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DEVELOPMENT OF HIGH SENSITIVITY X-RAY AND ELECTRON-BEAM RESIST --ETC(U)
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Development of High Sensitivity X-Ray and Electron-Beam Resist Processes

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RESEARCH OBJECTIVES

The goals of our research on high sensitivity electron beam and x-ray resist processes are threefold. First, newly discovered polymer formation techniques will be used to "build" highly sensitive polymers for resist applications, and to investigate novel methods of resist application to substrate surfaces. Second, chemical and physical methods of altering resist structure and thus properties will be studied in order to improve the plasma etch resistance of PMMA-type resist materials. Finally, a model will be developed which can predict resist thickness versus time, spin speed, and position on a silicon wafer, so that spin coating uniformity and reproducibility can be more efficiently attained. These studies will enhance our understanding of resists and resist processes, and will ultimately make possible improved processing methods and yields for higher performance and lower cost IC's.

STATUS OF THE RESEARCH EFFORT

Plasma-initiated polymerization (1) has been used to form ultrahigh molecular weight (UHMW) polymers. It can be demonstrated theoretically (see our continuation proposal No. 81-NE-074, entitled, "Development of High Sensitivity X-Ray and Electron-Beam Resist Processes") that such materials may display enhanced radiation sensitivity and lowered dissolution rates. For instance, the increase in sensitivity of a polymer can be described by (2-4)

$$\frac{M_n^f}{M_n^\circ} = \frac{1}{KG(s)\ D\ M_n^\circ} \qquad (1)$$

where M_n^f = final number average MW (after exposure)

M_n° = initial number average MW

K = constant for a particular polymer film

G(s) = number of main chain breaks produced when the polymer absorbs 100 eV of energy

D = exposure dose

It is clear from Eqn. (1) that the sensitivity of a resist can be increased either by increasing G(s) or by increasing M_n°. Both approaches have been pursued to improve resist sensitivity. However, only a few results have been published that relate initial molecular weight to resist sensitivity, and these data qualitatively support the hypothesis that increasing molecular weight increases sensitivity (5,6).

Plasma-Initiated Polymerization

For plasma-initiated polymerization, methyl methacrylate (MMA) monomer was purified by vacuum distillation at 38°C. The purified monomer was then transferred (under vacuum) to a polymerization ampule (Fig. 1). The ampule was immersed in liquid nitrogen, and copper electrodes positioned on either side of the ampule stem (Fig. 1). After warming the ampule until a pressure of 1 torr was established, an rf glow discharge was initiated in the tube between the electrodes. After one minute, the plasma was extinguished, the ampule was sealed and warmed to room temperature, and the monomer was mixed with the plasma initiation products. The ampule was then shielded from light and placed in a water bath at 25°C for 34 hours. At the end of the polymerization period, the polymer that had formed was

