Poly(methyl α-chloracrylate) as a New Positive Electron-Beam Resist

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Production of high density integrated circuits by electron-beam lithography relies heavily upon polymer resists for pattern delineation. Although there are many negative resists (1) known, far fewer positive e-beam (1) resists have been found. In this communication, we report positive e-beam resist behavior for poly(methyl α-chloracrylate) homopolymer. Previous radiation experiments (2, 3) with this material indicate that this polymer undergoes radiation degradation at a fairly high rate per unit radiation dose.

Methyl α-chloracrylate monomer was purchased from Polysciences, Incorporated, and was vacuum distilled before use. Poly(methyl α-chloracrylate) (PMCA) polymer was synthesized by conventional azodi-isobutyronitrile free-radial induced polymerization (4). The polymer was fractionally reprecipitated twice from dimethyl formamide using methanol as nonsolvent. The resulting polymer had a number average molecular weight ($\overline{M}_N$) of 125,000 as determined by membrane osmometry, and a polydispersivity of 2.6 as determined by gel permeation chromatography.

Electron-beam exposures were made with an AMR-900 scanning electron microscope operating at 10 kV, which was modified for raster scan pattern control with a flying spot scanner. The beam diameter was 1000Å. The electron dose was measured with a Faraday cup. The electron exposure charge density measurement was checked against the known sensitivity of PMMA using the standard developer (5). The test patterns consisted of sequential groups of lines with varying exposure densities; line widths were typically 1-2 μm with 1-3 μm spacings.

Electron-etched lines in PMCA films dissolved much faster than the unexposed resist when subjected to developer solutions. This occurs because the molecular weight of the irradiated polymer is much smaller (3) than that of the polymer in the unexposed region. The dependence of dissolution rate $\dot{d}$ upon polymer molecular weight has been shown to be (6)

$$\dot{d} = KM^{-A}$$

where M is the molecular weight, and K and A are constants. Although polymer solubility may change with radiation exposure, it is the dissolution rate that is most important for line development in positive resists. Table I lists line exposure charge densities employed for representative line groups in this study. Figure 1 is an SEM photograph of representative developed lines.

The e-beam developer composition is a very important consideration, but its selection is not scientifically clear-cut .Of the many developer solution compositions tried, two were fairly good. The first, a 1:1 $CHCl_3/CCl_4$ mixture, developed the lines, but with line edge blotchiness. The second, 1:1 $CHCl_3$/isopropanol (IPA), was an improvement over the first developer, but some unexposed polymer surface roughness was apparent. Isopropanol is probably a better nonsolvent for PMCA, because its larger molecular size could restrict molecular permeation of nonsolvent.

Our e-beam development charge densities indicate that PMCA is a significantly more sensitive resist than PMMA (see Table I). These findings are consistent with the higher observed radiation degradation susceptibilities (2, 3) observed for PMCA with respect to PMMA in other types of experiment. Since the only difference between PMMA and PMCA is the substitution of Cl for CH_3 at the α-acrylate group,

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Table I. Development charge densities and remaining resist thicknesses for PMCA positive e-beam resist samples

Resist	Exposure development charge density, C/cm²	Remaining resist thickness, A	Developer	Development time, min
PMCA	5.3×10^{-6}	3400 ± 300*	1:1 $CHCl_3/CCl_4$**	27
PMCA	1.0×10^{-5}	3500 ± 300*	1:1 $CHCl_3/CCl_4$**	17
PMCA	8.4×10^{-6}	2700 ± 300†	1:1 $CHCl_3$/IPA	40
PMCA	6.5×10^{-6}	2600 ± 300†	1:1 $CHCl_3$/IPA	91
PMMA	5×10^{-5}	5400 ± 300‡	1:3 MEK/IPA	1.5

* Original resist thickness 3700 ± 400A and measured by scanning electron microscope.
** Blotchy and poor line edge development which was improved by replacing CCl_4 nonsolvent with IPA.
† Original resist thickness 3900 ± 300A and measured by scanning electron microscope.
‡ Original resist thickness 6000 ± 300A.

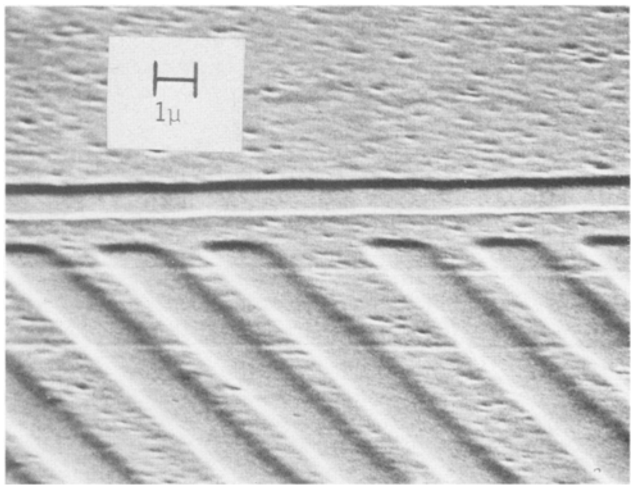

Fig. 1. Developed electron-beam etched lines in PMCA at 3800×. The substrate is a silicon wafer with a 4000Å thick oxide and the exposure dose is 8.4×10^{-6} C/cm². The other sample conditions are found in Table I and text.

the increased sensitivity in PMCA must be attributed to the chlorine substituent. The high electronegativity for chlorine is well known, and it is reasonable to expect a weakening of the main-chain C-C bond by electron polarization toward the halogen substituent (3).

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