Azido-*m*-meconine-'high ortho' Novolak resin-based negative photoresists for deep UV lithography[†]

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Abstract. Photoactive chemicals blended with polymers, solvents and certain other additives serve as photoresists. A new photoactive compound (PAC), azido-*m*-meconine absorbing in the deep UV region has been blended with 'alternating' and 'semi-alternating' and 'high ortho' alternating novolak resins, based on *m/p*-cresol. The new photoresists have been evaluated as a negative tone deep UV photoresist for mircolithography.

Keywords. Photoresists; NMR; deep UV; lithography.

1. Introduction

Most modern electronic gadgets are based on micro-lithography which allows one to draw electronic circuits at micron or sub-micron level to make the microchip. Precisely patterned array of conductors, insulators and semiconductors that can be made to perform a wide variety of electronic functions lead to Very Large Scale Integrated Circuits (VLSI).[1–5]

Photoactive chemicals blended with polymers, solvents and certain other additives are referred to as photoresists. These are the real workhorses of the burgeoning microelectronics industry. In positive photoresists the exposed parts of photoresists become soluble in the developer.[4,6,7] In case of positive resists, on photolysis often an acidic group is generated and the basic developer easily washes this out. On the other hand, in negative photoresists, on exposure to light cross-linking makes the exposed parts more insoluble in the developer, usually an organic solvent. This is shown schematically in figure 1.

The two main components of a negative photoresist are aromatic azides/bisazides and cyclized rubber, along with an organic solvent and certain other additives. The hydrogen abstraction and/or insertion reaction of nitrene, generated from the azide during photolysis, produces a cross linked network of polymers in the exposed part of the resist. This increases the molecular weight of the resin compared to the unexposed part, consequently changing its
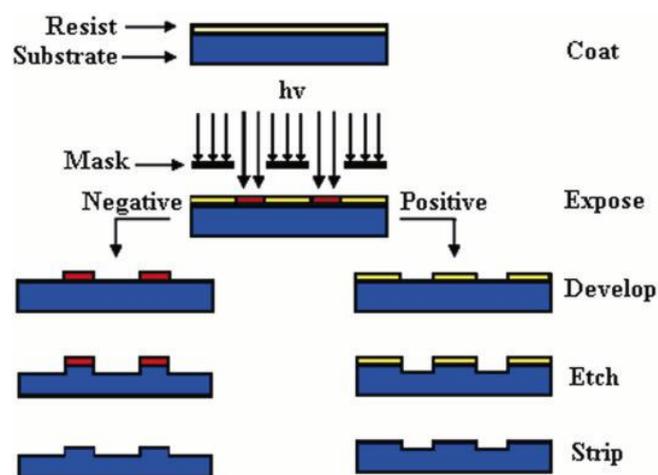

Figure 1. In positive photoresists the exposed parts become more soluble. On the other hand, in negative photoresists the exposed parts become more insoluble.

solubility characteristics (figure 1). Exploiting this change in the physical property a pattern can be generated on a substrate[1,4,6] by development, often using an organic solvent.

It was soon realized that negative photoresists have serious drawbacks such as swelling during development leading to a loss of resolution. Moreover, the organic solvent used as a developer was often an environmental pollutant. Another new class of negative photoresists introduced use aryl azides and novolak resins and used alkaline developers[8,9] combining features of both negative and positive photoresists and 'yet do not necessitate any change in the instrumental set-up'.[10] No swelling occurred in these cases and the resists were highly sensitive and led to high resolution as well. Improvements in the resolution of the lithographic process leads to smaller, faster devices and hence has been a continuous goal for microelectronics. Because the resolution is inversely related to the wavelength of exposure, the exposure source for patterning has shifted from the G and I-line (436 and 365 nm, respectively) to systems using 248-nm. More recently 193-nm and 157-nm excimer laser radiation are also being used. Deep UV lithography is of considerable importance for fabrication of 1–2 μm solid state devices.[11]

