Water-Soluble Chromophore Containing Copolymers for Bottom Antireflection Coating Applications in Lithography

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ABSTRACT: Regulatory concerns in the semiconductor industry from both VOC emissions and solvent handling have prompted the desire to introduce water-based formulations in spin-coating fabrication processes. As resolution demands for i-line lithography are driven to finer feature size and architecture, the need for antireflection coatings as a means of eliminating feature distortions from back reflected light is increasing. Common image irregularities, such as reflective notching and standing wave effects, can be effectively eliminated through application of an antireflection coating of optimal thickness between the resist layer and substrate. This work describes the design and development of novel side-chain methacrylate copolymers for use in water-based antireflection coating formulations. A pendant chromophore is incorporated into the polymer structure to allow optimization of the critical coating optical properties, refractive index, and absorption coefficient. The polymer solubility parameter and crosslinking density can be tailored by incorporation of appropriate functionality to allow compatibility with the device fabrication process. Terpolymers were designed, which were water-soluble, had a thermally activated crosslinking mechanism, and contained a keto-ester azobenzene chromophore that was highly absorbing at i-line wavelength. Optical properties of polymer films were collected by spectroscopic elipsometry and utilized in the design process to identify the optimum chromophore structure. Lithographic images, fabricated utilizing these coatings, were of excellent quality, allowing critical dimension resolutions of less than 0.3 μm. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1304–1316, 1999

ANTIREFLECTION COATINGS

Advances in DRAM chip manufacturing place continuing pressure on improving resist image resolution tolerances. This requires exposure sources of smaller wavelength, and both improved fabrication designs and materials. Resist image defects, including both reflective notching and thin film interference effects, are commonly observed as finer resolution features are obtained, caused by back reflected light from substrate topography. One way to eliminate these image defects is to introduce a bottom antireflection coating (BARC)[1–4] between the substrate and resist, as shown in Figure 1. This coating can be applied by a spin-casting procedure, similar to that used to apply the resist. In this process, however, there are significant VOC emissions, and aggressive solvents are used, leading to environmental and handling concerns. One solution to this is to apply the BARC coating from a water formulation.

A major design challenge has been to ensure that there was no dissolution of the postbaked BARC film on exposure to the solvents used in the
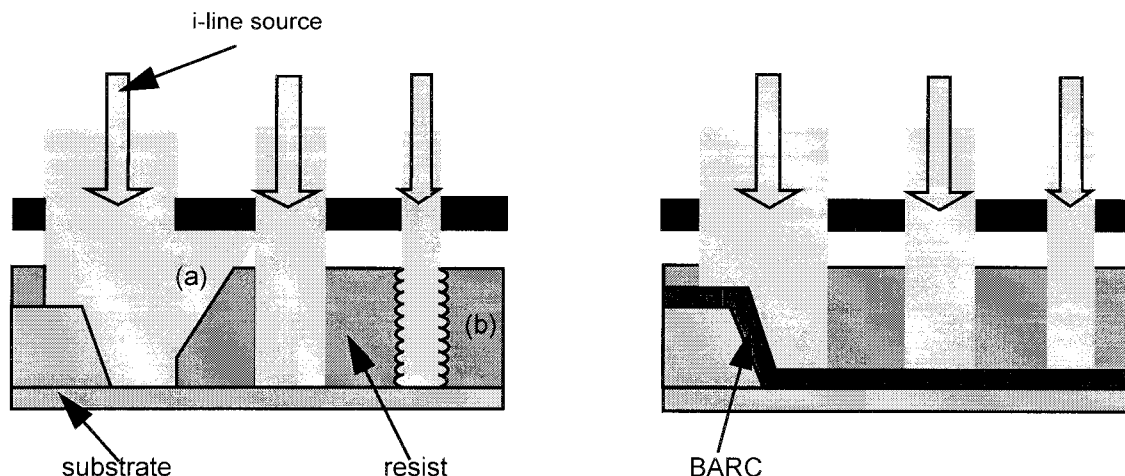
Figure 1 Utility of BARCs in elimination of resist image defects caused by reflection. (a) reflective notching, (b) standing wave effects.

lithography fabrication process. For a water-cast film, exposure to the resist solvent generally presents little problem due to the large difference in solubility parameters between film and solvent. However, exposure to the aqueous base developer can result in swelling and stripping, unless either the film, during baking, has undergone extensive crosslinking, or there has been a chemical reaction, resulting in a polymer solubility parameter change. Conversely, a resist solvent-cast film will have an affinity to the resist formulation dispensed onto the BARC film. This can lead to partitioning or intermixing of the BARC and resist layers, causing an image defect in processing called "foot formation" due to incomplete development. Either extensive crosslinking or a polarity switch during baking is needed to minimize these problems.

POLYMER DESIGN

Polymers designed for antireflection coating applications require incorporation of discrete functionality in the polymer structure in order to accommodate a diverse range of performance properties. Side chain copolymers were designed, in which one pendant group would contain the appropriate chromophore, another would contain a crosslinking functionality, and functional groups targeted at, enhancing solubility, providing reactive sites for crosslinking, and physical properties, would be incorporated throughout the polymer. Chromophores utilized in this application

must be highly absorbing at the i-line exposure wavelength and give rise to a high refractive index. This can be accomplished through incorporation of a high density of chromophore, which has an electronic absorption spectrum maximum at slightly shorter wavelength than 365 nm, thus enhancing refractive index through anomalous dispersion. In order to firstly design the chromophore, an understanding of the molecular origins of electronic absorption was necessary. The primary electronic transition is of the $\pi-\pi^*$ class. The intensity and wavelength of this transition has been shown to be dependent on, principally, a stabilization of the excited state through both π electron delocalization and intramolecular charge transfer. Both the presence of conjugated double bonds or aromaticity, and an asymmetric electron distribution, (facilitated through functional groups, which act as electron donors or acceptors) both enhances the absorption coefficient and shifts the absorption to longer wavelength. Through the use of both donor/acceptor functional groups and π orbital conjugation, a molecular engineering approach was taken to design a chromophore with a large absorption coefficient at i-line wavelength. Chromophores were designed, which had π electron conjugation at an appropriate length, and electron donator/acceptor groups of appropriate strength for absorption at i-line. Although the polymer composition includes the methylol acrylamide monomer, which can undergo a self-condensation crosslinking reaction at elevated temperature, enhancement of the film crosslinking density is often necessary. This can
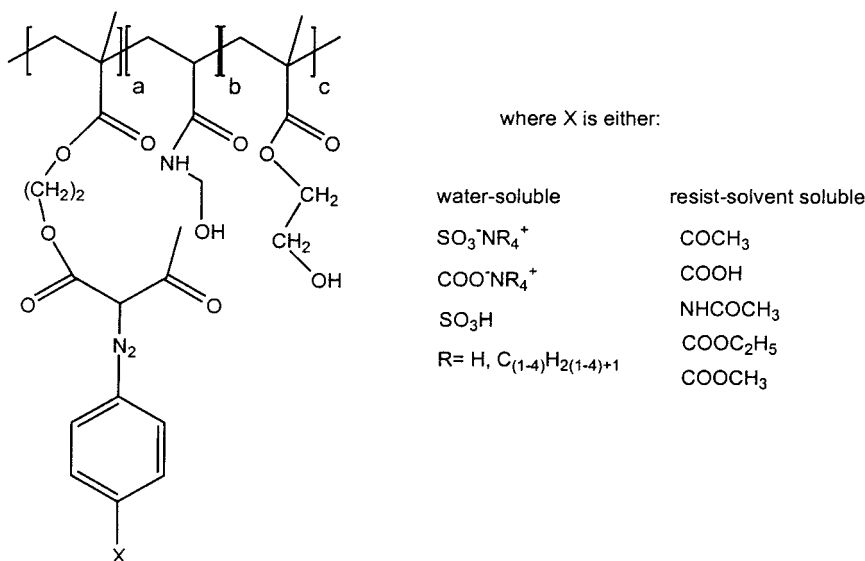
where X is either:

