

Polymer Communication

A novel organic bottom anti-reflective coating material for 193 nm excimer laser lithography

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Abstract

Bottom anti-reflective coatings (BARC) are useful to suppress the problems associated with reflection by the substrate during the lithographical processing. Now, we have proposed a new class of BARC material containing polyvinylphenol as a UV-absorber, poly(3,3'-dimethylpropene) (PDMP) as a crosslinker, and 2-hydroxycyclohexyl *p*-toluenesulfonate as a thermal acid generator. The PDMP was synthesized from acrolein by a two-step sequence reaction with a yield of 60%. The lithographic performance of photoresist with BARC that was proposed by us was evaluated and compared with those of photoresist without BARC. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Poly(3,3'-dimethylpropene); Thermal acid generator; Lithography

1. Introduction

The target of argon fluoride (ArF) excimer laser lithography is the fabrication of sub-0.15 μm design rule devices, which is the most promising candidate for the next generation of lithography techniques. The development of ArF excimer laser lithography has rapidly been accelerated to use practical process integration techniques such as advanced single-layer photoresist, [1–4] anti-reflective process, [5–9] attenuated phase-shifting mask, [10] and annular illumination. [5,11]

When the exposure wavelength is reduced to obtain a higher resolution, the interference and reflection from the interface between the photoresist and the substrate generally become stronger. The reflectance at 193 nm wavelength was slightly higher than that at 248 nm wavelength. In the semiconductor industry, the manufacture of high performance integral circuits requires tight control of critical dimensions (CDs) at poly pattern. In order to achieve these stable CDs and better resist profile, requirements force process engineers to eliminate line-width variation caused by inter-

ference and reflective notching. Implementation of a bottom anti-reflective coating (BARC) can reduce or eliminate line-width variations caused by interference and reflective notching. Therefore, the BARC is an essential technique in ArF excimer laser lithography with the practical resolution enhancement method. In *i*-line ($\lambda = 365$ nm) and krypton fluoride (KrF; $\lambda = 248$ nm) excimer laser lithography, many studies concerning BARC have been carried out. However, there is very little information about BARC for ArF excimer laser lithography. Ogawa et al. [6] discussed the use of hydrogenated silicon oxynitride ($\text{SiO}_x\text{N}_y\text{:H}$) inorganic film, that had already been used as a BARC film in *i*-line and KrF excimer laser lithography, and as a BARC for ArF lithography. [5,7] Yen et al. [12] and Kunz and Allen [13] developed an organic BARC for ArF lithography and investigated the anti-reflective effect at 193 nm. Both organic and inorganic BARCs have their own pros and cons but overall organic BARC seems to offer several advantages—reflective index reproducibility, throughput, stack issues, rework capability, thickness tolerance etc.

In this paper, we proposed a new organic BARC material, which had sufficient anti-reflectivity at 193 nm and the resist performance was improved by it. Also, we investigated the effect of substrate reflectivity on resist performance in order to improve the performance further.

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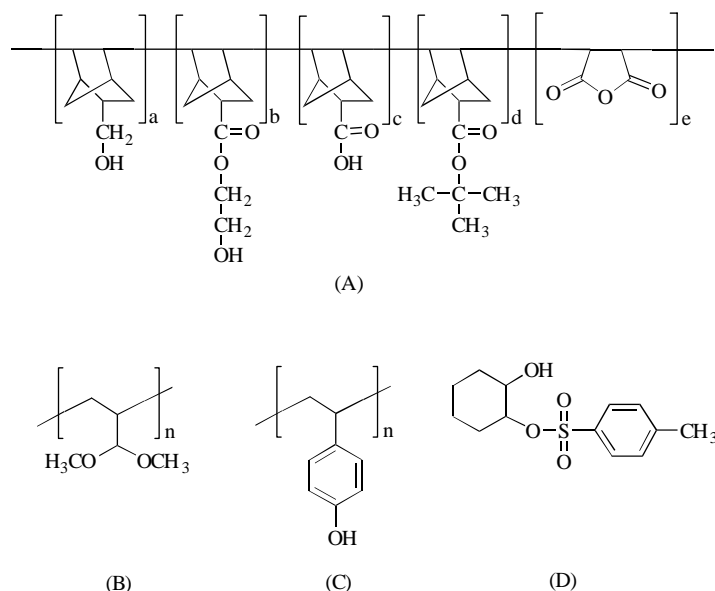


Fig. 1. Using materials in this study: (A) Poly(2-methanol-5-norbornene/2-(2-hydroxyethyl)carboxylate-5-norbornene/2-*t*-butylcarboxylate-5-norbornene/2-carboxylic acid-5-norbornene/maleic anhydride); (B) Poly(3,3'-dimethoxypropene); (C) Polyvinylphenol; and (D) 2-hydroxycyclohexyl *p*-toluenesulfonate.

