is the lack of nitrogen on the pitch-based fiber, thus eliminating the possibility of chemically shifted C–N groups, which can be found as close as about 0.7 eV from the main "graphitic" peak. PAN-based fibers have a significant residue of nitrogen-containing groups left on the surfaces from their precursors, which may contribute to the disordering of the surface graphitic lattice leading to further broadening of the C1s graphitic peak.

Thus the XRD and XPS results suggest differences in the surface and bulk chemistry of the fibers.

Conclusions

Pitch-based carbon fibers are clearly more graphitic in both surface and bulk structure, and the higher the modulus of the pitch fiber is, the more graphitic its structure.

Pitch-based carbon fibers have a lower level of surafce functionality than PAN-based carbon fibers. The surfaces of the graphite samples are also more active to the environment than the pitch-based carbon fibers.

Anodic oxidation of a highly graphitic pitch-based carbon fiber led to similar surface species as those seen on PAN-based fibers under similar oxidation conditions, though the pitch-based fibers showed more oxidation. One type of C/O surface species was produced. Decomposition during data collection leads to significant changes in the core regions but little change in the valence-band region, reflecting the greater surface sensitivity of the former regions.

Valence-band spectra provide a more sensitive monitor of changes in suface chemistry than the core region. Thus changes in surface functionality result in significant differences (including in some cases separately resolved peaks) in the O2s region, as well as in the region at binding energies below 20 eV. Calculations on model compounds, to be discussed in a later publication, broadly predict these features.

Registry No. Graphite, 7782-42-5.

Acid Formation and Deprotection Reaction by Novel Sulfonates in a Chemical Amplification Positive Photoresist

L. Schlegel, T. Ueno,* H. Shiraishi, N. Hayashi, and T. Iwayanagi

Central Research Laboratory, Hitachi Ltd., Higashi-Koigakubo, Kokubunji, Tokyo 185, Japan

In a positive deep-UV photoresist composed of tris(methanesulfonyloxy)benzene as a novel photo acid generator, bisphenol A protected with *tert*-butoxycarbonyl groups as a dissolution inhibitor, and a novolak matrix polymer, the deprotection reaction by the generated methanesulfonic acid was studied by using UV spectroscopy. The results were compared with exposure characteristics obtained with the same resist in lithography. The deprotection degree, the catalytic chain length of the deprotection reaction, and the quantum yield of the acid generation were determined. The amount of photogenerated acid was unexpectedly high. This could be due to a sensitizing effect of the strongly absorbing novolak matrix polymer to generate the acid with high efficiency. The results show that sulfonic acid esters have very high possibilities for application in deep–UV resist materials.

Introduction

For the fabrication of VLSI circuits with critical dimensions smaller than 0.5 μm, new resist materials are required that are sensitive to deep-UV light (200–300 nm). Resist systems that may be developed in aqueous alkaline developers are very advantageous, to avoid swelling phenomena during the development process. Moreover, these resists offer a high dry-etch resistance due to their high content of aromatic polymers such as novolak resin. A high photosensitivity is required, as the light intensity of the KrF excimer lasers, operating at 248.3 nm, is not so high. Moreover, a resist with a sensitivity of less than 10 mJ/cm^2 is necessary, if the even weaker intensity of a Hg lamp at 254 nm should be used in an exposure system. It has been shown that this photosensitivity can most easily be achieved by using the "chemical amplification" mechanism.[1] In this case a photosensitive acid generator is decomposed during the exposure. The following acid-catalyzed thermal reaction renders the exposed parts of the resist soluble, in the case of positive resists, or insoluble, in the case of negative resists. Positive resists of that type are generally composed of an acid generator and an acid-labile compound that leads to products soluble in an aqueous alkaline solution. It is also possible to use three-component systems in which the acid-labile compound acts as a dissolution inhibitor in a novolak matrix polymer. Resists of this type have been applied to mid-UV[2] (300–350 nm), deep-UV[3,4] X-ray[5] and electron beam lithography.[6] In these resists, onium salts,[2–4] halogen compounds,[5,6] and nitrobenzyl esters[7,8] have been used as

(1) Fréchet, J. M. J.; Ito, H.; Willson, C. G. *Proc. Microcircuit Eng.* **1982**, 260. Ito, H.; Willson, C. G.; Fréchet, J. M. J. *Ibid.* **1982**, 262. Willson, C. G.; Ito, H.; Fréchet, J. M. J.; Houlihan, F. *Proc. IUPAC 28th Macromol. Symp.* **1982**, 448. Ito, H.; Willson, C. G. *Polym. Eng. Sci.* **1983**, *23*, 1012.

(2) O'Brien, M. J.; Crivello, J. V. *Adv. Resist Technol. Processing V, Proc. SPIE* **1988**, *920*, 42.

(3) Ito, H.; Flores, E.; Renaldo, A. F. *J. Electrochem. Soc.* **1988**, *135*, 2328.

(4) McKean, D. R.; MacDonald, S. A.; Clecak, J.; Willson, C. G. *Adv. Resist Technol. Processing V, Proc. SPIE* **1988**, *920*, 60.

(5) Dössel, K. F.; Huber, H.-L.; Oertel, H. *Microelectron. Eng.* **1986**, *5*, 97.

(6) Menschig, A.; Forchel, A.; Dammel, R.; Lingau, J.; Scheunemann, U.; Theis, J.; Pongratz, S. *Microelectron. Eng.* **1989**, *9*, 571.

