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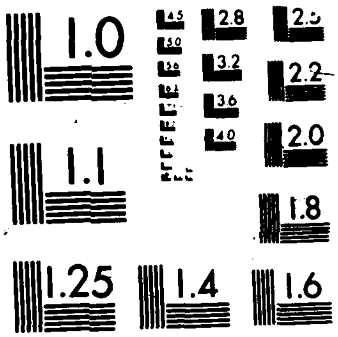
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Technical Report No. 3

SENSITIVITY OF POLYMER BLENDS TO SYNCHROTRON RADIATION

by

J. A. Jubinsky, R. J. Groele, F. Rodriguez,
Y. M. N. Namaste, and S. K. Obendorf

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Fall Meeting of the American Chemical Society
(Division of Polymeric Materials:Science and Engineering)
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Ithaca, NY 14853

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The sensitivity of poly(methylmethacrylate), PMMA, to x-rays is enhanced by the addition of poly(epichlorohydrin), CO rubber. The two polymers appear to be miscible over a wide concentration range. Films with 20 to 50% CO in PMMA require only 1/2 to 1/4 the exposure dose of synchrotron radiation to produce an equivalent pattern in PMMA alone. The sensitivity is confirmed by measurements of molecular weight of blends irradiated by gamma rays or electrons, a well as x-rays. Dissolution behavior of the blends also is similar to that for PMMA.

SENSITIVITY OF POLYMER BLENDS TO SYNCHROTRON RADIATION

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INTRODUCTION

When the resolving power of photolithography is to be exceeded, the two technologies that are most often called upon are electron-beam and x-ray lithography. For purposes of discussion, the lower limit of features using optical (deep UV) methods may be placed at about 0.5 μm. Electron beams currently can be used to produce features from 1.0 to 0.5 μm. Since backscattering is not a problem, the minimum dimensions obtainable with x-rays in deep films may well be smaller than those obtained with electron beams. Moreover, x-ray lithography is efficient for large volume production of chips. Electron-beam technology has been widely used for some time in mask-making and for customized, low-volume chip production, so a considerable body of information has been acumulated on the response of polymers to 20- to 50-keV electrons. A similar body of information does not exist on the response to x-rays.

There are currently three types of x-ray sources available to researchers: anodic, in which high-energy electrons act on a metal target; plasma, in which IR or UV laser radiation acts on a metal target; and synchrotron, in which a beamline is attached to a high-energy electron storage ring. Anodic sources are the least expensive type, but they are from 100 to 10,000 times less intense than the other sources. As source strength is increased and exposure times reduced, sensitivity is a less urgent matter. When the response of a given resist to x-rays is being measured, the wavelength of the radiation has to be taken into account also. While synchrotron radiation is intense, the energy distribution may not be concentrated in the regions corresponding to efficient absorption by the atoms making up the resist.

Several reports have been published on x-ray resists in recent years. Haelbich et al. (1) compared the performance of PMMA using synchrotron radiation with that using e-beam radiation. Yaakobi (4) et al. used a laser-ion x-ray source. The general topic of x-ray resists has been reviewed by Lane (3) and Taylor (4). A very optimistic view of the future for synchrotron-based lithography was taken by Wilson (5). More guarded predictions of eventual application of x-rays have been made by Broers (6) and Heuberger (7).

Poly(methylmethacrylate), (PMMA), is one resist which is especially favored by researchers due to its high resolution and contrast (γ = 2 to 3). Linewidths as small as 100 Å have been produced with an extremely high dose (10 J/cm^2) using PMMA. However, even PMMA's normal sensitivity of 600-1000 mJ/cm^2 is too slow for commercial use. There have been many attempts to improve the sensitivity of PMMA to electron beam irradiation mainly by copolymerization (8). In the current paper, we describe an alternative approach whereby a sensitive polymer is physically blended with PMMA to increase its sensitivity and yet maintain the good film qualities associated with PMMA as a positive x-ray resist.

Poly(epichlorohydrin), CO rubber* (Hydrin^R), was chosed fo various reasons. The main reason was that CO has been shown to be miscible with PMMA by Anderson based upon differential scanning calorimetry (DSC) which showed only one glass transition temperature (T_g) for the blend (9). Since T_g is very sensitive to the disruption of the local structure that results when two polymers are mixed, the existence of a single glass transition temperature is a good indicator of miscibility (10). CO contains chlorine which tends to enhance x-ray absorption especially near the absorption edge of 4.4 Å. It was hoped that the increase in absorption would produce more secondary electrons which would in turn increase the sensitivity of PMMA.

Our exploratory work indicated that CO degrades rapidly on gamma radiation. Taylor et al. (11), using a very high molecular weight CO, has reported that CO crosslinks appreciably when exposed to $Pd_{L\alpha}$ x-rays. In the present work no decrease in solubility has been observed and only a very slight broadening of the molecular weight distribution.

EXPERIMENTAL PROCEDURE

CO rubber (Hydrin 100) was obtained from the B.F. Goodrich Chemical Company. Based upon gel permeation chromatography (GPC) using tetrahydrofuran (THF) as a carrier solvent, the CO has a

---

*ASTM abbreviation for this polymer.

polystyrene equivalent number average molecular weight (M_n) of 303×10^3 and weight average molecular weight (M_w) of 598×10^3. DSC results by Anderson showed that it has a glass transition temperature of -20°C (9). The PMMA used was Rohm and Haas A-100 with M_n of 113×10^3 and M_w of 213×10^3.