2. Experimental

2.1. Materials

Acrolein, trifluoromethanesulfonic acid (TFMSA), azobisisobutyronitrile (AIBN), tetrahydrofuran (THF) and acetone were purchased from Fluka and Aldrich. The solvent, propylene glycol methyl ether acetate (PGMEA), was obtained from Aldrich. The polyvinylphenol (VP-8000) was obtained from Nippon Soda Co. The photoresist polymer used in this study was synthesized using the method of polymerization described in a previous paper [1]. Photo Acid Generator (PAG), triphenylsulfonium triflate was supplied by Korea Kumho Petrochemical Ind., Ltd.

2.2. Synthesis of polyacrolein and poly(3,3'-dimethoxypropene)

To synthesize polyacrolein, a 1000 ml three-necked round-bottom flask equipped with a reflux condenser and magnetic stirring bar was charged with 72 g of acrolein, 1.44 g of AIBN, and 108 g of THF under dry nitrogen atmosphere. After 5 h of reaction at 65°C, the white polyacrolein powder was precipitated in the solvent. The yield of polyacrolein is 75%. The obtained polyacrolein was washed with acetone for several times to remove the unreacted acrolein. To prepare the poly(3,3'-dimethoxypropene) (PDMP), 500 ml of round-bottom flask was charged with 20 g of polyacrolein, 200 g of methanol, and 0.5 g of trifluoromethanesulfonic acid (TFMSA). After refluxing for 10 h at 80°C, the solution was concentrated by removing the solvent using rotary evaporator. It was poured into 0.1 wt% tetramethyl ammonium hydroxide (TMAH) aqueous solution to precipitate the product with a yield of

60% and washed with distilled water for several times. The obtained product was dried in vacuum oven at 25°C for 3 days.

2.3. Preparation of BARC coated silicon wafer

To prepare BARC solution, PDMP (0.57 g) and polyvinylphenol (1.0 g) were dissolved in propylene glycol methyl ether acetate (40 g) and then stirred homogeneously. The thermal acid generator (0.1 g) was added in this solution. Finally, the mixed solution was filtered with a Gelman 0.2 μm filter. To prepare BARC coated wafer, BARC solution was coated on a silicon wafer with spin coating of 2300 rpm. For crosslinking BARC coated wafer was baked at 205°C for 90 s. The thickness of BARC of BARC coated wafer after crosslinking was 82 nm.

2.4. Preparation of resist solution

Poly(2-methanol-5-norbornene/2-(2-hydroxyethyl)carboxylate-5-norbornene/2-*t*-butylcarboxylate-5-norbornene/2-carboxylic acid-5-norbornene/maleic anhydride) (10 g) as resist polymer and 0.12 g of triphenylsulfonium triflate as photoacid generator were dissolved in 80 g of propylene glycol methyl ether acetate. This photoresist solution was used after filtering by using a 0.20 μm disk filter.

Fig. 1 shows materials used in this paper.

2.5. Characterization and measurements

The synthesized PDMP was characterized by Bruker, DPX 300 MHz ¹H-NMR spectrometer. FT-IR and UV spectrum were recorded on a Nicolet, Magna-550 series FT-IR spectrometer and on a Jasco 200 Vacuum-UV spectrometer. Thermal analysis was carried out on a Perkin-Elmer,

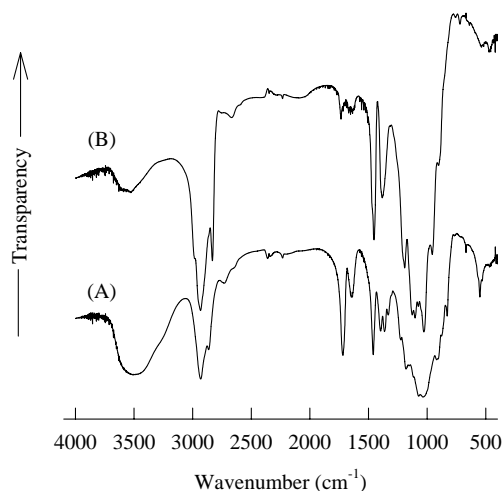


Fig. 2. FT-IR spectrum of: (A) polyacrolein; and (B) Poly(3,3'-dimethoxypropene).

