Novolak Resist Removal Using Laser (266/532nm)

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Positive-tone diazonaphthoquinone/novolak resist on a 42-alloy (Fe : Ni=42:58wt%) substrate was irradiated by the second harmonic of Nd:YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) laser (532nm). The resist was removed (stripped) completely, despite the presence of hexamethyldisilane (HMDS) and the pre-bake condition of the resist. There was no apparent damage to the substrate by the laser. In contrast, this resist on a Si wafer could not be removed completely, and the substrate was occasionally damaged as well. The fourth harmonic of Nd:YAG laser (266nm) was used to irradiate the resist on the Si wafer, ablation was effective. There was no apparent damage to the substrate. This resist does not absorb the energy of the laser at 532nm because it is optically transparent (over 90%) above 500nm. However, its transmittance was very low (under 5%) below 300nm. The resist therefore absorbed the energy of the 266nm laser, and was removed (ablated). This development addresses environmental concerns because expensive and toxic chemicals are not used.

Keywords: diazonaphthoquinone/novolak resist, 42-alloy substrate, Nd:YAG laser, hexamethyldisilane

1. Introduction

Until now, high-power lasers have been used only for manufacturing processes of valuable products because such lasers have a high photon cost. However, it is undesirable to disregard environmental costs because environmental problems have become increasingly important. It becomes important to evaluate costs including not only the added value of a product, but also those costs of manufacturing processes and industrial wastes

Transistors are formed on substrates in the manufacture of semiconductor devices and LCD by several repetitions of processes such as coating, patterning, etching, resist removal, and cleaning. Conventional methods for resist removal in semiconductor manufacturing use either oxygen plasma ashing or sulfuric acid/hydrogen peroxide/deionized water (SPM). However, oxygen plasma ashing causes some problems, including damage to devices on a Si wafer as a result of the plasma charge and reduction of the plasma uniformity [1]. The SPM process removes the resist at about 0.2 $\mu\text{m}/\text{min}$, although dissolution of the resist can be accelerated by heating the solution to above 100°C. In LCD production, solution 106 (mono-ethanol amine + dimethylsulfoxide) [2] is used, but is both harmful to the environment and expensive.

Ozone ashing [3-4] is being considered as an

environmentally friendly technique to remove resist. It is necessary to attain a temperature above 250°C, so devices are occasionally damaged by the high temperature. Ozonized water processing [5-8], and wet ozone process [9-10] using ozone and a small amount of water were reported, but the removal rate was very low.

Using a laser instead of chemical solvents to remove the resist has the advantage of reducing environmental risks. A laser can focus energy on the material without physical contact, and virtually any material can be laser machined. Therefore, excimer laser micromachining using resist has been studied by several researchers [11-13]. Resist removal by laser processing would be environmentally sensible since there is almost no waste. Fujita et al. [14] reported that poly acrylic resist used for printed circuit boards could be removed by irradiation with a 532nm laser.

Before we reported that a positive-tone diazonaphthoquinone (DNQ) / novolak resist used in semiconductor and LCD manufacturing was removed by laser (266nm). [15] There are no reports of a DNQ/novolak resist removal by laser whose wavelength is 532nm. Therefore, we examined the removal of a DNQ/novolak resist on some kinds of substrate by using a laser (532nm), and this result was compared with the resist removal system using laser (266nm). We also quantitatively evaluated the

adhesion between the resist and the substrate, because adhesion is closely related to resist removal from the substrate.

2. Experimental

2.1. Resist Preparation

Positive DNQ/novolak resist (OFPR-800 from Tokyo Ohka Kogyo) was spin-coated onto a Si wafer substrate and a 42-alloy (Fe : Ni=42:58 wt%) substrate using a spin-coater (ACT-300A from ACTIVE) at 2000rpm for 30sec. The resist thickness was found to be 1050nm by profilometry (Dektak6M from ULVAC). Four substrates were prepared by spin-coating hexamethyldisilazane (HMDS) at 5000rpm for 20sec and without coating on a Si wafer and on a 42-alloy substrate. The resist was pre-baked at 80°C, 100°C, and 120°C for 60sec. The film thickness of the HMDS was measured via profilometry, but it was too thin to detect. HMDS film is monomolecular, and the film thickness was probably a few nanometers.

