

NOTES

Relationship between Electron Sensitivity and Chemical Structures of Polymers as EB Resists. II. Acetalized Polyvinyl Alcohol as New Negative EB Resists

INTRODUCTION

The fabrication of a semiconductor-integrated circuit requires resist materials which are necessary to print fine patterns on silicon wafers in the lithographic process. In recent years, there has been a continuing demand for higher degrees of integration for LSI or VLSI and various types of EB resists with much better resolution than photoresists have been developed. Several EB resists containing epoxy groups, double bond, or halogen have been found to be negative acting with high sensitivity. Polymers such as poly(glycidyl methacrylate) (PGMA),^{1,2} poly(butadiene) (PB),³ or chloromethylated polystyrene (CMS)⁴ are used as negative EB resists.

Generally speaking, resist materials require many characteristics. These include not only high sensitivity and high resolution, but also good adhesion on the wafer, thermal stability, easy coating capability, excellent development characteristics, good resistance to etching, especially to a dry etching process, and so on. A great number of EB resists have been developed for the above-mentioned purpose.

We reasoned that the acetal group might have a high sensitivity to the EB irradiation, since the acetal group is susceptible to a radical scission reaction by a high energy irradiation just like the epoxy group. This paper deals with the synthesis and lithographic evaluation of acetalized PVA with various types of substituents in order to elucidate the relationship between EB sensitivity and chemical structure of the polymers.

EXPERIMENTAL

Synthesis of Polymers

Acetalized derivatives of poly(vinyl alcohol) (PVA) were synthesized from commercially available PVA and requisite aldehyde or ketone using hydrochloric acid as a catalyst.^{5,6} The structures of acetalized PVA are summarized in Figure 1.

A typical procedure for the synthesis is as follows: 1.0 g of PVA having a degree of polymerization of 1500 and 8.0 g of *p*-chlorobenzaldehyde were dissolved in 20 cm³ of chloroform, and two drops of hydrochloric acid were added to the solution. The reaction was carried out with stirring at 40°C for 40 h. The solution was poured into excess methanol containing an equimolar amount of sodium hydroxide and the acetalized polymer separated by filtration. It was further purified by reprecipitation from chloroform into methanol and finally dried under vacuum.

Acetalized PVA having a degree of polymerization of 500 or 2000 was synthesized according to the same method as mentioned above. The other acetalized PVA's using acetaldehyde (AA), cyclohexanone (CH), or benzaldehyde (BA) were also synthesized as mentioned above with appropriate reaction times. The different acetalized PVA's were synthesized using different solvents as follows: for AA-PVA, ethanol/water (10/1); for CH-PVA, benzene; and for BA-PVA, ethylene dichloride/methanol (7/3) or benzene/methanol (1/1).

Evaluation of Acetalized PVA as EB Resists

The polymers were spin-coated from solution on glass substrates precoated with a chromium film and then prebaked at 80°C for 30 min in order to remove the solvent and to promote adhesion on the plate. The film thickness was determined by a Talystep instrument.

The resists were exposed using an electron beam resist evaluation apparatus, ERE-301 (ELIONIX Co.). The accelerating voltage was 10 keV.

The exposed resists were developed in a solution of chloroform for 60 s. After development, the remaining film thickness was measured by the Talystep instrument and normalized with respect

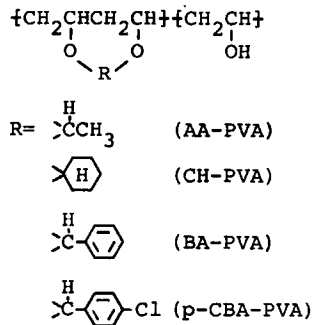


Fig. 1. Structures of acetalized PVA.

to the initial film thickness. The resist sensitivity is defined as the irradiation dose required to leave 50% of the original film thickness after development. The γ value is defined as the slope angle of the straight line which connects between two points in the thickness vs. log dose plot corresponding to the minimum dose required for any detectable gel formation and the dose for 50% film thickness.

After development and postbaking, reactive ion etching was performed using a planar type reactor in order to determine the durability of acetalized PVA to dry etching. The condition of dry etching was as follows: the etching gas contained 20% CCl_4 and 67% wet air. Gas pressure was 40 Pa and impressed rf power was 300 W.

After development and dry etching, the resist patterns were examined by SEM and optical microscopy.

RESULTS AND DISCUSSION

The physical properties of acetalized PVA (acetal group content: 70–80%) are summarized in Table I. The polymers had good solubility in several low boiling point organic solvents and showed good spin coating and development characteristics. The decomposition temperatures of these polymers were higher than that of the original PVA.

