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High-resolution Positive Resists for Electron-beam Exposure

Abstract: This paper examines the utility of four newly proposed positive resists whose processing combines electron-beam-induced degradation of certain polymers and, subsequently, *in situ* fractionation according to molecular weight. Positive-resist action in four systems formulated on this concept has been demonstrated. Typical sensitivity in electron-beam exposure is 10^{-4} coulomb/cm^2. Two resists exhibit resolution better than 1 micron. One resist investigated in detail yields extremely clean edges in electron-beam exposure, is resistant to hydrofluoric acid etching baths, and appears otherwise applicable to the fabrication of circuit elements of submicron size.

Introduction

To reduce the size of components of electronic circuits is important to their packaging and, more particularly, to the operational speed of components aggregated in systems. In present technology, where photoresists are exposed with optical masks or optical imaging so as to control etching and diffusion operations, the fabrication of very small circuit elements has been hindered by the fact that practical resolution is limited to about 2.5 microns (0.1 mil). Electron beams possess a much better resolution capability, both in theory and in practice. Beams having energy of the order of 10 keV and a diameter of approximately 0.1 micron can be produced with reasonable ease.[1] If a suitable resist material were available, such electron beams could be used to fabricate transistors and other circuit elements that invite extremely small geometries. Further, since positive-working resists are much more efficient than negative resists in applications where the ratio of open areas to protected areas is small, positive resists that are exposable by an electron beam would be particularly useful.

The use of electron beams as a means for exposing standard photoresists has been investigated and reported,[2] but the resolution and suitability of these resists for very small device fabrication is questionable. [Typically, a recent investigation of electron-beam-exposed lines on KTFR* (Kodak Thin Film Resist) revealed a smoothly sloping edge of about 2 microns on either side of a 10-micron-wide line exposed with a 10 kV beam.]

The exposure of negative photoresists involves chemical reactions of a type that generally can be initiated either by light or by electron bombardment. Photoresists of the standard positive type, on the other hand, undergo chemical reactions during exposure that can be initiated only by the absorption of light. Exposure of standard positive photoresists with an electron beam therefore cannot be expected to lead to results comparable even to the limited success that is possible in the case of negative photoresists.

The purpose of this paper is to present some results from work directed to the design, formulation, and evaluation of a resist system that is sensitive to electron beam exposure (but not to light), is positive working, and is capable of producing high-resolution etching masks.

Chemical and design considerations

Photoresists of the positive-working type are generally macromolecules containing functional groups that strongly influence the solubility characteristics of the molecule.

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*KTFR is a registered trademark of Eastman Kodak Co.

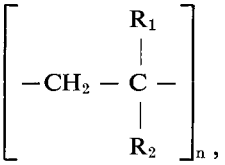
Upon illumination these functional groups are removed or replaced by others, thus rendering the molecule soluble in different kinds of solvents. For example, a photochemical reaction can be induced to replace certain functional groups with carboxyl groups, thus making the exposed photoresist soluble and developable in aqueous alkali solutions. This approach works well in the case of exposure by light because the light is absorbed by the functional groups only, and the subsequent photochemical reaction is limited to, or to the neighborhood of, the absorbing chromophores.

This method of changing the solubility, viz., by replacing certain functional groups photochemically, cannot be expected to work efficiently with electron beam irradiation. It is a well-known observation of radiation chemistry, which should also hold for low energy electron bombardment,* that energy from ionizing radiation is absorbed at every part of the molecule; hence neither the absorption nor the subsequent chemical reaction can be limited to functional groups.

A more promising approach is to change the solubility characteristics by using electron beam exposure to alter the size of macromolecules. The chemical effect of ionizing radiation of polymers is twofold, in that cross-linking of neighboring chains and random scission of the chains take place simultaneously. In individual polymers, generally only one of the two effects dominates and, on that basis, polymers thus categorize themselves into cross-linking and degrading types. On the assumption that the effect of low-energy electrons is similar to that of high-energy radiation, a positive-working resist can be made by taking advantage of the reduction that occurs in the average molecular weight of a degrading-type polymer when selected areas are exposed to an electron beam.