Spectral transmittance of the DNQ/novolak resist was measured. The DNQ/novolak resist was spin-coated onto a quartz plate to evaluate its characteristics in the UV region (200-500nm) (UV-3100PC from Shimadzu). The resist film thickness was measured as 1050nm using profilometry.

2.2. Laser Irradiation System

The fourth harmonic (266nm) and the second harmonic (532nm) of Nd:YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) laser were used for laser irradiation in this study. The resist was irradiated with a beam (pulse width=4ns) using an $f=100\text{mm}$ lens. 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. The energy intensity of the Laser irradiation was varied from 0 to 1000 mJ/cm^2 , in order to determine the relationship between the laser intensity and the residue resist film thickness.

2.3 Measurement of Adhesion between the Resist and Substrate by the SAICAS Method

The SAICAS method [16-17] was used to measure the adhesion between the resist and the substrate (Si wafer); NN-02 (from Daipura·Wintex). A single crystal diamond served as cutting blade (rake angle = 20° , relief angle = 10° , constant speed mode, horizontal speed = 300 nm/sec , vertical speed = 3 nm/sec).

3. Results and Discussion

3.1. Resist Removal from 42-Alloy Substrate by Laser Irradiation (532nm)

An optical microscope photograph (x50) of the resist on the 42-alloy substrate after irradiation with the second harmonic of Nd:YAG laser (532nm) is provided in Fig. 1 (a). This resist with HMDS was pre-baked at 80°C for 60sec. The energy applied to the resist was 133 mJ/cm^2 . The resist appeared to be completely removed (separated) from the substrate, as indicated in Fig. 1 (a). Moreover, no damage from laser irradiation was observed by visual examination under microscope. The resist could be removed from all substrates with or without HMDS treatment that were pre-baked at 80, 100, and 120°C, respectively, for 60sec. No ablation phenomenon was observed; it was resist separation.

(a)

(b)

Fig. 1. An optical microscope photograph of the resist after irradiating by laser (532nm) at an energy of 133 mJ/cm^2 : (a) 42-alloy substrate and (b) Si wafer substrate.

The resist was not stripped as a sheet of film, but rather it was split into 0.5mm square and could be removed by adhesive tape from the upper side. Pham et al. [13] reported the effects of laser ablation on many different polymers. However, we believe that this phenomenon was not ablation but resist separation from the substrate. The mechanism of resist removal under laser irradiation (532nm) is probably caused by a thermo-chemical phenomenon with laser absorption in the substrate.

Fig.2 shows transmittance of the DNQ/novolak resist measured by a spectrophotometer. The transmittance of this resist at 532nm for an 1100nm thickness is about 92%. Thus, the laser beam mostly passes through the resist and is absorbed in the substrate. It is considered that the temperature of the substrate then increases. Unfortunately, the surface temperature of the substrate could not be measured; the temperature increase rate of the substrate was evidently too rapid to measure by the usual temperature meter. The substrate absorbs 532nm laser energy, the temperature of both substrate and resist are raised continuously.

Fig 1.

Fig. 2. Transmittance of the DNQ/novolak resist measured by a spectrophotometer.

Because transmittance of this resist at 532nm is about 92%, we do not believe that photo-degradation and chain scission [17] of the resist takes place. As the DNQ/novolak resist was positive-tone, DNQ in the resist changes to carboxylic acid when exposed to a UV lamp (436nm), and the resist as a whole becomes acidic. The resist is then dissolved in alkaline developer [18]. However, this photo chemical reaction did not take place in the resist under laser irradiation (532nm), because the resist could be stripped as 0.5mm squares film.

The considerable difference in thermal expansion of the resist compare to the substrate is probably the reason that the resist was removed (separated) from the

42-alloy substrate (Fe : Ni=42:58 wt%). The thermal expansion coefficient of 42-alloy substrate is 4.5×10^{-6} to $5.3 \times 10^{-6}/K$ at 303 to 598K. The thermal expansion coefficient of the resist is 3.0×10^{-5} to $4.5 \times 10^{-5}/K$ at 303 to 598K. Thus, the thermal expansion coefficient of the resist was almost ten times greater than that of the 42-alloy substrate.