300 *Chem. Mater., Vol. 2, No. 3, 1990*

Schlegel et al.

the acid generator compound. In a previous paper[9] we reported that the use of novel sulfonates as acid generators are superior to onium salts, as with onium salts a negative tone side reaction occurs at relatively small overexposure. Moreover, these onium salts have a high nonbleaching absorbance at 248 nm and are very strong dissolution inhibitors.[10] It is desirable to have a deeper insight into the reaction mechanism for the sulfonate compounds as novel acid generators and to obtain fundamental data such as the intrinsic photosensitivity (e.g., quantum yield) and the ability of catalytic deprotection of dissolution inhibitors (e.g., catalytic chain length). In this paper we report on the photochemical reaction mechanism of a resist material composed of tris(methanesulfonyloxy)benzene as an acid generator, bisphenol A protected with *tert*-butoxycarbonyl (tBOC-BA) as a dissolution inhibitor, and a novolak matrix polymer. The deprotection reaction of the inhibitor compound was explored, as a function of the exposure dose and the postexposure bake (PEB) conditions, by using UV spectroscopy. Absolute values of the deprotection degree were obtained by IR spectroscopy. The experiments were completed by dissolution rate measurements and were compared with data obtained in lithography with the same resist. The quantum yield and catalytic chain length were calculated. Fundamental knowledge about the photolysis reaction of the sulfonic acid ester was obtained by test experiments in a different matrix polymer.

Experimental Section

Materials. The acid generator compound 1,2,3-tris(methanesulfonyloxy)benzene (MeSB) was prepared as follows: pyrogallol obtained from Tokyo Kasei Kogyo Co. was dissolved in pyridine. While the solution was stirred at room temperature, methanesulfonyl chloride was added dropwise. After this was stirred for 3 h at 70 °C, MeSB was precipitated in water and recrystallized from acetone solution. It was checked by thin-layer chromatography. The compound is well applicable in resists applying a prebaking temperature of at least up to 130 °C. In the experiments described below, a prebaking temperature of only 80 °C was used. Therefore possible losses of acid generator during the prebaking process due to thermal decomposition or evaporation can be excluded. The inhibitor compound tBOC-BA was synthesized as described in the literature.[11] The novolak matrix polymer was a m/p-cresol novolak supplied by Hitachi Chemical Co. The ratio of m-cresol/p-cresol used for polymerization was 50/50. The polystyrene equivalent molecular weights were M_w = 4800, M_n = 902, and M_W/M_n = 5.3. Its optical density at 250 nm was 0.5 μm^{-1}. The cellulose acetate polymer, with an acetylation degree of 40%, was supplied by Eastman Kodak Co. Methanesulfonic acid (MSA) and 2,4,6-trimethylphenol (TMP) were purchased from Tokyo Kasei Inc. Bisphenol A was obtained from Kanto Chemicals Co.

Methods. Resist films were spin-coated from solutions in 2-methoxyethyl acetate onto appropriate substrates and soft-baked at 80 °C for 10 min on a hot plate. The film thickness was measured with an Alphastep profilometer (Tencor Instr.). Deep-UV exposures at 250 nm were made with a Xe–Hg lamp through an interference filter. The light intensity was determined
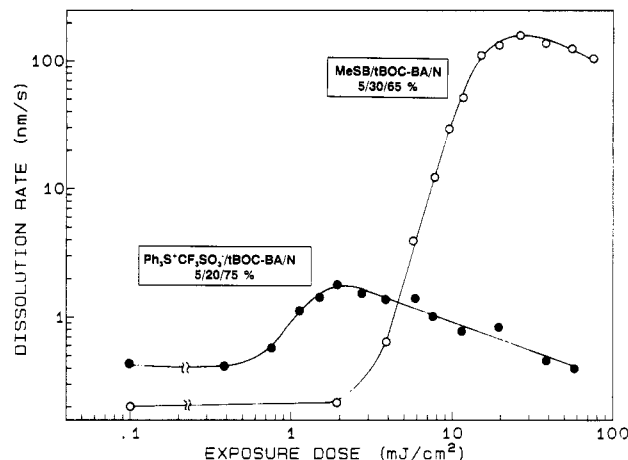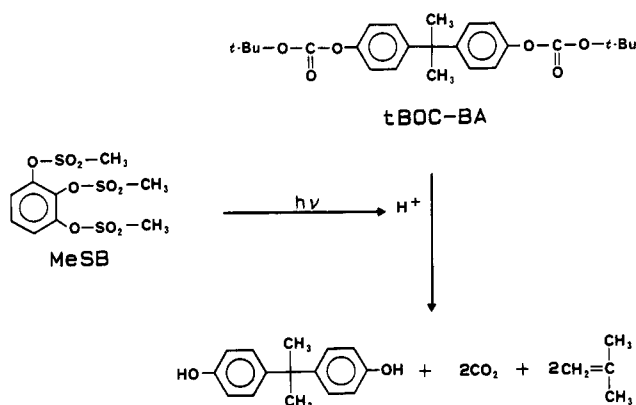
(7) Neenan, T. X.; Houlihan, F. M.; Reichmanis, E.; Kometani, J. M.; Bachman, B. J.; Thompson, L. F. *Adv. Resist Technol. Processing VI, Proc. SPIE* **1989**, *1086*, 2.

(8) Yamaoka, T.; Nishiki, M.; Koseki, K.; Koshiba, M. *Polym. Eng. Sci.* **1989**, *29*, 856.

(9) Ueno, T.; Shiraishi, H.; Schlegel, L.; Hayashi, N.; Iwayanagi, T. Chemical amplification positive resist systems using novel sulfonates as acid generators. Proceedings of the conference *Polymers for Microelectronics—Science and Technology*, Tokyo, October 1989; to be published.

(10) Schlegel, L.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Hesp, S.; Iwayanagi, T. *Jpn. J. Appl. Phys.* **1989**, *28*, 2114.

(11) Fréchet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* **1983**, *24*, 995.

