

Highly Sensitive Self-Developing Soft X-Ray Resists of Silicon-Containing Aldehyde Copolymers and Sensitive Novolac-Based Composite Resists Containing Aldehyde Copolymer

KAZUO NATE,* TAKASHI INOUE, and HITOSHI YOKONO,
*Production Engineering Research Laboratory, Hitachi, Ltd., 292
Yoshida-machi, Totsuka-ku, Yokohama 244, Japan;* and KOICHI
HATADA, *Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan*

Synopsis

Copolymers of aliphatic aldehydes containing a trimethylsilyl group were prepared at -78°C in toluene using diethylaluminum diphenylamide as an initiator. The copolymer depolymerized into monomeric aldehydes on exposure to soft X-rays. When the copolymer was used as a soft X-ray resist, almost complete development was accomplished by exposure alone. No development step was required. The soft X-ray sensitivity of poly(3-trimethylsilylpropanal-co-propanal) was $50\text{ mJ}/\text{cm}^2$ at the film thickness of $1.0\text{ }\mu\text{m}$. A composite resist system consisting of a novolac resin and an aldehyde copolymer containing trimethylsilyl groups has also been developed and used as an alkaline-developable positive electron-beam and soft X-ray resist.

INTRODUCTION

Very large-scale integrated (VLSI) technology continues to place demands for new materials and processes to achieve submicron resolution in the lithographic fabrication of integrated circuits. Electron-beam lithography and X-ray lithography have been shown to be promising techniques for resolution below $0.5\text{ }\mu\text{m}$.

Many papers have been published on positive electron-beam resists and soft X-ray resists. Most of these polymers are degraded upon electron-beam or soft X-ray irradiation. The resulting lower molecular weight polymer in the exposed area can be removed selectively by a specific developing solvent through differential dissolution between the exposed and unexposed areas. The dissolution rate ratio is a function of the initial molecular weight of the polymer and the degraded molecular weight.

Willson and co-workers reported that exposure of poly(phthalaldehyde) or poly(phthalaldehyde-co-*o*-nitrobenzaldehyde) to electron-beam, soft X-ray, and ultraviolet (UV) irradiation resulted in spontaneous formation of a relief image. They also found that the addition of certain cationic photoinitiators to poly(phthalaldehyde) allowed imaging of the $1\text{ }\mu\text{m}$ thick film of the polymer at $1.0\text{ }\mu\text{C}/\text{cm}^2$ without any development step.¹

*To whom correspondence should be addressed.

Self-development also occurred with poly(olefin sulfones), but complete development to the substrate could be achieved only in the case of thin films using high temperatures and low accelerating voltages.²

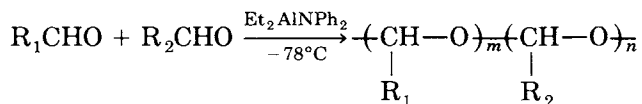
We have reported that copolymers of aliphatic aldehydes depolymerize when exposed to high energy electrons or soft X-rays and that almost complete development can be accomplished by exposure alone. The sensitivity is extremely high and no sensitizer is necessary.³ As a continuance of our investigations dealing with exposure characteristics of the aliphatic aldehyde copolymers, we have prepared copolymers of 3-trimethylsilylpropanal with aliphatic aldehyde. The copolymers are more soluble in common organic solvents, specifically, toluene than the aldehyde copolymers containing no silicon atoms.

This paper discusses the lithographic characteristics of copolymers of aliphatic aldehydes containing trimethylsilyl groups which act as highly sensitive self-developing soft X-ray positive resists. We also report our results on a novolac-based composite resist containing the aldehyde copolymer which acts as an alkaline-developable electron-beam and soft X-ray positive resist.

EXPERIMENTAL

Synthesis

Copolymers of the aliphatic aldehydes were prepared in toluene at -78°C using diethylaluminum diphenylamide as an initiator.⁴



(R_1 and R_2 are organic substituents.)

The polymerization was carried out in a 10 mL cylindrical polymerization vessel with a three-way stopcock. The apparatus was thoroughly dried and purged with dry nitrogen. All subsequent operations were carried out under dry nitrogen atmosphere.

