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Design and Synthesis of Novel Resist Materials for EUVL

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ABSTRACT

The design, synthesis and characterization of non-chemically amplified negative tone electron-beam and EUV resists based on the inclusion of a radiation sensitive sulfonium functional group are outlined.. MAPDST (4-(methacryloyloxy)phenyldimethylsulfoniumtriflate) and MANTMS (1-(4-(methacryloyloxy)naphthalen-1-yl)tetrahydro-1*H*-thiopheniumtrifluoromethane sulfonate) monomers each containing the sulfonium group underwent homo- and copolymerizations using free radical polymerization with 2,2'-azobisisobutyronitrile (AIBN) initiator. These resist materials were evaluated by EB lithography using 20 keV electron beam and EUV lithography to obtain sub-20 nm line patterns. These features were optimized ranging from resist coating, pre-exposure bake, exposure to e-beam, post-exposure bake, development and imaging. Our investigation showed that these newly synthesized resists are potential viable candidates for EUV lithography based on their ability to form flaw free thin films < 50nm, sensitivity, resolution and LER control.

Keywords: Non-chemically amplified negative tone resists, EB lithography, EUV lithography.

1. INTRODUCTION

Extreme ultraviolet (EUV) lithography is one of the most promising techniques for achieving sub-20 nm features as per the most recent ITRS roadmap.[1] EUVL/EBL are highly sensitive processes influenced by several factors, including the selection of resist material and the subsequent protocols ranging from spinning thin films to exposure, development and etching. Currently, the implementation of EUV lithography faces several issues, including the critical challenge of ensuring photoresists that can concurrently achieve narrow line width around 16 nm, low line edge roughness at 3σ (1.5nm), and high photosensitivity at 2-10mJ/cm^2. To address many of the inherent problems of currently used chemically amplified resist technology, e.g. acid diffusion, sensitivity, post exposure instability, the present project encompasses the design and synthesis of resists that are directly sensitive to radiation without utilizing the concept of chemical amplification (CARs). These new resist materials, while highly sensitive to photons of various wavelengths, function as non-chemically amplified resists. This resist design is accomplished by polymeric and molecular resists that are prepared from monomers containing sulfonium groups. In order for a polymer to be directly sensitive to wavelengths, a highly sensitive group must be introduced into the polymer units. Sulfonium groups have long been found to be sensitive to UV photons.[2-6] For this reason, sulfonium groups were chosen as radiation sensitive groups in non-CA resists. Herein the design and synthesis of non-chemically amplified negative tone electron-beam and EUV resists based on the sulfonium and methylmethacrylate functionalities with high sensitivity is presented. The principle behind the molecular design of these resists is predicated on the hypothesis that there is a polarity switch of the exposed regions from hydrophilic to hydrophobic.

2. EXPERIMENTAL

2.1 Materials

The structures of the synthesized monomers, homopolymers, copolymers and a molecular resist classification in this paper are shown in Figures 1 & 3. MAPDST (4-(methacryloyloxy)phenyl dimethylsulfonium triflate), MANTMS (1-(4-

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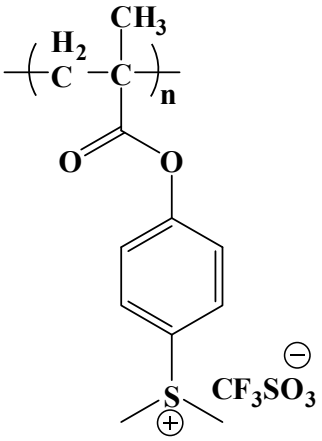
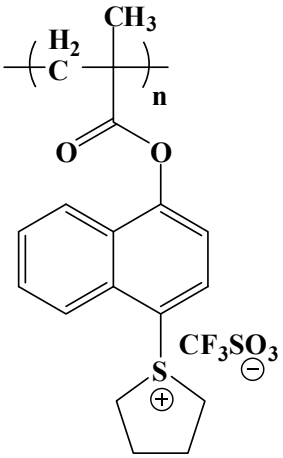
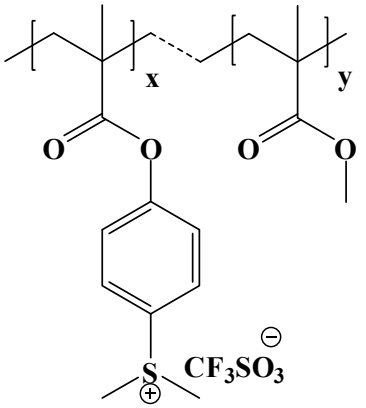
(methacryloyloxy)naphthalen-1-yl)tetrahydro-1*H*-thiophenium trifluoromethanesulfonate) and 4-Hydoxystyrene (STYOH) monomers were synthesized. The monomers, N-vinylcarbazole, 4-carboxystyrene and methylmethacrylate were purchased from commercial sources and used as received. Methylmethacrylate was distilled prior to polymerization.