Figure 1. Dissolution rate of resists $Ph_3S^+CF_3SO_3^-$/tBOC-BA/novolak = 5/20/75% and MeSB/tBOC-BA/novolak = 5/30/65% as a function of the exposure dose. PEB: 80 °C, 5 min. Developer: aqueous TMAH solution, 2.38%.

Scheme I

with a calorimetric flux detector (Thermopile). The UV spectra of films on quartz substrates were measured with a Hitachi U3410 spectrometer. IR spectra of films on NaCl substrates were measured with a Perkin-Elmer 1720X FTIR spectrometer. The dissolution rate of films on silicon substrates was measured with a home-made dissolution rate monitor. The developer was an aqueous solution of tetramethylammonium hydroxide (TMAH) with a concentration of 2.38%.

Results and Discussion

Performance of MeSB in Lithography Compared to Onium Salt. A negative tone behavior was found at quite small overexposure doses when deep-UV resists, containing tBOC-BA as a dissolution inhibitor and triphenylsulfonium triflate as an acid generator, were investigated.[9] To avoid this effect, several other acid generators were investigated in combination with tBOC-BA. We found that no negative tone effect occurred when MeSB was used as acid generator, even at very high exposure dose. This difference between both acid generators can clearly be seen in Figure 1, where the dissolution rate of resists, containing triphenylsulfonium triflate or MeSB as acid generator, is shown as a function of the exposure dose. The maximum increase in dissolution rate that could be achieved by exposure was quite small for the sulfonium salt (by a factor of ~5), and for exposure doses higher than ~2 mJ/cm² the dissolution rate decreased. On the other hand, with MeSB as acid generator, the dissolution rate increased by a factor of about 700. For exposure doses higher than about 12 mJ/cm², a slight decrease in dissolution rate was also observed, but even at a dose of 100

Acid Formation and Deprotection Reaction
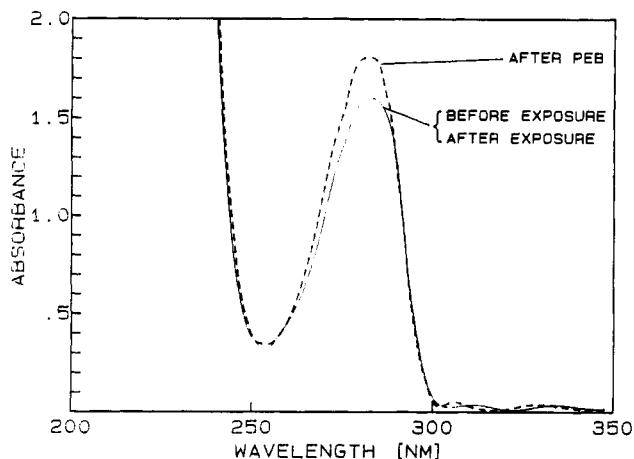
Chem. Mater., Vol. 2, No. 3, 1990   301

Figure 2. Spectral change in the resist MeSB/tBOC-BA/novolak = 5/30/65% during a PEB at 80 °C for 5 min. Exposure dose: 20 mJ/cm^2. Film thickness: ~1 μm.
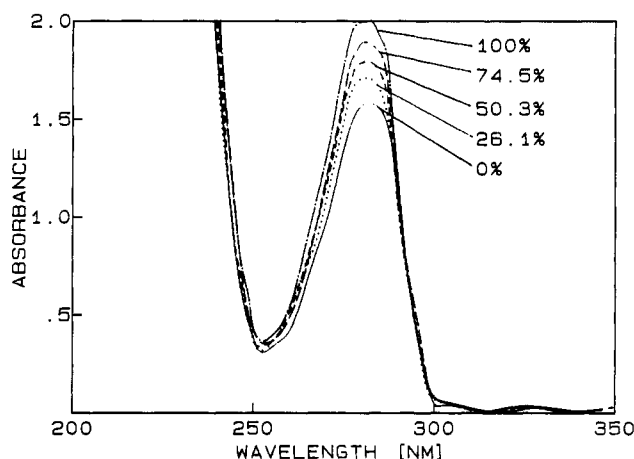

Figure 3. Spectra of model films with known amount of bisphenol A, simulating different deprotection degrees of a resist MeSB/tBOC-BA/novolak with a composition of 5/30/65%. Film thickness: ~1 μm.

Figure 4. IR spectra of the resist MeSB/tBOC-BA/novolak = 5/30/65% before exposure (upper part) and after exposure (50 mJ/cm^2) and PEB at 80 °C for 5 min (lower part). Film thickness: ~1 μm.

65%. The spectra of these films are shown in Figure 3. From the results shown in Figures 2 and 3 it can be concluded that the increase in absorbance at λ = 282 nm is a good indicator for the deprotection reaction.

Determination of the Deprotection Degree. The absolute value of the deprotection degree must be determined by an independent method. The content of tBOC groups in the resist can be estimated from the height of the carbonyl band in the IR spectrum. In Figure 4, the IR spectra of a resist MeSB/tBOC-BA/novolak = 5/30/65% are shown. These spectra were measured before an exposure of 50 mJ/cm^2 and after a PEB at 80 °C for 5 min. The carbonyl bands around 1730 cm^{-1} almost disappear completely during the PEB. This means that a nearly complete deprotection (>97%) can be achieved for a high exposure dose, as applied in the experiment in Figure 4. As the remaining absorbance around 1730 cm^{-1} might also be caused by traces of remaining solvent in the film, it is reasonable to assume a deprotection degree of 100% for very high exposure dose. The maximum increase in absorbance at λ = 282 nm in the UV spectrum, normalized for a film thickness of 1 μm ($\Delta ABS/d_0$), which occurred at similar high exposure dose and the same PEB conditions was $\Delta ABS/d_0$ = 0.21. The results shown in Figure 3 suggest that it is possible to assume a linear dependence of $\Delta ABS/d_0$ on the content of bisphenol A. Therefore the deprotection degree Dd can be determined from the increase in absorbance at 282 nm by the simple relation

$$Dd = \frac{100}{0.21} \frac{\Delta ABS(282)}{d_0} \%$$ (1)

The mean error in absorbance data can be estimated to about 1% and that in film thickness to about 3%. Additional errors are caused by slight drifts in light intensity and in the temperature of the hot plate. The absolute scattering in Dd for repetitive measurements was generally smaller than 10% in deprotection degree.