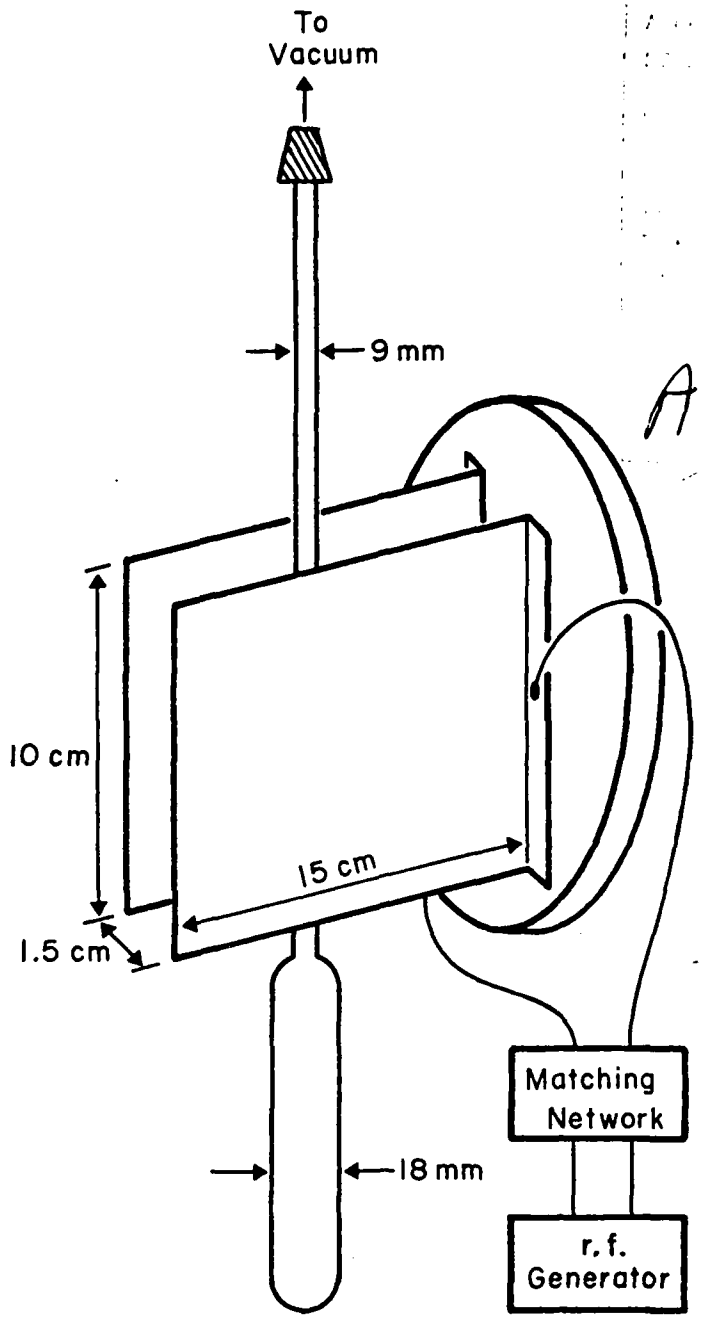

Fig. 1. Glass ampule positioned for plasma initiation.

precipitated from the monomer solution, and was dissolved in methyl-ethyl-ketone (MEK).

The specific viscosity of various polymer solutions was measured using a low-shear Ubbelohde-type viscometer (7), and by extrapolating this viscosity to infinite dilution, the intrinsic viscosity and thus the viscosity average molecular weight was determined (8). For comparison purposes, KTI PMMA electron beam resist was treated in the same manner, so that molecular weight determinations could be performed. The molecular weights obtained by this method were 3.1×10^7 g/mole for the plasma-initiated PMMA, and 6.9×10^5 g/mole for the KTI PMMA. Indeed, the plasma-initiated materials is ~15 times the molecular weight of conventional PMMA formed for the purpose of high molecular weight experiments (6).

Electron Beam Exposure

In order to determine the utility of the ultrahigh molecular weight (UHMW) PMMA as an electron beam resist, this material, dissolved in its monomer MMA, was spin-coated onto thermally oxidized silicon wafers and onto chromium-on-glass mask plates. For comparison, the KTI PMMA, which, as purchased, was dissolved in chloro-benzene, was spin-cast onto identical substrates. The thicknesses of both PMMA films were 0.42 μm.

Resist-coated samples were prebaked at 150°C for 30 min. in a vacuum oven to improve chemical etch resistance and adhesion, and to drive off any residual monomer (UHMW) or solvent (KTI). No degradation of the polymer films was observed. In addition, both films were pinhole-free.

E-beam exposures were carried out in an ETEC Autoscan scanning electron microscope and in an ETEC MEBES-1 exposure system, using 10 KV electrons. Using a 1:1 mixture of MEK and isopropanol (IPA) as a developing solution, the dissolution rates of unexposed UHMW and KTI PMMA were 170 Å/min. and 5 Å/min. respectively. Finally, the SiO_2 and the chromium were etched with buffered HF 1:7 HF:NH_4F) and chromium etch (Precision Photo Glass Chromium Etchant CR-8). Both resists adhered well during the etching of these two materials.

Figure 2 shows an SEM photograph of a pattern made in KTI PMMA, exposed at 9×10^{-6} C/cm^2. The 0.5 μm lines are a bit ragged, but the dose is a factor of 2-3 lower than normally used for commercial PMMA. In addition, ~ 40% of the unexposed resist is removed by the develop cycle.