	water-soluble	resist-solvent soluble
	$SO_3^-NR_4^+$	$COCH_3$
	$COO^-NR_4^+$	$COOH$
	SO_3H	$NHCOCH_3$
	$R= H, C_{(1-4)}H_{2(1-4)+1}$	$COOC_2H_5$
		$COOCH_3$

Figure 2 Structure of β-keto ester methacrylate copolymers. Comonomers shown are *N*-methylol acrylamide and 2-hydroxyethyl methacrylate, but can also include *N*-vinyl pyrrolidone, methacrylic acid, diethyleneglycol monovinylether, and itaconic anhydride.

be achieved through the use of external crosslinkers, such as melamine–formaldehyde resins added to the formulation. These resins can undergo a condensation reaction with hydroxyl functional groups present in either the polymer or resin itself. Other external crosslinking agents, such as bis-epoxies and β-hydroxyalkylamides, can also be used in combination with hydroxyl or carboxyl functionality present in the polymer. The polymer must also have sufficient solubility in the appropriate solvent for the formulation. This is facilitated through judicious choice of functional groups present in the polymer. Hydroxyl, acrylamide, carboxylate, and sulfonate groups were utilized to enhance the polymer solubility in water. As the exposed lithographic pattern is further subjected to a plasma etch, it is necessary to maximize the polymer film etch rate.[5] This can be theoretically determined by the Ohnishi Number,[6] which relates the etch rate to the number density of oxygen atoms present in the polymer. In order to ensure a high etch rate, therefore, oxygen containing functionality, such as esters and alcohols, should be present in the molecular structure. Finally, device contamination issues prohibit the presence of metallic ion impurities in the film. The synthetic route, therefore, must be metal-ion-free, an important consideration for the preparation of diazonium salts.

β-KETOESTER METHACRYLATE COPOLYMERS

β-keto ester methacrylate copolymer systems (shown in Fig. 2) were designed and synthesized. This polymer class offers advantages over current commercial systems in that the synthetic route circumvents a graft reaction to an existing polymer, through direct copolymerization of the chromophore monomer, thereby enabling greater reproducibility and a higher purity product. Additionally, the high chromophore extinction coefficient allows sufficient optical absorption to eliminate the requirement of additional free dye in the coating, which is often the source of contamination through sublimation. The chromophore exhibits π electron delocalization and asymmetry as well as planarization through hydrogen bonding, which generates a very high extinction coefficient. The optical properties of the coating are determined by the design of the diazo chromophore monomer. The choice of electron-withdrawing functional group on the chromophore is designed not only to optimize dye strength and absorption maximum, but also to influence the solubility of the polymer. If this group is either a carboxylic, or sulfonic acid or salt, then the polymer can be soluble in water; whereas, when the functional group is a carboxylic ester, amide, or ketone, then the polymer can
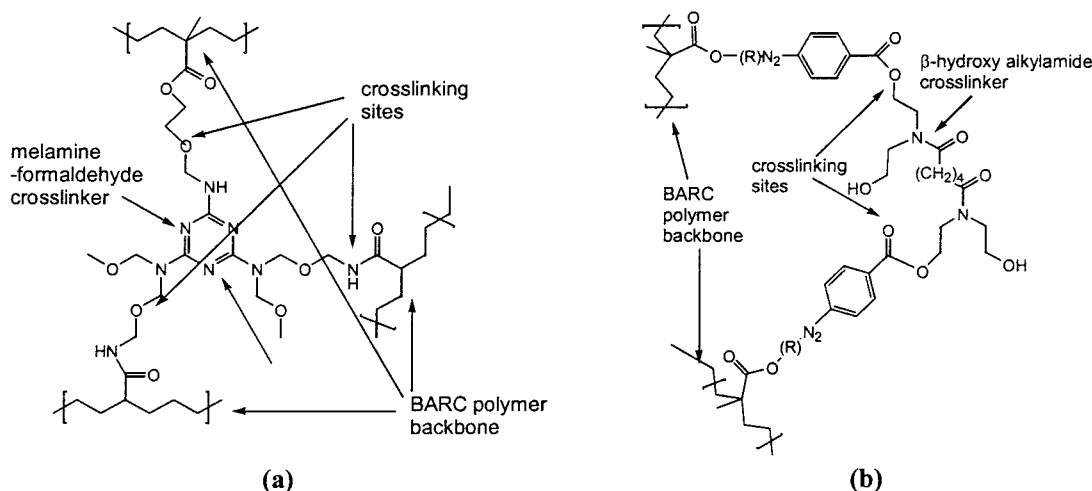
Figure 3 External crosslinking agents. (a) A melamine-formaldehyde resin structure crosslinking with the methylol and hydroxy ethyl functionality of a BARC copolymer. (b) A β-hydroxyalkylamide crosslinking with the chromophore carboxylate functionality of a BARC copolymer.

have solubility in common resist solvents, such as ethyl lactate, PGME, and PGMEA.

Comonomers are chosen to both further influence the polymer solubility and provide reactive sites for either internal or external crosslinking. They must also be compatible with a solution free radical copolymerization. Comonomers for polymerization have included hydroxyethyl methacrylate, diethylene glycol monovinyl ether, maleic anhydride (followed by hydrolysis), *N*-vinyl pyrrolidone, and *N*-methylolacrylamide. Both the hydroxyl and carboxylate functionality present in the comonomer structure are available for crosslinking reactions with either a melamine–formaldehyde or an epoxy crosslinking resin, whereas the carboxylate functionality is necessary for reaction with β-hydroxyalkylamide crosslinkers. Internal crosslinking can also be achieved through a self-condensation reaction of the methylolacrylamide comonomer.

