NON-CONJUGATED CYCLIC DIENES AND MALEIC ANHYDRIDE CO-POLYMERS, AND DERIVATIVES FOR BASE RESIN OF DEEP UV RESIST

TAKASHI YAMAMOTO, and TORU SEITA
*Advanced Materials Research Laboratory, TOSOH Corporation,
2743-1 Hayakawa, Ayase 252, Japan*

Non-conjugated cyclic dienes and maleic anhydride co-polymers were synthesized via co-polymerization which involves an addition cyclization process, and they were investigated an application to a photo resist base resin. Every these polymers, which have an alicyclic hydrocarbon main-chain, showed excellent transparency in the wavelength regions of deep UV rays, and some of these polymers have high reactive ion etch resistance as similar as phenolic base resin; i.e. polyvinyl-phenol. One of these polymers (EBH-MAH) was modified to a photo resist, which has diazo photo sensitive functional groups. This polymer appeared high sensitivity for exposure of the deep UV ray. Solubility rate of the polymer in an aqueous alkaline solution, which could be dissolved difficulty for the solution, increased excellently after deep UV exposure. Namely this polymer showed a function as a deep UV positive resist that could be developed in alkaline.

1. Introduction

With respect to semiconductor elements such as LSI or VLSI the degree of their working tends to be finer year by year for the purpose of improving their performance. At present, lithography using deep UV rays such as KrF excimer laser (248nm) is described as a fine working technique for the production of such semiconductor elements. However, just as the conventional novolac/diazoquinone resist used for G and I line lithography cannot be used at 248nm, because of their high optical absorbance and relatively low photospeed. The chemical amplification concept was proposed in 1982 by IBM Ito [1] to approach above the matter that demanded highly sensitive advanced resist systems. Using this mechanism, it is possible to combine very high sensitivity, due to the catalytic chain reaction induced by the photogenerated acid, with high resolution and high dry-etch resistance, even in case of applying a phenolic base resin. Many works, based on above results,

were investigated in recent years.[2] However these chemically amplification systems also have several disadvantages, such as pattern-width variability, wrong thermal stability and narrow process margin.[3] These disadvantages hinder to apply this mechanism to the commercial production of semiconductor elements.

Here, we aimed to approach a resist, except chemically amplification system. As a initial step of this, we examined a polymer that could both appear the high transparency to deep UV rays and the reactive ion etch (RIE) resistance. We have promptly noticed a polymer containing the alicyclic hydrocarbon structure.[4] The photoresist base resin which bear alicyclic pendant groups have already been reported by the workers at Fujitsu, Matsushita and IBM.[5] In a present report, we described the transparency and the RIE resistance of the polymers bearing an alicyclic main-chain, that were introduced it's synthesis and structures by Pledger.[6] We also described the result of modification of the polymer for Deep UV positive resist.

2.Method

Synthesis of Polymers

(1) Synthesis of non-conjugated cyclic dienes and maleic anhydride co-polymers

The co-polymers were prepared according to the method described by Pledger.[6] The non-conjugated cyclic dienes used as co-monomer were summarized with co-polymerization conditions and it's results in Table 1.

(2) Modification for Photoresist polymer

The co-polymer between 5-ethylidene-bicyclo(2.2.1)-hepta-2-ene and maleic anhydride [EBH-MAH] (1g) and pyridine (10ml) as a solvent were stirred under nitrogen atmosphere at r.t.,until the mixture become uniform. Then,to this solution, a pyridine solution containing 3-diazo-2,4-diketo-10-hydroxy-decane (1.43g) was added slowly, and the mixture was stirred at r.t. for 28 hrs. Then the reaction mixture was evaporated in order to remove the solvent, and a crude polymer was obtained. The obtained polymer was purified by precipitation from ethyl-ether after dissolving in tetrahydrofuran. Further, this co-polymer (1g) was dissolved dimethylformamide (10ml), and *n*-propylamine (0.75ml) and 1,3-dicyclohexylcarbodiimide (1.89g) was added to the solution. Then the solution was stirred at r.t. for 24 hrs. The reaction mixture was evaporated in order to remove the solvent, and a crude polymer was purified by using ethyl-ether and tetrahydrofuran again. The product was vacuum-dried at r,t, for 24 hrs to obtain 1.27g of the polymer for a photoresist.

