Copolymers of 2-hydroxyethyl methacrylate and methyl methacrylate: an electron beam resist study

Varinder K. Sharma, Stanley Affrossman and Richard A. Pethrick
Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland, UK
(Received 31 October 1983)

The electron beam development characteristics of copolymers of HEMA and MMA are reported. A copolymer with 4% of HEMA was found to have comparable sensitivity and enhanced contrast compared with conventional PMMA and this material would appear to be useful in lithographic applications.

(Keywords: 2-hydroxyethyl methacrylate; methyl methacrylate; electron beam resist; copolymer)

INTRODUCTION

Demands in the microelectronics industry for large scale integrated circuits places ever increasing demands on lithography to reduce component dimensions and increase the resolution. Concurrent developments in electron beam (EB) writing technology has also generated a requirement for high sensitivity, higher contrast, good resistance to dry etching and high thermal stability in EB resists. Many of the existing resists are capable of meeting these criteria but often fail due to poor adhesion to the substrate. Adhesion is particularly critical when the resist is subjected to a wet development process or when it is being plasma etched. Poor adhesion can lead to undercutting during etching and in the most severe situation to defects appearing in the mask or circuit element being written.

The most widely used positive resist is poly(methyl methacrylate)[1-5]. The polymer itself has poor sensitivity, typically having a value between 2×10^{-4} to 6×10^{-5} C cm^{-2}, however these slow resists have excellent resolution. An increase in the sensitivity and resolution may be achieved by the incorporation into the polymer of either methacrylic acid[6] or a mixture of methacrylic acid and methyl acrylic anhydride. These copolymers exhibit excellent adhesion and also increased sensitivity. In this paper we explore the effects of incorporation of 2-hydroxy ethyl methacrylate (HEMA) into the polymer. It is assumed that the incorporation of the hydroxyl group will increase the adhesion characteristics of the polymer but should also, through hydrogen bonding, stabilize the undeveloped polymer matrix without the necessity for thermally induced crosslinking.

EXPERIMENTAL

Monomers

Methyl methacrylate (MMA) was obtained from BDH and was washed with 5% NaOH to remove stabilizer. The monomer was then washed with distilled water several times before drying over calcium chloride and redistilling under reduced pressure. The 2-hydroxyethyl methacrylate (HEMA) was obtained from Aldrich and was redistilled under vacuum before use.

Synthesis of poly(methyl methacrylate)

In order to have a reference polymer, poly(methyl methacrylate) (PMMA) was prepared using the same initiator system as that used in the copolymerization. The MMA was polymerized at 343 K using benzoyl peroxide as initiator, the reaction being carried out under nitrogen. The degree of conversion was kept low, the contents of the solution being poured into methanol once the viscosity of the solution had visibly increased. The polymer so obtained, was dissolved in toluene and reprecipitated into methanol.

Copolymers of MMA and HEMA were prepared using benzoyl peroxide (0.2% w/v) as initiator. The initiator was added to the mixture in chloroform which was then removed using a rotary evaporator. The reaction was carried out at 343 K on a water bath. The degree of conversion was kept below 10% and the copolymer was precipitated using carbon tetrachloride. The precipitated copolymer was filtered and dried before use. The composition of the copolymer was determined by estimating the number of free hydroxyl groups present using an acetylation method[8]. A mixture of acetic anhydride and dried pyridine (1:3) was used in the titration of the free hydroxyl groups. The copolymers were prepared with HEMA contents in the range 4 to 10%. Copolymers containing more than 10% of HEMA were insoluble in most solvents, forming gels rather than solutions. Only copolymers which form true solutions are suitable for spinning into thin films. The molecular weights and distributions of the copolymers were determined using gel permeation chromatography. The tacticity and sequence structure of the copolymers were investigated using ^{1}H n.m.r. Details of the polymer characteristics are listed in *Table 1*.

Sample preparation for EB investigation

Resist films with thickness between 0.5–0.7 μm were

0032-3861/84/081090-03$03.00
© 1984 Butterworth & Co. (Publishers) Ltd.

prepared by spin coating a solution of the copolymer in chlorobenzene onto an oxidized silicon wafer using a Dage Precima Spinner. Films were then prebaked in air at 433 K for 1 h in order to remove the solvent and to promote adhesion on the wafer. The prebaked films of the copolymer were not readily soluble in solvents in which the original polymer were soluble indicating a strong interaction between the polymer and the substrate and also the possibility of side reactions.

