Improvement in 193 nm Photoresists Performance by 172 nm VUV Curing

Kazuhiro Takeda¹, Hirokazu Asahara^{1*}, Tetsurou Hanawa^{1**}, Kouichirou Tsujita¹,
Haruki Okumura², and Nobuyuki Hishinuma³

¹*Semiconductor Leading Edge Technologies, Inc.
16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan*

²*Toray Research Center, Inc.
3-3-7 Sonoyama, Otsu, Shiga 520-8567, Japan*

³*Ushio Inc.
1194 Sazuchi, Bessho-cho, Himeji, Hyogo 671-0224, Japan*
**Present address: Rohm Corp.*

21 Saiin-mizosaki-cho, Ukyo-ku, Kyoto 615-8585, Japan
***Present address: Renesas Technology Corp.*
4-1 Mizuhara, Itami, Hyogo 664-0005, Japan

In order to make the enhancement of dry etching durability of methacrylate-based ArF resists induced by VUV curing consistent with low film shrinkage, i.e., less CD deviation, characteristics of several methacrylate-based polymers were studied. It was found that the film shrinkage mainly depended on the side chain structures and polymers containing acrylate group in main chain and norbornane lactone group in side chain portion showed dry etching resistance equal to commercially available KrF resists with lower film shrinkage than methacrylate-based ArF resists by VUV curing and suitable for the process. Curing reaction mechanism of methacrylate-based polymers were also studied using an infrared micro spectrometry with gradient shaving preparation. It was confirmed that the linkage radiolysis around carbonyl sites, mainly lactone portion of methacrylate-based ArF resist polymers induced by 15sec VUV light irradiation proceeded from the film surface to the interface with the substrate. VUV curing less than 1 minute was noticed to be effective for improvement in methacrylate-based ArF resists performance and might be met with the process tact time required for mass production phase.

Keyword: methacrylate-based ArF resist, 172nm VUV Curing, film shrinkage, dry etch resistance, u-FT-IR, gradient shaving preparation

1. Introduction

ArF lithography is the most promising patterning technology for 90-65 nm nodes. Methacrylate-based polymers have been used as the platform of ArF resists since their transparency at 193 nm is high enough for achieving required resolution. However, methacrylate-based polymers also show high

reactivity toward chain secession reaction at carbonyl's alpha position induced by the energetic particles irradiation, and as a result, dry etching resistance and CD-SEM stability of ArF resists have not been sufficient for practical use and continuous improvements are required. Resist curing by UV light irradiation before dry etching step has been

widely used in order to enhance dry etching resistance and thermal durability with i-line and KrF lithography [1-3]. In ArF lithography, it was also reported that 172nm VUV curing for methacrylate-based polymer induced improvement of dry etch resistance and reduction of resist surface roughness [4]. However, since the illumination power of excimer lamp used in the former study [4] had been too low to take effect of VUV curing, sufficient improvement in the characteristic was not obtained.

Then we investigated the effect of 172nm VUV curing on the performance of methacrylate-based ArF resists, using the newly developed excimer lamp radiating the illumination power about 7 times stronger than the former one, and confirmed that line edge roughness(LER), dry etch resistance and SEM stability of VUV cured ArF resists were effectively improved. FT-IR spectra of methacrylate-based ArF resists showed that the carbonyl sites in the resist polymers were changing rapidly with VUV irradiation [5].

Although VUV curing has many advantages as mentioned above, several problems have been still left. One of the most serious one is the deformation of the trench pattern surrounded by large area of resist. Since mask sizing deteriorates the lithographic performance of the trench pattern, improvement in VUV curing process and/or resist material has been required.

In this study, dependence of polymer structures on VUV curing effect were studied using several methacrylate-based polymers in order to make the enhancement of dry etching durability induced by VUV curing consistent with low film shrinkage, i.e., less CD deviation.

Curing reaction mechanism of methacrylate-based polymers were also studied using an infrared micro spectrometry with gradient shaving preparation at TORAY RESEARCH CENTER, Inc..

2. Experimental

2.1. Materials

In order to investigate the dependence of polymer structures on VUV curing effect, several acrylate/methacrylate copolymers with similar structure to what were used in

Fig. 1. Structures of the model polymer samples.

methacrylate-based ArF resists offered from Sumitomo Chemical Co., Ltd. and a commercially available methacrylate-based ArF resist were used in this study. Structures of the model polymer samples are shown in Fig.1.

No additives, such as PAG and quencher were included in the model polymer samples.

These samples had acid labile adamantane group and dry etching resistive lactone group in the side chain portion. Two kinds of lactones, γ-butyrolactone and norbornane lactone were used. As a reference, commercially available PHS based KrF resist protected by acetal-substituent was used.

