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A New Negative Deep UV Resist Based on an Alternating Copolymer - Onium Salt System. Synthesis and Property of a 1:1 Alternating Copolymer of N-Vinylcarbazole with Ethyl Glycidyl Fumarate

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A new 1:1 alternating copolymer of N-vinylcarbazole with ethyl glycidyl fumarate was prepared. The copolymer film containing about 1 wt% diphenyliodonium tetrafluoroborate functions as a negative-working deep UV resist: it has a relatively high sensitivity of 70 mJ/cm^2 and a high contrast of 4.36 upon exposure to 248 nm light from a KrF excimer laser.

Recently short-wavelength UV lithograghy has been receiving great attention as a potential new technology in the fabrication of microelectronic devices. Much efforts have been made to develop deep UV resists with high sensitivity, high contrast, high resolution and dry-etch resistance. Poly(methyl methacrylate) and poly(methyl isopropenyl ketone), which are known as positive electron beam resists, function as deep UV resists; however, they are poorly dry-etch resistant. A copolymer of a methyl methacrylate (MMA) - 3-oximino-2-butanone methacrylate - methacrylonitrile system and a copolymer of MMA with indenone have been reported to be positive-working deep UV resists.[1,2] A two-component system composed of poly(vinyl phenol) and a bisazide compound, and chloromethylated polystyrene, are examples of negative deep UV resists with good dry-etch resistance: they show sensitivities of 100 mJ/cm^2 and 1 J/cm^2, respectively, upon exposure to 248 nm KrF excimer laser light.[3,4]

We report here a new negative-working deep UV resist based on a 1:1 alternating copolymer - onium salt system. Some alternating copolymers have been shown to function as electron beam resists. For example, certain poly(olefin sulfone)s have been used as positive electron beam resists,[5,6] and polymers derived from the reaction of unsaturated alcohols with alternating copolymers of maleic anhydride with ethyl vinyl ether or styrene have been reported to work as negative electron beam resists.[7,8] It has also been reported that an 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.[9] In this communication the synthesis of a new 1:1 alternating copolymer of N-vinylcarbazole with ethyl glycidyl fumarate and deep UV resist

property of the copolymer film containing an onium salt are described.

N-Vinylcarbazole (VCZ) (Tokyo Kasei Kogyo Co., Ltd, extra pure) was purified by repeated recrystallization from methanol and then from n-hexane, and dried in vacuo. Ethyl glycidyl fumarate (EGF) was prepared by the reaction of epichlorohydrin with potassium salt of fumaric acid monoethylester, which was derived from maleic anhydride by the reaction with ethanol, followed by the isomerization to the trans-form. The EGF monomer, bp 73-75 °C/0.05 mmHg, was identified by IR and ^{1}H NMR spectra and elemental analysis. The copolymerization of VCZ with EGF was carried out in benzene at 60 °C with 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The total monomer concentration and the initiator concentration were 1.0 mol dm^{-3} and 5.0 x 10^{-3} mol dm^{-3}, respectively.

The copolymer obtained at the equimolar monomer feed composition at 50 °C, which has a weight-average molecular weight of 110000 and a molecular weight distribution of 1.4, was used for the measurement of sensitivity and contrast by irradiation with KrF excimer laser light. A resist film of the copolymer of ca. 0.5 μm in thickness containing 1.2 wt% diphenyliodonium tetrafluoroborate was prepared on a silicon wafer by spin-coating (3000 RPM) from ca. 10 wt% cyclohexanone solution of the copolymer and dried at 90 °C for 20 min before exposure. The exposed film was developed with cyclohexanone for 60 seconds.

Table 1 shows compositions and molecular weights of copolymers of VCZ with EGF obtained at various monomer feed compositions. Copolymer compositions were found to be almost equimolar over a wide range of monomer feed molar ratios. The copolymers obtained at a wide range of monomer feed compositions exhibit essentially the same electronic absorption and fluorescence spectra. Figure 1 shows the fluorescence spectra of a copolymer and poly(N-vinylcarbazole) obtained