In most previous studies, the importance of novolak resin in promoting the dissolution of photoresists has not been explained, though the ratio of the photoactive component to novolak resin in conventional photoresists is ~5 : 1. It was soon realized that the matrix polymer holds the key for high resolution geometry. A proper engineering of the novolak microstructure is therefore very crucial for developing high performance photoresists.[12] Novolaks are phenol-formaldehyde resins obtained by acid/base catalysed polymerization of phenol and formaldehyde. Since the percentage of different precursors in the novolak microstructure is also very critical for good pattern formation, it is increasingly realized that the conventional 'one pot' synthesis of novolak resin should be replaced by a two-step procedure, to tailor the growth of the polymer chain.[10] For better lithographic performance cresol formaldehyde resins have replaced the phenol formaldehyde resins. The novolak resins used in the past were random structures and have been replaced by linear 'high ortho' novolaks (figure 2). To elucidate the exact microstructure of these polymers, NMR serves as the most useful and unambiguous characterization tool.[13,14]

2. Materials and methods

The NMR spectra were recorded on a Bruker 400 MHz Avance instrument operating at 400·13 MHz ^{1}H frequency. IR spectra were recorded on a Spectrum BX series spectrophotometer using KBr. TGA/DTA was recorded on Shimadzu DTG-60. UV spectra were recorded on Perkin Elmer UV spectrophotometer in methanol. DSC was recorded on Perkin Elmer. GPC instrument used was built by JASCO and equipped with UV and RI detectors. Calibration was done using polystyrene as standard.

3. Experimental

3.1 *m-Cresol and p-cresol-based 'semi-alternating' novolak resin (MS-6)*

10·8 g (0·1 mol) of *m*-cresol, 16·2 g (0·2 mol) of 37% formaldehyde and 4·0 g (0·1 mol) sodium hydroxide were stirred mechanically at room temperature (25°C) for 48 h. 10·8 g (0·1 mol) of
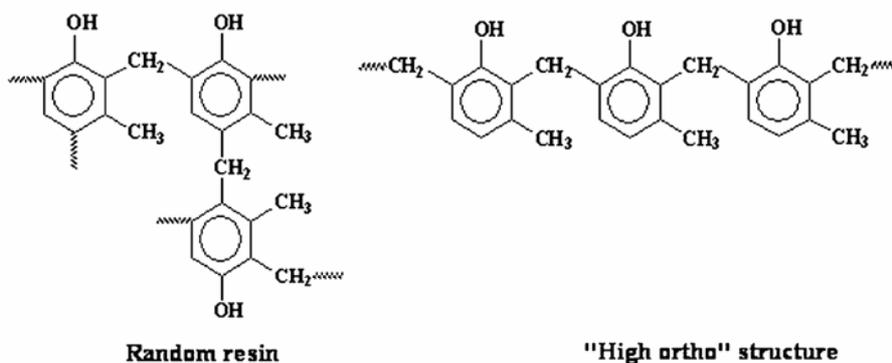
Figure 2. Random and 'high ortho' novolaks based on *m*-cresol and formaldehyde.

m-cresol was then added to the mixture and it was diluted with hydrochloric acid (1 : 1) in an ice bath and the pH brought down to 4–4·5. The *bis*-hydroxymethylated cresol (BHMC) was separated, and the organic layer was washed thoroughly twice with water containing 1% oxalic acid. In the second step, 10·8 g (0·1 mol) of *p*-cresol was mixed with liquid BHMC. 2·70 g of oxalic acid was used as catalyst and xylene was selected as the reaction medium. The mixture was then refluxed at 140–150°C for 45 min and then steam-distilled at 180°C for another hour. The molten resin was allowed to cool down and then the resin was leached with 30% NaOH. The alkali solution was filtered and in the filtrate dilute HCl was added drop-wise at 0°C until all the resin precipitated out. The precipitated resin was dried and then fractionated from ethyl acetate and hexane. Finally, the resin was dried in vacuum at 30°C for 24 h.

