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Organic-inorganic hybrid resists for EUVL

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ABSTRACT

Herein, we describe preliminary results on organic-inorganic hybrid photoresists, capable of showing line patterns up to 16 nm under e-beam exposure studies, prepared by incorporating polyoxometalates (POMs) clusters into organic photoresist materials. Various Mo and W based clusters such as $(\text{TBA})_2[\text{Mo}_6\text{O}_{19}]$, $(\text{TBA})_5(\text{H})[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ and $(\text{TBA})_4[\text{P}_2\text{Mo}_{18}\text{O}_{61}]$ (where TBA = tetrabutyl ammonium counter ion) have been incorporated into PMMA matrix by mixing POM solutions and standard PMMA polymer in anisole (MW ~ 95000, MicroChem) in 1:33 w/v ratio. E-beam exposure followed by development with MIBK solutions showed that these new organic-inorganic hybrid photoresists show good line patterns upto 16 nm, which were not observed in the case of control experiments done on pure PMMA polymer resist. The observed enhancement of resist properties in the case of hybrid resists could possibly be due to a combination of features imparted to the resist by the POM clusters such as increased sensitivity, etch resistance and thermal stability.

Keywords: Polyoxometalates, organic-inorganic hybrid materials, e-beam lithography.

1. INTRODUCTION

The semiconductor industry has progressed remarkably over the last few decades with the development of integrated circuits (ICs) technology based on resists that image under various exposures, DUV, e-beam and EUV down to the nanoscale. The ITRS-2011 roadmap predicts that next generation techniques such as EUV will realize 20 nm half pitch node and beyond.¹ However, many challenges still remain in the development of EUV photoresists. The ideal combinations of high sensitivity, low LER, high resolution, high etch resistance and other performance characteristics remains subtle. Incorporation of photoacid generating groups (PAGs) such as sulfonium salts is one of the approaches employed to enhance the sensitivity of resist materials.²⁻⁴ Recently, organic-inorganic hybrid photoresists incorporating inorganic components in organic polymeric materials have been developed in order to address issues like low sensitivity, pattern collapse and poor line-edge roughness (LER)⁵ of the polymeric resists. Inorganic components like polyhedral oligomeric silsesquioxane (POSS), Hf nanoparticles have been explored as inorganic components in organic-inorganic hybrid photoresist materials.^{6,7}

An approach that is currently being investigated by us to address the inherent problems of chemically amplified resists (CARs) such as acid diffusion, low sensitivity and post exposure instability encompasses the design and development of novel organic-inorganic hybrid photo resists that are directly sensitive to photons and hence do not require any chemical amplification. This approach is based on the use of various polyoxometalates (POMs) clusters as inorganic components in organic photoresist materials. Polyoxometalates (POMs) are a class of inorganic materials consisting of discrete, soluble, anionic metal oxide clusters of early transition metals like W, Mo, V and Nb, exhibiting enormous versatility in their structural features and properties.⁸ Electronic properties of POMs are often compared with that of semi-conductor (SC) nano particles. Excitation in SC promotes an

electron from valence band (VB) to the conduction band (CB), whereas in molecules such as POM clusters, the corresponding process is described as occurring from the highest occupied molecular orbitals (HOMO) to lowest unoccupied molecular orbitals (LUMO). In POM clusters, this corresponds to O→M charge transfer (CT) transition. O→M CT excitation leads to electron hole separation in POMs, which renders these clusters as powerful oxidizing reagents, capable of oxidizing a great variety of organic compounds.⁹ Moreover, due to the high atomic number of the metals present in POMs, their absorption cross section for X-rays and high energy e-beam radiation is typically much greater than that for organic materials. Radiation sensitive materials based upon mixtures of POMs and organic compounds therefore find application in nanolithography.¹⁰ Herein, we report new POM containing organic-inorganic hybrid resist materials capable of functioning as non-chemically amplified resists to attain the resolution upto 16 nm.

2. METHODOLOGY

2.1 Resist materials

Polyoxometalates used in the hybrid resists were prepared according to the reported procedures.¹¹ PMMA (MW ~ 95000) solution in anisole was purchased from MicroChem supplier. Acetonitrile was distilled over calcium hydride and dried in presence of 4Å molecular sieves prior to the use in resist preparation. POM based hybrid monomers, in which POM clusters are covalently attached to polymerizable organic units, were prepared by reacting methacryloyl chloride¹² with $(\text{TBA})_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ ¹³ and $(\text{TBA})_5(\text{H})[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}(\text{OCH}_2)_3\text{CNH}_2]$ ¹⁴ clusters. These hybrid monomers were then copolymerized with methylmethacrylate using 2,2'-azobisisobutyronitrile (AIBN) as initiator to generate organic-POM hybrid copolymers.

