Scanning Removal of Ion-implanted Novolak Resist by using a Laser Irradiation

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Laser resist stripping for the ion-implanted novolak resist was successfully performed without occurring laser damage to the Si wafer. In order for the advanced laser resist stripping method to be successful, it is important for the pulsed laser beam to pass through the ion-implanted resist and absorb into the Si wafer surface. The novolak resists which are implanted with B, P, and As ions, respectively, were irradiated with a pulsed 532nm laser. Regardless of the implanted ion species and density, more than 74 % of the laser power was found to absorb into the Si wafer surface. For the laser irradiation of 1 pulse, the ion-implanted resist with a density of 5.0×10^{13} atoms/cm² was completely stripped in the same way as that of a non-implanted resist. The optical absorption of the resist surface increased as the density of the ion-implantation increased. In case of the ion-implanted resist with a density of 5.0×10^{15} atoms/cm², the resist was stripped by 20 pulses irradiation without occurring laser-induced surface damage. A scanning removal of the highly ion-implanted resist was also successfully stripped by using an optimized irradiation condition. A highly ion-implanted resist was continuously stripped by the scanning laser irradiation with 20 pulses.

Keyword: resist stripping, ion-implanted novolak resist, laser irradiation, laser-induced damage, scanning removal

1. Introduction

In semiconductor manufacturing, there is an ion implantation process in which 13 and 15 group elements are implanted to a substrate. In this process, the resist plays the role of a mask, and ions are implanted to the resist also. It is difficult to remove the ion-implanted resist because the resist is hardened, and is denatured by the implanted ions [1-3].

Resist removal from substrates in a semiconductor manufacturing process conventionally makes use of oxygen plasma and/or sulfuric acid hydrogen peroxide mixture (SPM). These environmentally

unfriendly chemicals are used in large amounts and so cause environmental damage [4, 5].

In order to avoid using such chemicals, ozone with high oxidation potential is expected to remove the resist and organic residue. However, the resist cannot be removed using ozone alone at room temperature. The dry process using ozone requires temperatures higher than 250°C in order to generate oxygen radicals from the ozone through thermal decomposition. For this reason, the process using ozone may oxidize substrates and metal wiring [6, 7, 8].

The removal of the resist by laser

irradiation instead of chemicals has the advantage of reducing environmental risks [9, 10]. An advanced laser resist stripping method for the positive-tone diazonaphthoquinone (DNQ) / novolak resist was successfully developed without occurring laser damage to the Si wafer [11]. The pulsed laser irradiation in the water can improve the resist stripping effect when compared with that of conventional atmosphere irradiation. A laser irradiation of 532 nm, having large photon energy was found to have higher resist stripping efficiency than that of the wavelength 1064 nm. To apply this method to commercial contexts, ion-implanted photoresist is also surely removed from the Si wafer.

In this study, we have investigated the ion-implanted novolak resist removal by using laser irradiation. In order for the advanced laser resist stripping method to be successful, it is important for the pulsed laser beam to pass through the ion-implanted resist and absorb into the Si wafer surface. The optical characteristics of the ion-implanted resist were evaluated at the wavelength of 532 nm. For this purpose, novolak resists which were implanted with B, P, and As ions with density from 5.0×10^{13} atoms/cm² to 5.0×10^{15} atoms/cm², respectively, were prepared in this experiment. A stripping condition in which damage did not occur to the Si wafer was confirmed in the highly ion-implanted sample. In addition, demonstration of the ion-implanted resist stripping with laser beam scanning was performed by using optimized conditions.

2. Experimental Procedure

Ion-implanted novolak resists used in this experiment were prepared using the following procedure. HMDS was spin-coated onto the Si wafer substrate using a spin-coater (ACT-300A from ACTIVE) at 3000 rpm for 60 sec. Then, the positive DNQ / novolak resist (OFPR- 800 from Tokyo Ohka Kogyo Co., Ltd.) was spin-coated at 2000 rpm for 20 sec. The resist was pre-baked at 100 degrees Celsius for 60 sec. The resist thickness was found to be from 1.0 to 1.1 μ m by profilometry (Dektak6M from ULVAC). B, P, and As ions, were implanted to the novolak resist surface with the acceleration energy of 70 keV. The density of the ion-implants was

from 5.0×10^{13} atoms/cm² to 5.0×10^{15} atoms/cm².