3.2 *m-Cresol and p-cresol-based 'alternating' novolak resin (MS-8)*

10·8 g (0·1 mol) of *m*-cresol, 16·2 g (0·2 mol) of 37% formaldehyde and 4·0 g (0·1 mol) sodium hydroxide were stirred mechanically at room temperature (25°C) for 48 h. 10·8 g (0·1 mol) of *p*-cresol was then added to the mixture and it was diluted with hydrochloric acid (1 : 1) in an ice bath and the pH brought down to 4–4·5. The *bis*-hydroxymethylated cresol (BHMC) was separated, and the organic layer was washed thoroughly twice with water containing 1% oxalic acid. In the second step, 10·8 g (0·1 mol) of *p*-cresol was mixed with liquid BHMC. 2·7 g of oxalic acid was used as catalyst and xylene was selected as the reaction medium. The mixture was then refluxed at 140–150°C for 45 min and then steam-distilled at 180°C for another hour. The molten resin was allowed to cool down and then the resin was leached with 30% NaOH. The alkali solution was filtered and in the filtrate dilute HCl was added drop-wise at 0°C until all the resin precipitated out. The precipitated resin was dried and then fractionated from ethyl acetate and hexane. Finally, the resin was dried *in vacuo* at 30°C for 24 h.

4. Results and discussion

In this study two novolak *m/p*-cresol 'high ortho' semi-alternating[15] (MS-6) and *m/p*-cresol 'high ortho'

alternating[16] (MS-8) oligomers were synthesized using the two-step process. These novolaks were blended with the PAC (azido m-meconine).[17] Its UV spectrum recorded in methanol showed λ_{max} at 207 (0·621), 239 (1·378), 267 (0·423) and 302 (0·143) nm with strong absorptions in the deep UV region (figure 3) and hence it was evaluated as a negative tone resist for 'deep UV' microlithography.

In the first step, the cresol was reacted with formaldehyde in the presence of NaOH at room temperature to prepare the *bis*-hydroxymethyl cresol (BHMC). In the second step, another unit of cresol was allowed to react with the *bis*-hydroxymethyl cresol in the presence of acid. Using this two-step procedure one not only obtains 'high ortho' linear novolaks, but also 'tailor made' alternating or semi-alternating resins, starting from the appropriate phenolic precursors with the desired percentages of *p*-cresol content in resin structure.[10,14,18,19]

Two novolak oligomers were successfully synthesized using the two-step procedure. These were characterized using various techniques, viz. GPC, IR, ^{1}H-NMR, ^{13}C-NMR and 2D NMR experiments like COSY, NOESY and HSQC. For MS-8, the Polydispersivity (P.D.), was found to be 2·65 (Mw = 1385, Mn = 521, PD = 2·65), whereas for MS-6, P.D. was 1·6 (Mw = 574, Mn = 360, PD = 1·56). A broad absorption peak around 3300 cm^{-1} in the IR
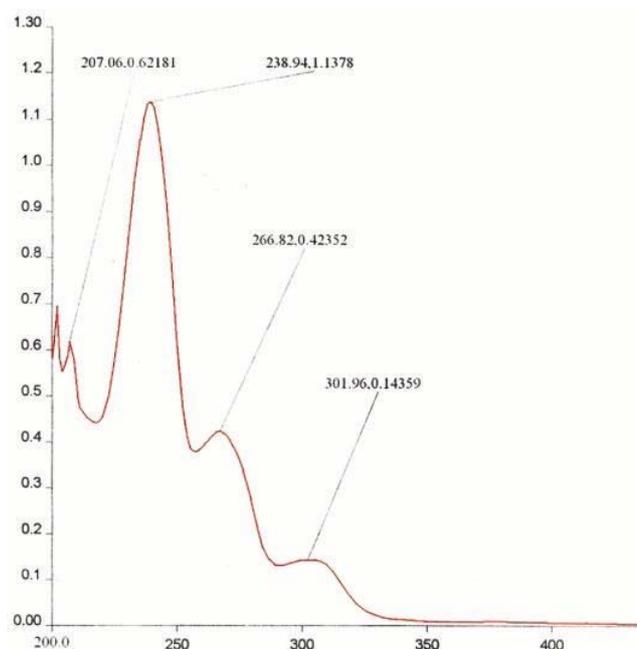

Figure 3. UV spectrum of the PAC, Azido-*m*-meconine.

Table 1. Spectral assignments of Novolak MS-8.

