Bismuth Resists for EUV Lithography

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We present the synthesis and preliminary lithographic evaluation of Molecular Organometallic Resists for EUV (MORE) that contain post-transition metals. These elements have high EUV optical density so they can utilize a large fraction of the incident photons. We will describe two technical approaches for EUV resist platforms that contain bismuth. Approach 1: Combination of organometallic compounds with photoacid generators. Approach 2: Combination of high-oxidation state metal-center oligomers that utilize carboxylate anions bound to the metal centers.
Key Words: Bismuth, EUV, Photoresist, MORE

1. Introduction

As the microelectronics industry continues to follow Moore's law, requirements for photoresists continues to advance. With 22-nm gate-lengths currently in production, many chip manufacturers are looking for ways to implement the 16 and 10-nm lithography nodes. Chip manufacturers currently use 193-nm scanners for printing these features, however, these systems have already surpassed their resolution capabilities and imaging is only made possible by multiple patterning. Extreme ultraviolet (EUV, 13.5-nm wavelength) lithography is thought to be the next imaging technology for fabricating microelectronic devices, however, there are still many obstacles that must be overcome. The traditional, chemically-amplified photoresist systems which have been successful in lithography since the 1980's are finally encountering extremely challenging [1] hurdles: poor photon absorption in thin-films [2], moderate etch selectivity [2,3] and limited gains in resolution [4,5].

Recently, two novel resist systems have been developed based on hafnium-oxide nanoparticles [6]. Researchers at Inpria Co., have demonstrated high resolution EUV resists capable of 8-nm dense line and space patterns at 200 mJ/cm^2. Christopher Ober's group at Cornell have demonstrated good sensitivity of

12 mJ/cm^2 at modest resolution of 36 nm. This pioneering work has demonstrated the great potential of inorganic systems as photoresists.

In this paper, we present on a subset of Molecular Organometallic Resists for EUV (MORE) that are comprised of organometallic compounds containing main group metals. The MORE approach utilises high EUV optical density metals to increase the photon absorbance of thin resist films. James Thackeray in his 2011 SPIE plenary presentation stated that the target absorption for EUV resist films is 50%. To print 10-nm lines with an aspect ratio of 2:1, film thickness must be around 20 nm. Polyhydroxystyrene at this thickness will stop only ~10% of the light (T ≅ 0.90) [7]. Loading organic polymers with fluorine will have limited impact. Teflon ($(C_2F_4)_n$) probably contains the most fluorine possible in an organic polymer, yet it only stops ~30% of the light in a film of 20 nm (T ≅ 0.70) [7]. A continuous, 20-nm film of HfO_2, on the other hand, will stop ~50% of the EUV light [7].

This work presents two approaches to create EUV photoresists using bismuth. These approaches leverage the free radical stability of and acid cleavability of metal phenyl bonds of main group metals. The EUV sensitivities of the two approaches as well as lithographic results of Approach 2 are reported in this work. The two

approaches are shown schematically in Figure 1 and are outlined below.

Approach 1. Main group metal-phenyl bonds are known to be acid sensitive [8,9]. When triphenyl bismuth is treated with three equivalents of triflic acid, bismuith tritriflate is formed. Triphenyl bismuth is organic soluble while bismuth tritriflate is water soluble [9]. Approach 1 utilizes these properties by blending metal-phenyl oligomers with a PAG. The proposed reactivity is the cleavage of metal phenyl oligomers in the exposed regions through photo-generated acid. Synthetic design of main group metal-phenyl oligomers is described in section II. These oligomers form the basis of Approaches 1 and 2.

