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Novel Organosilicate Polymer Resists for High Resolution E-Beam Lithography

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Over the past 10 years tremendous research efforts have been devoted to developing next generation lithography (NGL) such as e-beam lithography (EBL), extreme ultraviolet lithography (EUVL), and nanoimprint lithography (NIL) to achieve higher resolutions beyond the limits of photolithography.[1] Among the NGLs, EBL is used to direct-write sub-20-nm patterns to study new phenomena in nanostructures and to fabricate test devices for potential volume manufacturing with multiple beams. In addition, EBL is utilized to fabricate the imprint molds used for NIL as well as the photomasks for deep UV photolithography, due to its extremely high resolution and versatility, despite the low throughput.[2] New resist materials are essential to EBL and EUVL for high volume manufacturing since they determine not only the critical device dimension but also the throughput of the fabrication process. Up to now there are few reports on satisfactorily patterning sub-20-nm features using conventional resist polymers due to the pattern collapse and poor line-edge roughness (LER), attributed to their low glass transition temperature (T_g) and relatively large chain dimensions which cause entanglement effects.[3] Therefore, new resist materials have been investigated such as organic molecular glasses, calixarene derivatives, organometallic precursors, and hydrogen silsesquioxane (HSQ).[4−9] Among them, HSQ has been considered to be most prominent as (negative) e-beam resist for high resolution patterning because it has a high T_g and small molecular size leading to good LER, shows a high etching resistance, and is capable of forming very thin, defect-free, uniform films. Although sub-20-nm features with excellent LER have been obtained with HSQ e-beam resist,[10−12] there are still serious problems to be addressed for practical applications. The major drawback of HSQ is a rather low sensitivity which exacerbates the low throughput problem of EBL, as compared with chemically amplified resists.[11−13] Another drawback is the lack of long-term chemical stability, caused by the susceptibility of the Si−H bond to chemical reactions such as hydrolysis and subsequent secondary condensation.[14]

In this paper, we present new organosilicate polymers for e-beam resist application, which exhibit significant improvements in the sensivity and stability over those of HSQ while maintaining its high resolution capability and good LER. Organosilicate polymers are usually synthesized by acid or base catalyzed sol−gel reaction of organically modified trialkoxysilane monomers.[15] The properties of the resulting materials can be tuned by modifying the chemical structure of the organic group attached to the silicon (see Scheme 1). Therefore, appropriate organic groups could be attached to the silicon backbone which will enhance the sensitivity as e-beam resist by increasing the radical population generated upon e-beam irradiation and the cross-linking efficiency of subsequent radical reactions.[16] We chose bicycloheptenyl (normally called norbornene) and chloromethylphenyl groups to improve the characteristics of HSQ for the following reasons. First, it is expected that incorporation of the norbornene group as comonomer will enhance the sensitivity of HSQ as a result of the well-known tendency

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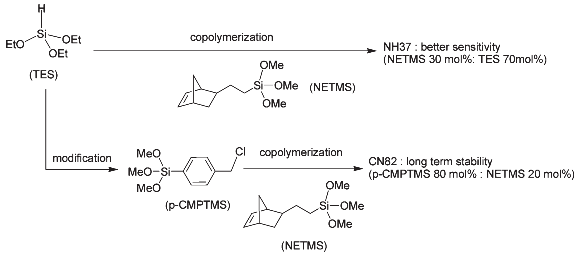
Scheme 1. Schemes for Synthesizing Organosilicate E-Beam Resists with Improved Sensitivity and Stability in Comparison to HSQ Resist



of its radical to undergo chain transfer reaction (see below).[17,18] Moreover, the relative stiffness of the norbornene-containing moiety is likely to minimize the loss of high resolution capability of HSQ, by suppressing a significant decrease in T_g. Second, the chloromethylphenyl moiety is quite stiff and known to be an efficient e-beam cross-linkable group.[19] The reaction schemes for synthesizing new organosilicate (negative) e-beam resists are shown in Scheme 1. Starting with triethoxysilane (TES) which is the precursor of HSQ, two new organosilicate polymer resists, denoted as NH37 and CN82, respectively, were synthesized step by step via preparation of monomers with designated organic functional groups bonded to silicon and subsequent copolymerization. To introduce norbornene groups, norbornene ethyltrimethoxysilane (NETMS) was used as a starting material. NH37 is synthesized by copolymerizing NETMS and TES in a 3:7 molar ratio. In the case of CN82, *p*-chloromethylphenyl trimethoxysilane (*p*-CMPTMS) was prepared to replace H in TES by a chloromethylphenyl group, followed by copolymerization with NETMS in an 8:2 molar ratio. Organosilicate copolymers with low molar masses were thus prepared (NH37: M_n = 1200, M_w = 1600; CN82: M_n = 1300, M_w = 1500), as described in the Supporting Information.