In order to eliminate intermixing and swelling, functional groups, which can undergo either self-crosslinking or can react with an external crosslinker, were also incorporated in the copolymer structure. Due to shelf life stability considerations, the choice of chemistry is restricted to functionality, which is inert in aqueous solution but can be activated during the thermal baking process. Self-crosslinking can be achieved through the condensation reaction of methylol acrylamides, which is effective at temperatures over 150°C. The efficiency of this reaction is lowered,

however, through the steric effects of the pendant chromophore comonomer, and it is often necessary to supplement the self crosslinking group with external crosslinking agents. One class of external crosslinker examined was the melamine–formaldehyde resins. This class of crosslinker can react through a condensation reaction with hydroxyl, carboxylate, or anhydride functionality present in the polymer backbone and can also self-condense. Both types of reactions give rise to crosslinked thermoset material. At lower pH, this reaction can occur at lower temperatures, which causes shelf life concerns. Less reactive crosslinking agents, β-hydroxyalkylamides, were also identified, in which the active hydroxyl group is available for esterification with a carboxylate or anhydride functionality present in the polymer. This reaction is only efficient for this polymer system at temperatures of over 170°C and is inert at room temperature. The molecular structure of crosslinked BARCs from both crosslinking agents is shown in Figure 3(a) and (b).

An optimum polymer was chosen, and herein referred to as Aquabar™, as a result of initial coating and lithographical evaluation, for both swing curve reduction experiments (Fig. 8), and the detailed lithographical analysis (Table IV; and Figs. 9 and 10). This was a terpolymer of the β-keto ester methacrylate chromophore, *N*-methylol acrylamide, and 2-hydroxyethyl methacrylate. The molecular structure and composition is
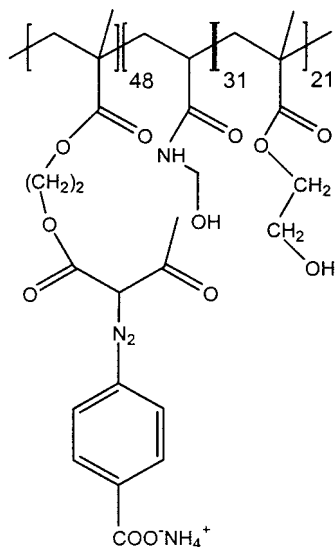
Figure 4 Molecular structure of Aquabar™.

shown in Figure 4, where the electron withdrawing group (X) was ammonium carboxylate (COO^-NH4^+), and the monomer ratio, as analyzed by ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectroscopy, was essentially determined by the monomer feed ratio $a : b : c = 48 : 31 : 21$. The synthesis of this particular composition is given as an example in the synthetic experimental section.

OPTICAL CHARACTERIZATION

β keto ester chromophore containing copolymers have extremely high absorption coefficients at i-
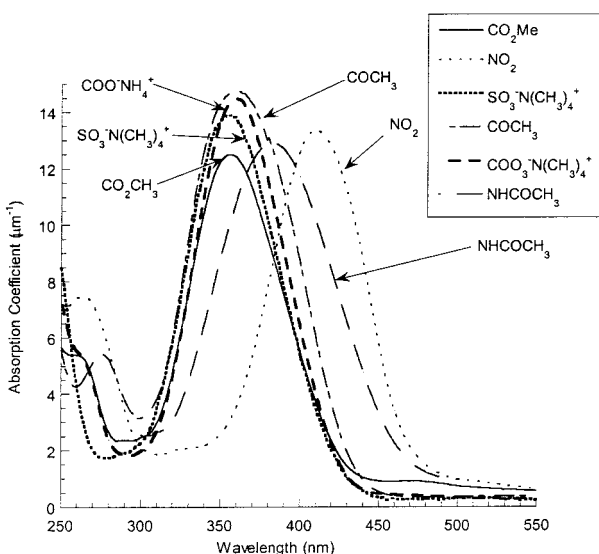

Figure 5 The electronic absorption spectra of polymer films on quartz.
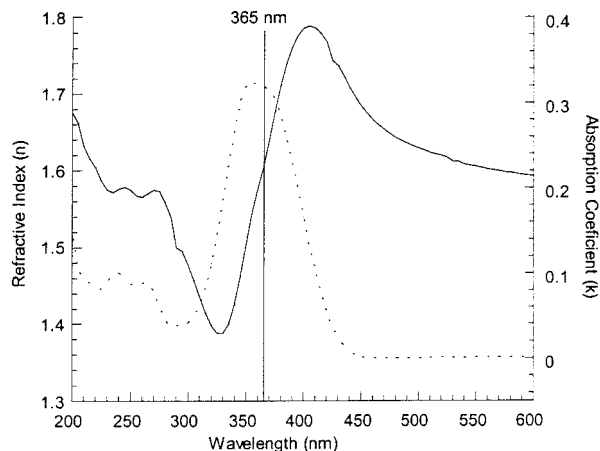

Figure 6 Dispersion curve for the optical constants n and k of Aquabar™.

line wavelength, with absorption maximums ranging from 355 to 410 nm, depending on the electron-withdrawing group. While the copolymer composition can be used to tailor absorption coefficients, the strength of the electron withdrawing group (X) on the chromophore has a large influence on the absorption maximum. For example, incorporation of the nitro group on the chromophore, the most effective common electron-withdrawing group, results in an absorption maximum of about 410 nm, while the less effective carboxylic esters give rise to a chromophore absorption maximum of about 355 nm. Neutralization of the carboxylate and sulfonate acids to form the ammonium salts had little influence on either the absorption coefficient or absorption maximum. Absorption coefficient data was collected from thin film samples of β-keto ester copolymers with a range of electron-withdrawing groups, on quartz slides using a standard ultraviolet–visible (UV-vis) spectrophotometer and are shown in Figure 5. Sample thicknesses were made as large as practically possible in order to minimize any interference effects. This was limited, however, by the power output of the spectrophotometer. As a result of this analysis, the ammonium carboxylate electron-withdrawing group was identified as having optimum optical characteristics, as well as suitable solubility properties. Subsequent lithographical studies utilized a polymer composition containing this chromophore exclusively. Both refractive index anomalous dispersion and absorption coefficient (k) can be more accurately determined by spectral elipsometry[7]; and data collected from the Aquabar™ polymer (Fig. 4) is