Approach 2. High resolution (18 nm) and good sensitivity (30 mJ/cm^2) have been achieved by a salt of CoBpy(Ox)$_2$ as presented by Daniel Freidman at SPIE Advanced Lithography 2014. From these results monomeric metal carboxylates of bismuth were synthesized. Compounds of the type BiPh$_3$X$_2$ where X = Cl and -O$_2$CR only achieved solubility contrast in protic solvents. This may be attributed to the high baseline solubility of these compounds in nonpolar organic solvents. Imaging results of these compounds using protic solvent developers were poor. This is likely due to the decomposition of these compounds in protic solvents. Approach 2 utilizes oxidized metal-phenyl oligomers. These oligomers have lower baseline solubility in non-polar organic solvents. Oxidized oligomers of bismuth have demonstrated solubility contrast under EUV exposure with development in non-polar organic developer.
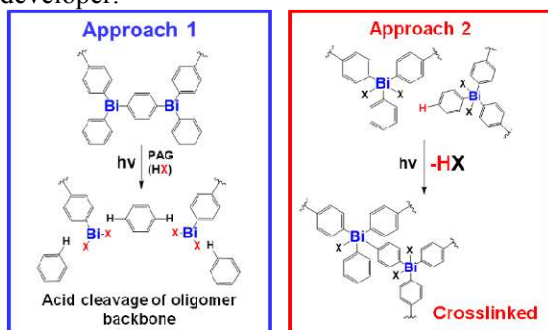

Figure 1. Schematic representation of approaches taken to develop EUV resists from main group metals.

2. Experimental

2.1 Synthesis of Main Group Metal Phenyl Oligomers

The synthesis of these oligomers is as follows. A disproportionation reaction occurs between triphenyl bismuth and bismuth trichloride when refluxed in THF [9]. Based on the equivalents of each reactant, the number of chloride substituents as compared to phenyl substituents can be modulated. For example, diphenyl bismuth chloride is the major product of 2 molar equivalents of triphenyl bismuth and 1 molar equivalent of bismuth trichloride. Phenyl bismuth dichloride is the major product of 1 molar equivalents of triphenyl bismuth and 2 molar equivalent of bismuth trichloride. In both cases, the end products will be a statistical distribution of triphenyl bismuth through bismuth trichloride.

Notice that when combined with a Grignard reagent, diphenyl bismuth chloride can react once while phenyl bismuth dichloride can react twice. The ability for phenyl bismuth dichloride to react twice allows it to serve as a "linking" substituent in an oligomeric chain. This chain is formed from the reaction of phenyl bismuth dichloride with a digrignard.

General reaction schemes and resulting GPC data are shown in Figure 2. By controlling the relative proportions of the dichloride and monochloride variants of bismuth, molecular weight can be controlled. The curve 3 in Figure 2 corresponds to the case where chain ends are preferentially selected by the stoichiometry of triphenyl bismuth and bismuth trichloride. Curve 1 corresponds to the case were "linker" molecules are preferentially selected.

Determination of molecular weight through a traditional polystyrene standard has proven challenging. The elution time for triphenyl bismuth is markedly longer then what is predicted by a polystyrene calibration curve. In order to properly calibrate the GPC, we would need fractions of the bismuth oligomers of known MW (such as the monomer and dimer). Notice that for the curves shown in Figure 2, distinct peaks appear from right to left. When triphenyl bismuth is run, the elution time agrees with the peak furthest to the right. If we assume

these peaks correspond to the monomer through tetramer molecular weights, then we can plot a calibration curve for the bismuth oligomer. This curve is shown in Figure 3. Notice the linear relationship. Using a polystyrene standard, a similar linear relationship is found. This gives some confidence to this calibration curve found in Figure 3.

Since the goal of this synthetic approach was to produce oligomers with lower baseline solubility than corresponding monomers, a method to isolate higher molecular weights was developed. This method consisted of precipitation of the quenched and purified reaction mixture in hexane. GPC data was collected for the supernatant fraction and precipitate. These curves are shown in Figure 4. Notice that the monomeric fraction is almost entirely removed and remains in the supernatant. Using the GPC calibration curve in Figure 3, it was found that the peak molecular weight (approx. number average) corresponded to 3400 g/mol or approximately nine metal centers. The resulting precipitate served as the acid cleavable oligomer employed in Approach 1 as well as the synthetic starting point for Approach 2.
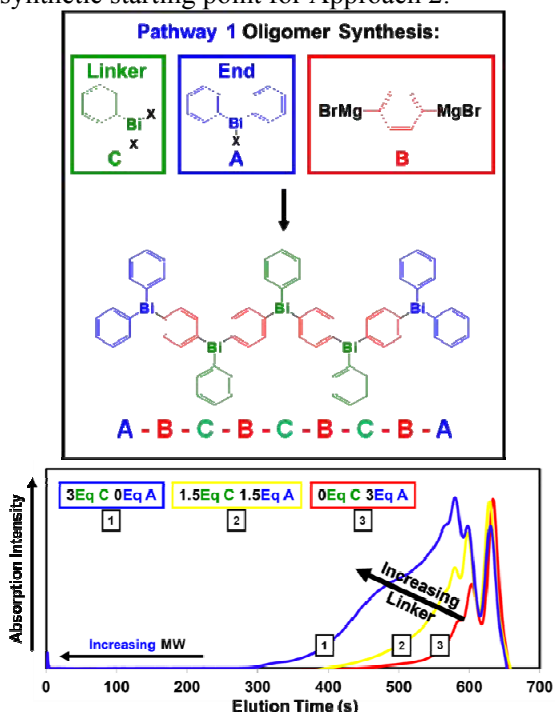

