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MODIFIED MALEIC ANHYDRIDE COPOLYMERS AS E-BEAM RESISTS

by

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Modified Maleic Anhydride Copolymers as E-Beam Resists

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ABSTRACT

Copolymers of maleic anhydride with styrene, ethylene, and methyl vinyl ether were modified and evaluated for use as negative working resist materials in electron beam lithography. The copolymers used were modified by reaction with an organometallic compound, which resulted in incorporation of tin in the pendant chains of the copolymers. The polymers were blended with a reactive plasticizer, dipentaerythritol pentaacrylate (DPEPA), to enhance sensitivity and to improve resolution. The esterified copolymer of styrene and maleic anhydride was fractionated to obtain fractions with a range of molecular weights and dispersities. The fractions obtained were used to determine effects of molecular weight and dispersity of the base polymer on sensitivity and contrast of the resist. The lithographic response of the modified copolymers was compared with that of the original unmodified base copolymer. Incorporation of tin into the copolymer resulted in an increase in sensitivity to electron beam. It also improved the dimensional stability of the resist material. There was a dramatic increase in oxygen reactive ion resistance by incorporation of tin, which was a result of formation of an etch-resistant passivating barrier. The etch resistance of the tin modified copolymer containing approximately 20 weight % tin was about twenty fold higher than that of poly(methyl methacrylate) under identical etching conditions. Blending the polymer with dipentaerythritol pentaacrylate resulted in a twenty fold increase in electron beam sensitivity over the base copolymer. Tin modified polymers blended with this plasticizer yielded sensitivities in the range of 0.2 to 1.5 $\mu C/cm^2$. Fractions of copolymer obtained were blended with DPEPA and evaluated for lithographic properties. Increase in molecular weight of the base polymer results in increase in sensitivity of the resist. Monodisperse polymers yielded higher contrast and better resolution. The effect of molecular weight of base copolymer on contrast was determined independent of molecular weight distribution.

1. EXPERIMENTAL PROCEDURE

1.1. Polymers and Monomers used.

The polymers evaluated for their lithographic properties were commercially available polymers, which were then modified to obtain the desired properties. Styrene maleic anhydride copolymers belonging to the SCRIPSET family of resins were obtained from Monsanto Chemical Co. Scripset 520 resin, also known as SMA 520 is a copolymer of styrene and maleic anhydride with a mole ratio of 1:1 and has a molecular

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weight of approximately 350,000 (1). Scripset 550, also known as SMA 550 is a styrene maleic anhydride copolymer (mole ratio of 1:<1) in which the maleic groups have been esterified by a low molecular weight alcohol (1). SMA 550 is used in this work to evaluate the effect of molecular weight and dispersity on the lithographic response. EMA 31 is a copolymer of ethylene and maleic anhydride with a mole ratio of 1:1, (obtained from Monsanto Chemical Co.) and has an approximate weight average molecular weight of 100,000 (2). Gantrez AN copolymer is a copolymer of methyl vinyl ether and maleic anhydride, (obtained from GAF Corporation). Gantrez 139 has an approximate weight average molecular weight of 41,000 and Gantrez 169 has a weight average molecular weight of 67,000 (3). Dipentaerythritol pentaacrylate (DPEPA) is a reactive monomer used to increase sensitivity of the base polymers to electrons. It was obtained from Monomer-Polymer and Dajac Laboratories Inc. Bis (tri-n-butyltin) oxide is used to bind a tin atom pendant to the main polymer chain. This compound (referred to as TBTO) was obtained from Pfaltz & Bauer Inc.

1.2. Fractionation

SMA 550 was the polymer used to determine effects of molecular weight and dispersity on contrast and sensitivity of the resist. Fractions with different molecular weights and dispersities were obtained using nonsolvent addition (4). The polymer was dissolved in tetrahydrofuran (THF), which is a strong solvent for the polymer. Hexane was the nonsolvent used. Eight fractions of the polymer SMA 550 were obtained. The molecular weights and dispersities were determined using High Performance Liquid Chromatography (HPLC) (Table 1).

1.3. Polymer Modification

The maleic anhydride copolymers were modified using bis (tri-n-butyltin) oxide (TBTO). This was done to attach the organometallic group to the side chain of the polymer (5). The polymer was dissolved in tetrahydrofuran and then refluxed with TBTO for 90 minutes. Evaporation of the THF resulted in modified polymer films. Incorporation of the amount of tin can be varied by changing the amounts of TBTO used.

