Polycarbonate Based Non-chemically Amplified Photoresists for Extreme Ultraviolet Lithography

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ABSTRACT

Some initial EUVL patterning results for polycarbonate based non-chemically amplified resists are presented. Without full optimization the developer a resolution of 60 nm line spaces could be obtained. With slight overexposure (1.4 x E_0) 43.5 nm lines at a half pitch of 50 nm could be printed. At 2x E_0 a 28.6 nm lines at a half pitch of 50 nm could be obtained with a LER that was just above expected for mask roughness. Upon being irradiated with EUV photons, these polymers undergo chain scission with the loss of carbon dioxide and carbon monoxide. The remaining photoproducts appear to be non-volatile under standard EUV irradiation conditions, but do exhibit increased solubility in developer compared to the unirradiated polymer. The sensitivity of the polymers to EUV light is related to their oxygen content and ways to increase the sensitivity of the polymers to 10 mJ cm^{-2} is discussed.

Keywords: Non-CAR, non-chemically amplified resists, EUV, polymer architecture, polycarbonates,

1. INTRODUCTION

Line edge roughness (LER) is becoming an increasing issue as the feature size for lithographic features decreases. For chemically amplified resists (CARs) a number of causes have been attributed, but diffusion of photogenerated acids has been reported to be one of the most significant contributing factors [1-3]. Our strategy has been to remove acid diffusion from the equation by investigating non-chemically amplified resists (non-CARs) for 193nm and EUV lithography [4-7]. The mechanism by which these resists function is through a molecular weight solubility switch, i.e. light interacts with the polymer resulting in chain scission of the backbone, which reduces the molecular weight of the polymer, making it more soluble in developer. Reports of poly(methylmethacrylate) (PMMA) as a non-CAR have shown that it can be patterned using EUV lithography to feature sizes as low as 22 nm with low LER [8]. However, PMMA lacks the required sensitivity and etch resistance for use in manufacture. The low sensitivity of PMMA is inherent to its chemical structure. We have screened a range of chemical structures for their propensity to degrade at 13.5 nm / 92 eV and generated a predictive model that is able to screen structures *in silico* [9]. One promising target that was identified using this model was substituted carbonates. This conference proceeding describes the lithographic performance of these materials.

2. EXPERIMENTAL

2.1 Example Synthesis of linear polycarbonates

2.1.1 Example Synthesis of Bis(imidazole) carboxylates: 2,5-dimethylhexane-2,5-diol (5.04 g, 33.4 mmol) was dissolved in anhydrous tetrahydrofuran (60 mL) under an argon atmosphere. Finely divided potassium (2 g) was added to the solution, which was then refluxed for 2 hours. The mixture was cooled to 30 ºC and the solution was transferred by cannula to a suspension of 1,1'-carbonyldiimidazole (11.26 g, 69.4 mmol) in anhydrous tetrahydrofuran (40 mL) under an argon atmosphere. The mixture was refluxed for 2 hours. The work up was achieved by adding 200 ml of ethyl acetate to the reaction mixture and washing the resultant solution (3 × distilled water). The washed organic layer was dried over anhydrous magnesium sulfate and then evaporated by rotary evaporation at reduced pressure to yield the crude product, which was then purified by passing through a silica gel column eluted with ethyl acetate. (7.5 g white crystals, 68%). 1H NMR 300 MHz (CDCl3): δ (ppm) 8.02-8.01(d, 2H), 7.32-7.31 (t, 2H), 7.00-6.99 (t, 2H), 1.97 (s, 4H),

