Time-resolved Analysis of Resist Stripping Phenomenon Using Laser Irradiation

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Resist stripping phenomenon with laser irradiation was observed by using a time-resolved analysis. The time change of the resist stripping phenomenon by a probe laser irradiation was observed from the viewpoint of the intensity change of the probe laser. As for the laser irradiation in the water, the probe laser intensity arrived at the maximum after around 40 μs. During the pump laser irradiation of 8 ns, a large compressive stress of -10 MPa was confirmed inside the resist from the FE analysis results. The generation of this compression stress is important for starting the resist stripping process, and is thought to improve the resist removal efficiency.

Keywords: Time-resolved analysis, Resist stripping phenomenon, Finite element (FE) method, Pump laser irradiation, Removal efficiency, Compressive stress

1. Introduction

Resist removal from substrates conventionally uses oxygen plasma [1,2] and/or chemicals (e.g., sulfuric acid hydrogen peroxide mixture). However, these resist removal methods include some technical problems. Oxygen plasma ashing may cause oxidation of substrates and metal wiring because this process requires high temperature (above 250 °C) [3,4]. Chemicals are used in large amounts and cause environmental damage [5,6]. Therefore, several resist removal methods have been developed (e.g., atomic hydrogen [7-10], UV/ozone [11,12]).

The removal of resist by laser irradiation has been investigated instead of the chemical method. [13,14]. An advanced laser resist stripping method was successfully developed without causing laser damage to the Si wafer [15]. 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 5.0×10¹⁵ atoms/cm² was continuously stripped by the scanning laser irradiation with 20 pulses [16]. 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 [17]. Poly(4-vinylphenol) (PVP) used as a base polymer of the KrF resist was also removed by laser irradiation in the water [18].
The resist removal phenomenon 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 radiation. In the normal atmosphere, any effective stress did not occur in the resist. In contrast, for the laser irradiation in the water, a large compressive stress was confirmed in the resist. This compressive stress in the resist is thought to improve the resist removal efficiency [19]. However, the FE model constructed in our research has difficulty in analysis after resist stripping from the Si wafer.

In this study, we have investigated the resist removal phenomenon by using a time-resolved analysis. A resist removal from the Si wafer was experimentally observed after 8 ns of pump laser pulse irradiation. The experimental result about laser irradiation in the water was compared with that in the atmosphere. And the analysis results of the FE method were also evaluated into details. The further clarification of the resist removal phenomenon was performed by combining an experimental time-resolved analysis and the FE analysis.

2. Experimental

A schematic depiction of the experimental system for the time-resolved analysis is shown in Fig. 1. The pulsed pump laser was operating at 532 nm, 8 ns full width at half maximum intensity (FWHM) and was focused onto the resist surface using a 300 mm focal length lens. The intensity of the pulses was varied with an attenuator consisting of a polarizer and a half-wave plate. The resist was stripped using a "1-on-1" method (irradiated place was changed with every pulse).

Positive DNQ / novolak resist (OFPR-800 from Tokyo Ohka Kogyo Co., Ltd.) was used in this experiment. The resist thickness was found to be 1100 nm by profilometry (Dektak6M from ULVAC). A He-Cd laser with CW operation was selected as a probe laser. The probe laser was irradiated to overlap with a pump laser on the resist surface by using a focusing lens units. For the He-Cd laser with a wavelength of 325 nm, an absorption coefficient to novolak resist was very high, and the reflectivity from a Si wafer was also high. When the irradiation angle of the probe laser was 45 degrees against the resist surface, the absorption to the resist was 88 %, and the reflectivity from the Si wafer was 57 %. By the considerable difference between these absorption coefficients and reflectivity, the time change of the resist removal phenomenon could be observed into details. The intensity change of the probe laser during the resist removal process was monitored with a biplanar phototube. A voltage signal from the biplanar phototube was measured with an oscilloscope. The pump laser of 8 ns was the trigger of the voltage signal from biplanar phototube. The time-resolved analysis about laser irradiation in the water was compared with that in the atmosphere.

3. Results and discussion

A Si wafer without resist was irradiated with a pump laser beam to easily confirm the intensity change of the probe laser. If a surface condition of the Si wafer does not show a change, the intensity of a probe laser reflecting from the Si wafer is constant. In contrast, the intensity of the probe laser decreases when laser damage occurred on the Si wafer surface by pump laser irradiation. Figure 2 shows the time-resolved analysis results when a pump laser beam of 532 nm was irradiated to a Si wafer both in the normal atmosphere and in the water. As for the intensity of irradiated pump laser, laser damage occurred to the Si wafer (Fig. 3). The intensity changes of probe laser from the Si wafer showed the same tendency for the experimental conditions in both the normal atmosphere and the water. After a pump laser
irradiation of 8 ns, the intensity of the probe laser suddenly decreased by 0.2 μs. These phenomena are almost similar to the results of time-resolved analysis of the laser damage generation of the fused silica [20]. It was found that a phenomenon of ns - μs field caused by the pump laser irradiation could be evaluated by this time-resolved analysis system.