Three mixtures of CO-PMMA were blended together for analysis of lithographic performance. Compositions of 20, 33, and 50% CO by weight were blended by dissolution in THF to form a 13% (total solids) solution. Cyclohexanone was added to the blend to form a 7% solution to impart proper viscosity and volatility for casting films. In the case PMMA with $M_n = 950 \times 10^3$, CO was dissolved in hot chlorobenzene and then mixed with PMMA (also in chlorobenzene).

The films were spun at 1250 RPM for 1 minute on three-inch silicon wafers. The wafers were baked at 150°C for 1 hour in a forced-convection air oven. Film thicknesses ranged between 0.8 and 1.3 micrometers. PMMA samples were also prepared using the same casting solvent mixture and baking conditions.

Gel permeation chromatography was used to determine polymer molecular weights. The model used was a Waters Associates 201 HPLC with 4 μStyragel columns (nominal pore sizes of 500, 10^3, 10^4, and 10^5 Å). THF was used as the carrier solvent. The molecular weights were reported as polystyrene equivalents with the exception of PMMA for which a PMMA calibration standard was used.

Glass transition temperatures (T_g) were measured using a Perkin Elmer Differential Scanning Calorimeter (DSC) model DSC-2C. DSC measures glass transition temperatures by supplying energy to the sample and to a reference to keep them both at the same temperature. At the glass transition temperature, there is a change in the specific heat of the sample. This causes a change in the amount of heat required to keep the sample and the reference at the same temperature. This will show up as a step change in the baseline of a heat supplied versus temperature curve.

The x-ray exposures were carried out using synchrotron radiation delivered by the National Synchrotron Light Source at Brookhaven National Laboratories. The beamline was built by IBM and has been described elsewhere (12,13). In summary, the storage ring operates with electron energies at 750 MeV and a magnetic radius of 1.91 meters. The current in the ring, which degrades with time, ranges between 75 and 250 mA. The actual power through the beryllium window and incident on the wafer ranged from 2.3 to 7.5 mW/cm^2 in the present work. Samples were exposed to synchrotron radiation through a gold-on-boron nitride mask and then developed using various mixtures of isopropyl alcohol (IPA) and methyl isobutyl ketone (MIBK). Development was conducted under stirred conditions using a constant temperature bath at 23°C and was terminated by blow drying with compressed air. Film thicknesses were measured by a Tencor Alpha Step.

Electron beam exposures were performed using a modified RCA model EMV-3 transmission electron microscope. The aperture was opened to allow the beam to spread out over an entire 3-inch wafer to give uniform exposure. The accelerating voltage was 50 keV, and the dose was measured using a faraday cup.

Gamma radiation was carried out in Cornell's Ward Reactor Laboratory. Using ^{60}Co, rates of about 0.5 Mrad/hour can be achieved. Bulk, rather than film, samples were used. They were held in nitrogen-purged test tubes during exposure.

Laser interferometry was used to study the dissolution rate of some of the films used in this work (14,15). A 632.8 nm wavelength beam of unpolarized light from a 2 mW He-Ne laser is directed on a submerged wafer coated with a polymer film. The angle of incidence is approximately 10°. Reflected light from the polymer-solvent and polymer-substrate interfaces is directed toward a photocell which is coupled to a chart recorder. As the polymer solvent interface begins to recede due to dissolution, constructive and destructive interference from the interface takes place, and a sinusoidal output is recorded. By measuring the period of the sinusoidal curve, the dissolution rate can be determined.

RESULTS AND DISCUSSION

Lithographic performance of the CO-containing samples was evaluated by constructing contrast and thinning curves. Contrast curves were constructed by measuring the dissolution rate for various doses and arbitrarily chosen development times. Typical contrast curves are shown for the 33% CO blend and for the PMMA (Figure 1). From the contrast curves, thinning curves were constructed by plotting the unexposed normalized thickness remaining versus the dose required for complete development (Figure 2).

The thinning curves show that the 33% CO blend is more sensitive than PMMA. However, the contrast of the blend is somewhat reduced. Resist contrast is very important in x-ray lithography because mask contrast tends to be low. This is due to the fact that the most absorbing materials such as gold are only about a factor of 50 higher in their absorption coefficients than the most transparent. In comparison, optical contrast can be as high as 10^{10}. Poor resist contrast in conjunction with the inherently poor mask contrast will result in increased thinning and sloping sidewalls. The gold on boron nitride mask used in the present work (see below), for example, had an effective ratio of 10:1 for intensity in the open versus the masked areas.

Referring to Figure 2, there is a trend toward increasing sensitivity as the percentage of CO is increased indicating that CO imparts its good sensitivity to the blend. For example, at 20% thinning, the dose required to completely develop the 33 and 50% CO blends are 2 and 3 times less, respectively, than that needed for PMMA. However, this occurs at the expense of contrast which is reduced by 25 to 40 percent. Furthermore, as the allowable percentage of thinning is reduced, the difference in sensitivity narrows. This is discussed later. One does not notice any trend with respect to contrast among the CO blends. The 33% blend appears to have the best contrast, but it is still significantly lower than that of the PMMA.

The mechanism behind the increase in the sensitivity of the blend appears to involve the scissioning and dissolution properties of CO. At low concentrations, CO initially speeds up the development rate of the blend as compared to PMMA. However, as the concentration of the CO is increased (between 20 and 33%), the dissolution rate does not increase as rapidly. When the blend is exposed to radiation, the CO scissions and its molecular weight is decreased. The decrease in molecular weight behaves as if one was decreasing the percentage of CO in the blend which results in the enhancement of the dissolution rate. This was confirmed by utilizing a lower molecular weight ($M_n = 86 \times 10^3$) CO sample obtained by gamma irradiation. A 33% by weight CO blend using the low molecular weight CO sample was spin coated under the same conditions as previously described. The dissolution rate of this unexposed blend was about 8 times faster than an unexposed higher molecular blend (using a 45% IPA-MIBK development mixture). Thus, the increase in the dissolution rate between the exposed and unexposed regions appears to be primarily due to the scissioning of the CO. This accounts for the increase in sensitivity.

