Enhanced plasma etch resistance of acrylic acid–calcium acetate modified poly(methylmethacrylate)

J. O. Choi, S. Y. Kim, J. A. Moore, J. C. Corelli, and A. J. Steckl
Center for Integrated Electronics, Rensselaer Polytechnic Institute, Troy, New York 12180

(Received 11 June 1986; accepted 1 October 1986)

Enhanced dry etch resistance of acrylic acid–calcium acetate modified poly(methylmethacrylate) was demonstrated. Selective pattern formation in the irradiated (DUV and e-beam) areas was accomplished using PMMA as a base film and acrylic acid as a modifying monomer. After the acrylic acid modified PMMA has imbibed calcium ion, a latent image was developed by exposure to an oxygen plasma. An involatile calcium oxide layer which had resistance against CHF_3 reactive ion etching was generated. The images of modified PMMA were transferred into the silicon dioxide layer.

I. INTRODUCTION

Poly(methylmethacrylate) (PMMA) is a standard photoresist which can be used for deep UV, e-beam, x-ray, and ion beam lithography.[1] The radiochemically induced scission of bonds in the main chain and the evolution of volatile fragments such as carbon monoxide, carbon dioxide, methane, and methanol, combine to generate the difference in solubility between the irradiated area and the original PMMA film.

In the usual positive processes, high radiation doses are generally required. In addition, PMMA has poor resistance against plasma etching and reactive ion etching (RIE) processes, so it cannot be effectively developed by dry development methods.

It is to be noted that the acyl stabilized, tertiary radicals in the cleaved main chain induce active sites for radical polymerization.[2]

It was found that the same reactive free radical fragments were generated, irrespective of the radiation source,[3,4] and that lithographic sensitivities enhanced by a factor of about 10–1000 were obtained using acrylic acid (AA) as the reactive monomer.[5–7] Acrylic acid modified PMMA (AA-PMMA) was still not plasma resistant enough to cause an effective difference in dry etch rate between it and unirradiated PMMA.

AA-PMMA has many functional carboxylic acid groups which can be easily exchanged with various ions (Ca^{++}, Mg^{++}, Na^{+}, K^{+}, Al^{+++}).[8,9] AA-PMMA can imbibe calcium ions when it is soaked in a saturated aqueous calcium acetate solution. After the imbibing of calcium ions, a latent image can be developed by exposure to an oxygen plasma which essentially generates an involatile layer of calcium oxide within the irradiated and modified portion of the resist.

The remaining modified PMMA has pronounced resistance against a CHF_3 reactive ion etching which erodes the oxide layer. Thus the image of modified PMMA is easily transferred into the silicon dioxide layer. Figure 1 shows an example of this dry development process.

II. EXPERIMENTAL METHODS

A. Modification of PMMA

Modification experiments were performed in a vacuum system designed so that a solution of purified acrylic acid (Aldrich) could be degassed in a reservoir and then siphoned directly into the reaction chamber without contact with oxygen. A detailed description of the irradiation, sample preparation, and grafting conditions are given elsewhere.[7]

