A Comparison of Removal Phenomena in Photoresist Materials Using Laser Irradiation

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Resist removal phenomena using laser irradiation were compared in the novolak resist and the PVP. Thresholds for stripping from the Si wafer and damaged at the Si wafer were evaluated for the laser irradiating condition in the normal atmosphere and in the water. The PVP was found to be easy to be stripped as compared with the novolak resist. Only in the water, the photoresist material was completely stripped from the Si wafer surface. The size of the changed area by the laser irradiation for the PVP was approximately 2 times larger than that of the novolak resist. Time-resolved images were also acquired in 400 ns and 7500 ns after the laser irradiation. The scattering condition of the PVP in the removal process was completely different from that of the novolak resist.

Keywords: Resist stripping phenomena, Stripping threshold, Time-resolved images

1. Introduction

Resist removal by using laser irradiation has been investigated instead of conventional processes such as oxygen plasma and chemical method [1,2]. Laser energy irradiated is absorbed to a Si wafer, and the resist is stripped from a Si wafer. For the normal atmosphere irradiation, laser damage occurs on a Si wafer easily. This is because that the condition of the occurrence of the laser damage and a stripping threshold of the resist are close. An advanced laser resist stripping method was successfully developed without causing laser damage to the Si wafer [3]. The pulsed laser irradiation in the water can improve the resist stripping effect when compared with that of the normal atmosphere irradiation. A laser irradiation of 532 nm, having large photon energy, was found to have higher resist removal efficiency than that of the wavelength 1064 nm. Positive-tone diazonaphthoquinone (DNQ) / novolak resists implanted with B, P, and As ions, respectively, were stripped by 20 pulses irradiation without causing laser-induced surface damage. The novolak resist implanted with a density of $5.0 \times 10^{15}$ atoms/cm$^2$ was continuously stripped by the scanning laser irradiation with 20 pulses [4]. And, irradiation with multiple laser beams with a small beam diameter was confirmed as one of the methods for improvement of a resist stripping rate with high efficiency [5]. Poly(4-vinylphenol) (PVP) used as a base polymer of the KrF resist was also removed by laser irradiation in the water [6].

The resist removal phenomena in the water was analyzed by using a finite element (FE) method. A two-dimensional (2-D) micro-FE model was constructed based on the boundary surface between the Si wafer, resist and water during laser irradiation. A large compressive stress in the resist is thought to improve the resist removal efficiency [7]. The
further clarification of the resist removal phenomena was performed by using a time-resolved analysis. A resist removal from the Si wafer was experimentally observed after 8 ns of pump laser pulse irradiation. When the resist was stripped from the Si wafer surface, the intensity of probe laser related to the surface shape change of the resist increased after the laser irradiation [8]. However, this method cannot find what kind of change occurs in a resist.

In this study, we investigated the resist removal phenomena in photoresist materials. Thresholds for stripping from the Si wafer and damaged at the Si wafer were compared for different resist materials. In our past research, novolak resists and PVP were measured for different time. To compare removal phenomena precisely, each photoresist material should be compared in the same irradiation condition again. For this purpose, the novolak resist and the PVP were evaluated on the same measurement condition. Changes for the surface shape during the stripping process were observed by using a time-resolved imaging technique. A change of the photoresist material surface related to the stripping process was confirmed directly.

2. Experimental

The photoresist material coated on the Si wafer was installed perpendicularly in a container having an aperture for laser beam incidence. Positive-tone DNQ/novolak resist (OFPR-800 from Tokyo Ohka Kogyo Co., Ltd.) and PVP were used as the photoresist material. The thickness coated on the Si wafer was around 1.1 μm. A pulsed laser with wavelength of 532 nm was used in this experiment. The pulse duration was 8 ns. The intensity shape of the laser beam was Gaussian shape, and beam diameter of 1/e² was 310 μm. The pulsed laser was irradiated using a "1-on-1" method (irradiated place was changed every pulse). A lens with a focal length \( f = 300 \text{ mm} \) was used to focus the laser irradiation onto the photoresist material surface. The intensity of the pulses was varied with an attenuator consisting of a polarizer and a half-wave plate. The laser irradiation to the photoresist material was carried out under two conditions. As for the condition of the normal atmosphere, a container did not have water. In contrast, a container was filled with water for in the water condition. The distance from the water surface to the photoresist material was kept to 2 - 3 mm in depth. The stripping threshold (the point at which the photoresist material begins being stripped from the Si wafer) and the surface laser damage threshold (the point at which laser damage occurs at the photoresist material and Si wafer interface) were evaluated for the normal atmosphere condition and in the water condition. The surface change after the laser irradiation was observed with a digital microscope (KEYENCE, VHX-950F). By using the optimal illumination method of the digital microscope, these thresholds were determined with high accuracy.

The stripping process of the photoresist material induced by the pump laser was captured by using the high-speed imaging system shown in Fig. 1. A He-Ne laser at 632.8 nm was used as a probe laser. Reflectance image on the sample was relayed and detected by a charge-coupled device (CCD) camera (640 × 480 pixels) equipped with an image intensifier (LaVision, PicoStar HR). The gate width of the image intensifier was set at 5 ns. A time delay between a pump pulse and a gating electronic pulse was changed by an electronic delay generator. Time-resolved images were acquired based on the “1-on-1” method described above.

