Chemically Amplified Main Chain Scission: Chopping the Influence of Polymer Dimensions on Line Edge Roughness

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The concept of Main Chain Scission of photoresist polymers (MCS) is used to reducing the influence of molecular dimensions on the quality of photoresist patterns. Independent from the wavelength or lithography technique, the concept will raise in relevance as critical dimensions approach molecular dimensions. After the introduction of the MCS concept on last years conference of photopolymer science and technology, initial results are given in this paper to verify this concept.[1] Starting with polymer synthesis, after optimization of resist formulation and process conditions, ebeam patterns with the MCS resist and a commercial ebeam resist were generated. The patterns were compared with respect to their roughness. It was found, that lines printed in the MCS resist show a significant lower LER than the same patterns in the ebeam resist.

Keywords: Line Edge Roughness, Main Chain Scission, Polycarbonate

1. Introduction

Line edge roughness and linewidth control will become a significant problem for semiconductor industry, as the dimensions required need to become as precise as the size of a polymer unit.[2] According to the ITRS structures down to 65nm have to be resolved for DRAM production until 2007. In 2016 22nm DRAM half pitch is required. Coming along with these dimensions, the demands on the photoresist raise. One of the first unsolved issues for lithography in the roadmap concerns the 80nm node already in 2004. The maximum line edge roughness must not exceed 4nm (3σ) for the 80nm node and has to be decreased down to 1nm until 2013.

The scope of this paper is to show initial results in reducing the influence of polymer size on printed patterns with the concept of main chain scission. Polymerization results followed by optimization of the resist formulation and first structures, obtained with ebeam lithography will be presented. The generated patterns will be compared to structures obtained with a commercial resist regarding LER.

2. Chemically Amplified Main Chain Scission of Polymers

The concept of chemically amplified main chain scission (MCS) of polymers for photoresist materials was introduced in 1985 by Jean M. J. Fréchet, C. Grant Willson *et al.* for DUV applications.[3]

Fig. 1. a) Schematic drawing of a common DUV resist with pendant protection groups; b) MCS: The protection groups are in the polymer backbone.

The polymers for the MCS approach are designed to have protection groups within the polymer backbone. As a result monomer units are formed in the exposed areas after the baking step. In contrast, common CAR polymers change their polarity in the exposed areas as a consequence of the exposure, since they have protection groups pendant to the polymer backbone. In Fig. 1 both approaches are sketched.

As displayed in Fig. 2a) for common resists, we expect partly exposed polymer units remaining in the pattern sidewall. With different polarity, compared to the bulk material, these polymer units have a strong tendency to form larger aggregates. The MCS approach (Fig. 2b) does not change the polarity of polymer units, but the exposed polymers chopped to monomer size by the generated acid.

Fig. 2. Schematic drawing of a) a common chemical amplified resist and b) a MCS resist before and after exposure, bake and development; "I" stands for insoluble, "S" for soluble groups.

3. Experimental

3.1. Instrumentation

NMR spectra were recorded on Bruker Avance300, Avance400 and Jeol JNM-EX400, respectively. Thermogravimetric data were collected on a Netsch STA 429 and on Perkin Elmer DSC 7 at a heating rate of 10 K/min in argon atmosphere. Sample structuring was done with an integrated E-beam combination of conventional Jeol Scanning Microscope (JSM-840A) with a linked E-beam Unit (nanobeam, Sietec) at an acceleration voltage of 40kV. Structures were inspected with a Jeol Scanning Microscope JSM 840A.

3.2. Synthesis of Bis(carbonylimidazolid) of 2,5-Dimethyl-2,5-hexanediol **2**

2 was prepared from 2,5-dimethyl-2,5-hexanediol **1** according to [8]. 15.9 g (70%). $M_p = 116^\circ\text{C}$; $^1\text{H-NMR}$ (CDCl_3 , 400MHz) δ 1.77 (s, 4H), 1.42 (s, 12H).

3.3. Synthesis of Bis-p-nitrophenylcarbonate of 2,5-dimethyl-2,5-hexanediol **3**

To a solution of 2,5-dimethyl-2,5-hexanediol **1** (2.96 g, 0.020 mol) and pyridine (3.27 g, 0.041 mol) in dichloromethane (60 g) a solution of p-nitrophenyl chloroformate (8.16 g, 0.040 mol) in dichloromethane (20 g) was added over 60 minutes. After 24h at reflux the mixture was cooled to room temperature and additional dichloromethane (50 g) was added followed by extraction with water (1 x 100 mL), HCl (5 %, 100 mL) and again water (2 x 100 mL). After drying with Na_2SO_4 , the organic phase was evaporated to result in 6.35g white solid. The raw product was further purified by column chromatography (SiO_2 , CHCl_3) to yield 3.41 g of **3** (0.007 mol, 36%). $M_p = 129^\circ\text{C}$; $^1\text{H-NMR}$ (CDCl_3 , 400MHz) δ 8.20 (d, 4H), 7.32 (d, 4H), 1.99 (s, 4H), 1.57 (s, 12H).

