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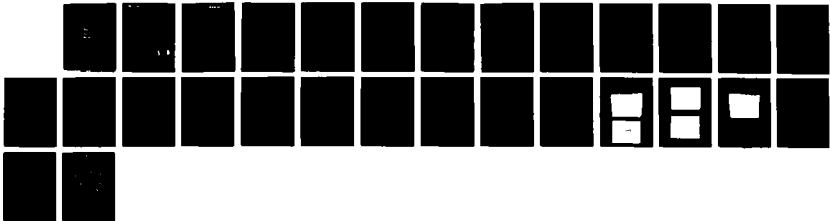
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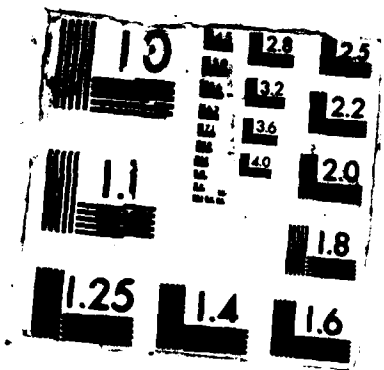
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Technical Report No. 6

CHOOSING POLYMER SOLVENTS FOR MICROLITHOGRAPHY

by

**D. Rosenthal, R. J. Groele, and F. Rodriguez
Y. M. N. Namaste, and S. K. Obendorf**

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Conference on Emerging Technologies in Materials
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Criteria for choosing solvents for coatings and dissolution processes in microlithography include: a) Thermodynamic interaction measured by viscosity level, intrinsic viscosity, or swelling, b) Dynamic interaction (transport) characterized by a diffusivity or some other rate process, such as rate of dissolution,		

- c) Volatility, control of removal, since the solvent is not a part of the final product,
- d) Safety (flammability and health hazards), and
- e) Cost.

Solvents based on ethylene oxide derivatives which contain both ether and ester linkages have been very useful in lithographic applications. However, health hazards such as fetotoxicity may be involved with such materials. In this work we found that PMAc (1-methoxy-2-propanol, acetate) and EEP (ethyl 3-ethoxy propionate) are suitable replacements for two popular ethylene oxide-based solvents, namely, MCA (2-methoxyethyl acetate) and ECA (2-ethoxyethyl acetate).

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CHOOSING POLYMER SOLVENTS FOR MICROLITHOGRAPHY

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INTRODUCTION

When solvents are selected for any polymer application, many of the same basic criteria are employed. The "goodness" of a solvent usually is stated in an equilibrium sense through the use of a thermodynamic property such as the polymer-solvent interaction parameter. However, when the specific use is microlithography, dynamic interactions should assume a prominent position. In addition, all the usual economic, safety, and engineering factors have to be included. A rather comprehensive list might be comprised of:

- a) Thermodynamic interaction measured by viscosity level, intrinsic viscosity, or swelling,
- b) Dynamic interaction (transport) characterized by a diffusivity or some other rate process, such as rate of dissolution,
- c) Volatility, control of solvent removal, since the solvent is not a part of the final product,
- d) Safety (flammability and health hazards), and
- e) Cost.

A concern for safety has always been the hallmark of the chemical industry. However, only recently have testing procedures evolved which

give a very broad basis for judging materials both as short-term and extended-time health hazards.

Solvents based on ethylene oxide derivatives which contain both ether and ester linkages have been very useful in lithographic applications. This can be ascribed in part to the specific interactions of the ether and ester bonds with polymer resists as well as the range of volatilities and viscosities obtainable. However, concerns have been expressed over health hazards such as fetotoxicity connected with these solvents (see Appendix).

Several alternative solvents have been proposed which resemble the ethylene oxide derivatives in having an ester and an ether group but which are based on a 3-carbon rather than a 2-carbon unit. In this work, two of the popular 2-carbon solvents are compared with two of the recently commercialized 3-carbon types (Table 1). The structures of these solvents are similar (Figure 1) and physical properties reported by the manufacturers and in the literature are summarized in Table 2. To date, toxicity testing has not shown Arcosolve[®] PM Acetate (PMAc) or Kodak EEP (EEP) solvent to exhibit the hazardous effects that the glycol-ether derivatives have. For PMAc and EEP, no overt toxic effects were seen even at exposure levels several-fold higher than toxic levels of the glycol ether acetates ^{1,2}. Both PMAc and EEP have a mild ester odor. EEP has no known specific exposure hazard, and PMAc is reported to have only slight inhalation, eye, and skin hazards.

EXPERIMENTAL

Two widely used glycol ether ester solvents, used for purposes of comparison, were obtained from Aldrich Chemical Company. These are referred to as MCA (methyl Cellosolve[®] acetate) and ECA (ethyl Cellosolve[®]) here, although a variety of synonyms are used in the literature (Table 1). The two recently introduced solvents suggested as replacements for MCA and ECA are 2-methoxy-1-methyl-ethyl acetate (PMAc) (supplied by Arco Chemical Company) and ethyl 3-ethoxy propionate (EEP) (supplied by Eastman Chemical Products Company). Both the PMAc and the EEP solvents were distilled before being used.