At high doses, the ability of the CO to influence the dissolution rate is diminished since its absolute molecular weight is no longer changing significantly. It appears that the main mechanism for increasing dissolution at higher doses is not due to the degradation of the CO, but the scissioning of the PMMA. This accounts for the apparent similarity in behavior of PMMA and the blends at high doses. Thus, the increased sensitivity of the blends is realized only in the "forced developing" regimes.

The relative response of CO/PMMA blends to various forms of radiation can be compared. In the first place, gamma radiation of bulk samples of CO or PMMA results in values of G(s) = 5.1 scissions/100 eV for CO compared to 0.8 for PMMA (Figure 3). It is not so surprising that a rubbery polymer like CO should have a high sensitivity. It is interesting that the structure leads primarily to scissioning with little crosslinking (G(x) = 0.5 at most). It is presumably the ether linkage in combination with the substituted chain carbon which leads to scission. Poly(ethylene oxide), in contrast, crosslinks readily, even in dilute solution as long as oxygen is excluded (16). Taylor (11) found that the disubstituted homolog, poly(cis-1,2-dichloromethyloxirane), was unequivocally a scissioning compound, but that CO appeared to crosslink somewhat. As mentioned earlier, this may have been due to the higher molecular weight CO which he employed.

Sensitivity of CO to electrons and x-rays was characterized by comparing a blend with PMMA to PMMA alone. In a beam of 50 keV electrons, a blend of CO to PMMA in the ratio 1:2 exhibits a slope about 2.9 times that of PMMA (Figure 4). However, the polydispersity, M_w/M_n, of the blend (shown on the same plot) reflects the fact that the CO is degrading faster than the PMMA. The polydispersity of neat PMMA remains between 1.9 and 2.3 under the same experimental conditions.

Synchrotron radiation yields a similar pattern to the e-beam result when the same blend and PMMA are compared (Figure 5). Once again, the slope for the blend is about 2.7 times the slope for PMMA.

Chlorine might be expected to enhance the sensitivity to x-rays over that to gamma radiation or electrons. The present work does not demonstrate the effect. The most probable reason is that the synchrotron beam was operating under conditions where the ~~energy~~ was not high at the absorption edge for chlorine (4.4Å).
intensity

The dissolution behavior of CO-PMMA blends was examined for two molecular weights of PMMA (Table 1):

Table 1. Dissolution in MIBK, 30°C

	PMMA alone		CO:PMMA, 1:4	
M_n of PMMA	Diss. Rate	f**	Diss. Rate	f
360×10^3	0.031	0.80	0.27	0.61
29×10^3	0.14	0.97	0.75	0.94

In each case, the dissolution rate was increased by addition of CO. Two additional features can be noted. The amplitude of the oscillations in reflected light intensity appears to remain constant as the blends dissolve. This would indicate that the undissolved portion of the film is not undergoing swelling or extraction to any noticeable extent. The second feature, observable especially in the high molecular weight PMMA blend, is an increased offset between the maximum amplitude during dissolution and the reflection from the bare wafer after dissolution is complete (Figure 6). This offset has been interpreted as representing a transition layer on the surface of the dissolving film (17).

**Oscillation amplitude reduction factor (17), f = (a - b)/(a - b + 2s), where a and b are maximum and minimum reflected light intensities during dissolution and s is the offset (Figure 6).

The increase in the offset means that the CO-PMMA blend has a thicker surface layer. On the other hand, the fact that the offset is only very slightly increased by high molecular weight CO with the lower molecular weights of PMMA means that the transition layer is probably not due to entangled CO molecules remaining on the surface.

Despite the rather low contrast available with a 1:2 blend of CO:PMMA, 0.5 μm lines and 0.3 μm spaces were developed with a dose of 400 mJ/cm^2 (Figure 7). Comparable resolution with PMMA would require a little over twice that dose.

CONCLUSIONS

The sensitivity of PMMA can be increased by adding CO as a blend. The sensitivity of the blend in comparison to the PMMA increases under more forced developing conditions (i.e. longer developing times for development of lower doses). However, under severe conditions, the contrast of the blends suffers greatly which would make it difficult to form good lithographic patterns. At 15 to 20% thinning, the 33 and 50% CO by weight blends still show a 2- to 3-fold increase in sensitivity over that of PMMA. However, this occurs at the expense of a 25 to 40% reduction in contrast.

The mechanism behind the increase in sensitivity is that at significantly high concentrations the CO acts as a dissolution inhibitor. Upon irradiation, the molecular weight of the CO decreases which enhances the dissolution of the blend.