3.2. Resist Removal from Si Wafer by Laser Irradiation (532nm)

An optical microscope photograph (x50) of the resist on a Si wafer after irradiation with the second harmonic of Nd: YAG laser (532nm) is presented in Fig. 1 (b). The energy applied to the resist was 133 mJ/cm^2 . This substrate was an HMDS-treated Si wafer, and the resist was pre-baked at 80°C for 60sec. The resist could not be completely removed in this case, some resist remained despite an increase in intensity of the laser beam. Furthermore, some damage was observed on the Si wafer when the energy dose was 443 mJ/cm^2 , as indicated in Fig. 3. The damage occurred on the Si wafer as the laser energy increased. The black wrinkles resulting from laser irradiation to the resist in Fig. 3 appear to be damage to the Si substrate.

Fig. 3. An optical microscope photograph of the resist on a Si wafer after irradiating by laser (532nm) at an energy of 443 mJ/cm^2 .

It is still not clear why resist removal performance differs between substrates (Si wafer and 42-alloy substrate); however, a possible explanation is as follows. The thermal expansion coefficient of Si is $3.0 \times 10^{-6}/K$, and that of the 42-alloy substrate is

4.5×10^{-6} to 5.3×10^{-6} /K at 303 to 598K, so they are almost the same. However, the laser energy absorption of the 42-alloy substrate is much greater than that of a Si wafer. The absorption coefficient of Si is $4 \times 10^4 \text{ cm}^{-1}$ at 530nm. The absorption coefficient of the 42-alloy substrate is not known, but it is probably 6×10^5 to $9 \times 10^5 \text{ cm}^{-1}$ at 530nm, considering that of Fe and Ni [18]. The laser energy absorption of the 42-alloy substrate was about ten times greater than that of the Si wafer, and thus the temperature increase of the 42-alloy substrate due to laser irradiation was greater than that of the Si wafer. Therefore, the thermal expansion of the 42-alloy substrate was probably greater than that of the Si wafer, and the resist on the 42-alloy substrate was removed (separated).

In addition, gas bubbles generated at the interface of the resist film and the substrate are thought to be the resist removal mechanism. Gas generally occurs [19] if resist film is exposed to UV light, such as that provides by laser energy. However, the resist removal phenomenon varies significantly among different substrates, even if the same resist is used. Therefore, it is uncertain whether generation of gas bubbles is the mechanism of resist removal.

3.3. Resist Removal Width by Laser Irradiation (532nm)

Fig. 4 illustrates the relationship between the width of the resist removed after laser irradiation (532nm) and the pre-bake temperature of the resist with and without HMDS. The energy applied to the resist was 443 mJ/cm^2 . The substrate here was the 42-alloy substrate. The length (see Fig. 1(a)) of the removed resist was measured three times, and the averages of the three measurements are plotted in Fig. 4. The width of the resist without HMDS removed by laser irradiation was 1.02 to 1.03 times longer than that of the resist with HMDS at all pre-baked temperatures. The resist with HMDS was demonstrably difficult to remove.

HMDS improves resist adhesion to the substrate and allows making finer patterns on the substrate than resist without HMDS [20-23]. This resist removal mechanism is considered to be the resist separation from the substrate. So HMDS, which improves resist adhesion to the substrate is important for resist separation. The laser removal width of resist without HMDS was clearly greater than that of the resist with HMDS. In addition, the resist tends to be more easily removed by laser at lower pre-baked temperatures,

Fig. 4. Relationship between the length of the removed resist and the pre-bake temperature of the resist on a 42-alloy substrate with and without HMDS after irradiating by laser (532nm) at an energy of 443 mJ/cm^2 .

probably because the adhesion between the resist and the substrate tends to decrease at lower pre-baked temperatures.

3.4. Adhesion between the Resist and the Substrate (SAICAS Method)

The adhesion between the resist and Si wafer was evaluated by the SAICAS method. Peeling strength is generally measured by crosscut testing [24] and scratch testing [24], however, these methods do not provide a quantitative evaluation. Peeling-off testing [25] is commonly used for quantitative evaluation but it is not suitable for thin films such as a resist. The SAICAS method, however, reveals the same trends as peeling-off testing for thick films [16-17]. Fig. 5 illustrates the relationship between the peeling strength determined by the SAICAS method and the pre-bake

Fig. 5. Relationship between the peeling strength and pre-bake temperature of the resist on a Si wafer with and without HMDS.

Fig. 6. Relationship between the laser fluence (266nm) and the residual film thickness of the resist.

temperature of a resist with and without HMDS. The peeling strength of the resist with HMDS (0.15 kN/m) was thus about three times greater than that of the resist without HMDS (0.05 kN/m). The width of the resist without HMDS removed by laser irradiation was greater than that of the resist with HMDS, as described in section 3.3. In addition, the peeling strength increases as the pre-baked temperature increases since the adhesion between the resist and the substrate tends to increase at higher pre-baked temperatures.

