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Photoresist Design to Address Stochastics Issues in EUV Resists

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Low stochastics, high sensitivity photoresists remain a goal for EUV lithography. Here we contrast two positive photoresist systems, polypeptoids (PPs) and poly(phthalaldehyde)s (PPAs), both of which are selected to minimize chemical stochastics. In the former, a chemically amplified resist with identical molecular weight, composition, and sequence is studied. In the latter, a PPA homopolymer enables preparation of a chemically homogeneous resist which can be chemically scissioned in exposed areas. We report the results of exposure of these materials to DUV, e-beam and EUV radiation and physical changes that occur. In addition, we highlight unexpected observations of the role of sequence on lithographic performance.

Keywords: EUV photolithography, Stochastics, Sequence control, Polypeptoid, Polyphthaldehyde

1. Introduction

The development of EUV photoresists continues to be hampered by the issue of stochastics, that is, the random probability distributions of exposure dose, and secondary electron generation that changes solubility in a photoresist with its inherent variation in molecular size and molecular composition which ultimately leads to imperfections in pattern formation. For example, in a classical chemically amplified photoresist there is: i) heterogeneity in polymer molecular size, composition and sequence and ii) in the mixing of the photoresist and photoactive additives [1]. The effect of inhomogeneity is believed to contribute to line edge roughness and defect formation among other issues. Most polymer preparation methods in which several building blocks are incorporated results in strong compositional heterogeneity due to the statistical nature of random copolymerization.

In recent studies, metal organic clusters (MOCs) have been shown to produce high resolution photoresists. It could be argued that the basic molecular structure of MOCs leads to molecular homogeneity [2]. Nevertheless, there remain advantages in working with polymer systems if chemical stochastics and thus patterning stochastics can be addressed. The chemical versatility of monomer building blocks remain very attractive if chemical control of synthesis can be implemented. In this report we discuss recent approaches to chemical control of stochastics in which: 1) a self-immolative resist is used to mitigate the effect of chemical variability in a photoresist by focusing on homopolymer design [3] and 2) solid supported synthetic chemistry is used to prepare polymer chains that eliminate chemical variability and are identical in composition, molecular weight and in sequence [4].

Self-immolative polymers have been previously studied as photoresists, particularly for mask writing. These polymers, with relatively low ceiling temperatures, will revert to monomer under the right thermal conditions after radiation exposure. They are generally homopolymers and while they may have high molecular weight the depolymerization process means that molecular size is not a critical factor in image formation. Poly(alkylene sulfone)s are one family of such polymers [5].

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Poly(phthalaldehyde)s are an alternative family of scissionable polymers [6] that we have studied in this context. We compare these highly sensitive resists that depend on a non-ionic photoacid generator for pattern formation [7] to the peptoid materials and what it implies for peptoid design.

Peptoids instead are aliphatic polyamides that mimic the structure and sequence control of proteins, are easier to synthesize, and yet are different because they both lack stereocenters present in proteins, and they have functional groups attached to nitrogen rather than carbon [8]. This polymer family, prepared using a robot synthesizer system originally developed for protein synthesis, depends on polymer supported chemistry and can result in multigram yields. The number of units in each chain is identical, the average composition is identical, and the sequence is identical thus minimizing issues of compositional stochastics.

In our prior report [9] on peptoid resists, we prepared sequences with tyramine as PHOST analog using the t-BOC protecting group in combination with hydrophobic comonomers such as phenyl ethylene amine and propargyl amine units. In this report we expand on the hydrophobic groups and explore the effect of sequence selection on patterning and development and to update our progress on the study of these new polymer systems.

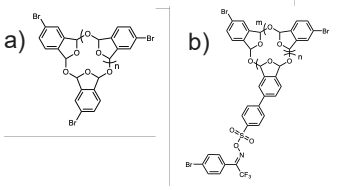
Ongoing studies of the lithographic behavior of these resist systems have been carried out using DUV, e-beam and EUV radiation and will be discussed.

2. Experimental

All reagents were purchased from Sigma Aldrich, Millipore Sigma, TCI America, and Oakwood Products at the highest purity available and used without further purification. Tyramine, diphenyl propyl amine and hexyl amine were purchased from Sigma Aldrich and used as received.

2.1 Synthesis of poly(phthalaldehyde) (PPA)

The PPA polymers with bromine substituents have been previously reported and are included here to compare with the peptoid resists [10]. In a sample synthesis of PPA, Br-phthalaldehyde monomer and boron trifluoride etherate initiator were added to a Schlenk flask [11]. The solids were dissolved in THF and then the solution cooled to -78 °C. The reaction was left stirring at -78 ℃ for 2 h, then pyridine was added. The reaction was stirred an additional *2 h* while maintaining at *-78 °C*. The solution was then warmed to room temperature and the polymer was precipitated by adding slowly into methanol. The white powder was collected by filtration, then further purified by dissolving in dichloromethane and re-precipitating from methanol and washing in diethyl ether The polymers were further purified by dissolving in dichloromethane and re-precipitating into methanol. The resulting polymers are shown in Scheme 1.

