Review Article

Development of an Environmentally Friendly Resist-Removal Process Using Wet Ozone

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We investigated the removal of polymers with various chemical structures and the removal of ion-implanted resists using wet ozone. The removal rates of polymers that have carbon-carbon (C–C) double bonds in the main chain were high. The main chain of these polymers may be decomposed. The removal rates of polymers that have C–C double bonds in the side chain were low. The benzene ring in the side chain changes into carboxylic acid, so their ability to dissolve in water increased. The polymers without C–C double bonds were not removed. Removal of B and P ion-implanted resists became difficult with increasing acceleration energy of ions at implantation. The resist with plastic-deformation hardness that was twice as hard as that of nonimplanted resist should be removed similarly to nonimplanted resist. Using TOF-SIMS, we clarified that the molecule of cresol novolak resin was destroyed and carbonized by ion implantation.

1. Introduction

Photosensitive resin (resist) is used in the semiconductor (IC, LSI) and liquid crystal display (LCD) manufacturing process. The pattern is transferred to the resist by three processes (spin coating, exposure and development). The substrate is etched by using resist as a mask, and ions are implanted. Finally, the unneeded resist is removed. Resist removal from substrates in a semiconductor manufacturing process conventionally uses oxygen plasma [1, 2] and/or chemicals (e.g., sulfuric acid hydrogen peroxide mixture, and ammonia hydrogen peroxide mixture). Environmentally unfriendly chemicals are used in large amounts and cause environmental damage [3, 4]. Also, oxygen plasma ashing may cause oxidation of substrates and metal wiring because this process requires high temperature (above 250°C) [5, 6]. Therefore, several resist removal methods have been developed (e.g., atomic hydrogen [7–10], UV/ozone [11, 12], and YAG laser [13–15]).

We examine the wet ozone process, which is an environmentally friendly, low-temperature process. In this process, ozone gas mixed with a small amount of water is irradiated to the resist at a temperature below 100°C, and the resist changes into hydrophilic carboxylic acid by the ozone and condensed water [16–18].

Figure 1 presents a schematic diagram of the experiment apparatus for wet ozone (Mitsubishi Electric-Corp. and SPC Electronics Corp.). Ozone gas mixed with a small amount of water vapor (wet ozone) is generated by bubbling ozone gas through hot water. Also, a small amount of water vapor condenses on the resist, due to the difference in temperature (ΔT = T₁ − T₂) between wet ozone (T₁) and Si wafer (T₂). The amount of water condensed on the resist was controlled by adjusting ΔT [19]. Figure 2 depicts the chemical reaction of the carbon-carbon double bond (C–C double bond) with ozone and the hydrolysis of ozonide. In resist removal using wet ozone, the C–C double bond in the benzene ring of the resist reacts with the ozone to generate ozonide [20, 21]. Ozonide is hydrolyzed by the water condensed on the resist, and carboxylic acid is generated. Finally, the carboxylic acid was washed down from the Si wafer by a pure-water rinse.

We removed base polymers that had different chemical structures and evaluated the chemical reactivity of wet ozone with the chemical structures of polymers. Also, we
investigated the relationship between ion-implanted resist removability and acceleration energy of ions at implantation. We examined the structure of ion-implanted resists by SEM observation and by stripping ion-implanted resists using chemicals. We clarified the characteristics ion-implanted resists by nanoindentation [22–24] and time-of-flight secondary ion mass spectrometry (TOF-SIMS).

## 2. Experimental

### 2.1. Removal of Polymers with Various Chemical Structures Using Wet Ozone.

The cycle consisted of 10 s at 2000 rpm for wet ozone irradiation, 5 s at 2000 rpm for pure-water washing, and 20 s at 1000 rpm for drying. The ozone gas concentration was 230 g/m³ (10.2 vol%), and the flow rate was 12.5 slm. The wet ozone temperature was $T_1 = 70\,^\circ\text{C}$, and the substrate temperature was $T_2 = 60\,^\circ\text{C}$. Polymer removal involved estimating novolak resin and cis-1,4-polyisoprene, which have C–C double bonds in the main chain; polyvinyl phenol (PVP) polystyrene (PS), which have C–C double bonds in the side chain; and polymethyl methacrylate (PMMA) and polyvinyl chloride (PVC), which have no C–C double bond. These polymers, which were dissolved in each solvent, were spin-coated onto an Si wafer using a spin coater (ACT-300A; Active) at 2000 rpm for 20 sec and prebaked at 100°C for 1 min on a hotplate (PMC 720 series; Dataplate). Table 1 lists polymers, solvents, and film thickness for this study. We also removed a positive-tone novolak photoresist (AZ6112; AZ-Electronic Materials) as a reference.