3.4. Preparation of polymer **5**

A mixture of 2,2-bis(4-hydroxyphenyl)hexafluoropropane **4** (4.94g, 0.012 mol), **3** (7.00g, 0.015 mol), 18-crown-6 (0.32 g) and K_2CO_3 (50.06 g) in dichloromethane (110 mL) was stirred under reflux conditions in an argon atmosphere for 5 days. The resulting suspension was cooled to room temperature, filtered and concentrated to approximately 50 mL. The polymer was then precipitated in methanol and dried *in vacuo* to yield 3.59 g (46%) of polymer **5**. T_g 91°C ; $^1\text{H-NMR}$ (CDCl_3 , 400MHz) δ 7.38 (d, 4H), 7.18 (d,

4H), 1.96 (s, 4H), 1.57 (d, 12H); GPC (THF) $M_n = 11200$ g/mol, $M_w = 13800$ g/mol, PDI 1.2.

4. Polymer Design and Synthesis

Essential for the polymer design is the availability of cleavable groups within the polymer backbone. Several cleavable groups were introduced by J.M.J. Fréchet.[4-8] We focused our investigations on polymers containing acid cleavable tertiary oxycarboxylates.

Fig. 3: Scheme of a polymer containing acid cleavable tertiary oxycarboxylates.

Usually polycarbonates are prepared by polycondensation of a dicarboxylic acid and a diol. To yield high molecular weight a high turnover number is essential in the polymerization step. However, since the reactivity of tertiary hydroxyl groups is reduced strongly due to sterical hindrance an activation step of the hindered hydroxyl groups is necessary. In a first approach, for activation the reaction of carbonyldiimidazole with 2,5-dimethyl-2,5-hexanediol **1** was used to receive the corresponding biscarbonylimidazolid **2** in good yields up to 70%. [8]

As second monomer 2,2-bis(4-hydroxyphenyl)-hexafluoropropane **4** was chosen, because the acidity and therefore the solubility of the molecule in TMAH after the imaging step is expected to be higher than for the non fluorinated derivative. According to literature, we used a solid-liquid phase transfer catalyzed polycondensation reaction to obtain the tertiary polycarbonates. Unfortunately, it turned out that the reaction of **2** with **4**, results in dimers and trimers only. Therefore we had to change the activation of **1**.

In a next approach the well established reaction of the sterically hindered 2,5-dimethyl-2,5-hexanediol with p-nitrophenyl chloroformate was used for activation.[7] This reaction runs in moderate yields of 40 – 50 %. For polymerization with **4** again a phase transfer catalyzed reaction was performed. Utilizing reaction times up to 5 days, we were able to prepare high molecular weight polymers with a narrow distribution. After purification molecular weight M_n typically was

found to be in the range of 11000 to 15000 g/mol with a polydispersity below 1.5

5. Lithography Results

5.1. Investigation of the resolution capabilities of a MCS based photoresist

To investigate the lithographic capability of the MCS based photoresists, open frame DUV experiments and ebeam lithography were used. Starting optimizing the process conditions 110°C softbake temperature were applied for 90s, followed by a variation of PEB temperatures from 60°C to 130°C. In this step isopropanol was used for development, to ensure that all fragments generated during PEB are dissolved. With 60°C post exposure bake temperature even a dose of 45 mJ/cm² was not sufficient to reach dose to clear (D(0)). Increasing PEB temperature to 70°C resulted in a D(0) between 4 and 6 mJ/cm² and a contrast between 2 and 4, depending on the development time. For 80°C PEB temperature the contrast was raised to approximately 12 while dose to clear decreased below 2 mJ/cm². Coming to higher PEB values of 110°C and 130°C, D(0) is further lowered. However, there is no increase in contrast at these temperatures. Taking the low T_g of 90°C into account, 80°C should be the most suited PEB temperature.

Fig. 4: Influence of PEB temperature on contrast and dose to clear D(0) at different exposure doses.

Based on the information of the 248nm greyscale analysis imaging experiments were performed to optimize the resist and the process conditions. 100nm L/S 1:1 pattern was printed with ebeam exposure into the resist and baked at 70°C and 80°C, respectively. For both temperatures the obtained pattern is similar. It turned out, that due to the use of isopropanol for development the structures were slightly overexposed, even at D(0).

