PLASMA POLYMERIZED RESIST FILMS IN A VACUUM LITHOGRAPHY

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ABSTRACT

As a positive resist in a vacuum lithography, methylmethacrylate and hexafluorobuthylmethacrylate were polymerized in a plasma. Styrene or tetramethyltin was co-polymerized with them. An electron-beam delineated pattern was developed by a plasma etching using oxygen-argon mixture or hydrogen. The sensitivity of resist was improved by co-polymerization and by hydrogen plasma etching.

1. INTRODUCTION

A vacuum lithography using plasma polymerization and plasma etching was proposed for a photomask fabrication by an electron-beam delineation [1,2]. Usually, a plasma polymerized film is crosslinked under an irradiation of high energy electron, ion and radiation from the plasma. An increase of crosslinked site will result in a decrease of sensitivity in both cases of positive and negative resists. Because it is important to obtain the polymer which has very few crosslinked site, a specially designed reactor is necessary to be used and a plasma polymerization must be controlled carefully.

A plasma etching development of electron-beam delineated pattern on a resist will be performed by a difference of etching rate on an electron-beam delineated and an undelineated area. Consequently, the plasma etching resistivity of resist becomes an important factor for a sensitivity, because the higher the sensitivity of resist, the larger the etching rate. But it is impossible to solve an inconsistency between a plasma etching resistivity and a sensitivity of resist. Whereas, the inconsistency must be minimized in the total process of vacuum lithography.

In this paper, optimum discharge condition was studied for the plasma polymerization of methylmethacrylate at first, and then, the qualities of several resists were evaluated in relation to plasma etching characteristics and self development.

2. EXPERIMENTAL

The resist film was formed on a glass substrate chromium evaporated using an argon flow type reactor, in which a monomer was introduced into a down stream of argon glow discharge (13.56 MHz) and the polymer was formed in a farther down stream [2]. A plasma

polymerized methylmethacrylate (PPMMA) was formed at various discharge conditions of gas flow rate, gas pressure and discharge power level. Properties of PPMMA were studied by IR measurements. In order to improve the properties of resists, styrene and tetramethyltin were co-polymerized with them. For a high sensitive resist, hexafluorobuthylmethacrylate (6FBMA) was also polymerized.

A delineation on a resist was carried out using an electron-beam delineation apparatus (Elionix, ELS-2A). An accelaration voltage was 20 KV and a shape of electron-beam was a square of 4 x 4 μm^2.

Delineated patterns were developed by a plasma etching apparatus (ULVAC, SBR-1104), which had parallel plane electrodes and was operated at 13.56 MHz using oxygen-argon mixture and hydrogen.

In comparison with the properties of plasma polymerized resists, conventional PMMA (Tokyo oka, OEBR-1000) was treated at the same condition.

3. RESULTS AND DISCUSSION

3.1. Plasma polymerization of MMA in a down stream of argon glow discharge

PPMMA was formed at 0.7 torr, 63 cm^3STP/min for argon, 6.3 cm^3STP /min for monomer and 10 watts. IR spectrum of the PPMMA film showed specific absoption peaks at 3400 cm^{-1}, 2900 cm^{-1}, 1730 cm^{-1}, 1450 cm^{-1}, 1370 cm^{-1}, and 1140 cm^{-1}. When the discharge power was increased while a gas flow rate and a gas pressure were constant, the two peaks at 1730 cm^{-1} and 1140 cm^{-1} behaved differently from other four peaks as shown in Fig. 1. The absorption peak at 3400 cm^{-1} will be assigned to OH strech caused on water absorped in air after the polymerization, and the three peaks at 2900 cm^{-1}, 1450 $cm^{-1}$and 1370 cm^{-1} will be assigned to CH strech and CH bend in CH_2 and CH_3 [3]. The behaviorsof two peaks varing with the discharge power are different. The absorption peak at 1140 cm^{-1} was largest peak in several peaks near 1140 cm^{-1} and the peak height was decreased with increasing the discharge power. But the absorption peak at 1730 cm^{-1} was replaced by two peaks at 1700 cm^{-1} and 1650 cm^{-1} at the higher discharge power level.

When an argon flow rate was changed as a discharge parameter, almost same behaviour of IR spectra was observed as shown in Fig. 2. With decreasing argon flow rate, the absorption peak at 1730 cm^{-1} replaced by two peaks at 1700 cm^{-1} and 1650 cm^{-1} and the peak height of absorption at 1140 cm^{-1} was decreased, but the four peaks were not affected by the argon flow rate.

IR spectrum of conventional PMMA has two peaks at 1730 cm^{-1} and 1140 cm^{-1} which are assigned to carbonyl and ether in ester structure of MMA, respectively.