Table I   Optical Properties of Polymer Films

Copolymer Composition βKE–NMA–HEM[a]	Electron Withdrawing Group	Absorption Maximum (nm)	Absorption Coefficient (μm^{-1}) (365 nm)
40/20/40	NO$_2$	417	9.7
40/10/50	COOH	357	13.5
50/10/40	COOC$_2$H$_5$	355	14.4
40/20/40	NHCOCH$_3$	383	6.8
40/20/40	COCH$_3$	362	14.3
40/20/40	SO$_3^-$NH$_4^+$	357	8.8
40/20/40	COO$^-$NH$_4^+$	359	7.8

[a] βKE is the β-keto ester methacrylate monomer; NMA is *N*-methylol acrylamide; HEM is hydroxyethyl methacrylate.

shown in Figure 6. At i-line wavelength (365 nm), the refractive index was measured to be 1.62 with a corresponding absorption coefficient (k) of 0.32. When the absorption maximum is slightly hypsochromically shifted from 365 nm, an enhancement in refractive index is observed. Both the strength and width of the absorption peak influence the extent of this refractive index dispersion behavior. It is necessary to control the refractive index of the coating[8] to determine the optimal film thickness for minimum reflectivity. Thermal stability of the chromophore through the baking cycles of the lithography process is also necessary. This was studied, and no changes in electronic spectra were observed. Representative data for polymer samples is collected in Table I.

COATING EVALUATION

To test swelling and/or intermixing of Aquabar™ after resist application, the polymer was coated and softbaked (SB) at elevated temperatures to ensure sufficient crosslinking. Both common resist casting solvents, for example, ethyl lactate and developer solution (2.38% tetramethyl ammonium hydroxide in water), were sprayed onto the Aquabar™-coated wafer for 30 s, which simulates typical solvent–BARC contact during resist fabrication process. The Aquabar™ film thickness changes before and after solvent exposure were measured by an automatic Nano AFT 215A to determine the extent of swelling/intermixing. The film thickness changes, collected in Table II, were observed to be negligible at temperatures of over 170°C, when either external crosslinker was used at 10 wt % of the active polymer.

LITHOGRAPHY

Swing Curve Analysis

Evaluation of the effectiveness of the BARC was carried out initially by swing curve simulation and analysis. The simulated swing curve amplitude of AZ® 7908 (an i-line photoresist product supplied by AZ Electronic Materials, Somerville, NJ) on Aquabar™ baked at 190°C, shown in Figure 7, was calculated from the optical constants n and k, obtained by spectral elipsometry (Fig. 6). From this, the optimum Aquabar™ thickness was identified as being in the range of 1900 Å. The reduction in swing amplitude was experimentally determined by plotting the dose-to-clear (DTC) of each wafer versus its corresponding resist thickness, as shown in Figure 8. AZ® 7908 i-line photoresist was coated on wafers precoated with 1900 Å Aquabar™ film to achieve resist thickness from 0.7 to 1.0 μm. The wafers were subsequently processed using the conditions described in the experimental section. The % swing reduction was calculated and reported in Table III.

Experimental

The Aquabar™ solution was coated to the targeted thickness, by solution spin-coating, followed by a postapply bake at 190°C for 60 s. (For minimum swing amplitude, the thickness was typically 1900 Å.) The AZ® 7908 i-line photoresist was applied onto the Aquabar™ coated wafers followed by a 90°C soft bake for 60 s to achieve a resist thickness of 0.974 μm. The coated wafers were imagewise exposed with a 0.54 NA NIKON NSR 1755i7B stepper, then a 110°C postexposure bake for 60 s, and single spray-puddle developed

Table II Aquabar™ Film Thickness Change on Solvent Exposure

Solvent	SB Temp (°C)	$FT_{initial}$ (Å)	FT_{final} (Å)	$_{Del}FT$ (°A)	Change (%)
Ethyl lactate	170	1943	1934	−9	−0.5
Developer	170	2130	2163	33	1.5
Ethyl lactate	190	1979	1964	−15	−0.7
Developer	190	2216	2226	10	0.4
Ethyl lactate	210	2001	1991	−10	−0.5
Developer	210	2044	2046	2	0.1

with AZ® 300 MIF developer for 60 s at 23°C. Resist images were analyzed by a Hitachi S-4000 SEM.

Etch Property

The Aquabar™ coating etch rate was designed to be as high as possible to avoid etch bias during image pattern transfer. This can be predicted by the polymer Ohnishi number,[6] calculated from molecular structure. Increasing the number density of oxygen atoms in the polymer, through inclusion of molecular functionality, such as esters, carboxylates, sulfonates, and even hydroxyl groups, contributes to enhance the Ohnishi number and increase the coating etch rate. Table IV gives the etch rate of Aquabar™ tested in a CHF_3/O_2 RIE in comparison to a typical DNQ-Novolak photoresist (AZ® 7900). The Aquabar™ sample measured exhibited high etch selectivity with a 1.7× high etch rate than typical DNQ-Novolak photoresist.

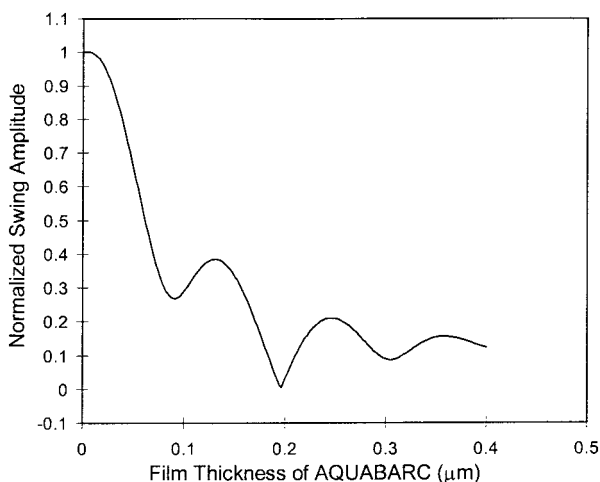**Figure 7** Normalized swing curve amplitude of AZ® Aquabar™ (bake temperature: 190°C).

Discussion

During formulation of the carboxylic-acid-containing copolymers, ammonium hydroxide solution was often added for two reasons. Firstly, addition was often necessary to render the polymer water-soluble through neutralization of the carboxylic acid to the more ionic carboxylate salt. In addition, a higher pH was necessary to ensure shelf life stability in water when the formulation also contained the external crosslinker Cymel. In acidic conditions, a condensation reaction of the Cymel resin methylol groups can occur, leading to crosslinking and, hence, gelling of the solution. Shelf life stability, which was defined as zero change in solution viscosity and absorption coefficient, was observed for over 3 months when the external crosslinker Primid (β-hydroxyalkylamides) was used. The esterification reaction necessary for crosslinking requires elevated temperature to occur. To obtain sufficiently crosslinked films after processing conditions, typically, the crosslinking agent was added at about a 10 wt % fraction of the polymer.