Laser interferometry was chosen as the method of dissolution rate measurement since the sample geometries and substrate materials of typical microlithographic processes can be used. A silicon wafer that has been coated with a 0.5 to 1.5 μm thick film of polymer is suspended in a glass beaker filled with the developing solvent. The solvent container includes a magnetic stirrer and a heating/cooling coil connected to a temperature bath maintained at 30 °C. The beam from an unpolarized He-Ne laser of wavelength 6328 Å is directed obliquely at the coated substrate with an incident angle of 10°. The reflected beam is directed to a silicon photocell operated in the zero bias photodiode mode so that the photocurrent produced is proportional to the reflected light intensity. A transimpedance amplifier is used to convert the photocurrent to a voltage which is displayed on a chart recorder. Hence the output of the chart recorder is a trace of the reflected light intensity as a function of time. As the polymer film dissolves, the reflected intensity should oscillate periodically due to thin film interference effects. The period of oscillation is inversely proportional to

the rate that the film dissolves. A more detailed description of the technique has been given in a previous publication³.

Films of poly(methylmethacrylate) (PMMA) were spin coated on three-inch silicon wafers with a native oxide layer. The PMMA used was Formula 950K from KTI Chemicals (6% in chlorobenzene). The resulting film thicknesses were about 1 μ m. After coating, the films were baked at 160 °C for 1 hour and annealed at 50 °C for 24 hours in a convection oven. Films were left either unexposed or flood-exposed to electrons at an incident dose of 10 or 75 μ C/cm² at 50 keV. The absorbed energy correspond to incident doses of 4 and 30 μ C/cm² when 20 keV electrons are used. The molecular weights before and after exposure as measured by GPC are shown in Table 3.

Viscosities of solutions containing 1% PMMA by weight were measured at 30 °C in an Ubbelohde viscometer for each of the solvents studied. The PMMA used was first precipitated from a commercial 6% solution of PMMA (Mw=950K) in chlorobenzene obtained from KTI Chemicals and then redissolved in each solvent.

Solutions of PMAc and EEP with 6% PMMA, respectively, were made to investigate the possible uses of PMAc and EEP as casting solvents. The solutions were spun on silicon wafers and then baked at 160 °C for 1 hour. Several thicknesses on each wafer were measured to determine the uniformity of the resist layer.

For lithographic evaluation, films were coated and baked as above, but not annealed. Patterns were exposed with an electron energy of 20 keV in a Cambridge EBMF-II-150 pattern generator. Developing was conducted in stagnant solutions and terminated with appropriate nonsolvents followed by blow drying with nitrogen. Patterns were post-baked at 100 °C for 15 minutes. Images and line profiles were observed using a Cambridge SEM. Contrast was determined by measuring film thicknesses after development of 20 μ m wide lines exposed at a series of 16 doses. The thicknesses were measured using a Tencor Alphastep thickness measuring device.

RESULTS AND DISCUSSION

Dissolution Rates

No swelling was observed in dissolution rate measurements of PMMA with MCA, ECA, PMAc, EEP, and a 1:1 mixture of MIBK and isopropanol (used as a standard) and the polymer films dissolved uniformly without leaving residue on the wafer. Figure 2 shows a typical computer readout from the interferometer dissolution rate monitor (DRM) and shows the uniform dissolution of PMMA in that particular solvent. This uniform sinusoidal output with constant period and amplitude indicates that the polymer film was dissolving at a constant rate and with negligible swelling. DRM outputs for the other solvents studied in this report are similar. MCA developed PMMA the fastest and 1:1 MIBK:IPA was the slowest (Table 4). All the dissolution rates in Table 4 are in a usable range for developing patterns produced with electron beam lithography.

The change in dissolution rate with molecular weight (Figure 3) is similar for the four ether-ester solvents. Cooper's data (based on unexposed PMMA with $M_n = 320K$) are included in Figure 3⁴. She used methyl ethyl ketone, MEK, as the developing solvent at 17.5 °C. The results are quite comparable. It should be noted that the lower molecular weights were obtained by exposure to electrons which causes them to dissolve faster than the same molecular weight spun on the wafers without exposure.

Dissolution rates were measured using both dry ether-ester solvents and the same solvents containing 2.5% water. It has been reported previously that water accelerates the dissolution of several polymers by ketones^{5,6}. The mechanism appears to be one of rapid diffusion by the small water molecules which act as a plasticizer thus increasing the diffusion rate of the larger solvent molecules. This process apparently occurs even though water itself is not a solvent for the polymer.

EEP is more sensitive to added water than the other three solvents (Table 5). Accelerated dissolution with added water was observed in all cases. Because the effect does not change when exposed films are used, there is no added differential sensitivity contributed by the added water. It is, however, good to be aware of the possible changes in dissolution rate brought about by the presence of water in these and most ketone and alcohol solvents. Variations in humidity during processing and storage of films and solvents can seriously affect the development of PMMA films.

Lithographic Evaluation

Electron beam lithographic patterns were developed with PMAc, EEP, MCA, ECA, and a 1:1 mixture of MIBK:IPA which is a standard developer for PMMA. Resolution, contrast, and thinning were evaluated. MCA and ECA are not commonly used as developers for PMMA, but they have been included in this comparison because of their use in developing other resist systems in microlithography. SEM images of the patterns developed by the PMAc, EEP, standard, MCA, and ECA solvents are shown in Figure 4. All five patterns were clearly developed, with both PMAc and EEP exhibiting resolution comparable to that observed using the standard developers. The linewidth in the five patterns is 1 μm . The developed patterns are free of scumming, and distortions due to swelling are not observed. The unexposed areas do not show any pitting or stress-cracking, and the resist adhesion is not altered by the use of these developers.