Usually, plasma polymerized ethylene showed an absorption peak at 1650 cm^{-1} which is assigned to C=C strech [3]. When this film was oxydized in air, an absorption peak at 1700 cm^{-1} appeared [3]. Whereas, it was concluded that the two peaks at 1700 cm^{-1} and 1650 cm^{-1} were caused on the degradation of MMA in the plasma. If PPMMA will be polymerized at a lower discharge power level and a higher argon flow rate, the structure of PPMMA will resemble to that of conventional PMMA.

3.2. Plasma etching development

(1) PPMMA and plasma etching using oxygen-argon mixture.

Plasma etching was performed at 2-3 mtorr using oxygen-argon mixture. Usually, an etching rate of PPMMA was smaller than that of conventional PMMA and the etching rate was propotional to oxygen content of the gas mixture [2]. However, a sensitivity and γ value of PPMMA were better than that of conventional PMMA. The evaluated sensitivity and γ value of PPMMA were 700 $\mu C/cm^2$ and 1, respectively, but a sensitivity of PMMA was 5000 $\mu C/cm^2$ or less[2]. These facts suggested that plasma etching resistivity was important for the plasma etching development.

(2) Plasma co-polymerized (MMA-St)

In order to improve the plasma etching resistivity, MMA and styrene were co-polymerized using MMA and styrene liquid mixture. By the plasma etching development using oxygen-argon mixture, a sensitivity of PP(MMA-St) became about 100 $\mu C/cm^2$ which was better than that of PPMMA, but still less than that of PMMA at a wet process.

(3) Plasma co-polymerized (MMA-TMT) and plasma etching using hydrogen

For a high sensitivity resist, a delineated pattern was developed without a treatment of etching. This phenomenon is known as a self development [4-6]. Plasma co-polymerized (MMA-TMT) was formed at the optimum discharge condition using MMA and TMT liquid mixture (mixing ratio; 25 : 1). Thickness removed by an electron-beam delineation was plotted against an exposure dose as shown in Fig. 4. The result of self development showed that the removal thickness of PP(MMA-TMT) was higher than that of conventional PMMA. In order to compar the etching characteristics of oxygen-argon mixture plasma and hydrogen plasma, relative etching rates of PPMMA and PMMA were shown in Fig. 5. Selectivity of hydrogen plasma etching was better than that of oxygen-argon plasma etching. Whereas, it was shown that the sensitivity of resist would be improved by adopting hydrogen plasma.

(4) Plasma polymerized 6FBMA and its copolymer

Poly6FBMA is presented as a high sensitivity electron-beam resist whose sensitivity is 0.4 $\mu C/cm^2$ at a wet process (Daikin FBM-110). A sensitivity of PP6FBMA was estimated to be higher than that of PPMMA. By plasma copolymerization, its quality as a resist will be improved. The removal thickness of PP(6FBMA-St) was plotted against the dose rate as shown in Fig. 6. PP(6FBMA) was sucessfully delineated by an electron-beam at 1 $\mu C/cm^2$ as shown in Fig. 7. These facts suggested that copolymers with 6FBMA showed higher sensitivity than that of MMA if a suitable developing method is used.

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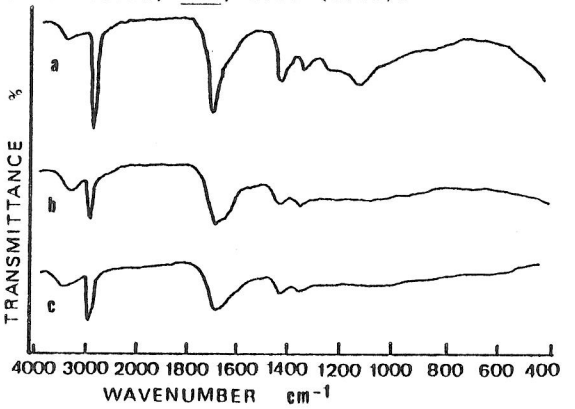


Fig. 1. The dependence of IR spectra on the discharge power at 0.7 torr, 63 cm^3STP/min (Ar) and 6.3 cm^3STP/min(MMA): (a) 10 watts, (b) 20 watts and (c) 30 watts.

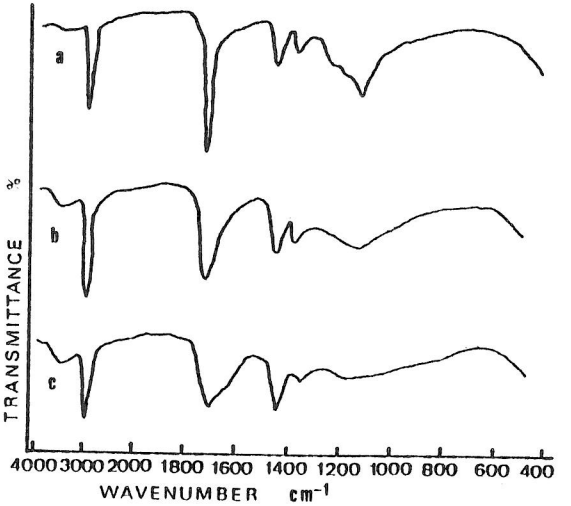


Fig. 2. The dependence of IR spectra on the gas flow rate of Argon at 0.7 torr and 10 watts: (a) 77 cm^3STP/min, (b) 63 cm^3STP/min and (c) 42 cm^3STP/min.