Figure 3 shows the same pattern, generated with UHMW PMMA, at a dose of 3.2×10^{-6} C/cm^2. Clearly, the line definition is improved, even though the dose is a factor of 3 lower than that used for KTI PMMA. Further, virtually no unexposed resist was removed during the develop cycle.

Spin Coating UHMW PMMA

Our efforts in utilizing UHMW PMMA have encountered some experimental difficulties in producing a uniform coating of this material by conventional spinning techniques. Because of the exceptionally high MW, the polymer chains are entangled even at concentrations of 1-2% in various solvents, and so high spin speeds (> 1000 rpm), which are usual for commercial spinners, are inconsistent with uniform coating. Therefore, a new spinner was designed and built, which allows low (< 400 rpm) spin speeds

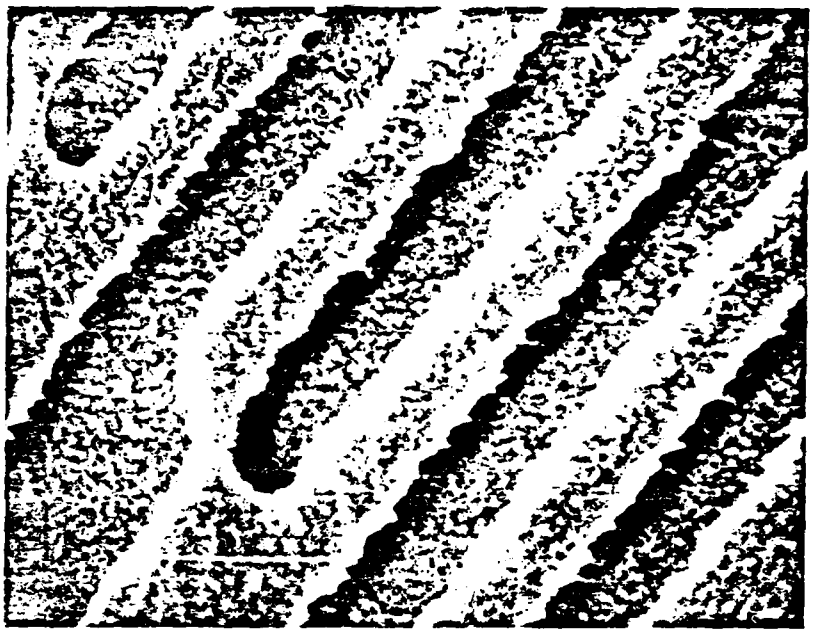

Fig. 2. SEM photograph of resist lines in KTI PMMA. Small lines are 0.5 μm. Dose is 9×10^{-6} C/cm^2.

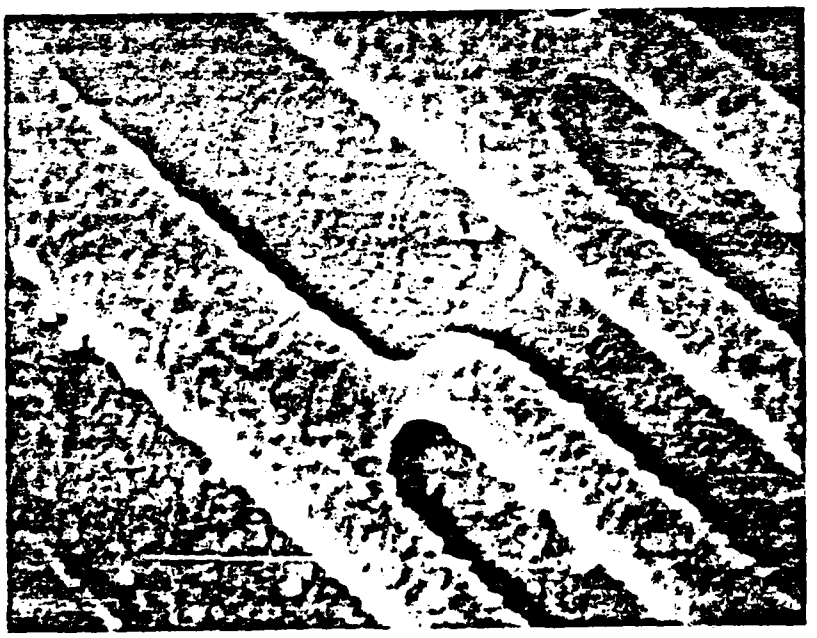

Fig. 3. SEM photograph of resist lines in UHMW PMMA. Small lines are 0.5 μm. Dose is 3.2×10^{-6} C/cm^2.