Compatibility of the BARC film with resist, resist solution, and developer solution are necessary to avoid fabrication failure and image pattern defects. As the polymer is water-soluble, the film was generally inert to the application of resist solution. After exposure, film stripping and image defects were observed with initial BARC polymer samples on development. Stripping was caused by either dissolution of the polymer film in developer solution (aqueous base) or swelling, leading to catastrophic adhesion failure, shattering, and cracking. To eliminate this stripping, two complimentary approaches were taken. Firstly, the polymer was designed to incorporate a large (50 mol %) quantity of functional groups that could either undergo self-crosslinking or would be amenable to crosslinking with an external crosslinking agent, which was also added to the
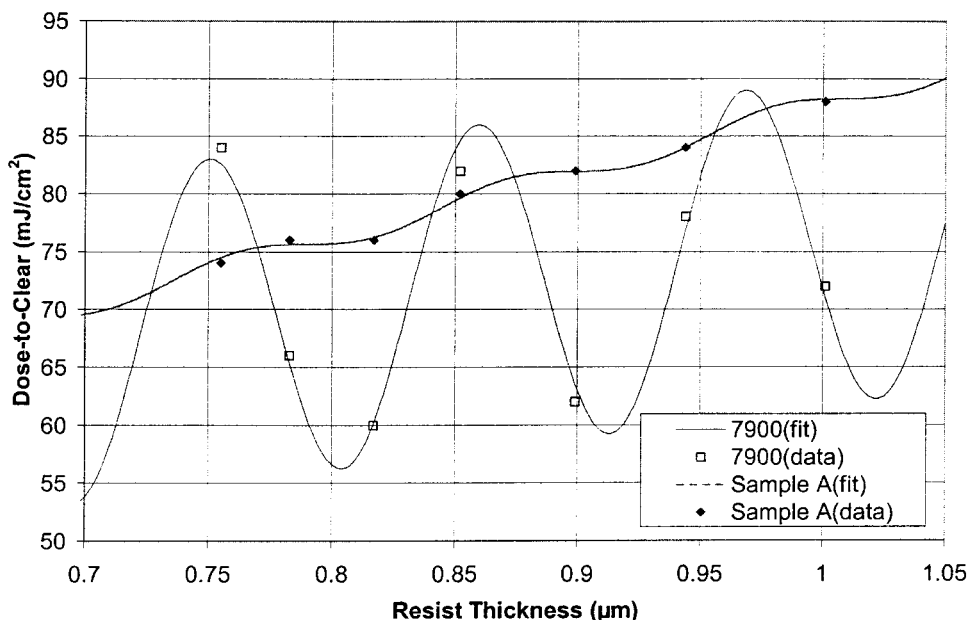
Figure 8   Swing curve of AZ® 7900 with and without Aquabar™.

formulation. In addition, the solubility parameter of the polymer was optimized by changing molecular composition, such that the polymer was only just insoluble in water. Thus, in formulation, a small amount (less than 10%) of a cosolvent was required for complete dissolution. An alternative to adjustment of the solubility parameter was to use a fugitive counterion in a sulfonate salt, such as ammonium. The ammonium ion, on baking, thermally liberates small amounts of ammonia which volatilize and diffuse from the film, leaving an insoluble polymer. This approach has the additional benefit of increasing the formulation pH, thus stabilizing the melamine formaldehyde external crosslinker present ensuring that crosslinking will only occur during the baking stage. Both approaches were successful in preventing film stripping on development.

Incomplete development defects were also initially observed and traced to the diffusion of alkyl amines into the resist film, inhibiting both photochemistry and dissolution. The amines were

formed by Hoffman degradation of alkyl ammonium counterions,[9] present in the polymer during the thermal baking step of the BARC. In this case, the amines were not sufficiently fugitive to completely volatilize and were still present to some extent on application of the resist solution. More thermally stable counterions, such as phosphonates which do not degrade, were also used and solved this problem. The most effective solution is to either use the ammonium ion, which volatilizes on baking, or, preferably, to use a nonionic chromophore. The resist-solvent-soluble BARC formulation generally formed good quality films and did not have the aforementioned stripping problems.

The performance of the BARC coatings was ultimately evaluated by the quality and feature size resolution of the lithographical images of re-

Table III   Swing Ratio Reduction of AZ® 7908 on Aquabar™, Calculated from Figure 7

Sample	FT (°A)	Amplitude	Reduction (%)
AZ® 7908	0	14.1	0.0
Aquabar™	1964	1.0	93.1

Table IV   Etch Properties of Aquabar™

Sample	Wafer No.	Etch Rate (Å/min)[a]	Etch Selectivity Versus AZ® 7900
Aquabar™	1	1101	1.796
Aquabar™	2	1075	1.754
AZ® 7900	1	613	1

[a] Etch conditions are as follows: Etcher, RIE-10N (SAMCO Inc.); Flow Rate CHF_3/O_2, 40/10 (sccm); RF Power, 60W; Etch time, 60 s.

(a)

(b)

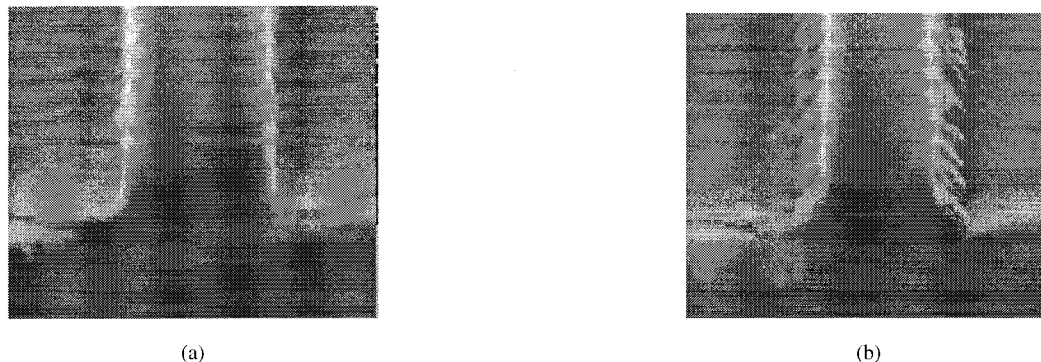**Figure 9** (a) and (b) SEM micrographs showing a 0.34-μm line width resist image profile on (a) sufficiently crosslinked and (b) insufficiently crosslinked Aquabar™ coating.

sist, coated on the BARC. Initial experiments examined the resist image profile and screened for evidence of an image irregularity known as foot formation. It was hypothesized that this occurred as a result of film layer intermixing during the application of the resist layer. In an effort to eliminate this defect, the crosslinking density of the baked BARC film was again increased through both the addition of an external crosslinker to the coating formulation, as well as incorporation of additional functional groups on the polymer which act as crosslinking sites. This is illustrated by Figure 9, which shows resist images on Aquabar™ formulated both with and without external crosslinker. In Figure 9(a), sufficient crosslinking occurs to prevent interlayer mixing, and the image sidewall makes a clean 90° angle with the BARC. However, foot formation can be observed when interlayer mixing occurred, due to the absence of external crosslinker and, hence, insufficient crosslinking, as shown in Figure 9(b). Figure 10 shows SEM resist image profiles of AZ® 7908 on Aquabar™ at decreasing line widths. Feature

sizes of 0.3 μm can be readily obtained with good process latitude.

