Oxide Nanoparticle EUV (One) Photoresist Studies

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Abstract:

Photo-acid generators (PAGs), key components in chemically amplified photoresists, are decomposed under mid-UV or deep-DV light to release strong acid. Such strong acid catalyzes the deprotection reaction or decomposition reaction of polymer resists, and leads to solubility changes between exposed and unexposed areas. However, PAGs are designed to absorb mid- or deep-UV, and strong acids are less-efficient in inducing solubility changes in metal-oxide nanoparticle resists, which are promising candidates in extreme ultra-violet (EUV) lithography. In this work, click chemistry is introduced into lithography to achieve high-contrast patterns under extremely low exposure dose, e.g., 7.5 mJ/cm², which is 10-20 times lower than the dose used in PAG resist chemistry. Under UV exposure, double bond modified zirconium oxide nanoparticles can quickly react with di-thiol compounds to form insoluble crosslinked networks and lead to clear patterns upon solvent development.

Summary of Research:

In a conventional lithography process, strong acids released by PAGs catalyze the deprotection reaction or decomposition reaction of the polymer resists and induce dissolution differences between exposed and unexposed areas. However, PAGs are usually aromatic compounds that are designed to absorb in the mid- or deep-UV regions, and strong acids are less-efficient in inducing solubility changes to metal-oxide nanoparticle resists. Utilizing zirconium/hafnium oxide (ZrO₂ or HfO₂) nanoparticles, the Ober group has developed a series of hybrid nanoparticles composed of an inorganic core with ZrO₂ or HfO₂ and various organic ligands [1]. These hybrid nanoparticles demonstrate excellent patterning efficiency under extreme ultraviolet (EUV) exposure conditions, due to their much smaller molecular size and higher EUV absorption than polymer resists.

However, the precise patterning mechanism is unclear, due to subtle changes that happen to these metal-oxide nanoparticles, and the role of PAG is rather confusing: PAG can improve the patterning performance; however, it is not an indispensable component in metal-oxide-nanoparticle EUV lithography. Patterns can be obtained without PAG, although there is a considerable decrease in quality; considering PAG’s inefficiency on absorbing EUV light, the entire mechanism becomes quite complicated, and thus leads to difficulty on improving patterning performance.

In this work, click chemistry is introduced into lithography, and high-contrast patterns under extremely low exposure dose are achieved. Thiol-ene click chemistry is a highly efficient, photo-initiated free-radical addition reaction, and under UV exposure, double bond modified zirconium oxide nanoparticles can quickly react with di-thiol compounds to form insoluble crosslinked networks (as shown in Figure 1) and lead to clear patterns upon development.

Middle Ultraviolet (mid-UV) Lithography. To demonstrate the dissolution behavior difference between the non-click and click reaction systems, preliminary lithographic evaluations were carried out using the CNF ABM contact aligner. For the non-click reaction test, the resist formulation contains 5 wt%
double bond modified nanoparticles, and propylene glycol monomethyl ether acetate (PGMEA) as solvent. The resist was spin-coated onto a silicon wafer at 2000 rpm for 1 min and then exposed with 254 nm mid-UV at 150 mJ/cm². For the click reaction system, the test resist formulation contains 5 wt% double bond modified nanoparticles, 0.5 wt% di-thiol compound as crosslinking agent and PGMEA as solvent. To highlight its superior sensitivity, the film was exposed with mid-UV at 150 and 7.5 mJ/cm², respectively.

For the non-click film, after being developed with 4-methyl-2-pentanone (4M2P) for 5s, negative tone patterns can be observed, however, with lots of residues (Figure 2A). Further development, e.g., 7s and 10s (Figure 2B and 2C), still allows the residue to be removed, but the desired patterns become weak and finally completely dissolved when developed for 15s (Figure 2D). For the case of the click reaction based film, after being exposed at the normal dose 150 mJ/cm², high-contrast patterns can be observed, even the film was developed in a much stronger solvent — acetone. Thiol–ene click reaction is a UV-sensitive and highly efficient reaction, meanwhile the reaction products are crosslinked networks (Figure 1), which are recognized for bad solubility or are totally insoluble in common developers. As a result, even the exposure dose was further decreased to 7.5 mJ/cm² — 20 times lower than the normal dose, clear patterns can be observed after being developed in acetone for 15s. It is noteworthy that the solubility change was remarkable, the pattern can be very well preserved after being developed in acetone for 12 or 24 hours (Figure 3C and 3D). Such obvious solubility change has not been observed in previous reports, although the dose used here is extremely low.

**Deep Ultraviolet (deep-UV) Lithography.** Using same the film fabricating condition, the click-reaction film was exposed using CNF ASML stepper (248 nm KrF laser). After being exposed at 25 mJ/cm² and developed in acetone for 15s, well-defined negative tone patterns were obtained, as indicated by scanning electron microscope (SEM) images (Figure 4), taken by CNF Zeiss Ultra SEM. 1:1 line-and-space patterns with the feature size from 1000 nm to 300 nm (Figure 4), in which the exposed area is slightly broader than the target feature size, suggest patterns are over-exposed, although the used dose is quite low.

In summary, click chemistry was introduced into lithography, and achieved high-contrast patterns under extremely low exposure dose. Utilizing click reaction between double bond modified ZrO₂ nanoparticles with di-thiol compound, good patterning performance was obtained under deep-UV exposure. Meanwhile, considering the thiol–ene click reaction is free-radical based reaction while the EUV-photoelectron and secondary electrons are good initiator for free-radicals, this preliminary work indicates such click reaction based patterning are promising candidates for EUV lithography.

**References:**