ACKNOWLEDGMENTS

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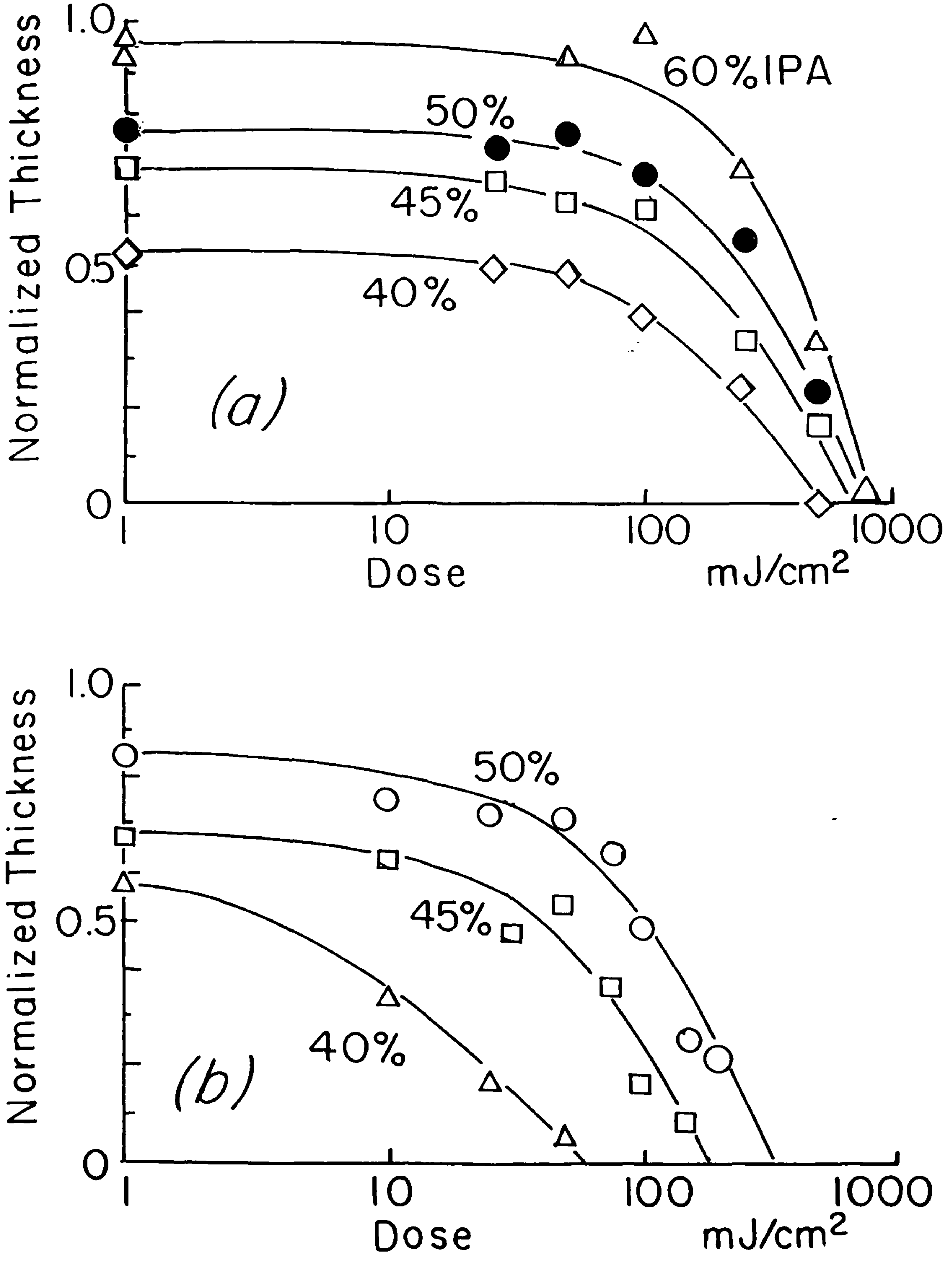
Figure Captions

1. Contrast curves for x-ray, flood-exposed films developed one minute in indicated mixtures of isopropyl alcohol and methyl isobutyl ketone,(a) PMMA and b) CO:PMMA, 1:2.
2. Thinning curves for PMMA and various blends containing (a) 50%, (b) 33%, (c) 20%, and (d) 0% CO by weight. The numbers in parentheses give the fraction of isopropyl alcohol in the solvent (balance is MIBK). The gamma value (contrast) also is given.
3. Sensitivity to gamma radiation (Cobalt source) for (a) CO, G(s) = 5.1, and (b) for PMMA, G(s) = 0.8.
4. Sensitivity to 50 keV electrons for (a) PMMA and (b) CO:PMMA, 1:2. The slope for the blend is 2.9 times that for PMMA.
5. Sensitivity to x-rays (flood exposure through berylium window) for same materials as in figure 4. The slope for the blend is 2.7 times that for PMMA. Polydispersity for PMMA ranges from 1.9 to 2.3 at all doses.
6. Dissolution rates measured by interferometry using MIBK at 30°C for (a) high molecular weight PMMA and (b) CO:PMMA, 1:4.
7. Pattern in CO:PMMA, 1:2. Conditions were 400 mJ/cm^2 synchrotron radiation through gold on boron nitride mask. Developed in MIBK-IPA mixture.