Dipentaerythritol pentaacrylate (DPEPA) was dissolved in Arcosolv PM acetate solvent, before being mixed with the polymer-casting solvent solution. Typically the amount of DPEPA used was 20 wt% of the polymer. DPEPA was blended with the original unmodified copolymers as well as the tin modified copolymers.

1.4. Electron beam exposure

The machine used to generate patterns of various doses on the wafer was the Electron Beam Microfabricator (EBMF) 10.5 (Cambridge Instruments). The EBMF 10.5 operates in the Vector-Scan mode. The accelerating voltage used for the exposures was 20kV. In addition to patterns at different doses, the machine was instructed to write a series of pads at different specified doses. Lines of 1 μm and

0.5 μm were also written primarily to check resolution of the resist.

1.5. Development

Electron beam exposure was followed by a development step. The wafer was diced into 9 parts (chips), each of which had a set of identical patterns written on it. Different developing schemes were employed for each one of those chips. The patterns were developed in suitable solvents, some developing schemes employed a rinse in a nonsolvent following the development step. The primary reason for a rinse in a nonsolvent is to decrease snaking and bridging effects caused due to the swelling of the polymer. An Alpha Step 200 surface profilometer (Tencor Instruments) was used to measure thickness retained after development. The normalized thicknesses obtained were plotted versus log dose (contrast curves).

1.6. Reactive ion etching

The tin modified copolymers as well as the original unmodified copolymers were etched in a custom-built, asymmetric diode reactive-ion etcher. The oxygen reactive ion etch rate of these copolymers was measured by dividing the intial film thickness (Alpha-Step) by the time required to strip the wafer. The end-point was detected using laser interferometry (6). The effect of tin content on the oxygen reactive ion etch resistance was studied. The etch conditions were fixed at 20 sccm oxygen flow, 35mTorr pressure, and 0.25 W/cm^2 nominal rf power density. The self-bias potential varied between 450 and 500 VDC.

2. RESULTS AND DISCUSSION

2.1. Electron beam response of unmodified maleic anhydride copolymers

Styrene maleic anhydride copolymers were investigated for their response to an electron beam. Pohl and Rodriguez reported that copolymers of maleic anhydride with alphamethylstyrene, ethylene, and methyl-vinyl ether chain scission upon exposure to radiation (7). In the present work, the electron beam response of styrene maleic anhydride copolymer (SMA 520), and the partially esterified form of styrene maleic anhydride copolymer (SMA 550) were obtained in the form of contrast curves. SMA 520, which is a perfectly alternating copolymer of styrene and maleic anhydride chain scissions upon electron beam exposure. Thus the material acts as a positive working resist with a sensitivity of 20 $\mu C/cm^2$ and contrast of about unity.

The esterified form (SMA 550) of the same copolymer was also exposed using the Cambridge EBMF 10.5. This esterified polymer behaved as a negative resist, crosslinking upon electron beam exposure. This polymer is however extremely sensitive to the development process. A negative tone image was obtained by development in MIBK. Rinsing in a nonsolvent such as toluene following the development step resulted in better resolution. The lithographic response for SMA 550 in the dose range of 20 to 200 $\mu C/cm^2$

is illustrated in Figure 1. A comparison of the responses of SMA 520 and SMA 550 clearly indicates that it is the presence of the anhydride group that enhances the chain scissioning of the polymer chains.

2.2. Blends of SMA 550 fractions with DPEPA

A blend of SMA 550 with DPEPA results in an increase in sensitivity (crosslinking) to electrons (20 and 50 kV). DPEPA upon exposure to electron beam crosslinks itself and possibly provides sites for crosslinking for the base copolymer (8). Blending the polymer with this monomer results in some sort of plasticization effect. The unexposed areas of the pattern are easily removed in a suitable developing solvent. The contrast curve for a blend of SMA 550 with 20 weight percent DPEPA shows a sensitivity of $6.5\mu C/cm^2$ which is a dramatic increase in sensitivity (decrease in dose) over SMA 550 alone (Figure 1). Resolution was typically 0.5 µm.

Fractionation of SMA 550 was used to determine effects of molecular weight and molecular weight distribution on sensitivity and contrast of the resist material. The weight average molecular weights determined by HPLC range from 58,000 to 265,000. The polydispersity index ranges from 1.42 to 2.86. Electron beam lithography on blends of these fractions with 20 weight % DPEPA clearly demonstrate effects of molecular weight and dispersity on lithographic performance (Table 2, Figure 2).

Fractions with high molecular weight show greater sensitivity than polymer fractions with lower molecular weight and monodisperse samples exhibit higher contrast and resolution. Figure 3 is a plot of molecular weight versus sensitivity of the resist. The slope of -1.3 is close to the predicted one of -1.0 (9). Similar trends have been reported for other copolymers of styrene by Choong and Kahn (10).