Exposure characteristics of these polymers to EB irradiation are shown in Figure 2. The sensitivity of BA-PVA (1500) which has a benzene ring in the acetal group was 2.1×10^{-6} coulombs/cm² which is higher than that of the CH-PVA (1500) and AA-PVA (1500). It is generally recognized that resist materials which contain aromatic groups in their fundamental structure show a high degree of resistance to dry etching environments,⁷ while conversely their sensitivity to the EB irradiation is decreased. From this point of view, the higher sensitivity of BA-PVA compared to the other acetals is to be unexpected. The crosslinking reaction of acetalized PVA may occur at the acetal group by the EB exposure. The high sensitivity of BA-PVA may be ascribed to stable benzyl radicals produced

TABLE I
Properties of Acetalized PVA

Polymer	Acetal group content (%) ^a	η_{sp}/C^b	$T_d/^\circ\text{C}^c$	Solubility				
				Ben- zene	CHCl_3	2-Ethoxyethyl acetate	Chloro- benzene	Ethyl alcohol
AA-PVA (1500) ^d	78	2.36	310	+	+	+	+	+
CH-PVA (1500)	74	2.12	286	+	+	–	+	–
BA-PVA (1500)	79	1.65	286	+	+	+	+	–
p-CBA-PVA (1500)	74	1.70	270	+	+	+	+	–

^a Determined by elemental analysis.

^b 0.1 g/10 cm³ in $\text{CH}_2\text{ClCH}_2\text{Cl}$ at 30°C.

^c Measured by DTA.

^d Polymerization degree of PVA is shown in parentheses.

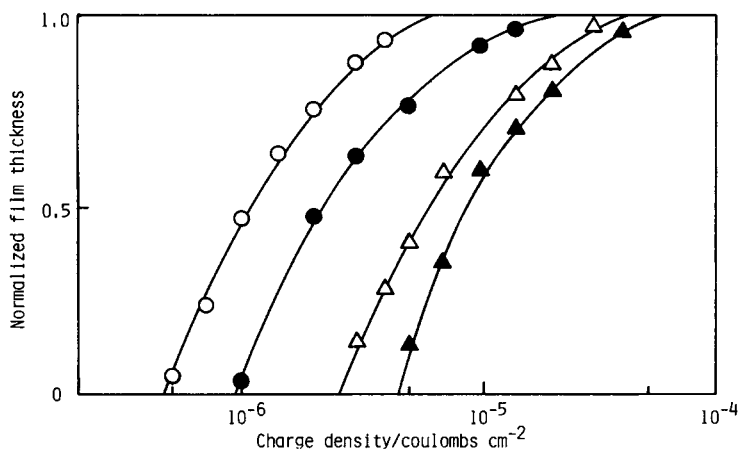


Fig. 2. Exposure characteristics of acetalized PVA (1500): (○) *p*-CBA-PVA^a; (●) BA-PVA^b; (Δ) CH-PVA^c; (▲) AA-PVA^d. Film thickness: (a) 5400 Å; (b) 6000 Å; (c) 6400 Å; (d) 5800 Å. Prebake: 80°C, 30 min. Developer: CHCl₃. Development time: 60 s.

TABLE II
Characteristics of Acetalized PVA as EB Resists

Polymer	Sensitivity ($\mu\text{coulombs/cm}^2$)	γ value
AA-PVA (500)	23	1.3
AA-PVA (1500)	8.2	1.3
CH-PVA (500)	11	1.5
CH-PVA (1500)	6.0	1.1
BA-PVA (500)	10	1.2
BA-PVA (1500)	2.1	1.1
<i>p</i> -CBA-PVA (500)	4.0	1.2
<i>p</i> -CBA-PVA (1500)	1.1	1.2
<i>p</i> -CBA-PVA (2000)	0.72	1.2

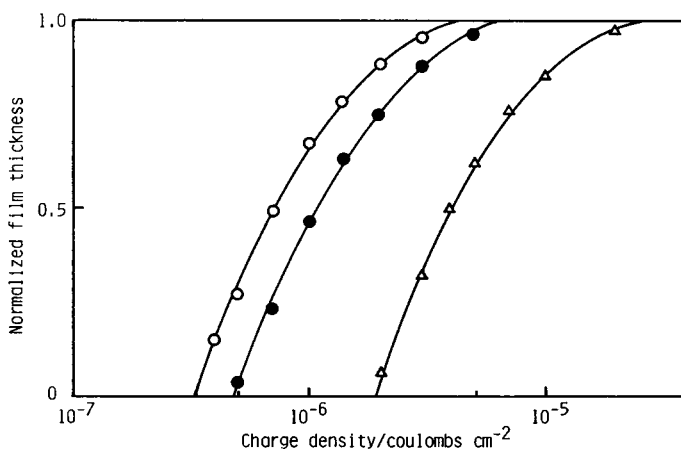


Fig. 3. Exposure characteristics of *p*-CBA-PVA: (○) PVA (2000)^a; (●) PVA (1500)^b; (Δ) PVA (500)^c. Film thickness: (a) 6300 Å; (b) 5400 Å; (c) 3600 Å. Prebake: 80°C, 30 min. Developer: (a) MEK; (b), (c) CHCl₃. Development time: 60 s.