(a)
Normalized Thickness
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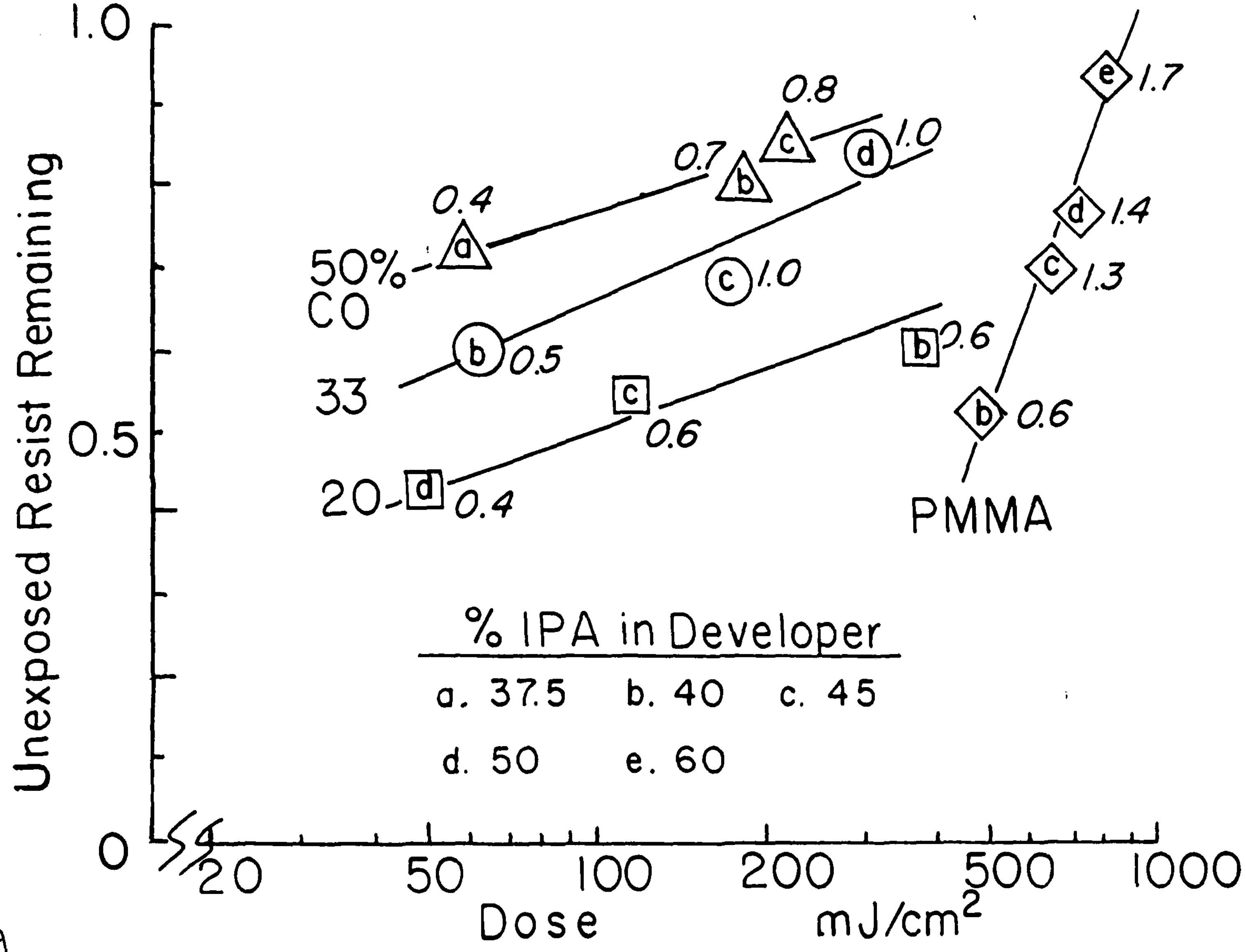
1
10
100
1000
Dose
mJ/cm2
60%IPA
50%
45%
40%
(b)
Normalized Thickness
1.0
0.5
0
1
10
100
1000
Dose
mJ/cm2
50%
45%
40%

