Removal of Positive-tone Diazonaphthoquinone/Novolak Resist Using UV Laser Irradiation

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This study developed a new method for removing positive-tone diazonaphthoquinone/novolak resist. The fourth harmonic wave ($\lambda=266\text{nm}$) of a pulse Nd^{3+} :YAG laser was used. Ablation occurred at the resist surface when it was irradiated with over $35\text{mJ}/\text{cm}^2$. The amount of removed resist increased with an increase in the laser energy, and it was possible to remove a 250nm thick resist layer by one pulse irradiation with $94\text{mJ}/\text{cm}^2$. Resist with an initial thickness of 1100nm and could be completely removed with no damage to the Si wafer after being irradiated seven times with $94\text{mJ}/\text{cm}^2$. The XPS measurement indicated that the residual amount of carbon from the Si surface irradiated by a laser under the vacuum was almost same to that from a Si wafer without resist coating. Resist removal method by laser is environmentally sound and will contribute to energy reduction.

Keywords: removing resist, DNQ/novolak resist, Nd^{3+} :YAG laser

1. Introduction

Transistors are formed on substrates in the manufacturing process of semiconductors and LCD electronic devices 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 are causing environmental damage.

Conventional resist removal from substrates in the semiconductor manufacturing process uses either single substrate oxygen plasma ashing[1] 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. The resist removal rate by the SPM process is about $0.2\mu\text{m}/\text{min}$, 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 (mono-ethanol amine + dimethylsulfoxide)[2], and it is harmful to the environment and expensive (several hundred yen/liter). The quantity consumed is also very high (several hundred cc/m^2), thus reducing the cost and environmental burden of the solvent are major issues to be resolved.

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 $1\mu\text{m}/\text{min}$ [3]. A wet ozone process using ozone

and a small amount of water was reported by Noda et al.[4,5], but the resist removal rate is about $1\mu\text{m}/\text{min}$.

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 micro-space 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 M.K.Ghantasala et al.[6]. 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 problems described above. Fujita et al.[7] reported that the polyacrylic type resist used for printed circuit boards was removed by irradiation with a 532nm laser.

However, there are no reports on the diazonaphthoquinone(DNQ)/novolak resist removal process using a laser. The DNQ/novolak resist is used for semiconductors and LCD electronic 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 sound and will contribute to energy reduction. Therefore, we decided to develop a new resist removal process using a UV laser with a wavelength of 266nm.

2.Experimental

2.1.Resist film preparation

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

2.2. UV transmittance of the resist

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).

2.3. Laser irradiation system

The fourth harmonic wave ($\lambda=266\text{nm}$) with the pulse width (4ns) of Nd^{3+} :YAG laser by using an $f=100\text{mm}$ was used in this study as the laser irradiation. Fig. 1 depicts a diagram of the 266nm laser irradiation system[8] for removal of the resist coated on the Si wafer.

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

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 intensity and the removed resist film thickness.

2.4. XPS measurement

The status of resist removal by laser irradiation was observed with an optical microscope and the amount of removed resist was measured with a film thickness meter. To confirm the resist removal from the Si surface, XPS (X-ray Photoelectron Spectroscopy) was measured with a SHIMADZU AXIS ULTRA electron spectrometer.

3.Results and Discussion

3.1. UV transmittance of the resist

The transmittance of the resist measured by a spectrophotometer is provided in Fig. 2. This resist is optically transparent above 500nm of laser light; however, its transmittance was significantly low

(under 5%) below 300nm in the UV region.

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

Even though after many repetitions of laser pulse irradiation onto the resist, its transmittance was not changed below 300nm (under 5% transmittance). Therefore, we chose 266nm as the laser irradiation source wavelength.

3.2. Relationship between laser irradiation intensity and resist film thickness

The relationship between the laser irradiation intensity and the residual resist film thickness is illustrated in Fig. 3. There was no change in the resist when it was irradiated with energy less than $35\text{mJ}/\text{cm}^2$. However, ablation occurred at the resist surface when it was irradiated at over $35\text{mJ}/\text{cm}^2$.

Fig.3 Relationship between the laser irradiation intensity and the residual film thickness of the resist.

The amount of removed resist increased with an increase of the laser energy. It was possible to remove a 250nm thickness by one pulse irradiation with $94\text{mJ}/\text{cm}^2$. More than five repetitions of laser pulse irradiation would thus be required to completely remove the film, since the initial thickness of the resist film was 1100nm.

3.3. Optical microscopic photograph

Fig. 4 presents an optical microscopic photograph taken after the resist was irradiated seven times with $94\text{mJ}/\text{cm}^2$.

Fig.4 The optical microscopic photograph taken after the resist was irradiated seven times with $94\text{mJ}/\text{cm}^2$.

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.

3.4. XPS measurement

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 during removal of the resist by laser irradiation and a Si wafer without resist coating are depicted in Fig. 5. The Si peak, C peak, and O peak were observed at 100eV, 280eV, and 520eV. The residual amount of carbon from the Si surface removed by the laser was about 1.8 times larger than that from the Si wafer without resist coating.

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

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 the vacuum (0.02Torr). The residual amount of carbon measured by XPS from the sample in this procedure was almost equivalent to that from the Si wafer without resist coating. Therefore we confirmed the complete resist removal from the Si surface under the vacuum.

Next we will discuss the Si peak and O 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.

On the other hand, the residual amount of oxide from the Si surface removed by the laser was a little less than that from the Si wafer without resist coating. It is considered that the oxide peak was not derived from the residual resist but SiO_2 on Si. The amount of SiO_2 on Si surface varies with the Si substrate. We found that the resist was completely removed by the irradiation with the laser beam under the vacuum.

4. Summary

We developed a new resist removal process using a UV laser for DNQ/novolac resist in semiconductor and LCD manufacturing. The fourth harmonic wave ($\lambda=266\text{nm}$) and the pulse width (4ns) of Nd^{3+} :YAG laser was used.

This resist was optically transparent above a wavelength of 500nm; however, its transmittance was very low below 300nm in the UV region. Therefore, we chose 266nm as the laser irradiation source wavelength.

Ablation occurred at the resist surface when it was irradiated with over $35\text{mJ}/\text{cm}^2$. The removed resist amount increased with an increase in the laser energy, and it was possible to remove a 250nm thick resist layer by one pulse irradiation with $94\text{mJ}/\text{cm}^2$. Resist with an initial thickness of 1100nm and could be completely removed with no damage to the Si wafer after being irradiated seven times with $94\text{mJ}/\text{cm}^2$.

The XPS measurement indicated that the residual amount of carbon from the Si surface irradiated by a laser in an ambient atmosphere was 1.8 times that from a Si wafer without resist coating; however, it was 1.1 times greater when irradiated in the vacuum. Reattachment may occur more easily in irradiation under atmosphere than under a vacuum since the diffusion length of the decomposed resist molecules removed by the laser is very short.

We found that the resist irradiated with the laser beam under a vacuum was completely removed.

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