PMR (δ)	CMR (ppm)	DEPT-135 intensity	Assignments
2·18–2·37	19–21	Positive	Methyl groups
3·92–3·94	29–33	Negative	Methylene bridges
6·73–7·12	121–131	Positive	Aromatic protons

spectra is assigned to the intramolecularly hydrogen bonded phenolic hydroxyl group and indicates the incorporation of cresolic monomers in the resin skeleton. The incorporation of *m*-cresol/*p*-cresol in the resin microstructure was further proved by the methyl group asymmetric stretching frequency around 2925 cm^{-1}. The absorption peaks at 1616–1464 cm^{-1} for in-plane skeletal vibration of the aromatic ring and 1275 cm^{-1} for C–O confirms the incorporation of cresolic monomer in resin microstructure. The –CH$_2$ symmetric stretching absorption peak at 2853 cm^{-1} confirms the formaldehyde incorporation and the formation of novolak type skeleton. The ^{1}H and ^{13}C NMR resonances range are tabulated (table 1) along with the intensity of the DEPT-135.

To zoom into the exact microstructure of the novolak resins, complete 2D characterization was done. The peaks at 19 ppm are due to the 'hindered' and 'unhindered' –CH$_3$ groups of *p*-cresol units in the resins. Similarly, the signals at 21·0 ppm are assigned to 'hindered' and 'unhindered' –CH$_3$ groups of *m*-cresol.[20] Using the HSQC spectrum, the ^{1}H chemical shifts corresponding to ^{13}C chemical shifts were then identified. The ^{13}C chemical shifts around 19·0 to 19·6 ppm correlated well with the ^{1}H chemical shift around $\delta = 2·1$ ppm, thereby identifying the ^{1}H chemical shift of methyl group of *p*-cresol to be at $\delta = 2·1$ ppm. Likewise, the signals around 20·5 to 21·0 ppm of *m*-cresol in ^{13}C-NMR spectrum are seen to be correlated with the signal at $\delta = 2·2$ ppm in ^{1}H-NMR spectrum.[15] For a decisive confirmation of the ^{1}H chemical shift assignments of MS-6, the TOCSY experiment was carried out, using a longer mixing time of 80 ms to allow magnetization transfer to remote protons, thus enabling the long range correlation between methyl proton and aromatic hydrogens to be seen in the TOCSY spectrum (figure 4). The protons of methylene bridges also show an expected correlation with the methyl protons. The ^{1}H chemical shift assignments for methyl protons of *p*-cresol at $\delta = 2·1$ ppm and of *m*-cresol at $\delta = 2·2$ ppm are therefore confirmed.[15]
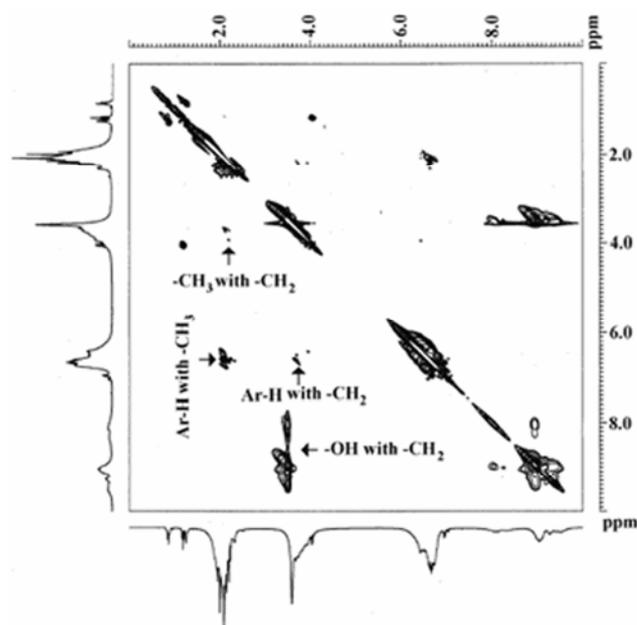
Figure 4. TOCSY of MS-6.
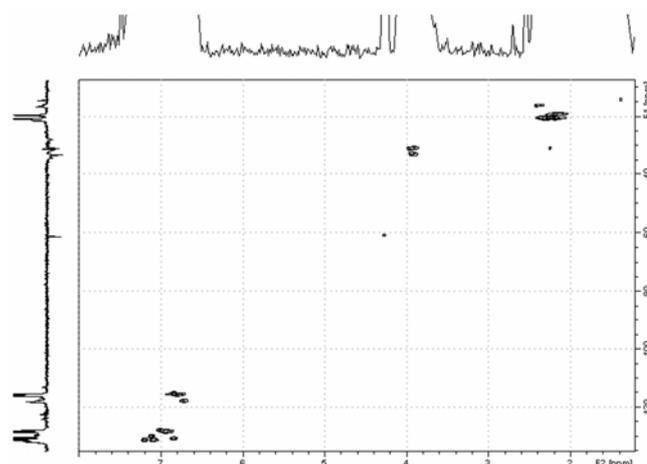
Figure 5. HSQC of the MS-8.