Fig. 2. Changes for intensity of the probe laser reflecting from a Si wafer.

Then, time-resolved analysis was performed to the resist removal phenomenon in the normal atmosphere and in the water (Fig. 4). The irradiated pump laser intensity was over the resist stripping threshold. When the resist stripped from the Si wafer surface, the intensity of probe laser increased after the pump laser irradiation. For the laser irradiation at the normal atmosphere, the maximum intensity of probe laser was arrived at after about 13 μs. The probe laser signal increased from 2.0 mV to 4.0 mV. This intensity change corresponds with the surface shape change of the resist during the stripping process.

In contrast, for the laser irradiation in the water, the probe laser intensity arrived at the maximum after about 40 μs. The initial probe laser intensity was 0.5 mV because the water absorbed a He-Cd laser. The probe laser signal increased from 0.5 mV to 4.0 mV. Figure 5 shows a photographs of the processed surface when a laser beam of 532 nm was irradiated to a positive-tone DNQ / novolak resist in the normal atmosphere and in the water.

Fig. 3. Optical microscope photograph of the laser damage at Si wafer surface after irradiating with 532 nm.

For the irradiation of pump laser to the resist in the normal atmosphere, the resist was stripped, but laser damage occurred to the Si wafer surface (Fig. 5(a)). As for the laser irradiation in the water, the resist was stripped from the Si wafer without occurring the laser damage (Fig. 5(b)). The small increase of the probe laser signal in the normal atmosphere was caused by the laser damage to the Si wafer. The time of resist removal phenomenon took 3 times longer in...
the underwater condition than in the normal atmosphere condition. There was a possibility that time necessary for the resist stripping became longer due to the resistance from water. The change of the surface shape of the resist immediately occurs after pump laser irradiation. The resist begins to strip from the Si wafer at an early stage after the pump laser irradiation. From these results, the pump laser irradiation at the start of resist removal is important to the initial process of the resist stripping.

Fig. 5. Optical microscope photographs of the resist striped surface after irradiating with 532 nm (a) in the normal atmosphere and (b) in the water.

The results of the FE method were analyzed about a shape change during the pump laser irradiation. Figure 6(a) shows the contour diagram for the shape change with the temperature distribution in the normal atmosphere condition. The laser energy irradiated was enough large for a resist removal phenomenon. At the Si wafer and the resist boundary surface, the temperature-rise caused by the laser energy absorption to a Si wafer showed the same tendency for the experimental conditions in both the normal atmosphere and the water. The temperature suddenly rose to 500 degrees Celsius or more by absorption of the laser energy. Shape displacement occurred with this temperature rise. The resist was transformed along a Si wafer by its thermal expansion of the Si wafer. The resist part is shown with the curve that a contour line was piled up densely. At the top of the resist surface, the displacement in the normal atmosphere was 8 nm while it was around 6 nm in the water.

Fig. 6. Analysis results for FE method during the pump laser irradiation. (a) Contour diagram for the shape change with the temperature distribution at normal atmosphere condition. (b) Stress inside the resist in a normal atmosphere. (c) Stress inside the resist in the water.
The stress inside the resist was not confirmed just after laser irradiation (Fig. 6(b)). In contrast, for the laser irradiation in the water, a compressive stress was found inside the resist was. The compressive stress becomes a maximum of -10 MPa after 5 ns (Fig. 6(c)). Because the resist could not be displaced by the water working as a wall, large compressive stress in the resist occurred in the underwater irradiation condition.

The resist stripping process in the water is explained as follows. The Si wafer surface thermally expands by pump laser irradiation. Then, the compression stress occurs inside the resist 5 ns later. Resist is stripped from the Si wafer surface subsequently after 20 μs. This compressive stress in the resist is thought to improve the resist removal efficiency.

4. Conclusion

We have investigated the resist removal phenomenon by using a time-resolved analysis. A He-Cd laser of CW was selected as a probe laser. When the resist was stripped from the Si wafer surface, the intensity of probe laser increased after the pump laser irradiation. For the laser irradiation in the water, the probe laser intensity arrived at the maximum after about 40 μs. This intensity change corresponds with the surface shape change of resist during the removal process. This result indicated that the pump laser irradiation at the start of resist removal is important to the initial process of the resist stripping. Shape changes of Si wafer and resist related to the temperature change during the pump laser irradiation were analyzed by the FE method. As for the underwater irradiation condition, a large compressive stress of -10 MPa was confirmed inside the resist from the FE analysis results. The generation of this compression stress is important for the starting the resist stripping process, and is thought to improve the resist removal efficiency. A resist stripping mechanism could be elucidated by combining experimental time-resolved analysis and FE analysis.

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