EB Resist Characteristics of Water Soluble Poly(siloxycethylene glycol)

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1. Introduction

Scaling down of minimum feature size on electronic devices have been progressed rapidly in semiconductor industry. To get a further integrated images, the development of a new high performance resist material toward light source having narrower wave length is required to next generation.[1-2] The new resist polymer have to show high sensitivity, high resolution and oxygen reactive ion etching (O₂ RIE) resistance. In addition, the polymer have to be safety for human and the earth.

Recently, we have synthesized a poly(divinylsiloxycethylene glycol) (PVSE300) (Scheme 1) by polycondensation reaction between poly(ethylene glycol) (molecular weight = 300) (PEG300) and bis(diethylamino)divinylsilane (DAVS).[3] Since the PVSE300 carries reactive vinyl groups on the Si atom in each repeating unit, the polymer was anticipated as a negative working resist toward UV and EB exposure. Actually, the PVSE300 film showed high sensitivity toward UV and EB exposure. For example, in the case of UV irradiation, the PVSE300 film coupled with cross-linking agent and sensitizer was irradiated by UV light generated from high pressure mercury lamp. A Dg50, which is exposure dose remaining 50% of initial thickness of polymer film after the development,[4-5] was estimated as 35 mJ/cm² from sensitivity characteristic curve. In the case of EB exposure, the Dg50 was estimated as 1 μC/cm² in the similar way.[6-7] Furthermore, the PVSE300 film showed high durability against oxygen plasma be-

![Scheme 1](image_url)

Poly(divinylsiloxycethylene glycol); PVSE
m = 7; PVSE300
m = 13; PVSE600

Poly(dimethylsiloxycethylene glycol), PSEG

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cause it was Si-containing polymer.[7] Alternatingly, PVSE300 showed unique behavior in aqueous media.[6-7] Since PVSE300 has alternating hydrophilic oligo(oxyethylene) unit and hydrophobic siloxane unit in the main chain, it is soluble in aqueous solution which shows a lower critical solution temperature (LCST).[8] The LCST of the PVSE300 phosphate buffer solution was 10.5°C.[3] Therefore, sensitivity characteristic curve and negative tone image toward UV and EB can be obtained by using 4°C water as a developer after exposure of light source.

For these reasons, the PVSE300 is expected for a new water soluble Si-containing photo and EB resist since it is interesting and important to employ water as a developer for microlithographic processing in the future.

In the case of PVSE300, however, the development must be carried out below 10.5°C due to the low LCST of PVSE300. For industrial point of view, it is much convenient if the water development can be done at ambient temperature. As we reported previously, the LCST of poly(siloxyethylene glycol) homologues can be controlled by their composition.[8] If this tendency can be applied to PVSE, the LCST must be varied by its composition.

This paper describes the synthesis of PVSE polymer having the structure of stronger hydrophilicity than PVSE300 and its characteristics as a negative EB resist (Scheme 1).

2. Experimental

2.1. Materials

Poly(ethylene glycol) (PEG600) (molecular weight 600) was dried at 110°C for 2 days in vacuo. Diethylamine (Wako) and divinylchlorosilane (Shin-etsu Chemical Co., Ltd.) were used as received. Bis(diethylamino)divinylsilane (DAVS) was synthesized by the reaction between diethylamine and divinylchlorosilane in the same manner as reported in previous paper.[3] The obtained DAVS was purified by fractional distillation under the reduced pressure (63.5 - 64.5°C / 2mmHg). Other materials were used as received.

2.2. Polymer Synthesis

PVSE600 (600 denotes molecular weight of PEG) was synthesized by polycondensation reaction between PEG600 and DAVS. In a 100-mL round-bottomed flask equipped with a mechanical stirrer, 9.0g of PEG600 and 3.39g of DAVS were added and the mixture was allowed to react for 48h at 80°C. After the reaction, the liberated diethylamine was removed by evaporation at 80°C for 2 days in vacuo. The obtained polymer was analyzed by GPC and 1H-NMR.

2.3. Temperature Dependency of Aqueous solution

After the obtained PVSE600 sample was dissolved in phosphate buffer (1.5 wt.% pH = 7.0 I = 0.05) at room temperature, the change in transmittance of the PVSE600 aqueous solution was measured by the same manner as described in our previous paper.[8] The LCST was defined as the temperature at which the solution started to decrease its transmittance.

2.4. Resist processing

On a Si wafer surface, THF solution of the PVSE600 (10 wt.%) was spin-coated by 3000 r.p.m for 30 second. The thickness of the PVSE600 film thus obtained was about 1.9 µm, and EB was generated using a JEOL JSM-5200 scanning electron microscope (SEM) equipped with a Tokyo Technology L&S Pattern Generator LSPG 1-1S (probe currents: 100 pA, accelerating voltage: 20 kV). A dose that ranged from 0.4 - 70 µC/cm² was employed. The PVSE600 film on the Si wafer was developed by soaking in water (room temperature) for 60 second after EB exposure. The remaining film thickness was measured with a Tencor ALPHA STEP 500. The sensitivity and resolution parameter were calculated from the sensitivity characteristic curve as D₅₀ and γ value. The γ value was calculated from the following equation.

\[ \gamma = \left[ \frac{2\log(D_{\text{g}50}/D_{\text{g}})}{D_{\text{g}50}} \right]^{-1} \]

where D₅₀ represents the minimum dose in which the crosslinking reaction is proceeded by EB.[4-5]

2.5. Observation of Negative Tone Image

For evaluation of negative tone line & space image, the film of PVSE600 was exposed by EB dose of 10 µC/cm². The exposed film was developed in water at room temperature for 2 minutes. The obtained image was observed using a Hitachi, Ltd; 5-4200 type scanning electron microscope (SEM; 1 kV).