Fractions 3A and 8 have approximately the same dispersity, 1.4. However it is clear from Table 2 that fraction 8 with a molecular weight of 58×10^3 has a higher contrast than fraction 3A, which has a weight average molecular weight of 180×10^3. Contrast is improved slightly (c. 15%) when the molecular weight is increased at the same polydispersity. Polydispersity could be varied at the same weight average molecular weight by blending fractions. It was found that contrast was improved by about 35% when polydispersity was reduced from 2.05 down to 1.45. Contrast for a negative resist is related to the rate of formation of the crosslinked network at a constant input dose (11). When two samples with the same molecular weight distribution are exposed to an electron beam, the higher molecular weight polymer has a lower crosslink density, hence it exhibits more swelling and suffers from poorer contrast.

2.3. Lithographic response of tin modified copolymers

Maleic anhydride copolymers such as EMA, Gantrez, and SMA 520 chain scission upon exposure to electrons. The presence of the tin atom in the side chain of the copolymer results in a sharp increase in absorption of electrons, probably due to the large absorption cross section of the tin atom (12).

The reaction of bis (tri-n-butyltin) oxide with EMA and Gantrez results in a reversal in lithographic response. These copolymers when modified by tin exhibit negative-working behavior. Reaction with TBTO results in the opening of the anhydride linkage, which may be a cause of negative working behavior. The contrast curves are shown on one plot in Figure 4 for purposes of comparison. EMA / TBTO has a sensitivity of ~ 40 $\mu C/cm^2$, Gantrez / TBTO and SMA 550 / TBTO have a sensitivity in the range of 90 to 100 $\mu C/cm^2$. This plot clearly indicates that negative working resists are obtained by tin modification of maleic anhydride copolymers. The individual responses of the tin modified copolymers cannot be compared due to differences in molecular weight and molecular weight distribution. However they serve as indicators of a general trend.

A comparison of the lithographic response of SMA 550 with 10 and 20 weight % tin demonstrates that as the tin content increases, the sensitivity of the polymer to electrons increases. The sensitivity of SMA 550 with a tin content of 20% is 32 $\mu C/cm^2$ as compared to 115 $\mu C/cm^2$ of SMA 550 with no tin at all. However SMA 550 with a tin content of 10 % by weight is only slightly more sensitive than the unmodified SMA 550 copolymer. The increase in sensitivity can be attributed to the absorption cross section of the metal atoms. Another interesting observation is a definite increase in contrast upon tin modification. The original unmodified copolymer has a contrast of 1.1, the same copolymer containing 10 weight % tin has a contrast of 2.1, and the copolymer containing 20 weight % tin has a contrast of approximately 2.4.

2.4 Blends of tin modified copolymers with DPEPA

SMA 550 reacted with TBTO (equivalent to 10 weight % tin) was blended with DPEPA (20 weight % of polymer). A comparison of the sensitivity of SMA 550 blended with DPEPA which is 6.5 $\mu C/cm^2$, with that of the tin modified SMA 550 blended with DPEPA which is approximately 1 $\mu C/cm^2$ also clearly indicates that the presence of tin in the side chain makes it more sensitive to electrons (Figure 1).

The tin modified copolymers EMA and Gantrez were also blended with DPEPA equivalent to 20 % by weight. Figure 5 is a comparison of the lithographic responses of tin modified SMA, EMA, and Gantrez blended with DPEPA. The tin modified SMA 550 blended with DPEPA exhibits a sensitivity of approximately 1$\mu C / cm^2$. The Gantrez blend has a sensitivity of ~ 0.2 $\mu C /cm^2$ and the tin modified EMA blend has a sensitivity of ~ 1.5 $\mu C /cm^2$.

2.4. Oxygen RIE resistance of tin modified copolymers

The oxygen reactive ion etch resistance of the tin modified copolymers was compared with that of the original unmodified copolymers. Figure 6 is a plot of oxygen reactive ion etch rate versus tin content of the copolymer for EMA, Gantrez, and SMA 550. There is a dramatic increase in oxygen reactive ion etch resistance with increase in tin content of the base copolymer (13). SMA 550 has an oxygen reactive ion etch rate of 315 nm/min. Incorporation of 10 weight % tin results in a drop of etch rate to 70 nm/min, and incorporation of 20 weight % tin results in a further decrease of etch rate to 20 nm/min. Blending the polymers with DPEPA does not affect reactive ion etch resistance in oxygen.