Fig. 5: 100nm L/S 1:1 ebeam imaging at different post exposure bakes; developer: isopropanol; left: SB 130°C / 90s, PEB 70°C / 90s; right: SB 130°C / 90s, PEB 80°C / 15s.

As a consequence of overexposure, for the next experiment the developer was changed to TMAH 2.38%. Again 70°C and 80°C PEB temperatures were compared. In Fig. 6 70nm L/S 1:1 are displayed. For the lower PEB temperature the structures were well resolved. However, with the higher bake conditions the lines show pattern collapse at the resolution limit. This phenomenon could be due to the low Tg of the polymer. The overexposure effect was not observed with the TMAH development.

Fig. 6: 70nm L/S 1:1 ebeam imaging at different post exposure bakes; development TMAH 2,38%/90s; left: SB 130°C / 90s, PEB 70°C / 90s; right: SB 130°C / 90s, PEB 80°C / 15s.

For further optimization of the process conditions the influence of the soft bake temperature was investigated. Softbake conditions were adjusted to 110°C/90s and 130°C/90s, respectively. As exemplified in Fig. 7 starting at 100nm dense L/S a lower soft bake temperature leads to pattern collapse. The reason could be found in a larger amount of solvent remaining in the resist material at lower bake temperature.

Summarizing the conditions tested so far, it can be concluded, that for this material for soft bake a higher temperature of 130°C and for post exposure bake a lower temperature of 70°C are favorable to enhance resolution. TMAH for development is also suited and helps to prevent overexposure.

Fig. 7: 100nm L/S 1:1, PEB: 70°C / 90, Dev. TMAH 2,38%; left: soft bake 110°C / 90s; right: soft bake 130°C.

To get information on the profiles as well, cross sections were made. For this experiment the optimized conditions, SB 130°C/90s and PEB 70°C/90s, were applied. In Fig. 8 350nm and 150nm dense L/S patterns are shown. No scumming or corner rounding can be observed, but especially the smaller structures show t-topping.

Fig. 8: Cross sections left: 350nm L/S 1:1; right: 150nm L/S 1:1; SB 130°C / 90s, PEB 70°C / 90s, TMAH 2.38%/90s.

To reduce t-topping we added 1.0 % triethanol amine (TEA) as a quencher to the resist. Using favorite process conditions the resolution capability was compared to the resist without base. Although capable to resolve 70nm L/S 1:1, the additive leads to enhanced pattern collapse.

Fig. 9: Comparison of the resolution capability; left: no additive; right: 1% TEA.

However, the quencher reduces t-topping significantly, as can be seen in Fig. 10. But, together with the loss of t-topping, footing occurs.

Fig. 10: 1% TEA reduces t-topping significantly; left: without base; right: 1% TEA.

So far in this paper, only 80nm thick films were discussed. To investigate the influence on pattern collapse and resolution, film thickness was doubled. It turned out, that again 130°C soft bake temperature yield better resolution than 110°C. However, even at elevated temperature the higher film thickness lowers resolution to 125nm L/S. For smaller CDs pattern collapse occurs (see Fig. 11).

Fig. 11: At 160nm film thickness, the resist is capable to resolve 125nm L/S 1:1 (right); with a CD of 100nm pattern collapse is observed.

We therefore can conclude, that for thin films the MCS approach is capable to resolve at least L/S 1:1 pattern with CD = 70nm at optimized conditions. Coming to thicker film thickness, pattern collapse limits the resolution capability. A similar behavior is observed at lower soft bake and higher post exposure bake temperatures. The reason for this behavior might be found in the low T_g of the polymer used. In addition, solvent residues, especially at low soft bake temperatures can contribute to soften the resin.

5.2. Line Edge Roughness - Comparison with commercial ebeam resist

Scaling resist patterns to smaller CDs, lithographic requirements will reach molecular dimensions in future.[9-11] Maybe the first limit that will be violated is pattern roughness. To get an impression of the influence of the polymer dimensions onto the roughness, the MCS resist was compared to a commercial ebeam resist. For that purpose, again ebeam lithography was used to print dense L/S pattern into both resists.

To exclude an influence coming from missing resolution capabilities, investigation of LER was started at uncritical dimensions. Both resists resolve 350nm L/S pattern at 80nm film thickness. As shown in Table 1, the CD was tightened down to 100nm stepwise. Although sometimes very similar to the ebeam resist, in all experiments the main chain scission resist showed smaller values for LER. Especially for 100nm and 125nm lines the MCS resist without base showed significantly lower line edge roughness.

Table 1: Comparison LER of commercial ebeam resist and MCS resist at 80nm film thickness.