Contrast curves (lithographic response curves) are shown for each of the developing solvents in Figure 5. Contrast data and developing times are presented in Table 6. For purposes of comparison, the contrast (at doses of 40 $\mu\text{C}/\text{cm}^2$ and 60 $\mu\text{C}/\text{cm}^2$) was estimated for each of the solvents by interpolation and extrapolation of the contrast data (Table 7). After an exposure dose of 40 $\mu\text{C}/\text{cm}^2$, development with the PMAc provides a high contrast

($\gamma = 4.1$), nearly as high as that of the standard developer (1:1 MIBK:IPA, $\gamma = 5.6$) (Table 7). EEP exhibits an acceptable contrast (3.3). MCA, ECA, and EEP all give roughly the same contrasts at 40 and 60 $\mu\text{C}/\text{cm}^2$. At a dose of 60 $\mu\text{C}/\text{cm}^2$ the standard exhibits the highest contrast (8.0) but the PMAc still shows very good contrast of (5.7). In all cases, the contrast is greater than that required for development of patterns with adequate resolution ($\gamma = 1$).

The standard developer for PMMA (1:1 mixture of MIBK and 2-propanol) is a very selective solvent for dissolving low molecular weight PMMA, and dissolves PMMA much more slowly than any of the other solvents evaluated (Table 4). For this reason, there is somewhat less thinning of unexposed resist with the standard developer than with the other solvents. However, the thinning behavior of these solvents might be similar when developing lower doses in the regime of forced development. Further lithographic evaluation would be required to complete the thinning comparison for the low dose region. Less thinning was suffered when developing with EEP and PMAc than with the glycol ether derivatives.

Casting Solvents

PMMA films made by spinning solutions of PMAc and EEP, each with 6% PMMA, exhibited uniform film thickness and were free of defects. The uniformity of the thicknesses of the resist layer for all the wafers tested were all within 10 nm.

Other Physical Properties

The physical properties of MCA and ECA, are similar to those of PMAc and EEP, except that EEP exhibits a somewhat lower vapor pressure and lower evaporation rate than the other solvents (Table 2). The lower volatility of the EEP may be desirable in that it could reduce exposure levels of the vapors to

workers. The viscosities of all the solvents are approximately equal and their boiling points range from 140 °C to 165 °C. The high boiling points and low evaporation rates of these solvents are desirable for developing lithographic patterns, because volatile developing solvents will cool the substrate and cause moisture condensation. If the evaporation rate of the casting solvent is too high, the solvent will evaporate during spin-coating producing poor film thickness uniformity. Therefore, high boiling solvents are also desirable for casting resist films. It is also important that the boiling points of the developing solvents be well below 200 °C so that the post-bake temperature used for removing residual developer does not need to be too high. This reduces the risk of thermal deformation of the developed patterns, and possible crosslinking of the resist during the prebake step.

The solubility parameters of the PMAc and EEP solvents are similar to those of ECA and MCA (Table 2). This indicates that these solvents should be suitable for developing similar polymer resists. This range of total solubility parameters is similar to that reported for PMMA ($d = 17.8-19.4 \text{ MPa}^{1/2}$)⁷.

Viscosity measurements were made with the four solvents using concentrations of 1% by weight PMMA (950,000 weight average molecular weight). The calculated relative viscosities were all around 2.4 except for that of MCA which was slightly higher (Table 8), indicating that these solvents are thermodynamically similar in their ability to dissolve PMMA.

CONCLUSIONS

The glycol ether derivatives have gained widespread use in the microelectronics industry as resist developing solvents, casting solvents, and stripping solvents for various resist systems. However, the recent reports of toxic and teratogenic effects have caused serious concern for the industry. The PMAc and EEP solvents thus far have not been found to exhibit

these toxic effects, although their structures are similar to those of the glycol ether derivatives.

PMAc and EEP are suitable alternative solvents for typical applications in resist processing. Our evaluation of dissolution behavior and microlithographic performance has shown that PMAc and EEP are similar to ECA and MCA in sensitivity to water and molecular weight and are superior to ECA and MCA in lower vapor pressure and evaporation rate, contrast, and thinning behavior. PMAc and EEP were also found to be suitable as casting solvents.

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research. ARCO Chemical Company and Eastman Chemical Products Company supplied PMAc and EEP solvents, respectively. The authors also acknowledge the use of equipment at the National Research and Resource Facility for Submicron Structures and the assistance of Brian Whitehead with the electron exposures.

Appendix : Toxicity Hazards

"The National Institute for Occupational Safety and Health (NIOSH) recommends that 2-methoxyethanol (2ME) and 2-ethoxyethanol (2EE) be regarded in the workplace as having the potential to cause adverse reproductive effects in male and female workers. These recommendations are based on the results of several recent studies that have demonstrated dose-related embryotoxicity and other reproductive effects in several species of animals exposed by different routes of administration. Of particular concern are those studies in which exposure of pregnant animals to concentrations of 2ME and 2EE at or below their respective Occupational Safety and Health administration (OSHA) Permissible Exposure Limits (PEL's) led to increased incidences of embryonic death, teratogenesis, or growth retardation. Exposure of male animals resulted in testicular atrophy and sterility. In each case the animals had been exposed to 2ME or 2EE at concentrations at or below their respective Occupational Safety and Health Administration Permissible Exposure Limits" ⁸.