to be reproducibly attained, permits ramp speeds to be changed over a wide range, and permits "instantaneous jumps" in spin speed if desired. Thus far, our experience with this tool is most gratifying - significant improvements in thickness uniformity have been obtained. Currently, we can spin films of UHMW PMMA with $\pm$ 4% across a wafer.

The above spinner offers the possibility of performing modeling studies on spinning of resist films in general. Since processes for resist spinning are presently determined by trial and error, development of models would greatly facilitate process development and enhance fundamental understanding. The current approach takes into account the non-Newtonian nature of the resist solution and the solvent evaporation (which changes viscosity) during spinning, in an attempt to predict film thickness as a function of position, solution viscosity, and spin speed.

Plasma Etch Resistance

Electron-beam and x-ray resists must be capable of withstanding ion/electron/photon bombardment incurred during plasma etch processes. However, under the proper plasma exposure conditions (9) PMMA has been observed to cross-link, and so become more resistant to bombardment effects normally encountered during dry etching. Preliminary experiments on UHMW PMMA using an argon plasma have suggested that indeed cross-linking has occurred, as evidenced by a significantly reduced solubility of the plasma-treated polymer in acetone. Further, patterns of UHMW PMMA treated in this way showed no signs of pattern size degradation; however, a loss of ~25% in thickness was observed, suggesting

that some sputtering or ablation was occurring. Additional, more quantitative tests are now beginning.

Halogen-Substituted Methacrylate Resists

The substitution of a halogen atom such as chlorine or bromine, for the α methyl group in PMMA has been shown to generate a polymer that is a significantly more sensitive e-beam or x-ray resist material than PMMA (10,11). Since brominated MMA is not generally stable, and is difficult to purchase from commercial chemical houses, and since chlorinated MMA is expensive, both monomers are being prepared in our laboratory.

Methyl-α-chloroacrylate was synthesized by a two-step process involving direct chlorination of methyl acrylate, followed by vacuum distillation to separate methyl-α, β - dichloropropionate from the starting materials and side products. The methyl-α, β - dichloropropionate was then reacted with quinoline to give methyl-α-chloroacrylate (12). The yield of this monomer based upon methyl acrylate was 75%, and the purity was established by refractometry, infrared spectroscopy, and gas chromatography. Plasma-initiated polymerizations with this material are now underway.

Direct Thin Film Resist Formation

In an attempt to directly form thin films of UHMW PMMA from monomer films, a simple bell-jar apparatus, shown in Fig. 4, was constructed. Monomer vapor (MMA) was introduced into the chamber via the top electrode, and was condensed on substrates lying on the cooled lower electrode. The monomer film was allowed to warm-up, and a plasma was ignited by supplying rf