In case of MS-8, using the HSQC spectrum (figure 5), the ^{1}H chemical shifts corresponding to ^{13}C chemical shifts were then identified.[16] The ^{13}C chemical shifts at 19·2 and 19·6 ppm are seen to correlate well with the ^{1}H chemical shift at $\delta = 2·2$ ppm, thereby identifying the ^{1}H chemical shift of methyl

group of *p*-cresol to be at $\delta = 2 \cdot 2$ ppm. Likewise, the signals at $20 \cdot 6$ and $21 \cdot 0$ ppm of *m*-cresol in ^{13}C-NMR spectrum correlate with the signal at $\delta = 2 \cdot 3$ ppm in ^{1}H-NMR spectrum. The NOESY–COSY overlay (figure 6b), clearly evidenced that the methyl protons of m-cresol ($\delta = 2 \cdot 3$ ppm) exhibit a COSY cross-peak to *m*-cresol aromatic protons at ($\delta = 7 \cdot 1$ ppm), and this is the stronger of the two NOE cross-peaks observed from the methylene protons. Similarly, the '*m*-cresol methyl to the methylene protons' NOESY (figure 6a) cross-peak is far stronger than the p-cresol NOESY cross-peak to the methylene protons.[16]

5. Lithographic evaluation

The photosensitive resins were prepared by dissolving the oligomer and the photoactive component, PAC in the ratio $5 : 1$, in ethyl lactate, keeping the total solid content at 30%, using a vertex and left for homogenization for 36 h. The matrix was then filtered using a $0 \cdot 2 \mu$ filter, protected from light. A few drops of the resist were poured over the silicon wafer, and spin coated at 3000 rpm for 25 s and soft

