch durability. Resist films were prepared by spin coating on hydrogen terminated silicon substrates, followed by a post application bake (PAB). Lithographic patterning was performed with an FEI XL30SFEG scanning electron microscope equipped with a Raith lithography system, and followed by a post exposure bake (PEB), and development. Resist sensitivity was evaluated at a beam energy of 20 kV, whilst high-resolution lithography was performed at 30 kV with electron current of 30 pA.

We have studied the effects on resolution, sensitivity and LWR of varying the casting solvents; PAB temperature and time; composition of the resist with respect to component ratios; crosslinker; PEB temperature and time; post exposure delay (PED) and developing solvents. Casting solvents included anisole, propylene glycol methyl ether acetate (PGMEA) and chloroform, whilst chlorobenzene, anisole, IPA:H₂O, PGMEA, xylene, methyl isobutyl ketone (MIBK) and TMAH were examined as developer. PABs of 75 to 100 °C and 1 to 30 minutes duration; and PEBs of 75 to 135 °C for 1 to 9 minutes were applied.

The resist sensitivity, resolution and LWR were not significantly affected by the range of PEB temperatures and times. Indeed a PEB was not required at all in order to observe high resolution high sensitivity behavior from the material implying that this is a low activation energy resist. However, the resist was extremely stable under ambient conditions and for PEDs of more than 24 hours, regardless of whether a PEB was applied, showing that the PEB step can be eliminated for this resist (see Fig 2), and furthermore that the chemical amplification reaction in the material is in some way self limiting. PAB improved sensitivity and reduced pattern collapse. Resist component ratio, developing solvents, density of a line-space pattern or exposure dose were found to significantly impact resist LWR. The resist LWR was between 3 and 4 nm for sparse patterns under standard processing conditions, and slightly higher in dense patterns (see Fig 3). LWR of less than 2.0 nm was seen under certain conditions (see Fig 4).

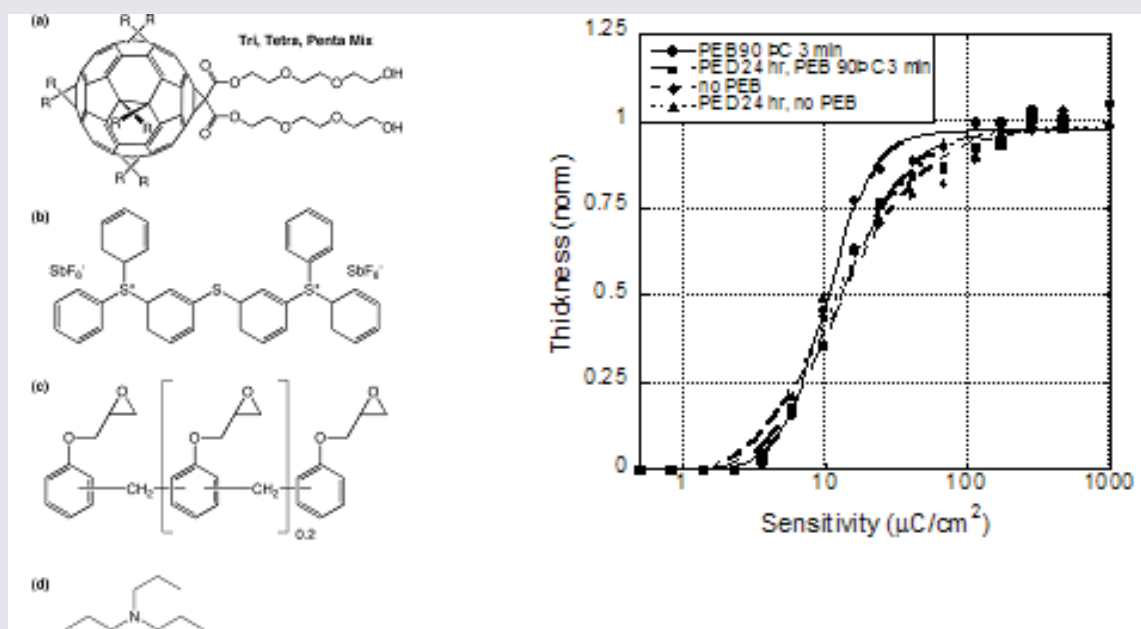


Figure 1. Three component chemically amplified fullerene resist system: a) the fullerene MF07-01, b) a photoacid generator triarylsulfonium hexafluoro antimonate salt (Dow, UVI-6976) and c) epoxy novolac crosslinkers. Figure 2. Response of resists cast with PGMEA to 20 keV electrons. PAB was 75 °C for 15 minutes. Combinations of PEB and PED were applied. Development was in MCB:IPA for 10 s, with IPA rinse.

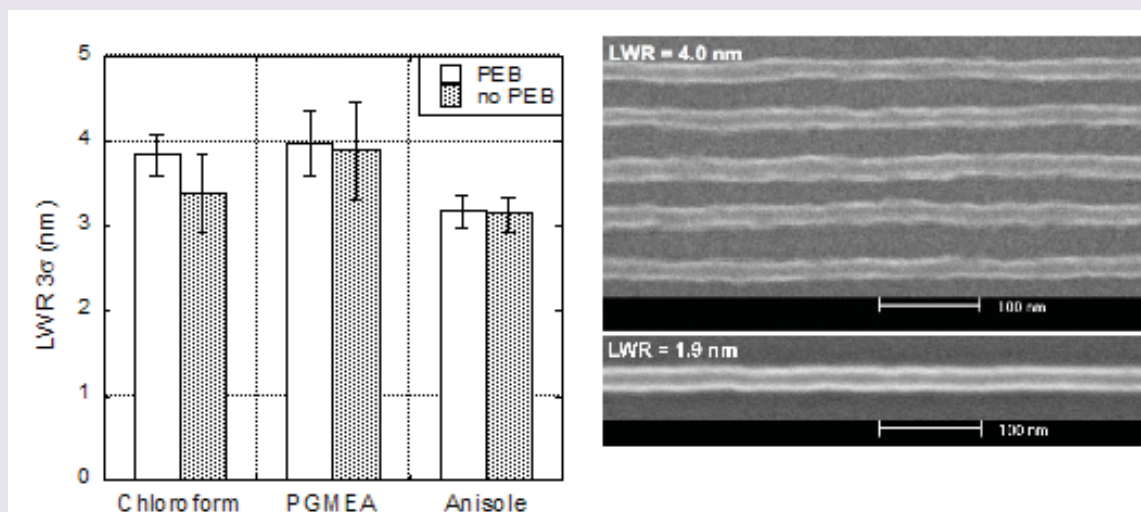


Figure 3. Comparison of LWR of sparse lines in the resist cast with chloroform, PGMEA or anisole. PAB was varied. PEB was 90 °C for 3 minutes or not applied. Development was in MCB:IPA for 10 s, with IPA rinse. Figure 4. 25 nm half-pitch dense patterns with LWR of 4 nm, and a 21 nm sparse line with LWR of 1.9 nm.