(3) Charactarization of polymers

The shynthesized polymers were charactarized using standard techniques. The molecular weight of

Table 1. Co-polymerization of Non-conjugated Cyclic Dienes(I) and Dienophiles (II)

Run. No.	Monomers		Co-polymerization Conditions					Results		Polymer Structure [6]
	Diene (I)	Dienophile (II)	Moles I Moles II	Initiater Mol %	Solvent ℓ / mol II	Temp (°C)	Time (hr)	Yield (%)	Mw ^j	
1.	EBH ^a	MAH ^f	1 : 1	BPO ^h 1	Torueue 6	90	4	52	3000
2.	MBH ^b	MAH ^f	1 : 2	BPO ^h 1	Xylene 3	90	4	81	3200
3.	VCH ^c	MAH ^f	1 : 2	AIBN ⁱ 0.4	Dioxane 1	70	4	35	2800
4.	BHD ^d	MAH ^f	1 : 2	BPO ^h 1	Xylene 5	90	3	78	2100
5.	COD ^e	MAH ^f	2 : 1	BPO ^h 1	Xylene 6	90	24	89	2300
6.	EBH ^a	MI ^g	4 : 1	BPO ^h 1	Torueue 15	90	4	80	1700

^aEBH=5-Ethylidene-bicyclo(2.2.1)-2-heptene

^bMBH=5-Methylene-bicyclo(2.2.1)-2-heptene

^cVCH=4-Vinyl-1-cyclohexene

^dBHD=Bicyclo(2.2.1)-2.5-diene

^eCOD=Cycloocta-1.5-diene

^fMAH=Maleicanhydride

^gMI =Maleimide

^hBPO =Dibenzoyl peroxide

ⁱAIBN=2.2'-Azobis(isobutyronitrile)

^jPeak molecular weight determined with polystyrene as standard polymer.

the polymers were measured by gel permeation chromatography (Tosoh corp. CP-8000 systems) using polystyrene as standard. The polymer structure were determined by infrared measurements (Nihon Bunko IR-910).

Measurement of the Transmittances of the Polymer Films

The films with 1 μm thickness of the polymers were prepared by spin-coating on a quartz glass substrate. The film thickness was measured with a stylus instrument (Tencor Instruments Co. α-step 200). The transmittances at 248nm and UV spectra of the films on quartz substrates were measured by UV-visible spectro-photometer(Shimadzu UV-260).

Measurement of the RIE rate of the Polymer Films

The etching rates for the polymers were measured under CF₄ gas plasma conditions by using

reactive ion etching (RIE) equipment (Nichiden Anelva DEM-45M). The polymer films as etching sample were prepared by spin-coating on silicon wafer from solutions in cyclohexanone. The etching condition was 8Pa gas pressure, 30 sccm flow speed, and 200 W acceleration power. The film thickness were measured with a stylus instrument.

Measurement of the Solbility Rate of the Polymer Films in Alkaline Developer

The polymer films, coated on silicon wafers, were dipped into tetramethylammonium hydroxide (TMAH) 2.38% aqueous soln. (Tokyo Ohka NMD-3), and dissolved thickness were measured with a stylus measurement.

Irradiation of Deep UV Rays to Polymer Films

Deep UV exposure at 254nm were made with a ultra high pressure Hg lamp (Ushio Inc. ML251A/A) through an interference filter.

3. Results and discussion

Polymer Structure

Table 1 shows the structures of the synthesized co-polymers, which was described by Pledger.[6] Every these polymers have an alicyclic main-chain as a result of co-polymerization which involves an addition cyclization process between the non-conjugated cyclic diends and maleic anhydride. These structures were confirmed by IR analysis of the co-polymers as shown in Figure 1. IR spectral data of the co-polymers are summarized in Table 2.

Figure 1. IR spectra of co-polymer between 5-Ethylidene-bicyclo(2.2.1)hepta-2-ene and Maleicanhydride [EBH-MAH].

Table 2. IR Spectral Data of Non-conjugated Cyclic Dienes and Maleic Anhydride Copolymers

Co-polymer	IR (KBr) cm ⁻¹			
	C-H	C=O	-C-O-C-	N-H
1. EBH-MAH	2955 2830	1855 1775	910	
2. MBH-MAH	2950 2840	1860 1780	920	
3. VCH-MAH	2925 2830	1850 1775	920	
4. BHD-MAH	2950 2880	1855 1775	915	
5. COD-MAH	2940 2860	1850 1775	910	
6. EBH-MI	2950 2860	1770 1710		3200

Transparency of polymers

Table 3 shows the transmittances of several polymer films with a thickness of $1\mu\text{m}$ at 248nm UV ray. Moreover in the Figure 2, UV spectra of 5-ethylidene-bicyclo(2.2.1)hepta-2-ene /maleic anhydride co-polymer [EBH-MAH], a typical polymer including the alicyclic main-chain, can be seen in comparison with phenolic resins. Every present polymers showed the excellent transparency in the wavelength regions of deep UV rays, compared with phenolic polymers, e.g. polyvinylphenol [PVP] or novolac resin, and were equal to that of polymethylmetacrylate [PMMA] well-known as high transparent polymer at deep UV regions.

Figure 2. UV spectra of several polymer films for photoresist base resin with $1\mu\text{m}$ thickness coated on quartz substrates.

Table 3. Transmittance and RIE Rate of Non-conjugated Cyclic Dienes and Maleic Anhydride Co-polymer Films

Ex.No.	Co-polymer	Transmittance ^a (%)	RIE Rate ^b (Å/min)
1.	EBH-MAH	81	120
2.	MBH-MAH	80	122
3.	VCH-MAH	71	166
4.	BHD-MAH	82	134
5.	COD-MAH	83	120
6.	EBH-M I	78	124
7.	PVP ^c	45	121

^a Transmittances at 248 nm of the polymer films with $1\mu\text{m}$ thickness coated on quartz substrates

^b Etch rate under CF_4 ion etching condition.