To evaluate the e-beam sensitivities of new organosilicate resists, lithographic results obtained with their thin films were compared to those obtained with the conventional HSQ (Dow Corning) as a reference. (Detailed e-beam lithographic processes are described in the Supporting Information.) Figure 1 displays the contrast curves obtained for new organosilicate resists, NH37 and CN82, in comparison with HSQ, upon exposure to 20 and 100 keV e-beam at varying doses. As shown in Figure 1, the critical dose (x-axis intercept D_0) of NH37, approximately 70 μC cm^{-2} (at 20 keV), is much lower than D_0 of HSQ, approximately 120 μC cm^{-2}. In addition, the magnitude of the slope (γ) in the initial linear region, which determines the contrast, is much higher for NH37 ($\gamma = 25$), as compared with the contrast of HSQ ($\gamma = 5.9$). In comparison, CN82 exhibits a higher sensitivity as seen by the lower D_0, as compared with HSQ, but its contrast is slightly lower ($\gamma = 4.7$) than HSQ. Contrast curves of the resists irradiated at 100 keV show similar trends to those at 20 keV, except that the contrast curves shift to higher doses as expected. Therefore, the experimental results clearly demonstrate that our new organosilicate resists exhibit significantly higher sensitivity than HSQ.

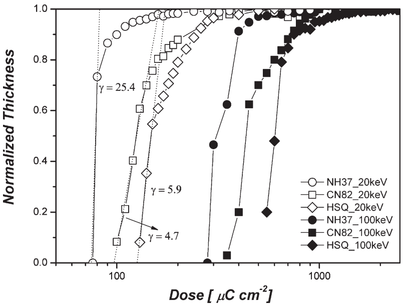


Figure 1. Contrast curves of HSQ and new organosilicate polymer resists upon exposure to e-beam of 20 and 100 keV, respectively, followed by development in TMAH 25 wt % solution.

The resolution limit of new organosilicate e-beam resists was quantified by examining the developed line-grating patterns written with varying e-beam doses of 100 keV (VB 300 from Vistec). Arrays containing line gratings with varying line widths from 5 to 100 nm were written on resist films of 30 nm thickness. Exposed samples were then developed in various developer solvents including aqueous basic solution, isopropanol (IPA), and acetone to investigate the effects of developers on pattern quality. (Detailed description of the development characteristics for each resist in various developers is presented in the Supporting Information.) NH37 produces high resolution patterns when developed in concentrated tetramethylammonium hydroxide (TMAH) solution in water (25% by weight), in a manner very similar to the characteristics of HSQ. In contrast, CN82 generates more reliable high-resolution patterns upon developing in organic solvents such as IPA and acetone. Scanning electron microscope (SEM) images of sub-20-nm line gratings of HSQ and new organosilicate resists are shown in Figure 2. NH37 generates reliable line-grating structures of 25 μm in length and sub-20 nm in width without any pattern collapse at one-half the dose required for generating similar features with HSQ. The smallest line width obtained with NH37 is approximately 15 nm, comparable to the results achieved with HSQ using TMAH developer solution. Therefore, NH37 exhibits a significantly improved e-beam sensitivity as compared with HSQ without sacrificing sub-20 nm high resolution with good LER as seen by cursory SEM investigation. CN82 also generates high resolution line-grating patterns 20 nm in width with apparently good LER in SEM micrographs at 75% of the e-beam dose for HSQ.

The long-term stability of NH37 is also improved over HSQ, but it is still not satisfactory, since deterioration of the pattern quality (resolution and LER) and the occurrence of unprocessable gel formation were still observed after several days in ambient solutions. This lack of long-term stability may be attributed to the remaining

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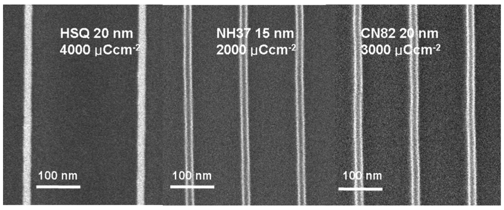

Figure 2. SEM images of high resolution line-grating patterns: high-resolution line width gratings achieved with HSQ and synthesized organosilicate resists; 20 nm line width for HSQ exposed at 4000 μC cm^{-2} (left-hand side) and 15 nm line width for NH37 at 2000 μC cm^{-2} (middle), and 20 nm line width for CN82 at 3000 μC cm^{-2} (right-hand side). The images were developed in 25 wt % TMAH solution for HSQ and NH37 and in acetone for CN82 after exposure to e-beam of 100 keV, as denoted in the figure.

