146-nm Light Induced Crosslinking of Poly(vinylphenol) and Its Silylation

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146-nm Light induced photolysis of poly(vinylphenol) (PVP) thin film (50-60 nm) and vapor phase silylation of the irradiated PVP film were studied. On irradiation at 146 nm under nitrogen atmosphere, insolubilization of PVP film was observed and the efficiency increased with molecular weight of PVP. A crosslinking mechanism was proposed based on the FT-IR spectroscopy which showed the decrease of the peaks due to O-H (3360 cm⁻¹), C=C (1515 cm⁻¹) and C-O (1242 cm⁻¹) bonds on irradiation. Vapor phase silylation of PVP thin film was carried out using dimethylsilyldimethylamine (DMSDMA) as a silylating reagent. The silylation of PVP was inhibited on irradiation at 146 nm. The inhibition was enhanced when molecular weight of PVP increased.

Keywords: TSI process, poly(vinylphenol), photocrosslinking, silylation, 146-nm light

1. Introduction

To fabricate sub-100 nm or smaller pattern, vacuum ultraviolet (VUV) lithography using F₂ laser at 157 nm has been proposed. However, there is a serious issue on resist materials with regard to transparency at 157 nm and dry-etch durability. Most organic polymers which have been commonly used for i-line, 248- or 193-nm lithography show strong absorbance at 157 nm. Therefore the conventional resist systems using solution development could not be used for 157-nm lithography. Top surface imaging (TSI) process is an important technology for 157-nm lithography because, for the TSI process, photoreaction is required to occur at the film surface and transparency of the resist films to the irradiation light is not important. Thus, it is possible to use many types of polymeric materials as TSI resists. Although several types of TSI process have been reported [1-12], poly(vinylphenol) (PVP) and its derivatives are most commonly used as a resist base polymer. In the TSI process the OH groups of the irradiated or unirradiated areas of PVP film were silylated. Since the silylated areas show a high etch resistance to O₂ RIE, images can be obtained after dry etching.

Irradiation of polymers with vacuum ultraviolet light like 157-nm light sometimes induces undesirable photochemical reactions such as crosslinking and/or main-chain scission which are not significant on UV or deep UV irradiation. Photochemical reactions of well-known resists for ArF or KrF lithography have been studied using a Kr₂ excimer lamp (146 nm) [12,13]. Main-chain scission was observed for poly(methacrylates) based resists but crosslinking was observed for polystyrene based resists. In this paper we report the photocrosslinking of PVP using 146-nm light and the effect of crosslinking of PVP film on silylation.

2. Experimental

2.1. Materials

Poly(vinylphenol)s with molecular weights of 20000 and 8000 were obtained from Aldrich and used as received. Poly(vinylphenol)s with molecular weight of 4400 and 3100 were prepared by the living radical polymerization as follows:
p-t-butoxystyrene (3.0 g), benzoylperoxide (18.6 mg) and 2,2,6,6-tetramethyl-1-piperidinyloxy (13.2 mg) were placed in a glass tube and degassed with freeze-thaw cycles. The mixture was heated at 95 °C for 1 h and then at 125 °C for 1 h. The reaction mixture was poured into an excess of hexane to precipitate poly(p-t-butoxystyrene). The polymer was purified by reprecipitation. The purified polymer (0.5 g) was dissolved in dioxane (25 ml) and 0.7 ml of HBr (8.6 N) was added. The mixture was reacted at room temperature for 24 h. Small amounts of dioxane was added to the reaction mixture and the solution was poured into an excess of hexane to precipitate poly(vinylphenol). Characteristics of poly(vinylphenol)s used in this study are shown in Table 1.

Table 1. Properties of PVP.

<table>
<thead>
<tr>
<th>M_n</th>
<th>M_w/M_n</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20000</td>
<td>. c)</td>
<td>166</td>
</tr>
<tr>
<td>8000</td>
<td>1.1</td>
<td>169</td>
</tr>
<tr>
<td>4400</td>
<td>1.1</td>
<td>169</td>
</tr>
<tr>
<td>3100</td>
<td>1.1</td>
<td>152</td>
</tr>
</tbody>
</table>

a) From Aldrich. b) Synthesized. c) Not measured.

