Cashew Nut Shell Liquid–Based Tailor-Made Novolac Resins: Polymer Morphology Quantitation by 1-D and 2-D NMR Techniques and Performance Evaluation

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ABSTRACT: The application of cashew nut shell liquid (CNSL) and CNSL-based polymers in the burgeoning microelectronics industry is rare. "High ortho" alternating and semialternating tailor-made novolac copolymers based on CNSL and *m*-cresol and/or *p*-cresol and have been made and successfully used as photoresists for microlithography. The microstructure of one of the representative *m*-cresol copolymer is exhaustively elucidated based on 1-D and 2-D NMR techniques. Incorporation of different monomers in the resin backbone has been quantitatively estimated based on an improved NMR methodology. The lithographic performance of photoresists using novolac resins based on cardanol (fractionated CNSL) and diazonaphthoquinone ester was also evaluated. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1959–1965, 2003

Key words: resins; microstructure; NMR; copolymers

INTRODUCTION

The economy of tropical and subtropical countries is highly influenced by the cashew tree, *Anacardium occidentale,* because of the edible value of its nut and the widespread use of the shell liquid in technical applications.[1] Cashew nut shell liquid (CNSL), a most abundant natural phenolic liquid with a long aliphatic side chain, has many potential applications such as brake linings, surface coatings, foundry core oil, laminating and rubber compounding resins and adhesives, as composites and flame retardants. However, it is felt that CNSL-based applications have "yet to find a niche" for themselves.[2] For example, application of CNSL and CNSL-based polymers in the burgeoning microelectronics industry is very limited.[3] The construction of most modern electronic gadgets is based on microlithography, which deals with drawing of electronic circuits at micron or submicron level and enables one to make very large scale integrated (VLSI) circuits.[4,5]

Photoresists are the real workhorses of this multibillion-dollar industry and usually consist of photoactive chemicals such as diazonaphthoquinone, novolac polymers, acid-catalyzed phenol formaldehyde resin, solvents, and certain additives. It is realized that the current need for nanoscale fabrication can be met only through careful design and engineering of the matrix polymers (i.e., novolac resins).[6] An extensive study of the novolac polymer and copolymers reveals that the "high ortho" linear polymers show better lithographic performance than that of random resins.[7] Because the percentage of different precursors in the novolac microstructure is also very critical for good pattern formation, it is increasingly realized that the conventional "one-pot" synthesis of novolac resin should be replaced by a two-step procedure to tailor the growth of the polymer chain.[8] To elucidate the exact microstructure of these polymers, NMR turns out to be the most useful and unambiguous characterization tool.[9,10]

In this study, we have demonstrated a methodology for the synthesis of a new series of CNSL/cardanol-based "high ortho" novolac copolymers and have used GPC and both 1-D and 2-D NMR spectroscopic techniques to elucidate their exact microstructure and to calculate the percentage incorporation of different monomers in the polymer microstructure. Use of these natural product–based polymers is demonstrated by preparing photoresists and evaluating their lithographic performance.

EXPERIMENTAL

CNSL and cardanol-based copolymers were prepared by a two-step procedure.[8] In the first step, the first

Patent application has been filed.
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TABLE I
Cardanol and/or CNSL-Based Novolak Copolymers[a]