We have found several polymers that do indeed degrade upon low-energy-electron bombardment, and in combination with the development method to be described below, form a novel resist system sensitive to electron beam exposure. The suitable polymers fall into two classes:

Class 1: Vinyl-type polymers and copolymers in which one-half of the carbon atoms of the main chain are quaternary, as in



where $R_1 = CH_3$, C_6H_5, $COOCH_3$, etc., and $R_2 = CH_3$, etc.

Class 2: Cellulose derivatives.

To be preferred for resist purposes are those members of the two classes that exhibit good adhesion to the substrate surface and are capable of withstanding the conditions of etching.

Development is based on a technique of fractionation of polymers according to molecular weight. Given a liquid, A, which is a good solvent for a particular polymer of any molecular weight, and a different liquid, B, which is not a solvent for the same polymer irrespective of its molecular weight, it is, in general, possible to find a composition of a mixture of A and B that will act as a solvent for the polymer below a critical molecular weight, but will act as a nonsolvent for the same polymer above the critical molecular weight. In the formulation of the developer, one adjusts the proportion of the two liquids until the molecular weight corresponding to the composition will be between the molecular weight of the starting material and that of the degraded polymer.

A few other considerations in the design of a positive-resist system are worth mentioning. Polymers, as prepared, are generally not monodisperse, i.e., the individual molecules do not all have identical molecular weights. It is obvious that the broader the initial distribution, the farther must the degradation be carried before a good distinction between exposed and unexposed areas can be made. As will be seen later, the distribution of molecular weights is narrow enough, in all the polymers used here, to result in satisfactory resists. It is possible, however, to increase the sensitivity to exposure by using more nearly monodisperse polymers. The choice of average molecular weight for the starting material is based on practical considerations, such as viscosity for coating solutions, availability, and, of course, final performance. Finally, in the choice of components for the developer, relative evaporation rates must be considered; namely, to avoid attack on the unexposed areas during drying after development, the solvent-to-nonsolvent ratio in the developer must not be allowed to increase by evaporation.

Experimental

- *Materials*

The following polymers were investigated individually:

1. Cellulose Acetate, **CA**, obtained from Eastman Organic Chemicals; Acetyl 39.8%, ASTM Viscosity 3.
2. Poly-isobutylene, **IB**, obtained from Monomer Polymer Laboratories, Borden Chemical Co.
3. Poly-(α-methyl-styrene), **MS**, obtained from Dow Chemical Co.
4. Poly-(methyl methacrylate), **MM**. This material was synthesized in this laboratory from the monomer, using azo-bis-isobutyronitrile catalyst.

The coating solutions were prepared by dissolving the polymers in suitable solvents or solvent mixtures. The

* The chemistry of the interaction of low-energy (20 keV or less) electrons with organic materials in condensed phases has been only randomly investigated. (However, see Refs. 3 & 4.) Nonetheless, some guidance as to the expected reactions can be obtained by extrapolating the knowledge available in the well-studied field[5] of effects of high-energy (MeV) radiation.

Table 1 Composition of resist solutions.

Polymer	*Solvent*	*Concentration*
CA	1:1 cyclohexanone/ methyl ethyl ketone mixture	4%
IB	Trichloroethylene	5%
MS	Trichloroethylene	15%
MM	Methyl isobutyl ketone	10%

Table 2 Poly-(methyl methacrylate): effect of resist solution concentration on layer thickness.

Polymer Concentration	*7%*	*10%*	*15%*
Thickness of resist layer on 1-inch wafers spun at 5000 rpm	3000 Å	5000 Å	7000 Å

solvents were chosen so as to have a conveniently long drying time in the coating process, while the concentrations were determined so as to gain the required resist thickness (about 5000 Å) for a given spinning speed and acceleration. The appropriate solvents and concentrations are listed in Table 1.