A mixture of aldehyde monomers and toluene was placed in the polymerization vessel through the three-way stopcock using a hypodermic syringe. The apparatus was cooled in an ice-water bath. A toluene solution of diethylaluminum diphenylamide was added slowly with vigorous stirring. After 5 minutes, the apparatus was cooled in a dry ice-acetone bath and kept at -78°C for 24 h. Then, the reaction mass was quickly transferred to a blender containing anhydrous ammoniacal methanol precooled at -70°C . The blender was turned to high speed for about 20 seconds, and the mixture was allowed to stand overnight at room temperature. The polymer was collected by filtration, washed several times with methanol, and dried *in vacuo* at 30°C for 10 h.

Synthesis of 3-Trimethylsilylpropanal⁵

A 2-liter, three-necked, round-bottomed flask was fitted with a motor-driven stirrer, a pressure-equalized dropping funnel, and a thermometer. This apparatus was thoroughly dried and purged with dry nitrogen.

Dried tetrahydrofuran (1200 mL), 12.32 g (1.76 mol) of lithium fine powder, and 236 g (2.17 mol) of trimethylchlorosilane were placed in the flask and cooled to -10°C . Then, 100 mL of tetrahydrofuran solution containing 44.8 g (0.8 mol) of acrolein was added dropwise from the dropping funnel for about 2 h with violent stirring so that the temperature of the reaction mixture remained in the range of -10 to -5°C . The resulting solution was stirred for another 5 h at room temperature, and then unreacted lithium powder was filtered off. The filtrate was subjected to distillation to remove tetrahydrofuran, and 100 mL of methanol containing a few drops of conc. HCl was added to the residual solution. The mixture was stirred for 3 h at room temperature, and then methanol was removed by distillation. After removal of methanol, 3-trimethylsilylpropanal was isolated by the distillation under reduced pressure. Yield 10%; B.P. $86^{\circ}\text{C}/110$ mmHg (lit. b.p. $58^{\circ}\text{C}/30$ mmHg).

Ethanal, propanal, butanal, hexanal, 3-phenylpropanal, and benzaldehyde were obtained commercially.

Synthesis of Diethylaluminum Diphenylamide⁴

A 200 mL, four-necked, round-bottomed flask was fitted with a motor-driven stirrer, a pressure-equalized dropping funnel, a three-way stopcock, and a thermometer. This apparatus was thoroughly dried and purged with dry nitrogen. All subsequent operations were carried out under dry nitrogen atmosphere.

Triethylaluminum (14.5 g, 0.127 mmol) and toluene (33 mL) were placed in the flask through the three-way stopcock using a hypodermic syringe. A solution of diphenylamine (21.4 g, 0.127 mmol) in 40 mL of toluene was added dropwise from the dropping funnel with agitation while cooling the flask in an ice-water bath. After the addition was complete, stirring was continued for 2 h at 60°C . The solution of diethylaluminum diphenylamide thus obtained was diluted with toluene to 0.5 mol/L and stored in the flask with a three-way stopcock under nitrogen atmosphere.

Resist Processing

Resist preparation. Resist solutions were prepared by dissolving the aldehyde copolymer in xylene or cyclohexanone at a concentration of 0.5–1.0 wt%. The solutions were then filtered through a $1.0\ \mu\text{m}$ Teflon filter.

Coating. Resist films were spin-coated or dip-coated on silicon wafers.

Prebake. The resist films coated on silicon wafers were prebaked in a conventional oven at 80°C for 30 minutes.

Exposure. Electron-beam experiments were carried out using an Elionix ERE 301 electron-beam exposure system at 20 KeV electron-beam. Soft X-ray exposure was performed by a Rigaku SX-7F soft X-ray generator under reduced pressure using Mo L_{α} or Al K_{α} soft X-ray.

RESULTS AND DISCUSSION

Copolymerization of 3-Trimethylsilylpropanal

Copolymerizations of 3-trimethylsilylpropanal (TMSPA) with several aliphatic aldehydes and benzaldehyde were carried out in toluene at -78°C

TABLE I
Copolymerization^a of 3-Trimethylsilylpropanal (TMSPA) by
Diethylaluminum Diphenylamide in Toluene at -78°C for 24 h

No.	Comonomer	Amount of total monomer (mmol)	Toluene (mL)	Polymer	
				Yield (%)	TMSPA (mol%) ^c
1 ^b	—	6.4	1.03	54.8	100
2	Ethanal (EA)	11.6	1.13	33.1	50.2
3	Propanal (PA)	11.1	0.97	44.0	47.7
4	Butanal (BA)	11.1	0.97	44.9	48.3
5	Benzaldehyde (PhA)	11.6	1.13	9.3	100
6	3-Phenylpropanal (PhPA)	11.6	1.13	47.1	42.6

^a Monomer/Initiator = 50 mol/mol. TMSPA/Comonomer = 1 mol/mol.