Copolymer	First cresolic monomer **I**	BHMC $R = C_{15}H_{25-31}$ $R_1 = CH_3$	Second cresolic monomer **II**	Third cresolic monomer **III**	Nature	Base solubility
1	Cardanol (C)	OH, HOH_2C, CH_2OH, R	*m*-Cresol (M)	*m*-Cresol	"High ortho," alternating (M-C-M-C. . . M)	Base soluble
2	Phosphorylated cardanol (R)	OPO_4, HOH_2C, CH_2OH, R	*m*-Cresol	*m*-Cresol	"High ortho," alternating (M-R-M-R. . . M)	Base soluble
3	Cardanol	OH, HOH_2C, CH_2OH, R	*m*-Cresol	*p*-Cresol (P)	"High ortho," semi-alternating (P-C-M-C. . . P)	Base insoluble
4	Cardanol	OH, HOH_2C, CH_2OH, R	*p*-Cresol	*m*-Cresol	"High ortho," semi-alternating (P-C-M-C. . . P)	Base insoluble
5	Cardanol	OH, HOH_2C, CH_2OH, R	*p*-Cresol	*p*-Cresol	"High ortho," alternating (P-C-P-C. . . P)	Base insoluble
6	Cardanol	OH, HOH_2C, CH_2OH, R	CNSL (C)	*m*-Cresol	"High ortho," semi-alternating (C-C-M-C. . . C)	Base insoluble
7	CNSL	OH, HOH_2C, CH_2OH, R	*m*-Cresol	*m*-Cresol	"High ortho," alternating (M-C-M-C. . . M)	Base insoluble
8	CNSL	OH, HOH_2C, CH_2OH, R	*m*-Cresol	*p*-Cresol	"High ortho," semi-alternating (P-C-M-C. . . P)	Base insoluble
9	*m*-Cresol	OH, HOH_2C, CH_2OH, R_1	Cardanol	*m*-Cresol	"High ortho," semi-alternating (C-M-M-C. . . C)	Base insoluble
10	*m*-Cresol	OH, HOH_2C, CH_2OH, R_1	*m*-Cresol	CNSL	"High ortho," semi-alternating (C-M-M-C. . . C)	Base insoluble
11	*m*-Cresol	OH, HOH_2C, CH_2OH, R_1	CNSL	Cardanol	"High ortho," alternating (C-M-C-M. . . C)	Base insoluble
12	*p*-Cresol	OH, HOH_2C, CH_2OH, R_1	Cardanol	*m*-Cresol	"High ortho," semi-alternating (C-P-M-P. . . C)	Base insoluble
13	*p*-Cresol	OH, HOH_2C, CH_2OH, R_1	Cardanol	Cardanol	"High ortho," alternating (C-P-C-P. . . C)	Base insoluble

TABLE I *Continued*

Copolymer	First cresolic monomer **I**	BHMC $R = C_{15}H_{25-31}$ $R_1 = CH_3$	Second cresolic monomer **II**	Third cresolic monomer **III**	Nature	Base solubility
14	Cardanol	OH, HOH_2C, CH_2OH, R	CNSL	Cardanol	"High ortho" (C-C-C-C. . . C)	Base insoluble
15	Cardanol	OH, HOH_2C, CH_2OH, R	Cardanol	Cardanol	"High ortho" (C-C-C-C. . . C)	Base insoluble

[a] BHMC of cardanol and phosphorylated cardanol give only base soluble resin. The bulky side chain (cardanol/CNSL) or the less reactive *p*-cresol incorporation generally terminates the chain. *p*-Cresol or cardanol/CNSL thus occupies the end group of the polymer chain.

cresolic monomer (designated as "**I**" in Table I) was mixed with formaldehyde (37%) and sodium hydroxide in a 1 : 2.2 : 1 ratio. The mixture was stirred mechanically at room temperature (25°C) for 48 h. The ratio of formaldehyde : cresolic monomer was carefully optimized and the reaction temperature was kept below 25°C to avoid oligomer formation in the presence of base. The reaction time was found to be sufficient to consume almost all (95%) the formalin solution.[8] The second cresolic precursor (designated as "**II**" in Table I) was then added to the first cresolic monomer in a 1 : 1 ratio. The mixture was diluted with hydrochloric acid (1 : 1) in an ice bath and the pH was lowered to 4–4.5. The bishydroxymethylated cresol (BHMC) was separated, and the organic layer was washed thoroughly twice with water containing 1% oxalic acid.

In the second step, the third cresolic monomer (designated as "**III**" in Table I) was mixed with liquid BHMC in a 1 : 1 ratio with the first phenolic monomer.[11] A 1% molar equivalent of oxalic acid (with respect to the total cresolic components) was added. Xylene was selected as the reaction medium to produce an azeotropic mixture with water produced during polymerization, and the water was tapped out by using the Dean–Stark trap. The mixture was refluxed at 140–150°C for 45 min and then steam-distilled at 180°C for another hour.