Electron beam exposure

The resists were exposed using Philips PSCM 500 scanning electron microscope at Glasgow University. The accelerating voltage was 25 kV with a beam size of 320–640 Å and a beam current of 7.3×10^{11} A and 2.65×10^{-10} A respectively. Exposed areas of $3\times10^{-4}\ cm^2$ were then developed at 293 K in suitable developer with gentle agitation to enhance the dissolution of the soluble material. After development the remaining film thickness was measured using a Talystep and normalized with respect to the initial film thickness.

RESULTS

The sensitivities and contrast of the copolymers were determined from the graphs of the normalized thickness against the log of the exposure dose (*Figures 1* and *2*). The remaining thickness after development can be taken as the gel fraction. The dose, when the gel fraction becomes zero, defines the sensitivity. The contrast was determined from $\log(D_0/D)^{-1}$ where D_0 is the extrapolated dose for complete exposure and D_i is the extrapolated dose for full thickness of the film. The estimates of D_0 and D_i were taken from the linear portions of the curve shown in *Figures 1* and *2*. The results of this analysis are presented in *Table 2*.

Table 1 Physical characteristics of resist materials

Resist	% of HEMA in copolymer	Code	$M_w \times 10^5$	M_w/M_n
PMMA (BDH)	0	R_1	1.23	2.12
PMMA (Benzoyl peroxide)	0	R_2	4.70	2.14
MMA–HEMA	4.3	R_3	6.06	2.40
MMA–HEMA	6.23	R_4	7.34	2.35
MMA–HEMA	9.61	R_5	–	–

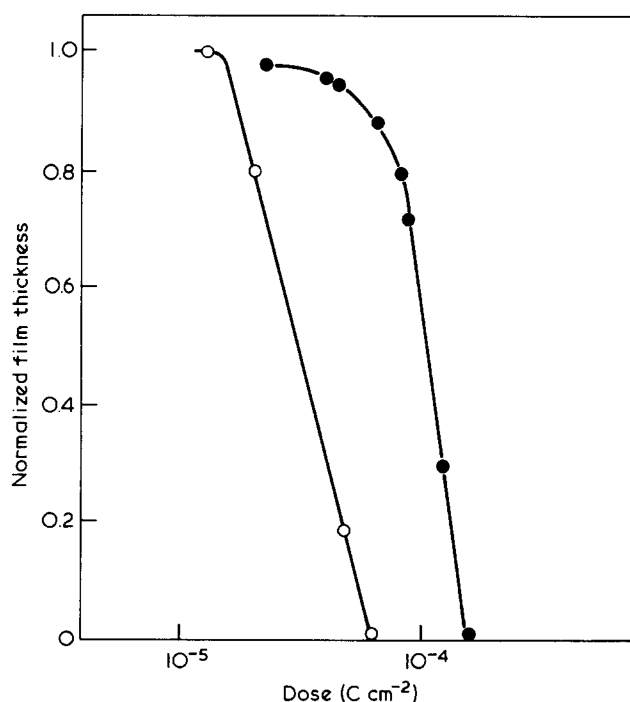

Figure 1 Development curves for PMMA's: ○, ($M_w=1.23\times10^5$); ●, ($M_w=4.7\times10^5$)

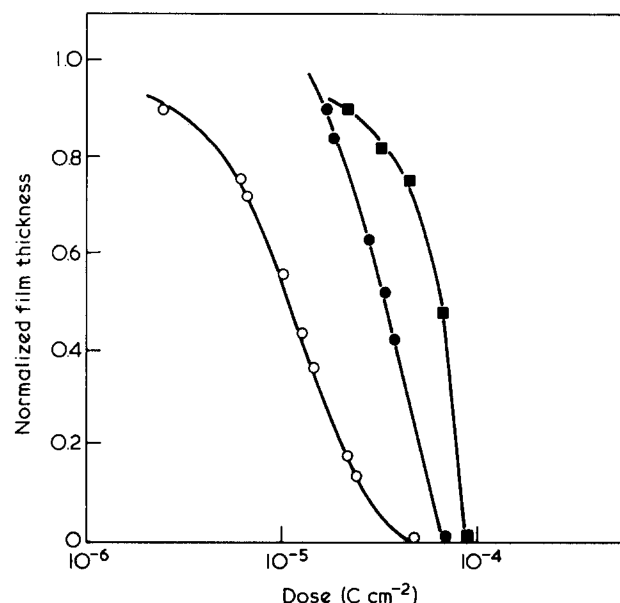

Figure 2 Development curves for copolymers of MMA–HEMA: ■, R_3; ●, R_4; ○, R_5

Table 2 Electron beam development characteristics

Code	Developer	Time (s)	Electron beam sensitivity at 25 KeV (cm^{-2})	Contrast γ
R_1	MIBK:IPA 2:3	60	6×10^{-5}	1.70
R_2	MIBK:IPA 2:3	60	1.5×10^{-4}	3.05
R_3	Dioxane:IPA 2:1	60	8.5×10^{-5}	4.00
R_4	Dioxane:IPA 2:1	60	6.7×10^{-5}	1.75
R_5	Dioxane:IPA 2:1	60	4.2×10^{-5}	1.16

