Enhanced sensitivity in the electron beam resist poly(methyl methacrylate) using improved solvent developer

Mahmood A. Mohsin and John M. G. Cowie*
Department of Chemistry, University of Stirling, Stirling FK9 4LA, UK
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Poly(methyl methacrylate) (PMMA) has been used widely as a positive working resist in electron beam lithography, and so the solubility of this polymer in organic solvents increases upon exposure to electron beam irradiation. Considerable efforts have been directed towards increasing the sensitivity of this resist to electron beam irradiation, but only a few have focused on careful and proper solvent selection for the development process. In this study we have investigated the way in which the selection of the best solvent or combinations of solvents can lead to a significant improvement in resist performance by influencing both the sensitivity and the contrast on development.

The solubility of PMMA in cosolvent and solvent-precipitant systems has been examined, and a number of developers were chosen which fulfilled the basic requirement that the observed pattern distortion was minimized on exposure to the developer. Comparison with the standard developer for PMMA, which is a mixture of methyl isobutyl ketone and isopropyl alcohol (1:3), showed that an improved sensitivity of at least threefold was achieved when isopropyl alcohol and water (9:1) was used as a developer. This enhancement in sensitivity was achieved at the expense of an increase in the development time to about 4–5 min. On the other hand, the development time could be greatly reduced by using a developer selected from solvent–precipitant systems.

(Keywords: poly(methyl methacrylate); positive resist; cosolvent system; solvent–precipitant system; sensitivity; contrast)

INTRODUCTION

Electron beam lithography is one of the important new technologies in direct wafer writing for fabricating semiconductor devices and circuits with submicrometre dimensions, and has been in use for several years. Polymers have played an important role in the fabricating technology of these devices. During the last 20 years, large numbers of common polymers have been investigated for possible use as electron beam resists[1–4], but much of the recent work has been focused on the development of a new generation of resist materials that possess desirable and improved properties for microelectronics applications. Currently the most widely used and extensively studied electron-sensitive material is the positive acting resist poly(methyl methacrylate) (PMMA). On exposure to high-energy radiation, this polymer undergoes predominantly chain scission and decomposition of its ester side groups, thus causing a reduction in molecular weight and formation of volatile products such as CO_2, CO, CH_4, CH_3OH and H_2. The evolution of these volatile fragments increases the polymer free volume, thereby allowing a substantial increase in the diffusion rate of the developing solvent into the polymer matrix[5]. Although many polymers exceed PMMA in sensitivity, its combination of attractive properties has maintained its popularity, and it remains a standard by which to judge the performance of other positive resists. The performance of any resist is measured in terms of its sensitivity to the incident radiation, where sensitivity is expressed in terms of the incident dose of radiation per unit area required to produce a particular resist pattern of the desired thickness.

PMMA has the advantages of extremely high resolution together with a relatively good thermal stability, fairly good etch resistance, excellent film forming and good processing properties[1–4]. Its main disadvantage, however, is that its sensitivity to degradation is lower than is considered desirable by many workers, and an exposure dose in the range 5×10^{-5} to 5×10^{-4} C cm^{-2} is required to initiate free-radical production[6–10]. The lack of sensitivity has stimulated interest in the development of more sensitive electron beam resist materials, but attempts to improve the sensitivity of PMMA by modifying its chemical structure, while preserving desirable processing characteristics, have also been considered[10–14]. An interesting approach to improving the sensitivity of a polymer resist involves copolymerization with another monomer which is itself more sensitive[10], and polymers with both a higher sensitivity and a higher degree of main-chain scission have been prepared. In addition, these improvements have often been further enhanced by optimization of the development process. The intention of this work, however, is not to optimize the development process or the developer exhaustively, but rather to demonstrate that an improvement in the sensitivity and the contrast of PMMA can be achieved without altering the processing characteristics or the chemical structure, by using solvent developers that are more finely tuned to dissolution of the degraded PMMA sections while leaving the unexposed regions relatively unaffected.