Figure 2. Bismuth oligomer synthetic approach. As linking bismuth dichloride unit is increased as compared to the ending monochloride unit, molecular weight increased.

2.2 Synthesis of Oxidized Metal-Phenyl Oligomers

Oligomers of bismuth were oxidized with sulfuryl chloride in dichloromethane [10]. This yielded the dichloride variant. These chlorides could be exchanged for carboxylates through the use of a corresponding carboxylic acid and an excess of triethyl amine. The resulting triethylamine hydrochloride was then filtered off, and the carboxylate functionalized oligomer precipitated into hexane.
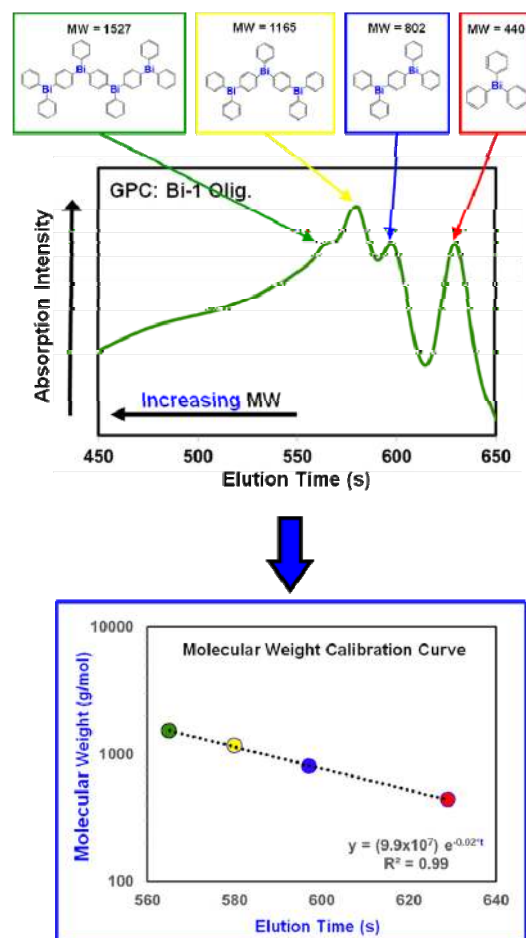

Figure 3. Molecular weight calibration for bismuth oligomer. Sharp peaks of reaction mixture GPC spectrum were assigned to Monomers through tetramers. A molecular weight calibration curve was then plotted.
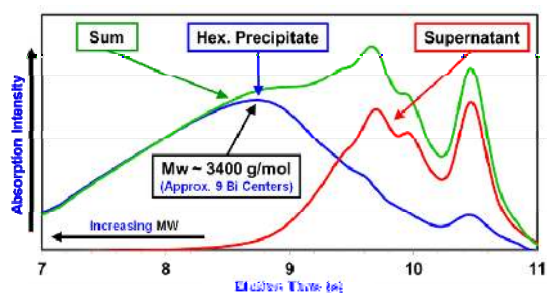
Figure 4. Control of bismuth oligomer through precipitation of reaction mixture into hexane.

3. Results and Discussion

3.1 Approach 1: Noncatalytic Acid Cleavage of Main Group Oligomers

This approach leverages the acid cleavability of main group metal-phenyl bonds. These cleavage events consume the acid. Approach 1 is to formulate the main group oligomeric materials discussed in Section II with a Photoacid Generator (PAG). We propose that the generation of acid in the exposed regions will cause the cleavage of the oligomeric chain as well as changing the lipophilicity as a result of the metal counterion complex formed.