As the film is spun from solution, film quality on drying, topographical coverage, and coverage uniformity are all important. By designing the BARC material to be a homogeneous amorphous polymer system, film quality was generally excellent; whereas coating behavior and topography coverage was optimized through synthesis of polymer with a number-average molecular weight of at least 50,000 (solution viscosity becomes a problem at a high molecular weight).

Synthesis

The synthetic route outlined in Scheme 1 was successful for the synthesis of most keto-ester methacrylate polymers. Synthesis of the monomer involves firstly formation of the diazonium salt of a substituted aniline derivative using the metal ion free reagent *t*-butyl nitrite. This salt then undergoes azo coupling at the active methylene site of the acetoacetate monomer. One com-
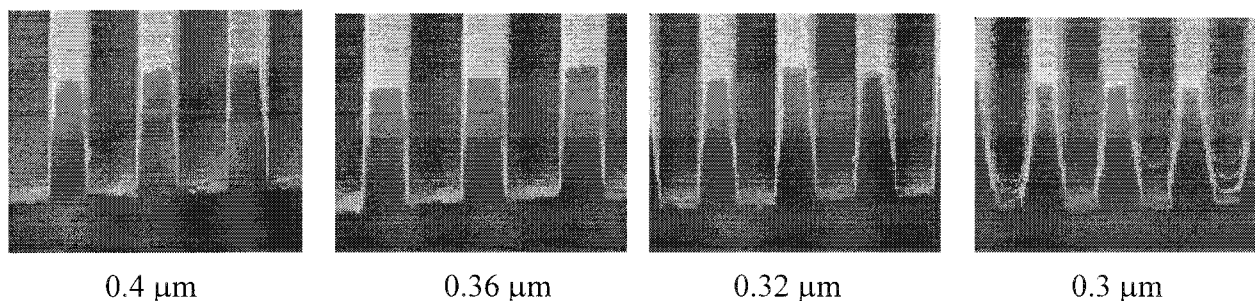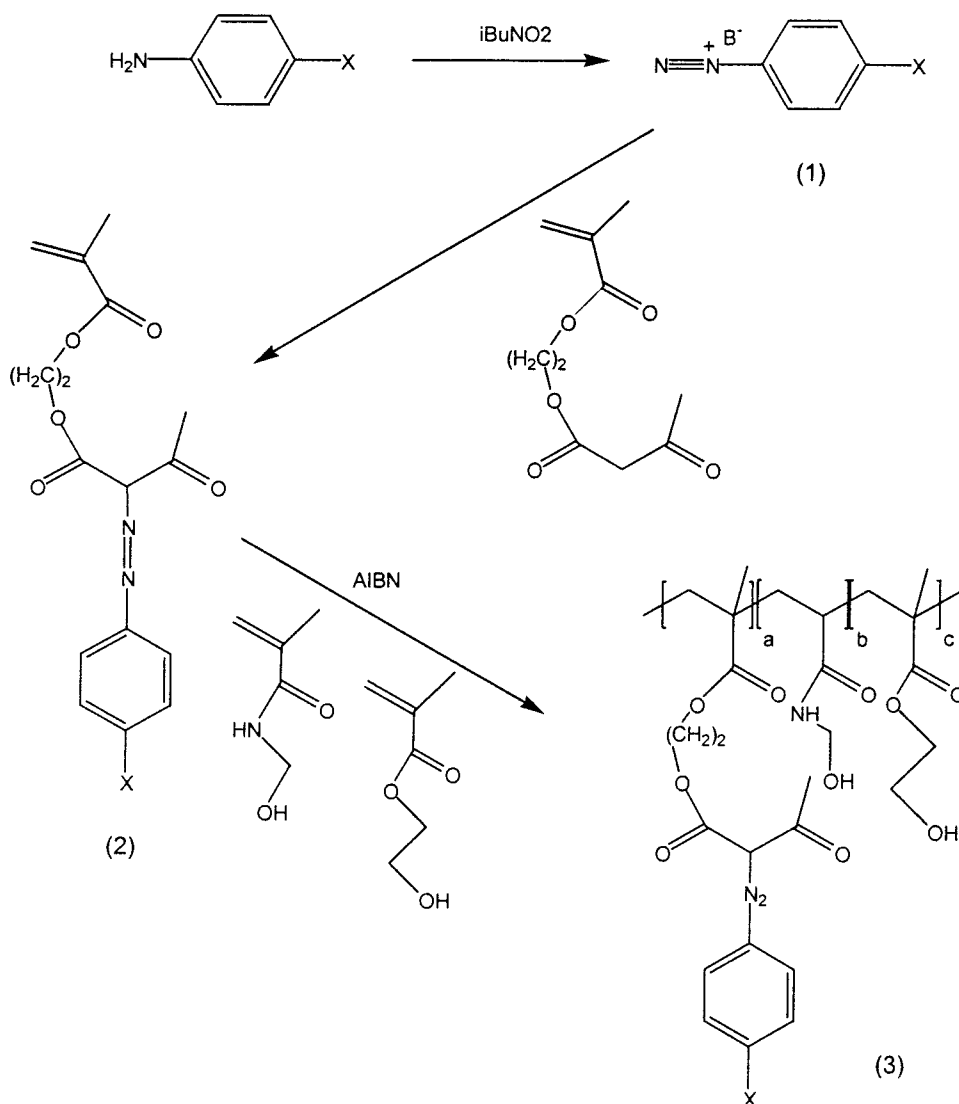

0.4 μm   0.36 μm   0.32 μm   0.3 μm

Figure 10. SEM micrograph showing resolution & DOF of AZ® 7908 on Aqueous B.A.R.C.