1.57-1.56 (d, 12H); 13C NMR 75 MHz (CDCl3): δ (ppm) 148.8, 138.9, 132.3, 128.9, 118.9, 88.7, 36.3, 27.8; FTIR (cm-1) 3180.1, 3122.6, 2964.9, 2938.2, 2858.6, 1752.0, 1376.9, 1297.5, 1285.7, 1087.1; elemental analysis Exp. C% 57.4, H% 7.3, O% 19.0, N% 16.3 Theoretical. C% 57.5, H% 6.6, O% 19.1, N% 16.8.
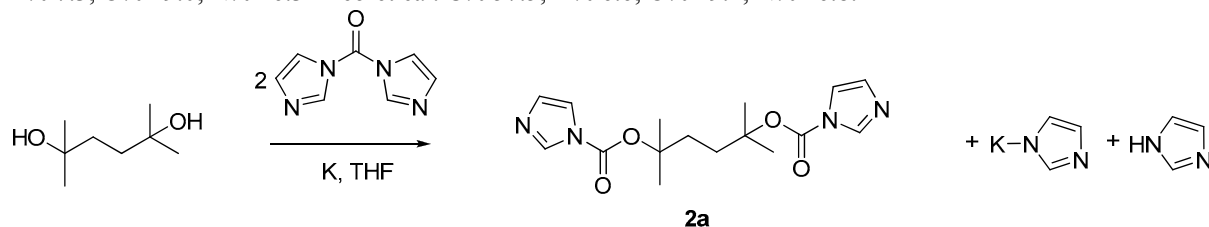
2.1.2 Example Synthesis of Linear Polymer Carbonate:
The above bis(imidazole carboxylate (1.00 g, 3.0 mmol) and cyclohexane-1,4-diol (1c, 0.345 g, 3.0 mmol) were dissolved in dichloromethane (2.5 mL). 18-crown-6 ether (0.11 g) and anhydrous potassium carbonate (2.0 g) were added to the solution under an atmosphere of argon. The suspension was refluxed for 24 hours. The reaction was worked up by diluting the mixture with dichloromethane (100 mL) and centrifuging the suspension. The decanted, clear solution was filtered and most of the solvent was removed by rotary evaporation at reduced pressure. The remaining solution was added drop-wise into methanol (100 mL) with stirring. A white precipitate was obtained, which was dried under vacuum at room temperature. (0.45 g, 48.3%). 1H NMR 300 MHz (CDCl3): δ (ppm) 4.58 (m, 2H), 2.36 (d, 2H), 2.00-1.86 (m, 5H), 1.69- 1.14 (m, 22H) 13C NMR 125 MHz (CDCl3): δ (ppm) 152.8, 83.5, 83.3, 73.9, 72.8, 34.2, 29.2, 28.2, 27.1, 25.8, 25.8, 25.7; FTIR: (cm-1) 2943, 1728, 1446, 1367, 1324, 1262, 1228, 1199, 1148, 1120, 1079; GPC (pSty calibration):   11 200 Da; ÐM 1.3; DSC Tg 95.6 °C.
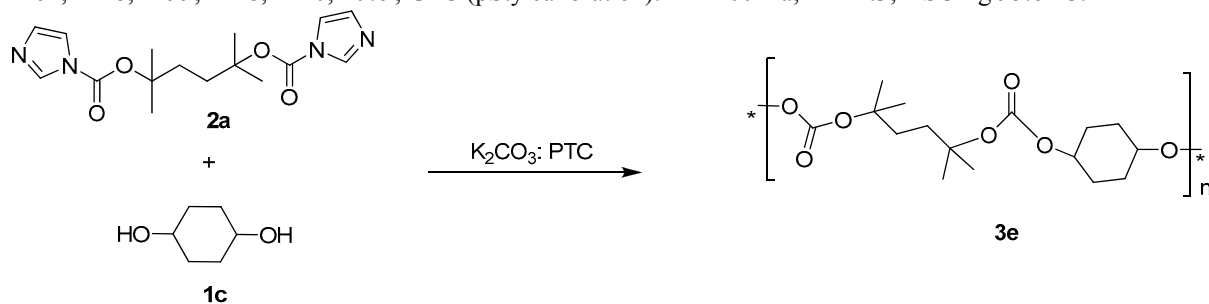
2.2 Irradiation conditions

EUV lithography (EUVL) exposures were performed at the Sematech Advanced Light Source micro-exposure tool at LBNL (known as the ALS-MET or BMET)[10, 11] Multiple calibration wafers were run using TOK EUVR-P1123 ME to ensure proper targeting of dose and focus. 200 μm x 600 μm open frame exposures were made using a 5% exponent increase in dose over the range of 0.5-150 mJ cm-2 (30 steps). Large array focus exposure matrix (FEM) wafers were obtained using 7 mJ cm^{-2} linear dose increments, from 27-153 mJ cm-2 (17 steps) and a focus range of best focus ± 50 nm (2 steps). Patterns were obtained using the Berkeley Pseudo Dark Resolution (SPDR2) microcell on the Samsung SU-451 mask. All exposures used standard annular illumination (0.35 < δ < 0.55) which is known to have resolution to approximately 26 nm half pitch [10, 11].