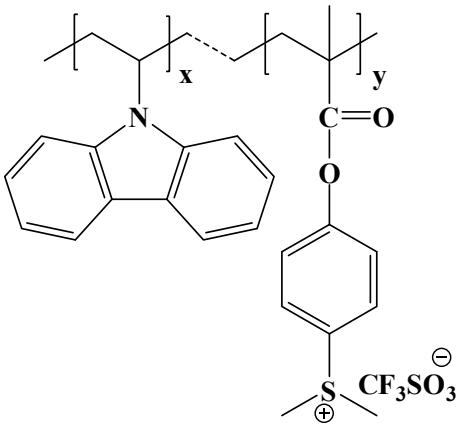
MAPDST homopolymer



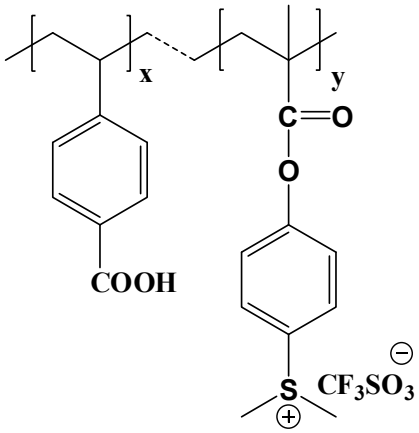
MANTMS homopolymer



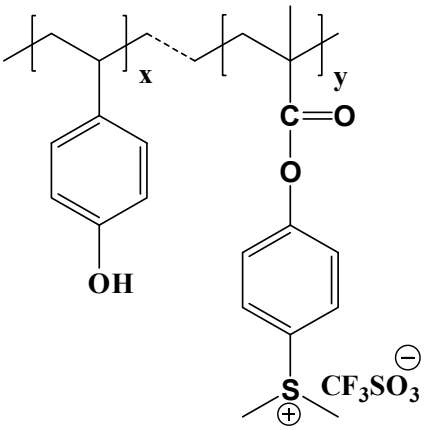
Poly(MAPDST-*co*-MMA)



Poly(MAPDST-*co*-NVK)



Poly(MAPDST-*co*-STYCOOH)



Poly(MAPDST-*co*-STYOH)

Figure 1. Library of photosensitive polymeric resist materials for EUV lithography.

4-Hydroxystyrene was prepared by treating 4-acetoxystyrene with sodiumhydroxide (NaOH) and hydrochloric acid (HCl). Acetonitrile (CH_3CN) and tetrahydrofuran (THF) used for polymerizations were dried using calcium hydride and Na metal, benzophenone, respectively. The MAPDST & MANTMS homopolymers and MAPDST copolymers were synthesized using free radical polymerization method using 2,2'-azobisisobutyronitrile (AIBN) as initiator.