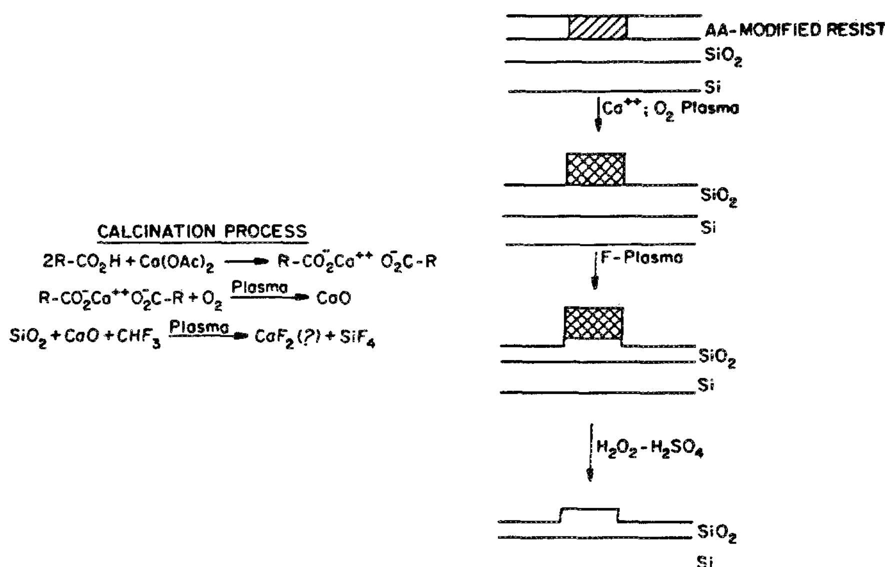

FIG. 1. Processing sequence schematic for dry developed process by acrylic acid modification and calcination.

 0734-211X/87/010382-04$01.00 © 1987 American Vacuum Society

The purified monomer was diluted with deionized water to a 10% (by volume) solution. The monomer solution was degassed by repeatedly freezing it with liquid nitrogen and then allowing it to thaw slowly.

The monomer solution was introduced into the evacuated chamber (10^{-5} Torr) where the irradiated samples were mounted on wafer holders so that the monomer could be easily vaporized. The reaction chamber was immersed in a water bath and the temperature was increased from 20 to 60 °C. The reaction with acrylic acid was continued at 60 °C until the patterns on the wafer could be detected visually.

The modified wafers were rinsed with deionized water and immersed in 20% aqueous calcium acetate solution at 60 °C. After treatment with calcium acetate solution for a specific time, samples were rinsed with deionized water, blown dry with nitrogen, and baked at 120 °C for 1 h.

B. Oxygen plasma etching

The dry etch durability of Ca-AA-PMMA was investigated by oxygen plasma etching with a Technics Planar Etcher II. PMMA films were irradiated with deep UV at 20 mJ/cm^2 and modified. Each sample was dry etched for 0.5, 1.5, 2.5, 4, and 6 min, at an oxygen pressure of 110 mTorr and a power setting of 255 W. The plasma etching was stopped after each time interval and the film thickness was measured with a Dektak profilometer.

Similar experiments were performed for e-beam irradiated samples at dose levels in the range of 10^{-6}–10^{-7} $\mu C/cm^2$. Each of five different samples prepared with the same modifying condition was plasma etched for 0.5, 1, 1.5, 2.5, and 5 min, at an oxygen pressure of 110 mTorr and a power setting of 255 W. The remaining thickness of each sample was measured after dry etching.

C. CHF_3 reactive ion etching (RIE)

The CHF_3 RIE durability of PMMA, AA-PMMA, Ca-AA-PMMA, and SiO_2 was investigated with a Plasma Therm etcher. The flow rate of CHF_3 gas was 20 cm^3/min, its pressure was 34 mTorr, and the power setting was 300 W at a dc bias voltage of − 474 V.

III. RESULTS AND DISCUSSION

Figure 2 shows the dry etch characteristics of DUV-modified Ca-AA-PMMA. Soaking of the modified resist in 20% aqueous calcium acetate solution for 10 min incorporated sufficient calcium ions to yield oxygen plasma etch resistance as shown by the change in etch rate from 3040 to 1160 Å/min before and after modification, respectively.

Figure 3 shows the oxygen plasma etching characteristics of e-beam modified PMMA. The etch rate of Ca-AA-PMMA was influenced by the exposure dose in addition to the modification condition because more active sites were produced in the more highly irradiated sample.

The etch rate of PMMA in Fig. 3 was faster than that in Fig. 2 which was obtained with several stopping intervals. The net result was an increase in O_2 plasma etch rate due to only one initial etch state.