• *Procedures for general evaluation*

The resist solutions were coated on 1-inch-diameter oxidized silicon wafers (oxide-layer thickness $\approx$3000 Å) using a spinning table revolving at $\approx$4000 rpm. In a few instances wafers coated with aluminum were used as substrates. The samples were air-dried for 60 minutes or longer and were then exposed to an electron beam, as described below. The composition of developer solutions was optimized by immersing exposed wafers in a series of mixtures containing a solvent and a nonsolvent in varying ratios until one was found that removed the exposed areas cleanly and rapidly without attacking unexposed areas. The resolution was determined by observing under an optical microscope sets of parallel lines which had been defined by electron beam exposure. Resistance to chemical etching solutions was determined by immersing the resist-coated (but in most instances unexposed) wafers in the etchants. Etchants used were buffered HF solution (15 g NH_4F, 22 ml H_2O, 3 ml concentrated hydrofluoric acid solution), and hot (80°C) 20% hydrochloric acid solution. Layer thicknesses, when necessary, were measured with a Taylor-Hobson "Tallysurf" instrument.

• *Electron-beam exposure*

The electron-optical equipment used for exposure was, with minor modifications, identical to apparatus developed by Thornley, Brown, and Speth.[1]

Two types of electron beam exposures were made: one to determine the sensitivity of the resist at various beam accelerating voltages, and one to determine resolution. In determining sensitivity, the beam was scanned over an $8\mu \times 37\mu$ area with the line frequency adjusted so that the line detail was not resolved. Exposures were made at 7.5, 10, and 14 kV over the range of 2×10^{-3} to 10^{-5} coulomb/cm^2. In determining resolution, a 2000 Å beam was scanned over a $1\mu \times 37\mu$ area with the fast line scan running along the short direction of the area (width of line). Several lines were exposed with line spacing varied from 2.0 to 2.5 μ. Lines of various widths were also exposed with the same method.

• *Procedure for the poly-(methyl methacrylate) resist*

In the course of this work it appeared that the resist based on poly-(methyl methacrylate) would be the one best suited to the fabrication of high-speed transistors. A rather detailed study of its properties was therefore undertaken. The following procedure was used. The samples used for coating were oxidized silicon wafers (n-type with resistivity of from 0.1 to 0.2 ohm-cm) having an oxide thickness of about 2600 Å. The resist solution was applied to the wafer while stationary, after which the wafer was spun at 5000 to 10,000 rpm for one minute. The thickness of the resist layer seems to be independent of spinning speed so long as the speed is sufficient to produce a uniform layer over the wafer surfaces (over 4000 rpm). The layer thickness is a function of solution concentration; the results of various concentrations of MM on 1-inch wafers spun at 5000 rpm are shown in Table 2. Thickness measurements were obtained with a Watson Interferometer after metalizing the samples with $\approx$1000 Å of aluminum.

Prebaking at 170°C for 30 minutes in air was found necessary to improve adhesion and resistance to chemical etching. The wafer was then inserted into the vacuum chamber of the electron gun, pumped down to a pressure of approximately 10^{-5} Torr, and exposed to the electron beam as described above.

All wafers were developed immediately after exposure by soaking in a 3:1 solution of isopropyl alcohol and methyl isobutyl ketone for one minute followed by a 30-second spray with the same solution. The samples were dried by blowing Freon-12* gas over the surface, and were then observed in the optical microscope and photographed. In the resolution runs the wafers were postbaked at various temperatures before etching in order to determine the degree of undercutting. These wafers were subsequently etched by immersion in a solution consisting of 10 cm^3 of 48% solution by volume of HF in water, and 90 cm^3 of 40% solution of NH_4F in water. The wafers were etched for 3 to 4 minutes

*Freon-12 is a registered trademark of E. I. duPont Co.

Table 3 Properties of positive electron-beam resists.

