PLASMA POLYMERIZED METHYL-METHACRYLATE AS AN ELECTRON BEAM RESIST

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ABSTRACT

Plasma polymerized methyl-methacryrate films were formed by a radiofrequency glow discharge of a monomer gas on a glass substrate coated with chromium. Two discharge frequencies of 5KHz and 13.56MHz were used for this polymerization. Delineations were done by an electron beam. The figures were developed by CCl_4 plasma etching.

1. INTRODUCTION

Finer precise geometry pattern generation and delineation is necessary for an advanced very Large Scale Integrated circuit (v-LSI). For these demands, the uses of electron beam and X-ray lithographies have been proposed. Also, there are interests in simplifying process throughout the lithograph[1]. Though, there are significant progresses in recent dry process techniques, resist film formation and pattern development were still done by a wet process in a conventional electron beam and X-ray lithography[2]. For instance, if the resist film for a lithography was formed and developed by dry methods and if the entire fablication process of v-LSI could be changed to a dry process, we can expect a remarkable increase in the reliability at total process. Gas plasma techniques are successfully used in the fablication of v-LSI like as etching and stripping techniques [3,4,5,6,7]. It is well known that plasma polymerized film is fundamentally pin hole free and uniform and that the film is highly crosslinked and has a good adhesive property to the substrate[1,8]. But there is not any report concerned on the resist film formation by this technique according to our knowledge. As a matter of course, the properties of plasma polymerized film as a resist film is not known. In this paper, plasma polymerized methyl-methacryrate (PPMMA) was selected as a possible candidate for an electron beam resist and the properties were studied.

2. EXPERIMENTAL

Resist film formation, delineation and development of a figure were

conducted separately in this study as shown in Fig. 1.

Methyl-methacryrate was distilled in vacuo after being washed several times with 5% aqueous NaOH and deionized water. The distilled monomer was degassed by repeated freezing-pumping-thawing cycles before presentation to the plasma polymerization. A bell-jar type reactor (230mmID) which was provided with two circular electrodes (70mmOD) set in parallel was used. The monomer was introduced into the bell-jar through a needle valve, but a flow rate was not measured. The pressure in the reactor was controlled by using another needle valve located between the reactor and a liquid N_2 trap. A glass plate coated with chromium was used as a substrate and holded on the lower electrode. The substrate had a area of $5x5cm^2$. The thickness of evaporated chromium film on the glass plate was about 0.07μm and the chromium film was connected electrically to the lower electrode. Two kinds of frequencies of 5KHz and 13.56MHz were chosen as the frequency of power source. The power source of 5KHz was consisted of an oscilator (Torio AG-8) and amplifier. The discharge current was measured by a thermocouple type high frequency current meter. The power source of 13.56MHz was consisted of a generator (SAMUCO) and a impedance matching unit. The discharge power level was measured by a wattmeter (Bird 43). Sample I and II were formed at 5KHz and 13.56MHz, respectively. The polymerization conditions are listed in Table I. The thickness of the film was evaluated by weighing.

The delineations were carried out by an electron beam (Elionix ERE-301). The acceleration voltage and the diameter of electron beam were 20KV and 0.5μm, respectively. Twenty lines were delineated in the width of 10μm as a line bandle. 25 line bandles were figured in a rectangle area of 0.5x0.5 mm^2 as a picture element, and six picture elements were delineated in six grades on one sample surface. The exposed dose rate was ranged from $8x10^{-5}$ to $6.4x10^{-4}C/cm^2$ and from $2x10^{-5}$ to $4.8x10^{-4}C/cm^2$ for Sample I and II, respectively.

The delineated figures were developed by a CCl_4 plasma etching. The discharge electrodes of etching reactor were parallel electrodes whose diameter and space between the electrodes were 210mm and 150mm, respectively. Plasma etching was performed at a discharge frequency of 13.56MHz, a pressure of 10^{-3}torr, a gas flow rate of $30cm^3/min$ and a discharge power level of 300watts (ULVAC). The discharge duration was changed for each specimen depending on the polymerization condition. Generally, the operating duration was 15-30min and 5-20min for sample I and II, respectively.

The structure of PPMMA was observed by an infrared spectrometer (JASCO IR-G). For the infrared measurements, the PPMMA films of sample II were formed on NaCl crystal. But for sample I, the glow of discharge did not cover the NaCl crystal. Therefore, the film for the infrared measurement was formed on aluminum foil and was craped from it, then a transparent sheat of craped film was formed by using a conventional method mixed with KBr. In order to compair the infrared spectra of PPMMA films with PMMA film polymerized in a conventional manner, the film was prepared on NaCl crystal from benzen solution of commercially supplied PMMA (SUMIPET).

3. RESULTS AND DISCUSSION

Infrared spectra of the three kinds of sample were shown in Fig. 2. Many

sharp absorption peaks were recorded for PMMA film, while blunt absorption peaks were observed for PPMMA. However, most peaks of PPMMA corresponded to those of conventional PMMA except the peaks at $750cm^{-1}$ and $680cm^{-1}$ which may be referred to residual benzen in PMMA film[9]. The characteristic differences were observed between sample I and II. The absorption peak at $3400cm^{-1}$ for sample I is assigned to O-H stretch[9]. This peak may be attributed to absorbed water in the specimen, which was introduced during sample preparation. The absorption peak at $1650cm^{-1}$ observed for sample I was negligibly small for sample II. This peak is assigned to C=C stretch[9]. Even if the infrared spectrum of MMA monomer shows a large peak at 1650 cm^{-1}, the peak of sample I may not be attributed to the residual monomer in the film because the film of sample I was harder than that of sample II. The peak at $1680cm^{-1}$ is probably attributed to the crosslinking of sample I which was induced by an ion bombardment during the polymerization of sample I[10].