Scheme 1 Two-step synthesis of β-keto ester copolymers via polymerization of chromophore monomer.

mon factor in all synthesis was that no metallic species be present. Synthesis of the diazonium salt and the subsequent azo coupling step was found to be very pH-sensitive. In most cases, diazotization was carried out in acidic conditions, unless the amine was insoluble, such as sulfanilic acid. In this case, dissolution in base was preferred, and, on addition of the nitrite reagent, the reaction mixture was made acidic. Azo coupling was routinely carried out in basic conditions in high yield. On purification, the resulting chromophore containing monomer can be readily copolymerized by a solution free radical polymerization technique, with a range of comonomers discussed previously. The polymerization can be carried out in the formulation solvent, thus eliminating a processing step in production. The monomer must be scrupulously pure to allow a high-molecular-weight product, and γ-butyrolactone solvent was identified as a good solvent for both dissolution of monomer and polymer, as well as having good chain transfer properties for free radical polymerization. Polymer molecular weights from 20,000 to 400,000 can be obtained, depending on composition and conditions. Molecular weight polydispersity is usually slightly over 2, typical for methacrylate free radical polymerizations; although when the initiator is added in aliquots, the molecular weight profile can often be asymmetrical and even multimodal, leading to
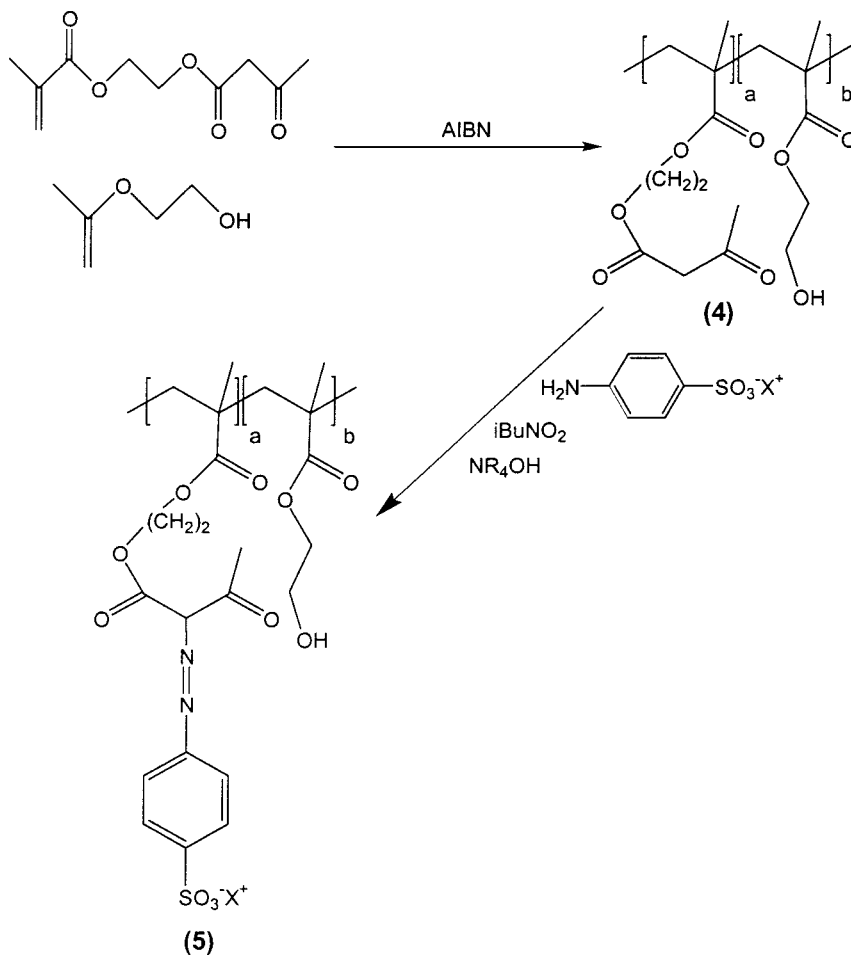
Scheme 2 One-pot synthesis of β-keto ester copolymers via polymer graft reaction.

higher polydispersity. Analysis of the ^{13}C-NMR spin-coupling constants indicated that the monomer incorporation within the polymer chain was random.

An alternative scheme (Scheme 2) involves firstly solution free radical copolymerization of methacryloyloxyethyl acetoacetate monomer. The prepolymer formed subsequently undergoes azo coupling with the appropriate diazonium salt, in an analogous manner to that previously described for the monomer. Utilization of this graft technique allows formation of polymers in which the chromophore contains functional groups with high chain transfer constants which normally inhibit free radical polymerization. When the chromophore contained an ammonium sulfonate salt, this route was identified as being preferable. The prepolymer was not isolated, and the polymerization solution made basic to facilitate direct azo coupling with the diazonium salt of sulfanilic

acid. Polymers obtained through this route were in both higher yield and molecular weight than conventional polymerization of the chromophore monomer. Optimization of initiator, polymerization solvent, and conditions may, however, provide a route to conventional polymerization.

PREPARATION OF THE DIAZONIUM-SALT OF AMINOBENZOIC ACID (1)

4-aminobenzoic acid (13.75 g, 0.1 mol) was dissolved in a mixture of concentrated hydrochloric acid (22.3 mL, 0.25 mol) and methanol (150 mL). The flask was then immersed in a bath of crushed ice and cooled until the temperature of the solution was below 3°C. The solution became a white suspension. Diazotization was then facilitated by the slow addition of *tert*-butyl nitrite (11.3 g, 0.11 mol) at a temperature below 5°C. The diazonium

solution was then stirred in an ice water bath for about 1 h. The product formed as a yellow solution and was not isolated but was used directly in the following reaction.

PREPARATION OF THE METHACRYLATE MONOMER (2)

2-(methacryloyloxy)ethyl acetoacetate (22.08 g, 0.10 mol) and triethylamine (25.3 g, 0.25 mol) were dissolved in methanol (200 mL), and the solution was stirred and cooled below 5°C in an ice water bath. To this solution, the cold diazonium salt solution (1), formed as described previously, was then slowly added, while the temperature was maintained between 5 to 10°C. The reaction mixture was allowed to stir for 3 h while warming to room temperature, resulting in the formation of the product as a yellow suspension. This was then filtered, washed with methanol, and dried under vacuum to yield 32.7 g (90%) of yellow product.

NMR: ^{1}H-NMR (200 MHz, DMSO-d_6, δ ppm): 7.95 (m, 2H, aromatic); 7.50 (m, 2H, aromatic); 6.05 (s, 1H, =CH$_{cis}$H$_{trans}$); 5.65 (m, 1H, =CH$_{cis}$H$_{trans}$); 4.35–4.55 (m, 4H, —CO$_2$CH$_2$CH$_2$CO$_2$—); 3.30 [s, 1H, —COCH(N=)CO—]; 2.45 (s, 3H, CH$_3$C=); 1.85 (s, 3H, —COCH$_3$).