The pronounced growth of the PMMA film broadens the

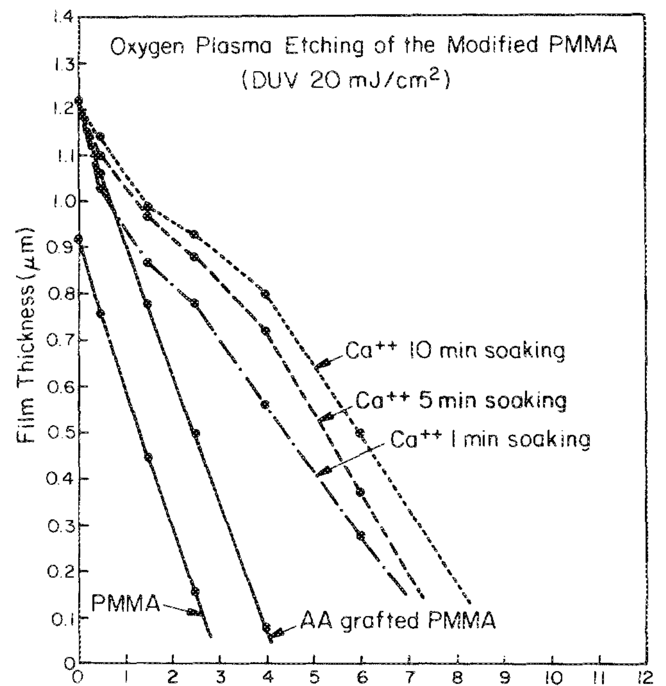

FIG. 2. Etching characteristics of DUV-modified PMMA. Ramp time from 20 to 60 °C: 40 min. Reaction time at 60 °C: 15 min.

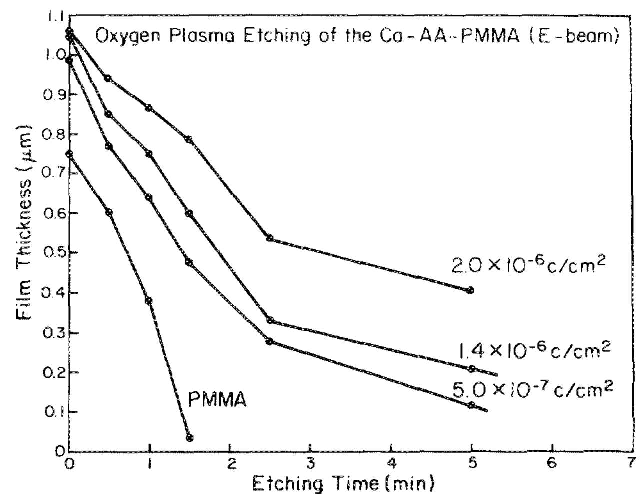

FIG. 3. Etching characteristics of e-beam-modified PMMA. Ramp time from 20 to 60 °C: 40 min. Reaction time at 60 °C: 20 min, Ca^{++} soaking for 10 min at 60 °C.

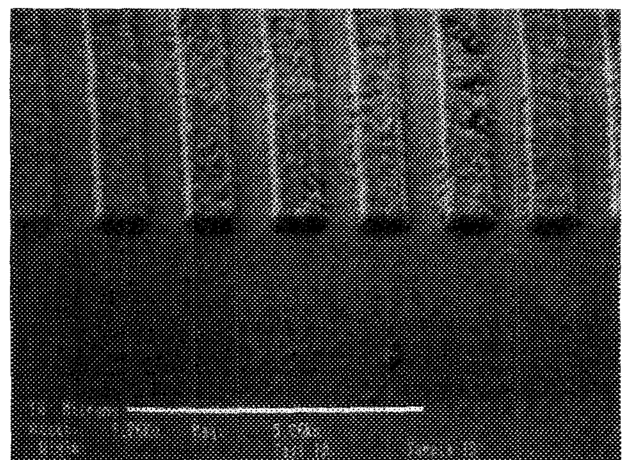

FIG. 4. Oxygen plasma etched patterns of Ca-AA-PMMA (20 mJ/cm^2 DUV).

