MULTICOMPONENT E-BEAM RESISTS CONTAINING ORGANOMETALLIC COMPOUNDS AND REACTIVE MONOMERS

by

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1. A 3-component blend consisting of VMCH (a terpolymer with 86% vinyl chloride, 13% vinyl acetate, and 1% maleic acid), dipentaerythritolpentaacrylate (DPEPA) and an organotin stabilizer (OTS). A blend of 55% VMCH, 20% DPEPA, and 25% OTS exhibits a sensitivity (20 kV electron beam) of 0.4 μC/cm² and etches in O₂/RIE at about 1/10 the rate of PMMA. Baked films of this blend exhibit a high surface concentration of tin (confirmed by EDS) which provides an effective SiOₓ etch-inhibiting barrier. Exposed films of this blend do not form a high Sn concentration on the
19. Abstract, continued.

during baking, and this phenomenon has been utilized for a plasma-development lithographic technique.

2. Modification of host polymer by reaction with an organometallic compound with pendant reactive groups on the polymer chain: poly(ethylene/ maleic anhydride), EMA, reacts with bis(tri-n-butyl tin) oxide (TBTS) to form polymers with varying tin content. EMA/TBTS with 25% Sn etches in O2 RIE at less than 50 nm/min. Addition of 20% DPEPA provides for a sensitivity of 1 µC/cm².

3. Using a metal-containing reactive monomer blended with a host polymer: Tributyl tin acrylate (TBTA) blended with WCH results in little or no increase in etch durability and only a two-fold increase in sensitivity over that of WCH alone. Although this particular plasticizer performed poorly, other reactive organometallic plasticizers could be investigated.

These blended systems offer the advantage of a wide processing latitude. The properties of the blends can be varied greatly without complete new synthesis and characterization of individual polymers.
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INTRODUCTION

Many of the properties desired in a negative-working e-beam resist have been attained with a single polymer or a polymer with one additional ingredient. The combination of an azo compound with cyclized rubber was one of the first widely-used optical resists. Properties which are desirable in a negative resist include: dimensional stability, sensitivity to radiation, resistance to plasma etching, adhesion, and strippability after image transfer.

It is of interest to see whether these properties can be provided by blends in which a multiplicity of individual components contribute some properties without interfering with the action of the other components. In the present work, negative-working resists with combined e-beam sensitivity and oxygen etch resistance have been formulated using three components: 1. A host polymer for dimensional stability during radiation processing. 2. An unsaturated, non-volatile monomeric component for control of sensitivity, and 3. An organometallic compound to contribute RIE resistance in an oxygen plasma.

Addition of reactive monomers to host polymers can increase sensitivity dramatically relative to that of the host. These blends exhibit sensitivity in the $\mu$C/cm$^2$ range, but offer little improvement in etch resistance relative to polymethylmethacrylate (PMMA) and other aliphatic polymers.

The oxygen etch resistance can be improved by incorporating metals in the form of organometallic compounds. The incorporation of metals into resist materials has received considerable attention in recent years because some metals form oxides in an oxygen plasma, leading to high O$_2$ RIE durabilities. Such resists are particularly useful for bi-level and tri-level lithography which use O$_2$/RIE for providing images with very high aspect ratios. The incorporation of metals is also expected to improve sensitivity because of the increased cross-section for energy absorption that they provide.

In the present study, we have investigated incorporating metals into resist materials in three ways:

1. Forming a 3-component blend consisting of host polymer, reactive monomer, and an organotin stabilizer.
2. Modifying the host polymer by reacting an organometallic compound with pendant reactive groups on the polymer chain. This modified polymer is then blended with a reactive monomer for enhanced sensitivity.
3. Using a metal-containing reactive monomer blended with a host polymer.
EXPERIMENTAL

Materials:

VMCH (a commercial terpolymer consisting of 86% vinyl chloride, 13% vinyl acetate and 1% maleic acid) was obtained from Union Carbide. The reactive monomer, dipentaerythritol pentaacrylate (DPEPA), was obtained from Monomer-Polymer & Dajac Laboratory, Inc. The organotin stabilizer (OTS) is a commercially available dialkyl organotin compound, being marketed as Thermolite 42 by M & T Chemicals Inc.

Tin derivatives of poly (ethylene/maleic anhydride), EMA, were produced by reaction of EMA with bis (tri-n-butyltin) oxide (TBTO). EMA was obtained from Monsanto (as EMA 31), and TBTO was obtained from Pfaltz and Bauer. EMA was dissolved in tetrahydrofuran (THF) and refluxed with the desired amount of TBTO for 90 minutes. The EMA/TBTO polymers were recovered by evaporation of THF. Tin contents of the derivatives range from 5 to 25 wt. %.