Optical characteristic of ion-implanted resist was evaluated by using a second harmonics (532 nm) of a pulsed Nd:YAG (Y₃Al₅O₁₂) laser. The laser beam was irradiated to the Si wafer coated with ion-implanted resist. The relations between the irradiation power and the reflection power from the Si wafer coated with an ion-implanted resist were measured precisely. To calculate the absorption of ion-implanted resists, the same measurement was performed on the Si wafer surface only.

Prepared ion-implanted resists were sunk underwater to obtain an improved stripping condition identical to a non-implanted novolak resist. The pulsed laser was irradiated using a "1-on-1" method (irradiated place was changed every pulse). A lens with a focal length $f = 300$ mm was used to focus the laser radiation onto the resist surface. The intensity of the pulses was varied with an attenuator consisting of a polarizer and a half-wave plate. The prepared ion-implanted resist was installed perpendicularly in a container having an aperture for laser beam incidence as shown in Figure 1. The distance from the water surface to the resist was controlled using the quantity of the water put in the container. The resist was irradiated with a laser beam of 532 nm in the water at a depth of 2 mm.

Figure 1. Experimental setup of the laser irradiation for ion-implanted resist stripping in the water.

3. Results and Discussion

The absorbance of the ion-implanted resist obtained from the optical characteristic

measurement is summarized in Figure 2. At the wavelength of 532 nm, novolak resist is transparent optically. The irradiated laser beam arrives at the interface of the Si wafer and the resist. For the non-implanted photoresist, approximately 90% of irradiated laser power was absorbed at the Si-resist interface. In contrast, the absorbance of ion-implanted resists was from 74 to 90 %. Even a highly ion-implanted resist with a density of 5.0×10^{15} atoms/cm² showed the same absorbance of approximately 90% as the non-implanted resist. Ion-implanted novolak resists were also transparent optically in the wavelength of 532 nm. No dependence on ion-implanted density and implanted ions species was identified in the difference of the absorbance between the samples. The single-layered novolak resist film having low index of refraction against a Si wafer works as AR coating. Thus, the difference of slight film thickness among the samples was thought to cause dispersion of the absorbance. From these results, irradiated laser power pass through the ion-implanted resist surface which changed in quality chemically and mechanically.

Figure 2. Optical characteristic of ion-implanted resist samples at 532 nm wavelength.

Resist stripping threshold (the point at which the resist begins stripping from the Si wafer) and laser-induced damage threshold (LIDT) of the Si wafer surface under the ion-implanted resist were measured at the laser wavelength of 532 nm. In order not to generate laser damage to the Si wafer in this advanced laser resist stripping method, resist stripping threshold must be lower than the LIDT of the Si wafer surface coated with the ion-implanted resist. If the difference of these

two thresholds is large, resist stripping is enabled in a safe laser irradiation condition. Table 1 shows the resist stripping threshold and LIDT of the Si wafer surface coated with the ion-implanted resist.

For the laser irradiation of 1 pulse, ion-implanted resist with a density of 5.0×10^{13} atoms/cm² was completely stripped in the same way as that of non-implanted photoresist. The difference of the type of an implanted ion was not found in the resist stripping threshold obtained.

The resist stripping threshold was 42~48 mJ. It was half a degree of the LIDT of the Si wafer surface coated with the ion-implanted resist. In case of the ion-implanted resist with a density of 5.0×10^{15} atoms/cm², the resist stripping threshold decreased in 15~19 mJ. Only an outer side of the resist was stripped with 1 pulse irradiation. It is thought that optical absorption of the surface of the resist increased with a high-density ion implantation. The irradiated laser comes to be absorbed at the resist surface with the increase of the optical absorption of the resist. Therefore, after irradiating multiple pulses, the ion-implanted resist with a density of 5.0×10^{15} atoms/cm² could be stripped without damaging the Si wafer.

