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Communications to the Editor

Synthesis of Poly[*N*-(1-adamantyl)vinylsulfonamide-*co*-2-(2-methyl)adamantyl methacrylate] for 193 nm Lithography

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Chemically amplified resists (CAR) based on poly(hydroxystyrene) are widely used for KrF (248 nm) lithography in the semiconductor industry because of the high sensitivity and chemical etch resistance properties they possess and needed for device fabrication.[1] The CAR technology continues to be one of the most promising candidates for the next generation lithography below sub-100 nm features with good fidelity and process margins. ArF (193 nm) resists such as poly(acrylate)s,[2] poly(cycloolefin-*co*-maleic anhydride)s (COMA),[3] and poly(vinyl ether-*co*-maleic anhydride)s (VEMA)[4] begin to replace KrF resists in 2004, producing imaging feature sizes of 90 nm. Control of the critical dimension (CD) during photolithographic process is becoming more and more serious as the CD size decreases and wafer size increases. However, ArF resists based on acrylate and methacrylate copolymers are apt to swell during the development process with an aqueous base developer, giving image distortion.[5] On the other hand, COMA and VEMA are so hydrophobic that they display poor adhesion and poor aqueous base solubility.[6]

The ArF resists have been exclusively based on carboxylic acid derivatives, which provide extremely fast dissolution rates in aqueous base solution. Thus, it is important to develop a novel ArF resist based on another functional groups in place of carboxylic acid derivatives.

Sulfonamides are well-known alkaline soluble groups;[7] thus, several reports have been published for deep UV lithography (248 nm) using styrylmethylsulfonamides as a component.[8] We reported that an attempt to incorporate a novel base-solubilizing sulfonamide functionality and a bialicyclic structure into a polymer backbone through anionic ring-opening polymerization of camphorsultam failed.[9]

In this paper, we report that poly(vinyl sulfonamide) [poly(VnSA)] derivatives are very transparent in the 193 nm region and show good aqueous base solubility and good adhesion. Brief lithographic properties of a novel resist system based on poly{*N*-(1-adamantyl vinylsulfonamide)-*co*-[2-(2-methyl)adamantyl methacrylate]} [poly(VnSAAd-*co*-MAdMA)] and a photoacid generator (PAG), triphenylsulfonium perfluoro-1-butanesulfonate (TPS-Nf), as an attractive single layer ArF photoresist are also reported.

Synthesis and Characterization of VnSAs. To investigate the transparency of VnSA derivatives at 193 nm wavelength, *N*-propyl (VnSAPr), *N*-(1-adamantyl) (VnSAAd), and *N*-(2,2,2-trifluoroethyl) (VnSATf) VnSAs were prepared by the reaction of 2-chloroethanesulfonyl chloride with the corresponding amines in the presence of triethylamine as an acid acceptor.[10] The structures of these VnSA were identified by infrared (IR), ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis.

The IR spectra of these compounds exhibited characteristic sulfonamide and sulfonyl absorptions at 3282 cm^{-1} (−NH) and 1365 cm^{-1} (−SO$_2$−), respectively. The ^{1}H NMR spectrum of VnSAAd in CDCl$_3$ consisted of two doublet and doublet−doublet for vinyl protons ($\delta = 5.82$, 6.23, and 6.61 ppm), a singlet at 4.59 ppm for a sulfonamide proton, and three signals at 2.09, 1.93, and 1.64 ppm for adamantyl protons (see Supporting Infor-

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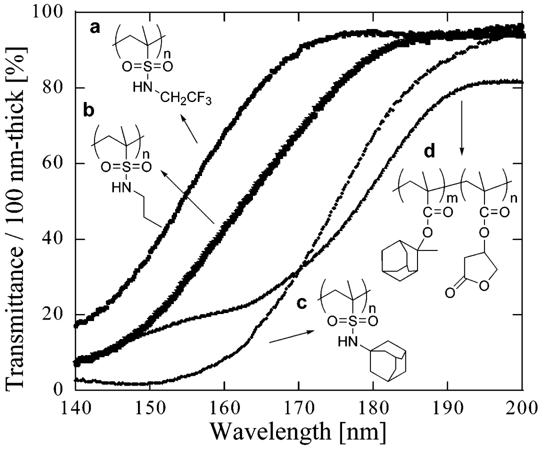