RIE Apparatus

Etch rates were determined in a parallel-plate, reactive ion etcher. The aluminum chamber was made in-house, and the electrode was powered by a Plasma Therm Inc., model HFS 2000 D rf generator operating at 13.56 MHz. This RIE apparatus is described in more detail in a previous publication. The reactive gases used include pre-purified oxygen and a commercial mixture of CF₄ with 8% O₂ (Matheson Corp., LFE-100). All RIE experiments in this study were done with the following conditions, unless otherwise stated: O₂ flow rate: 20 sccm, pressure: 35 mtorr, and power density: 0.25 W/cm².

Etch rates are monitored in-situ with a laser interferometer, consisting of a 2 mW laser aimed at the wafer surface through a quartz window the chamber lid. The reflected light intensity was monitored with a photocell whose signal was amplified and monitored with a chart recorder. Initial etch rates were also estimated using an Alpha-Step 200 stylus profilometer for film thickness measurements before and after etching for specified time intervals. Etch rates were measured in the center of a 3-inch wafer to minimize edge effects.

Lithographic Evaluation

Electron-beam lithographic responses of the blended resists were determined by exposures with a Cambridge Instruments EBMF 10.5 pattern generator at the National Nanofabrication Facility (NNF) at Cornell University. Films of the blends were spin-cast onto silicon wafers from appropriate solvents, exposed, and developed in various developing solvents. Contrast curves were determined by measurement of residual film thicknesses after development of pads exposed at a series of doses. The accelerating voltage used for all evaluations was 20 KV.

Rutherford Backscattering:

Rutherford Backscattering Spectrometry (RBS) measurements of the resist films were made at the Tandetron Accelerator Facility at Cornell University. The technique measures the profile of
elemental concentrations through the entire film. Of particular interest in the present work are the profiles for tin.

RESULTS

I. Three Component Blends

Blends of VMCH and DPEPA have previously been shown to exhibit electron sensitivity of about 1 \(\mu C/cm^2\). However, the RIE resistance of these blends is poor, being only slightly better than that of PMMA. Films of pure VMCH etch in an \(O_2/RIE\) at a rate of 330 nm/min at standard conditions. For comparison, PMMA etches at 420 nm/min under these conditions. Addition of DPEPA to VMCH has no discernable effect on the \(O_2\) etch rate. Prebaking (100°C) and electron exposure (10 \(\mu C/cm^2\)) of the VMCH/DPEPA blends also have no effect on etch rate.

An organotin stabilizer (OTS) has been added to the VMCH/DPEPA blends to increase etch resistance. Mixtures of VMCH, DPEPA and OTS form compatible blends with up to 50 wt. % DPEPA and up to 25% OTS. These blends form homogeneous films that are free of any signs of phase separation when spin-cast onto silicon wafers. Addition of OTS to VMCH/DPEPA blends affords good etch resistance in oxygen RIE. The initial etch rate of baked VMCH-OTS-DPEPA films decreases linearly with increasing OTS concentration (Figure 1). Addition of 25 wt. % OTS reduces the initial etch rate in oxygen by a factor of ten.

Films of VMCH/OTS without DPEPA exhibit cracking and other damage towards the end of etching. Plasticization with DPEPA greatly reduces the damage observed during etching.

The initial etch rate of VMCH-OTS-DPEPA in \(CF_4/O_2\) plasma strongly depends on the relative concentration of oxygen in the plasma (Figure 2). It was believed that the terblend would prove to be etch resistant in a fluorocarbon plasma since SnF\(_x\) compounds are non-volatile. However, with only 8% \(O_2\), the blend etches at a rate of 250 nm/min. This amount of reduction in etch rate could be attributed to deposition of fluorocarbon-based polymer on the film surface. Increasing the percent \(O_2\) in the plasma increases the etch rate to a maximum of 350 nm/min for 40% \(O_2\). The increase in etch rate with increasing \(O_2\) concentration is probably due to a reduction in polymer deposition by scavenging of pre-polymer moieties by oxygen atoms. As the oxygen content is further increased, the formation of SnO\(_x\) dominates which leads to a reduction in etch rate.

Wet development of the VMCH-OTS-DPEPA blends results in negative resist images using very low electron doses. The 50% gel dose (at 20KV) for a blend containing 25% OTS and 20% DPEPA is about 0.4 \(\mu C/cm^2\) (Figure 3). This compares to a 50% gel dose of 0.8 \(\mu C/cm^2\) for VMCH/DPEPA without the organotin compound. The high-atomic-weight tin atoms may be contributing to increased electron stopping power, leading to greater energy absorption and enhanced sensitivity. The contrast \((\gamma)\) of this resist blend is about 0.6, and the resolution attained is 0.5 \(\mu m\). It is likely that contrast and resolution could be improved by fractionating the VMCH host polymer as was demonstrated.
previously for VMCH/DPEPA blends (Fig. 3 and Ref.1).