Oligomers were treated with an excess of triflic acid and a GPC spectrum collected before and after treatment. The results of this experiment are shown in Figure 5. Curve 1 shows the GPC of the sample before treatment with acid and curve 2 shows the GPC after treatment. Notice that the elution times post treatment are longer and the resulting peaks are sharper. This indicates a decrease in molecular weight after treatment with acid.

Contrast curve measurements taken at the Berkeley Micro Exposure Tool (BMET) have demonstrated poor photospeeds of the Bi-1 oligomer blended with 25 wt% PAG. The Emax vales measured was 60 mJ/cm^2. We believe that the poor photospeeds of this system result from the noncatalytic nature of the acids generated. Because of this, a high wt% of PAG must be used in order to achieve photosensitivity. With this wt% of PAG, PAG segregation will likely be an issue. As such, this approach has not been our primary focus.
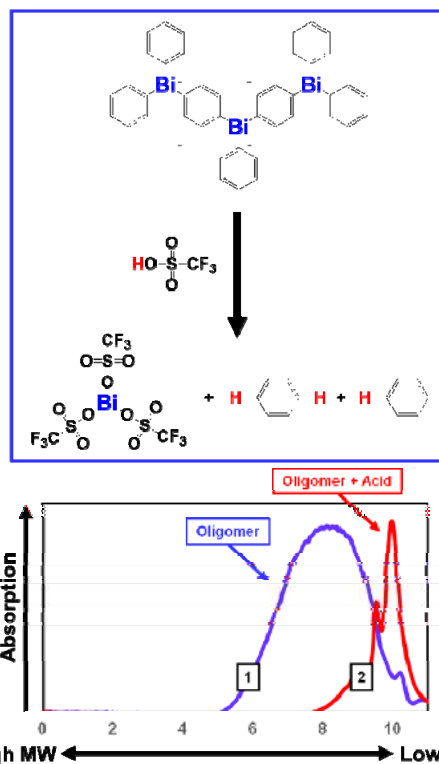

Figure 5. Cleavage of bismuth oligomer backbone by triflic acid.

3.2 Approach 2: Oxidized Metal Phenyl Oligomers

This approach is based on the oligomers discussed in Section II. In this case oligomers are oxidized to the representative metals higher oxidation state. In the case of bismuth, the metal center may be readily oxidized from its lower oxidation state of 3+ to its higher oxidation state of 5+ with a stoichiometric amount of sulfuryl chloride. This acts to bond two chlorides to each metal center. The resulting chlorines may be readily substituted for a variety of substituents including carboxylates and other halogens. Substitution of carboxylates in the place of halogens dramatically increases solubility of these oligomers. Contrast curves were recorded using the Berkley DCT. A representative contrast curve is shown in Figure 6 for the bismuth oligomer X = Cl.

Exposures were carried out on four variants of the bismuth oligomer. The results are shown in Figure 7. In all cases, the developer employed was 50/50 dichloromethane/hexane. Notice that the best resolution was obtained from the

dichloride variant (21 nm) and the best sensitivity from the diacetate variant (30 mJ/cm^2). All of the SEM's displayed are of negative tone development. When the dichloride variant was developed in acetic acid instead of non-polar organic solvent, it displayed positive tone imaging.
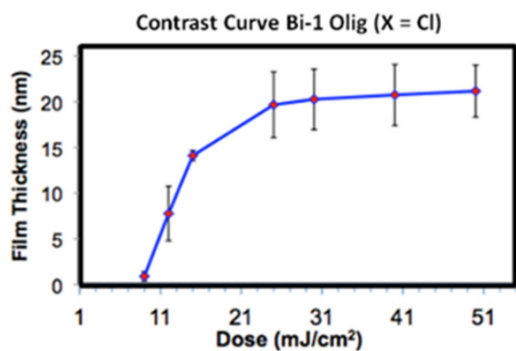

