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Removal of Diazonaphthoquinone/Novolak Resist Using UV Laser (266 nm)

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ABSTRACT: This study revealed a promising method for removing positive-tone diazonaphthoquinone/novolak resist. The fourth harmonic of an Nd^{3+}:YAG ($Y_3Al_5O_{12}$) pulsed laser (266 nm) was irradiated onto the resist. Resist was removed when laser power exceeded 35 mJ/cm^2, and a 250 nm-thick resist was removed with a laser power of 94 mJ/cm^2. X-ray Photoelectron Spectroscopy (XPS) proved that 1100 nm-thick resist could be completely removed from a Si surface when it was irradiated almost 700 mJ/cm^2. The resist onto three inch Si wafer (45.58 mm^2) was removed in two minutes by laser. No damage to the processed Si wafer could be detected by optical microscopic observation. This method is good for environment. [DOI 10.1295/polymj.37.813]

KEY WORDS Removing Resist / Diazonaphthoquinone / Novolak Resist / Nd^{3+}:YAG Laser / Laser Power / Environment /

Transistors are formed on substrates in the manufacturing process of semiconductors and Liquid Crystal Display (LCD) by several repetitions of processes such as coating, patterning (resist coat, exposure, development), etching, and resist removal and cleaning. The repeatability number is about twenty in semiconductor manufacturing and about five in LCD manufacturing. Large amounts of sulfuric acid, hydrogen peroxide, and amine type organic solvents are used in the resist removal process, and the chemical wastes is causing environmental damage.

Conventional resist removal from substrates in the semiconductor manufacturing uses either single substrate oxygen plasma ashing or a batch process using sulfuric acid/hydrogen peroxide/deionized water (SPM). However, oxygen plasma ashing causes some problems, such as damage to the device on a Si wafer as a result of the plasma charge and reduction of the plasma uniformity due to the charged Si wafer.[1] The resist removal rate by the SPM process is about 0.2 μm/min, although the decomposition and dissolution of the resist can be accelerated by heating the solution above 100 °C.

The substrate in LCD production is larger than that of a semiconductor, and uniform resist removal cannot be obtained by a dry process using oxygen plasma ashing. Therefore, a chemical stripping method is generally used. The chemical solvent commonly used for LCD resist removal is known as solution 106 (monoethanol amine + dimethylsulfoxide),[2] and it is harmful to the environment and expensive, and the quantity consumed is also very high. Consequently, reducing the cost and environmental burden of the solvent are major issues to be resolved.

Ultra Violet (UV)/ozone ashing is being considered as an environmentally friendly process for resist removal. It is necessary to attain a temperature above 250 °C to achieve a resist removal rate exceeding 1 μm/min.[3,4] However, the device is occasionally damaged due to the high temperature. Ozonized water processing for removing the resist was also studied.[5–8] A wet ozone process using ozone and a small amount of water under 100 °C was reported by Noda *et al.*,[9,10] but the resist removal rate is about 1 μm/min.

Using a laser instead of chemical solvents for resist removal has the advantage of reducing the environmental impact. A laser can focus energy in a microspace without direct contact with the processing material, and basically any material can be laser machined. The excimer laser micromachining using resist has been studied by several researchers.[11–13] Moreover, laser processing is environmentally sensible since there is almost no wastage. Therefore, we considered laser processing to be a promising tool to solve the

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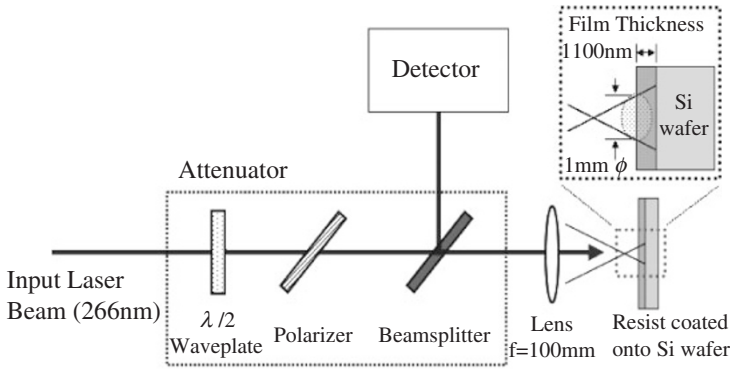

Figure 1. The diagram of 266 nm laser irradiation system for the resist removal of the resist coated onto Si wafer.

problems described above. Fujita *et al.*[14] reported that the poly acrylic type resist used for printed circuit boards was removed by irradiation with a 532 nm laser.