3.5. Resist Removal from Si Wafer by Laser Irradiation (266nm)

The resist on the Si wafer was not completely removed by laser irradiation (532nm), as indicated in Fig. 1(b). Furthermore, some damage was observed on the Si wafer, as depicted in Fig. 3. The transmittance of the resist measured by a spectrophotometer (UV-3100PC from Shimadzu, 200-500nm) is provided in Fig. 2. This resist was optically transparent (over 90%) above 500nm; however, its transmittance was quite low (under 5%) below 300nm in the UV region. Therefore, 266nm was chosen as the laser irradiation source wavelength, since the resist would absorb laser energy.

The relationship between the laser fluence and the residual film thickness of the resist on a Si wafer is illustrated in Fig. 6. The resist on a Si wafer was irradiated with a 266nm beam (pulse width=4ns) using an f=100mm lens. There was no change in the resist when it was irradiated with energy less than 35 mJ/cm². However, the ablation phenomenon occurred at the resist surface when the resist was irradiated at fluence greater than 35 mJ/cm². The amount of ablated resist

increased with an increase of the laser energy. It was possible to ablate a 150nm thickness with one pulse of irradiation at 94 mJ/cm². The initial thickness of the resist film was 1050nm, and thus seven or more repetitions of laser pulse irradiation should be required at 94 mJ/cm². Fig. 7 presents an optical microscope photograph (x50) taken after resist on a Si wafer was irradiated seven times with 94 mJ/cm² (658 mJ/cm²), the original Si surface was obtained at this energy. Microscope observation revealed no apparent damage to the Si wafer.

Fig. 7. An optical microscope photograph taken after the resist on a Si wafer was irradiated seven times with 94mJ/cm² (658mJ/cm²) at a wavelength of 266nm.

The mechanism of the resist ablation with laser irradiation (266nm) can be explained as follows. The transmittance of the resist was significantly low (under 5%) below 300nm, so the resist absorbed most of the laser energy. We consider that the resist was ablated as carbon dioxide and water vapor by the thermal energy. An odor associated with resist burning was detected in this experiment, which supports our hypothesis.

Laser ablation is the following processes. If the irradiation density of laser exceeds a threshold fluence (in this case, this value corresponds to 35mJ/cm²), 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 [26]. 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 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 [26].

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 [25].

Fig. 8. Relationship between the normalized film thickness of the resist on a Si wafer and the pre-bake temperature of the resist with and without HMDS using an irradiating laser (266 nm).

Fig. 8 depicts the relationship between the normalized film thickness of the resist and the pre-bake temperature of the resist with and without HMDS. All the resists were ablated in the same way despite the existence of HMDS and the resist pre-bake condition. This mechanism was not resist removal (separation) from the substrate but laser ablation. Therefore, it is likely that these phenomena occurred similarly, even though HMDS improved the resist adhesion to the substrate.

The resist on a three-inch Si wafer (45.58mm^2) was completely removed in two minutes by laser scanning. Conventional resist removal methods that use chemicals are usually performed in one minute. Thus, the resist removal rate of the process using a laser under the present conditions is slower than that of

chemicals. Laser power will be increased in the future, and we believe that the resist removal rate using a laser will then be equivalent to those using chemicals.

4. Conclusion

(1) Positive-tone diazonaphthoquinone (DNQ)/novolak resist on a 42-alloy substrate was irradiated by the second harmonic of Nd:YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) laser (532nm). The resist appeared to be removed completely from the 42-alloy substrate. This phenomenon was not ablation but separation. Microscope observations revealed that the resist could be removed from all of the substrates despite the existence of hexamethyldisilane (HMDS) and differences in the pre-bake conditions (80, 100, and 120°C , each for 60sec) of the resist. In contrast, the resist could not be removed completely from a Si wafer substrate, and some damage due to the laser was observed.

(2) The peeling strength of the resist (SAICAS method) with HMDS treatment was about three times greater than that of the resist without HMDS. The length of the resist without HMDS removed by laser irradiation was 1.02 to 1.03 times greater than that of the resist with HMDS.