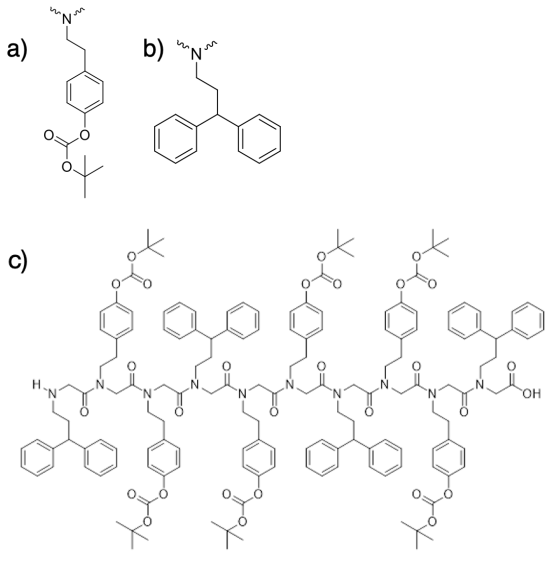


Scheme 1. PPA Polymers a) without PAG attached and with b) PAG attached.

Photoresist solution containing *5 wt.%* polymer in cyclohexanone blended with PAG was prepared in varying ratios of *10-20 wt.%* to PPA. The solution was then spin coated onto a silicon wafer at *3000 rpm* for *1 min* and post baked at *90°C* for *1 min* to remove excessive solvent.

2.2 Synthesis of peptoid photoresists

The peptoid syntheses were conducted using a CSBio Peptide Synthesizer, Model CS336X. The important structural units and a typical sequence are shown in Scheme 2. For the solid-phase supported synthesis of the peptoids *1g* of 2-chlorotrityl chloride resin with a loading of *1.7 mmol* g^{-1} was swollen in dichloroethane (DCE) for 10 minutes and washed with dimethyl-formamide (DMF). The first



Scheme 2. Key building blocks in peptoid photoresist: a) t-Boc protected tyramine and b) diphenylpropyl amine. c) Peptoid sequence prepared for these studies. These components produce e-beam and EUV resists capable of sub-20 nm resolution.

bromoacetylation step was carried out by adding *10 mL* of a *1.3 M* bromoacetic acid (BAA) in DMF and *10 mL* of a *1.3 M N, N*-diisopropylethylamine (DIEA) in DMF to the resin and bubbling with nitrogen and shaking for 30 minutes. The resin was then washed repeatedly with DMF. Amination was performed by reacting the acylated resin with *1-2 M* of the amine in DMF for *60 minutes* constantly bubbling nitrogen and shaking the reactor. Additional bromoacetylation steps were conducted with *1.2 M* BAA and *1.4 M N, N'*-diisopropylcarbodiimide (DIC) in DMF. Cleavage was accomplished by treatment with *20%* hexafluoroisopropanol in dichloromethane (DCM). The resin was filtered, and the solution was concentrated via rotary evaporation and lyophilized. The resulting solid was dissolved in 1:1 acetonitrile/water and purified using a preparative HPLC and lyophilized and characterized using a Bruker Matrix Assisted Laser Desorption - Time of Flight (MALDI-TOF) Bruker AutoFlex Max tool. To introduce solubility switching groups the tyramine hydroxyl groups were protected with of di-tert-butyl dicarbonate (tBOC). For the *1*g peptoid synthesis, it was dissolved in *10 mL* acetone and *1.3 equivalents* of tBOC and *0.1 mol* equivalent 4-dimethylaminopyridine (DMAP), were added and the solution was stirred for *24 hours* at room temperature. Afterwards, the sample was concentrated, purified by preparative HPLC and lyophilized. The resulting solid was characterized using MALDI-TOF.

2.3 Lithographic characterization:

For deep-ultraviolet (DUV) exposures *25 mg* peptoid were dissolved in *1ml* of propylene glycol methyl ether. To this solution *20 wt%* (with respect to peptoid) photoacid generator (TPS-nonaflate) was added and the solution was sonicated for 5min. The solution was filtered, and spin coated on a UVO cleaned silicon wafer. The coated wafer was post-apply baked for *60s* at *110℃*.