2.3 Process Conditions:

All resists were coated to 50 ± 3 nm film thickness on HMDS primed silicon wafers. A post apply bake was undertaken at 120 °C for 90 s. Following EUVL exposures, most samples a PEB step was not used. Our standard development procedure was undertaken by immersing the wafer in 100% isopropanol for 45 seconds, followed by drying the wafer with a stream of nitrogen flow. Selected samples, as detailed below, were treated with either (1) no PEB and solvent development using 95% isopropanol / 5% methylisobutylketone mix for 45 seconds or (2) a post exposure bake at 100°C for 60 seconds and solvent development with 95% isopropanol / 5% methylisobutylketone mix for 45 seconds. At that point, wafers were analyzed without additional processing.

2.4 SEM Measurements:

Patterning was observed top-down by scanning electron microscopy (SEM), using a Hitachi S-4800. Image capture was performed using an accelerating voltage of 2 kV, a working distance of 2.2 mm, 150k magnification, and integration of

64 frames. Images were imported into EUV Technology Corporation's SuMMIT software package for critical dimension and LER analysis using the same parameter set employed for analysis of the calibration wafers (Details of EUV Technology Corporation's SuMMIT software suite can be found at http://www.euvl.com/summit/summit.htm). The characterization of 30 - 100 nm hp features on each SEM wafer through both dose and focus provided the information reported in the text regarding each material's resolution, depth of focus, and exposure latitude.

3. RESULTS & DISCUSSION

The polymers in this project are linear polycarbonates that have been prepared by a polycondensation reaction between bis(imidazole) carboxylates and diols, using methods adapted from Frechet et al. [12-14]. To achieve high yields and molecular weights for these polymers, it was important to ensure that the reaction was dry. The polymers have been designed to incorporate polycyclic structures with the aim of giving a high glass transition temperature (T_g) and etch resistance. By modifying the structure of the repeat units it was found that the T_g could be tuned between about 50-170°C [7]. The structure that was chosen for further lithographic evaluation is shown in Figure 1. This polymer was selected due to its T_g of 127 °C. The molecular weight was 11k Da with a polydispersity index of 1.6.
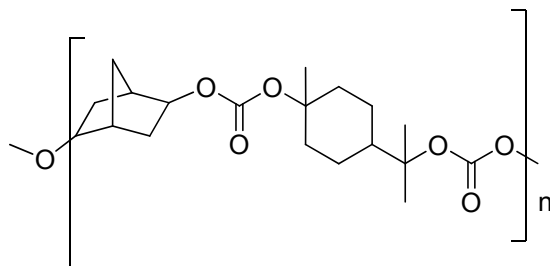

Figure 1 Structure of polycarbonate used for patterning by EUVL in this study.

The carbonate structures in the polymer backbone have been incorporated to increase the sensitivity of the polymer to EUV photons. Oxygen has been reported to have a higher absorbance than carbon at 13.5 nm.[15] Hence, incorporation of carbonates, which are comprised of three oxygens, increases the absorbance of the polymer. Following this primary absorption process thermalized secondary electrons will be produced which will generate free radical and / or ionic species.[16-18] The carbonate structures are secondary or tertiary in nature, so ionic species that are formed will be stabilized and will promote chain scission rather than recombination reactions.