DSC-7 at a heating rate of 20°C/min under nitrogen. Molecular weight and molecular weight distribution of polymer were determined in THF at 35°C using TOSOH, HLC-8020 gel permeation chromatography apparatus. Imaging experiments were done by an ISI ArF ($\lambda = 193$ nm) exposure tool (0.6 NA). The obtained SEM photographs were observed using a Jeol, JSM-6400 scanning electron microscope.

3. Results and discussion

3.1. Synthesis of poly(3,3'-dimethoxypropene)

The synthesized PDMP that was designed by us was a white color powder with good film-forming property and very soluble in organic solvents. The glass transition temperature and melting temperature of PDMP are 136.7 and 183.8°C, respectively. The molecular weight of

synthesized PDMP were $M_n = 4225$, $M_w = 6887$, and polydispersity = 1.63, respectively. These inherent properties of PDMP imply that it can be used as a BARC material in the semiconductor industries. The chemical structures of polyacrolein and PDMP were confirmed by $^1\text{H-NMR}$ as below. $^1\text{H-NMR}$ (CDCl_3) (ppm): 3.3–3.6 (m, hydrogens in two methoxy groups, 6H); 0.8–2.0 (m, hydrogens in main chain, 3H); 4.2–5.8 (s, $\text{CH-CH}(\text{OCH}_3)_2$, 1H). Fig. 2 shows FT-IR spectrum of polyacrolein and PDMP. In order to obtain the FT-IR spectrum, we prepared the KBr window that was prepared by KBr powder and synthesized the polymer powder and measured it. As shown in Fig. 2, the characteristic peak of carbonyl ($-\text{CH}=\text{O}$) group in polyacrolein at 1718 cm^{-1} disappeared in PDMP. This implies that the polyacrolein converted to PDMP successfully. Through the structural characterization of FT-IR and NMR, we ascertained that the synthesized compound is poly(3,3'-dimethoxypropene).

3.2. Deep-UV absorbency measurements

In order to measure the UV absorbency at 193 nm wavelength, the BARC solution was spin-coated on the quartz wafer with a thickness of 850 Å, followed by baking at 205°C for 2 min. The thermal hardening process of BARC results in the crosslinking by transacetalization between the methoxy groups of PDMP and hydroxy groups of polyvinylphenol by forming the new acetal unit. The UV spectrum of cured BARC material is shown in Fig. 3. At the 193 nm radiation, the UV absorption peak of BARC shows the maximum value as 0.8. This peak was induced by the aromatic benzene ring in polyvinylphenol. Absorption at 193 nm radiation of BARC protects the standing wave which was induced by the interference and reflective notching phenomenon during the ArF lithographic processing. These results indicated that the BARC containing acetal

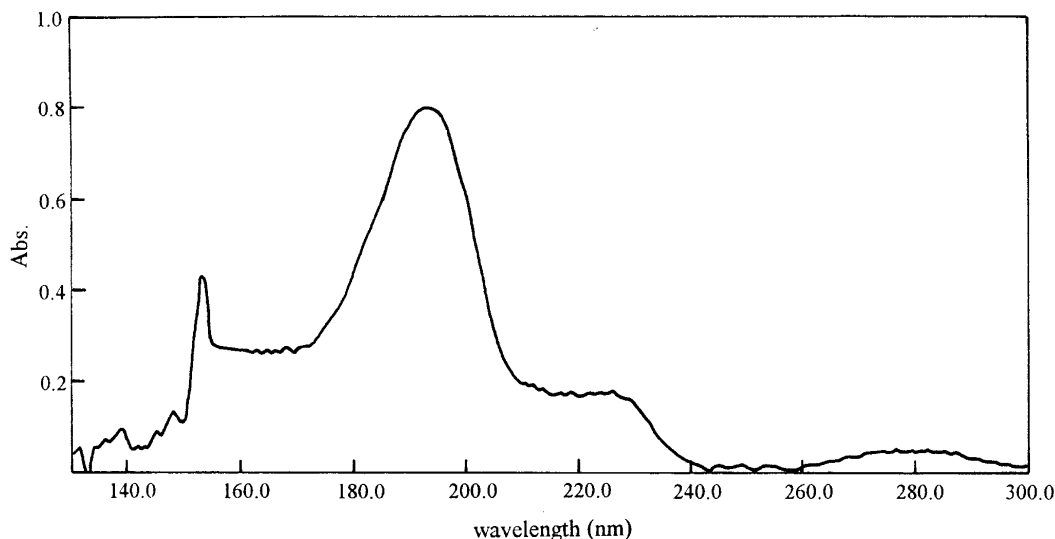


Fig. 3. UV spectrum of cured BARC.