This improvement in oxygen reactive ion etch resistance can be explained by the formation of a passivating layer of SnO_x (tin oxide) which prevents further etching (13). The etch rate of the tin modified copolymers is approximately 10-15 times less than that of poly(methyl methacrylate) under identical conditions of etching. This makes the resist system suitable for bilevel or trilevel applications. It is also clear from Figure 6 that, for films containing 10% tin or less, the etch rate of the original unmodified copolymer is lowest for the styrene maleic anhydride copolymer. This is probably due to the presence of the styrene group, since it is known that polymers with an aromatic group are more etch resistant than aliphatic polymers.

2.5. Glass Transition Temperatures

The results of the DSC done on the copolymers containing different amounts of tin revealed that the glass transition temperature of the copolymer increases linearly as the tin content of the copolymer increases. This trend was observed for all three copolymers, EMA, Gantrez, and SMA. For EMA, T_g increased from 144° to 168°C by incorporation of 20% tin. For Gantrez, the T_g increased from 130° without tin to 180° with 20% tin and for SMA, from 110° to 145°. Thus, incorporation of tin not only provides for an increase in sensitivity of the base copolymer and oxygen etch resistance, but also an improvement in dimensional stability of the polymer. The bulky groups containing tin atoms probably contribute to an increase in stiffness of the polymer chains which is manifested as an increase in glass transition temperature.

3. CONCLUSIONS

Electron beam lithography on maleic anhydride copolymers reveals that the copolymer of styrene and maleic anhydride in which the anhydride groups have been esterified, primarily crosslinks upon electron beam exposure. However the unesterified copolymer primarily chain scisions upon electron beam exposure. This is consistent with the results observed for anhydride copolymers in literature.

Incorporation of tin into the maleic anhydride copolymers results in an increase in sensitivity to electrons. This can be explained on the basis of the high absorption and scattering cross section of the metal atoms. Reaction with tin results in improvement of contrast from 1.1 of the unmodified SMA 550 copolymer to 2.4 of the same copolymer containing 20 weight % tin.

Reactive ion etch studies of tin modified copolymers indicate that the oxygen RIE resistance of these polymeric resists dramatically improves with increase in tin content. SMA 550 copolymer with a tin content of 20 weight % etched 20 nm/min, a factor of 20 less than that of PMMA or unmodified SMA 550 under identical etching conditions.

Blending the polymers with dipentaerythritol pentaacrylate (DPEPA) results in a significant improvement in sensitivity relative to the unmodified copolymers. DPEPA crosslinks itself and possibly provides sites for crosslinking for the polymer. The electron beam sensitivity of the SMA 550 copolymer increased from 115 to 5.7 $\mu C/cm^2$ upon blending with 20 weight % DPEPA. Blends of the tin modified copolymers with DPEPA show an extremely high sensitivity, in the range of 0.2 to 1.5 $\mu C/cm^2$.

Results of lithography on the fractionated copolymer SMA 550 blended with DPEPA helped in clearly establishing the effects of molecular weight and molecular weight distribution on sensitivity and contrast obtained. As the molecular weight of the base copolymer is increased there is an increase in sensitivity of the resist. The sensitivity of fraction 2 of SMA 550 copolymer (MW= 174 $\times 10^3$) blended with 20 weight % DPEPA is 2.0 $\mu C/cm^2$. However the sensitivity of fraction 8 (MW= 58 $\times 10^3$) blended with DPEPA is 12.0 $\mu C/cm^2$, which is 6 times less. As the base polymer becomes closer to monodisperse, there is a distinct improvement in contrast and resolution. The unmodified SMA 550 copolymer (polydispersity =2.32) blended with DPEPA has a contrast of 1.2, the fractionated copolymer (polydispersity =1.44) blended with DPEPA has a much higher contrast of 3.1. This effect has been studied independent of molecular weight. Studies of the effect of molecular weight on contrast for same molecular weight distribution indicate that as molecular weight increases, contrast decreases.

The copolymers exhibit an increase in glass transition temperature with increase in tin content of copolymer along with the increase in sensitivity. This effect is the reverse of what is observed for most polymeric resist systems in which an improvement in dimensional stability results in a decrease in radiation sensitivity.

Thus, a resist system with high sensitivity, excellent oxygen reactive ion etch resistance, good adhesion and thermal properties has been developed. Improvement in sensitivity and contrast may be obtained by modification of the polymer by fractionation to obtain desired molecular weight and dispersity.