2.2 Process Condition

VUV Cure Condition

VUV curing was carried out using Xe type dielectric barrier discharge excimer lamp unit radiating wavelength of 172 nm with Full Width Half Maximum (FWHM)=14 nm (Ushio Inc.). The wafer was set in the lamp house and the atmosphere of which was replaced by Nitrogen before irradiation. The distance from lamp to wafer was 20 mm and the illumination power on the wafer was 70 mW/cm², about 7 times stronger than what was used in the former study [4].

Sample preparation

The materials were spin-coated on 300 mm wafers to get the target thickness of 400 nm. For the evaluation of the dry etching resistance, samples were prepared on SiN film (200nm), and were applied to SiN hard mask opening etching process, which

comprised of BARC step (CHF₃/CF₄/Ar/O₂, 35sec) and SiN step (CHF₃/CF₄/Ar/O₂, 74sec), using UNITY III -305SD (Tokyo Electron Ltd.).

2.3 Measurements

The changes in film thickness of the materials induced by VUV curing were measured using an ellipsometer (KLA-Tencor ASET-F5). The changes in surface roughness of the materials induced by dry etching process were measured using AFM (Seiko Instruments SPA500). To investigate the curing reaction mechanism of methacrylate-based ArF resists, FT-IR spectrometry was used. Bulk measurements were performed using QS-312J+ (Bio-Rad) and depth direction analyses were done using the samples prepared by gradient shaving method at TORAY Research Center, Inc.. Fig.2 shows the schematic illustration of the shaving preparation. The shaving length obtained was about 300 μm and the spot size of each measurement was 20 μm . After sample preparation, FT-IR spectra were taken with Spectrum Spotlight-300 (PerkinElmer) in transmission mode. 8 to 10 spectra were obtained at intervals of about 50nm in the depth direction of the film examined.

3. Results and Discussion

3.1. Dependence of polymer structures on VUV Curing effect

Fig.3 shows the film thickness change of the ArF resist and the model polymer samples with VUV curing. The model polymer

Fig. 2. Schematic diagram of FTIR spectrometry with gradient shaving preparation.

Fig. 3. Film shrinkage of ArF resist and model polymer samples with VUV curing.

samples, M1 and M2, have γ -butyrolactone, while the model polymer samples, M3~M6, have norbornane lactone, in the side chain portion of the copolymer respectively.

These results showed that film shrinkage mainly depended upon side chain structures and polymers containing acrylate group in main chain and norbornane lactone group in side chain portion were suitable for VUV curing as concerning about film shrinkage. It was also found that 15 seconds of VUV curing led considerable film shrinkage to the model polymer samples, M1-M4. This suggests that VUV curing with high illumination power excimer lamp would meet with the process tact time required for mass production phase.

Fig. 4 shows the changes in FT-IR spectra of the model polymer sample films resulted from 4 minutes of VUV curing. All the samples examined showed three bands between 1700 cm^{-1} and 1800 cm^{-1} . Higher band around 1790 cm^{-1} can be assigned to the carbonyl site of lactone in side chain portion and two bands around 1720 cm^{-1} can be assigned to carbonyl sites of ester linkage of acrylate main chain, respectively.

With VUV curing for 4 minutes, all the samples examined showed almost the same spectra. The band assigned to a carbonyl site of lactone nearly disappeared, although two bands related to carbonyl sites of ester linkage of acrylate main chain still could be noticed. It is concluded that the lactone structures were easily decomposed by 4 minutes of VUV curing comparing with ester structures.

Fig. 4. FT-IR spectra of the model polymer sample films before and after VUV curing.

Fig.5 (a) and (b) show the changes in FT-IR spectra of model polymer sample films of M1 and M3 resulted from 15 seconds of VUV curing, respectively. It was found that the change in relative absorbance intensity of the band assigned to the carbonyl site of lactone to those of the bands assigned to carbonyl sites of ester linkage of acrylate main chain is larger in M1 than M3. As the difference between M1 and M3 is just the lactone structure, it is concluded that reactivity of polymer decomposition induced by VUV curing strongly depends upon lactone structure introduced into the resist polymer.

In this study, the effect of VUV curing on the dry etching resistance was evaluated by surface roughness measurement using AFM. Fig.6 shows the surface roughness (RMS) of plasma etched samples with and without 4 minutes of VUV curing. It was found that surface roughness of model polymer samples mainly depended on the side chain structures and polymers containing acrylate group in main chain and norbornane lactone group in side chain portion showed relatively small surface roughness, i.e., high dry etching resistance. This tendency is similar to what

Fig. 5. Changes in FTIR spectra of the model polymer sample films of M1 (a) & M3 (b) with VUV curing.

was observed in the evaluation of film shrinkage. With VUV curing for 4 minutes, surface roughness of the model polymer samples, i.e., dry etching resistance of them were improved to almost the same level of KrF resist, except for the model polymer sample M1. Decrease in the dependence of surface roughness on sample structure induced by VUV curing suggests that cured samples have almost the same structures.