TABLE III
Dry Etching Rate for Reactive Ion Etching

Resist	Etching rate (Å/min)
AA-PVA (1500)	340
CH-PVA (1500)	250
BA-PVA (1500)	250
<i>p</i> -CBA-PVA (1500)	300
<i>p</i> -CBA-PVA (2000)	280
OEER-100	540
AZ-1350	250

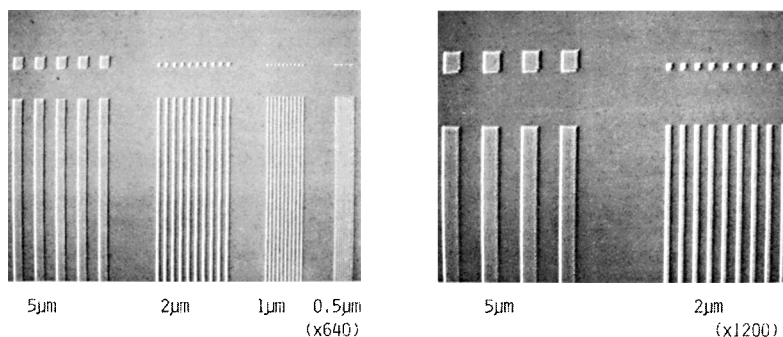


Fig. 4. SEM micrographs of *p*-CBA-PVA (2000) resist patterns after development. Film thickness: 0.57 μm . Beam diameter: 0.5 μm . Exposure: 2.0×10^{-6} coulombs/cm². Developer: MEK. Rinse: IPA.

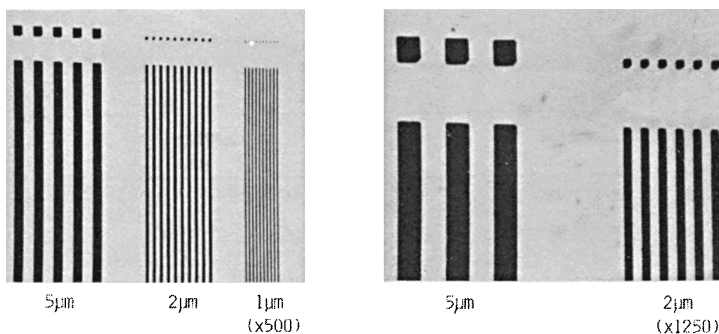


Fig. 5. Photomicrographs of etched patterns of chromium using *p*-CBA-PVA (2000) resist.

by EB exposure, which initiate crosslinking among polymer chains. The sensitivity of *p*-CBA-PVA having a chlorine substituent on the benzene ring was higher than that of BA-PVA, presumably due to the presence of the electron withdrawing chlorine group.

Sensitivity and γ value of these acetalized PVA's are summarized in Table II; exposure characteristics of *p*-CBA-PVA (500,1500,2000) are shown in Figure 3.

It is known that the sensitivity of a polymer depends on its molecular weight. As shown in Table II and Figure 3, for *p*-CBA-PVA, sensitivity increased with increasing molecular weight, although the γ value tended to decrease. This may be due to poor dissolution characteristics of the high molecular weight sample. The sensitivity of *p*-CBA-PVA (2000) was the highest with the value of 7.2×10^{-7} coulombs/cm².

Dry etching rates of acetalized PVA and commercial resists are summarized in Table III. The dry etching durability of resists is usually estimated by their etching rates so that low etching rate implies high durability. It is clear from Table III that BA-PVA and CH-PVA have good dry etching durability due presumably to the cyclic structures in the polymer. The durability of *p*-CBA-PVA to dry etching is slightly lower than that of BA-PVA because of having a chlorine in the benzene ring.

Figure 4 shows the SEM micrographs of *p*-CBA-PVA (2000) resist patterns on a chromium film after development. Resolution of 1 μm line and space could be clearly obtained by *p*-CBA-PVA (2000) resist. Figure 5 shows the photomicrographs of etched patterns of chromium delineated with *p*-CBA-PVA (2000) resist. It was found from Figures 4 and 5 that the resist patterns were clearly copied into the chromium.

In summary, acetalized PVA's are easily crosslinked by EB exposure. The polymers with a benzene ring in the acetal group have high sensitivity with good adaptability to dry etching processes and are good potential EB resists.

Other acetalized PVA's will be published in the near future.

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