After the delineation by an electron beam, any change was not observed on the surface of PPMMA film by an optical micro scope. However, by a CCl_4 plasma etching, the figures were developed and visualized by an eye sight. The photographic figure was obtained by Scanning Electron Microscopy (SEM) are shown in Fig. 3 for sample II. This photograph showes the delineated figure on the chromium film. The PPMMA film had been etched away. The delineated figures were also developed for sample II by a wet etching method which was operated for min in methyl-isobutyl-ketone (MIBK). For sample I, visible figure was not developed by a wet etching method for the same etching duration of sample II. From the discharge period that PPMMA film endured the CCl_4 plasma etching, the etching rate of PPMMA film which was not exposed to an electron beam was estimated to be 100A/min and 700A/min for sample I and II, respectively. The difference of etching rate on two samples is explained as being correlated to the degree of cross linking of polymer.

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REFERENCES

1) J.R.Hollahan and A.T.Bell ed."Techniques and Application of Plasma Chemistry"(J. Wily & Sons, New York 1974). 2) A.N.Broors, J.M.E.Harper and W.WMolzen, Appl. Phys. Lett., 33, 392(1978). 3) H.Abe, International Round Table on Plasma Polymerization and Surface Treatment, IUPAC, Limoges(1977) 4) K.Suzuki, S.Okudaira, N.Sakudo and I.Kanomata, Jpn J. Appl. Phys., 16, 1979(1977). 5) H.F.Winter, J.W.Coburm and E.Kay, J. Appl. Phys., 48,4973 (1977). 6) C.J.Mogab, A.C.Adams and D.L.Flamm, J. Appl. Phys., 49,3796 (1978). 7) H.F.Winters, J. Appl. Phys., 49, 5165(1978). 8) M.Shen ed., "Plasma Chemistry of Polymer"(Marcel Dekker, New York 1976). 9) J.M.Tibbitt M.Shen and A.T.Bell, J. Macromol. Sci.-Chem., A10, 1623(1976). 10) S. Morita, S.Ishibashi, M.Shen and A.T.Bell, ACS Organic Coating and Plastic Chemistry, 40, 451 (1979).

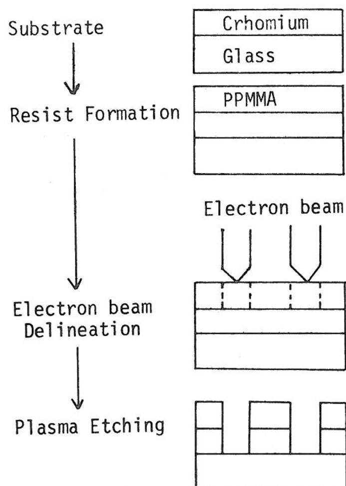


Fig. 1.
Electron Beam Lithography Process

Table I. Polymerization Parameter of PPMMA

No	R1	R2	R3	R4	R5
Discharge frequency (Hz)	13.56M	13.56M	13.56M	5k	5k
Discharge power (W)	30	30	20	-	-
Discharge current (mA)	-	-	-	20	40
Gas pressure of MMA (Torr)	1.0	0.5	0.5	0.5	0.5
Discharge duration (min)	16	10	10	11	10
Deposition weight (mg)	2.05	1.77	1.00	0.61	3.68
Deposition rate $x10^{-3}$(mg/(minxcm^2))	5.13	7.00	4.00	2.22	14.7
Film thickness* (μm)	0.82	0.71	0.40	0.24	1.47

*Specific gravity was estimated to be 1 for PPMMA.

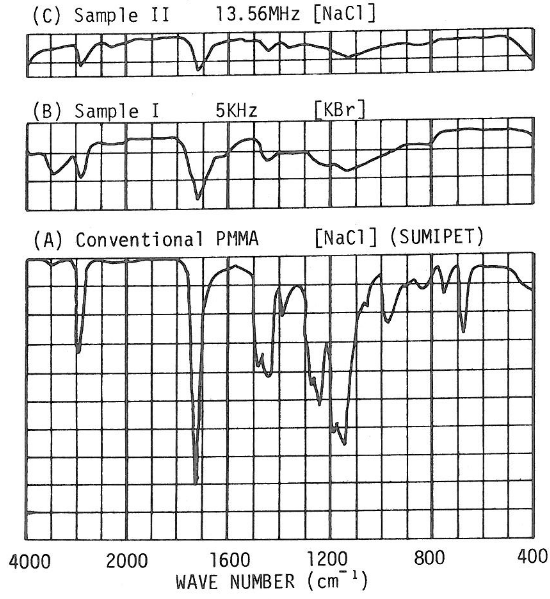
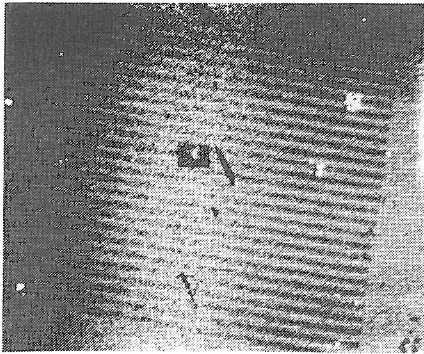
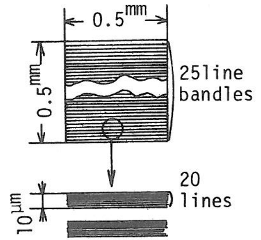


Fig. 2. Infrared Spectra





Delineated Figure

Fig. 3. Developed Figure by ESCA

Sample II (R - 3)

[Delineation Condition]

Electron beam diameter 0.5μm

Acceralation voltage 20KV

Exposed Dose Rate $1.6x10^{-4}C/cm^2$