Table 1. Optical characteristic of the resist sample in the second harmonics (532 nm) of a Nd:YAG laser.

Sample name	Photoresist stripping threshold (mJ/cm ²)	LIDT at the Si-photoresist interface (mJ/cm ²)
B-ion 5×10^{13}	42	98
B-ion 5×10^{15}	19	65
P-ion 5×10^{13}	48	110
P-ion 5×10^{15}	15	41
As-ion 5×10^{13}	44	99
As-ion 5×10^{14}	16	51
As-ion 5×10^{15}	15	37

Figure 3 shows a photograph of the processed surfaces when a laser beam with 532 nm was irradiated to the B ion-implanted resist in water. The energy of irradiated laser beam was adjusted to the intensity at which laser damage did not occur to the Si wafer surface. On the optimized condition, the non-implanted novolak resist was completely stripped by the laser irradiation with 1 pulse (Fig 3. (a)). The Boron ion-implanted resist

with a density of 5.0×10^{13} atoms/cm² was stripped similar way (Fig 3. (b)). The Boron ion-implanted resist with a density of 5.0×10^{15} atoms/cm² was stripped by 20 pulses irradiation without occurring surface laser-induced damage (Fig 3. (c)). Therefore, it was found that even the highly ion-implanted resist could be stripped by using an advanced laser stripping method.

(a) non-implanted resist (1 pulse).

(b) Boron ion-implanted resist with density of 5.0×10^{13} atoms/cm² (1 pulse).

(c) Boron ion-implanted resist with density of 5.0×10^{15} atoms/cm² (20 pulses).

Figure 3. An optical microscope photograph of the resist surface after irradiating with 532 nm.

In addition, the ion-implanted resist stripping with laser beam scanning was carried out in the water. A pulsed 532 nm

laser was irradiated to the boron ion-implanted resist (density of 5.0×10^{15} atoms/cm²) with 20 pulses per spot. The laser beams were scanned every 20 μm after the laser irradiation of 20 pulses. The micro photograph of the stripped ion-implanted resist surface after 532 nm laser scanning is shown in Figure 4. At the laser irradiated surface, the resist has been continuously stripped from the Si surface without occurring laser damage.

In contrast, the ion-implanted resist coated on the Si wafer remains on the surface without the laser irradiation. The stripping rate of the ion-implanted resist depends on the number of laser pulses. Thus, a laser light source with a large beam diameter and high repetition rate is required for its industrial application.

Figure 4. Micro photograph for Boron ion-implanted resist with density of 5.0×10^{15} atoms/cm² after 532 nm laser scanning.

4. Conclusion

We have investigated the ion-implanted photoresist removal by using an advanced laser resist stripping method. The optical characteristics of the ion-implanted resist were evaluated at the wavelength of 532 nm. B, P, and As ion-implanted novolak resists with a density from 5.0×10^{13} atoms/cm² to 5.0×10^{15} atoms/cm² were prepared in this experiment. Regardless of implanted ion species and density, more than 74 % of laser power was found to absorb into the Si wafer surface. A highly ion-implanted resist with a density of 5.0×10^{15} atoms/cm² showed the absorbance of approximately 90% as the non-implanted resist. The difference of slight film thickness of the samples is thought to cause the dispersion of absorbance. For the laser irradiation of 1 pulse, the ion-implanted resist with a density of 5.0×10^{13} atoms/cm² was completely stripped in the same way as

that of non-implanted photoresist. In contrast, the ion-implanted resist with a density of 5.0×10^{15} atoms/cm² was could be stripped by irradiating 20 pulses without damaging the Si wafer.

Furthermore, the ion-implanted resist stripping with laser beam scanning was carried out on B the ion-implanted resist with a density of 5.0×10^{15} atoms/cm². The ion-implanted resist was continuously stripped from the Si surface without causing laser damage. From these results, the irradiation of the 532nm pulsed laser to the resist in the water also enables ion-implanted resist stripping from the Si wafer. In addition, it is indicated that an advanced laser resist stripping method is a promising technique for reduction of environmental load in lithography process.

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