3. Results and Discussion

3.1. Synthesis and Characteristics of PVSE600

The PVSE600 was synthesized by polycondensation reaction between PEG600 and DAVS. The reaction was proceeded smoothly and was not observed a side reaction such as gel formation though DAVS has two vinyl groups. The GPC profile of product obtained by polycondensation was shown...

Fig. 1. GPC curve of PVSE600 through polycondensation reaction between poly(ethyleneglycol) and bis(diethylamino)divinylsilane

in Figure 1. The number average of molecular weight (Mn) and molecular weight distribution (MWD) (Mw/Mn) of product was 7700 and 1.59, respectively. It is generally known that condensation of diol with dichlorosilane compounds provides fairly large amount of cyclic compounds. [9] When bis(diethylamino)silane derivatives was used instead of dichlorosilanes, such the cyclic reaction suppressed very much. [8] Actually, almost no oligomeric cycles were observed in the GPC profile. This may be one of the reason for a rather arrow MWD of the obtained PVSE600. In the 'H-NMR spectrum of the obtained polymer, which was purified by fractionation by GPC, both signals originated with oxymethylene and vinylsilyl protons appears at 3.6 and 6.0 ppm, respectively. The integral ratio of -CH2CH2O-/CH=CH2 was 49/6, which agreed well with the polycondensation repeating unit of PVSE600 as shown in Scheme 1. On the basis of these results, PVSE600 having alternating oligo(oxyethylene) unit and siloxane unit in the main chain was synthesized by polycondensation reaction without side reaction such as production of gel and cyclic oligomers.

3.2. LCST of PVSE600

Polymers which possess suitable hydrophilic/hydrophobic balance are soluble in aqueous media and show a LCST. [10] Negative dissolution entropy governed their characteristics. As mentioned above, PVSE300 shows its LCST at 10.5°C. PVSE600, which possesses longer hydrophilic PEG segments than that of PVSE300, is anticipated to show much higher LCST than one in PVSE300 in aqueous solution. Actually, PVSE600 solution in phosphate buffer (1.5 wt.% pH = 7.0 I = 0.05), the solution became turbid at ca. 50°C. Thus, PVSE600 can be developed by neutral water at ambient temperature.

3.3. Sensitivity against EB Exposure

As reported previously, PVSE300 showed remarkable high sensitivity against EB exposure due to the high extent of vinylsilyl groups. [7] Since PVSE600 possesses also repeating divinylsilane moieties, it is anticipated a high sensitivity against EB exposure. To evaluate lithographic performance, a sensitivity characteristic of PVSE600 was investigated. The PVSE600 film (thickness = 1.9 µm) was prepared by spin-coating from 10 wt.% THF solution. After the film was exposed by EB in the range from 0.4 to 70 µC/cm2, the film was developed by neutral water at ambient temperature. Figure 2 shows the sensitivity characteristic curve of PVSE600 film against EB exposure. The Dg50 and γ value against EB exposure was determined from Figure 2 to be 1.0 µC/cm2 and 0.5, respectively. These lithographic parameters were as high as that of PVSE300 though the vinyl extent was lower than that of PVSE300. This indicates that the vinyl extent in PVSE600 is enough for high sensitive crosslinking reaction as EB resist.

3.4. Negative Tone Image of PVSE600

On the basis of the above results, PVSE600 can be utilized as a negative EB resist which is developed by water at ambient temperature. Figure 3 shows the line & space (L&S) pattern of the
PVSE600 film which is exposed by EB (10 µC/cm², 20 kV). As can be seen in the figure, a 1 µm line and 4 µm space pattern was formed by low exposure dose. It should be noted again that water of room temperature was employed as a developer to obtain this pattern.

4. Conclusion
The PVSE600 was synthesized by polycondensation reaction without side reaction. Since the PVSE600 has alternating hydrophilic oligo(oxyethylene) unit and hydrophobic siloxane unit, aqueous solution of the polymer showed a LCST. Since the PVSE600 has oxyethylene units larger than that of PVSE300 in the main chain, the LCST of the PVSE600 was higher (about 50°C) than one in PVSE300. In other words, the PVSE600 is soluble in water at ambient temperature. The PVSE600 film showed high sensitivity toward EB exposure. The Dg⁵₀ examined from sensitivity characteristic curve for EB was 1.0 µC/cm². The L&S pattern of 1µm width was obtained by exposing low EB dose and developing in water under the room temperature. On the basis of these results, PVSE polymer is anticipated as a new water soluble Si-containing EB resist in next generation.

References