The production of an image or a pattern depends on the differential solubility of the exposed and unexposed

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* To whom correspondence should be addressed

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regions of the polymeric films. Phenomena such as swelling and film cracking can cause distortion of the patterns, and these effects have been shown[2] to be dependent on the solvent used during the development process.

The basic requirements of a developer can be summarized as follows. First, it must have thermodynamic properties that render it a minimal solvent for the resist, thereby sharply reducing the swelling volume of the defined features. Secondly, it must be a kinetically good solvent so that the soluble areas of the resist are completely dissolved and washed away in the requisite development time. The solubility of a polymer matrix after exposure will depend on the molecular weight of the polymer as well as on the thermodynamic quality of the solvent, and so the developer, required to generate the pattern, should then be a solvent that is just capable of dissolving the low-molecular-weight fragments resulting from irradiation while leaving the rest of the film with little or no swelling or distortion.

It was brought to our attention that isopropanol containing 5% water is capable of developing a PMMA pattern[15], and since both isopropanol and water are non-solvents for PMMA at room temperature, this developer must be a cosolvent system. Classical cosolvent systems are defined as those in which a polymer is insoluble in either of the two pure non-solvents, yet is soluble in a binary mixture of the two, and this interesting behaviour has been reported for several polymer–binary solvent combinations[16–21]. In order to obtain a clear idea of this effect, the phase behaviour of PMMA in mixtures of isopropanol and water was examined to establish both the temperature and the solvent composition limits of solubility. These results, which are published elsewhere[22], have indicated the most suitable composition range for a more detailed study.

Two approaches have been examined: one is to use a cosolvent system and the other is to use a solvent–precipitant system where the polymer is dissolved in a solvent and can be precipitated on addition of a non-solvent. These two methods are compared using the best combination examined in each case.

EXPERIMENTAL

Determination of phase boundaries

A number of cosolvent systems have been identified for a PMMA sample ($M_w = 86\,000$) and the phase boundaries have been established and reported[22]. The systems used were t-butanol/water, n-propanol/water, isopropanol (IPA)/water, ethanol/water and methanol/water. The phase behaviour of poly(methyl methacrylate) of different molecular weights dissolved in IPA/water has also been established[22]. The most suitable solvent–precipitant systems selected from a study of several possible combinations were methyl ethyl ketone (MEK) used as a good solvent and ethanol or methanol used as a precipitant. Several good solvent–precipitant systems were investigated by determining the composition of the binary mixture that would just precipitate the PMMA sample. This binary composition should then be an increasingly good solvent for PMMA as the molecular weight is lowered by electron beam degradation, thereby allowing rapid pattern development while leaving the unirradiated PMMA undissolved when exposed to the developer.

Resist preparation

The sample of atactic PMMA was obtained from BDH, and has been previously characterized in this laboratory[21]. Two different molecular-weight samples of $M_w = 86 \times 10^3$ and 110×10^3 g mol^{-1} with $M_w/M_n \sim 1.8$ were used in this study. Solutions of 5% PMMA were prepared in methyl ethyl ketone and filtered through a 0.2 μm sintered glass filter. The filtered solutions were spun onto a chromium-coated substrate at 5000 rpm for 60 s using a Headway Research Inc. spinner. The resist film was then prebaked at 120°C for 60 min prior to use. The film thicknesses obtained were typically between 0.3 and 0.5 μm.

Electron beam exposure and sensitivity measurements

Electron beam exposures were carried out with a computer-controlled exposure system, which was an International Scientific Instrument Model SMS-2 'SUPER II' scanning electron microscope. The resist specimens were exposed to electron beam radiation at an acceleration voltage of 20 keV on an area of approximately 28×16 μm. The exposure doses were varied between 10^{-5} and 10^{-2} C cm^{-2}, and the electron dose was determined by varying the exposure time of the beam at a given beam current. After a series of progressive exposures, the patterns were developed by immersion of the substrate with gentle agitation in the chosen developer. Periodically, the substrate was removed from the solvent and subsequently rinsed with neat IPA for 30 s (in order to halt any further development), then dried by blowing dry nitrogen gas over the sample. The resist thickness was measured using a Sloan Dektak IIA profilometer. The sensitivity of the resist was measured as the minimum dose required to obtain complete removal of the resist and was derived from the exposure curves, which were obtained by plotting the normalized remaining thickness against the logarithm of the incident dose. The contrast (γ) was calculated from $\log(D_0/D_{100})^{-1}$, where D_0 is the extrapolated dose for complete exposure and D_{100} is the extrapolated dose for full thickness. Generally, a high value of contrast indicates that the material is capable of high resolution, and this is one of the parameters used to characterize the lithographic response of a polymer resist.