From a series of these prepared polymers (Table I), the *m*-cresol–cardanol and *m*-cresol phosphorylated cardanol–based alternating novolac copolymers (copolymers 1 and 2) alone were found to be soluble in base. These two resins were dissolved in 30% aqueous NaOH and precipitated by adding dilute HCl (1 : 1). The resulting resins were purified by dissolving them in ethyl acetate and reprecipitation was done using *n*-hexane. Molecular weights of the resins were determined by gel permeation chromatography (GPC) using a polystyrene standard column with paraffin as

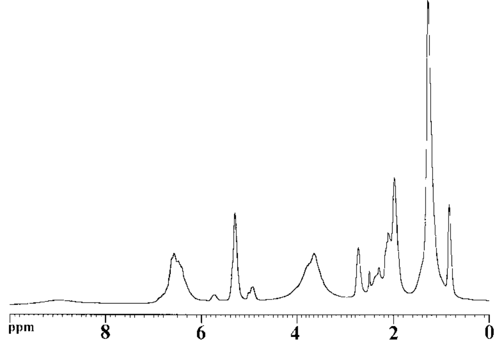

Figure 1 A 300-MHz ^{1}H-NMR spectrum of cardanol and *m*-cresol–based "high ortho" novolac resin.

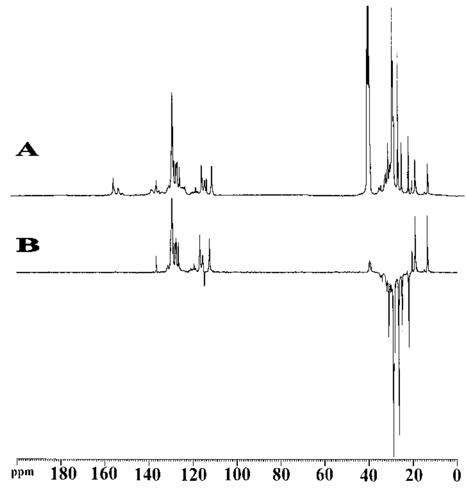

Figure 2 (A) 75.4-MHz ^{13}C-NMR spectrum and (B) DEPT-135 spectrum of the "high ortho" novolac copolymer: the signals attributed to $-CH_3$ and $-CH$ are pointed upward, whereas the signals of $-CH_2$ are pointed downward in the DEPT-135 spectrum.

A B C D

Figure 3 Natural cardanol is a mixture of four compounds having different types of side chains: (A–C) the terminal group is the methyl group; (D) a double-bonded methylenic group is the end group.

the reference standard and tetrahydrofuran as the eluent. The number-average molecular weight (M_n) was found to be 6920 for copolymer 1 (Table I). The weight-average molecular weight (M_w) and polydispersity (P.D., [M_w/M_n]) values for this polymer were 7394 and 1.05, respectively. The M_n, M_w, and P.D. of novolac copolymer 2 were determined to be 2016, 13,556, and 6.7, respectively.

For photoresist preparation, copolymer 1 (Table I) was selected for its lower P.D. value. A photoresist solution was made by mixing the above-mentioned novolac resin and diazonaphthoquinone-5-sulfonic acid esterified with 2,3,4-trihydroxybenzophenone in a 4 : 1 ratio, using ethyl cellosolve acetate as the solvent. The photoresist solution was filtered without application of pressure through a 0.45-μm Teflon filter. The resist films were coated on a silicon wafer by spin coating at 2000 rpm for 20 s. Baking was then done at 60°C for 30 min. A 200-W "g-line" UV light was used for exposure of the film and the exposure time was set at 10 s. The developer used was prepared by dissolving 5.0 g of sodium hydroxide in 15 mL of water and 5 mL of absolute methanol.