2.2 Preparation of photoresist

The resist solutions (blends) were prepared by mixing solutions (3.3 wt % of POM to polymer) of the corresponding polyoxometalates i.e. $(\text{TBA})_2[\text{Mo}_6\text{O}_{19}]$, $(\text{TBA})_5(\text{H})[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ and $(\text{TBA})_4[\text{P}_2\text{Mo}_{18}\text{O}_{61}]$ with 1 ml standard PMMA solution in anisole (MW ~ 95000, MicroChem). The resulting solutions were filtered through a 0.2 µm Teflon[®] filter to remove particles. The resist solutions were then spin coated on HMDS treated p-type Si wafer pieces of 2 cm X 2 cm size to obtain ~50 nm thick films. The prebake annealing of the resists were performed at 180 °C for 90s on hot plate.

2.3 E-beam evaluation

The samples were exposed on a Raith-150 E-beam system using 20 KeV energy for different doses, 45, 50 and 75 µC/cm², with an aperture size of 20 µm. Exposed samples were developed in standard 1:3 MIBK solution for 30s followed by 15s in IPA and then dried with nitrogen gas. Developed resists were carefully examined with SEM attached to Raith 150 lithography system at energy of 5 keV. HRSEM images were also taken using Nova Nano SEM 450 FEI instrument.

3. RESULTS AND DISCUSSION

3.1 E-beam exposure studies on hybrid photoresists

In the present study, we prepared a series of organic-inorganic hybrid resists by blending various Mo and W based POM clusters such as $(\text{TBA})_2[\text{Mo}_6\text{O}_{19}]$, $(\text{TBA})_5(\text{H})[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ and $(\text{TBA})_4[\text{P}_2\text{Mo}_{18}\text{O}_{61}]$ (where TBA = tetrabutyl ammonium counter ion) with commercially available PMMA polymer in anisole (MW \sim 95000, MicroChem) in 1:33 w/v ratio and tested their properties using 20 KeV e-beam lithography. In the case of hybrid blend resist prepared from PMMA (MW \sim 95000) and $(\text{TBA})_2[\text{Mo}_6\text{O}_{19}]$ cluster, 20 nm line patterning was observed at $45 \mu\text{C}/\text{cm}^2$ dose using 20 KeV e-beam energy. The films were developed in 1:3 MIBK solution for 30s followed by 15s in IPA. Exposed regions (patterns) of the $(\text{TBA})_2[\text{Mo}_6\text{O}_{19}]$ -PMMA hybrid resist film readily dissolved in aqueous MIBK developer, while the unexposed regions remained intact in the developer. The prebake of the resist were performed at 180°C for 90s. 20 nm line patterns with 500 and 80 nm line spaces were successfully observed in the case of $(\text{TBA})_2[\text{Mo}_6\text{O}_{19}]$ -PMMA blends (Fig. 1(a)), which were not observed in control experiments done using pure PMMA polymer in anisole (MW \sim 95000, MicroChem) resist. Under similar experimental conditions, we have also tested organic-inorganic hybrid resists prepared by mixing $(\text{TBA})_5(\text{H})[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ and $(\text{TBA})_4[\text{P}_2\text{Mo}_{18}\text{O}_{61}]$ clusters with PMMA in 1:33 w/v ratio. We were able to get 20 nm line patterns with L/2 space by using $50 \mu\text{C}/\text{cm}^2$ dose in the case of $(\text{TBA})_5(\text{H})[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ based resist, Fig. 1(b). Down to 16 nm features were successfully observed with L/S and L/2S at a higher dose, $70 \mu\text{C}/\text{cm}^2$, in the case of hybrid containing the Mo based cluster $(\text{TBA})_4[\text{P}_2\text{Mo}_{18}\text{O}_{61}]$, Fig. 1 (c). High resolution SEM images of 20 nm L/S was taken at 120KX magnification of the hybrid resist a) $(\text{TBA})_2[\text{Mo}_6\text{O}_{19}]$ -PMMA (Fig. 2) which clearly shows line patterns having line edge roughness around 2.1 nm and line width roughness 3.4 nm.

The above results suggest that POM based organic-inorganic hybrid resists show improved patterning properties compared to standard PMMA solution in anisole (MW \sim 95000, MicroChem) resists. This observed improvement in resist properties could possibly be due to a combination of features imparted to the resist by the POM clusters such as increased sensitivity, thermal stability, etch resistance etc. Studies to understand the exact reasons behind the improved properties of the hybrid resists are currently underway.