RESULTS AND DISCUSSION

Cosolvent and solvent–precipitant systems

Prior to conducting any lithographic assessment, the solubility phase diagrams for PMMA in several cosolvent systems were established to serve as a guide for developer solvent selection[22], and isopropanol/water was chosen as a suitable cosolvent for the development of PMMA resist. The polymer is soluble at room temperatures when the volume fraction of alcohol lies between 0.9 and 0.7. The alternative method of establishing polymer–solvent interaction and miscibility as a function of polymer concentration is to study solvent–precipitant systems. Methyl ethyl ketone was selected as a good solvent for PMMA, and ethanol or methanol were used as precipitant. The miscibility boundaries for these solvent–precipitant pairs were measured in order to establish the optimum

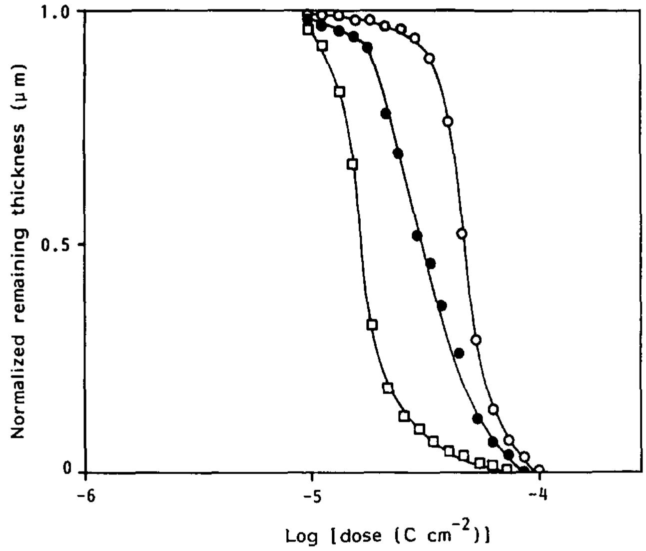

Figure 1 Exposure characteristics curves for PMMA 110×10^3 mol. wt developed in IPA/water: (○) 70/30 for 3 min; (●) 80/20 for 2 min; and (□) 90/10 for 4 min

concentration of the two components that dissolves the species lower in molecular weight than the starting material but not the original PMMA itself. The potential developers have been chosen on the basis of equilibrium experiments only, but the optimum developer must be selected from these candidates on the basis of actual lithographic performance in terms of contrast and sensitivity, and can only be accurately assessed by examining the electron micrographs of the developed patterns.

Electron beam assessment

Resolution is the minimum feature size that can be clearly defined in the resist and depends on factors such as adhesion and extent of swelling during development and contrast. Resist contrast is more difficult to define precisely but is related to how responsive the extent of development is to small changes in exposure dose. The sensitivity of a resist is then a measure of the speed with which one part of the microelectronic circuit can be fabricated. In general terms, sensitivity is defined as the exposure to form satisfactorily a relief image in a resist layer, and is interpreted here as the minimum radiation dose (C cm^{-2}) required to remove, upon development, the irradiated polymer completely, i.e. 100% of the initial resist thickness. In order to optimize the development process, significant changes had to be made both to the ratio of the mixture of isopropanol with water and also in the length of the development time. According to the phase separation diagram for the cosolvent system of PMMA 86×10^3 molecular weight for a development temperature of 20°C, the polymer will be soluble in the range of IPA from 90% to 70%[22]. The polymer films of 110×10^3 molecular weight were exposed and developed in 90% IPA for 4 min, 80% IPA for 2 min and 70% IPA for 3 min. The decrease in the thickness of the unexposed areas during the development stage using each of the above-mentioned developer compositions was minimal, and the film retained almost all of the original thickness.