^b Monomer/Initiator = 100 mol/mol.

^c Determined by elemental analysis.

using diethylaluminum diphenylamide as an initiator. The results are shown in Table I. The copolymers with the aliphatic aldehydes had nearly the same composition as that of the initial monomer mixture, whereas only the homopolymer of TMSPA was formed in the copolymerization with benzaldehyde. Unlike the homopolymers of the aliphatic aldehydes, the copolymers are soluble in organic solvents such as toluene, xylene, chloroform, or tetrahydrofuran in a certain range of copolymer composition.⁶

The solutions of aldehyde copolymers prepared by diethylaluminum diphenylamide were usually highly viscous, making it difficult to obtain uniform films on silicon wafers by spin-coating.³ The copolymers containing TMSPA were more soluble in organic solvents than the copolymers of ordinary aliphatic aldehydes as shown in Table II, and the solution viscosities were lower. Thus it was easier to spin-coat films. The weight-average molecular weights of the poly(ethanal-co-butanal)s prepared in toluene at -78°C by diethylaluminum

TABLE II
Solubilities in Toluene of Several Copolymers of Aliphatic Aldehydes

No.	Copolymer ^a of aliphatic aldehydes	Solubility ^b in toluene
1	Ethanal-co-propanal	+
2	Ethanal-co-butanal	++
3	Ethanal-co-hexanal	++
4	Propanal-co-3-phenylpropanal	+++
5	TMSPA-co-ethanal	+++
6	TMSPA-co-propanal	+++
7	TMSPA-co-butanal	+++
8	TMSPA-co-3-phenylpropanal	++++

^a Copolymerization: Monomer/Comonomer = 1/1.

^b The number of + 's means the grade of the solubility.

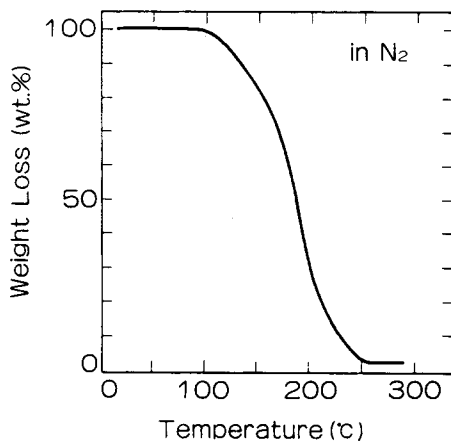


Fig. 1.

diphenylamide were reported to be more than 1×10^6 .⁷ It would seem reasonable to assume that the molecular weight of the aldehyde copolymers used in this work is of a similar magnitude.

The thermal gravimetric analyses (TGA) of these polymers were measured in air and in nitrogen. The TGA curve of poly(TMSPA-co-PA) obtained under nitrogen is shown in Figure 1. The weight loss started to occur at about 100°C and the copolymer was depolymerized into monomeric aldehydes.

Electron-Beam and Soft X-Ray Resist of Aldehyde Copolymers

Since the ceiling temperature for the copolymerization of aliphatic aldehydes is usually below 0°C, it is not unusual that the copolymers should depolymerize at temperatures above 150°C under vacuum. We found that depolymerization also occurred on the exposure to electrons or soft X-rays, at room temperature as evidenced by combined gas-liquid partition chromatography-mass spectrometry. As a result, these copolymers behave as self-developing positive resists and almost complete development can be accomplished without any solvent treatment.³

The sensitivities of poly(TMSPA-co-EA), poly(TMSPA-co-PA), and poly(TMSPA-co-BA) as electron-beam resists were in the order of 0.1–1 $\mu\text{C}/\text{cm}^2$ at the film thickness of 0.4–3.8 μm and increased with decreasing film thickness.³

The soft X-ray exposure characteristics of the aldehyde copolymers were determined and summarized in Table III. The exposure characteristic of poly(TMSPA-co-PA) is shown in Figure 2. A positive resist pattern was obtained by exposure alone. No development step was required, although a thin residual film (about 10%) remained in the exposed area in the case of poly(TMSPA-co-PA), poly(TMSPA-co-BA), and poly(TMSPA-co-PhPA). The resist film appeared to be completely removed in the case of poly(TMSPA-co-EA) by the exposure. The degradation products of poly(TMSPA-co-BA) produced by the soft X-ray exposure were collected and analyzed by combined