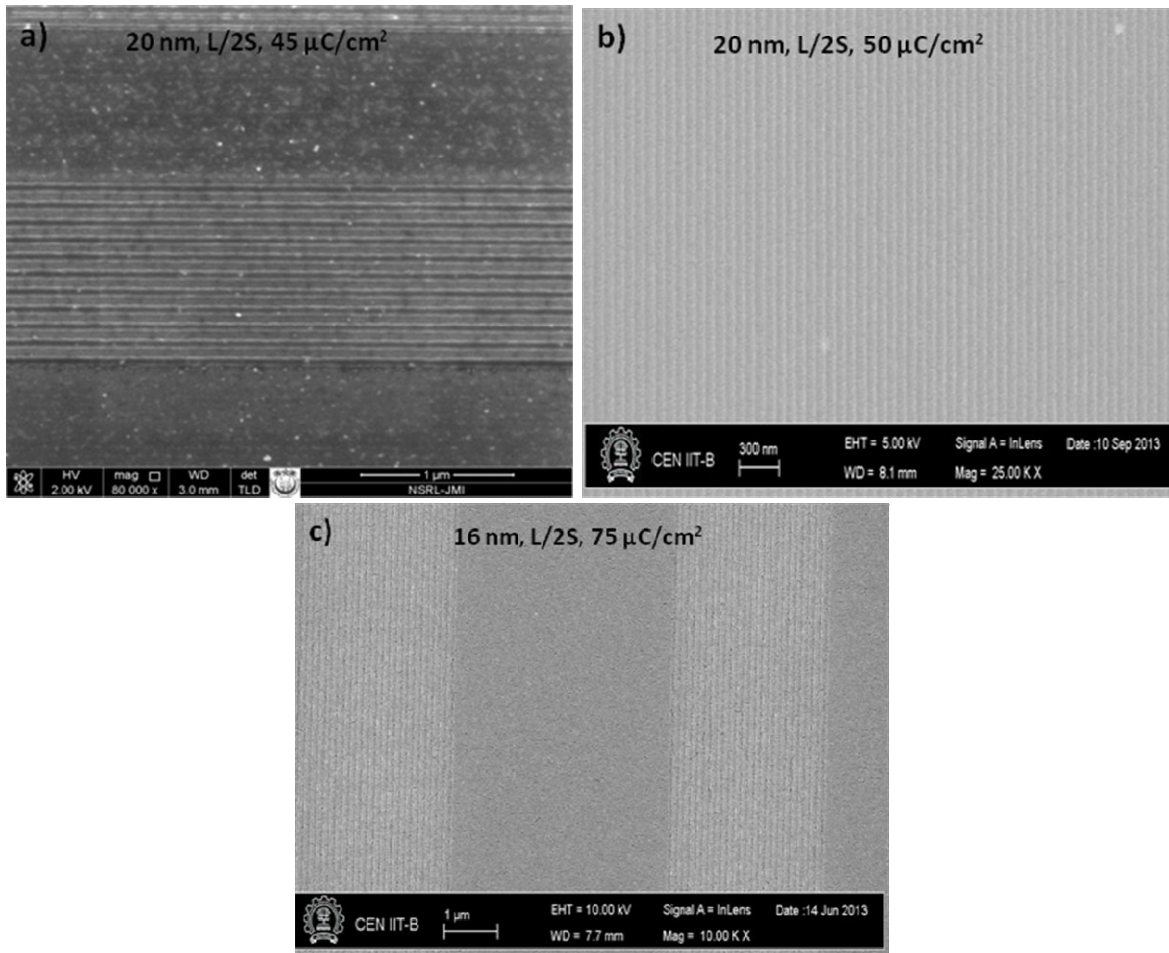


Figure 1. SEM images of the exposed hybrid resist a) $(TBA)_2[Mo_6O_{19}]-PMMA$ b) $(TBA)_5(H)[P_2V_3W_{15}O_{62}]-PMMA$ and resist c) $(TBA)_4[P_2Mo_{18}O_{61}]-PMMA$.

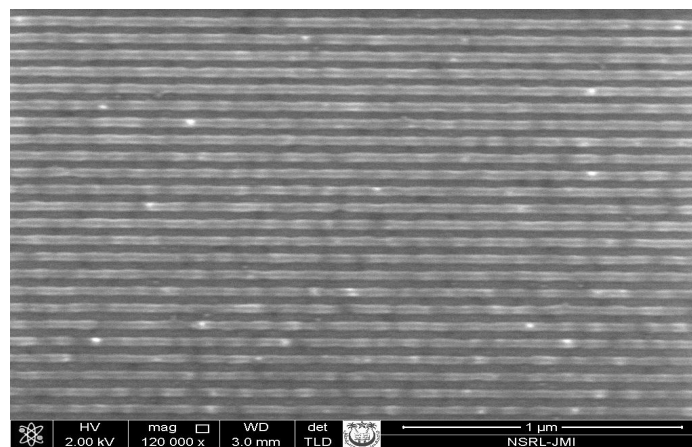


Figure 2. HRSEM image of 20 nm L/S of the hybrid resist $(TBA)_2[Mo_6O_{19}]-PMMA$ exposed at $70 \mu C/cm^2$.