DUV exposures were conducted on an ASML PAS 5500/300C Wafer Stepper. When carried out, E-beam exposures were performed using a JEOL 6300, *100kV* e-beam tool. After exposure, the patterns were post-exposure baked for *60s* at *110℃* for 60s and developed in the appropriate developer (aqueous base or solvent depending on the sequence). The resulting patterns were characterized using a Zeiss-Gemini-500-FESEM.

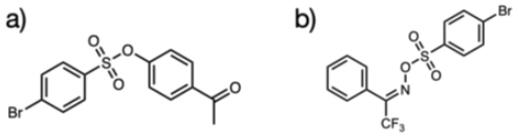
Extreme-ultraviolet exposures were conducted at the Paul-Scherrer Institute (PSI) in Switzerland. After exposure, the patterns were post-exposure baked for *60s* at *110℃* for *60s* and developed in the appropriate developer (aqueous base or solvent depending on the sequence). The resulting patterns were characterized using a Zeiss-Gemini-500-FESEM.

3. Results and discussion

3.1 Patterning. Behavior of Brominated PPA Resists

In our study of PPA photoresists we incorporated Br as a substituent for subsequent modification of each repeat unit and on the hope that Br might enable direct radiation induced depolymerization. Instead, we found that the presence of Br enhances the stability of the PPA and gives it better shelf life, but it does require a PAG to induce depolymerization [10]. The resulting polymer had a molecular weight of ~3,000 g/mol and was soluble in solvents such as cyclohexanone. We chose non-ionic PAGs for incorporation as a free component and for direct attachment to the polymer itself. Active and inactive PAGs are shown in Scheme 3.

Interestingly, not all non-ionic PAGs are active under EUV conditions even though they work under DUV and e-beam conditions and as shown in Scheme 3 similar PAGs do have different activities which we ascribe to the nature of bonding around the groups that lead to release of the sulfonic acid.



Scheme 3. Non-ionic PAGs investigated with Br-PPA EUV resists. PAG a) is EUV inactive while PAG b) is very EUV active.

An EUV active and EUV inactive PAG are shown in the figure. We consider the actions of secondary electrons in bond cleavage events to be the source of this difference. PAGs with a C-O-S linkage are EUV inactive whereas PAGs with an N-O-S linkage is very active. DFT studies suggest that the O-S bond is weaker in the C-O-S PAGs while the N-O bond is weaker in the N-O-S PAGs [10]. We will pursue EUV active PAGs in our future peptoid studies for incorporation directly the polymer backbone.

Resolution in photoresists is controlled by the solubility difference between the exposed and unexposed regions. Similarly, line edge roughness has been correlated to inhomogeneities in regions of the resist possessing both soluble and insoluble components after exposure [12]. These inhomogeneities are partially the result of stochastics in the initial distribution of photoacid generators and solubility change groups [13]. Minimizing such variations via control of the polymer's molecular size is crucial to achieving the

lithography performance requirements set by the IEEE IRDS [14].

In order to minimize stochastics variability, we explored incorporating PAG groups on each and every repeat unit in our PPA photoresists. Monomers were modified before polymerization and tested under various exposure conditions. The all PAG resists were found to be extraordinarily sensitive requiring doses well under 5 *mJ/cm*^{2} by EUV exposure. Only when 1 PAG was incorporated per chain (or per macrocycle in the tested materials)

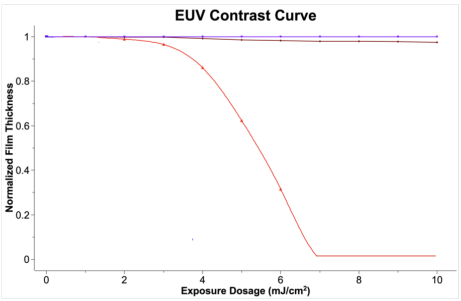


Figure 1. EUV contrast curves for inactive Br-PPA resist alone (Scheme 1a), with inactive PAG on macrocycle and active PAG on macrocycle (Scheme 1b) exposed to EUV source. Data from reference 15.

were we able to produce reasonable results.

Figure 1 shows the contrast curves for the EUV inactive Br-PPA homopolymer resist alone (Fig. 1a), with the Br-PPA with inactive PAG, both with unchanging contrast curves and the active PAG on macrocycle (Fig. 1b) exposed to EUV. Several other PAGs were tested and showed in the fastest case maximum contrast at *2mJ/cm*^{2} or faster with a single PAG per macrocycle. Importantly, this suggests that we can think about stochastics more broadly than all repeat units are identical and design macromolecular units that have identical size, composition and sequence but made from different components.