4. ACKNOWLEDGMENTS

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Table 1 **Fractions obtained upon fractionation of 30 grams of SMA 550 copolymer**

Fraction	Amount Obtained (gms)	Weight Average Molecular Weight x 10^{-3}	Number Average Molecular Weight x 10^{-3}	Polydispersity Index M_w/M_n
Unfractionated		126	54.3	2.32
Fraction 1	1.16	265	92.5	2.86
Fraction 2	4.50	175	84.4	2.07
Fraction 3	7.37	148	79.1	1.86
Fraction 4	5.44	124	71.1	1.74
Fraction 5	3.33	96.3	63.6	1.51
Fraction 6	5.08	76.7	45.4	1.69
Fraction 7	1.87	64.6	40.4	1.60
Fraction 8	0.74	58.4	41.0	1.42
Fraction 3A	1.0	180	125	1.44

(Recovered by reprecipitation from Fraction 3)

Table 2. **Lithographic Response of SMA 550 Fractions blended with 20 weight % DPEPA**

Sample	Weight Average Molecular Weight x 10^{-3}	Polydispersity Index M_w/M_n	Sensitivity ($\mu C/cm^2$)	Contrast
Unfractionated	126	2.32	5.7	1.2
Fraction 2	174	2.06	2.0	1.6
Fraction 3A	180	1.44	2.4	2.5
Fraction 4	124	1.74	3.1	2.1
Fraction 5	96.0	1.51	6.7	2.2
Fraction 8	58.0	1.42	12.0	3.1

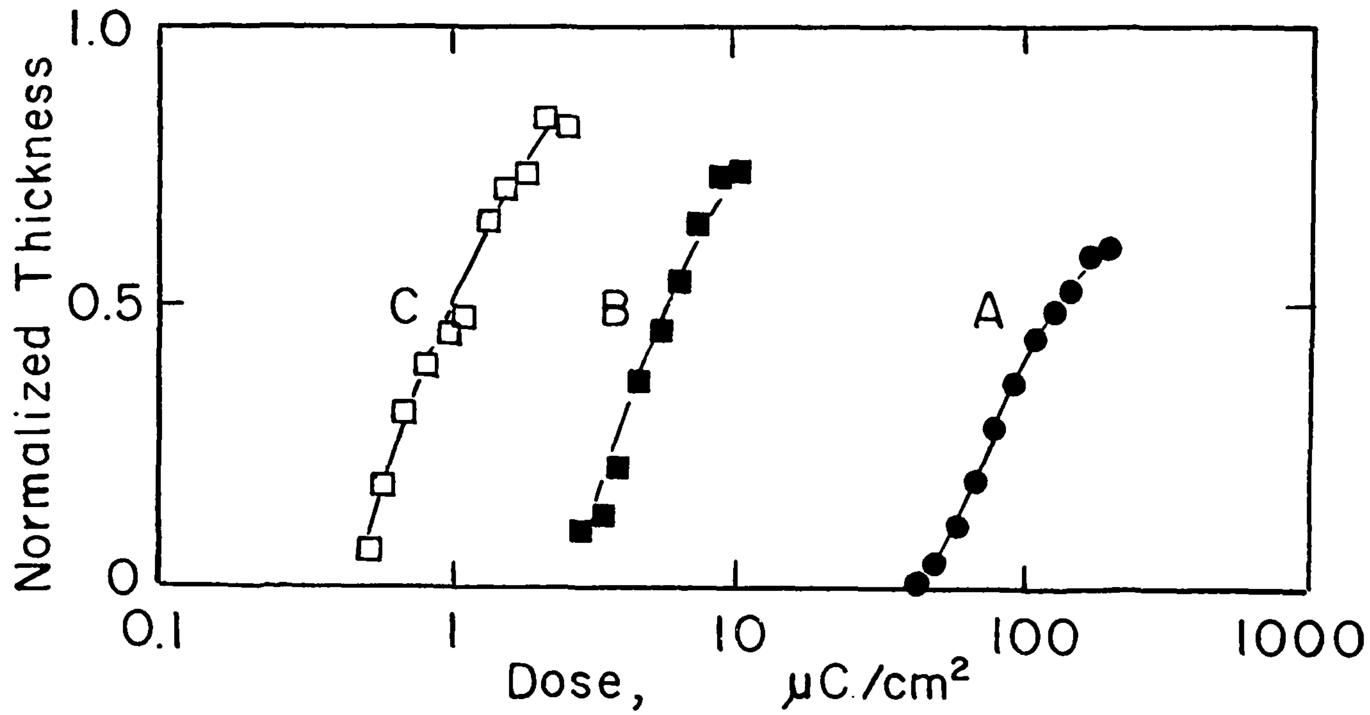

Figure 1. Contrast curves for SMA 550 (partly-esterified styrene-maleic anhydride copolymer), A. SMA as received, B. SMA blended with 20 % DEPEPA, C. Tin-modified SMA (10% tin) with 20% DPEPA. Films prebaked 30 min/80°C, developed in MIBK followed by toluene rinse.