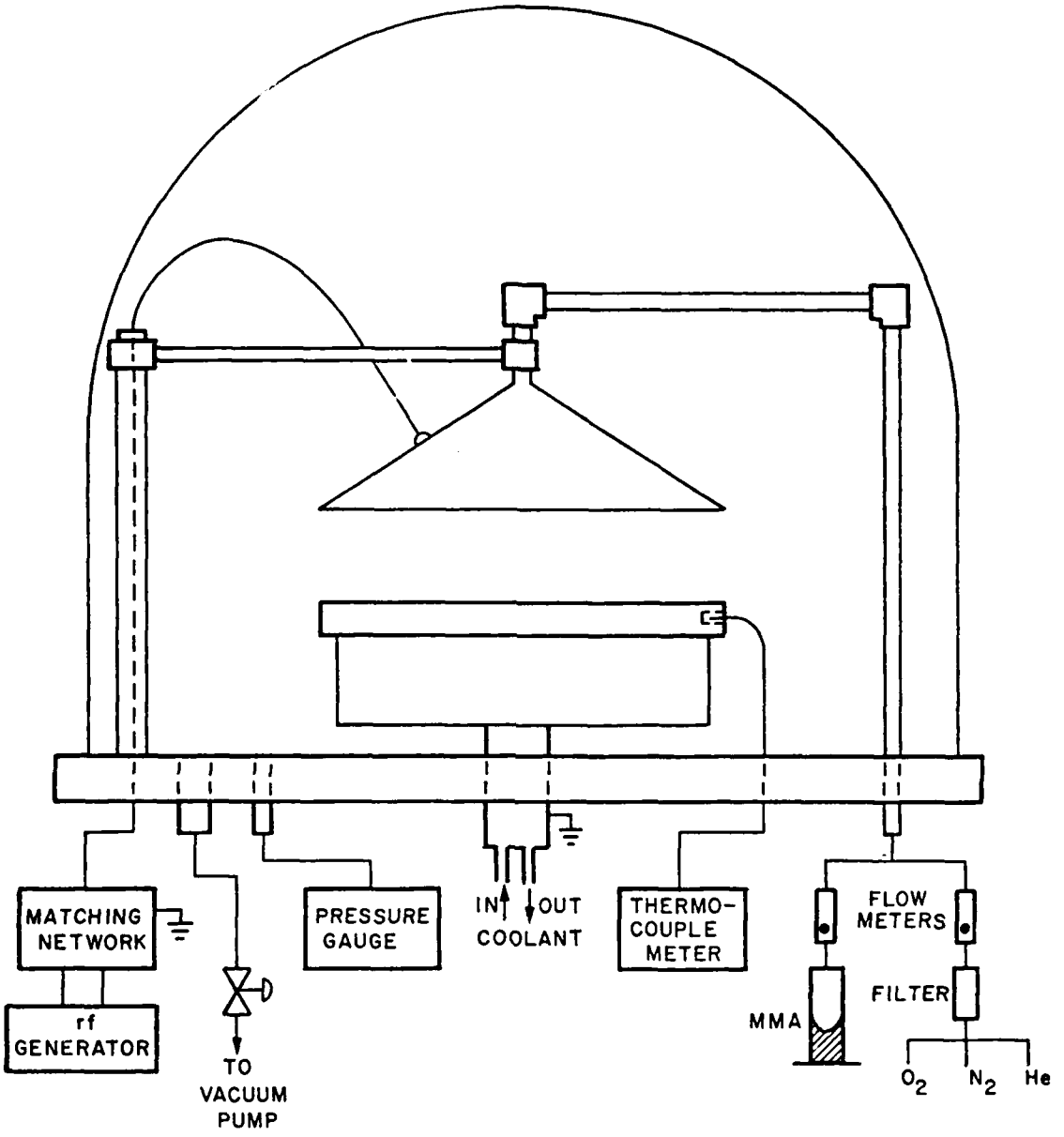

Fig. 4. Bell jar apparatus for direct plasma-initiation of monomer films.

power to the top electrode. After approximately one minute, the plasma was extinguished, and the monomer film was permitted to polymerize.

Initial experiments demonstrated that a polymer film does form, but the formation time is long (10-20 hours). Further, the film was not as uniform as is necessary for resist applications. These non-uniformities disappeared when plasma cleaning of the substrates prior to monomer condensation was performed using either oxygen or helium glow discharges. Unfortunately, under all conditions of rf power, pressure, and substrate temperature attempted, only thin ($\sim$ 0.1 μm) polymer films were obtained.

Currently, two possiblities exist for the inability to form thick ($>$ 0.2 μm) films by the direct deposition method. First, as the substrate warms, a temperature gradient is established between the substrate and the electrode so that the monomer evaporates off the sample surface and condenses on the cooler electrode. Second, surface tension forces draw the MMA off the top of the substrate to the space between the substrate and the electrode. The likelihood of these possibilities is established by the fact that thick layers ($\sim$ 0.3 μm) of polymer form on the side of the substrate in contact with the electrode surface.