The initial lithographic characteristics of PMMA are summarized in the exposure curves shown in *Figure 1*. The sensitivity was best when developed in 90% IPA and the worst when developed in 70% IPA, while the contrast (γ) was greatest when 90% IPA was used. The development times required to produce these patterns using IPA/water mixtures are shown in *Table 1* but are longer than might be acceptable, particularly for the 70/30 mixture. The sensitivity was improved at least threefold when using 90/10 IPA/water than when using the 70/30 IPA/water mixture, and the value of the contrast observed is also significantly higher when using 90/10 IPA/water as the developer. No thinning of the unexposed resist occurred with the IPA/water developers, regardless of the length of the developing time, and this is a distinct advantage in the development process, as excessive thinning of unexposed areas is often the limiting factor when developing patterns at low exposure doses. The developer containing 90/10 IPA/water also gave a reasonably good level of sensitivity of 24 μC cm^{-2} compared with 33 μC cm^{-2} for the 70/30 system. It is important to note from the electron micrographs that there is no evidence of scumming or other undesirable characteristics on the resist pattern, such as have been observed with other developers. The use of 95/5 IPA/water and mixtures with lower than 65% IPA at 20°C had no significant effect on either the exposed or unexposed areas, and no pattern was found to have developed even after a period of about 30 min development time.

On comparing the results for PMMA obtained in this work with those reported in the literature using methyl isobutyl ketone/IPA as a standard developer, the resist appears to be more sensitive and has a good gain in contrast when developed in IPA/water. Furthermore, the increase in the sensitivity is accompanied by retention of the full resist thickness. However, this process suffers from the fact that a 4–5 min developing time might be considered undesirable for the automated manufacturing lines in microlithographic technology.

The electron beam exposure characteristics of PMMA of 110×10^3 molecular weight were also studied using the developer selected from the solvent–precipitant system. The exposure curves obtained are shown in *Figures 2* and *3*. Different compositions of MEK/methanol were studied and the development time was varied in order to give a fully developed pattern; the exposure curves for this developer combination are shown in *Figure 2*. It is clear that by using 40/60 MEK/methanol for 40 s development time, the results obtained in terms of sensitivity and contrast are reasonably good, compared with the other compositions. The exposure curve of PMMA 110×10^3 molecular weight developed using MEK/ethanol for different lengths of time is given in *Figure 3*, showing the variation of the sensitivity and contrast with developing time. The longer the developing time the higher the loss in the unexposed film thickness in this system, and it was calculated that there would be a total loss of about 600 Å if 60 s had been used for development. If the developing time is reduced to 20 s then there is only a 160 Å loss and a 10 s development time will reduce the loss even further to a minimum acceptable level. As the development time was reduced the contrast improved from 1.97 to 2.42. This suggests that when the development process involves a solvent selected from the cosolvent systems there is a minimum loss in film thickness whereas the solvent–precipitant system has the advantage of providing a faster development time. Because the loss of the unexposed resist is

Table 1 Comparison of clearing dose and contrast values for PMMA resists in different developers at different immersion times