Figure 1. Transmittance of (a) poly(VnSATf), (b) poly(VnSAPr), (c) poly(VnSAAd), and (d) poly(MAdMA$_{50}$-*co*-*g*-LacMA$_{50}$). All polymers contain 3 wt % of PAG (TPS-Nf).

mation). Further spectral evidence for the structure of VnSAAd was provided by 75 MHz ^{13}C NMR spectroscopy with the assignment of each peak (see Supporting Information). Elemental analysis of VnSAAd also supported the proposed structure. The acid dissociation constant (pK_a) of VnSA was determined by the acid−base titration method to be 10.2, which is comparable with that of phenols.[11]

Polymerization and Characterization of VnSAs. Free radical polymerizations of VnSAs were conducted using AIBN as an initiator, giving white powders after the precipitation in methanol. These films were prepared by spin-casting cyclohexanone solutions on silicon wafers. Transmittance of the resulting poly(VnSA)s was measured with a VUV spectrophotometer (Figure 1), and it was found that these films are more transparent than the conventional ArF-resist material [poly(MAdMA$_{50}$-*co*-LacMA$_{50}$); LacMA: 4-(4-methyl)-δ-valerolactonyl methacrylate] at a 193 nm region. The optical densities (OD) of VnSAPr, VnSAAd, and VnSATf are 0.26, 0.41, and 0.22 μm^{-1}, respectively. The dissolution rates of these polymers to a 2.38 wt % tetramethylammonium hydroxide (TMAHaq) solution are 15, 0.035, and 300 nm s^{-1}, respectively, depending on the N-substituents. The dissolution rate of conventional ArF resists based on carboxylic acid derivatives is almost zero to 2.38 wt % TMAHaq solution, which induces swelling during development. On the other hand, the dissolution rate of poly(VnSAAd) is 0.035 nm s^{-1}, which means the swelling will be suppressed. Noteworthy is that poly(VnSA) films show good adhesion to silicon wafers because of polar sulfonamide units.

On the basis of these findings, copolymers from VnSAAd and MAdMA were decided as the first generation matrix for ArF resists.

Copolymerization and Characterization of VnSAAd with MAdMA. Free radical copolymerization of VnSAAd and MAdMA in an equimolar ratio was carried out in tetrahydrofuran (THF) using AIBN at 60 °C for 48 h (Scheme 1, Table 1). The copolymers were obtained as a white powders from 17 to 41% yield with the number-average molecular weights (M_n)s in the range of 2000−6600. Molar ratios of VnSAAd and MAdMA in the copolymers were determined by a sulfur analysis. The higher molar ratio of VnSAAd in the copolymer is required to decrease the solubility to 2.38 wt % TMAHaq solution and has the advantage of adhesion and solubility to a casting solvent, cyclohexanone. When the monomer feed ratio of VnSAAd and MAdMA was 2:1, the copolymer composition ratio of VnSAAd and MAdMA was 40:60 in mol %. On the other hand, the copolymer composition of VnSAAd (62 mol %) and MAdMA (38 mol %) was obtained when the monomer feed ratio of VnSAAd and MAdMA was 3:1.

Scheme 1

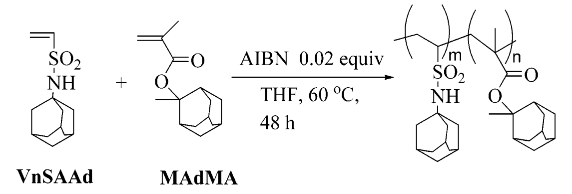

Table 1. Polymerization of VnSAAd[a]

R	conc [mol/L]	temp[°C]	M_n[c]	M_w[c]	yield [%]
CH$_2$CF$_3$	10[b]	60	9500	13000	20
Pr	bulk	60	17000	29000	18
1-Ad	bulk	95	2500	4800	45

[a] For 48 h. [b] In ethanol. [c] Detected by GPC (PSt standards DMF).