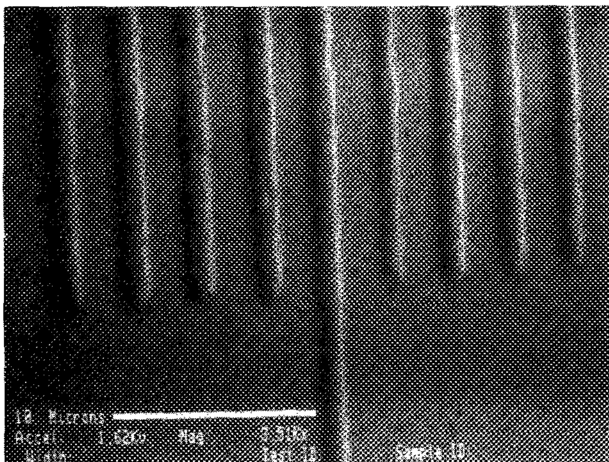

FIG. 5. Oxygen plasma etched patterns of Ca-AA-PMMA ($2.4\,\mu C/cm^2$ e-beam).

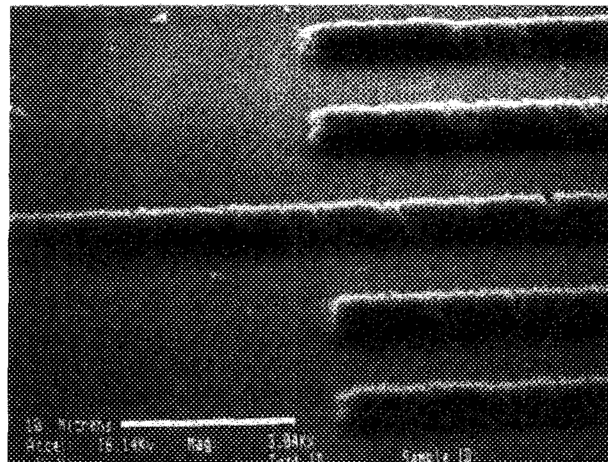

FIG. 6. SEM of CHF_3 reactive ion etched patterns ($2.0\,\mu C/cm^2$ e-beam).

images during the acrylic acid modification.[10] The incorporation of only a small amount of acrylic acid is required to generate a high fidelity image. It was found that the amount of vertical image growth necessary for optimal image fidelity was $0.1 \sim 0.2\,\mu m$. The grafting conditions were controlled to attain optimal growth of PMMA.

Figures 4 and 5 show SEM micrographs of fine oxygen plasma etched patterns obtained by DUV and e-beam induced modification. The nominal linewidth was $1.5\,\mu m$ with $1.5\,\mu m$ space for DUV and $1\,\mu m$ line with $2\,\mu m$ space for e-beam modification, respectively.

Once the modified resist has been exposed to an oxygen plamsa, it generated a protective coating of involatile oxide within the irradiated (negative) portions of the PMMA resist.

Table I shows the CHF_3 RIE etch resistance of PMMA, of modified PMMA, and of SiO_2.

The CHF_3 RIE etch rate of SiO_2 was very fast compared with that of Ca-AA-PMMA which was oxygen plasma etched. Therefore, the image of Ca-AA-PMMA was easily transferred into the $0.5\,\mu m$ thick oxide layer grown by a wet oxidation process.

The formation of CaO by O_2 plasma and CaF_2 by CHF_3 RIE was demonstrated with Auger electron spectroscopy. Residual CaO and converted CaF_2, which were involatile, permitted the selective erosion of the oxide layer.

Figure 6 shows a scanning electron micrograph of the pattern transferred to the SiO_2 layer under the CHF_3 RIE conditions for e-beam modified Ca-AA-PMMA. Two layers of Ca-AA-PMMA and SiO_2 are shown in this figure.

SiO_2 images were achieved by stripping Ca-AA-PMMA with Caro's acid (H_2O_2–H_2SO_4) after CHF_3 RIE. Figure 7 shows a micrograph of a SiO_2 pattern showing a $0.75\,\mu m$ line after stripping of the modified PMMA.

TABLE I. Comparative CHF_3 RIE etch resistance.