HSQ moieties in NH37. In this regard, CN82 devoid of HSQ moiety indeed exhibits the long-term stability as CN82 maintains its pattern quality with no gel formation even after storing over 1 year as dried powder. (See the results on the resist stability in the Supporting Information.)

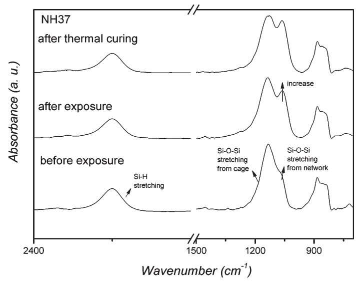

Figure 3. FT-IR spectra of NH37 films before and after e-beam irradiation at 450 μC cm^{-2} with 200 kV and upon curing for 15 min at 200 °C.

To understand the mechanism of enhanced sensitivity, we carried out Fourier transform infrared (FT-IR) measurments of the initial soluble films and the exposed insoluble films. It is well-known that organosilicate materials show two distinct IR absorption peaks attributed to the asymmetric stretching modes of Si$-$O$-$Si moieties.[20−22] The peak at approximately 1150 cm^{-1} is most prominent in highly symmetric molecular structures such as perfect cages or partially open cages. The other peak centered at approximately 1050 cm^{-1} is most prominent in low-symmetry structures such as branched and network-like structures.[22] On the basis of such FT-IR characteristics, it was reported previously that when HSQ resist was irradiated by e-beam and became highly cross-linked and insoluble, the absorption patterns of Si$-$O$-$Si stretch changed strongly such that the peak around 1050 cm^{-1} became more prominent than the cage-like peak of 1150 cm^{-1}, which was most prominent in the unexposed film.[23] Figure 3 shows the FT-IR spectra of NH37 film before and after relatively low e-beam exposure dose (450 μC cm^{-2} with 200 kV[24]). Also shown for comparison is a partially thermally cured film heated for 15 min at 200 °C with no e-beam exposure. There are noticeable changes in the relative intensities of two Si$-$O$-$Si absorption peaks, while there is practically no change in Si$-$H absorptions at 2250 cm^{-1} due to the e-beam irradiation and thermal curing at 200 °C. The relative change of the intensites of the two peaks is slightly larger for the thermally cured film as compared with e-beam exposed film, indicating the presence of a greater amount of branch/network Si$-$O$-$Si bonding in the thermally cured film. But the e-beam exposed NH37 film is insoluble in all the developers we tested while the thermally cured film is soluble in the same developers. This result shows that the main cause of enhanced sensitivity of NH37 (and CN82) as a negative e-beam resist is not the cross-linking reaction that changes the characteristics of Si$-$O$-$Si moieties as found in HSQ. Therefore, the enhanced sensitivity of NH37 and CN82 is most likely caused by the well-known radical reactions involving the norbornene groups. It is well-known that the carbon centered radical is generated when the double bond in norbornene group is irradiated, followed by radical rearrangement and polymerization reaction. But the radical polymerization of norbornene is easily terminated by a strong tendency of the chain transfer reaction producing a proton radical cation, which initiates another polymerization, so on. (See Scheme S1 in the Supporting Information.) Such chain transfer reactions involving norbornene moieties in resists will result in a high cross-linking efficiency of radicals generated by e-beam irradiation. Currently, this proposed mechanism is being investigated by FT-Raman experiments.

In summary, novel organosilicate polymers have been developed to overcome the major shortcomings of conventional HSQ as high resolution e-beam resist for potential volume manufacturing. Organosilicate copolymers containing norbornene and chloromethylphenyl moieties exhibit a significant improvement of the sensitivity and stability as compared with HSQ without sacrificing sub-20-nm high resolution with good LER. As a result, high resolution line gratings 15 nm in width are fabricated at half the exposure dose required for HSQ. It is expected that further investigations of reaction mechanisms and development characteristics will lead to better e-beam resists with much higher sensitivity and sub-10-nm resolution.

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Supporting Information Available: Description of experimental procedures, resist stability results, and the schematic drawing of chain transfer reaction involving norbornene moieties (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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