DISCUSSION

Two samples of the homopolymer were studied (R_1) and (R_2). They have the same molecular weight distributions, same tacticities (syndiotactic 57%, heterotactic 43%) but have different weight average molecular weights M_w. Both samples respond differently to electron beam exposure. The contrast increases by a factor of 1.8 while the sensitivity decreases by a factor of three with increasing M_w. It is well known that in positive resists that sensitivity increases at the expense of contrast and *vice versa*. Bowden[9] has reported that in PMMA sensitivity increases with an increase in M_w for $(M_w/M_n)(=1.6)$ constant. We do not have information on the tacticity of the polymers used and our earlier studies[10] have indicated that this is a very important parameter when considering the behaviour of PMMA. It is still a little strange that there should exist this apparent contradiction in observations and we anticipate that it is the result of a number

of factors influencing the EB behaviour of the resist. For example, the molecular weight distribution, tacticity, development times used and the current densities employed, all these may influence the nature of the entities generated during EB exposure and the effects on the observed development behaviour.

In the copolymers, the sensitivities increased with an increase in the amount of HEMA present. This observation agrees well with an earlier study which indicated that incorporation of HEMA in allylmethacrylate enhanced the sensitivity and plasma etch resistance[11]. The copolymer containing 4% HEMA shows optimum lithographic performance. It has a sensitivity of the order of $0.8\ \mu C\ cm^{-2}$ and a contrast value of 4.3. When the amount of HEMA was increased to 6%, the γ value decreased to 1.7. At this copolymer composition the EB behaviour is similar to that of PMMA, however, the adhesion to the substrate is better. At 9.6% HEMA, the copolymer starts swelling in most solvent systems and becomes unusable for most practical purposes. The lithographic evaluation of this sample was done on the soluble part. Although the sensitivity has improved to $0.4\ \mu C\ cm^{-2}$ the contrast is very poor. The copolymer exhibits excellent adhesion to the substrate. The prebaked film in most of the above systems was not easily removed from the substrate. This is presumably due to the presence of highly polar hydroxyl groups which form hydrogen bonds with the substrate and thereby increase resist adhesion. These polymers would be very suitable for applications using SiO_2 and other substrates which have a mildly acid character.

CONCLUSIONS

The presence of HEMA in the backbone of PMMA has a dramatic effect on the overall performance of these materials as EB resists. The introduction of 4% HEMA into the copolymer gives the optimum improvement in performance and leads to a material which has a higher contrast than conventional PMMA and is better than the related crosslinking resists. This material would appear to be attractive.

ACKNOWLEDGEMENTS

One of us (V.K.S.) wishes to thank the SERC for financial support for the period of this study and Professor C. D. Wilkinson of Glasgow University for assistance with the electron beam lithography studies.

REFERENCES

1. Hatzakis, M. *J. Electrochem. Soc.* 1969, **116**, 1033
2. Miller, R. T. *Solid State Technol.* 1973, July, p. 25
3. Hatzakis, M., Chang, H. P., Wilson, A. D., Speth, A. J. and Kein, A. *Elektron* 1977, **51**, 8
4. Atoda, N., Komuro, M. and Kawakatsu *J. Appl. Phys.* 1979, **50**, 3707
5. Need, O. U., Johnson, D. E., Ouano, A. C. and Gipstein, E. *IBM J. Res. Develop.* 1977, p. 143
6. Matzakis, M. *J. Vacuum Sci. Technol.* 1979, **16**, 1984
7. Moyer, W., Merritt, D. and Moreau, W. *J. Vacuum Sci. Technol.* 1979, **16**, 1989
8. Vogel, A. I. Elementary Practical Organic Chemistry, Part III, 1958, 677
9. Bowden, M. J. *J. Polym. Sci., Polym. Symp.* 1975, **49**, 221
10. Sharma, V. K., Pethrick, R. A. and Affrossman, S. *Polymer* 1982, **28**, 1732
11. Tan, Z. C. H., Petropoulos, C. C. and Rauner, F. J. *J. Vacuum Sci. Technol.* 1981, **19**, 1348