Material	CHF_3 RIE etch rate (Å/min)
PMMA	330
AA-PMMA[a] (20 mJ/cm^2 DUV)	110
Ca-AA-PMMA[b] (20 mJ/cm^2 DUV)	10
SiO_2	270

[a] Ramp time from 20 to 60 °C: 40 min. Reaction time at 60 °C: 20 min.
[b] Oxygen plasma etching: 110 mTorr, 255 W, 2 min.

IV. CONCLUSIONS

A technique for dry development of modified PMMA has been shown to be effective. Selective pattern formation in the irradiated areas was performed using PMMA as a base film, acrylic acid as a modifying monomer, and calcium as an exchangeable ion.

Base film images can be fabricated by oxygen plasma etching. The oxygen plasma etched patterns were transferred into the oxide layer by using Ca-AA-PMMA as a mask under CHF_3 RIE conditions.

Submicron pattern formation was demonstrated with this dry developable DUV modification system.

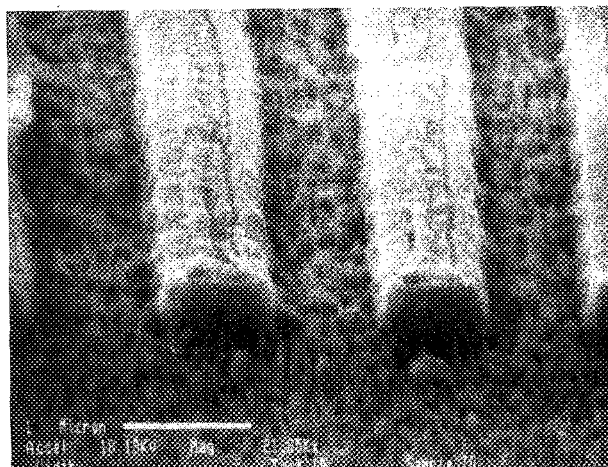

FIG. 7. SiO_2 patterns after stripping the modified PMMA (20 mJ/cm^2 DUV).

ACKNOWLEDGMENTS

This research was supported, in part, by the Semiconductor Research Corporation and the International Business Machine Corporation. We also thank Mr. J. Bachur, President of Hybrid Technology Groups, Inc. for giving us the DUV light source.

[1]C. G. Willson, in *Introduction to Microlithography*, edited by L. F. Thompson, C. G. Willson, and M. J. Bowden, ACS Symposium Series No. 219 (American Chemical Society, Washington, DC, 1983), p. 123.

[2]A. Gazard, C. Duchesne, J. C. Dubois, and A. Chapiro, Polym. Eng. Sci. **20**, 1069 (1980).

[3]J. A. Moore, J. C. Corelli, A. J. Steckl, W. T. Liu, J. T. Warden, R. Tarro, and J. N. Randall, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. **25**, 105 (1984).

[4]R. M. Tarro, J. T. Warden, J. C. Corelli, J. A. Moore, A. J. Steckl, and S. Kumar, in *Microcircuit Engineering*, edited by A. Heuberger and H. Beneking (Academic, New York, 1985), p. 537.

[5]W. T. Liu, J. A. Moore, J. C. Corelli, M. Bourgeois, and A. J. Steckl, J. Electrochem. Soc. **83-2**, 331 (1983).

[6]W. T. Liu, J. C. Corelli, A. J. Steckl, J. A. Moore, and J. Silverman, Appl. Phys. Lett. **44**, 973 (1984).

[7]S. Y. Kim, J. Choi, D. Pulver, J. A. Moore, J. C. Corelli, and A. J. Steckl, J. Vac. Sci. Technol. B **4**, 403 (1986).

[8]C. C. Anderson and F. Rodriguez, J. Vac. Sci. Technol. B **3**, 347 (1985).

[9]J. Economy, J. R. Lyerla, and L. A. Pederson, IBM, U.S. Patent No. 4 289 573 (15 September 1981).

[10]M. Morita, S. Imamura, T. Tamamura, O. Kogure, and K. Murase, J. Vac. Sci. Technol. B **1**, 1171 (1983).