Resist	Optimum developer: Solvent	Optimum developer: Nonsolvent	Optimum developer: Ratio	Minimum exposure at 10 kV (C/cm²)	Resolution (microns)	Resistance to etchants[a]: HF	Resistance to etchants[a]: HCl
CA	1:1 methyl ethyl ketone/ethanol mixture	toluene	40:60	5×10^{-4}	<0.8	P	P
IB	1:1 methylene chloride/ benzene mixture	ethanol	70:30	5×10^{-5}	2.0	S	S
MS	benzene	ethanol	10:60	1×10^{-4}	2.0	P	S
MM	methyl ethyl ketone *or* methyl isobutyl ketone	isopropanol	30:70	5×10^{-5}	<0.8	S	G

(a) Code for etch resistance: P = Poor, S = Satisfactory for short period, G = Good.

at room temperature without agitation. Stripping of the unexposed resist was accomplished by soaking in acetone or ethyl acetate for 5 minutes, followed by a 30-second spraying with the same solvent.

Results and discussion

• *General evaluation*

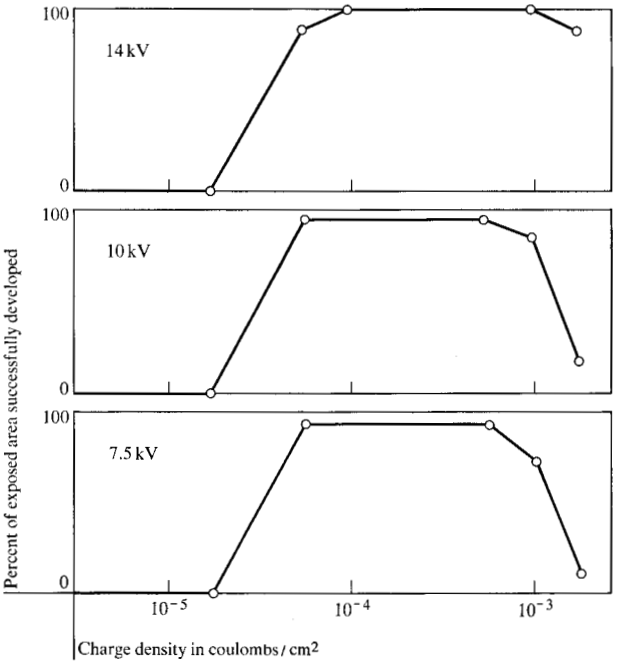
All four of the polymers evaluated performed well as positive resists, i.e., under electron-beam exposure they degraded with high sensitivity, and the exposed images could be developed with solvent-nonsolvent mixtures. The results are summarized in Table 3. The optimum developer compositions listed therein are for typical film thicknesses at one-minute development time. If the proportion of the solvent component is increased, more rapid development is possible. The best proportions also depend on the resist film thickness and exposure.

No major differences in sensitivity were found among the four materials. The resolution of the **CA** and **MM** resists was better than the accuracy in measurement that can be achieved with an optical microscope (the values given in Table 3 are upper limits). The resolution of the polyisobutylene resist was limited by the creep of this rubbery material.

The resistance of the resists to chemical etchants seems to be governed mainly by adhesion effects. The failures in etch baths, if any, appear as flaking off rather than disintegration of the resist. The great improvement in etch resistance of **MM** films upon prebaking is more easily explained in terms of relaxation of strains and an increase in the adhesive forces due to molecular reorientation at elevated temperatures than in terms of chemical reactions in this polymer. With prebaking the etch resistance of **MM** is very good. Evaluation of adhesion promoter additives promises further improvement with all of the resists.

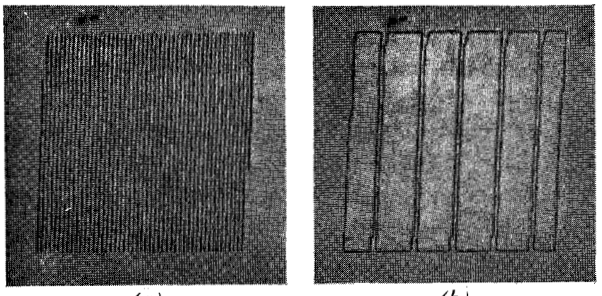
Cellulose acetate, of course, is subject to acid-catalyzed hydrolysis and cannot be expected to withstand acidic etching baths for an extended period of time. Its good resolution capability recommends its use when ion etching[6] (reverse sputtering), rather than chemical etching, is preferred in the fabrication process.