Unbaked films of the VMCH-DPEPA-OTS blends show little or no increase in etch resistance with increasing OTS concentration (Fig. 1). It is probable that the tin compound is diffusing to the surface of the film during baking, allowing for the rapid formation of a SnO2 etch barrier and a slower etch rate for the baked film. Unbaked films, which have a more homogeneous distribution of OTS, etch at a constant, more rapid rate. Using laser interferometry to monitor the etching process, unbaked films are seen to etch at nearly a constant rate from beginning to end as indicated by a nearly constant period of oscillation of the reflected signal (Fig. 4a). In contrast, baked films exhibit a characteristic "passivation" or induction period where etching is very slow for the first 2 to 3 minutes and then increases (Fig. 4b). Presumably, a tenacious SnOx layer forms initially and is slowly sputtered away until a critical Sn surface concentration is reached where it no longer can sustain an adequate SnOx etch barrier. This phenomenon results in the very large difference in initial etch rate between baked and unbaked films, as seen in Figure 1. The hypothesized high surface concentration of tin on baked films of VMCH-DPEPA-OTS is confirmed using Rutherford backscattering spectrometry (RBS) (Fig. 5). Tin is initially distributed uniformly throughout the unbaked resist film (Fig. 5A). A one hour bake at 100°C results in about a three-fold increase in the surface concentration of tin (Fig. 5c). RBS also shows that high surface concentrations of tin are formed during O2/RIE etching of both unbaked (Fig. 5b), and baked (Figs. 5d and 5e) films of VMCH-DPEPA-OTS.

We have attempted to utilize the difference in etching behavior of the baked and unbaked films of this blend in a dry-developing scheme. When unbaked films are exposed to an electron dose of 5 to 10 μC/cm², the OTS is effectively locked into place by the polymerization and crosslinking of the DPEPA, preventing diffusion of OTS during a post-exposure bake. Thus, films exposed prior to baking etch uniformly without induction period, just like an unbaked film (Fig. 4d). Unexposed resist, on the other hand, forms a high surface concentration of tin during the post exposure bake, leading to the formation of a SnOx etch barrier.

The lithographic process for the dry-developing scheme is shown schematically in Figure 6. Patterning is accomplished by electron exposure (5 to 10 μC/cm²) of the lithographic pattern in an unbaked film, followed by a post-exposure bake for one hour at 100°C. The film is then etched in O2/RIE until the exposed regions are etched to the substrate. The unexposed regions etch at a slower rate and experience an induction period due to the surface concentration of tin compound. The resulting pattern is then a positive image with about 50% thinning. Unfortunately, the resolution of these patterns is severely limited by inhomogeneity of the etched film, and possibly by lateral diffusion of the tin compound during the post-exposure bake step.

Optimum conditions for the dry-developing technique have been estimated by determining the RIE induction period for a series of post-exposure bake conditions and exposure doses. For the
conditions investigated in this experiment, electron exposure at 10 \( \mu \text{C/cm}^2 \) followed by a 30 minute post exposure bake at 100°C yields the maximum differential in induction period between exposed and unexposed films (Table I).

II. Tin-Modified Host Polymer with Reactive Plasticizer

Another approach to incorporating metals into resists is to modify the host polymer by reaction of pendant groups with an organometallic compound. This approach is particularly useful in that it avoids problems with blend compatibility and phase separation.

As an example of this approach, we have modified poly(ethylene/maleic anhydride), EMA, by reaction with bis(tri-n-butyl tin) oxide (TBTO). As expected, the initial O\(_2\)/RIE rates of the EMA/TBTO polymers decrease rapidly with increasing tin concentration (Fig. 7). The TBTO-modified polymers etch in O\(_2\) until the formation of a passivating layer prevents further etching. The residual film is then removed only by sputtering in the O\(_2\) environment. This is in contrast to the VMCH/DPEPA/OTS blends which etched to the substrate in O\(_2\)/RIE. Prebaking has no effect on the etch rate of these modified polymers as it did with the VMCH-OTS-DPEPA blends. This is not surprising because the Sn atoms are covalently bonded to the host polymer restricting their mobility.