Resist	Developer	Ratio	Development time (s)	Sensitivity ($\times 10^{-5}$ C cm^{-2})	Contrast, γ
PMMA 110×10^3 mol. wt	MEK/methanol	30/70	65	8.3	2.6
			120	7.6	2.3
		40/60	20	4.1	2.8
			40	2.3	5.0
		50/50	5	1.6	5.8
	MEK/ethanol	30/70	60	10	1.4
			120	8.3	1.5
			240	6.7	1.7'
		40/60	10	4.9	2.4
		20/80	3.6	2.0	–
		60/40	2.9	2.0	–
		50/50	30	2.0	2.6
PMMA 86×10^3 mol. wt	MEK/methanol	30/70	45	6.7	1.8
			120	9.1	1.4
		32/68	5	3.4	2.8
		35/65	2	4.9	2.1
			5	2.5	2.5
			50	2.4	3.7
	MEK/ethanol	30/70	15	5.4	2.1
		40/60	4	2.7	2.4
PMMA 110×10^3 mol. wt.	IPA/water (cosolvent)	70/30	180	9.0	2.1
			360	6.3	2.3
		80/20	120	3.3	3.1
			240	3.6	2.5
		90/10	180	3.3	2.8
			240	2.4	4.2
PMMA 86×10^3 mol. wt	IPA/water (cosolvent)	70/30	300	6.5	3.9
		80/20	360	8.5	1.7
		90/10	360	8.3	2.2

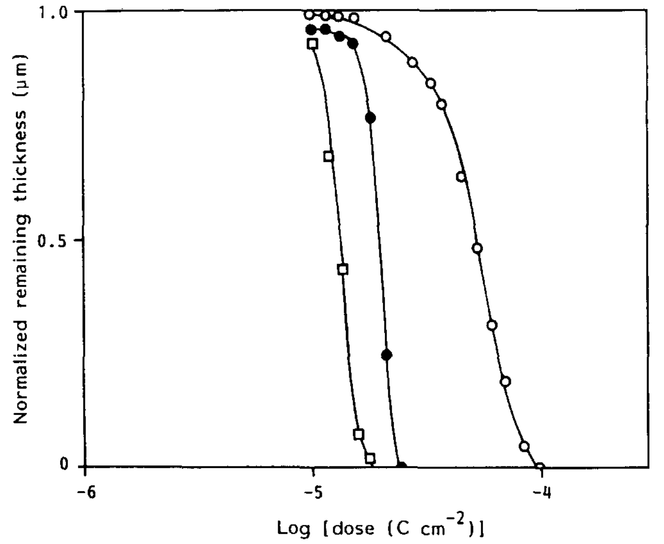

Figure 2 Exposure characteristics curves for PMMA 110×10^3 mol. wt developed in MEK/methanol: (○) 30/70 for 65 s; (●) 40/60 for 40 s; and (□) 50/50 for 5 s

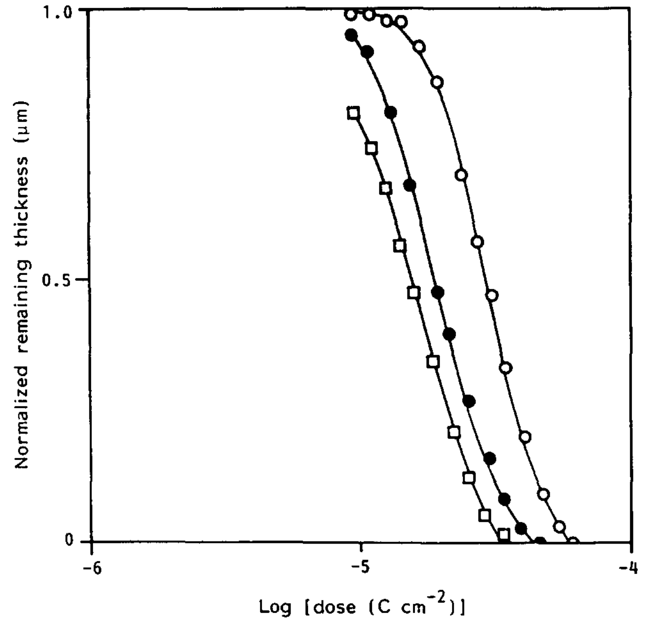

Figure 3 Exposure characteristics curves for PMMA 110×10^3 mol. wt developed in 40/60 MEK/ethanol for different times: (○) 10 s; (●) 20 s; and (□) 60 s

less than those observed in other systems, the resist will then provide an important and improved protection for the substrates during the subsequent processing, especially during plasma or reactive ion etching. The other resist sample examined in this study was PMMA with a molecular weight of 86×10^3, and the characteristic exposure curves for the various solvent developers are shown in *Figure 4*. As expected, the sensitivity of this polymer is lower than obtained for the higher-molecular-weight sample; however, the contrast remains at least as high. The influence of solvent quality, as illustrated in *Figure 4*, indicates that forced development using stronger solvent combinations leads to enhanced sensitivity, but

