Electron-Beam Resist Properties of New 1:1 Alternating Copolymers of N-Vinylcarbazole with Allyl Glycidyl Fumarate and Ethyl Glycidyl Fumarate

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Alternating copolymers are of interest because they have regular structures of alternation. Certain 1:1 alternating copolymers, e.g., poly(olefin-alt-SO₂), have found successful application as positive electron-beam resists [1,2]. Polymers derived from reactions of unsaturated alcohols with alternating copolymers of maleic anhydride with ethyl vinyl ether or styrene have been reported to function as negative electron-beam resists [3,4]. It has also been reported that the alternating copolymer of α-methylstyrene with maleic anhydride has a higher sensitivity and a higher contrast than the corresponding random copolymers upon exposure to the electron beam [5]. We report here the synthesis of new 1:1 alternating copolymers containing N-vinylcarbazole (VCZ) as one monomer component and their electron-beam resist properties.

The AIBN-initiated copolymerizations of VCZ with allyl glycidyl fumarate (AGF) and with ethyl glycidyl fumarate (EGF) produced copolymers as white powders. The compositions of copolymers of VCZ and EGF were found to be almost equimolar over a wide range of monomer feed ratios [6]. Likewise, the compositions of copolymers of VCZ and AGF were found to be almost equimolar over a wide range of monomer feed compositions; however, the copolymers obtained at low VCZ molar fractions in the monomer feed (VCZ mole fraction: ∼0.2) were rich in AGF. The deviation of the copolymer composition from the 1:1 molar ratio at the low VCZ molar fractions may be due to the participation of the copolymerization at the allyl group as well as at the fumarate double bond in AGF. The 1:1 alternating copolymers, poly(VCZ-alt-AGF) and poly(VCZ-alt-EGF),
which contain alternately cross-linking epoxy or epoxy and allyl groups and a dry-etch resistant carbazole moiety as pendant groups, are expected to function as dry-etch resistant, negative electron-beam resists.

\[ \text{CH}_2=\text{CH}_2 + \text{HCOOCH}_2\text{CH}-\text{CH}_2 \xrightarrow{\Delta} \text{CH}_2=\text{C} = \text{N} - \text{C} = \text{O} - \text{CH}_2=\text{CH}_2 + \text{COOCH}_2\text{CH}-\text{CH}_2 \]

R: \( \text{CH}_3\text{CH}_2^-, \text{CH}_2=\text{CHCH}_2^- \)

The alternating copolymers obtained at the equimolar monomer feed ratio at 50°C were used for the measurements of resist properties by irradiation with electron beam at 20kV accelerating voltage. They have number-average molecular weights of 80,000 and 60,000, molecular weight distributions of 4.3 and 1.8, and relatively high glass-transition temperatures of 130°C and 140°C, for poly(VCZ-alt-AGF) and poly(VCZ-alt-EGF), respectively. They have a good film-forming property.

Resist films of the copolymers of ca. 0.4 μm in thickness were prepared on a silicon wafer by spin coating from ca. 10 wt% cyclohexanone solutions, and dried at 80°C for 20 min before exposure. The exposed films were developed with cyclohexanone at 20°C for 90 sec and then rinsed with isopropyl alcohol. It was found that the poly(VCZ-alt-AGF) film has a high sensitivity of 2.5 μC cm\(^{-2}\), which is one-order of magnitude higher than that for the poly(VCZ-alt-EGF) film (Fig. 1). The result indicates that the allyl group is more effective than the epoxy group for the cross-linking upon irradiation with electron beam. Both films have a resolution of ca. 0.2 μm line width and 1 μm spacing with vertical sidewalls.

![Fig. 1. Characteristic film thickness vs. electron beam exposure dose (at 20kV); (a) poly(VCZ-alt-AGF), (b) poly(VCZ-alt-EGF).](image)

References