Influence of the PEB Conditions on the Deprotection Degree. Films of the resist MeSB/tBOC-BA/no-

mJ/cm^2, the dissolution rate of the resist was still higher than that of the neat novolak polymer (65 nm/s). As the clear advantages of MeSB, compared to onium salts, became evident we decided to investigate the mechanisms working in this new type of photoacid generator.

Effect in the UV Spectrum. When a resist, composed of the acid generator MeSB, tBOC-BA, and novolak, is heated after an exposure to deep-UV light, the compound tBOC-BA is deprotected according to Scheme I, resulting in the formation of bisphenol A, carbon dioxide, and isobutene.[12] The deprotection of tBOC-BA can be observed by UV spectroscopy, as is shown in Figure 2. The resist composed of MeSB/tBOC-BA/novolak, with a composition of 5/30/65 wt %, shows a clear increase in absorbance at λ = 282 nm during the PEB process, following an exposure with about 20 mJ/cm^2, whereas no spectral change was observed due to the exposure. To be sure that the increase in absorbance at 282 nm is due to the formation of bisphenol A, model films composed of MeSB, tBOC-BA, bisphenol A, and novolak were prepared. The molar contents of tBOC-BA and bisphenol A corresponded to assumed deprotection degrees of 0, 26.1, 50.3, 74.5, and 100%, in the system MeSB/tBOC-BA/novolak = 5/30/
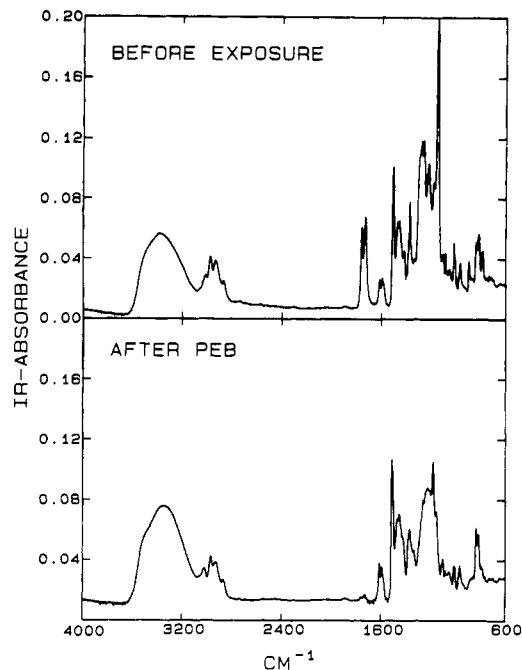
(12) Ito, H.; Willson, C. G. In *Polymers in Electronics*; Davidson, T., Ed.; ACS Symposium Series No. 242; Americal Chemical Society: Washington, DC, 1984; p 11.
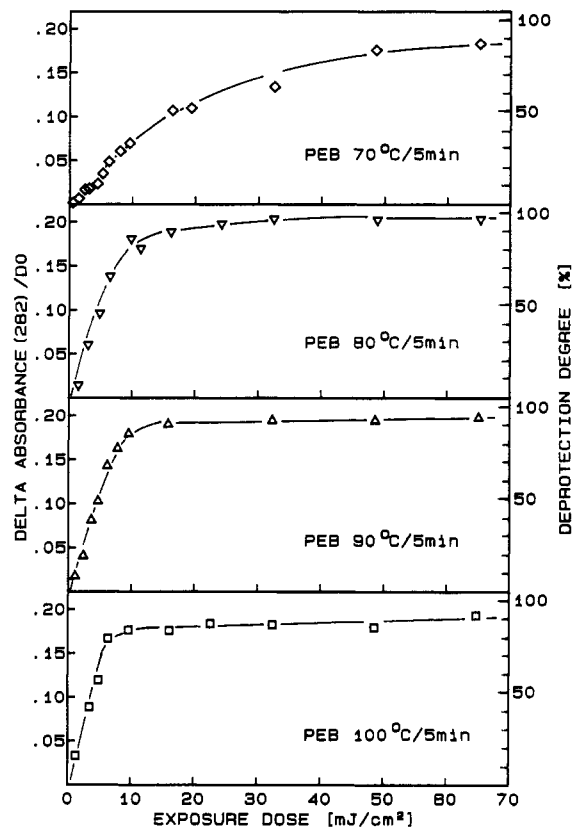
302 *Chem. Mater., Vol. 2, No. 3, 1990*

Schlegel et al.

Figure 5. Increase in absorbance at 282 nm (normalized for 1-μm thickness) as a function of the exposure dose for a PEB temperatures of 70, 80, 90, and 100 °C. PEB time = 5 min. Resist composition: MeSB/tBOC-BA/novolak = 5/30/65%. Scale at the right margin: deprotection degree obtained from eq 1.

Figure 6. Increase in absorbance at 282 nm (normalized for 1-μm thickness) as a function of PEB time for different PEB temperatures. Exposure dose: 9.75 mJ/cm². Resist composition: MeSB/tBOC-BA/novolak = 5/30/65%. Scale at the right margin: deprotection degree obtained from eq 1.