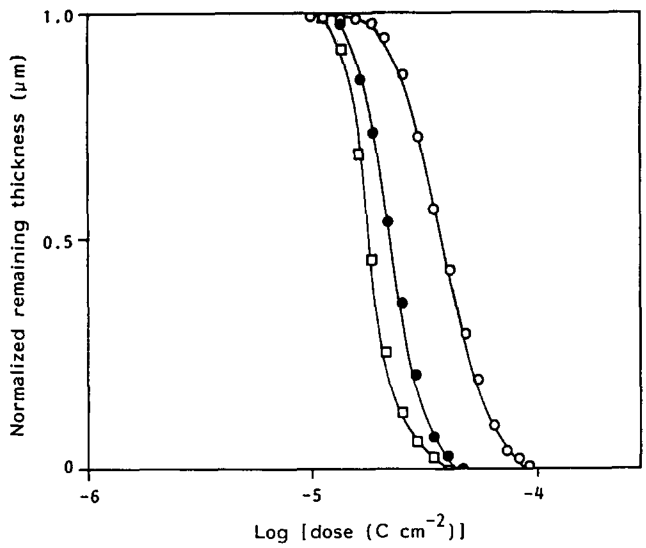

Figure 4 Exposure characteristics curves for PMMA 86×10^3 mol. wt developed at different developers and times: (○) 70/30 IPA/water for 5 min; (●) 30/70 MEK/ethanol for 15 s; and (□) 35/65 MEK/methanol for 50 s

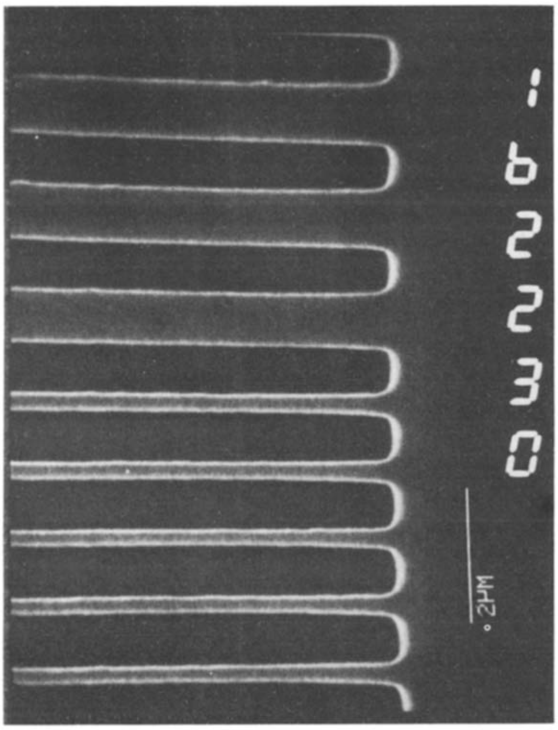

Figure 5 SEM micrograph obtained for PMMA 86×10^3 mol. wt at exposure dose of 7.7×10^{-5} C cm^{-2}, developed in 70/30 IPA/water for 5 min (0.5 and 1.0 µm lines and space)

this is often accompanied by pronounced swelling and dissolution of the unexposed regions to a significant extent. A satisfactory performance is again exhibited by this PMMA sample, which can be developed with little or no swelling using the cosolvent system containing the IPA and water mixtures. The results for each system are gathered in *Table 1*.