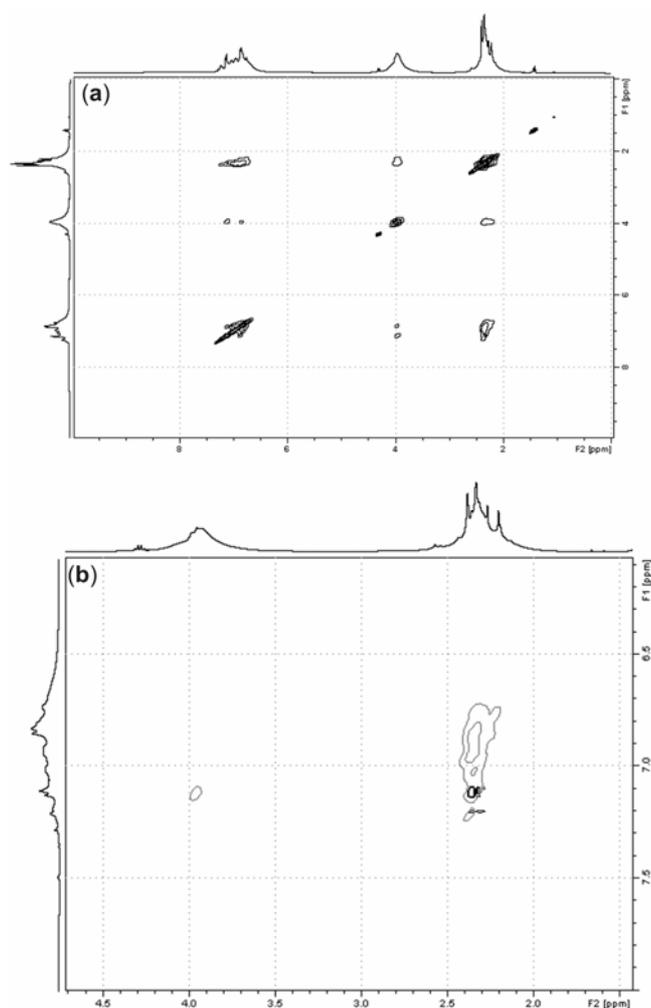**Figure 6.** NOESY (**a**) and NOESY–COSY, (**b**) overlay of MS-8.
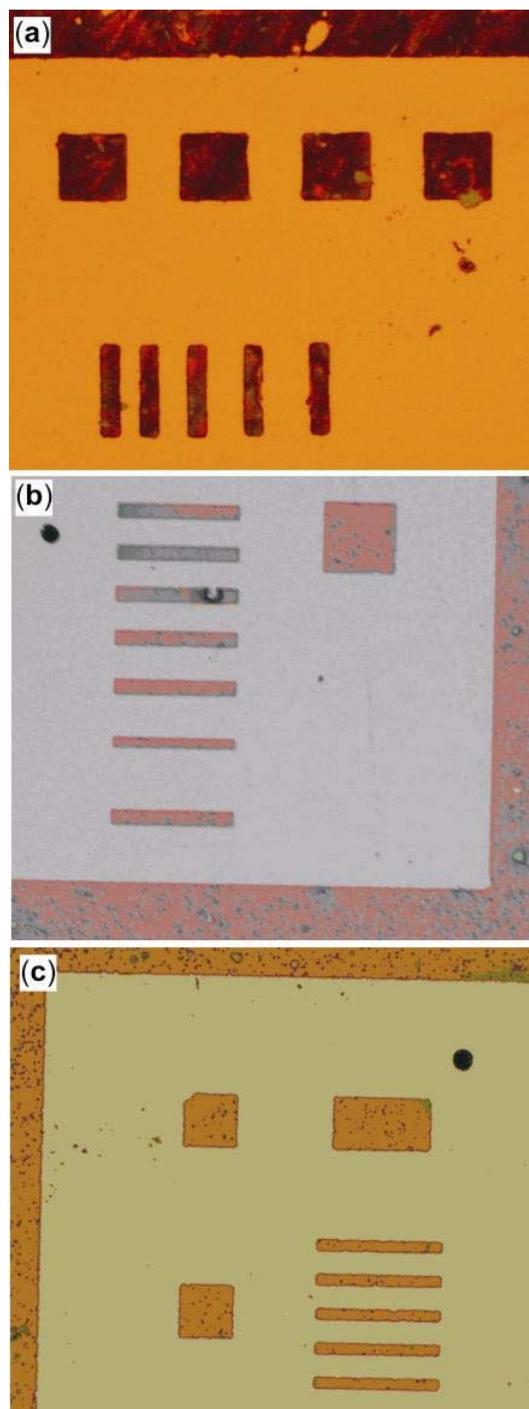

Figure 7. Optical micrograph of patterns obtained using the new photoresists based on: (**a**) MS-8 and (**b**), (**c**) MS-6.

baked at 80°C. The masks used were up to 5 μm. The exposure was carried out on a DUV stepper operating on Hg-Xe lamp 500 W delivering a dosage of 3·2 mJ. Development was done using tetra methyl ammonium hydroxide (TMAH).

The developed wafers were observed under the optical micrograph (figure 7). Both the resist compositions showed negative tone behaviour. The MS-6 composition showed a contrast but sharp resolution was not obtained. The film thickness was less than 1 μm, moreover the resist tend to wash away very fast. In the case of MS-8 composition, better film formation was observed. Film thickness was 1–2 μm with improved patterns. This is consistent with earlier reports that incorporation of the *p*-cresol in the given resin affects lithographic performance. 'semi-alternating' novolaks are better for positive photoresists, while 'alternating' novolaks yield better performance as negative tone resists.

6. Conclusion

Novolak resins MS-8 and MS-6, based on *m*- and *p*-cresols, were prepared and characterized by using 2D-NMR techniques. There were formulated with azido-*m*-meconine, the photoactive component (PAC) and evaluated as possible 'deep UV' negative photoresists for microlithography. The MS-8 composition showed better film formation compared to the one based on MS-6. In the former case, better resolution was obtained and the film thickness after development was determined to be around 1 μm.

Acknowledgements

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