These EMA/TBTO polymers function as negative resists, but the sensitivity is limited to about 70 \( \mu \text{C/cm}^2 \) (50% thinning). To improve sensitivity, we combined the EMA/TBTO derivatives with reactive plasticizer (DPEPA). Incorporation of 20% DPEPA improves the sensitivity to approximately 1 \( \mu \text{C/cm}^2 \) (Fig. 8). The addition of DPEPA has little or no effect on the O\(_2\) etch rate of the EMA/TBTO polymers. Thus, we have combined both sensitivity and etch resistance by the blending of EMA/TBTO polymers with DPEPA.

III. Host-Polymer with Tin-Bearing Reactive Plasticizer

A third approach is to combine the metal-containing compound with the reactive plasticizer into a single component in blends with an appropriate host polymer. As an example, VMCH can be mixed with tributyl tin acrylate (TBTA) which contains tin as well as a reactive acrylate group. TBTA forms homogeneous films with VMCH. However, the TBTA only enhances sensitivity by a factor of two, and it has little or no effect on etch rate. Other organometallic plasticizers may be investigated, particularly multifunctional monomers, which may prove to be more useful than TBTA.

CONCLUSIONS

Organotin compounds have been incorporated into resist films in three ways: 1) Blending VMCH with OTS and DPEPA results in a resist with high O\(_2\) RIE etch durability and high sensitivity. 2) Modification of EMA with TBTO provides good O\(_2\) RIE durability, and when combined with DPEPA, also provides high sensitivity as a negative resist. This resist material offers the advantage of a guaranteed homogeneous distribution of metal during etching. 3) Reactive organometallic plasticizers hold some promise, but further work with other compounds will be necessary to demonstrate their utility.
The majority of this work involved the use of organotin compounds. Additionally, preliminary work with titanium, barium, zinc and silver compounds indicates that incorporation of these metals can yield similar improvements in \( O_2 \) RIE resistance. For example, 3-component blends of PMMA, DPEPA and an organic titanate yield high sensitivities as well as a dramatic improvement in etch resistance.

**ACKNOWLEDGMENTS**

This work was supported in part by the Office of Naval Research. Work was performed in part at the National Nanofabrication Facility at Cornell University which is partially supported by the National Science Foundation.

**REFERENCES**


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**TABLE I**

**Induction Period During \( O_2 \) RIE of VM/DPEPA/UTS Blend.**

**Effects of Electron Dose and Post-exposure Bake Conditions.**

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<th>Electron Dose (( \mu C/cm^2 ))</th>
<th>Induction Period (min) One Hour Post Exposure Bake Temp. (( ^\circ C ))</th>
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*Bake time of 5 min. @ 100\(^\circ\)C resulted in no induction period (similar to one hour, 80\(^\circ\)C bake after 5 \( \mu C/cm^2 \) exposure).
*Bake time of 30 min. @ 100\(^\circ\)C yielded results similar to one hour post bake @ 100\(^\circ\)C, after 5 \( \mu C/cm^2 \) exposure.*
1. Effect of organotin compound, OTS, on initial etch rate of VMCH.
Bake 1 hr/100°C. RIE conditions:
20 sccm at 36 mTorr and
0.25 W/cm², DC bias = 570 V.

2. Initial RIE etch rates in CF₄/O₂ mixtures for VMCH with 25% OTS & 20% DPEPA.
Baked 1 hr/100°C.

3. Lithographic response.
(A) same blend as in Fig. 2,
(B) same without OTS,
(D) VMCH alone,
(C) same as (B) but with fractionated polymer.
4. Interferometer traces during Oxygen/RIE of same blend as Fig. 2.
   - Exposure = 10 μC/cm², Bake = 1 hr/100°C.
5. Rutherford Backscattering Profiles for unbaked (A,B) and baked (C,D,E) films (1 hr/100°C). (A,C) unetched, (B,D) etched 1.5 min, (E) etched 3 min.
6. Dry developing scheme based on OTS diffusion.

1. COAT WAFER with VMCH/DPEPA/OTS Blend

2. EXPOSE PATTERN in unexposed film with 5 to 10 μC/cm² (Crosslinking in exposed regions locks OTS into polymerized matrix)

3. POST-EXPOSURE BAKE for 30 min at 100°C (OTS diffuses to surface in unexposed areas but remains uniformly distributed where exposed)

4. OXYGEN/RIE (Exposed areas etch more rapidly since etching is inhibited in unexposed regions because of surface tin concentration; resulting image is positive)

7. Oxygen/RIE rates for tin-modified polymer (EMA). Conditions: 20 sccm at 36 mTorr and 0.25 W/cm².

8. Lithographic response of EMA derivative with 10% tin. (A) 20% DPEPA, prebaked 2.5 hr/80°C, (B) 20% DPEPA, no prebake, (C) no DPEPA, no prebake.
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