Figure 1 Exposure characteristics of poly-(methyl methacrylate) positive resist.



• *Poly-(methyl methacrylate) resist: detailed evaluation*

The characteristics of the **MM** resist have been investigated in more detail than those of the other resists. The exposure characteristics are presented in Fig. 1. It can be seen that the satisfactory exposure range at 7.5 and 10 kV lies between 5×10^{-5} and 5×10^{-4} coulomb/cm², while at 14 kV it is 10^{-4} to 10^{-3} coulomb/cm². Overexposure of the



(a) (b)

Figure 2 Fine line resolution of poly-(methyl methacrylate) resist: (a) 50 lines of exposed resist on 100 × 100 micron field (exposed at 12 kV, 10^{-4} C/cm²); (b) large areas of exposed resist with 1-micron separation.

Table 4 Effect of postbaking temperature on resist undercutting.

Postbaking temperature	100° C	120° C	130° C
Widening (after etching) of a line 2 microns wide	50%	20%	0%

resist beyond these charge densities causes the reactions leading to cross-linking to dominate, and the resist in overexposed areas cannot be removed with acetone or ethyl acetate. Prebaking at 170°C does not seriously affect the exposure characteristics of the resist while it increases its hardness and resistance to scratching. As expected, this resist is insensitive to white or ultraviolet light exposure comparable to the exposure used for commercial photoresists.

The resolution of the resist is demonstrated in Figs. 2 and 3, and particularly in the latter, where fine lines are shown at various stages of sample processing. An electron-beam accelerating voltage of 12 kV was chosen for these runs as a compromise accommodating both resist resolution and electron gun performance. Also, a charge density of 1.3 × 10^{-4} coulomb/cm² was used, chosen within the proper exposure range of Fig. 1.

Undercutting in the resist, that is, the widening of the bottom of the trough beyond the width of the top of the trough, is generally a serious problem when narrow lines (width of the same magnitude as depth) are formed in photoresists. In the case of the MM resist, undercutting was estimated by baking 2-micron-wide lines at various temperatures after developing, and before chemical etching. The results are tabulated in Table 4, where it can be seen that postbaking at 130°C for 30 minutes eliminated the undercutting to the point where the dimensions of the original developed pattern are preserved after chemical etching. This can also be seen in Fig. 3.

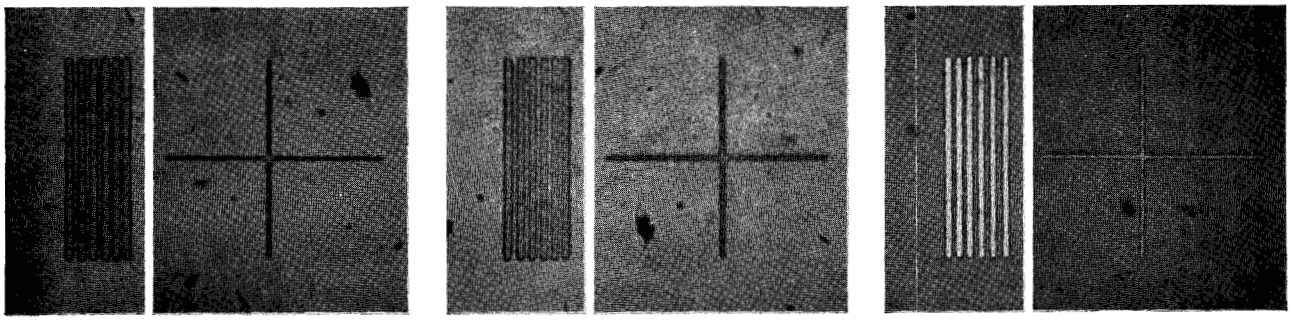
The results summarized in Table 4 indicate that an undercut of approximately 0.5 micron on either side of the 2-micron-wide line exists after baking at 100°C. It appears that at higher temperatures controlled flow of the resist at the edges fills in the undercut portion of the edge.