3.2 Development of organic-POM hybrid copolymers

In order to enhance the stability and homogeneity of the POM containing hybrid resists, we are currently engaged in the development of POM based hybrid monomers in which POM clusters are covalently attached to polymerizable organic units (examples: $(TBA)_3[MnMo_6O_{18}\{(OCH_2)_3CNH\}_2(CH_2=CCH_3CO)_2]$ and $(TBA)_5(H)[P_2V_3W_{15}O_{59}\{(OCH_2)_3CNH\}(CH_2=CCH_3CO)]$) and co-polymerizing them with organic monomers such as MMA and MAPDST¹² to develop improved hybrid copolymer resists as shown in Fig.3 a) & b). The copolymers of hybrid monomers with MMA were synthesized by using free radical polymerization with 2,2'-azobisisobutyronitrile (AIBN) initiator at 70 °C temperature in acetonitrile solvent for 2 days under nitrogen atmosphere. The synthesized copolymers were characterized using FT-IR, NMR analysis and the molecular weights of the polymers were calculated using GPC analysis using polystyrene standards. The weight average molecular weight of the $(TBA)_3[MnMo_6O_{18}\{(OCH_2)_3CNH\}_2(CH_2=CCH_3CO)_2]$ -MMA copolymer was found to be ~35000 with polydispersity index (PDI) of 2.24; whereas, weight average molecular weight of the $(TBA)_5(H)[P_2V_3W_{15}O_{59}\{(OCH_2)_3CNH\}(CH_2=CCH_3CO)]$ -MMA copolymer was ~30000 with PDI 1.87. These hybrid copolymers are readily soluble in chloroform, dichloromethane and acetone at room temperature. Detailed E-beam exposure studies on these organic-POM hybrid copolymers are currently underway.

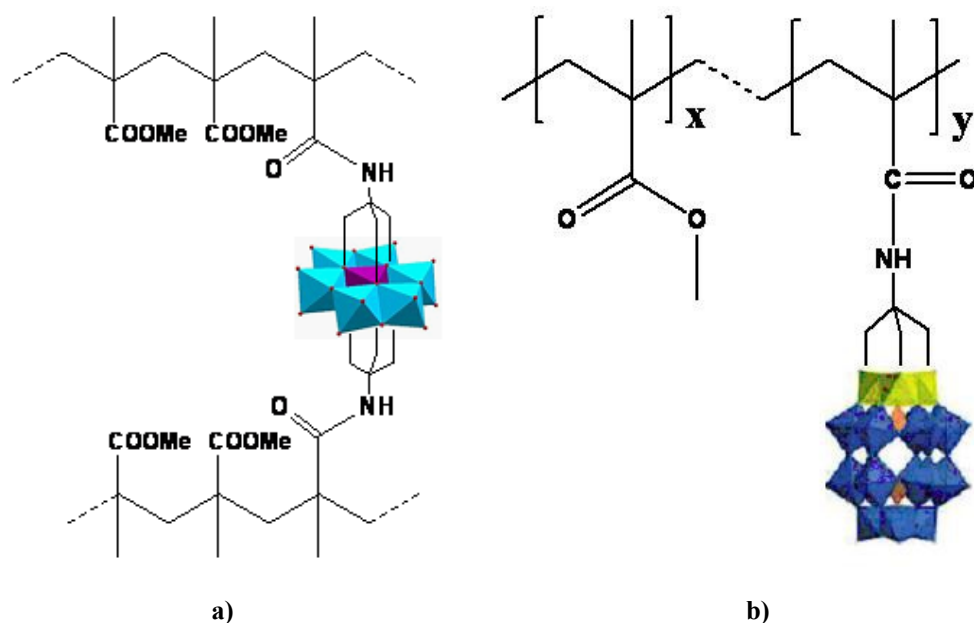


Figure 3. Structures of the hybrid copolymers a) $(TBA)_3[MnMo_6O_{18}\{(OCH_2)_3CNH\}_2(CH_2=CCH_3CO)_2]$ -MMA and b) $(TBA)_5(H)[P_2V_3W_{15}O_{59}\{(OCH_2)_3CNH\}(CH_2=CCH_3CO)]$ -MMA

4. CONCLUSIONS

In summary, we have tested the hypothesis that Mo and W polyoxometalates (POMs) and PMMA based organic-inorganic hybrid photoresists showed line patterns upto 16 nm under electron beam exposure studies. These hybrid resists show improved properties compared to standard PMMA polymer solution in anisole (MW ~ 95000, MicroChem) resists and these observed improvement in properties could possibly be due to a combination of features imparted to the resist by inorganic POM units such as enhanced sensitivity, etch resistance and thermal stability. This proof of concept is now being applied to organic-POM hybrid copolymers to increase their sensitivity.¹⁵

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