The resolution capability of PMMA is demonstrated in the SEM micrographs given in *Figures 5* and *6*. The most common solvent mixture, which has been considered by many workers as a standard developer, is a mixture of 3:1 methyl isobutyl ketone (MIBK)/IPA[6,7,23,24] and *Figure 7* showed the scanning electron micrograph obtained for a PMMA sample of 110×10^3 molecular weight developed in 1:3 MIBK/IPA for 60 s, followed by another 30 s in the same developer following the procedure outlined by Haller *et al.*[23]. From this micrograph one can see that the resist profile is not very clear and that swelling and stringing are very much in evidence. The resist performance and the lithograhic profile are not nearly as good as those obtained when

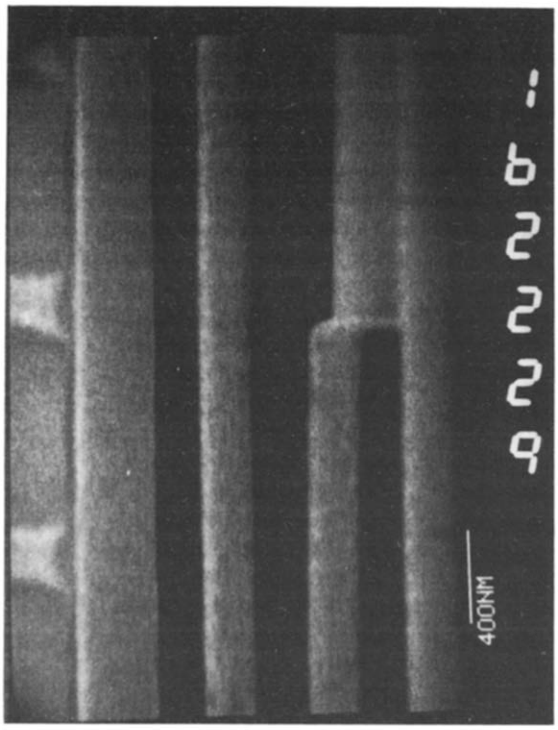

Figure 6 SEM micrograph obtained for PMMA 86×10^3 mol. wt at exposure dose of 7.7×10^{-5} C cm^{-2}, developed in 70/30 IPA/water for 5 min

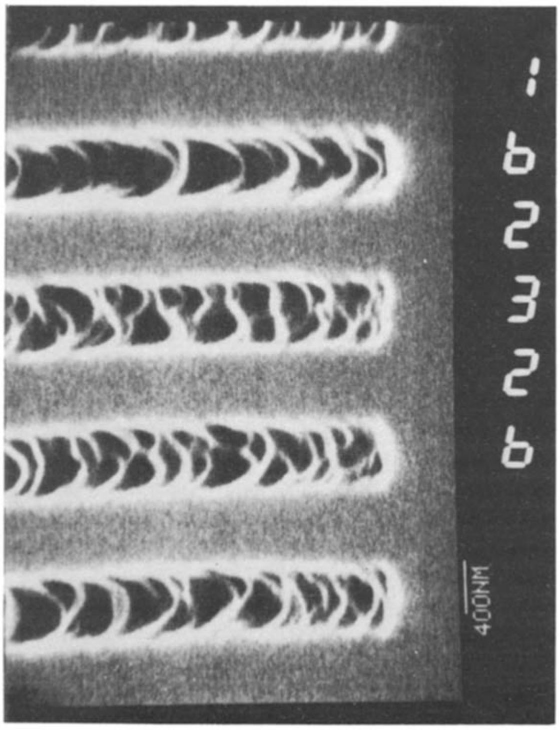

Figure 7 SEM micrograph obtained for PMMA 110×10^3 mol. wt at exposure dose of 11×10^{-5} C cm^{-2}, developed in 1:3 MIBK/IPA for 60 s then 30 s in the same developer[23]

