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Highly Sensitive Self Developing Electron-Beam Resist of Aldehyde Copolymer

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Summary

The copolymers of aliphatic aldehydes were prepared in toluene with diethylaluminum diphenylamide at -78°C. It was found that the copolymer was depolymerized into monomeric aldehydes on the exposure to electron-beam or X-ray. When the copolymer was used as an electron-beam resist, almost complete development was accomplished by exposure alone. No development step was required. The sensitivities of poly(ethanal-co-propanal), poly(ethanal-co-butanal), poly(ethanal-co-heptanal) and poly(ethanal-co-3-phenylpropanal) at the film thickness of $0.4 \sim 0.7$ μm were 8×10^{-7}, 7×10^{-7}, 1.7×10^{-6} and 6.5×10^{-6} C/cm^2, respectively. The copolymer acts also as an X-ray resist of high sensitivity.

Introduction

Among many positive electron-beam resists, poly(methyl methacrylate) is an exemplary resist of high resolution. However, it requires fairly high dose of $10^{-4} \sim 10^{-5}$ C/cm^2, which limits the throughput of the electron-beam system. Very recently Willson and his coworkers (WILLSON et al., 1982) reported that the exposure of poly(phthalaldehyde) or poly(phthalaldehyde-co-o-nitrobenzaldehyde) to electron-beam, X-ray and ultraviolet radiation resulted in spontaneous formation of relief image, which was corresponding to $10 \sim 60$% loss in film thickness in the exposed regions. They also found that the addition of certain cationic photoinitiators to poly(phthalaldehyde) allowed imaging of the 1 μm thick film of the polymer at 1.0×10^{-6} C/cm^2 and 20 KV with electron-beam exposure without any development step. The similar phenomenon was also observed in the polyolefinsulfones but complete development to substrate can be achieved only with thin film using high temperatures (∿100°C) and low accelerating voltage (5KV) (BOWDEN and THOMPSON 1974).

The appearance of Willson's paper prompted us to make a preliminary report of our own studies on alde-

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hyde copolymer, in which the copolymers of aliphatic aldehydes were exposed to electron-beam and X-ray and almost complete development was accomplished by exposure alone. The sensitivity to electron-beam was extremely high ($10^{-6} \sim 10^{-7}$ C/cm^2) without any sensitizer.

Experimental

The copolymers of aliphatic aldehyde were prepared in toluene at -78°C by using diethylaluminum diphenylamide as an initiator (TANAKA et al., 1964a, TANAKA et al., 1964b, TANAKA et al., 1965a, TANAKA et al., 1965b, TANAKA et al., 1965c, TANAKA et al., 1965d). Unlike the homopolymers of aliphatic aldehydes, the copolymers were soluble in organic solvents such as toluene, xylene or chloroform in a certain range of copolymer composition (TANAKA et al., 1964a, TANAKA et al., 1964b, TANAKA et al., 1965a). The soluble copolymers containing approximately equal amounts of both monomer units were used for making the resist films, which were spin-coated or dip-coated on a silicon wafer substrate and were $0.04 \sim 3.4$ µm in thickness. The weight-average molecular weights of the poly(ethanal-co-butanal)s prepared in toluene at -78°C by diethylaluminum diphenylamide were reported to be more than 1,000,000 (TANAKA et al., 1965c). It is reasonable to assume that the molecular weight of the aldehyde copolymers used in this work is at least the order of 10^6.

The coated silicon wafer was exposed to a 20 KV electron-beam or an Al-K_α soft X-ray. The film thickness before and after exposure was measured by using Talystep film thickness gauge (Rank Taylor Hobson Co., Ltd).

Results and Discussion

The ceiling temperature for the copolymerization of aliphatic aldehyde is usually below 0°C and the copolymer was easily depolymerized into monomeric aldehydes above 150°C under vacuum. The depolymerization into monomers also occurred on the exposure of aldehyde copolymer to electron-beam or X-ray, which was evidenced by combined gas-liquid partition chromatography-mass spectrometry. Electron-beam and X-ray exposure characteristics of several aldehyde copolymers are shown in Table 1. Almost complete development was obtained at the dose of $\sim 10^{-6}$ C/cm^2, 20 KV and the film thickness of $0.4 \sim 0.7$ µm with electron-beam exposure without any solvent treatment. The sensitivity increased with decreasing the thickness of film. The poly(ethanal-co-propanal) of 0.04 µm thickness showed the sensitivity of 1×10^{-7} C/cm^2. The sensitivity decreased in the increasing order of the boiling points of aldehyde monomers. The results indicate the dependence of the

Table 1
Electron-beam and X-ray Exposure Characteristics of Aldehyde Copolymers[a]

Copolymer[b]	(mol%)[c]	Thickness (μm)	Sensitivity (C/cm^2)	γ-value
AA-PA	51.3	0.04	1×10^{-7}	0.74
AA-PA	51.3	0.4	8×10^{-7}	0.70
AA-BA	50.0	0.65	7×10^{-7}	1.3
AA-BA	50.0	1.8	1.7×10^{-6}	0.61
AA-BA[d]	50.0	2.4	30 mJ/cm^2	1.0
AA-HA	54.4	0.38	3.3×10^{-7}	1.0
AA-HA	54.4	0.70	1.7×10^{-6}	0.75
PA-PhPA	52.0[e]	0.65	6.5×10^{-6}	0.86
PA-PhPA	52.0[e]	1.2	2.1×10^{-5}	0.72
PA-PhPA	52.0[e]	3.4	5.0×10^{-5}	0.57

[a] Prebaked at 80°C for 0.5 hr and without any development step, accelerating voltage 20 KV

[b] AA: ethanal, PA: propanal, BA: butanal, HA: heptanal, PhPA: 3-phenylpropanal. The films of poly(AA-co-BA), poly(AA-co-HA) and poly(PA-co-PhPA) were made from the solution in xylene and that of poly(AA-co-PA) from chloroform solution

[c] The content of AA unit in the copolymer

[d] Exposure to X-ray (Al-Kα)

[e] The content of PA unit in the copolymer

sensitivity on the volatility of the aldehyde formed under the irradiation.

Recently it was disclosed in a Japanese patent that the copolymers of hexanal with propanal, butanal and isobutanal could be used as a self-developing X-ray resist of 200 ∿ 400 mJ/cm^2 sensitivity (SUKEGAWA et al., 1982). Our aldehyde copolymer also acted as a positive resist on the exposure to X-ray and poly(ethanal-co-butanal) showed the sensitivity of 30 mJ/cm^2 without any development step.

As judged from the measurement of thickness by Talystep gauge, the resist film was completely removed at the dose shown in Table 1. However, a very thin residual film ($\simeq$ 0.01 μm) was found remained by scratching the exposed pad. Higher exposure doses did not decrease the thickness of residual film. It may be possible to etch substrate through the remaining thin film. Another inconvenience of polyaldehyde resist was the low solubility of the polymer and the softness of the film. These were fairly improved with poly(propanal-co-3-phenylpropanal) in association with a little decrease in the sensitivity probably owing to the incorporation of phenyl group. The γ-value of polyaldehyde resist was generally low as shown in Table 1, but it increased with a decrease in the thickness of the film. These factors, which hinder the full utilization of the polyaldehyde resists, may be eliminated by the chemical modification of the polymer. Further studies are now under way on various kinds of aldehyde copolymers and the results will be published in near future.

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