To understand the mechanism of photodegradation the polymers were subjected to outgassing analysis. The mass spectrometry trace of the out gassed species during exposure to EUV photons is shown in Figure 2. When the polymer is exposed to EUV photons the primary species that are observed to be ejected are carbon dioxide and carbon dioxide. This indicates that photochemistry is indeed occurring at the at the carbonate functional group. Interestingly, we do not observe peaks that can be assigned to oligomers or monomer units in the mass spectra, which indicates that the other photoproducts that are formed are not volatile under EUV exposure conditions. This result is promising because it indicates that only carbon dioxide and carbon monoxide are produced in significant quantities during outgassing, so these polymer systems should not contribute significantly to mirror contamination. However, witness plate testing is required to demonstrate this conclusively. The inset in Figure 2 shows a number of molecules evolved versus dose plot. This plot shows that there is a linear increase in the number of molecules evolved with dose. This indicates that for the dose range studied the photoproducts produced as a result of loss of car bon dioxide and carbon monoxide are not having a significant influence on subsequent chain scission events.
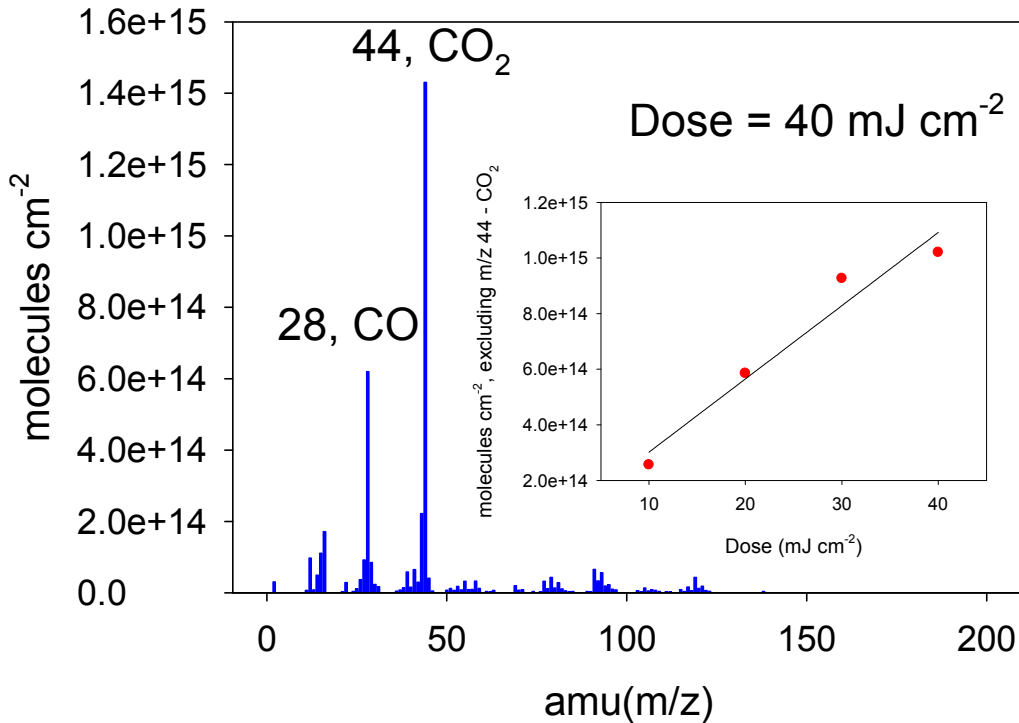
Figure 2 Mass spectrum from EUV outgassing experiment at a dose of 40 mJ cm^{-2}. The inset shows a linear increase in evolved molecules with increasing dose

Figure 3 shows top-down SEM images of patterned films after exposure to an EUV dose of 48 mJcm^{-2} at a variety of half pitches and developed with isopropanol. It should be noted that there has been no attempt to optimize the developer. In these examples no post exposure bake (PEB) step was used. This is because the mechanism for the solubility switch is by direct polymer chain scission, which in the absence of a PAG will not be improved by a PEB step The top row of images shows elbow patterns, while the second row the second shows line spaces. Using IPA as a developer the ultimate resolution for 1:1 line spaces can be seen to be 70 nm. At a half pitch of 60 nm the main defects can be seen to be micro-bridging. It was found that by increasing the strength of the developer, by using 5% MIBK in IPA, that the ultimate resolutions of 60 nm could be achieved with no micro-bridging defects (data not shown)
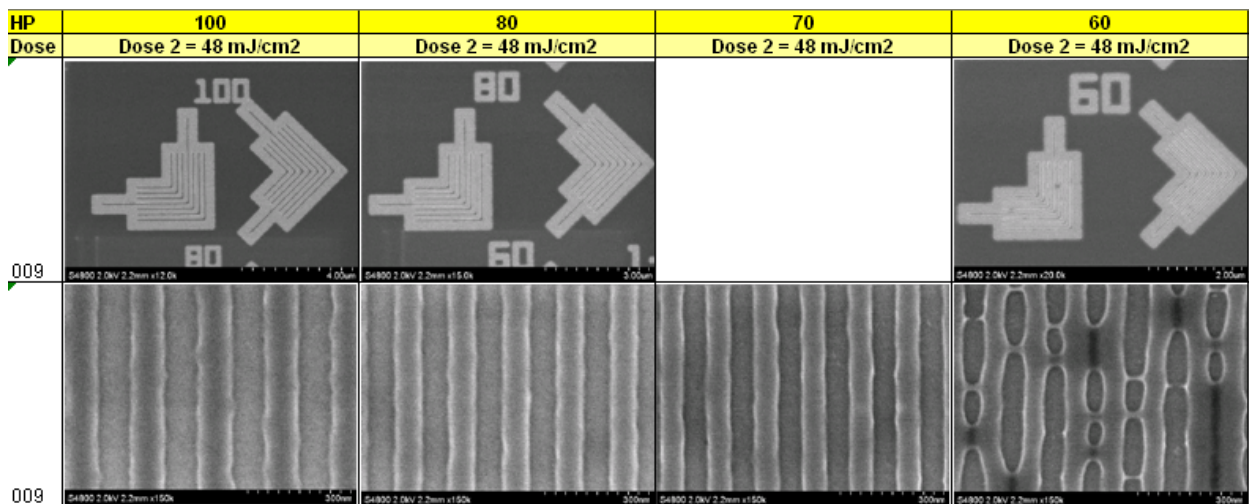