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PUBLICATIONS

Within the next several months, a paper entitled, "Electron Beam Resists Produced by Plasma-Initiated Polymerization of Methyl Methacrylate," will be written. The authors of this paper will be L. M. Gavens, D. W. Hess, A. T. Bell, and D. S. Soong, and submission will most likely be to the Journal of Applied Physics.

PERSONNEL ASSOCIATED WITH THE RESEARCH EFFORT

1. L. M. Gavens - M.S. in Ch.E., awarded December, 1980. Thesis title: Electron Beam Resists Produced by Plasma Initiated Polymerization of Methyl Methacrylate.
2. W. W. Flack - Ph.D. candidate in Ch.E.
3. B. J. Wu - M.S. candidate in Ch.E.
4. D. W. Hess - Associate Professor, Department of Chemical Engineering, U.C. Berkeley.
5. A. T. Bell - Professor and Chairman, Department of Chemical Engineering, U.C. Berkeley.
6. D. S. Soong - Assistant Professor, Department of Chemical Engineering, U.C. Berkeley.

INTERACTIONS

1. Presented paper entitled, "Use of Ultrahigh Molecular Weight PMMA as an Electron Beam Resist," at Fairchild R&D Laboratory, Palo Alto, CA, February 5, 1981.
2. Will present a paper entitled, "Electron Beam Resists Produced by Plasma-Initiated Polymerization of Methyl Methacrylate," at the IUPAC 5th International Symposium on Plasma Chemistry, Edinburgh, Scotland, August 10-14, 1981.

NEW DISCOVERIES

The use of plasma initiation generates the opportunity to investigate ultrahigh molecular weight polymers for resist applications. Due to the extensive entanglements of polymers with molecular weights greater than 10^7 g/mole, developing solutions swell and dissolve this material at a low rate, thereby enhancing the contrast observed between exposed and unexposed resist. This makes possible the use of lower exposure doses for electron beam resist materials such as PMMA.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Plasma-initiated polymerization was used to form ultrahigh molecular weight (greater than ten million grams per mole) poly (methylmethacrylate) (UHMW PMMA) from liquid methyl methacrylate (MMA). The PMMA thus obtained was exposed to beams of 10 KV

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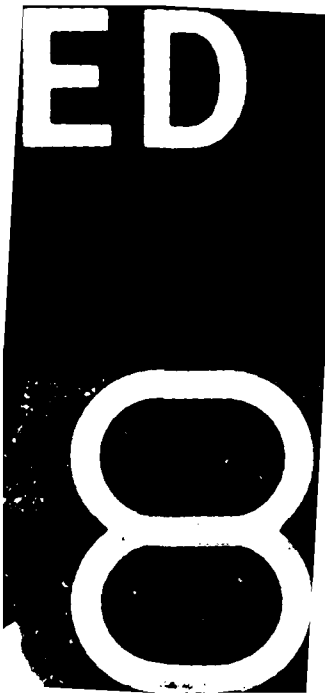
electrons ranging in dose from 0.1-10 mico-coulombs per square centimeter. For comparison, identical exposures were carried out using commercial PMMA resist (KTI) with a molecular weight of ~0.7 million grams/mole. Using 1:1 methyl ethyl ketone and isopropanol to develop the exposed resist, 0.5 micron pattern sizes were formed in both resist materials. Pattern fidelity in the UHMW PMMA was virtually identical to that obtained with KTI PMMA, but a factor of three lower dose could be used with the UHMW material. This lowered dose arose because the dissolution rate of the unexposed resist was a factor of 30 lower for UHMA than for KTI PMMA.

A new spinner was designed and built to allow improved control of spin-cast films. Modeling studies based upon non-Newtonian behavior were initiated to enable prediction of film thickness as a function of position on a wafer, solution viscosity, and spin speed.

In an attempt to further improve the sensitivity of UHMW materials, synthetic studies were undertaken to introduce halogen atoms into the MMA molecule. Chlorinated MMA was synthesized and is currently being investigated for its plasma-initiation susceptability.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