2.2 Resist formulation

Resist solutions were prepared using 3 percent by weight of polymer in methanol and filtered through a 0.2 µm Teflon® filter to remove larger particles if any. These prepared solutions were used in all experiments. Resist formulations were spun cast on 2″ diameter p-type Si (100) wafers purchased from Wafer world, Inc. To remove organic contaminants on Si wafers, they were cleaned by RCA method and given a dehydration bake at 200 ºC for 10 min and finally cooled to room temperature. To dry out the solvent completely on the resist coated wafers, soft-bake was done using hot plate. Resist coated films were exposed at 20 keV beam energy with 20 µm aperture, beam current was 196.8 pA by covering a broad range of doses. For EUV the E_0 was determined using SEMATECH Berkeley Microfield Exposure Tool (MET). Post-exposure bake (PEB) method was followed to obtain good resist edges using hot plate. All the exposed resist coated films were developed using standard concentration TMAH aqueous solutions by maintaining pH = 11.5 at room temperature and finally dried by passing pure nitrogen gas over the films. Figure 2 represents different steps involved in the lithographic process.[7]

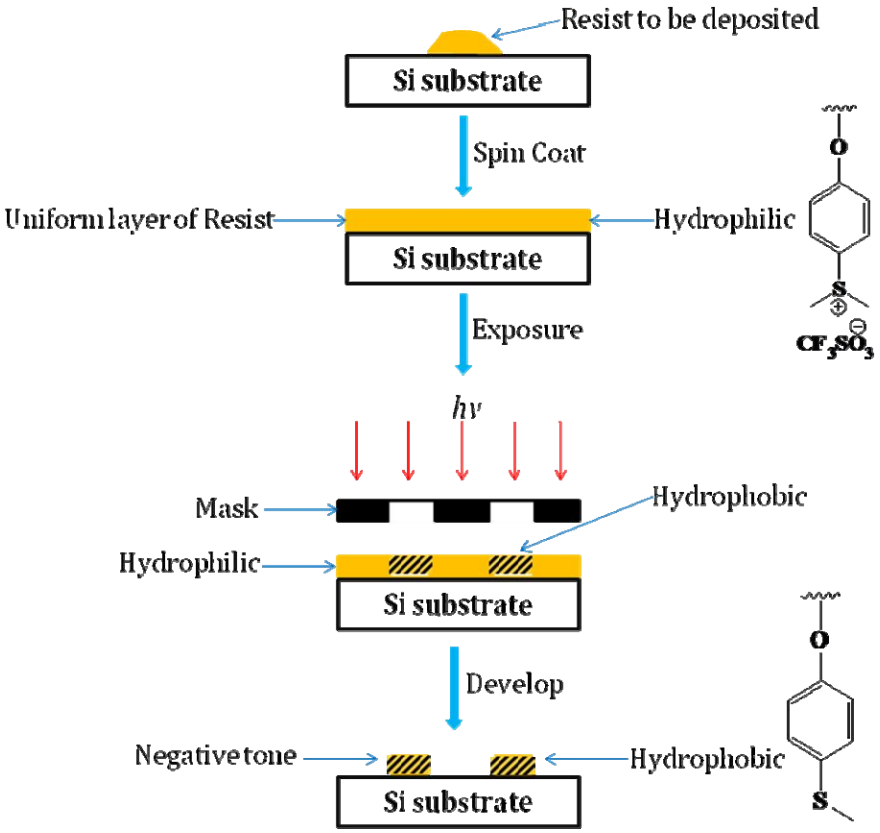


Figure 2. Schematic diagram of lithographic process.

2.3 Imaging

Resolution and image quality were determined by examining the developed resist profiles with SEM attached to Raith 150 lithography system. The exposed features were evaluated at energy of 5 keV. HRSEM images were taken using Nova Nano SEM 450 FEI instrument.