Figure 7. Dissolution rate of resist films MeSB/tBOC-BA/novolak = 5/30/65% as a function of the deprotection degree. PEB: 80 °C/5 min. Developer: aqueous tetramethylammonium hydroxide solution, 2.38%.

volak were exposed, and the increase in absorbance at 282 nm during the PEB process was determined. The results are plotted in Figure 5, where the PEB temperatures were 70, 80, 90, and 100 °C, respectively, and the PEB time was 5 min for all measurements. The scale for the deprotection degree, obtained from eq 1, is drawn in the right margin of each part in the figure. As can be seen in Figure 5, a bend occurred in the curves at a deprotection degree of about 84%, for PEB temperatures between 80 and 100 °C. The doses necessary for that deprotection degree were 10 (T_{PEB} = 80 °C), 9 (T_{PEB} = 90° C), and 8 mJ/cm² (T_{PEB} = 100 °C). By application of higher exposure doses, only a slight additional increase in the deprotection degree could be achieved. As this variation is quite small, a good process latitude in respect of PEB temperature can be expected in this temperature range. The difference between T_{PEB} = 70 °C and T_{PEB} = 80 °C is quite large; therefore, the effects of small fluctuations in PEB temperature on the result in lithography would be large for T_{PEB} < 80 °C. In the case of T_{PEB} = 70 °C, no sharp bend in the curve was found. In this case the applied PEB time of 5 min was too short to achieve high deprotection degrees at doses below 50 mJ/cm², as becomes more evident from Figure 6. In Figure 6, the increase in absorbance, normalized for 1 μm film thickness, is shown as a function of the PEB time. The applied PEB temperatures were 70, 80, 90, and 100 °C, respectively, and all samples had been exposed with a dose of D = 9.75 mJ/cm². The exponential increase found in Figure 6 can be explained by first-order kinetics. In the case of T_{PEB} = 100 °C, a slight decrease in absorbance was observed for longer PEB time due to a partial evaporation of Bisphenol A from the film. From Figure 6 the appropriate PEB time can be obtained for each PEB
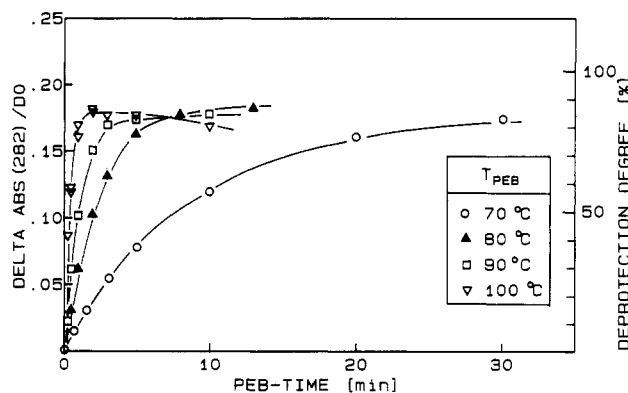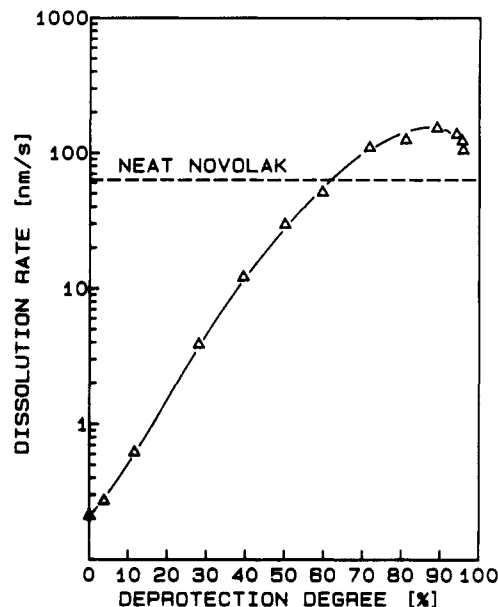
temperature. It is advantageous to choose process conditions that result in deprotection degrees near the saturation value. From Figure 6 it follows that the appropriate PEB time would be about 30 min for T_{PEB} = 70 °C, 7 min for T_{PEB} = 80 °C, 3 min for T_{PEB} = 90 °C and 1 min for T_{PEB} = 100 °C. Longer baking times would not improve the result, as the deprotection degree would not increase significantly, whereas negative effects, like the diffusion of acid out of the exposed regions, would become stronger. Of course, the recommended PEB times depend on the applied exposure dose, which was D = 9.75 mJ/cm² in the experiments shown in Figure 6. The rate constants of the deprotection reaction can be determined from Figure 6. An evaluation according to the Arrhenius equation reveals an activation energy of E_{act} = 107 kJ/mol.

Dependence of the Dissolution Rate on the Deprotection Degree. To obtain a relation between the deprotection degree and the characteristics of the resist observed in lithography, resist films of the same composition as described above were exposed and postexposure baked at 80 °C for 5 min. The dissolution rate in a metal-ion-free developer, with a concentration of 2.38%, was measured
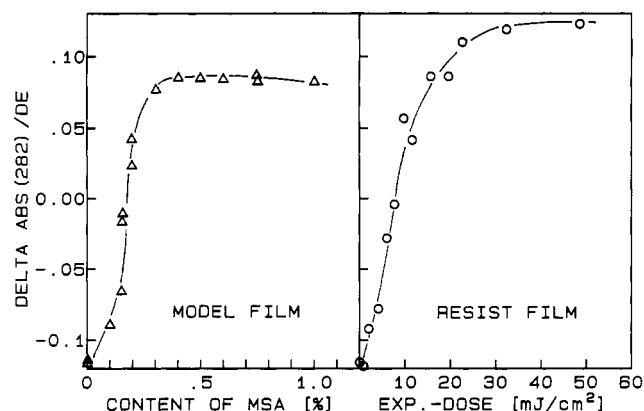
Figure 8. Increase in absorbance (normalized for a final film thickness of 1 μm) during a bake at 80 °C/10 min by addition of MSA to a resist MeSB/tBOC-BA/Novolak = 4/30/65% (left) and by photoexposure of a resist MeSB/tBOC-BA/Novolak = 5/30/65% (right).