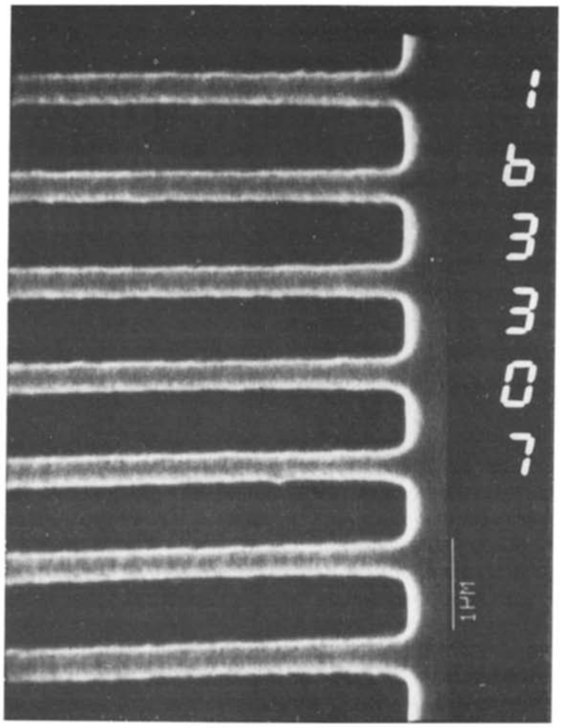

Figure 8 SEM micrograph obtained for PMMA 110×10^3 mol. wt at exposure dose of 8.7×10^{-5} C cm^{-2} developed in 40/60 MEK/ethanol for 60 s

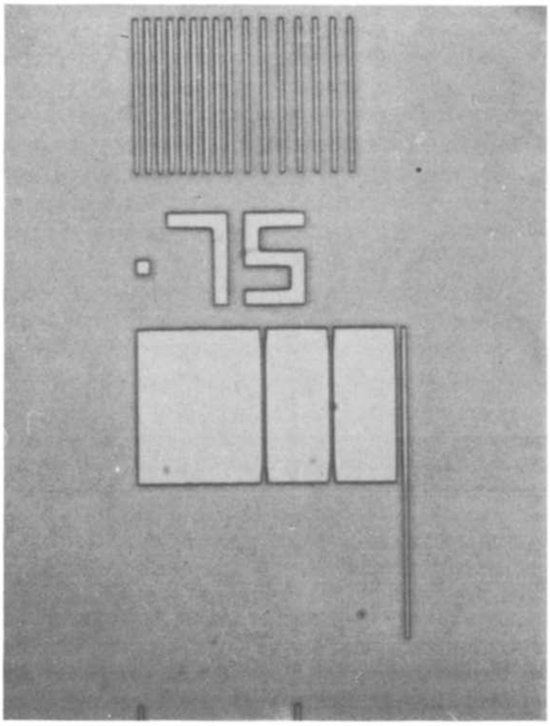

Figure 9 Optical micrograph for PMMA 110×10^3 mol. wt developed in 90/10 IPA/water for 4 min, showing a complete pattern

IPA/water is used for development, as is clearly demonstrated in *Figures 5* and *6* where virtually no stringing or swelling can be observed. The influence of the developer selected from a solvent–precipitant system is illustrated this time in the SEM micrograph shown in *Figure 8* obtained for the PMMA sample (110×10^3mol.wt) which was developed in 40/60 MEK/ethanol mixture for 60 s. This indicates that fast development with satisfactory lithographic performance can be achieved with this solvent mixture. Also the residual film thickness and pattern profile of the resist were again improved compared to the standard developer of (1:3) MIBK/IPA. *Figure 9* shows the optical micrograph for a complete pattern for PMMA developed in 90/10 IPA/water for 4 min, which was believed to be the optimum combination for the cosolvent series.

CONCLUSIONS

The micrographs obtained suggest that the cosolvent system developer gives the best results in terms of feature resolution and resist profile. The results gained from this study give some insight into the performance of different developer systems and the crucial importance of selecting the best one. Further work is being undertaken to optimize the selected developer in terms of the dissolution rate and temperature. One can conclude that development of PMMA with an IPA/water mixture, particularly the 90/10 composition, results in improved contrast and sensitivity when compared with the patterns obtained using MIBK/IPA, which has been regarded as the standard developer for this polymer. The developing time may, however, be too long for IPA/water mixtures but this can be improved by using MEK/methanol or MEK/ethanol combinations, which are also superior to the MIBK/IPA system.

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