Fig. 1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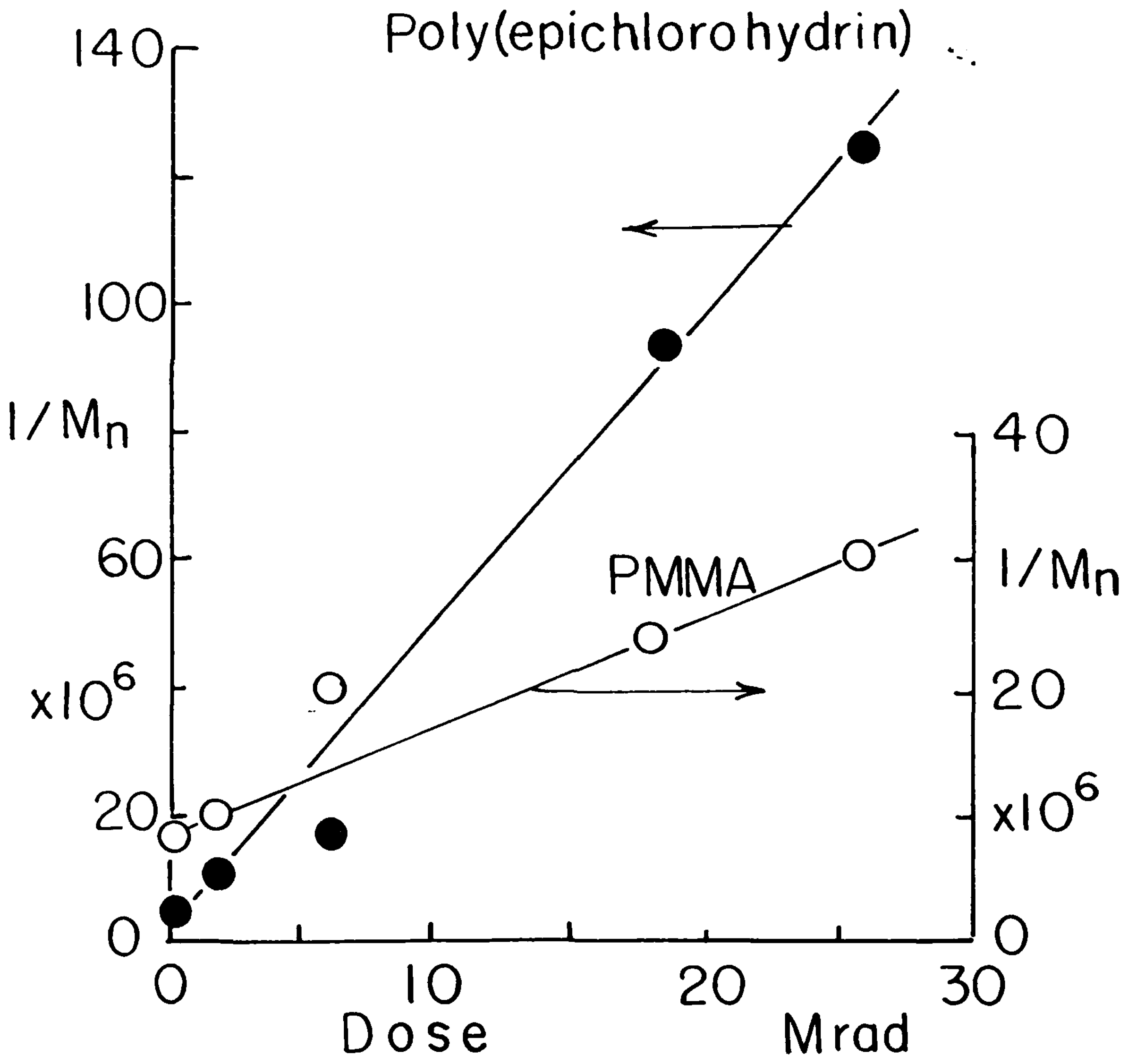
0.5
0
Unexposed Resist Remaining
20
50
100
200
500
1000
Dose
mJ/cm²
50%
CO
33
20
PMMA
a
0.4
b
0.7
c
0.8
b
0.5
c
1.0
d
1.0
d
0.4
c
0.6
b
0.6
b
0.6
c
1.3
d
1.4
e
1.7
% IPA in Developer
a. 37.5
b. 40
c. 45
d. 50
e. 60