with the dissolution rate monitor. The dissolution curves were nearly linear. From Figure 5 the deprotection degree corresponding to the exposure dose was determined. In Figure 7 the dissolution rate is plotted as a function of the deprotection degree. For deprotection degrees smaller than approximately 60%, the dissolution rate increased nearly exponentially with the deprotection degree. With deprotection degrees higher than about 60%, the resist dissolved faster than the neat novolak polymer, which indicates that the deprotected bisphenol A acts as a dissolution promoter in the system. The slight decrease in the dissolution rate, which occurred for very high exposure dose, is caused by other exposure effects such as radical reaction beside the deprotection reaction (see Figure 1). When the dissolution characteristics (Figure 7) are compared with exposure characteristic curves of the resist, it turns out that about 50% deprotection is necessary for a development of the resist within 45 s. From Figures 5 and 6 it can be seen that at this deprotection degree the curves still have a high slope, which indicates that the dependence on exposure dose and PEB time is still quite high. This finding is in accordance with the common experience in lithography that, for a good-quality pattern transfer, the exposure dose should be higher than the sensitivity value, obtained from the characteristic curve, by a factor of about 1.5-2.

Determination of the Yield of Photogenerated Acid. The acid generator MeSB is decomposed during the exposure. Although the exact reaction mechanism is not known, it is quite certain that methanesulfonic acid (MSA) is generated. To estimate the amount of photogenerated acid, small amounts of MSA were added to a resist solution of MeSB/tBOC-BA/novolak with 4/30/65 weight parts, respectively, and the increase in absorbance at 282 nm during a baking process was compared with data from resist films that were exposed with UV light. In Figure 8, the change in absorbance, normalized with the final film thickness, is plotted as a function of the content of MSA in the model films (left part) and as a function of the exposure dose of the resist film (right part).

The deprotection reaction occurred during the prebake process, of 80 °C for 10 min, in films already containing MSA. Therefore, the absorbance had to be measured before and after that baking process. The resist films that were to be compared with the films containing MSA were photoexposed directly after the spin coating, and the absorbance was measured before and after the following baking process, also at 80 °C for 10 min. If data from these measurements are to be compared with those obtained

Table I. Calculation of the Catalytic Chain Length in a Resist MeSB/tBOC-BA/Novolak = 5/30/65% for PEB Temperatures of 80 and 100 °C

	T_{PEB}, °C	
	80	100
exposure dose, mJ/cm^2	2.77	2.77
amount of acid formed	0.0527%, 6.58 × 10^{-6} mol/cm^3	0.0527%, 6.58 × 10^{-6} mol/cm^3
deprotection degree, %	29.7	48
original content of tBOC units, mol/cm^3	1.68 × 10^{-3}	1.68 × 10^{-3}
deprotected tBOC units, mol/cm^3	5.0 × 10^{-4}	8.06 × 10^{-4}
catalytic chain length	76	123

from resist films, which were exposed after a prebaking process (see the sections above), it must be presupposed that the photolysis of MeSB is not affected by solvent remaining in the film after spin coating.

It turned out that, due to the evaporation of solvent (2-methoxyethyl acetate), the absorbance at 282 nm decreased during the baking when the amount of methanesulfonic acid in the model films was small or when the exposure dose for the resist films for comparison was low. As can be seen in Figure 8, the increase in absorbance was small for very small amounts of MSA. At about 0.2% MSA, the absorbance increased strongly, and for the films containing more than 0.4% MSA, the absorbance decreased slightly. For contents of MSA ≤0.3%, the curve can be well compared with that obtained by the exposure of resist films (right part of Figure 8), thus allowing a direct estimation of the amount of photogenerated acid at different exposure doses. The maximum value in absorbance, which was observed with the resist films for high exposure doses, could not be obtained with model films containing a corresponding high amount of MSA. For higher MSA concentration it is possible that the deprotection reaction by MSA had already occurred to some degree in the solution. Therefore the effect during the baking process decreased when the content of MSA was higher than 0.3%.

The comparison of the reliable range of both curves (ΔABS/d_e between −0.05 and 0.07) gives a conversion ratio of 0.019% acid per 1 mJ/cm^2. It should be possible to extrapolate this value of the conversion efficiency to an exposure dose of about 105 mJ/cm^2, corresponding to 50% conversion of MeSB.

Catalytic Chain Length of the Deprotection of tBOC-BA. To determine the number of tBOC groups deprotected by one acid molecule (catalytic chain length), the amount of acid formed at a certain exposure dose must be compared to the resulting deprotection degree after the baking process. To obtain significant results, it is necessary that the PEB process is extended until the reaction has stopped and the saturation must not be caused by a total consumption of tBOC-BA. For that reason the results in Figure 6 cannot be used for the determination of the catalytic chain length, as in that case the final deprotection degree was nearly 100%. Therefore resist films were exposed with a relative low dose of 2.77 mJ/cm^2, and the PEB at 80 and 100 °C was continued until a saturation value in the absorbance was obtained ($\sim$30 min). The amount of acid formed at the given exposure dose was estimated by using the result of the previous section. The deprotection degrees Dd were calculated from eq 1. The outline of the calculation of the catalytic chain length is given in Table I. The higher catalytic chain length at 100 °C is caused by the higher mobility of MSA at higher temperature.

The results can be compared with data from the literature. For a system containing 1% of Ph$_3$S$^+$SbF$_6^-$ in neat

304 *Chem. Mater., Vol. 2, No. 3, 1990*

Schlegel et al.