All of the information above also pertains to the glycol ether acetate derivatives of 2ME and 2EE⁸ which, in this paper, are called MCA and ECA respectively (Table 1) . It has been reported that oral doses of ECA and MCA produced marked testicular atrophy and leukopenia⁸. More recently, in a NIOSH-sponsored teratology study, test animals (pregnant rats) exposed to 130, 390, and 600 ppm of ECA by inhalation showed adverse results in the offspring characterized by cardiovascular and skeletal defects. In the test animals exposed to 600 ppm, total embryo lethality, fetotoxicity, and severe cardiac malformations were observed. One fetus in the test animals exposed to 130 ppm showed the same type of cardiac malformation as one of those exposed to 390 ppm⁹. Both ECA and MCA have toxic effects on the blood, kidney, liver, central nervous system as well as the reproductive system. On January 24, 1984, the Environmental Protection Agency (EPA) published in the Federal Register their intent to start developing regulations to reduce exposure to four basic glycol

ethers and acetates : ethyl glycol ether, methyl glycol ether, ethyl glycol ether acetate, and methyl glycol ether acetate ¹⁰. All this evidence points to the need to move away from the 2-carbon based solvents and their acetate derivatives and to find feasible replacement solvents which are safer.

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Table 1

Solvent Synonyms

Methyl Cellosolve[®] acetate (MCA)

Ethylene glycol methyl ether acetate

Ethylene glycol monomethyl ether acetate

Glycol monomethyl ether acetate

2-methoxyethyl acetate

Methyl glycol acetate

Monomethyl ether of ethylene glycol acetate

Ethyl Cellosolve[®] acetate (ECA)

Cellosolve[®] acetate

Cellosolve[®] acetate solvent

2-Ethoxyethyl acetate

Ethylene glycol ethyl ether acetate

Glycol ethyl ether acetate

Glycol monoethyl ether acetate

Hydroxy ether acetate

Ethylene glycol monethyl ether acetate

Arcosolve[®] PM Acetate (PMAc)

1-methoxy-2-propanol, acetate

PGME acetate

Propylene glycol methyl ether acetate

"EKTAPRO"[®] EEP solvent (EEP)

EEP solvent

Ethyl 3-ethoxypropionate

Table 2

Physical Properties

<u>Solvents</u>	<u>Boiling point, °C</u>	<u>Vapor pressure @25°C, mm Hg</u>	<u>Evaporation rate (BuAc=1)</u>	<u>Viscosity @30°C, cp</u>	<u>Solubility parameter (MPa)^{1/2}</u>
MCA	143	3.46	0.31	0.993	20.6
ECA	156	2.12	0.20	1.135	19.8
PMAc	140	3.80	0.34	1.100	19.7
EEP	165	1.11	0.12	1.124	19.1

Table 3

Molecular Weights of PMMA on Exposure to 50 keV electrons

<u>Dose ($\mu\text{C}/\text{cm}^2$)</u>	<u>Mn</u>	<u>Mw</u>
unexposed	360,000	930,000
10	71,000	115,000
75	14,000	32,000

Table 4

Dissolution Rates of unexposed PMMA

<u>Solvent</u>	<u>Dissolution rate ($\mu\text{m}/\text{min}$), 30 °C</u>
MCA	0.2164
ECA	0.0710
PMAc	0.0352
EEP	0.0213
1:1 MIBK:IPA	0.0022

Table 5

Effect of 2.5% water on Dissolution Rate

<u>Solvent</u>	<u>$\frac{(\text{DR})_{\text{water}}}{(\text{DR})_{\text{dry solvent}}}$</u>			
	<u>$M_n=14\text{K}$</u>	<u>$M_n=71\text{K}$</u>	<u>$M_n=360\text{K}$</u>	<u>Average</u>
MCA	1.36	1.45	1.43	1.41
ECA	2.05	1.81	1.82	1.89
PMAc	1.76	1.74	1.74	1.75
EEP	2.89	2.59	2.53	2.67

Table 6**Contrast Comparison**

<u>Solvents</u>	<u>Developing time (min)</u>	<u>Contrast (γ)</u>
ECA	1.1	3.7
	1.5	3.6
MCA	0.5	3.8
	0.8	2.5
EEP	3	3.8
	5	3.3
	7	3.5
	10	3.2
PMAc	1.5	5.7
	3	4.2
	5	3.7
	10	3.1
1:1 MIBK:IPA	7	6.8
	10	6.3
	15	5.9

Table 7**Contrast obtained with the various solvents for development**

<u>Solvent</u>	<u>$\gamma @ 40 \mu\text{C}/\text{cm}^2$</u>	<u>$\gamma @ 60 \mu\text{C}/\text{cm}^2$</u>
EEP	3.3	3.5
PMAc	4.1	5.7
ECA	3.5	3.9
MCA	2.7	3.9
1:1 MIBK:IPA	5.6	8.0