Fig. 6. Bulk surface roughness of the resist and the model polymer samples after dry etching process with/without VUV curing.

It is concluded that film shrinkage mainly depended on the side chain structures and polymers containing acrylate group in main chain and norbornane lactone group in side chain portion showed dry etching resistance equal to commercially available KrF resists with lower film shrinkage than methacrylate-based ArF resists and suitable for VUV curing. Further improvement on methacrylate-based ArF resist for VUV curing would be possible by optimizing the lactone group in the side chain portion.

3.2. Structure analysis of VUV cured films by micro-FTIR spectroscopy with gradient shaving preparation.

In order to investigate the detailed mechanism of the reaction induced by the VUV curing in film, the structural change for VUV cured films were analyzed using micro FT-IR spectroscopy with gradient shaving preparation. The gradient shaving preparation which creates a physical slope to the thin film below sub-micron order is an original technology developed at TORAY Research Center, Inc. [Fig.2]. Various analyses of the depth direction are enabled by developing the information on the depth direction in the direction of the plane using this method.

Fig.7 shows the FT-IR spectra at varied depths in film of model polymer sample M1 with/without 15 seconds of VUV Curing. Fig. 8 shows the intensity ratio of the higher band assigned to the lactone site (1790cm^{-1}) to the lower band assigned to the ester linkage in main chain (1720cm^{-1}) plotted to depth in film.

Without VUV curing, FT-IR spectra and intensity ratio at varied depths in film were almost the same throughout the film. This means that film structure of the model polymer sample M1 is uniform in the depth direction. On the contrary, for VUV cured films, differences were observed in FT-IR spectra. The intensity ratio of two bands, parameter of structural change, gradually decreased from the interface with substrate to the surface. These results suggest that VUV curing led the more elimination reaction or the more decomposition reaction of lactone than those for ester linkage in the model polymer sample film and reaction sites were distributed with an inclination from the film

Fig. 7 The depth profiling spectra in film of the model polymer sample M1 before and after VUV curing.

Fig. 8 parameter of structure change, carbonyl peak intensity ratio ($1790\text{cm}^{-1}/1720\text{cm}^{-1}$) of model polymer sample 1 within film.

surface to the interface with substrate.

It was also found that the spectra near the interface of cured film differ from what was observed in the film without VUV curing. This means that the reaction induced by VUV curing proceeded to ground interface of the film within 15 seconds, and was not limited at the film surface region.

More research on the reactivity of lactone group with VUV curing in depth direction would develop the materials more suitable for VUV curing than the commercially available methacrylate-based ArF resists nowadays.

4. Conclusion

In order to make the enhancement of dry etching durability of methacrylate-based ArF resists induced by VUV curing consistence

with low film shrinkage, i.e., less CD deviation, characteristics of several methacrylate-based polymers were studied. It was found that the film shrinkage mainly depended on the side chain structures and polymers containing acrylate group in main chain and norbornane lactone group in side chain portion showed dry etching resistance equal to commercially available KrF resists with lower film shrinkage than methacrylate-based ArF resists by VUV curing and suitable for the process.

Curing reaction mechanisms of methacrylate-based polymers were also studied using an infrared micro spectrometry with gradient shaving preparation. It was confirmed that the linkage radiolysis around carbonyl sites, mainly lactone portion of methacrylate-based ArF resist polymers induced by 15sec VUV light irradiation proceeded from the film surface to the interface with the substrate. VUV curing less than 1 minute was noticed to be effective for improvement in methacrylate-based ArF resists performance and might be met with the process tact time required for mass production phase.

References

1. S.Kishimura, Y.Kimura, J.Kasai, K.Tsujita and Y.Matsui, "Improvement of Dry Etching Resistance of Resists by Deep UV Cure", *Jpn.J.Appl.Phys.*, vol.38, 1999, 250.
2. G.Becker, M.Ross, S.Wong, J.Minter, T.Marlowe and W.R.Livesay, "A Comparative Study of Resist Stabilization Techniques for Metal Etching Processing", *Proc. SPIE*, vol.3678, 1999, 1126.
3. Y.Takasu, T.Ohkuma, and Y.Todokoro, *Proc. 6th Symp. On Dry Process, Tokyo*, The Institute of Electrical Engineers of Japan, 1984, 60.
4. I.Okabe, "Examination of Surface Roughness of ArF Resist after Dry Etching", *9th Symp. of Photoactive Electronic Material*, The Society of Polymer Science, Japan, 2000.
5. H.Ashahara, T.Hanawa, W.Wakamiya, N.Endou, T.Arikado, and N.Hishinuma "Improvement in 193nm Photoresists Performance by 172nm VUV Curing", *ISSM 2002*, Japan, 2002, 203.