Table II. Calculation of the Quantum Yield of Acid Formation by the Photolysis of MeSB

incident light intensity I_0	0.396 mW/cm^2
abs coeff of MeSB ϵ	229 L mol^{-1} cm^{-1}
film thickness d	1.085 μm
film abs A_F	0.3993
conc of MeSB	0.167 mol/L
intensity abs by MeSB	6.248 × 10^{-3} I_0
photon flux (λ = 250 nm)	8.276 × 10^{-10} einstein/cm^{2}s
photons abs by MeSB	4.766 × 10^{-8} einstein/cm^{3}s
conversion efficiency (Figure 7)	0.019%/(mJ/cm^2)
acid density	9.438 × 10^{-7} g/(cm^3 s)
quantum yield Φ	19.7

poly(*tert*-butoxycarbonyloxy)styrene, a catalytic chain length of ~1000 was obtained by applying a PEB at 100 °C for 1 min.[13] These data are not easily compared with the results described here, as in ref 13 the baking time was not extended until all the acid was used up. In that case the value of the catalytic chain length should be even higher. It must also be noted that the acid in that case was not methanesulfonic acid. From the density of the film and the catalytic chain length it is calculated that all tBOC groups that are deprotected by one proton are located within a sphere with a diameter of about 100 Å. When the same calculation is done for the system MeSB/tBOC-BA/novolak 5/30/65%, it is found that the corresponding spheres have diameters of about 60 and 51 Å at T_{PEB} = 100 and 80 °C, respectively. This would mean that the higher catalytic chain length obtained in ref 13 is caused, to a large part, by the much higher density of tBOC units in that system. Moreover, it must be pointed out that it is not certain that the deprotection reaction is a diffusion-controlled reaction. Therefore it is not possible to calculate the migration range of one acid molecule from the catalytic chain length, as was done in ref 13, and to estimate the resolution limit in lithography from this value.

Quantum Yield of Acid Formation by the Photolysis of MeSB. The outline of the calculation of the quantum yield Φ is shown in Table II. The absorption coefficient of MeSB was measured in acetonitrile solution. As is shown in Table II, only 0.62% of the incident light is absorbed by MeSB. From the calculation in Table II a quantum yield (number of generated acid molecules per photon absorbed by MeSB) of Φ = 19.7 is obtained. Theoretically the highest possible value would be Φ = 3, as three sulfonic acid ester units are attached to one ballast molecule. As the probability that the excitation by one photon results in the production of three acid molecules is quite low, a value of $\Phi \approx 20$ is too high by about 2 orders of magnitude. This discrepancy is much too large to be caused by experimental errors in the determination of the amount of photogenerated acid, or in the measurement of the absorption coefficient.

The discrepancy could be explained only by the assumption not only that photons absorbed by MeSB contribute to the formation of acid, but also that photons absorbed by other components of the resist, via sensitization, also contribute to the formation. When the amount of photogenerated acid is compared to the total number of photons absorbed in the film, a modified quantum yield

$$\Phi' = 0.205 \qquad (2)$$
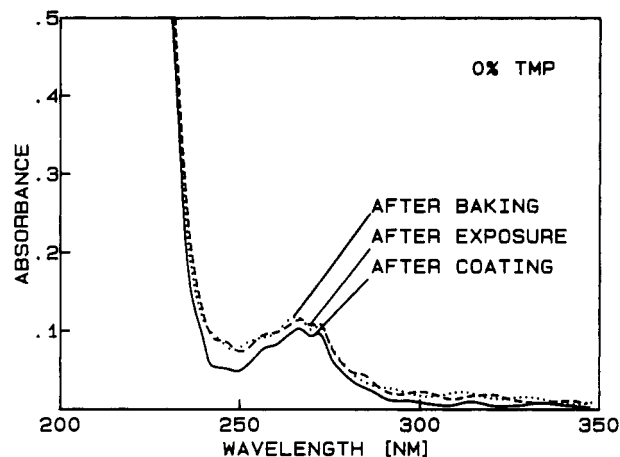
is obtained, which would be an acceptable result.

(13) McKean, D. R.; Schaedeli, U.; MacDonald, S. A. In *Polymers in Microlithography*; Reichmanis, E., McDonald, S., Iwayanagi, T., Eds.; ACS Symposium Series No. 412; American Chemical Society: Washington, DC, 1989; p 27.


Figure 9. Spectral effects in a resist MeSB/tBOC-BA/CA = 5/15/80% that was exposed after spin coating (450 mJ/cm^2) and baked at 80 °C for 10 min. Final film thickness: ~1.5 μm.

Studies of Model Compounds in Cellulose Acetate Films. When the sensitization effect supposed above would be present in the resist system, only the novolak matrix polymer can be a possible candidate for the sensitizer compound, as the light is mainly absorbed by the novolak. For that reason it would be interesting to know whether the acid formation and deprotection of tBOC-BA occur when MeSB and tBOC-BA are used in a matrix polymer that does not absorb at the irradiation wavelength of 250 nm. A matrix polymer appropriate for that purpose must meet the following requirements: besides its transparence at 250 nm it must be soluble in a common solvent of MeSB and tBOC-BA, it should have a glass transition temperature similar to novolak, and it must be a hydrophilic polymer, as certain amounts of water might be required in the system for the acid formation from MeSB and the deprotection of tBOC-BA. It was found that cellulose acetate (CA) with an acetylation degree of 45% is appropriate for that purpose. 2-Methoxyethyl acetate could be used as solvent. The content of tBOC-BA in resist films using cellulose acetate as a matrix polymer could not be higher than about 15%, as higher contents of tBOC-BA caused a phase separation.