(3) We used the fourth harmonic of Nd:YAG laser (266nm). Ablation occurred at the resist on a Si wafer when it was irradiated with over $35\text{mJ}/\text{cm}^2$. The ablated resist amount increased concomitantly with an increase in the laser energy, and it was possible to ablate a 150nm thick resist layer by one pulse irradiation of $94\text{mJ}/\text{cm}^2$. Resist with an initial thickness of 1050nm could be completely ablated after being irradiated seven times with $94\text{mJ}/\text{cm}^2$. The resist on a three-inch Si wafer (45.58mm^2) was completely removed in two minutes by laser scanning.

Positive-tone DNQ/novolak resist used in semiconductor and LCD manufacturing can be removed by laser irradiation. This new development eliminates the use of expensive and environmentally hazardous chemicals in resist removal process.

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References

1. H. Tanaka, I. Aikawa, and T. Ajioka, *J. Electrochem.*

- Soc., **137** (1990) 644.
2. H. Kikuchi, *Monthly FPD Intelligence*, Chap. 4. p.169, Press Journal (1999) [in Japanese].
3. K. Omiya and Y. Kataoka, *J. Electrochem. Soc.*, **145** (1998) 4323.
4. W. I. Gardner, A. P. Baddorf, and W. M. Holber, *J. Vac. Sci. Technol. A*, **15** (1997) 1409.
5. N. Narayanswami and S. Nelson, in *Proceedings of the 3rd International Symposium on Ultra Clean Processing of Silicon Surfaces*, p. 66, Oostende, Belgium (1998).
6. S. De Gendt, P. Snee, D. M. Knotter, P. W. Mertens, M. Meuris, and M. M. Heyns, in *Proceedings of the 3rd International Symposium on Ultra Clean Processing of Silicon Surfaces*, p. 70, Oostende, Belgium (1998).
7. I. Kashkoush, R. Matthews, R. Novak, E. Brause, F. Carrillo, and B. Rajaram: *Mater. Res. Soc. Symp. Proc.*, **477** (1997) 173.
8. K. Wolke, T. Riedel, R. deGendt, R. Haug, M. M. S. Heyns and M. Meuris, in *Cleaning Technology in Semiconductor Device Manufacturing VI*, eds. R. E. Novak, J. Ruzyllo and T. Hattori, Pennington, NJ, (Electrochemical Society, 1999) *Electrochem. Soc. Proc. Ser.*, PV99-36, p. 204.
9. S. Noda, H. Horibe, M. Kuzumoto, and T. Kataoka, *J. Adv. Oxidation Tech.*, **6** (2) (2003) 132.
10. S. Noda, M. Miyamoto, H. Horibe, M. Kuzumoto and T. Kataoka, *J. Electrochem. Soc.*, **150** (2003) 537.
11. M. K. Ghantasala, J. P. Hayes, E. C. Harvey, and D. K. Sood, *J. Micromech. Microeng.*, **11** (2001) 133.
12. K. Suzuki, M. Matsuda and N. Hayashi, *Applied Surface Science*, **127** (1998) 905.
13. D. Pham, L. Tonge, J. Cao, J. Wright, M. Papiernik, E. Harvey, and D. Nicolau, *Smart Materials and Structures*, **11** (2002) 668.
14. M. Fujita, A. Yoshikado, and H. Horibe, *Photopolymer Conference*, (2004) A-11.
15. H. Horibe, T. Kamimura, and K. Yoshida, *J. Photopolym. Sci. Tech.*, **18**(2) (2005) 181.
16. I. Nishiyama, *Tosougijutsu*, **4** (1995) 123 [in Japanese].
17. I. Nishiyama, K. Teramoto: *Material Life*, **11** (1999) 124 [in Japanese].
18. T. A. Shankoff, J. H. Bruning, and R. L. Johnston, *Polym. Eng. Sci.*, **20** (1980) 1102.
19. O. Sus, *Ann*, **556** (1944) 85.
20. P. B. Johnson and R. W. Christy, *Phys. Rev. B*, **9** (1974) 5056.
21. M. Endo, A. Katsuyama, *Polymer Material Form*, **6** (1997) 353.
22. H. Maruyama, *Electronic Material*, **12** (1988) 78.
23. J. C. Marinace and R. C. McGibbon, *J. Electrochem. Soc.*, **129** (1982) 2389.
24. JIS K-6854.
25. JIS C-6481.
26. Y. Kawamura, "Laser engineering", 1st edition, S. Nakai ed., p. 91, Ohm, Tokyo (1999) [in Japanese].