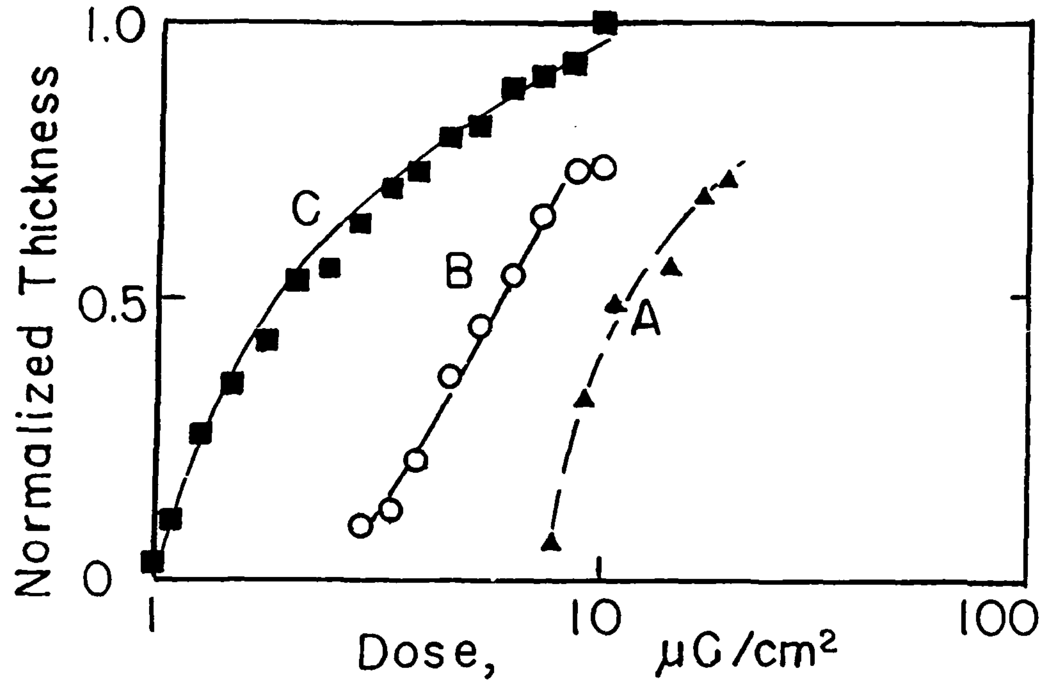

Figure 2. Contrast curves for SMA 550 samples blended with 20% DPEPA, A. Fraction 8, B. Unfractionated SMA, C. Fraction 2 (See Table 1).