Fig. 2



Poly(epichlorohydrin)
140
100
1/Mn
60
x10^6
20
0
PMMA
40
1/Mn
20
x10^6
0
0
10
20
30
Dose
Mrad

Fig. 3

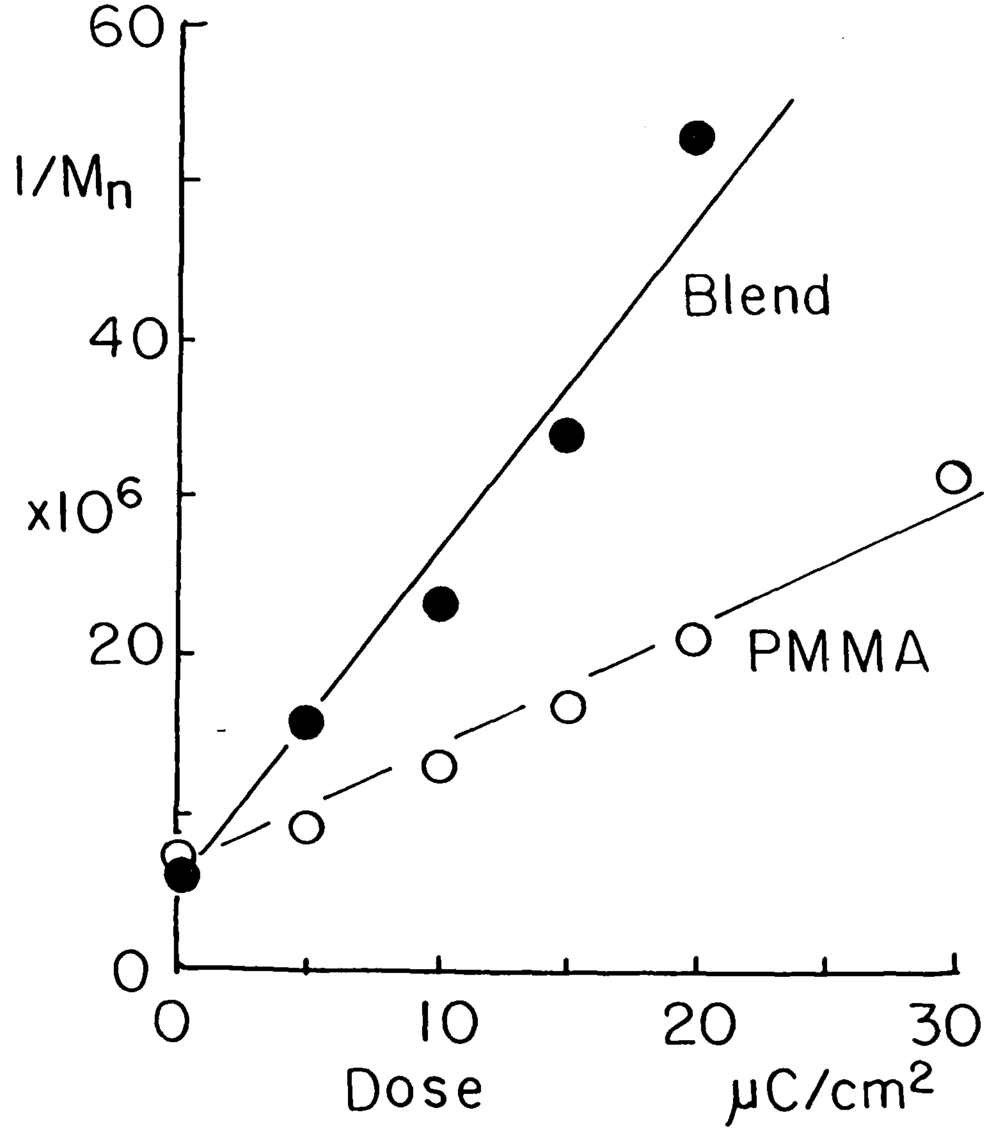
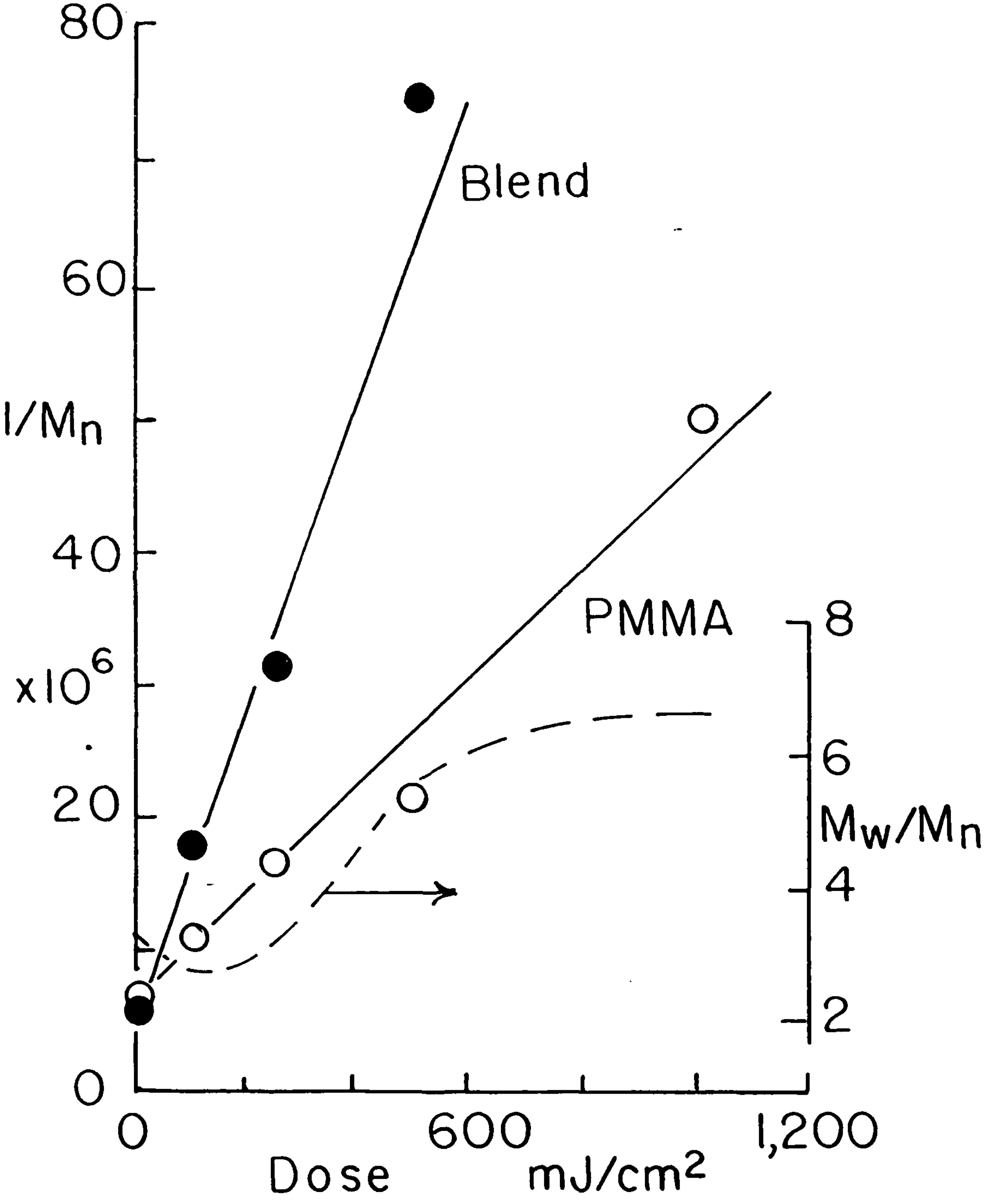


Fig. 4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60
40
20
0
1/Mn
x10^6
Blend
PMMA
8
6
4
2
Mw/Mn
0
600
1,200
Dose
mJ/cm²