In Fig. 4, the edge quality of the resist before postbake and of the etched 2-micron line is demonstrated in photographs obtained with a scanning electron microscope with 300 Å resolution. As can be seen from these photographs, both edges look very good, with some undercutting in the resist edge. The detail visible on the top of the edge is due to 60-cycle modulation of the electron beam. The edge quality of the resist makes it particularly suitable for ion etching, where the edge detail is usually duplicated on the oxide edge.

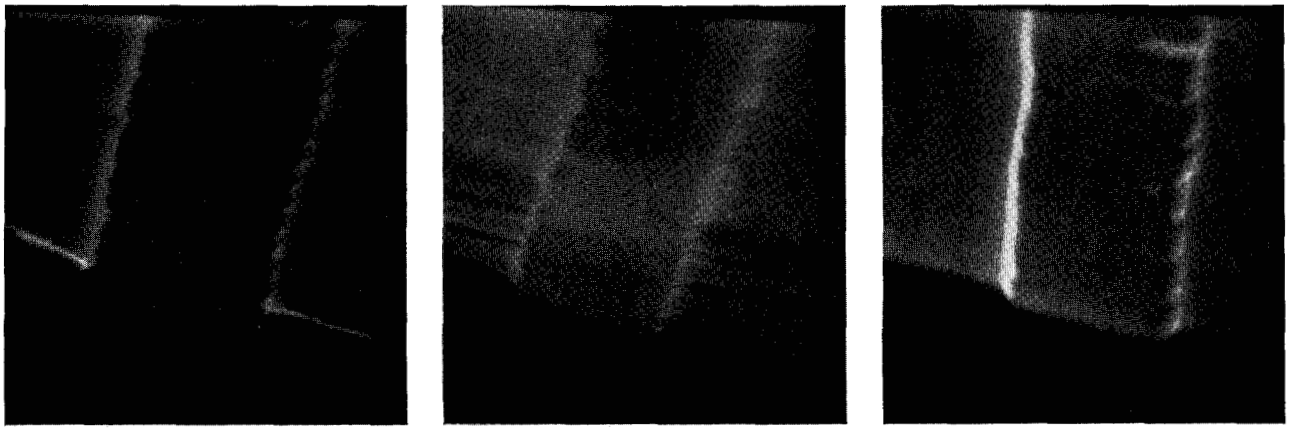
Summary

A novel concept for the design of positive resists for electron-beam exposure has been described and resists formulated upon that concept have been evaluated. Two of the

Figure 3 Resolution patterns for poly-(methyl methacrylate) resist: (a) developed resist patterns before baking; resist thickness, 5000 Å; exposed at 12 kV, 1.3 × 10^{-4} C/cm²; (b) the same patterns after baking at 130° C for 30 minutes; (c) the same patterns chemically etched through 2600 Å of SiO_2.



10μ (a) (b) (c)



(a) (b) (c)

Figure 4 Scanning electron micrographs of positive resist and SiO_2 profiles: (a) profile of a 2-micron-wide line written with a 10 kV electron beam on 4000 Å methyl-methacrylate (viewing angle, 27°); (b) the same line at a viewing angle of 10°; (c) the same line as chemically etched through 2600 Å of SiO_2.

resists, cellulose acetate and poly-(methyl methacrylate), possess a better resolution capability than any previously available resist or, for that matter, any other known forming technique. The superior resistance of poly-(methyl methacrylate) to HF etching baths renders it preferable for device fabrication on oxidized silicon wafers.

The edge profiles of line images were seen to be very good, both in the exposed and in the developed poly-(methyl methacrylate) resist and, subsequently, in the chemically etched silicon oxide. The reproducibility of the process proved good. To employ it in the fabrication of devices of 1-micron or smaller geometry appears feasible.

Acknowledgment

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