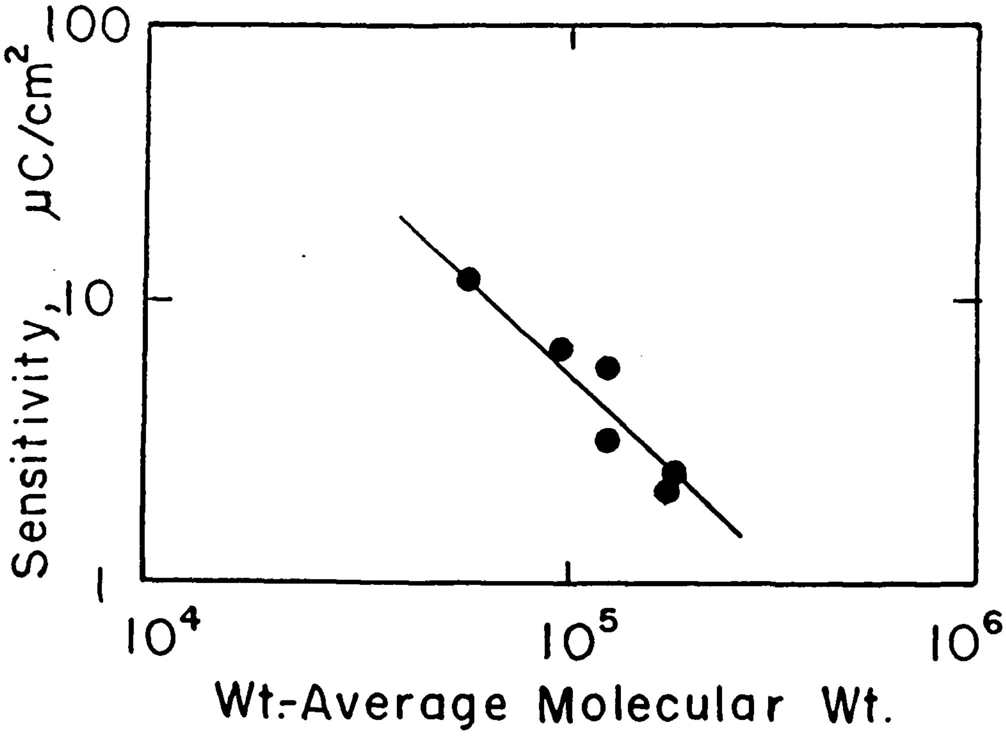

Figure 3. Dependence of sensitivity on molecular weight (SMA 550).

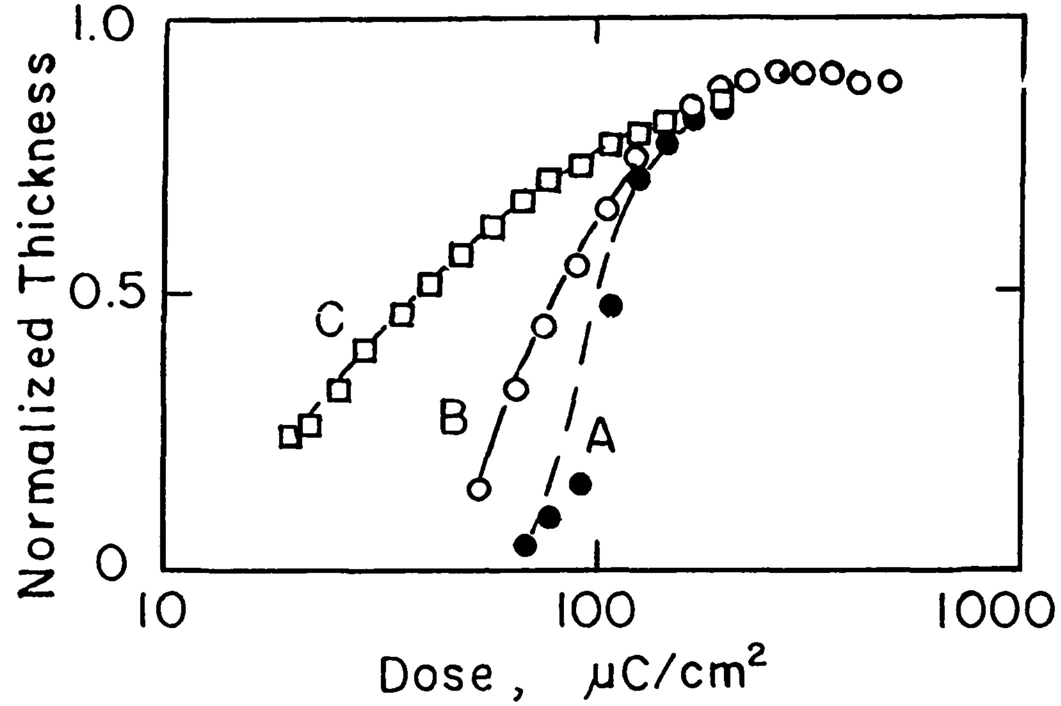

Figure 4. Contrast curves for tin-modified (10% tin) copolymers, A. SMA 550, prebaked 30 min/80°C, B. Gantrez, prebaked 60 min/100°C, C. EMA, prebaked 5 min/80°C. All developed in Arcosolv PM Acetate solvent. Toluene rinse used with A.