NMR spectra were recorded at room temperature on a Bruker Spectrospin DPX-300 MHz spectrometer (Bruker Instruments, Billerica, MA). The sample solutions were prepared by dissolving 30 mg of sample in 0.5 mL DMSO-d_6 for the 1-D spectra and 100 mg of sample in 0.5 mL DMSO-d_6 for the 2-D NMR spectra. ^{1}H-NMR spectra were recorded at 300.13 MHz, whereas "proton decoupled" ^{13}C-NMR spectra were recorded at 75.4 MHz. The mixing time used in the total correlation spectrum (TOCSY) was 80 ms.

RESULTS AND DISCUSSION

From a series of polymers prepared in our laboratory (Table I), the representative *m*-cresol and cardanol–based copolymer was chosen for full characterization, and its lithographic performance in a photoresist after blending with DNQ ester was evaluated. The 1-D ^{1}H-NMR spectrum (Fig. 1) of *m*-cresol and cardanol–based copolymer is fairly broad, with unresolved chemical shift peaks, making it difficult to assign the individual signals of *m*-cresol or cardanol, incorporated in the polymer.

The proton decoupled ^{13}C-NMR spectrum of the same polymer was comparatively sharper, and the signals were well separated. The assignments of the peaks in the ^{13}C-NMR spectrum were carried out using distortionless enhancement by polarization transfer (DEPT) experiments and then correlated with signals of the ^{1}H-NMR spectrum using the heteronuclear single quantum correlation (HSQC) spectrum followed by double quantum filtered correlation spectroscopy (DQF-COSY) and total correlation spectroscopy (TOCSY) experiments.

Figure 2 shows a comparison of the ^{13}C-NMR and DEPT-135 spectra of this novolac polymer. The structures of *m*-cresol and cardanol are almost similar, the only difference being that the methyl group of *m*-cresol is replaced by the $C_{15}H_{25-31}$ group (depending on the number of double bonds) in cardanol (Fig. 3). Signals in the aromatic region arising out of *m*-cresol and cardanol components of the resin thus have almost similar ^{13}C chemical shift values, and it is very difficult to identify the individual peaks arising out of *m*-cresol and cardanol. In the ^{1}H-NMR spectrum (Fig. 1) it is even worse, given that only one broad signal with weak shoulders is observed in the aromatic region. We thus focused our attention on the aliphatic region of the spectrum. In Table II, the ^{13}C chemical

TABLE II
Assignments of Aliphatic Region of Novolac Copolymer Based on *m*-Cresol and Cardanol

^{13}C chemical shift (ppm)	DEPT-135 signal pointed	Type of carbon atoms	Assignment
42.7			Solvent DMSO-d_6
39.8–25.3	Downward	Methylene ($-CH_2$)	Benzylic methylene bridge
22.2	Downward	Methylene ($-CH_2$)	Aliphatic methylene groups (in cardanol side chain)
20.8 and 19.4	Upward	Methyl ($-CH_3$)	Benzylic methyl group (in *m*-cresol)
13.9	Upward	Methyl ($-CH_3$)	Aliphatic methyl group (in cardanol side chain)