Table 8**Viscosity data**

<u>Solvent</u>	<u>Solvent viscosity, cp, 30 °C</u>	<u>Relative viscosity, cp, 30 °C of a 1% PMMA* Solution</u>
MCA	0.99	3.22
ECA	1.14	2.37
PMAc	1.00	2.47
EEP	1.12	2.42

* $M_w = 950,000$

Figure 1

Chemical Structure of Ether-Ester Solvents

<u>Solvent</u>	<u>Structure</u>	<u>Formula Weight</u>
MCA	$\text{H}_3\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	118.13
ECA	$\text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	132.16
PMAc	$\text{H}_3\text{C}-\text{O}-\overset{\text{CH}_3}{\underset{ }{\text{CH}_2}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	132.16
EEP	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$	146.2

Figure 2

**Dissolution Rate Monitor output for unexposed PMMA
developed with Kodak EEP at 30 °C**

Calculated Dissolution Rate = 0.034 $\mu\text{m}/\text{min}$

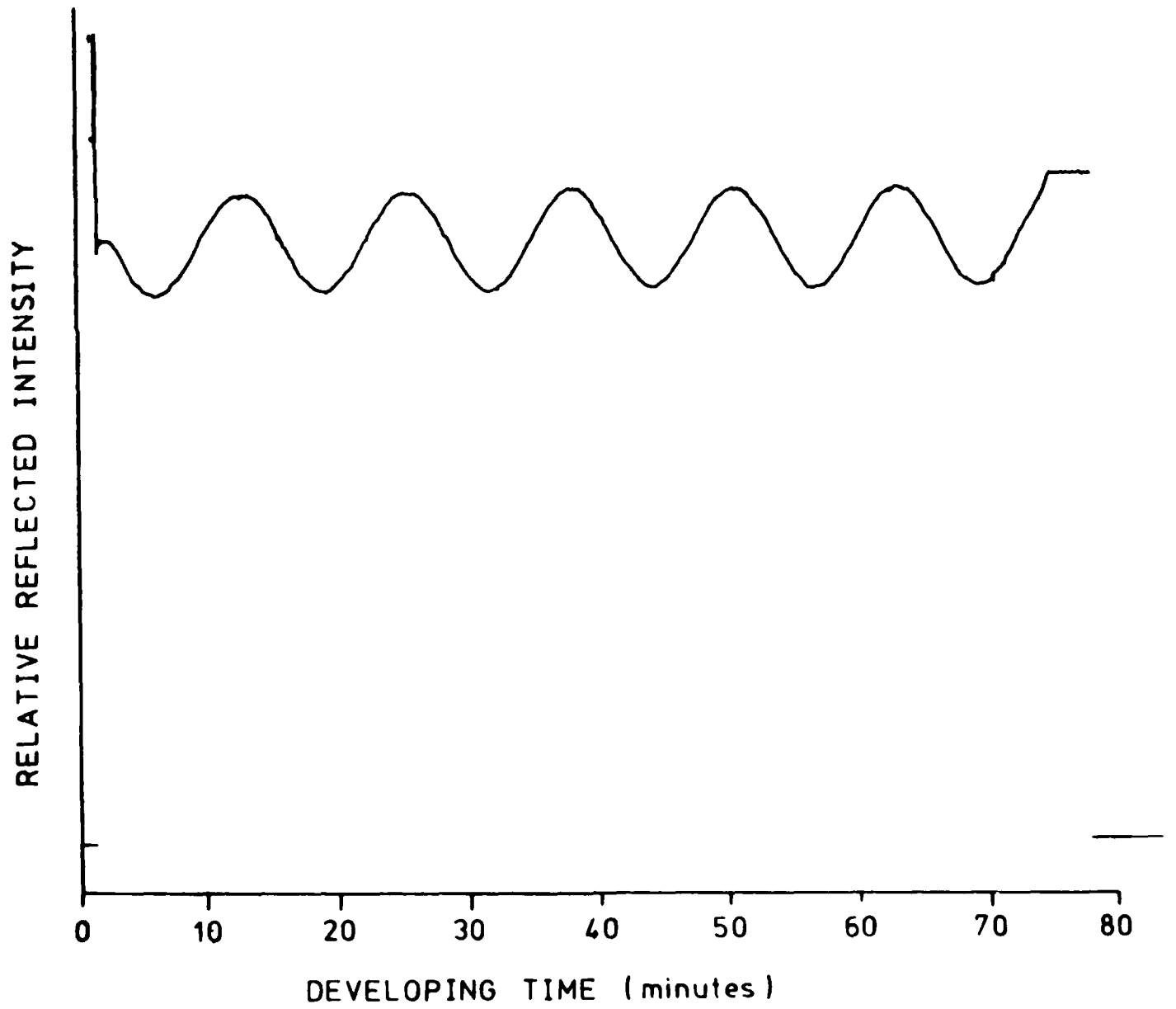


Figure 3

The dissolution rate (DR) divided by DR for the unexposed, high molecular weight PMMA (DR^*) is shown for the four ether-ester solvents. Similar data were obtained by Cooper using MEK as the solvent.