^c Poly-vinylphenol

Reactive Ion Etch Resistance

It was assumed and estimated that alicyclic structure has some kind of efficiency to the RIE resistance. At the result, the following good relationship between polymer etch rate and the content of the aliphatic hydrocarbon structure in the whole structure was found out. In Figure 3, the number-ratio of C-C and C-H bonds in the repeat unit are plotted against the RIE rate. Also Figure 4 shows that the weight-ratio of carbon and hydrogen atoms in the repeat unit are plotted against the RIE rate. Both those data support the above mentioned relationship, that the polymer etch durability was given by the aliphatic hydrocarbon structures in the present polymers.

Figure 3. RIE rate vs. number-ratio of C-C and C-H bonds.

Figure 4. RIE rate vs. weight-ratio of C and H atoms.

No.	Co-polymer
1.	EBH-MAH
2.	MBH-MAH
3.	VCH-MAH
4.	BHD-MAH
5.	COD-MAH
6.	EBH-M I
7.	PVP

We suggest the following a reason to support the result. If the polymer contained much oxygen or nitrogen atoms, stable low molecular substances such as CO₂ or NO₂ would be produced through the process of dissociation of the bond under the RIE etching conditions. Then the polymer would be easily decomposed, so that it would lead to appear the low RIE durability. On the contrary, the hydrocarbon structure would be hard to produce low molecular substances comparatively. Therefore, our estimation goes to that the higher RIE resistance would be guaranteed in the polymer of higher ratio of C-C bonds or carbon atoms, with the alicyclic hydrocarbon structures. This estimation consists with the result examined by Ohnishi.[7]

Molecular Design for Photoresist

Among the examined polymers, [EBH-MAH] was selected and modified for a positive photoresist, that can be developed in an aqueous alkaline solution. The modification for the resist was attempted according to the following concepts, based on the foresaid results. The alicyclic main-chain in this polymer was remained for the appearance of high RIE resistance. Then photo sensitivity and alkaline solubility functions were added to the polymer by ring-opening esterification at acid anhydride rings in it. 3-diazo-2,4-dione group, which was not chemically amplified system, was adapted as photo sensitive functional group. This group is well-known to decompose directly by irradiation of deep UV rays, and to produce carboxylic acid after exposure. Further, some of carboxylic groups in the polymer, which were co-generated through ring-opening reaction, were

converted to amido groups in order to control the initial solubility rate in an alkaline developer. The polymer structure of modified [EBH-MAH] is described in Figure 5. Figure 6 shows IR spectra of the polymer.

Figure 5. Structure of modified [EBH-MAH] as a deep UV positive resist.

Figure 6. IR Spectra of modified [EBH-MAH]

Estimation of Photoresist

(1) Photosensitivity to deep UV irradiation

Figure 7 shows the UV spectra of produced resist film with 1 μ m thickness. The film had a high absorption at 248nm, and the absorption decreased to almost the same transmittance of original polymer [EBH-MAH] after 254nm UV irradiation with 75mJ/cm². This result exhibits decomposition of diazo functional group high sensitively.

(2) Solubility rate in alkaline developer

The solubility rate of the resist film in tetramethylammoniumhydroxide (TMAH) 2.38% aqueous solution was investigated before and after exposure. The film, that was very slowly solved before exposure, was seen the rapid solubility after 254nm UV irradiation with 45mJ/cm². (Figure 8) The data shows that this polymer functions as a deep UV positive resist which can be developed in alkaline developer. The preferable solubility balance was also possible to appear by using diluted an alkaline developer (1% TMAH soln.). So far, the ratio between photo sensitive functional group and amido group has not been investigated efficiently. If it is optimized, further preferable solubility balance will be expected to appear.

Figure 7. UV spectra of modified [EBH-MAH] positive resist before and after exposure with a thickness of $1\ \mu\text{m}$.

Figure 8. Solubility rate of modified [EBH-MAH] positive resist in alkaline developer before and after exposure.

4. Conclusion

It was investigated that the RIE rate of non conjugated cyclic diens and maleic anhydride co-polymers, hence, some of these polymers showed high RIE resistance, that is equal to that of phenolic resin. It was found out that high RIE durability was related to the high ratio of the aliphatic hydrocarbon structure, as a result of analysis of correlation between the polymer structure and the RIE rate. On the basis of the results, a photoresist polymer was designed and synthesized. This polymer having diazo photo-sensitive group had high sensitivity to deep UV rays, and appeared function as a deep UV positive resist, by means of estimation for solubility rate of the polymer film in alkaline developer before and after exposure.

Those whole results suggest to realize an advanced deep UV resist, that dose not owe to chemically amplified system. Therefore, it is expected the capability of the supply with more practical resist, that has high sensitivity, high resolution, and wide process margin at the same time in deep UV lithography.

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