However, there are no reports on the diazonaphthoquinone/novolak (DNQ/novolak) resist removal process using a laser. The DNQ/novolak resist is used for semiconductors and LCD devices. There would no longer be any need to use harmful and expensive chemical solvents if the laser processing method can remove the resist. Moreover, this technology is environmentally sensible and will contribute to energy reduction. Therefore, we decided to develop a new resist removal process using a laser.

EXPERIMENTAL

Resist Preparation

We used the DNQ/novolak resist (OFPR800 from Tokyo Ohka Kogyo Co., Ltd.) in this work. It was spin-coated onto new Si wafer whose diameter is three inch by using a spin coater (ACT-300A from ACTIVE) at 2000 rpm for 30 s. It was pre-baked at 100 °C for 60 s in a hot-plate (PMC from Dataplate). The resist film thickness was 1100 nm by using a profilometry (Dektak 6M from ULVAC).

The spectral transmittance of the DNQ/novolak resist was measured to determine the wavelength of the laser. The DNQ/novolak resist was spin-coated onto a quartz plate to evaluate the characteristics in the UV region (UV-3100PC from SHIMADZU). The resist film thickness was 1100 nm by using a profilometry.

266 nm Laser Irradiation System

The fourth harmonic wavelength (266 nm) of the pulsed Nd^{3+}:YAG ($Y_3Al_5O_{12}$) laser was used in this study as the laser irradiation. Figure 1 depicts a diagram of the 266 nm laser irradiation system[15] for removal of the resist coated on the Si wafer. The resist surface was irradiated with a 266 nm beam (pulse width = 4 ns) by using an f = 100 mm lens under atmosphere or under a vacuum (0.02 Torr). The intensity of the laser beam was adjusted with an attenuator and the energy variation was examined with the laser beam separated by a beam splitter. Laser irradiation was applied with a change in the energy intensity at every irradiation to determine the relationship between the laser fluence and the removed resist film thickness.

Status of Resist Removal by XPS Measurement

The status of resist removal by laser irradiation was observed with an optical microscope and the removed resist amount was measured with a profilometry. We measured by XPS (X-ray Photoelectron Spectroscopy) to confirm the resist removal from the Si surface. XPS is made from SHIMADZU Co. AXIS ULTRA.

RESULTS AND DISCUSSION

Laser Irradiating onto the Resist

The transmittance of the resist onto a quartz plate measured by a spectrophotometer is provided in Figure 2. The resist film thickness was 1100 nm. This resist is optically transparent above 500 nm of laser light; however, its transmittance was significantly low (under 5%) below 300 nm in the UV region. Even though after many repetitions of laser pulse irradiation

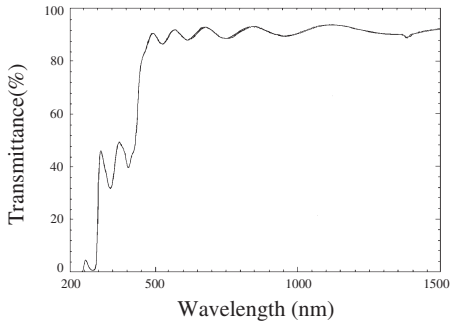

Figure 2. The transmittance of the positive-tone diazonaphthoquinone/novolak resist measured by a spectrophotometer.