PREPARATION OF COPOLYMER (3)

The methacrylate monomer (2) (9.79 g, 0.03 mol) was dissolved in γ-butyrolactone solvent (40 mL) and DMF (45 mL). The solution was warmed to 65°C while stirred. On complete dissolution, the solution was degassed by vigorously bubbling argon, via an inlet needle in a sealed rubber septum, through the solution for about 2 h. N-(hydroxymethyl)acrylamide (3.6 mL, 0.018 mol) and 2-hydroxyethyl methacrylate (1.23 mL, 0.012 mol) were then injected into the solution through the septum, and the polymerization mixture was further degassed for 30 min. An aliquot from a solution of AIBN (0.10 g, 0.65 mmol, 1 mol % total monomer) in γ-butyrolactone (1 mL) was then injected, and the solution was degassed further for 30 min. In total, two aliquots were added at intervals of 5 h. Both inlet and outlet needles were then removed, and the sealed vessel allowed to stir at 65°C for 20 h. This solution was then precipitated into a five-fold excess of 2-propanol. The polymer forms as a yellow solid, which was

then collected by filtration and dried [yield, 12 g (85%); M_n (gel permeation chromatography), universal calibration method, 95,000; T_g, 126°C.

NMR: ^{1}H-NMR (200 MHz, DMSO-d_6, δ ppm): 7.70–8.00 (aromatic); 7.20–7.50 (aromatic); 5.20–5.40 (—NHCH$_2$OH); 4.00–4.30 (—CO$_2$CH$_2$CH$_2$CO$_2$, —); 3.80–3.90 (—OCH$_2$CH$_2$OH), —); 3.50–3.60 (—OCH$_2$CH$_2$OH); 3.30 [—COCH(N=)CO—); 2.30–2.50 (—CHCONH—, backbone); 1.50–2.00 (—CH$_2$—, backbone); 0.80–1.00 (—CH$_3$). ^{13}C-NMR (200 MHz, DMSO-d_6, δ ppm): 193 (=CCO—); 176 (=CCONH—); 174 (—OCOPh—); 165 (—CO—OCH$_2$—); 162 (—COCH$_3$); 146.5 (—CHN=N—); 132, 131, 125, 124, 116, 114 (aromatic); 63, 62 (—CO$_2$CH$_2$CH$_2$CO$_2$—); 66 (—OCH$_2$CH$_2$OH); 61 (—CH$_2$OH); 59 (—OCH$_2$CH$_2$OH); 51–54 (—CH$_2$—, backbone); 45 (=C=, backbone); 38 (—CHCONH—, backbone); 23 (—COCH$_3$); 18 (—CH$_3$).

PREPARATION OF PREPOLYMER (4)

2-(methacryloyloxy)ethyl acetoacetate (8.83 g, 0.04 mol) and 2-hydroxyethyl methacrylate (5.21 g, 0.04 mol) were dissolved in DMF solvent (140 mL). The solution was warmed to 65°C while stirred. The solution was then degassed by vigorously bubbling argon, via an inlet needle in a sealed rubber septum, through the solution for about 0.5 h. An aliquot from a solution of AIBN (0.335 g, 2 mmol, 1 mol % total monomer) in DMF (2 mL) was then injected, and the solution was degassed further for 15 min. Both inlet and outlet needles were then removed, and the sealed vessel was allowed to stir at 65°C for 24 h. A sample of the product was isolated by precipitation into 2-propanol and analyzed. To the remaining polymer solution was added tetramethyl ammonium hydroxide solution in MeOH (16.8 mL, 0.04 mol), and the mixture was stirred while cooling to below 10°C.

NMR: ^{1}H-NMR (200 MHz, DMSO-d_6, δ ppm): 4.20–4.30 (—CO$_2$CH$_2$CH$_2$CO$_2$—); 3.80–3.90 (—OCH$_2$CH$_2$OH), —); 3.50–3.60 (—OCH$_2$CH$_2$OH); 3.30 (—COCH$_2$CO—); 2.20 (—COCH$_3$); 1.60–1.90 (—CH$_2$—, backbone); 0.70–1.00 (—CH$_3$). ^{13}C-NMR (200 MHz, DMSO-d_6, δ ppm): 201 (CH$_3$CO—); 177 (—CCO—); 176 (—CCO—); 167 (—CH$_2$CO—); 68 (—CO$_2$CH$_2$CH$_2$CO$_2$—); 66 (—OCH$_2$CH$_2$OH); 59 (—OCH$_2$CH$_2$OH); 51–54 (—CH$_2$—, backbone); 49 (—COCH$_2$CO—); 45 (=C=, backbone); 30 (COCH$_3$); 17–19 (—CH$_3$).

PREPARATION OF COPOLYMER (5)

To the polymer solution (4) prepared in the previous reaction was added sulfanilic acid (7 g, 0.04

mol) and water (20 mL), followed by isobutyl nitrite (5.1 mL, 0.041 mol). The resulting suspension temperature was maintained below 10°C. A solution of HCl (37.8 wt % in water) (3.2 mL, 0.04 mol) was added to water (10 mL), and the solution was slowly added to the reaction mixture, forming the diazonium salt, which was then transferred to a pressure equalizing dropping funnel. This solution was then added dropwise to the polymer solution (4), and the resultant red solution was allowed to stir at room temperature for 3 h. The solution was then precipitated into 2-propanol (3 : 1), allowing the polymer to form as a solid product [yield, 18.5 g (87%); T_g, 123°C; M_n (GPC, universal calibration method), 64,000].

NMR: ^{1}H-NMR (200 MHz, DMSO-d_6, δ ppm): 7.80–8.00 (aromatic); 7.10–7.50 (aromatic); 4.20–4.30 (—CO$_2$CH_2CH_2CO$_2$—); 3.80–3.90 (—OCH_2CH$_2$OH), —); 3.50–3.60 (—OCH$_2$CH_2OH); 3.30 (—COCH_2CO—); 2.20 (—COCH_3); 1.60–1.90 (—CH_2—, backbone); 0.70–1.00 (—CH_3).

SUMMARY

A side chain methacrylate copolymer was designed and synthesized for use as water-soluble bottom antireflection coatings in lithography. The polymer composition was optimized as a result of extensive optical and lithographic evaluation. The β-keto ester azo benzene chromophore with carboxylate withdrawing group was identified as having suitable absorption maximum for i-line wavelength and had a high absorption coefficient (k). Solubility of the BARC copolymer in water was achieved through incorporation of highly polar functional groups, such as hydroxyl and carboxylate salts, in the polymer structure. A two-step synthetic route

was designed to produce the polymer in high yield. In the lithographic fabrication process, to prevent stripping failure, the polymer film must be inert during exposure to both organic and aqueous solutions. This was achieved by both internal and external crosslinking mechanisms, which were thermally activated during the baking fabrication steps. External crosslinkers, which were inert at room temperature, were identified and incorporated into coating formulations. Effective crosslinking also prevented interlayer mixing between resist and BARC. This ensured good quality resist images without scumming and foot at the resist/BARC interface. High CD resolution tolerances, and good swing curve reductions, were obtained.

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