It turned out that changes in the spectrum of a film MeSB/tBOC-BA/CA of 5/15/80% were very small during the exposure and PEB, even at very high exposure dose and long baking time as shown in Figure 9. This finding supports the hypothesis of a sensitization of MeSB by the novolak in a resist with novolak as matrix polymer. To prove that hypothesis, the compound 2,4,6-trimethylphenol (TMP) as a model compound for the cresol–novolak was added to certain contents to a system MeSB/tBOC-BA/CA. It was found by UV spectroscopy that the compound TMP evaporated from the film during the prebake at 80 °C for 10 min. Therefore, no prebake could be applied in the experiments described below. The films were treated in the following way: spin coating, exposure of the films to deep-UV light, baking at 80 °C for 10 min, measurement of the absorption spectrum, and measurement of the film thickness d_e after baking. The results are summarized in Figures 9 and 10. In Figure 9, the spectral change is shown for a resist MeSB/tBOC-BA/CA = 5/15/80%, which did not contain TMP.

In Figure 10, results are shown obtained with films containing TMP with contents of 5.4%, 10%, and 15.2%, respectively. This figure shows the final spectra after a sequence coating–exposure–baking at 80 °C/10 min. The exposure dose was varied between 0 and 450 mJ/cm^2 for all three cases. It can clearly be seen that the final ab-

Acid Formation and Deprotection Reaction

Chem. Mater., Vol. 2, No. 3, 1990 **305**
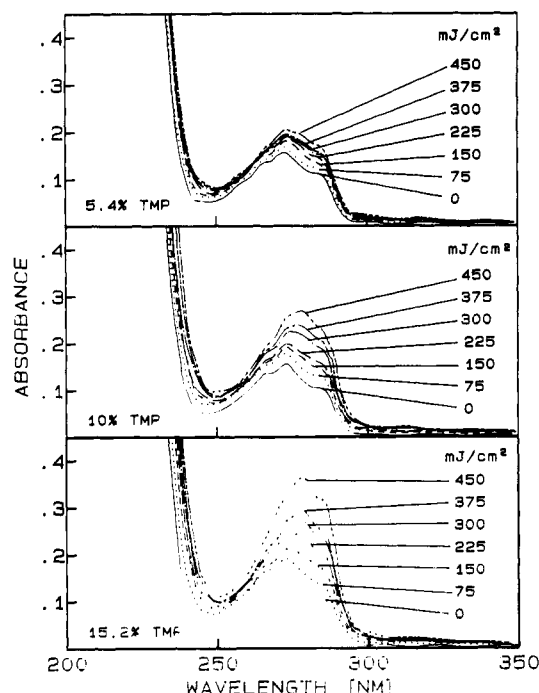
Figure 10. Absorption spectra of resists MeSB/TMP/tBOC-BA/CA = $5/x/15/80 - x\%$ after a sequence coating–exposure–baking 80 °C/10 min with different exposure doses. Final film thickness: ~1.5 μm.

Figure 11. Increase in absorbance (normalized for a final film thickness of 1 μm) as a function of exposure time for different contents of TMP. Light intensity: 0.396 mW/cm^2.

sorbance at 282 nm increases with exposure dose. Moreover, this effect itself increases when the content of TMP becomes higher. It is evident from the results in Figure 10 that the compound TMP acts as a sensitizer molecule at 250 nm for the acid generation by the decomposition of MeSB. This finding proves that a sensitization of MeSB by the novolak compound occurs in a resist MeSB/tBOC-BA/novolak, resulting in very high amounts of acid after the exposure.

The results in Figure 10 were evaluated in more detail. All absorbance data were corrected for a final film thickness d_e of 1 μm. When the increase in absorbance, which is caused by the exposure (e.g., $ABS(D)/d_e(D) - ABS(0)/d_e(0)$), is plotted as a function of the exposure time, a linear increase of the absorbance at 282 nm with increasing exposure time was obtained, as shown in Figure 11. The slope of the straight lines in Figure 11 increases
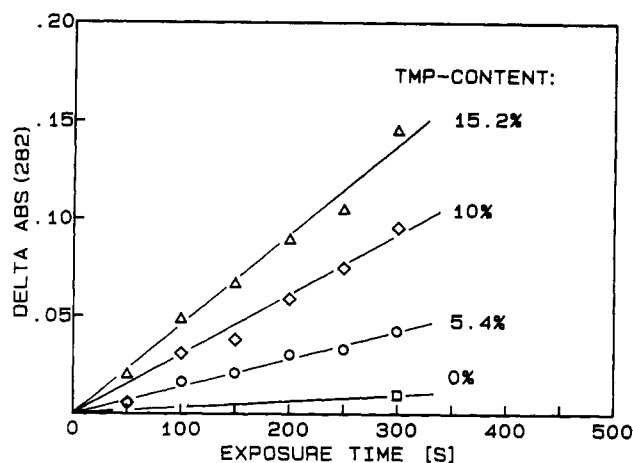
with higher TMP content. The linear dependence found in Figure 11 shows that the deprotection reaction did not approach any saturation value in the investigated dose range.

Conclusion

The deprotection degree and yield of photogenerated acid in a positive resist containing the methanesulfonic acid ester MeSB were determined by UV spectroscopy. The method applied here is advantageous in that only compounds used in actual resist formulations are involved. The use of acid-sensitive dyes and the transfer of the film into solution was not necessary. The results show that a novolak matrix polymer can be strongly involved in the photochemical reaction mechanism of deep-UV resists. The strong absorbance of novolak polymers, which is one of the main obstacles for the generation of fine-line patterns with high quality, can be utilized quite efficiently for the generation of acid by addition of sulfonic acid esters. The use of sulfonic acid esters causes no increase in absorbance of the resist, in contrary to other acid generators where the high absorbance caused by the acid generator may be problematic.

Registry No. MeSB, 126615-05-2; tBOC-BA, 117458-06-7; MSA, 75-75-2.