Dimethylsilyldimethylamine (DMSDMA) as a silylating reagent and propylene glycol methyl ether acetate (PGMEA) as a casting solvent were used as received.

2.2. Measurements

Sample films were prepared by spin-casting onto silicon wafer (1.0 X 4.5 cm) using a Mikasa Spincoater 1H-D7. PGMEA was used as a casting solvent. Sample films were baked at 90 °C for 1 min to remove the residual solvent. Film thickness was adjusted to be 50-60 nm which was measured by interferometry using Nanospec M3000. Thin films were necessary to pass the incident light at 146 nm.

Irradiation at 146 nm was carried at room temperature under N₂ (99.99%) flow using a Kr₂ excimer lamp (Ushio UER20H-146V). A sample holder was placed in a chamber equipped with a MgF₂ window for incident light. Distance between the sample and lamp was 3 cm. Light intensity was about 3 mW/cm².

FT-IR measurements were carried out by the reflection absorption infrared spectroscopy method at accumulation of 100 scans using a JASCO FT-IR 7300 spectrophotometer equipped with a PR-500 attachment. A polarizer (KRS-5) was used and the incident light angle to the sample film was 85 degree. Sample films (50-60 nm thick) were prepared on silicon wafer (1.0 X 4.5 cm) with Al-Cr mirror surface.

Insoluble fraction of the film on irradiation was calculated by measuring the thickness change before and after developments in tetrahydrofuran for 5 min.

Refractive index of the films was measured using a laboratory-constructed ellipsometer (light source: He-Ne laser at 632.8 nm).

Silylation of sample films was studied as follows: the film on Si wafer was placed in a test tube with a rubber septum. The tube was kept in a thermostatic bath at 45 °C. DMSDMA (0.1 ml) was introduced with a micro syringe into the bottom of the tube. The silylation was performed under atmospheric pressure. The degree of silylation of the film was calculated using the peak at 930 cm⁻¹ due to Si-O bonds. The peak at 840 cm⁻¹ due to PVP was used as a reference peak.

3. Results and Discussion

3.1. Photoreaction of PVP

Polystyrene has tertiary hydrogen atoms in the main chain and, on irradiation with UV light, these hydrogen atoms can be abstracted radically to generate main-chain radicals which induce the crosslinking [14]. On irradiation of PVP film at 146 nm an efficient crosslinking was observed as shown in Figure 1. The crosslinking ability of PVP judged from insoluble fraction increased with its molecular weight. Although PVP (Mn = 20000) showed a similar sensitivity to PVP (Mn = 8000), PVP (Mn = 4400) and PVP (Mn = 3100)
PVP (Mn = 4400) and PVP (Mn = 3100) showed lower sensitivity than PVP with higher molecular weights. It is well-known that insolubilization of polymers by crosslinking is strongly dependent on their molecular weight.

Thickness changes of PVP films on irradiation were studied by ellipsometry. The thickness of PVP film (52 nm) decreased 1% after irradiation for 30 sec. Furthermore, refractive index of the film increased from 1.565 to 1.590 after 30 sec irradiation. These findings suggest the release of small molecules from the PVP film by the photoreaction.