Figure 3 Top down SEM images for EUVL imaging at 48 mJ cm-2 at a variety of half pitches

To investigate the effect of overdose a dose skew for patterning at a half pitch of 50 nm is shown in Figure 4. The polymer is performing well at overdose. At a dose equal to $1.4 \times E_0$ (69 mJ cm^{-2}) it was possible to resolve a line/space pattern with a critical dimension of 43.5 nm at a half pitch of 50 nm. At higher doses, 1.8 and $2.1 \times E_0$, it was possible to achieve critical dimensions of 32.3 and 28.6 nm respectively. LER for these exposures was approximately 5.2 ± 0.5 nm. For these systems there will be no LER contribution from acid diffusion, because these polymers operate through a molecular weight solubility switch resulting from direct scission of the polymer chain. However, other LER contributions such as mask roughness and developer effects may result. For example, the roughness of the absorber in the Sematech-Berkley micro-field exposure tool is known to be in the order of 8.9 nm and this along with other factors such as flare or scattered light can result in mask induced LER in the patterned photoresist of approximately 3.5 nm [11]. Hence, the LER observed is only 1.7 nm greater than that of the mask roughness, which may be attributed to developer-resist interactions.

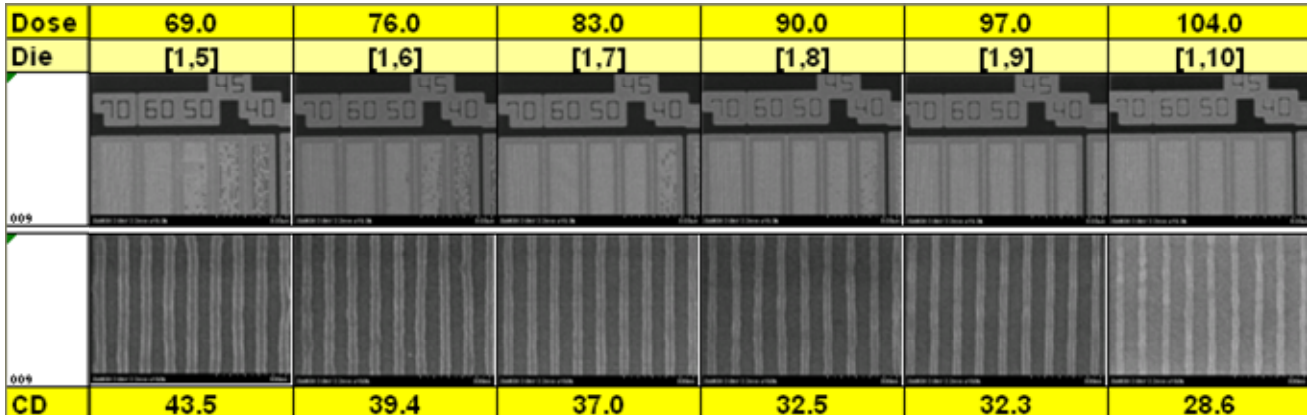| Dose	69.0	76.0	83.0	90.0	97.0	104.0
Die	[1,5]	[1,6]	[1,7]	[1,8]	[1,9]	[1,10]
CD	43.5	39.4	37.0	32.5	32.3	28.6

Figure 4 Top down SEM images of EUVL patterning at a half pitch 50 nm where a dose skew has been performed.