### 2.2. Removal of Ion-Implanted Resists Using Wet Ozone.

The wet ozone irradiation conditions were the same as those described in Section 2.1. In this study, the ion-implanted resist was a positive-tone novolak resist (AZ6112; AZ-Electronic Materials) with B and P ions implanted at a dose of $5 \times 10^{14}$ atoms/cm² at each acceleration energy (10 keV, 70 keV, and 150 keV).

We observed cross-sections of ion-implanted resists using scanning electron microscopy (SEM: JSR-6360; JEOL Ltd.). SEM images were secondary electron images with an acceleration voltage of 20 kV. Also, after dissolving the ion-implanted resist into ethylene carbonate (EC), we measured the thickness of the stripped resist film. We previously clarified the presence of a damaged layer at the surface of ion-implanted resists [25–28]. Ion-implanted resists were composed of two layers (the damaged layer and the normal layer). We calculated the percentages of the damaged layer among of the ion-implanted resist. The temperature of EC was 70°C.

We examined plastic-deformation hardness by varying the maximum load from 1 to 260 mgf by nanoindentation. The loading rate was 1/2000 for loads exceeding 8 mgf and 0.004 mgf/ms (lower limit) below 8 mgf. We used a Berkovich diamond indenter with an apex angle of 115°. Also, in order to evaluate the effect of ion implantation on resists, we normalized the plastic-deformation hardness of the ion-implanted resists with that of nonimplanted resists. We refer to this value as normalized plastic-deformation hardness $H_2$.

In order to evaluate the composition of ion-implanted resists, we cut resists at a slant using SAICAS (NN-04; DAIPLA WINTES) and conducted composition depth profile analysis using TOF-SIMS (TOF-SIMS 5; ION-TOF). The primary ion was Bi$_3^{2+}$, and the acceleration voltage was 25 kV. In order to clarify the degree of hardening, we used ion-implanted resists in which B ions were implanted at a dose of $5 \times 10^{15}$ atoms/cm² and some acceleration energies (10 keV, 70 keV, and 150 keV).

## 3. Results and Discussion

### 3.1. Removal of Polymers with Various Chemical Structures Using Wet Ozone.

Figure 3 plots the results of removing polymers using wet ozone. Table 2 presents removal rates of each polymer using wet ozone. The removal rates of polymers that have C–C double bonds in the main chain (novolak resin and cis-1,4-polyisoprene) were highest. The removal rates of polymers that have C–C double bonds in the side chain (PVP and PS) were lower compared to those of novolak resin and cis-1,4-polyisoprene. In novolak resin and cis-1,4-polyisoprene, the main chain may be decomposed by reaction of wet ozone. In PVP and PS, the benzene ring in the side chain changes into carboxylic acid by reaction with wet ozone. Thus, PVP and PS should be removed because their ability to dissolve in water increased. In contrast, the polymers that have no C–C double bond (PMMA and PVC) were not removed.

### 3.2. Removal of Ion-Implanted Resists Using Wet Ozone.

Figure 4 plots the removal of B and P ion-implanted resists using wet ozone. Removal of B and P ion-implanted resists...
became difficult with increasing acceleration energy of ions at implantation. Resist with B ions implanted at an acceleration energy of 150 keV could not be removed, nor could resist with P ions implanted at acceleration energies of 70 keV and 150 keV. Removal rate decreased with increasing acceleration energy. It was assumed that the reactivity of ozone and resists decreases with increasing acceleration energy. After the ion-implanted resist surfaces were removed, the resists were removed at the same rate as nonimplanted resists. The damaged layer formed at the surface of ion-implanted resists, and the lower layer was normal layer (nonimplanted resist). The estimated thicknesses of the damaged layer of B ion-implanted resists were 40 nm (10 keV) and 200 nm (70 keV) and that of P ion-implanted resist was 30 nm (10 keV).

3.3. SEM Images of Ion-Implanted Resist. Figure 5 presents SEM images of B and P ion-implanted resists with various acceleration energies. The ion-implanted resists are composed of two layers. The percentage of ion-implanted resist damaged layer increased with increasing acceleration energy. Table 3 lists the damaged layer thickness measured by resist removal using wet ozone, SEM images, and resist removal using chemicals. Table 4 lists the percentage of ion-implanted resist damaged layer determined by SEM and stripping of
ion-implanted resist using chemicals. The percentage of ion-implanted resist damaged layer increased with increasing acceleration energy.

3.4. Plastic-Deformation Hardness of Ion-Implanted Resist. Figure 6 plots depth profiles of normalized plastic-deformation hardness $H_2$ of B and P ion-implanted resists versus photoresist depth. Normalized plastic-deformation hardness $H_2$ was obtained by dividing the plastic-deformation hardness of ion-implanted resists by that of non-ion-implanted resists. The plastic-deformation hardness and the thickness of ion-implanted resists increased with increasing acceleration energy. Therefore, removability of the ion-implanted resist using wet ozone decreased with increasing acceleration energy because the hardness of resist increases with increasing acceleration energy as determined by nanoindentation measurement. Based on the results of the removal of ion-implanted resists using wet ozone and nanoindentation,
the resist with plastic-deformation hardness five times that of normal resist should not be removed. After the ion-implanted resist surfaces were removed, the resists were removed at the same rate as nonimplanted resist. The ion-implanted resists whose plastic-deformation hardness was less twice than that of normal resist should be removed similarly to nonimplanted resist.