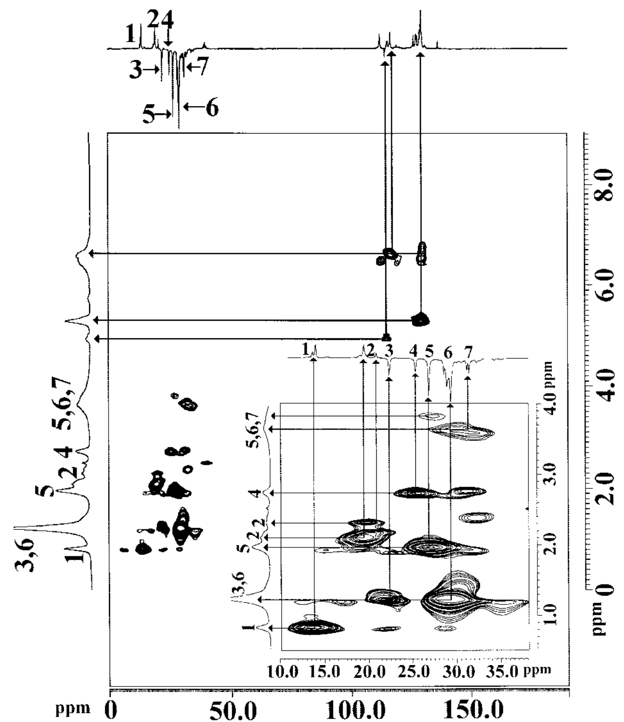

Figure 4 HSQC spectrum of m-cresol and cardanol-based novolac resin: the DEPT-135 spectrum is plotted along the *x*-axis, whereas the ^{1}H-NMR spectrum is plotted along the *y*-axis. In the inset, the expanded aliphatic region correlations are shown for clarity.

shift values are tabulated.

The ^{13}C chemical shifts assignments are confirmed by the 2-D HSQC experiments (Fig. 4). The ^{13}C chemical shift of benzylic methylene carbons (signals 5, 6, and 7 of the ^{13}C-NMR spectrum in Fig. 4) are correlated (one bond correlation) well with the ^{1}H chemical shift at $\delta = 3.6$ ppm, which are attributed to methylene protons. There are some additional correlations of signal 5 of ^{13}C-NMR with $\delta = 1.95$ ppm and signal 6 of ^{13}C-NMR with the ^{1}H chemical shift at $\delta = 1.2$ ppm, possibly attributed to the "through-space" couplings (long-range correlation) brought about by the sterical polymer macrostructure. Signal 4, at 25.3 ppm of the ^{13}C-NMR spectrum (Fig. 4), correlates well with the lower field ($\delta = 2.7$ ppm) signal of the ^{1}H-NMR spectrum. As expected, the aliphatic methylene signals of the side chain of cardanol at $\delta = 1.2$ ppm are connected with the ^{13}C chemical shift at 22.2 ppm. The signals of the methyl protons on the aromatic moiety of *m*-cresol observed at $\delta = 2.1$ and 2.3 ppm (attributed to the "hindered" and "unhindered" methylene protons) are correlated well with the ^{13}C chemical shifts at 20.8 and 19.4 ppm,[12] whereas the signals attributed to the terminal methyl group of the side chain of cardanol at $\delta = 0.8$ ppm correlate with the ^{13}C chemical shift at 13.9 ppm.

A comparison of the intensities of the two ^{1}H chemical shifts at $\delta = 2.1$ and 2.3 ppm in the case of *m*-cresol and with that of $\delta = 0.8$ ppm for cardanol could thus be a measure of the relative incorporation of these two moieties in the novolac polymer. However, upon critical examination of the aromatic region of the DEPT-135 spectrum (Fig. 2), a signal at 114.7 ppm could be seen to be pointing in the downward direction, indicating that this is a methylenic carbon atom. Furthermore, this signal correlates well with the signal attributed to the olefinic hydrogens at $\delta = 4.9$ ppm in the HSQC experiment (Fig. 4). The signal at $\delta = 4.9$ ppm is thus attributable to the double-bonded methylenic group ($=CH_2$). The double-bonded methylenic group can only be the end group of the aliphatic side chain of cardanol [Fig. 3(D)].[1]

The other signals for olefinic hydrogens seen at $\delta = 5.7$ and 5.3 ppm in the ^{1}H-NMR spectrum (Fig. 1) are attributed to the double-bonded methine group,