PVP film showed a strong absorption peak at 210 nm due to phenyl ring. This peak slightly decreased on irradiation at 146 nm, suggesting the destruction of resonance structure of phenyl ring or release of phenyl moiety from the polymer backbone. Photoinduced degradation of PVP with different molecular weight was studied by FT-IR spectroscopy. A representative spectral change is shown in Figure 2. Although the intensity change was not large because very thin films (50-60 nm thick) were used, peaks due to O-H (3360 cm\(^{-1}\)), C=C (1515 cm\(^{-1}\)) and C-O (1242 cm\(^{-1}\)) bonds decreased on irradiation. The decrease of these peaks is plotted against irradiation time (Figures 3a-c). In the case of decrease of C=C bonds, PVP (Mn = 20000) was slightly slower than PVP (Mn = 8000) and PVP (Mn = 3100). On the other hand, in the case of C-O bond decrease, PVP (Mn = 3100) was slightly slower than PVP (Mn = 8000) and PVP (Mn = 20000). Furthermore, in the case of O-H bond decrease, PVP (Mn = 8000)
was slightly slower than PVP (Mn = 3100) and PVP (Mn = 20000). The effect of molecular weight on the decrease of those peaks was complicated. Thus, it is difficult to fully discuss it. However, a distinct difference of the rate of decrease between O-H bonds and C=C and C-O bonds was observed. The initial rate for the OH group decrease was higher than that for C-O bonds. Although, after 60 sec irradiation, OH decrease was about 40%, C-O bond decrease was about 20%. The disagreement of both values suggests that the C-O bonds may regenerate after the photolysis of OH groups of PVP as shown in a proposed mechanism (Scheme 1). The initial photochemical reaction of PVP may be generation of OH, phenyl and phenoxy radicals. The radicals generated in the polymer chains can induce the crosslinking. The phenoxy radicals generated photochemically may couple with other radicals to form the C-O-C linkage. Furthermore, any radicals generated may abstract hydrogen atom from phenolic OH groups to generated phenoxy radicals in the polymer chain. α-Hydrogen atoms in the main chain of PVP can be abstracted by radical species to form main chain radicals.

3.2. Silylation

Effect of photocrosslinking on silylation was studied using DMDSDMA as a silylating reagent. Silylation was monitored using FT-IR spectroscopy. Silylated PVP film (50-60 nm thick) showed new peaks at 930 (Si-O) and 1280 cm⁻¹ (Si-CH₃) and OH peak at around 3360 cm⁻¹ disappeared (Figure 4). Degree of silylation was estimated using the characteristic peak at 930 cm⁻¹. Figure 5 shows the relationship between silylation degree and irradiation time. Very similar silylation curves were obtained irrespective of silylation time (15, 30, 60 and 600 sec). This means that the silylation can be accomplished within short time in the present experimental conditions. Silylation
degree started to remarkably decrease after irradiation for about 30 sec. This finding was roughly consistent with the photocrosslinking behavior of PVP shown in Figure 1. Thus, the photoinduced crosslinking of PVP film strongly suppressed its silylation reaction because of the inhibition of diffusion of DMSDMA molecules into the film.

Effect of thickness of PVP film on the silylation is shown in Figure 6. Almost the same silylation curves were obtained for PVP films (50 and 200 nm thick). Silylation degree for the unirradiated PVP films was 100%, suggesting that the diffusion of DMSDMA molecules occurred from surface to bottom of both films under the present experimental conditions. For the 200 nm thick film, photocrosslinking occurs only at the surface because the incident light cannot be reached to the bottom of the film. However, no silylation for 200 nm thick film occurred on irradiation as observed for the thin film (50 nm). Thus, it may be conclude that the crosslinked surface layer significantly inhibits the diffusion of DMSDMA molecules into thick film.

Figure 7 shows the effect of molecular weight of PVP on the silylation when irradiated. Silylation degree of PVP largely decreased after irradiation for 30-60 sec, depending on its molecular weight. The irradiation period needed to inhibit the silylation decreased with the molecular weight of PVP. This finding was consistent with the photocrosslinking efficiency of PVP with different molecular weight.

The TSI process based on the photocrosslinking of PVP might be a useful lithography using vacuum ultraviolet light.

4. Conclusion

Insolubilization of PVP occurred on irradiation at 146 nm. The crosslinking efficiency increased with molecular weight of PVP. It was suggested that the crosslinking was induced by coupling reactions of polymer radicals generated by the photolysis and subsequent thermal reactions. Although vapor phase silylation of PVP occurred easily, it was strongly inhibited by the photocrosslinking using 146-nm light. The crosslinked surface layer effectively prevented the diffusion of silylating reagent into films.

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References