3.5. TOF-SIMS Measurement of Ion-Implanted Resist.

Figure 7 presents the secondary negative ion mass spectra of ion-implanted resists with various acceleration energies. “Counts” of the vertical axis of Figure 7 is a number of ions which entered the detector, and it becomes the number of counts for each area. The \( C_8H_9O^- \) (m/z 121.08) Chemical structure is drawn in Figure 7) from cresol novolak resin was detected as a component of non-ion-implanted resists. In addition, \( C_{10}H^- \) (m/z 121.01), which is a hydrocarbon with a saturated bond, was detected as a component of the damaged (hardened) layer of ion-implanted resist. \( C_{10}H^- \) is described as follows. Hydrogen is escaped from the resist \( C_8H_9O^- \) by ion implant, and we think that it is
the compound such as graphitized and amorphous carbon. We do not understand whether the material is composed only of a saturated bond. The ion intensity of \( C_{10}H^- \) increased with increasing acceleration energy. Therefore, it was assumed that removing ion-implanted resists would become difficult because cresol novolak resin was carbonized by ion implantation. The reason why the count of \( C_{10}H^- \) of 150 keV is smaller than that of \( C_{10}H^- \) of 70 keV is that the area where \( C_{10}H^- \) in 150 keV is smaller than that of 70 keV. When Figure 8 is seen, it is understood that the area (h: hardener layer) of \( C_{10}H^- \) of 150 keV is narrower than that of 70 keV. Figure 8 presents the second negative ion images of ion-implanted resists with various acceleration energies. \( C_{10}H^- \) was detected from the lower layer of resist with increasing acceleration energy.

In contrast, the ion intensity of \( C_8H_9O^- \) was weak at the surface and strong at the lower layer. Therefore, resists are carbonized deeply with increasing acceleration energy. Also, the ion intensity of \( C_8H_9O^- \) was greater than that of non-ion-implanted resist for all ion-implanted resists. It was assumed that the molecules of cresol novolak resin were easily ionized. For 10 keV, \( C_8H_9O^- \) was detected at the lower layer than at the surface because the surface was stripped when it was cut at a slant. It was assumed that the hardened layer fell away.

Next, we measured the surface profile of the resist that was cut by SAICAS using a stylus-type surface-profile measurement instrument (DekTak 6 M; ULVAC). From the result of surface profile measurement, at the resist with ions implanted at 10 keV, the resist layer of 100 nm depth from the surface was stripped. At 70 keV, the resist of 400 nm depth was stripped and that at 150 keV was 600 nm. Therefore, the estimated thickness of the hardened layer of ion-implanted resist at 10 keV was above 100 nm, that at 70 keV was above 400 nm, and that at 150 keV was above 600 nm.

### 4. Conclusion

We investigated the removal of polymers with various chemical structures and the removal of ion-implanted resists using wet ozone. The removal rates of polymers that have C–C double bonds in the main chain (novolak resin and cis-1,4-polyisoprene) were the highest. The removal rates of polymers that have C–C double bonds in the side chain (PVP and PS) were lower than those of novolak resin and cis-1,4-polyisoprene. In novolak resin and cis-1,4-polyisoprene, the main chain may be decomposed by reaction with wet ozone. In PVP and PS, the benzene ring in the side chain changes into carboxylic acid by reaction with wet ozone. Thus, PVP and PS should be removed because their ability to dissolve in water increased. However, the polymers that have no C–C double bond (PMMA and PVC) were not removed.

Removal of B and P ion-implanted resists became difficult with increasing acceleration energy. Resist with B ions implanted at an acceleration energy of 150 keV could not be removed nor could resist with P ions implanted at acceleration energies of 70 keV and 150 keV. It was assumed that the reactivity of ozone and resists decreases with increasing acceleration energy. From the results of removal of ion-implanted resist using wet ozone and nanoindentation, a resist with plastic-deformation hardness five times that of normal resist could not be removed, and a resist with plastic-deformation hardness twice that of normal resist should be removable similarly to nonimplanted resist. Using TOF-SIMS, the \( C_8H_2O^- \) (m/z 121.08) from cresol novolak resin was detected as a component of non-ion-implanted resists. \( C_{10}H^- \) (m/z 121.01), which is a hydrocarbon with an unsaturated bond, was detected as a component of the damaged (hardened) layer of ion-implanted resist. The ion intensity of \( C_{10}H^- \) increased with increasing acceleration energy. We clarified that the molecule of cresol novolak resin was destroyed and carbonized by ion implantation.

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### References


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