TABLE III
Soft X-Ray Sensitivities and γ -Values for the Copolymers
of 3-Trimethylsilylpropanal (TMSPA) with Aliphatic Aldehydes

No.	Aldehyde copolymer	Thickness (μm)	Sensitivity ^a (mJ/cm^2)	γ -value
1	Poly(TMSPA-co-EA)	0.75	160	1.03
2	Poly(TMSPA-co-PA)	1.00	50 ^b	0.86
3	Poly(TMSPA-co-BA)	0.84	50 ^b	0.72
4	Poly(TMSPA-co-PhPA)	0.60	240 ^b	0.96

^aExposure to soft X-ray ($\text{Mo } L_{\alpha}$).

^bMeasured from the doses with 90% loss in the film thickness.

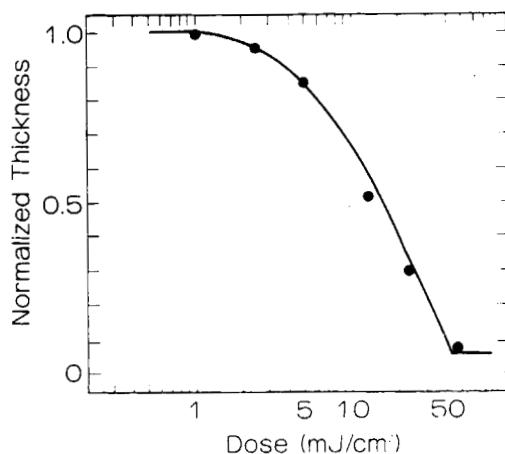


Fig. 2.

gas-liquid partition chromatography-mass spectrometry, which showed them to consist of a mixture of both aldehyde monomers as shown in Figure 3.

It has been disclosed in a Japanese patent by Sukegawa that the copolymers of hexanal with propanal, butanal, and isobutanal can be used as self-developing X-ray resists of 200–400 mJ/cm^2 .⁸ Our copolymers of 3-tri-

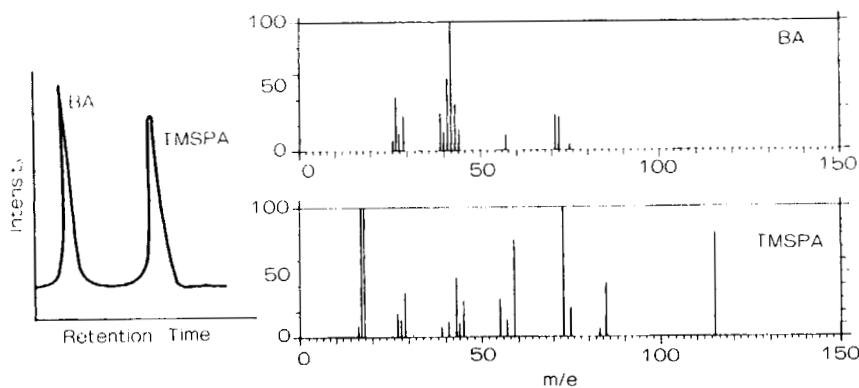


Fig. 3.

methylsilylpropanal with aliphatic aldehydes showed higher sensitivities on exposure to soft X-ray irradiation than did Sukegawa's copolymers.

Composite Resist System Consisting of Novolac Resin and Aldehyde Copolymer

We have seen that the copolymers of TMSPA with aliphatic aldehydes are highly sensitive self-developing soft X-ray positive resists. Although many polymers containing silicon atoms in the main chain or side groups are known to exhibit high resistance to an oxygen plasma, the silicon-containing aldehyde copolymer resists used in this study exhibited poor resistance to dry-etching environments such as plasma-etching and ion-beam milling. The etching rate of the aldehyde copolymer films was fairly high under mild oxygen plasma conditions which would seem to preclude their practical application in manufacture of high-resolution devices.

Positive-acting photoresists, which are based on novolac resins exhibit excellent dry-etch resistance. They are generally composed of an alkaline-soluble novolac resin and a photoactive dissolution inhibitor. Substituted naphthoquinone diazides are usually employed as the photosensitive dissolution inhibitor, which becomes soluble in aqueous alkaline developers after UV irradiation. This change in solubility depends on the photochemical decomposition of the naphthoquinone diazide into the indene ketene, which is hydrolyzed into indene carboxylic acid. The resistance of these resists to dry-etch processes is due to the excellent radiation and thermal stability of the novolac resins.