Figure 5 shows the 50 nm half pitch analysis of the images shown in Figure 4. From this chart it can be seen that the E_{50} for this polymer is 51.2 mJ cm^{-2}, which is 1.07 x E_0.
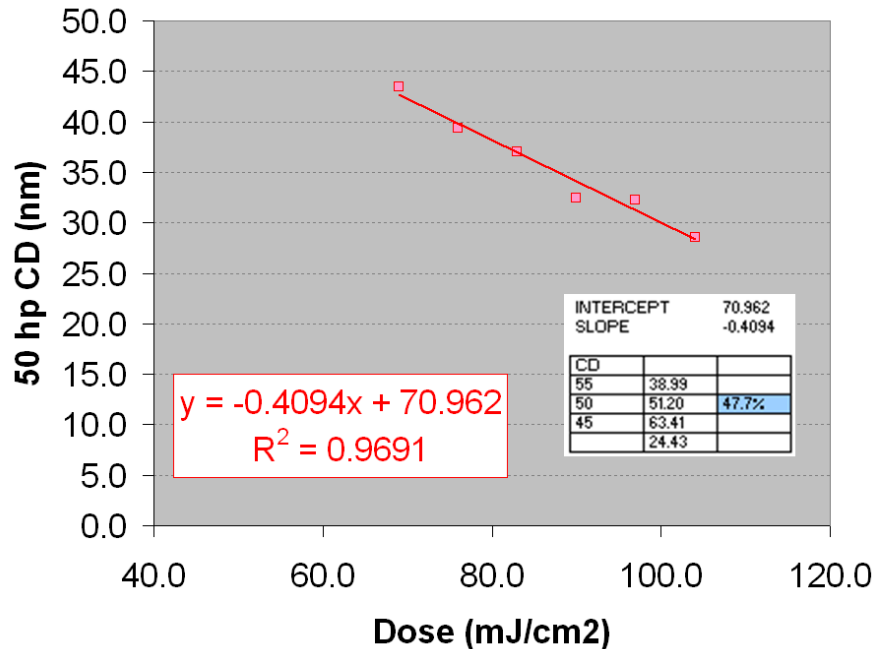

Figure 5 50 nm half pitch versus dose plot for images shown in Figure 4.

The E_0 values for three different polycarbonates has been plotted versus their calculated absorbance values at 13.5 nm in Figure 6. Extrapolation of this curve shows that if the absorbance of the polymer could be increased to approximately 4.8 μm^{-1} then an E_0 value of 10 mJ cm^{-2} could be achieved. For patterning at the 22 nm node it is expected that the film thickness will be low, so these higher absorbance values should not be issue, in terms of obtaining a good aerial image through the resist. One possible way to achieve higher absorbance values would be to incorporate fluorine into the polymer structure. This would increase the absorbance and also the etch resistance of the polymers. It should also be noted that the strength of the developer and the interaction of the developer with the resist will also have a large impact on the sensitivity.
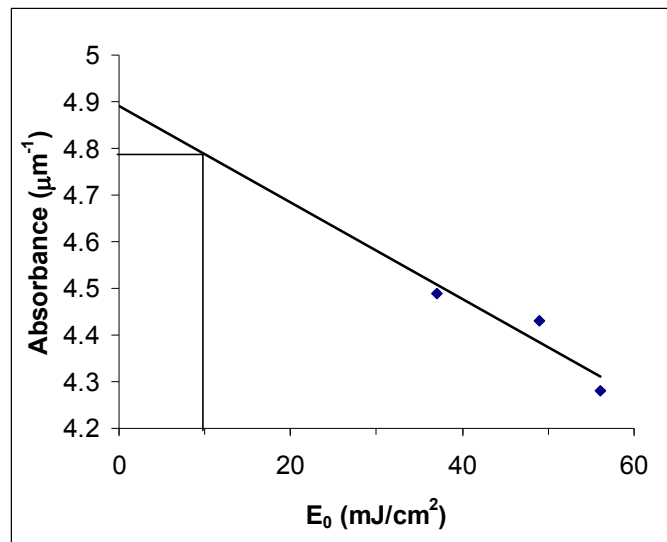

Figure 6 Absorbance versus E_0 plot showing predicted absorbance required to result in an E0 of 10 mJ cm^{-2}.

4. CONCLUSIONS

Initial results on the patterning of polycarbonate based non-chemically amplified resists using EUV lithography have been presented. The ultimate resolution for 1:1 patterns was shown to be 70 nm, however this could be improved by optimization of the developer strength as well as overdosing the polymers. By increasing the absorbance of the polymers and further optimizing the developer-resist interactions it was hypothesized that non-chemically amplified resists based on polycarbonates could be developed with E_0 values as low as 10 mJ cm-2.

5. ACKNOWLEDGEMENTS

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