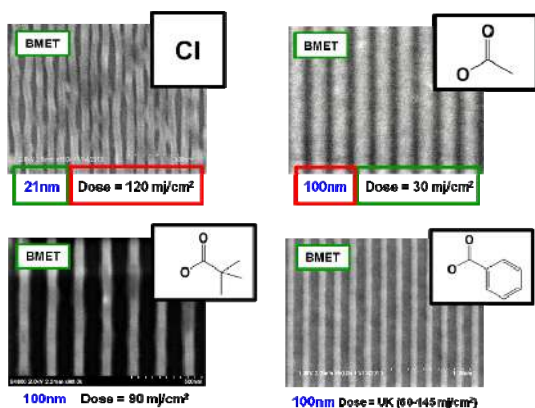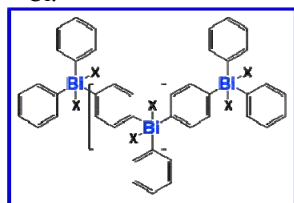Figure 6. Contrast curve for oxidized bismuth oligomer X = Cl.

Figure 7. Lithographic results for oxidized bismuth oligomer with various X group substituents. Dose of 30 mJ/cm^2 is achieved for X = OAc, resolution of 21 nm is achieved for X = Cl.

3.3 Proposed Mechanism For Solubility Contrast

In an attempt to improve this system, an effort was made to understand the photo-reactive mechanism of these bismuth phenyl oligomers. Outgassing experiments were conducted for this oligomer system. By analyzing the mass spectrum recorded for the bismuth oligomer X = Acetate (OAc), and comparing to literature results of acetic acid, it is conceivable that the resist is alleviating acetic acid upon exposure to electrons. Using this information, we propose a crosslinking mechanism that alleviates HX as a byproduct (Figure 9). This mechanism proposes that under EUV exposure, the bismuth-X bond homiletically cleaves. The resulting medal radical may then attack the phenyl ring of an adjacent oligomer. The remaining X radical may then abstract the proton at this cite thus restoring aromaticity to the phenyl ring. The end result of this proposed mechanism is to form a bond between the bismuth of one oligomer and the phenyl of an adjacent oligomer thus crosslinking the two oligomers. Through this proposed mechanism, HX would be generated.

This mechanism also supports the positive tone imaging observed. When bismuth is oxidized to its 5+ state, the axial positions become acid sensitive [10]. An equilibrium is set up as shown in Figure 10. Notice that the predominant group bound to the axial positions is the group whose conjugate acid is stronger. For this reason a phenyl is easily displaced by acetic acid. This property of bismuth should make the new bond in Figure 10 acid cleavable. Cleavage of this bond with acetic acid would act to remove the crosslink between the two oligomers and add an acetate group to the bismuth center. This would increase the solubility of this oligomer and may explain the positive tone imaging observed in acetic acid.

A connection may exist between the bismuth-X bond strength and photo speed. It appears that the photo speed for X = Cl are considerably slower than for X = OOCR. A bismuth halogen bond is known to be stronger than a bismuth carboxylate bond [8] and as a result, bond strength seems to correlate with photo speed. This supports the proposed mechanism but also indicated that breaking the bismuth-X bond is likely a key component of the photo-reactive mechanism.
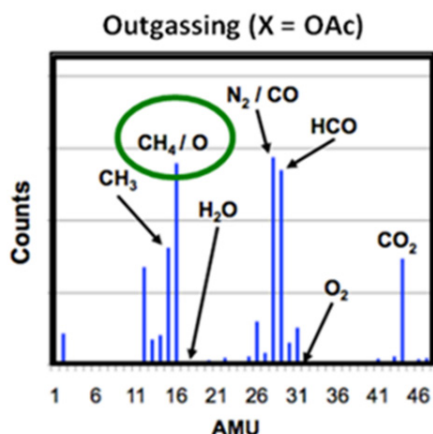
Figure 8. Outgassing data for bismuth oligomer X = Cl. Strong outgassing signals are shown that may represent decomposition fragments for acetic acid.
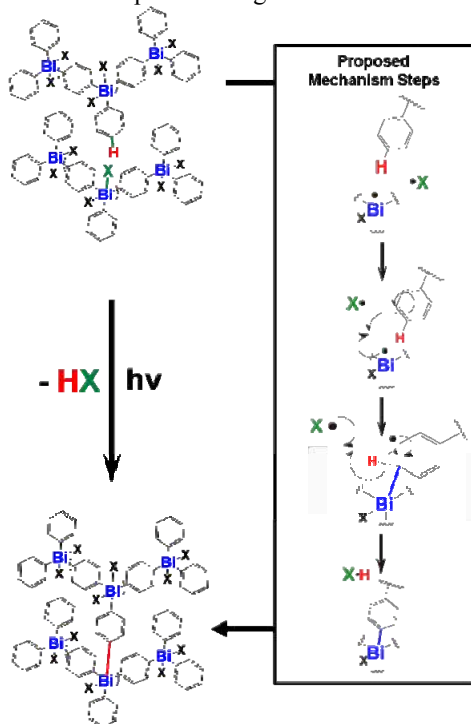