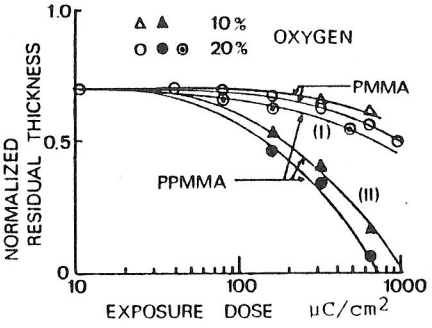


Fig. 3. Normalized residual film thickness against the exposure dose.

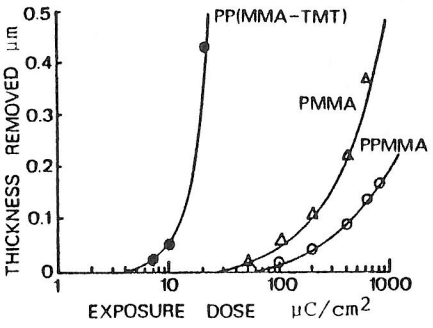
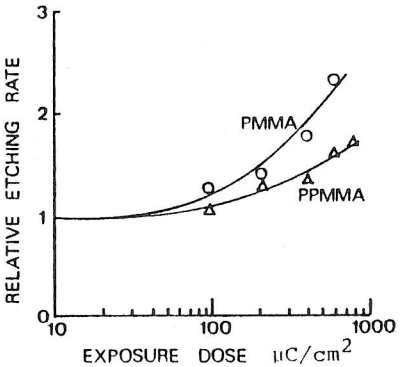
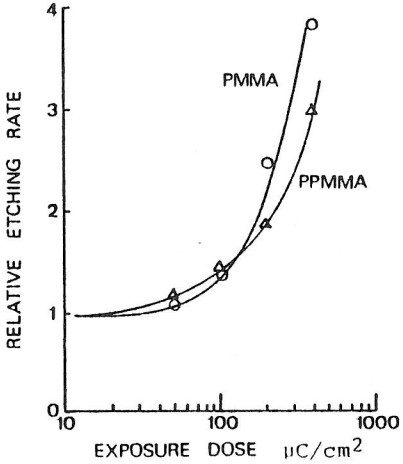


Fig. 4. The dependence of thickness removed on exposure dose; PP(MMA-TMT), PPMMA and Spin coated conventional PMMA.



(a) Plasma etching with O_2-Ar mixture



(b) Plasma etching with H_2

Fig. 5. The dependence of relative plasma etching rate (the etching rate of unexposed film is normalized to unity) on exposure dose.

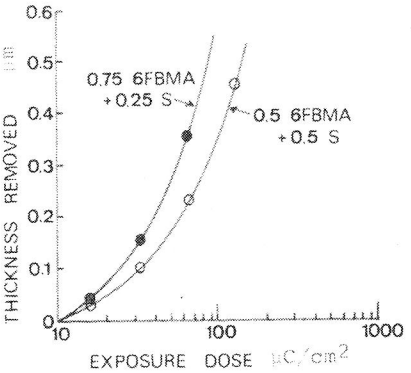


Fig. 6. The self development of plasma copolymerized 6FBMA-Styrene

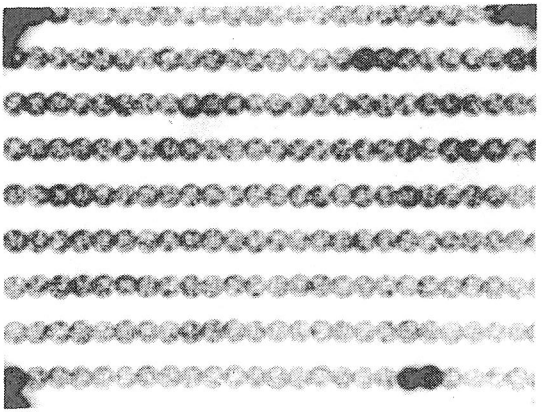


Fig. 7. Picture of self developed pattern on plasma co-polymerized 6FBMA-TMT; 6FBMA : TMT = 30 : 1, Dose rate of electron beam : 1 μC/cm^2, and Width of line and space : 4 μm.