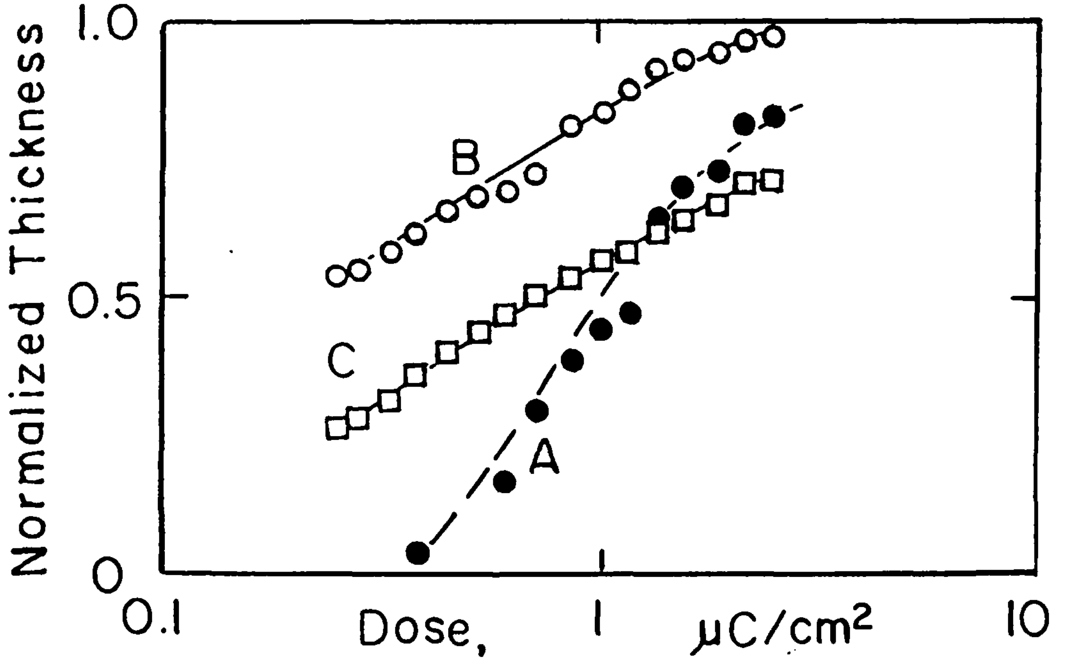

Figure 5. Contrast curves for polymers containing 10% tin and blended with 20% DPEPA, A. SMA 550, prebaked 30 min/80°C, developed in MIBK followed by toluene. B. Gantrez, prebaked 60 min/100°C, developed in Arcosolv PM solvent., C. EMA, prebaked 2.5 h/80°C, developed in Arcosolv PM solvent.

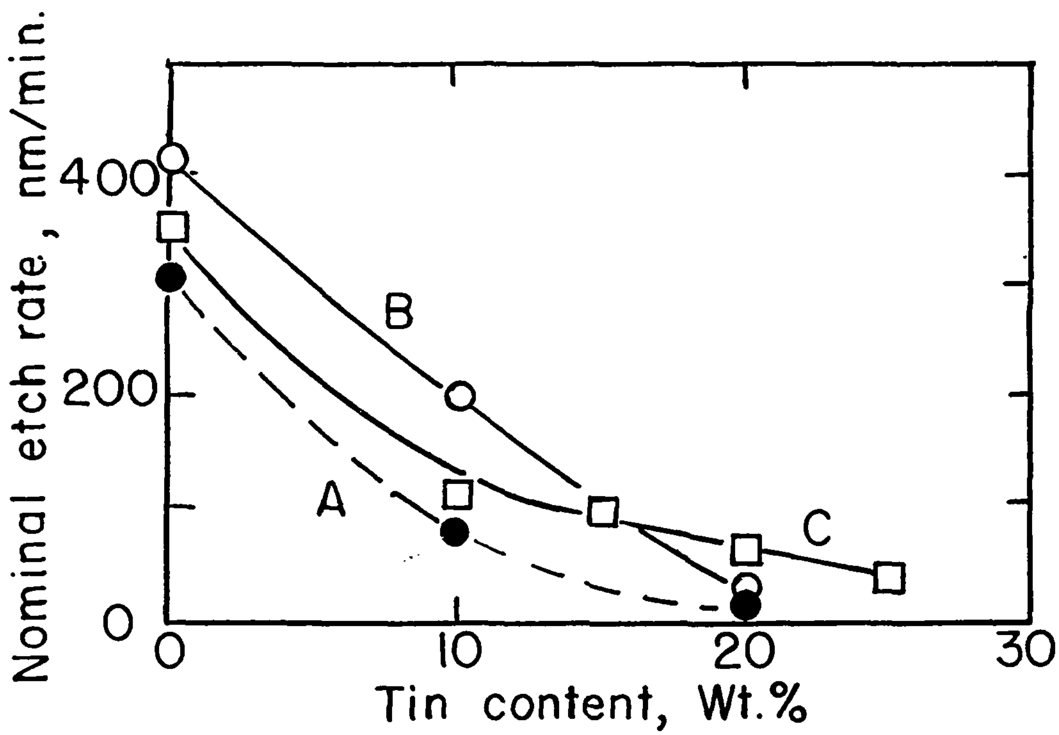

Figure 6. Effect of tin content on RIE etch rate in oxygen, A. SMA 550, B. Gantrez, C. EMA. Oxygen flow rate = 20 sccm, pressure = 35 mTorr, power density = 0.25 W/cm^2.

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