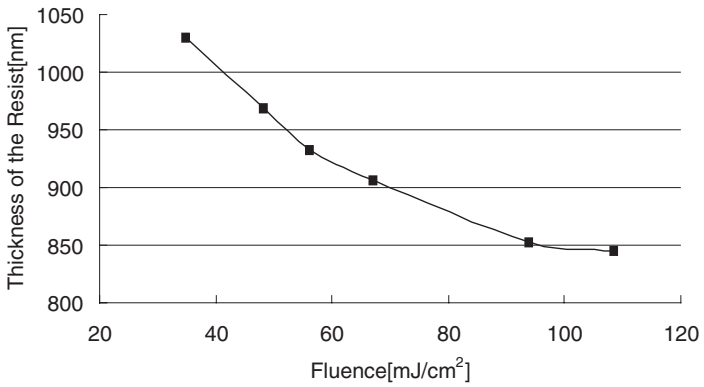

Figure 3. Relationship between the laser fluence and the residual film thickness of the resist.

onto the resist, its transmittance was not changed (under 5% transmittance) below 300 nm. Therefore, we chose 266 nm as the laser irradiation source wavelength.

The resist was irradiated with a 266 nm beam (pulse width = 4 ns) by using an f = 100 mm lens under atmosphere. Laser irradiation was applied with a change in the energy intensity at every irradiation. The relationship between the laser fluence and the residue film thickness of the resist is illustrated in Figure 3. The threshold fluence for laser ablation of the resist is measured to be about 35 mJ/cm^2. Laser ablation happens when the irradiation density of laser exceeds a threshold fluence, and less than it, it does not happen. Exceeding a threshold, the molecule combination of polymer will be cut and the molecule will jump out of the solid surface.

The removed resist amount increased with an increase of the laser fluence. It was possible to remove a 250 nm thickness by one pulse irradiation with 94 mJ/cm^2. More than five repetitions of laser pulse irradiation would thus be required since the initial thickness of the resist film was 1100 nm. Figure 4 presents an optical microscopic photograph (×50) taken after the resist was irradiated seven times with 94 mJ/cm^2 (almost 700 mJ/cm^2) under atmosphere. Laser beam was 200 μm in diameter. The original Si surface could be obtained in the region irradiated with the laser beam. From the outset, the beam shape was warped, though we made an effort to adjust it. No damage to the Si wafer was observed after laser irradiation to the Si wafer by microscope measurement. In future, we will examine whether the damage to actual device structure will generate by laser resist removal.

All the resist onto three inch Si wafer (45.58 mm^2) was removed in two minutes by laser irradiation. The resist removal method using chemicals is usually performed in one minute. So under present conditions, the resist removal rate of the process using laser is slower than that of process using chemicals. Future, laser power will be increased and we think the resist removal rate using laser will be as same as that of chemicals.

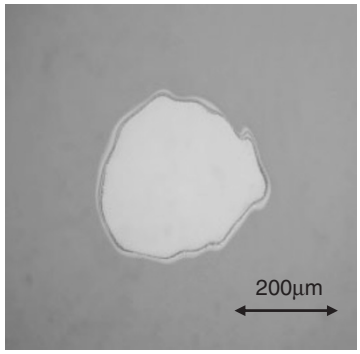

Figure 4. The optical microscopic photograph taken after the resist was irradiated seven times with 94 mJ/cm^2.

The Mechanism of Resist Removal under Laser Irradiation

The mechanism of resist removal under laser irradiation is probably caused by the thermo-chemical phenomenon with absorption of laser energy in the resist. The transmittance of the resist was significantly low (under 5%) below 300 nm, so the resist had much absorption of laser energy. It is considered that this phenomenon was caused by laser ablation. Laser ablation is the following processes. If the irradiation density of laser exceeds a threshold fluence (in this case, this value corresponds to 35 mJ/cm^2), laser energy will be exchanged for an electron, heat, light, and dynamics energy, on the solid surface. As a result, a neutral atom, a molecule, an ion, a cluster, an electron, and a photon are ejected.[16]

When the laser is condensed and the resist is irradiated, the temperature of the resist rises rapidly locally. A quick temperature rise makes the resist liquefy and evaporate rapidly. However, the temperature of the surface of the resist becomes lower than that of an