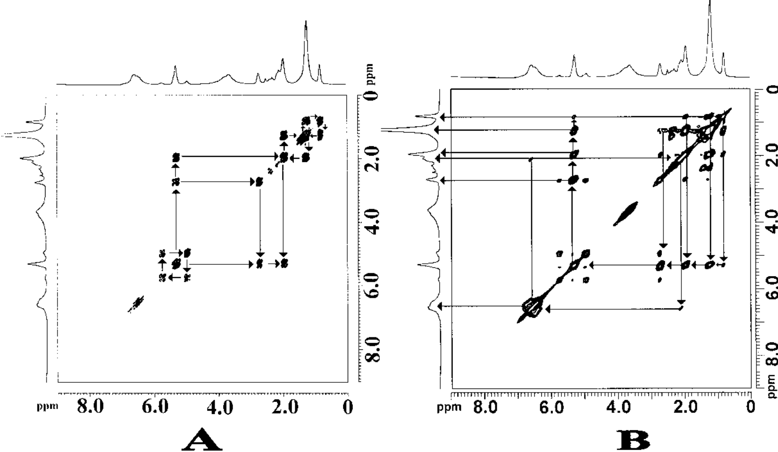

Figure 5 (A) DQF-COSY and (B) TOCSY spectra of the novolac resin based on cardanol and *m*-cresol: all correlations in the same spin system are seen in the TOCSY spectrum because the mixing time is very high (80 ms) in the TOCSY experiment compared to that in the DQF-COSY experiment.

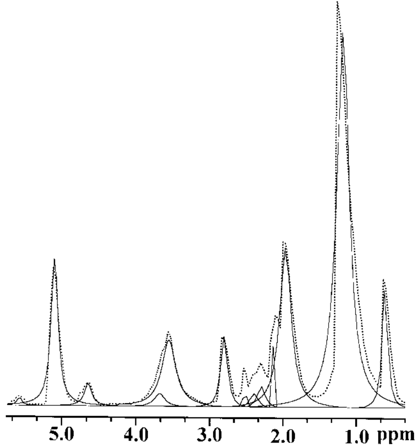

Figure 6 Deconvoluted ^{1}H-NMR spectrum. The dotted line corresponds to the original ^{1}H-NMR spectrum, whereas the solid traces are the Lorentzian curve-fitting lines.

A

OH OH CH$_2$ CH$_3$ $C_{13}H_{22-26}$—CH$_2$—CH$_3$ n

and

B

OH OH CH$_2$ CH$_3$ $C_{13}H_{22}$—CH=CH$_2$ n

Figure 7 *m*-Cresol and cardanol-based alternating novolac copolymer, where the two end groups are *m*-cresol units. (A) The novolac polymer where cardanol has a terminal methyl group. (B) The cardanol polymer possessing a methylenic end group.

given that they correlate with the signal at 129.6 ppm in the HSQC spectrum (Fig. 4), which is pointed upward, indicating that it is a secondary (–CH) carbon atom. These two signals thus cannot arise from the end group of the side chain in cardanol [Fig. 3(B–D)]. The comparative incorporation of the precursor compounds in the resin should scale according to the ratio of the area under the curve of the peaks at $\delta = 2.1$ and 2.3 ppm (methyl groups of *m*-cresol) to that of the signals at $\delta = 0.8$ and 4.9 ppm (terminal "–CH_3" and "–CH_2" of cardanol).

A further confirmation of the above assignments is crucial because the relative incorporation of the different precursors becomes critical for lithographic performance of the novolac resin. Calculations based only on the intensities of signals of the ^{13}C-NMR spectrum are not usually reliable because of (i) the low natural abundance of ^{13}C nucleus and (ii) the nuclear Overhauser effect (NOE) and the consequent unequal polarization transfer from the attached hydrogen to carbon atom.[9,13] Calculations based on ^{1}H-NMR intensities would be much more dependable for quantitative estimation of the incorporation of the different monomers in the resin. The exact assignments of the ^{1}H-NMR chemical shifts are thus very important, particularly in the case of polymers, because the range of molecular weights (higher P.D. values) makes the signal very broad and overlapping.[14] For further confirmation of our ^{1}H chemical shift assignment, we recorded the DQF-COSY and a TOCSY spectra (Fig. 5) of this new polymer. TOCSY has the well-known additional important practical advantage that all the components of the cross peaks are "in phase" and there is thus no "peak-cancellation."[15]

The signal at $\delta = 5.7$ ppm is correlated with the signal at $\delta = 4.9$ ppm in the DQF-COSY spectrum [Fig. 5(A)], indicating that the former is attributed to the hydrogens of the methine group, which in turn is attached to the terminal methylene group [Fig. 3(D)]. The signal at $\delta = 2.7$ ppm is correlated with the signal at $\delta = 5.3$ ppm, whereas the peaks at $\delta = 1.95$ ppm are also correlated with the peaks at $\delta = 5.3$ ppm in the DQF-COSY spectrum [Fig. 5(A)], confirming that these signals at $\delta = 5.7$ and 5.3 ppm are attributed to the centrally placed double bonds in the cardanol side chain [Fig. 3(B) and (A), respectively].