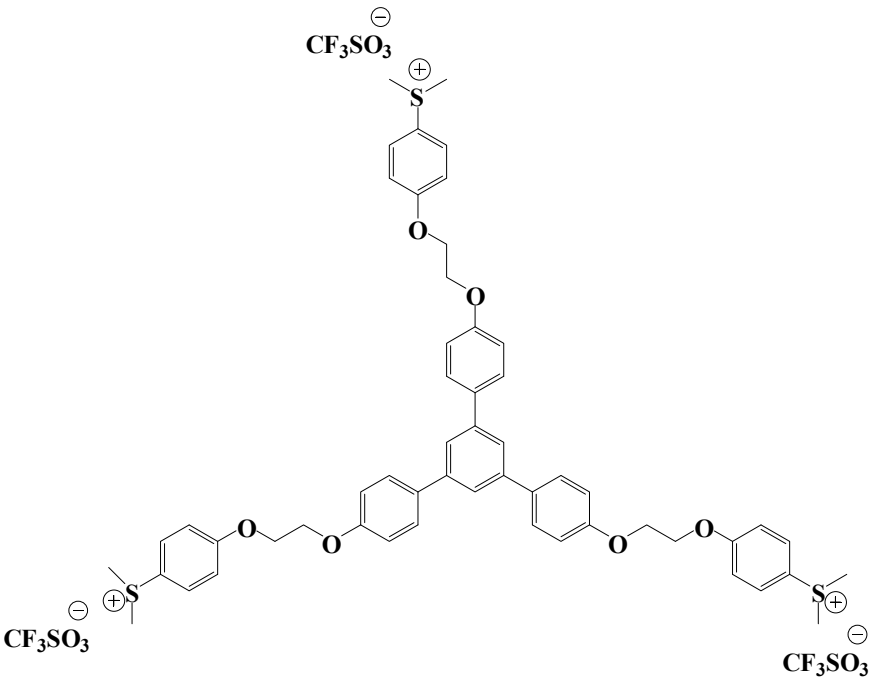


Figure 3. Structure of molecular resist having photosensitive sulfonium groups.

3. RESULTS AND DISCUSSION

3.1 Resist Materials

MAPDST (4-(methacryloyloxy)phenyl dimethylsulfonium triflate), MANTMS (1-(4-(methacryloyloxy)naphthalen-1-yl)tetrahydro-1*H*-thiophenium trifluoromethanesulfonate) and 4-hydroxystyrene monomers were synthesized according to the reported procedures and confirmed by comparing with the literature data.[8-11] The homopolymers of MAPDST and MANTMS monomers were synthesized using free radical polymerization with 2,2'-azobisisobutyronitrile (AIBN) initiator at 60 °C temperature in tetrahydrofuran (THF) solvent for 2 days under nitrogen atmosphere (Figure 1). Also, we have synthesized copolymers of MAPDST with MMA (methyl methacrylate), VCBZ (9-vinyl carbazole), STYCOOH (4-carboxy styrene) and hydroxyl styrene monomers using the same free radical polymerization method initiated by AIBN at 60 °C in a combined organic solvent, acetonitrile (CH_3CN) and THF for 2 days under N_2 atmosphere. A sulfonium functionality containing molecular resist has also been prepared (Figure 3). The synthesized homopolymers, copolymers of MANTMS and MAPDST monomers and a molecular resist have been characterized using FT-IR, NMR analysis and the molecular weights of the polymers were calculated using GPC analysis.[12,13] The copolymer compositions and glass transaction temperature (T*g*) values are calculated using ^{1}H NMR and DSC analysis.

3.2 EB Lithography Evaluation

Initially, the homopolymer of MAPDST, poly(MAPDST-*co*-MMA), poly(MAPDST-*co*-NVK) and poly(MAPDST-*co*-STYCOOH) copolymers were evaluated by EB lithography (Figure 4). Resist solutions (3% w/v) were prepared in methanol solvent and coated on a 2″ silicon wafers with a soft-bake at 100 ºC and 90 ºC, respectively. The resist coated films were exposed to e-beam using 20 keV electron beam under low electron dose values (10 to 55 μC/cm^2) to achieve 20 nm line patterns with L/S or L/2S line space. The exposed resist coated films were subjected to post exposure bake at 115 ºC and 100 ºC and developed in aqueous TMAH solutions by maintaining pH = 11.5 at room temperature. Thickness of films was measured around 50-120 nm using optical profilometer. Our investigation showed that these new materials can be useful for the development of highly sensitive non-chemically amplified photoresists for sub 20 nm EUVL.