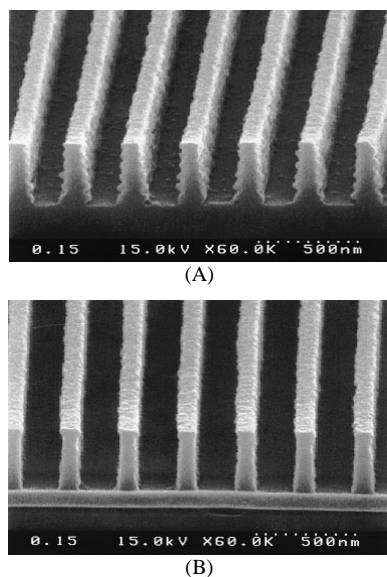


Fig. 4. Cross-sectional SEM micrographs of line and space grating pattern: (A) To obtain without BARC at the exposure energy of 12 mJ/cm^2 ; and (B) To obtain with BARC at the exposure energy of 14 mJ/cm^2 .

type polymer acts as a good eliminator of the standing wave effect on the wall of the photoresist pattern.

3.3. Lithographic performance

The BARC performance of the lithographic process was investigated by the following procedures. A resist film was prepared by spin-coating of photoresist solution on a BARC treated silicon wafer substrate followed by soft baking at 110°C for 90 s. Exposure was carried out on an ArF exposure tool and the film was baked again at 110°C for 90 s. After baking, the wafer was developed in 2.38 wt% tetramethyl ammonium hydroxide (TMAH) aqueous solution for 40 s [1].

The thickness of the crosslinked BARC after immersing in PGMEA solvent for 90 s was not changed. This result indicated that the BARC was crosslinked perfectly at 205°C .

Fig. 4 shows the cross-sectional SEM morphologies of $0.15 \mu\text{m}$ L/S photoresist patterns at the steps without and with organic BARC, respectively. As shown in Fig. 4(A), L/S pattern shape is very irregular on the wall surface. But, using the BARC reduces irregularity of surface on wall, drastically. The lithographic performance clearly shows that the pattern resolution in ArF lithography can be enhanced efficiently by employing a new organic BARC.

In summary, we have proposed a new class of BARC material containing polyvinylphenol as a UV-absorber, poly(3,3'-dimethoxypropene) as a crosslinker, and 2-hydroxycyclohexyl *p*-toluenesulfonate as a thermal acid generator. The PDMP was synthesized from acrolein by a two-step sequence reaction with a yield of 60%. The lithographic performance of photoresist with BARC that was proposed by us was evaluated and compared with those of photoresist without BARC. We ascertained that this organic BARC absorbs successively at 193 nm wavelength and it has an improved photoresist pattern performance.

References

- [1] Jung JC, Bok CK, Baik KH. *J Photopolym Sci Technol* 1997;10:529.
- [2] Hwang SH, Jung JC. *Polym Int* 1999;10:529.
- [3] Okoroanyanwu U, Byers J, Shimokawa T, Willson CG. *Chem Mater* 1998;10:3328.
- [4] Okoroanyanwu U, Shimokawa T, Byers J, Willson CG. *Chem Mater* 1998;10:3319.
- [5] Ogawa T, Uematsu M, Onodera T, Nakazawa K, Takahashi M, Ohfuji T, Ohtsuka H, Sasago M. *Jpn J Appl Phys* 1997;36:7482.
- [6] Ogawa T, Nakano H, Gocho T, Tsumori T. *Proc SPIE* 1994;2197:722.
- [7] Ogawa T, Sekiguchi A, Yoshizawa N. *Jpn J Appl Phys* 1996;35:6360.
- [8] Schiltz A, Terpan JF, Amblard G, Paniez PJ. *Microelectronic Engng* 1997;35:221.
- [9] Jun BH, Han SS, Lee JS, Kim YB, Kang HY, Koh YB, Jiang ZT, Bae BS, No K. *Semicond Sci Technol* 1997;12:921.
- [10] Sohn JM, Kim BG, Choi SW, Kim JM, Cha BC, Yoon HS. *Jpn J Appl Phys* 1998;37:6669.
- [11] Yan P, Qian Q, Langston J. *Proc SPIE* 1993;1972:167.
- [12] Yen A, Smith HI, Schattenburg ML, Taylor GN. *J Electrochem Soc* 1992;139:616.
- [13] Kunz RR, Allen RD. *Proc SPIE* 1994;2195:447.