That the signals at $\delta = 2.1$ ppm arise from the methyl group of *m*-cresol incorporated in the polymer is borne out by the TOCSY experiment. The signals at $\delta = 2.1$ ppm are coupled (long range) with the aromatic hydrogens, which was not seen in the low "mixing time" DQF-COSY spectrum [Fig. 5(A)]. The expected correlations are visible in TOCSY spectrum [Fig. 5(B)] between all the hydrogens of the side chain of cardanol, given that the longer mixing time of 80 ms allows magnetization transfer to remote protons.

TABLE III
Details of Lithographic Experiment Using Positive Photoresist Prepared from DNQ Ester and Novolac Resin, Based on *m*-Cresol and Cardanol

Process steps	Typical conditions
Spin coating	2000 rpm; 20 s
Prebake	60°C; 30 min
Exposure	200-W UV light for 10 s
Developer	5 g of NaOH dissolved in 20 mL of water and 5 mL of absolute MeOH
Thickness	1.4 μm

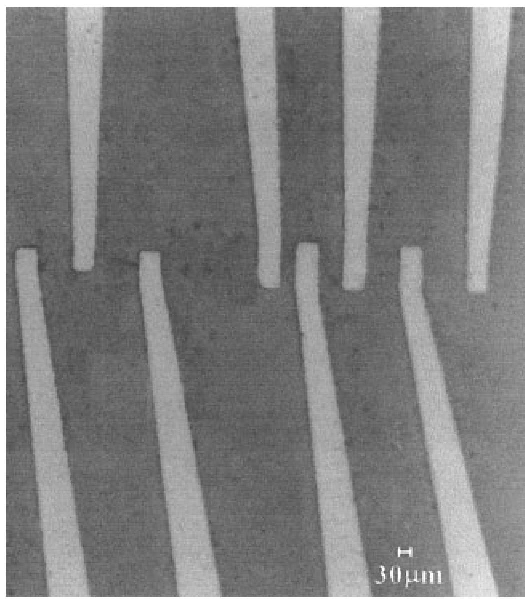

Figure 8 A typical pattern obtained on a silicon wafer using the new positive photoresist after exposure and development (magnification ×5).

It remains for us to quantitate these peak assignments by exact curve-fitting techniques. Based on 1-D and 2-D NMR techniques, it is proved that the ratio of area of the signals at $\delta = 2.1$ and 2.3 ppm to that of the signals at $\delta = 0.8$ and 4.9 ppm is a measure of the relative *m*-cresol and cardanol incorporation in the novolac copolymer. Deconvolution was done using Origin 6.1 software and a Lorentzian curve-fitting technique was used to measure the areas under the curves (Fig. 6). The percentage of *m*-cresol incorporation was calculated to be 50.34% [$341.3 \times 100/(341.3 + 336.7)$]. We therefore concluded that this copolymer is an alternating "high ortho" novolac resin, whose probable structure is given in Figure 7.

The lithographic performance of the new positive photoresist was then evaluated. The detailed results of the lithographic experiments are tabulated in Table III. A typical pattern obtained on a silicon wafer using the new photoresist, after exposure and development, is shown in Figure 8.

CONCLUSIONS

Natural product (CNSL, cardanol)–based tailor-made "high ortho" novolac copolymers were prepared, and the microstructure of the representative cardanol/*m*-cresol copolymer was fully elucidated using 1-D and 2-D NMR spectroscopy. The incorporation of monomers in the resin was also quantitatively assessed by use of a new methodology based on the 1-D and 2-D NMR techniques. Such quantitative structural data are of help in critically evaluating the lithographic performance of photoresists. Our methodology opens up a strategy for improved use of CNSL/cardanol products in the burgeoning microelectronics industry.

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