Table 1. Compositions and Molecular Weights of Copolymers of VCZ with EGF

VCZ Mole Fraction in Monomer Feed	VCZ Mole Fraction in Copolymer	Mn x 10^{-4}	Mw x 10^{-4}
0.10	0.47	0.8	2.1
0.20	0.48	1.8	3.5
0.30	0.49	2.1	4.9
0.40	0.49	2.6	6.8
0.50	0.50	6.5	11
0.60	0.50	6.6	11
0.70	0.50	5.6	12
0.80	0.51	12	36
0.90	0.51	7.7	18

by radical polymerization of N-vinylcarbazole. Unlike poly(N-vinylcarbazole), which shows mainly excimer fluorescence, these copolymers exhibit mostly monomer fluorescence with peaks at 345 and 358 nm in a dilute solution, the shape of which resembles that of ethylcarbazole. Generally the intramolecular excimer formation in aryl vinyl polymers in a dilute solution using good solvents occurs by interactions between the nearest-neighbor pendant chromophores. The fluorescence spectral data as well as the equimolar composition of the copolymers over a wide range of monomer feed compositions indicate that the copolymer of VCZ with EGF is a 1:1 alternating copolymer.

The 1:1 alternating copolymer, poly(VCZ-alt-EGF), contains alternately a crosslinkable epoxy group and a dry-etch resistant carbazole moiety as pendant groups. It is expected that the copolymer functions as a dry-etch resistant, negative-mode deep or mid-UV resist in the presence of an onium salt. Onium salts are known to generate the proton acid by photoirradiation, which initiates photocationic polymerization of epoxy compounds and vinyl ethers.[10] In the present polymer system, cross-linking will take place.

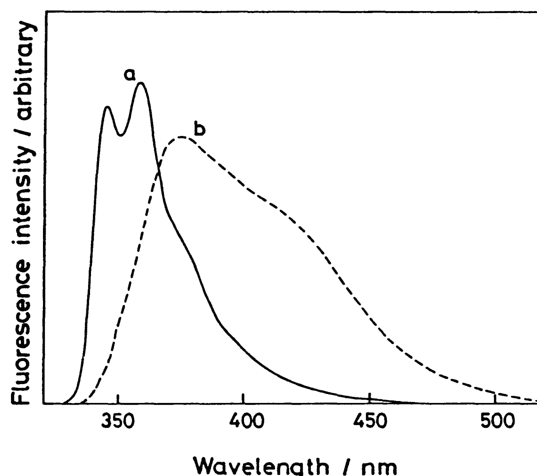

Fig. 1. Fluorescence spectra of (a) poly(VCZ-alt-EGF) obtained at the equimolar monomer feed and (b) poly(VCZ) obtained by radical polymerization, in THF at room temperature. Concentration: ca. 2×10^{-4} mol dm^{-3} based on the carbazole unit.

Figure 2 shows the characteristic curve of the remaining film thickness vs. exposure energy when the poly(VCZ-alt-EGF) film containing diphenyliodonium tetrafluoroborate was exposed to 248 nm light from a KrF excimer laser. It was found that the two-component film has a relatively high sensitivity of 70 mJ/cm^2 and a high contrast of 4.36 upon exposure to 248 nm light.

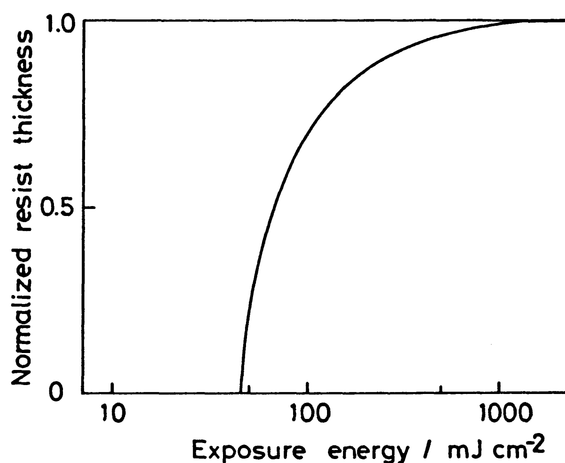

Fig. 2. Characteristic curve of poly(VCZ-alt-EGF) film containing 1.2 wt% diphenyliodonium tetrafluoroborate on exposure to KrF excimer laser light.

Resist materials containing onium salts have been reported. Examples are given of an end-capped poly(phthalaldehyde) - onium salt system[11] and poly(styrene) derivatives that undergo radiation-induced changes in polarity of polymer repeating units in the presence of onium salts.[12] In the present poly(VCZ-alt-EGF) - diphenyliodonium

tetrafluoroborate system, the onium salt absorbs 248 nm light to generate proton, which initiates the ring cleavage of the epoxy group, leading to the cross-linking of the copolymer. The present system composed of an onium salt and a polymer containing alternately a dry-etch resistant group and a cross-linkable epoxy group presents a new approach for the search for negative-mode deep UV or mid-UV resists.

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