Figure 9. Proposed crosslinking mechanism of bismuth oligomer.

4. Conclusions

Two systematic approaches have been developed to create EUV photoresists comprised of organometallic compounds that contain
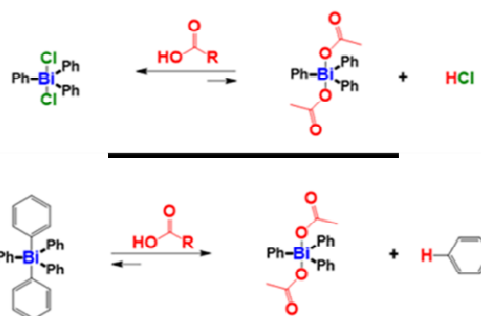

Figure 10. Acid equilibrium for bismuth in 5+ oxidation state with chloride and phenyl substituents in axial positions.

bismuth. The first approach has demonstrated poor EUV sensitivity. This is likely due to the non-catalytic nature of cleaving a bismuth phenyl bond with acid. The second approach has shown the most promise. Bismuth oligomers in this class have produced modest photo speeds of 30 mJ/cm^2 at poor resolutions of 100 nm and modest resolution capabilities of 21 nm at poor photo speeds of 120 mJ/cm^2. A mechanism has been proposed for the photo reactivity of this system and has been supported by the data collected thus far. Further investigations are required to refine this system such that good photo speed and resolution may be simultaneously obtained.

References
1. G. Moore, *Electronics*, 1965, **38**.
2. J. Paul, M. Rudolph, S. Riedel, S. Wege, C. Hohle and V. Beyer, *The Electrochemical Society Abstract* 2012.
3. J. Paul, M. Rudolph, S. Riedel, X. Thrun, S. Wege and C. Hohle, *Advanced Etch Technology for Nanopatterning II, Proc.SPIE,* **8685**.(2013) 86850V.
4. S. Kang, W. L. Wu, K. W. Choi, A. DeSilva, C. K. Ober and V. M. Prabhu, *Macromolecules*,**43** (2010) 4275-4286.

5. G. P. Patsis, V. Constantoudis and E. Gogolides, *Microelectron. Eng.*, **75**, (2004) 297-308.

6. Y. Ekinci, M. Vockenhuber, M. Hojeij, L. Wang and N. Mojarad, *Extreme Ultraviolet Lithography IV, Proc. SPIE*, **8679** (2013) 867910.

7. B.L. Henke, E.M. Gullikson, and J.C. Davis. X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000 eV, Z=1-92, Atomic Data and Nuclear Data Tables Vol. 54 (.2), 181-342 (July 1993).

8. Haiduc, Ionel, and Jerry J. Zuckerman. Basic Organometallic Chemistry: Containing Comprehensive Bibliography. Berlin: W. De Gruyter, 1985.

9. Suzuki, Hitomi. Organobismuth Chemistry. Amsterdam: Elsevier Science, 2001. Print.

10. Barton, Derek H.r., Neerja Yadav Bhatnagar, Jean-Pierre Finet, and William B. Motherwell. "Pentavalent Organobismuth Reagents. Part Vi. Comparative Migratory Aptitudes of Aryl Groups in the Arylation of Phenols and Enols by Pentavalent Bismuth Reagents." *Tetrahedron*, **42**(12) (1986) 3111-3122.