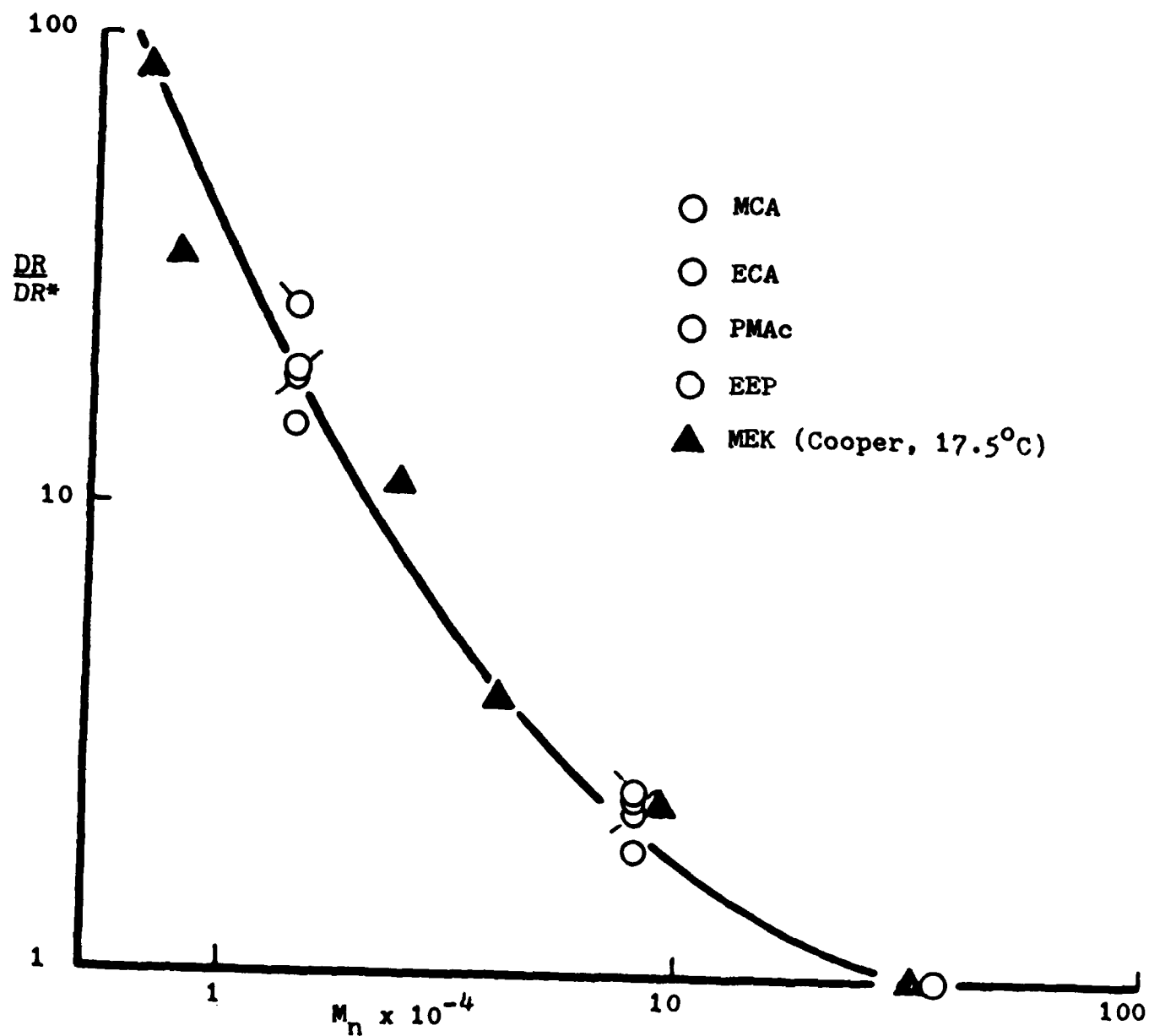
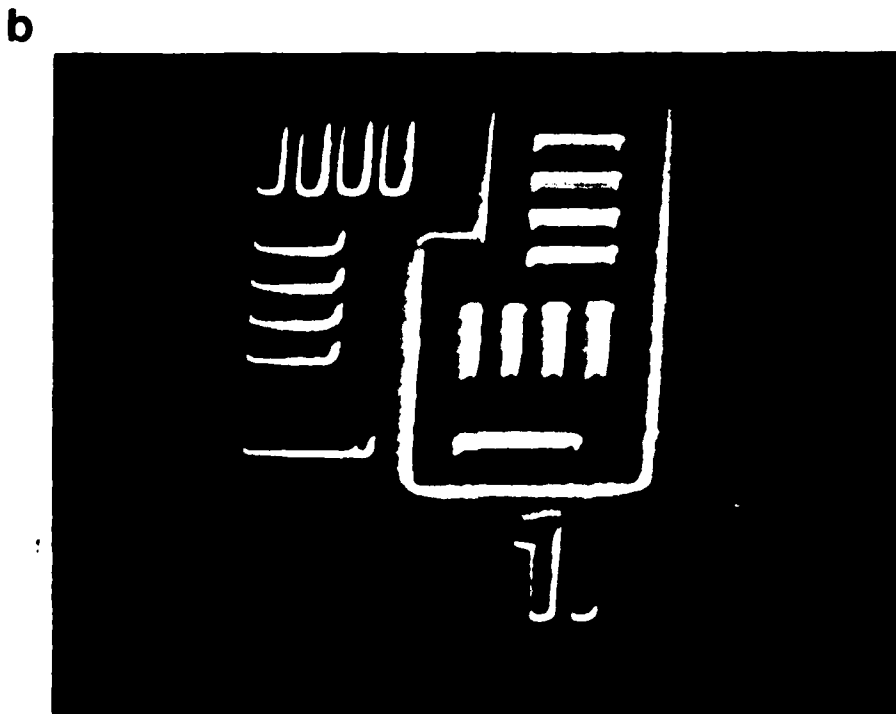