An alkaline-developable positive electron-beam resist also has been developed using a novolac resin and poly(2-methyl-1-pentene sulfone).⁹ In this case, the poly(olefin sulfone) acts as a dissolution inhibitor of novolac resin in aqueous base solution. The polymeric dissolution inhibitor is spontaneously depolymerized by electron-beam irradiation, thereby facilitating subsequent development in the aqueous base.

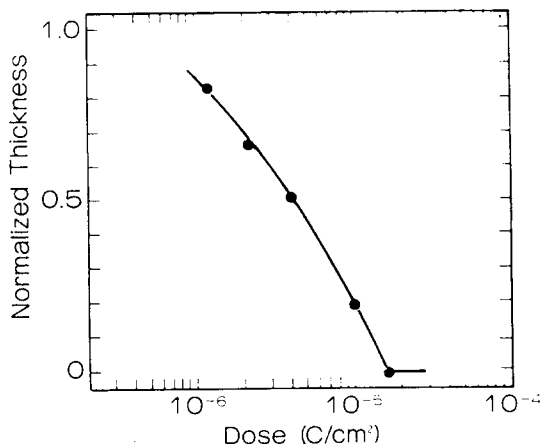


Fig. 4.

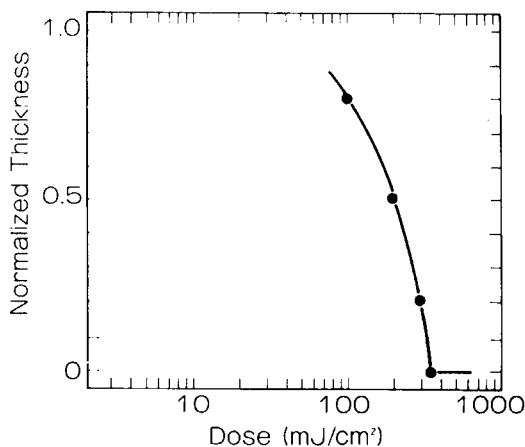


Fig. 5.

Several composite systems composed of a novolac resin and the silicon-containing aldehyde copolymer were investigated for resist application. Poly(TMSPA-co-EA), poly(TMSPA-co-PA), and poly(TMSPA-co-BA) were insoluble in solvents for the novolac resin and could not be used as a component of the composite. However, copolymers of TMSPA with PhPA were soluble in cyclohexanone which was also a solvent for the novolac resins investigated in this work. The phenolic novolac resins ($M_w \approx 1000$) and poly(*p*-hydroxystyrene) ($M_w = 3400$) could be used as alkaline-soluble polymers, and we usually used poly(*p*-hydroxystyrene) as an alkaline-soluble polymer. The composite system composed of poly(TMSPA-co-PhPA) and poly(*p*-hydroxystyrene) gave uniform films by spin-coating. Aqueous solution of tetramethylammonium hydroxide (2.38 wt%) was used as a developer.

Typical exposure characteristics generated for the resist containing 10 wt% poly(TMSPA-co-PhPA) are shown in Figures 4 and 5. The electron-beam sensitivity was $17 \mu\text{C}/\text{cm}^2$ at 20 KeV with a film thickness of $0.7 \mu\text{m}$ and a contrast of 0.84 was obtained. The soft X-ray sensitivity was $360 \text{ mJ}/\text{cm}^2$ at Mo L_α with a film thickness of $1.0 \mu\text{m}$ and a contrast of 1.9 was obtained. Further investigations are needed to enhance the sensitivities.

CONCLUSIONS

A new class of positive self-developing resists of aldehyde copolymers containing trimethylsilyl groups and a sensitive novolac-based positive composite resist system containing the aldehyde copolymer were developed and investigated in regard to the lithographic properties. Our conclusions are summarized below:

1. The copolymers are highly sensitive self-developing soft X-ray positive resists.
2. Almost complete development can be accomplished by exposure alone. No development step is required.

3. The copolymers are more soluble in organic solvents than the copolymers of ordinary aliphatic aldehydes, making spin coatings of uniform films easier to achieve.
4. The composite resist system, novolac resin/aldehyde copolymer is an alkaline-developable electron-beam and a soft X-ray positive resist.

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