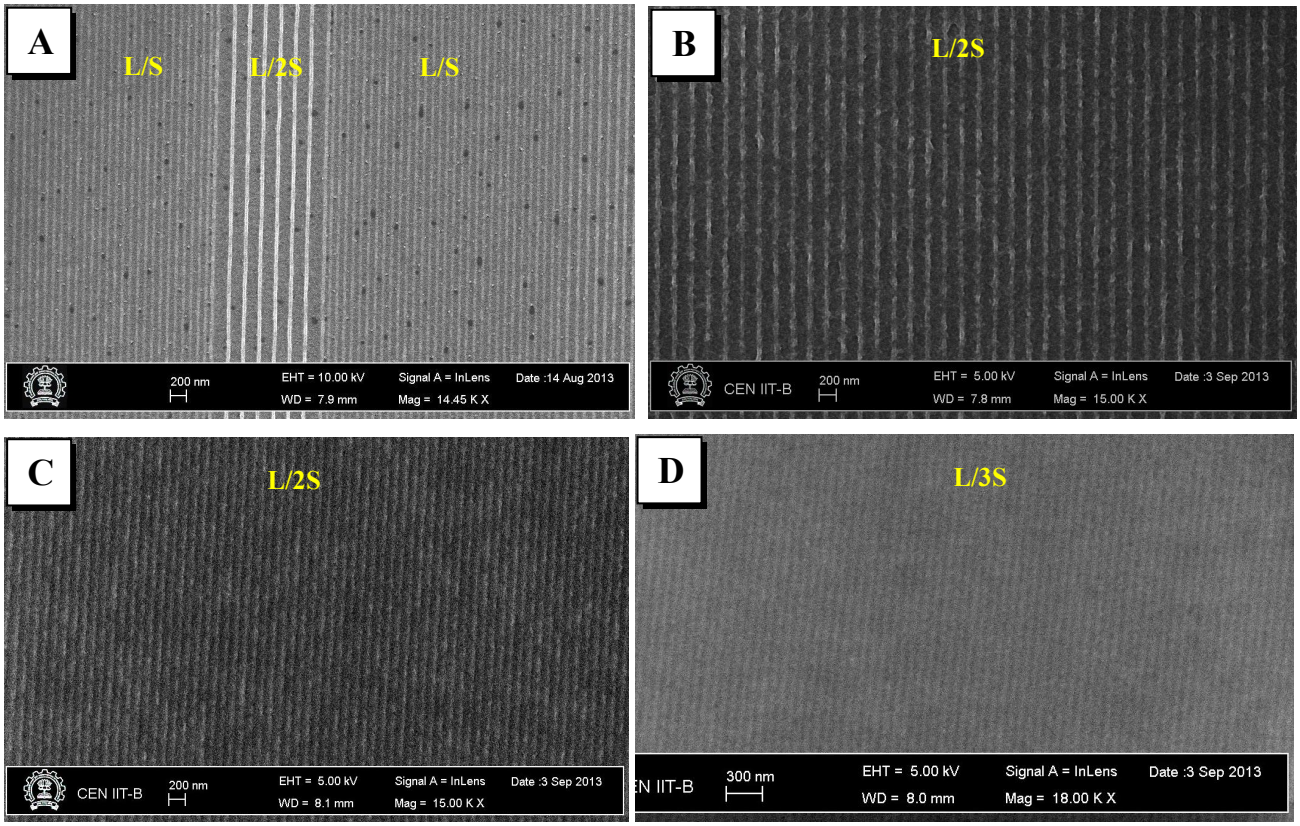


Figure 4. SEM results of the e-beam patterning of negative tone MAPDST homopolymer resist (**A**), poly(MAPDST-*co*-MMA) (**B**), poly(MAPDST-*co*-NVK) (**C**) and poly(MAPDST-*co*-STYCOOH) (**D**) resists for 20 nm with different line/space, patterns exposed at dose value 40, 30, 35 and 50 μC/cm^2, respectively.

3.3 EUV Lithography Evaluation

The resist solutions were prepared in methanol and were filtered by 0.2 micron Teflon filter before EUV exposure evaluation and spin-coated onto a 200 mm silicon wafer that was treated with a hexamethyldisilazane (HMDS), and pre-baked at 100 °C for 90 sec for MAPDST homopolymer resist, pre baked condition for poly(MAPDST-*co*-MMA) copolymer was 90 °C for 90 sec to give a film thickness of around 40 nm. The resulting photo resist layer was flood exposed using an E0 array using SEMATECH Berkeley Microfield Exposure Tool (MET) which is the world's highest resolution EUV (EUV radiation 13.5 nm) lithography tool. The Mask IMO228775 with field R4C3 was used to EUV exposure to these resists. The wafers were post exposed baked at 115 °C /90s for MAPDST homopolymer and 115 °C /90s for poly(MAPDST-*co*-MMA) copolymer resist samples. After the post bake, samples were developed with aqueous TMAH solution to obtained EUV lines patterns of these resists. Figure 5 shows line patterns of MAPDST homopolymer and poly(MAPDST-*co*-MMA) copolymer resists.