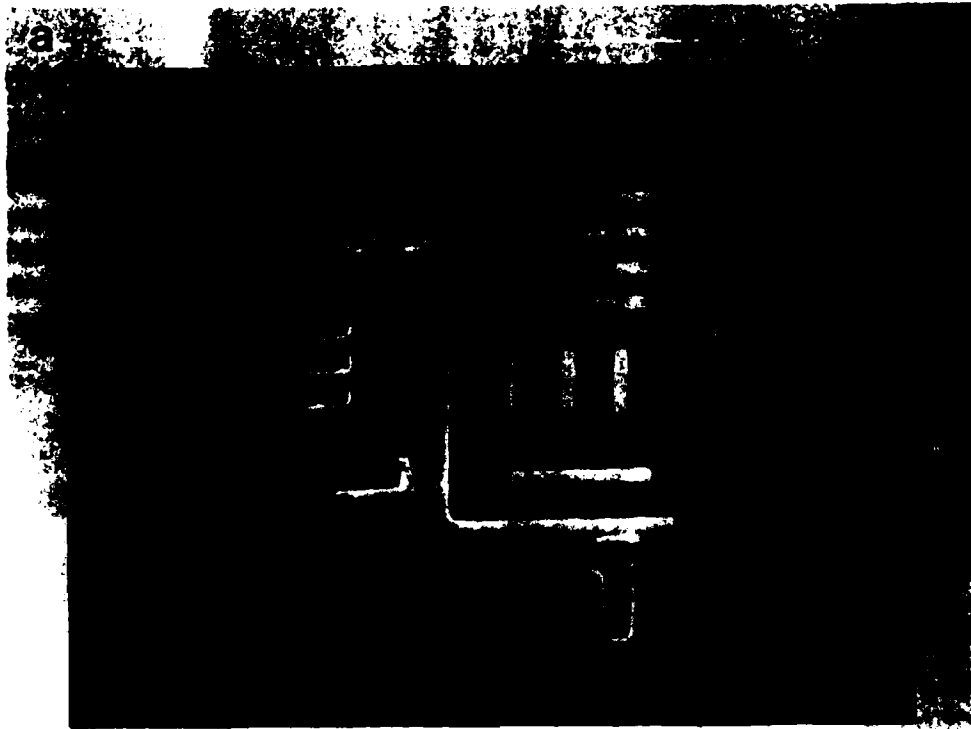