Fig. 5

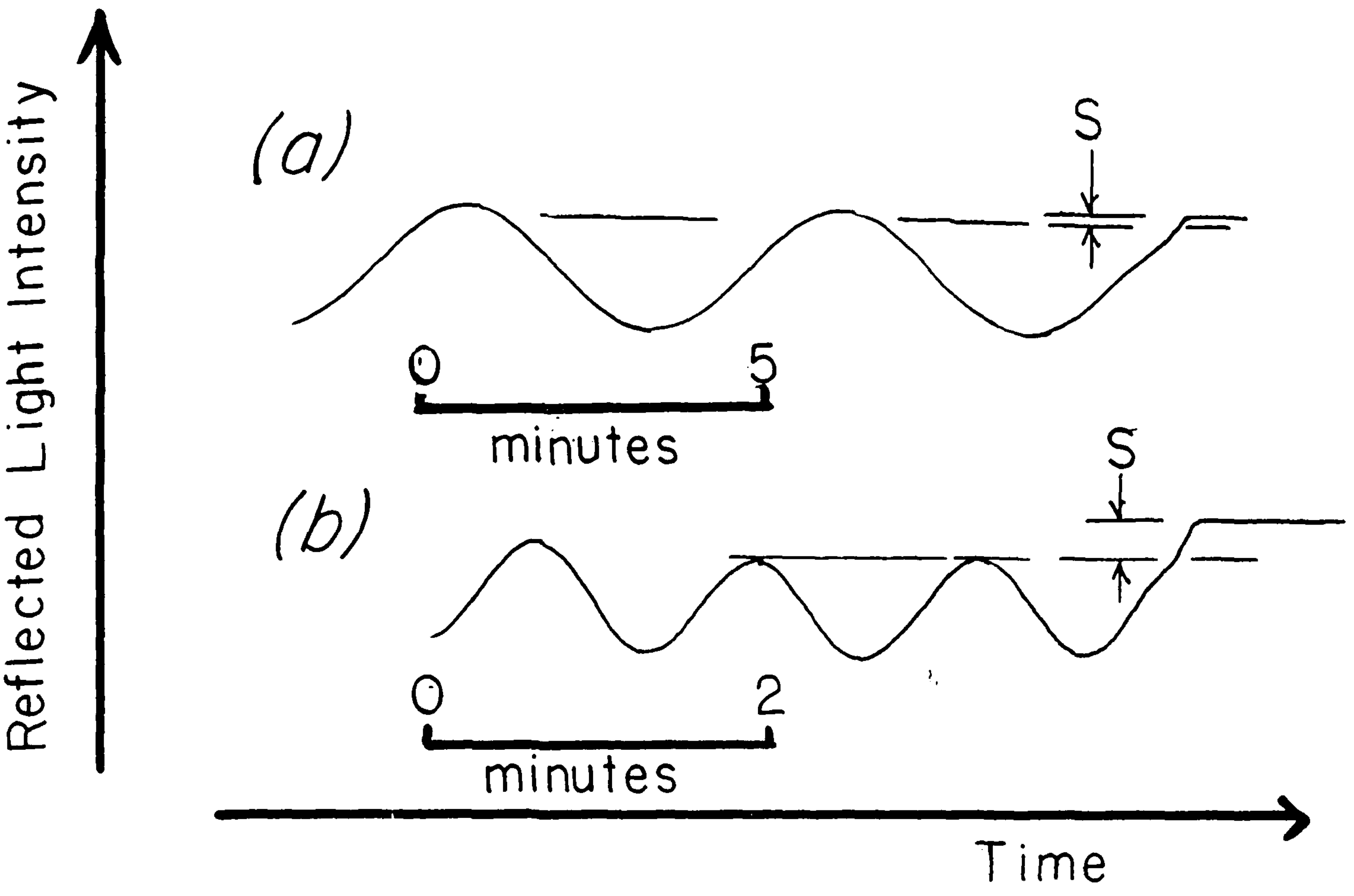

Fig. 6

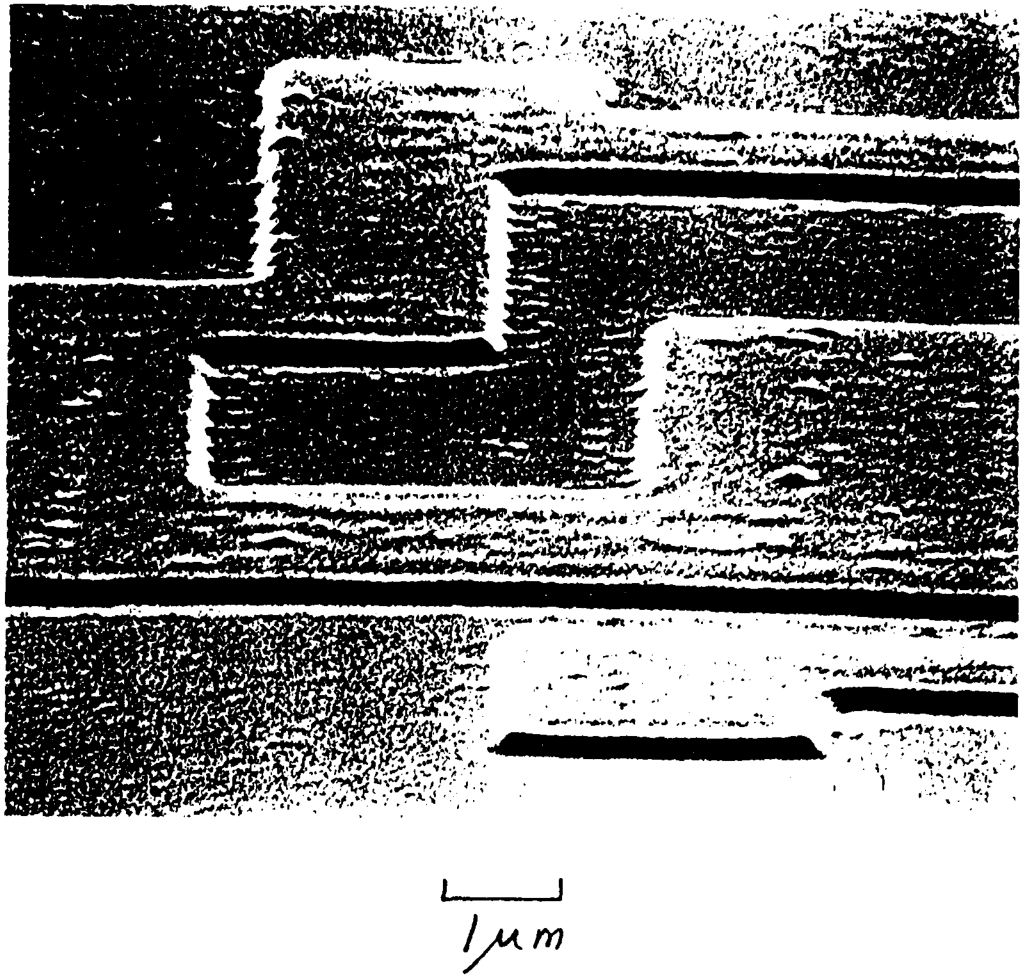

Fig. 7

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