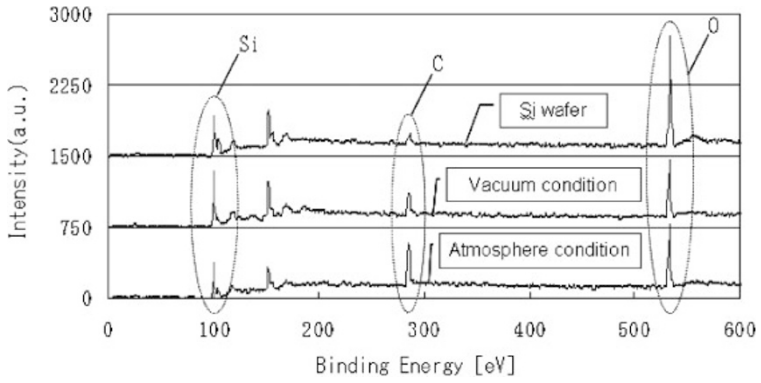

Figure 5. XPS spectra of Si wafer without resist coating, and Si wafer after removing resist by laser irradiation in the vacuum or in the atmosphere.

inside of the resist, for the evaporation heat and the radiation cooling. Since an inside of the resist becomes a higher temperature, the volume expansion takes place explosively, the resist changes as a cluster, ion and vapor, and it jumps out of the surface. The material which jumped out is again irradiated to laser, and it is re-excited and it changes to the thermal-plasma.[16]

It is said that the temperature of the plasma goes up to thousands of times and the solid is finally etched. The mechanism of the laser ablation is complicated with the character of a substance (absorption coefficient, surface state, thermal conductivity, etc.), and the character of laser light (wavelength, peak energy, pulse width, etc.) and the elucidation is still under progress.[16]

Resist Removal Status by XPS

The residual amount of carbon from the laser-irradiated surface was measured by XPS to confirm the resist removal from the Si surface. The XPS peaks of a Si wafer after removal of the resist by laser irradiation and a Si wafer without resist coating are depicted in Figure 5. The Si2p peak, C1s peak, and O1s peak were observed at 99, 285, and 530 eV. The residual amount of carbon from the Si surface removed by the laser was about 1.8 times that from the Si wafer without resist coating. Reattachment generally occurs in laser ablation when the diffusion length (the mean free path) of the laser-ablated material is short. This resist removal experiment was performed under atmosphere and the decomposed resist could have reattached at the Si surface because its diffusion length was somewhat short. Therefore, resist removal by laser irradiation was performed under a vacuum (0.02 Torr). The residual amount of carbon from the sample in this procedure was almost equivalent to that from the Si wafer without resist coating. Therefore we confirmed the resist removal from the Si surface under a vacuum by the C1s peak.

Next we will discuss the Si2p peak and O1s peak. The residual amount of silicon from the Si surface removed by the laser under a vacuum was almost as same as that from the Si wafer without resist coating by the Si2p peak. The residual amount of silicon from the Si surface removed by the laser under atmosphere was a little smaller than that from the Si wafer without resist coating. Because it is probably caused by reattachment of carbon occurring in laser ablation.

On the other hand, the residual amount of Oxide from the Si surface removed by the laser was a little smaller than that from the Si wafer without resist coating. It is considered that the O1s peak was derived from the residual resist and SiO_2 on Si. The amount of SiO_2 on Si surface varies with each Si substrate. We thought that the resist irradiated with the laser beam under a vacuum was almost removed measuring by XPS of Si2p, C1s peak.

SUMMARY

This study revealed a promising resist removal process using the fourth harmonic wave (266 nm) of a pulse Nd^{3+}:YAG laser for DNQ/novolak resist. The threshold fluence for ablation of the resist is measured to be about 35 mJ/cm^2. The removed resist amount increased with an increase in the laser energy. Resist with an initial thickness of 1100 nm could be completely ablated with no damage to the Si wafer after being irradiated with 700 mJ/cm^2. The mechanism of resist removal under laser irradiation is probably caused by the thermo-chemical phenomenon with absorption of laser energy in the resist. The resist onto three inch Si wafer was ablated in two minutes by laser. The XPS measurement indicated that the residual amount of carbon from the Si surface irradiated by a laser was 1.1 times that from a Si wafer without resist coating. This development benefits the environment since expensive and toxic chemicals are not used.

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