4. CONCLUSIONS

In this study, we presented a library of six different kinds of polymers and a molecular resist, which are having photosensitive sulfonium groups to improve the sensitivity and LER towards the e-beam and EUV lithography. Initially, MAPDST homopolymer and a copolymer of MAPDST with MMA were evaluated by EB and subsequently by EUV lithography. The results show that these polymeric resist materials containing photosensitive sulfonium groups have improved sensitivity towards e-beam. We are currently optimizing the sensitivities of these resists to EUV by strategies incorporating inorganics[14] as well as dissolution inhibitors. The inclusion of metals such Mo and W are expected to increase the absorption cross sections of these resists to EUV radiation. Based on our initial synthetic strategies, multiple

polymeric resist materials are available to improve the non-chemically amplified negative tone resist properties for nano lithography. From the resist requirement point of view, results of the present study are expected to promote EUVL technology for semiconductor fabrication functional applications.

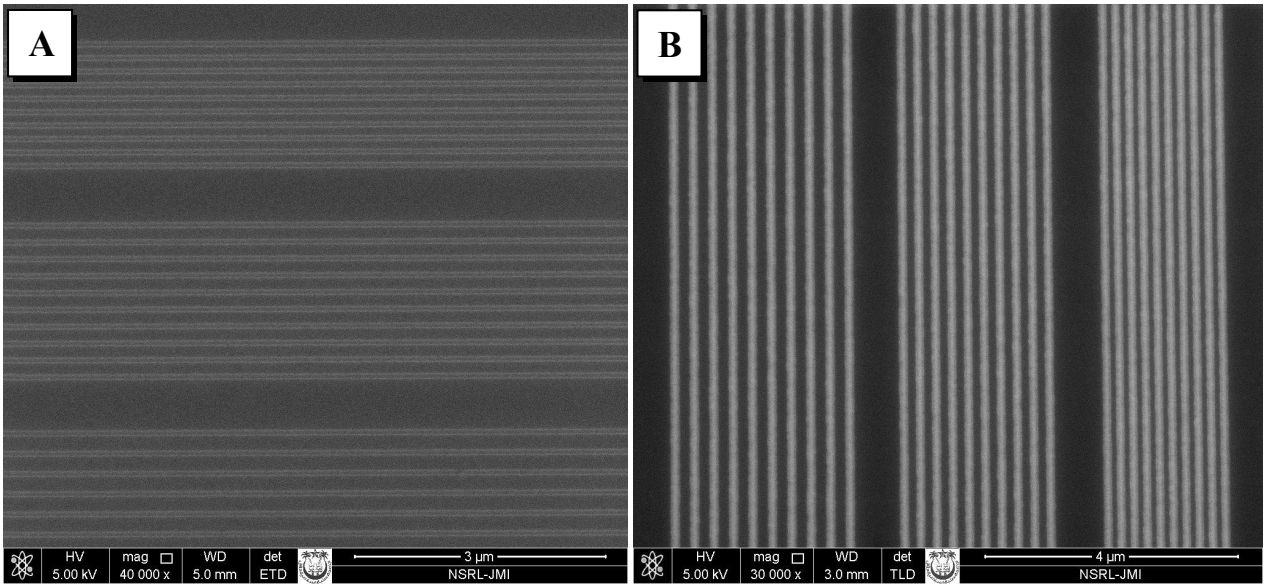


Figure 5. SEM results of the EUV patterning of negative tone MAPDST homopolymer resist (**A**) and poly(MAPDST-*co*-MMA) resist (**B**) for 25, 30, 35 nm with L/S and L/2S line/space, respectively.

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