Figure 4

SEM photomicrographs of patterns exposed in PMMA at a dose of $80 \mu\text{C}/\text{cm}^2$ and developed with (a) Arcosolve[®] PM Acetate, (b) Kodak EEP, (c) 1:1 MIBK:2-propanol, (d) Methyl Cellosolve[®] Acetate (MCA), (e) Ethyl Cellosolve[®] Acetate (ECA).



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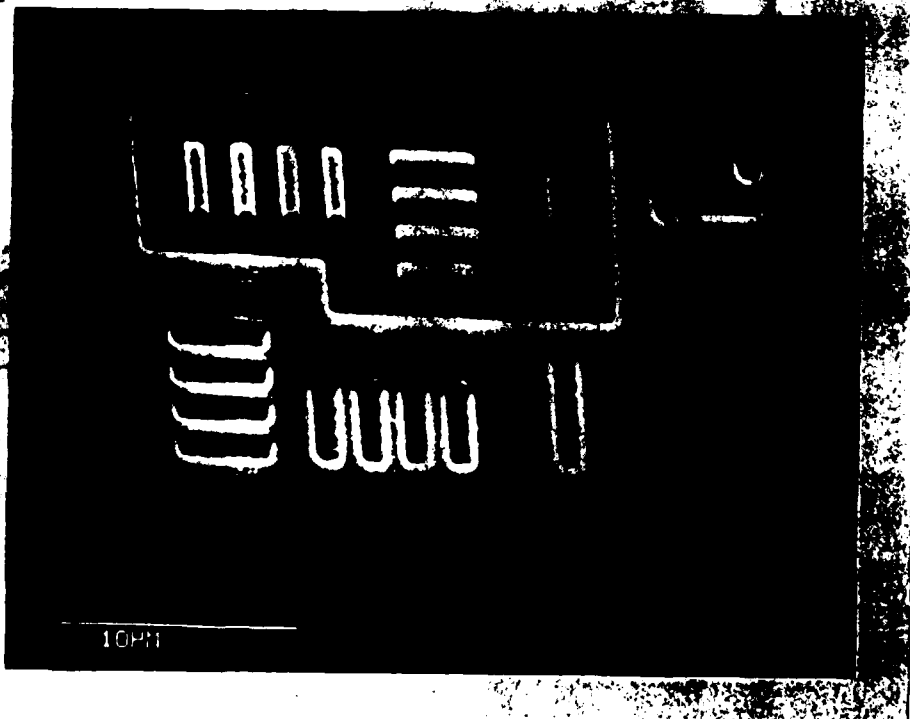
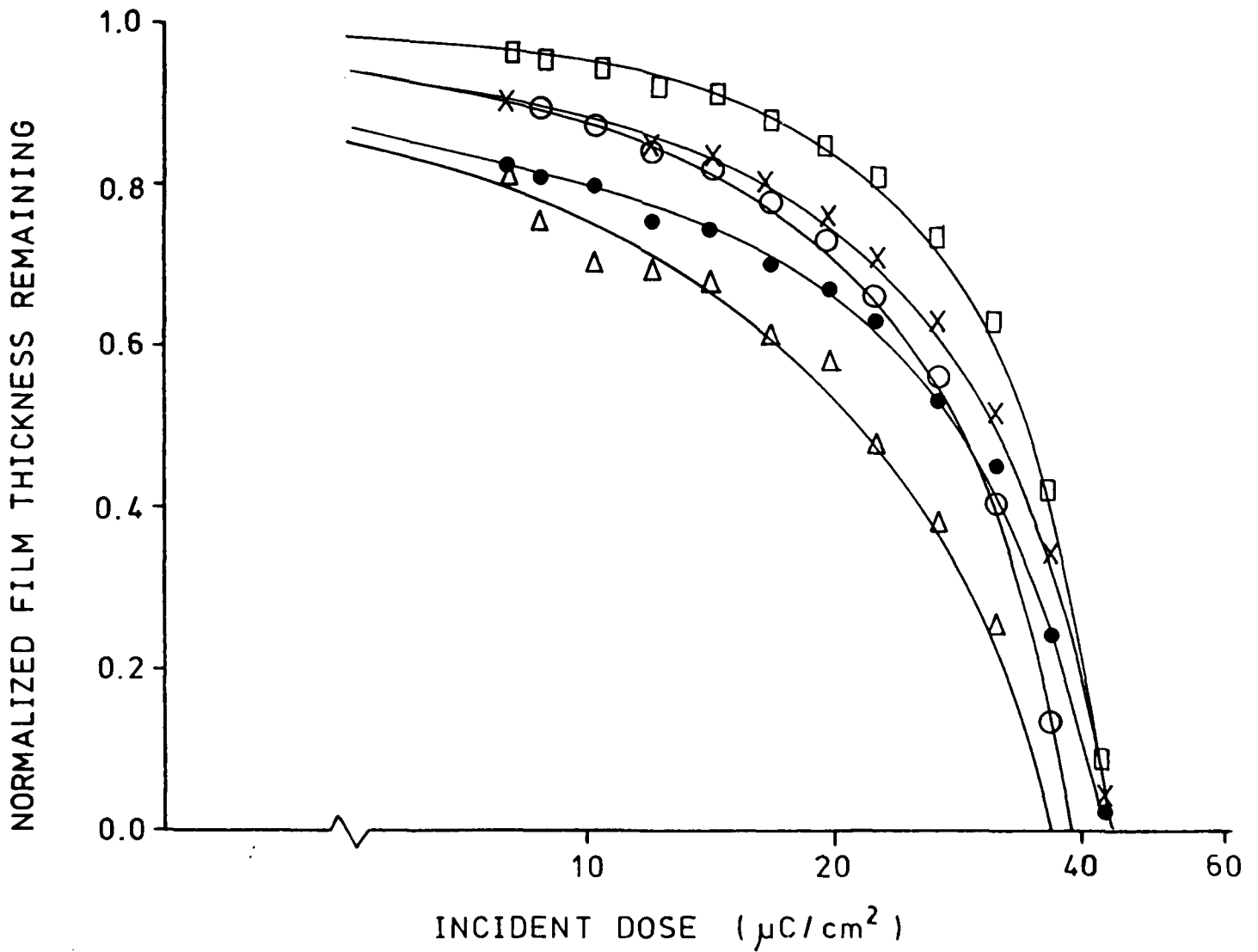
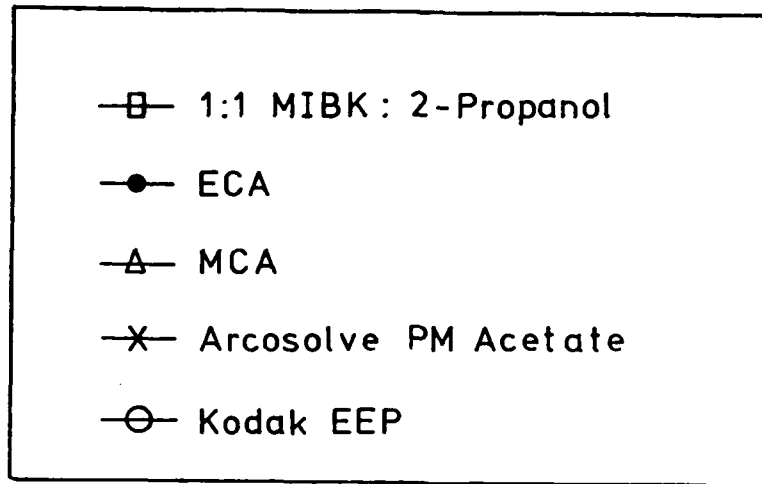




Figure 5

CONTRAST CURVES FOR PMMA WITH VARIOUS SOLVENTS



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