3.2 Patterning. Behavior of Peptoid Resists

Peptoids possess repeat units built from *N*-substituted glycines. Compared to peptides, peptoids present numerous advantages including a wider range of functional groups and lower-cost. More efficient synthesis enables production of higher molecular weights with high precision when compared to protein synthesis in molecular weight ranges suitable for photoresists [16]. The most well-developed solid-phase method is the submonomer synthesis (SMS), which combines two types of repeat units, primary amines and bromoacetic acid, in a stepwise manner [17]. Following synthesis, preparatory HPLC is used to remove any excess lower molecular weight segments that might have been produced [18].

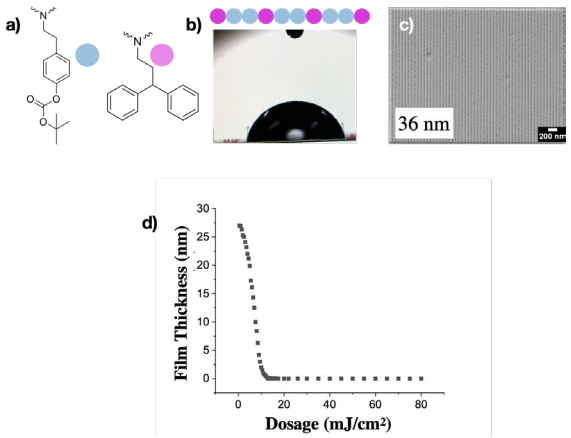


Figure 2. a) Structure of amine units in peptoid repeat. t-Boc protected tyramine is colored cyan and diphenylpropyl amine is colored magenta. B) An effective sequence is shown with 4 diphenylpropyl amine units and 6 tyramine units in a decamer (Scheme 2c). All peptoids in a sample have the same quantity of each unit type in the same length chain with the same sequence. The resist is moderately hydrophobic. c) The micrograph shows a 36 nm line/space pattern made using e-beam exposures. Recent results from both e-beam and EUV patterning are approaching *15 nm* resolution. d) Contrast curve for tyramine/diphenyl propyl amine peptoid exposed to EUV radiation.

In this report we briefly describe resists made with tyramine and diphenylpropyl amine (Figure 2) [19]. The molecular weight of each molecule of peptoid is 2687 g/mol.

This polypeptoid can be dissolved in acetone, isopropyl alcohol, N,N-dimethylformamide and acetonitrile. In these sequences we have used our understanding of the importance of the distribution and sequence of the tyramine (PHOST mimic) in the sequence and observed the effect of architecture of lithographic performance first using DUV patterning of these materials. Subsequently we used e-beam patterning and most recently EUV patterning at the Paul Scherer Institute.

Development conditions originally required inorganic solvent due to the high polarity of the peptoid backbone, but with the introduction of hydrophobic peptoid units (diphenyl propylamine), we are now able to develop patterns in dilute aqueous base. The appropriate selection of sequence and the more hydrophobic peptoid sequence has led to a dramatic improvement in peptoid resolution

under e-beam and EUV exposures (see Fig. 2c). The result of patterning studies has shown the ability to produce patterns that are comparable to those produced by all but the best metal organic cluster photoresists.

As we relate sequence to enhanced development, we find that the overall sensitivity of the peptoid resists is showing marked improvement. At present we are using free ionic PAGs (TPS-nonaflate) and anticipate even more improved performance when we incorporate PAGs (non-ionic) into the peptoid sequence. As an example of the current sensitivity of these peptoid resists, we provide a contrast curve for EUV exposure in Fig. 2d [20].

At present there remains much to explore as we continue to introduce new functions into these peptoid systems including units for etch resistance, units that enhance resist adhesion or compatibility with ARC materials. We need to understand how their inclusion content and placement in a sequence influence resist performance.

4. Conclusion

To summarize, these photopolymers have shown high sensitivity EUV photoresponse and each family brings advantages to high resolution patterning. Through the PPA polymers and the covalently attached PACs we have shown that certain non-ionic PAGs are effective while others are not and we believe that characteristic depends on bond breakage behavior due to secondary electrons. Active PAGs produce very sensitive self-immolative PPA photoresists and our original idea of placing a PAG on each repeat to minimize stochastic variability becomes impractical due to the high speed of the resist. Instead, we obtain our best PPA performance using a single PAG per chain.

In the peptoids, we take the idea that good stochastics can be achieved through identical molecules without needing to make each repeat unit in a polymer identical. In the case of peptoids, sequence, function location, overall size and solubility contrast are all important and can be achieved by use of multiple monomers. We will also in future incorporate non-ionic, EUV active PAGs to enable control of PAG location and incorporation into each molecule. Both avenues (PPA and peptoid) have not been fully explored and given the progress to date, offer real potential to continue to improve on resolution, sensitivity and EUV resist performance.

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