CD [nm]	LER 3 σ [nm]			
	ebeam resist	MCS	MCS	MCS
	SB: 120°C/90s PEB: 120°C/90s FT: 80nm	SB: 130°C/90s PEB: 70°C/90s FT: 80nm Base: 0%	SB: 130°C/90s PEB: 70°C/90s FT: 80nm Base: 0.5%	SB: 130°C/90s PEB: 70°C/90s FT: 80nm Base: 1.0%
350	11	7	10	7
250	10	6	7	6
200	8	5	6	5
175	8	4	6	6
150	7	5	6	5
125	7	3	6	6
100	7	3	6	5

In Fig. 12 350nm and 100nm patterns for ebeam and the MCS resist are shown. LER for patterns with MCS resist with 0.5% base content is slightly better, but almost identical to the ebeam resist. Similar to 0.5% base, but more consistent at 350nm lines are the values for the resist with 1% quencher.

Fig. 12: Comparison of LER (top: CD = 350nm; bottom: CD = 100nm); left: commercial ebeam photoresist; right: MCS resist.

At 160nm film thickness the MCS resist was tested with 1% quencher. For all dimensions investigated, LER was found to be only half as much as for the ebeam resist (see Table 2).

Table 2: Comparison LER of commercial ebeam resist and MCS resist at 160nm film thickness.

CD [nm]	LER 3 σ [nm]	
	ebeam resist	MCS
	SB: 120°C/90s PEB: 120°C/90s FT: 160nm	SB: 130°C/90s PEB: 70°C/90s FT: 160nm Base: 1%
350	13	6
250	13	5
200	12	4
175	10	4
150	11	4
125	10	4
100	8	-

To avoid measurement errors due to degraded profiles, cross sections were prepared. Both resists show some footing, but no scumming. While there was found a small t-top for the ebeam resist, the profile of MCS patterns is somewhat rounded. The surface of the MCS resist seems to be smoother (Fig. 13).

Fig. 13: Comparison of LER (CD = 350nm); left: commercial ebeam photoresist; right: MCS resist.

6. Conclusion and Outlook

After first introduction of the MCS concept at last years conference, in this paper the synthesis of a new polymer for the MCS concept is published. The synthesis was optimized to get access to high molecular weight polymers at reasonable yields. After polymer characterization, a photoresist was formulated and the process conditions were adjusted with respect to resolution and profile quality. Elevated softbake conditions and lower PEB temperature turned out to be most suited. After optimization, 70nm dense L/S patterns were resolved. Finally the line edge roughness of the MCS resist was identified and compared to a commercial ebeam resist acting as reference system. It was found, that the MCS resist concept shows 50% less LER compared to the ebeam resist.

To get a final conclusion, more experiments have to be performed. Especially optical lithography has to be taken into account. However, the first results obtained are very promising. To avoid pattern degradation and pattern collapse, for future experiments, the Tg of the resist has to be enhanced. Finally etch tests have to be performed.

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8. References

1. C. Eschbaumer, N. Heusinger, C. Hohle, and M. Sebal, *J. Photopolym. Sci. Technol.*, 15 (2002) 673.
2. ITRS, *Internet* <http://public.itrs.net/Files/2001ITRS/Home.htm>.
3. J. M. J. Fréchet, F. M. Houlihan, F. Bouchard, B. Kryczka, and C. G. Willson, *J. Chem. Soc., Chem. Commun.*, (1985) 1514.
4. J. M. J. Fréchet, F. Bouchard, F. M. Houlihan, B. Kryczka, E. Eichler, N. Clecak, and C. G. Willson, *J. Imag. Sci.*, 30 (1986) 59.
5. J. M. J. Fréchet, F. Bouchard, F. M. Houlihan, E. Eichler, B. Kryczka, and C. G. Willson, *Makromol. Chem., Rapid Commun.*, 7 (1986) 121.
6. J. M. J. Fréchet, E. Eichler, M. Stanciulescu, T. Iizawa, F. Bouchard, F. M. Houlihan, and C. G. Willson, *ACS Symp. Ser.*, 346 (1987) 138.
7. J. M. J. Fréchet, F. Bouchard, E. Eichler, F. M. Houlihan, T. Iizawa, B. Kryczka, and C. G. Willson, *Polym. J.*, 19 (1987) 31.
8. F. M. Houlihan, F. Bouchard, J. M. J. Fréchet, and C. G. Willson, *Makromolecules*, 19, (1986) 13.
9. A. Kawai, *J. Photopolym. Sci. Technol.*, 15 (2002) 371.
10. Q. Lin, R. Sooriyakumaran, and W.-S. Huang, *Proc. SPIE*, 3999 (2000) 230.
11. T. Yamaguchi, H. Namatsu, M. Nagase, K. Yamazaki, and K. Kurihara, *J. Photopolym. Sci. Technol.*, 10 (1997) 635.