The Chemistry of Single Layer 157 nm Photoresists

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The continuing demand for device performance improvements in microelectronics has driven the need for printing ever-smaller features on integrated circuits.[1] The minimal feature size that can be printed by optical lithography is directly proportional to the exposure wavelenth.[1,2] Photolithography at 157 nm (F_2 excimer laser) has emerged as the leading contender for the next generation of lithography.[3] A key obstacle for 157 nm technology is the development of photoresists that are capable of high resolution imaging at the 157 nm wavelength.[4]

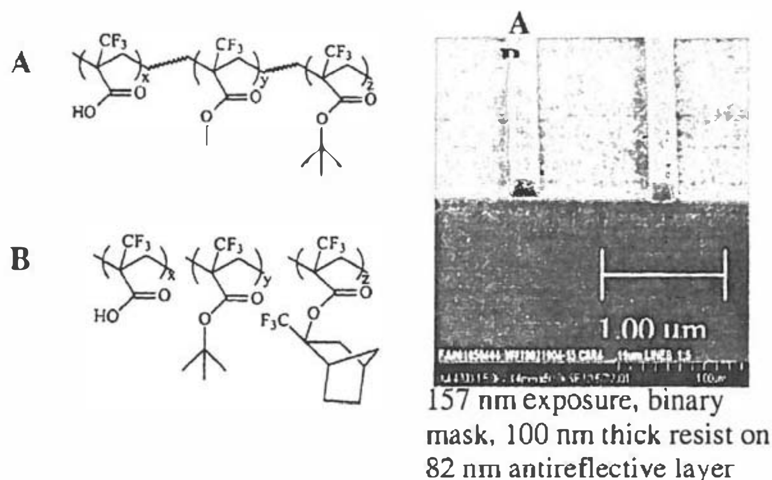
Fundamentally, the design of 157 nm photoresists is the same as that used in previous lithographic technologies.[5,6] Potential resists must meet three requirements common to all chemically-amplified resists. They must have high transparency at the wavelength of exposure, resistance to plasma etching, and the ability to undergo efficient photochemical reactions that change the resist solubility in developer solutions.[5-7] Using a modular approach, the polymer design is broken down into the subunits of etch resistance, developer solubility, and protecting group.[7] These can then be addressed independently of each other.[7] The transparency requirement must be addressed for each subunit.

The transparency of the polymer at the exposure wavelength is crucial to ensure an equal rate of photochemical reaction throughout the exposed resist. The photochemical species is often dispersed throughout the polymer and if the irradiating light cannot pass equally through the resist a gradient of photoproduct will result.[8] This gradient leads to a gradient in solubility of the exposed resist towards the developer, which can deteriorate the resist profile.[8] It has been demonstrated that the higher the fluorine content in polymer the lower the photoresist's absorptivity will be at 157 nm.[9-11]

High plasma etch resistance is desirable to reduce the erosion of the resist material. Plasma etch resistance is achieved by incorporating a high carbon to hydrogen number ratio into the photoresist.[12] Previous photoresist designs have incorporated benzene rings into the polymer to increase the carbon to hydrogen ratio. Unfortunately, π-systems absorb strongly at 157 nm and therefore can not be used in 157 nm photoresists.[9] Alicyclic groups, such as norbornane, that have strategically placed electron withdrawing groups, are being employed in the development of 157 nm resists to increase the etch resistance while minimizing the increase in absorptivity of the polymer. Photoresists that do not incorporate an etch resistant subunit often result in features with poor wall profiles (Figure 1).[1]

Photoresists for 157 nm technology employ chemical amplification technology to change solubility. Chemically amplified resists consist of a polymer that after an acid catalyzed reaction changes solubility and a photoacid generator (PAG).[8] The PAG is the photochemical species and upon exposure to UV radiation will decompose into an acid and other molecules. Triarylsulfonium salts are commonly used as PAGs.[8,13-14] Photoresists for 157 nm technology often incorporate a protected carboxylic acid group; this protecting group is often a tert-butyl or other acid cleavable group.[15] The acid

generated from the PAG catalyzes the deprotection of the carboxylic acid transforming the exposed resist from a base insoluble species into a base soluble species.[8]

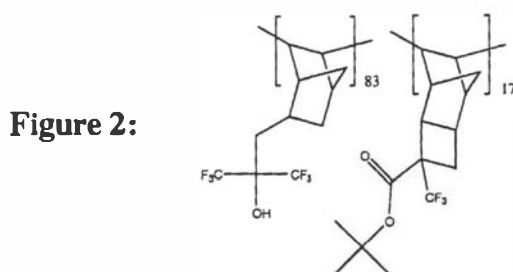


157 nm exposure, binary mask, 100 nm thick resist on 82 nm antireflective layer

Figure 1: Polymer A, a photoresist lacking etch resistance. Polymer B, a photoresist incorporating an etch resistant subunit.

Successes have been achieved in recent years towards the goal of designing a resist with an absorptivity below 1.00 μm^{-1}. Willson recently synthesized a polymer using the monomers 3-(bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)-propan-2-ol and *tert*-butyl 3-(trifluoromethyl)tricyclo[4.2.1.0]non-7-ene-3-carboxylate (Figure 2) with an absorptivity of 1.8 μm^{-1}.[15] While not below 1.00 μm^{-1} it is a significant improvement on the 6-8 μm^{-1} absorptivity typical amount the first 157 nm resists.

Figure 2:



While the major obstacles have been overcome, challenges still remain in designing 157 nm photoresists. One such challenge has been to balance the absorptivity lowering properties of fluorine with its dissolution hindering hydrophobic properties.[11] Research is also being done to eliminate the need for the greatly absorbing carboxylic acid groups. Current research in photoresist chemistry suggest that the first chips using 157 nm technology will be commercialized in 2006.[4]

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