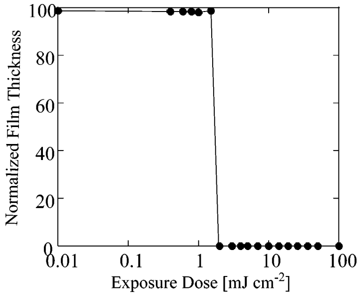

Figure 2. Film thickness change of poly(VnSAAd$_{40}$-*co*-MAdMA$_{60}$).

Copolymers were identified as the expected poly(VnSAAd-*co*-MAdMA)s by IR and ^{1}H NMR spectroscopy and elemental analysis. The IR spectrum of the poly(VnSAAd-*co*- MAdMA) exhibited a characteristic N−H bond stretching at 3263 cm^{-1} and a sulfo stretching at 1311 cm^{-1}. In the ^{1}H NMR spectrum, the vinyl protons of VnSAAd and MAdMA around 6.5 ppm completely disappeared.

Transparent films were prepared by spin-casting a cyclohexanone solution of poly(VnSAAd-*co*-MAdMA)s on a silicon wafer. The transmittance of the resulting poly(VnSAAd-*co*-MAdMA) film was measured with a VUV spectrophotometer, and it was found that poly(VnSAAd-*co*-MAdMA) film was transparent at 193 nm region.

Lithographic Evaluation. A preliminary formulation of a resist material was performed by dissolving poly(VnSAAd-*co*-MAdMA) and 3 wt % TPS-Nf as a PAG in cyclohexanone. Lithographic characteristics were studied using an ArF laser exposure system. When poly(VnSAAd$_{20}$-*co*-MAdMA$_{80}$) was used as a resist matrix, the maximum dissolution rate reached more than 3500 nm s^{-1} in 2.38 wt % TMAHaq solution after the exposure. Increasing the composition ratio of VnSAAd from 20 to 80 in the copolymer, the solubility decreased. The appropriate dissolution rate of 200 nm s^{-1} was obtained when the poly(VnSAAd$_{40}$-*co*-MAdMA$_{60}$) was used. Figure 2 depicts the sensitivity curve of the resist, in which the sensitivity and contrast are 2 mJ cm^{-2} and 8, respectively, when a 220 nm thick resist film prebaked at 100 °C for 60 s was exposed to 193 nm excimer laser, postbaked at 120 °C for 60 s, and followed by developing with 2.38 wt % TMAHaq solution.

Table 2. Copolymerization of VnSAAd with MadMA[a]

run	feed ratio[b]	M_n[c]	M_w[c]	copolymer composition (VnSAAd:MAdMA)	yield [%]
1	1	6600	20000	28:72	41
2	2	3800	9500	40:60	35
3	3	2700	5800	62:38	32
4	10	2000	3200	80:20	17

[a] In THF at 60 °C for 48 h. [b] Momomer feed ratio of VnSAAd to MAdMA. [c] Detected by GPC (PSt standards, chloroform).

In conclusion, poly(VnSA)s are good candidates for the matrix of the ArF resists because of their high transparency at the 193 nm region, appropriate aqueous base solubility, and good adhesion to a silicon wafer. Novel copolymers from VnSAAd and MAdMA were prepared by free radical copolymerization, in which the VnSAAd unit was responsible for the minimum dissolution, transparency, and adhesion. The resist system based on the poly(VnSAAd-*co*-MAdMA) (optical density 0.25/μm) and 3 wt % TPS-Nf showed a high transparency and excellent sensitivity as the ArF resist. Poly(VnSA) derivatives open up a new design of ArF resists and will provide an excellent resists with better properties than the conventional ArF resists based on carboxylic acid derivatives.

Supporting Information Available: Synthesis and polymerization of vinyl sulfonamide derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) 4 g of VnSA was dissolved in 50 mL of 0.1 mol/L NaOH solution. After predetermined amounts of 0.05 mol/L HCl solution were added and pH was stabilized, the change in pH was monitored by HANNA HI8424 microcomputer pH meter. The pH change was recorded, and the pK_a was determined at an inflection point of a titration curve. The temperature was controlled by a thermostat circulator to be 30 °C within the limit of 1 °C.

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