3. Results and discussion

Measurement results of the stripping threshold and the surface laser damage threshold for photoresist material are shown in Table 1. The difference of the laser irradiation condition was not found in the stripping threshold and the surface laser damage threshold at Si wafer. In case of novolak resist, the resist stripping threshold was about 0.17 J/cm², and the surface laser damage threshold was about 0.44 J/cm². In order not to generate laser damage to the Si wafer, differences between the stripping threshold and the surface laser damage threshold are required. If the difference of these two thresholds is large, resist stripping is completed in a safe condition.
Table 1. Stripping threshold and the surface laser damage threshold of Si wafer for laser irradiation in the normal atmosphere and in the water.

| Photoresist materials | Laser irradiating condition | Stripping threshold (J/cm²) | Surface laser damage threshold at Si wafer (J/cm²) |
|-----------------------|-----------------------------|----------------------------|-----------------------------------------------|
| Positive-tone DNO / novolak resist | Normal atmosphere | 0.16 | 0.44 |
|                        | In the water | 0.17 | 0.47 |
| PVP                   | Normal atmosphere | 0.11 | 0.43 |
|                        | In the water | 0.11 | 0.44 |

Digital microscope photographs of the novolak resist surface after irradiating with 532 nm were shown in Fig. 2. The energy of irradiated laser beam was adjusted to an intensity of about 0.4 J/cm² at which laser damage did not occur to the Si wafer surface. For the irradiation in the normal atmosphere, the novolak resist slightly rises from the Si wafer surface by a difference of the coefficient of thermal expansion between the Si wafer surface and the resist material. The resist surface changed by laser irradiation was central around 100 μm of the laser beam. Furthermore, if the laser energy intensity was increased, the resist started being stripped with laser damage to the Si wafer surface. In contrast, for the laser irradiation in the water, the resist was stripped from the Si wafer without occurring laser damage. Resist stripping effect clearly improves under the laser irradiation to the resist in the water.

In case of the PVP, the stripping threshold was 0.11 /cm² that was slightly lower than that of the novolak resist. The surface laser damage threshold was 0.44 /cm² which was the same as the novolak resist. Therefore, the surface laser damage threshold is thought to be decided by the transmittance of photoresist materials at 532 nm. As for both of these materials, optical transparency at 532 nm is the same. Figure 3 shows digital microscope photographs of the PVP surface after irradiating with an intensity of about 0.4 /cm². The area that is changed by laser irradiation becomes larger than that of the novolak resist. For the irradiation in the normal atmosphere, a rise and breaking that

Fig. 2. Digital microscope photographs of the novolak resist surface after irradiating with 532 nm (a) in the normal atmosphere and (b) in the water.

Fig. 3. Digital microscope photographs of the PVP surface after irradiating with 532 nm (a) in the normal atmosphere and (b) in the water.
occurred to the PVP was approximately 200 \text{μm} in size. However, the PVP was not stripped from the Si wafer surface. For the laser irradiation in the water, the PVP was stripped from the Si wafer without occurring laser damage. The size of the stripped area was of a diameter of 200 \text{μm} that was wider than that of the novolak resist. Because laser beam with the almost same intensity was irradiated to both the novolak resist and the PVP, the PVP was found to be easy to be stripped as compared with the novolak resist.

In this removal process, about 60% of laser energy is absorbed to the Si wafer during 8 ns of pulse duration. The temperature of the Si wafer surface rapidly rises by absorbing laser energy and causes local thermal expansion. Therefore, the material change occurring subsequently depends on material characteristics such as the hardness and adhesive power to the Si wafer. In this experiment, the thermomechanical property of the PVP in the thin film condition is thought to be lower than that of the novolak resist.

Then, the removal processes in photoresist materials were monitored with a high-speed camera directly. The observation for the underwater irradiation had a bad resolution for an influence of the water. Therefore, the observation results of every material for the irradiation in the normal atmosphere are shown in Figs. 4 and 5. To monitor the clear change in the removal process, the irradiating laser energy is larger than the laser damage threshold to the Si wafer. Time-resolved images were acquired in 400 ns and 7500 ns after the laser irradiation. In case of the novolak resist, a change has already occurred at the laser irradiating spot after the laser irradiation of 400 ns (Fig. 4(a)). The resist was completely stripped from the Si wafer surface after 7500 ns (Fig. 4(b)). The time change of these resist shapes corresponds to the result of the time-resolved analysis by the reflected probe laser intensity change from the resist and the Si wafer surface [8]. The stripped resist was scattered to the group of small lumps.

Fig. 4. Time-resolved images of the novolak resist surface after laser irradiating (a) after 400 ns (b) after 7500 ns.

Fig. 5. Time-resolved images of the PVP surface after laser irradiating (a) after 400 ns (b) after 7500 ns.
As for the PVP, cracks already occurred in the irradiating area after 400 ns (Fig. 5(a)). The PVP was stripped from the Si wafer in split conditions after 7500 ns (Fig. 5(b)). The condition of the PVP in the process to be scattered was completely different from that of the novolak resist. These results are very useful to apply this technique to a real resist removal process.

4. Conclusion

We investigated the resist removal phenomena in photoresist materials. Positive DNQ/novolak resist and PVP were used as the photoresist material. The stripping threshold and the surface laser damage threshold at Si wafer were evaluated for the normal atmosphere condition and the water condition. The stripping threshold of PVP was slightly lower than that of the novolak resist. In contrast, as for the surface laser damage threshold, there was not the difference in laser irradiation condition. However, for the laser irradiation in the normal atmosphere, the photoresist material was not stripped from the Si wafer. Only in the water, the photoresist material was completely stripped. The size of the changed area by the laser irradiation for the PVP was approximately 2 times larger than that of the novolak resist. From these results, the PVP was found to be easy to be stripped as compared with the novolak resist. The removal processes were monitored with a high-speed camera directly. Time-resolved images were acquired in 400 ns and 7500 ns after the laser irradiation. The scattering condition of the PVP in the removal process was completely different from that of the novolak resist. These results are very useful to apply this laser removal technique to a real resist removal process.

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