Evaluation of Decomposition Property of Photoresist by Oxygen Radicals Using Helium-Oxygen Mixtures

Masashi Yamamoto^{1*}, Koki Akita¹, Shiro Nagaoka²,
Hironobu Umemoto^{3,4}, and Hideo Horibe⁴

¹ Department of Electrical and Computer Engineering, National Institute of Technology,
Kagawa College, 355 Chokushi-cho, Takamatsu, Kagawa 761-8058, Japan

² Department of Electronic Systems Engineering, National Institute of Technology,
Kagawa College, 551 Kohda, Takuma-cho, Mitoyo, Kagawa 769-1192, Japan

³ Shizuoka University, Johoku, Naka, Hamamatsu, Shizuoka 432-8561, Japan

⁴ Department of Applied Chemistry and Bioengineering, Graduate School of Engineering,
Osaka City University, 3-3-138, Sugimoto-cho, Sumiyoshi, Osaka 558-8585, Japan

*m-yamamoto@t.kagawa-nct.ac.jp

We have previously demonstrated that photoresist removal rate is enhanced by adding a trace amount of O₂ to the atmosphere in which H radicals are produced from H₂ on a hot metal filament. In this case, not only H radicals but also O and OH radicals are produced. The populations of O and OH radicals are a few hundredth parts of that of H radicals, but these radicals must play important roles. It is not clear which radicals contribute more to the enhancement of the removal rate. We used He/O₂ mixtures in this study, instead of H₂/O₂, to produce O radicals without co-producing H and OH to make clear the contribution of O radicals on the removal rate. The removal rate increased slightly with increasing the O₂ additive amount when the filament was unheated. This may be caused by thermal oxidation. On the other hand, the removal rate with a hot filament decreased by the addition of O₂. In short, the removal rate is not enhanced by O radicals. The enhancement in H₂/O₂ mixtures must only be ascribed to OH radicals.

Keywords: Photoresist, Removal, Hardening, Crosslinking, O Radical, He/O₂ mixture

1. Introduction

Photoresists are widely used to fabricate fine patterns on the substrate in the manufacturing process for nano- and micro-devices. The role of photoresist is to protect the predetermined area from some processes, e.g. deposition, etching and ion implantation. Photoresists must be removed for the next step, except in some photoresists such as SU-8, which is used for MEMS process. Chemicals, which are hazardous to humans and the environment, are widely used to remove photoresists [1,2]. An enormous amount of chemicals is used to shorten the process times in batch processes. There are several problems in this technique, such as environmental impacts and costs of chemicals in photoresist removal.

To overcome the above issues, we have examined a way of photoresist removal using H radicals [3,4].

H radicals can be produced efficiently by decomposing molecular H₂ on metal hot catalysts [5-7]. The removal rate comparable to oxygen plasma has been accomplished by optimizing the removal conditions with H radicals [3]. On the other hand, as far as only H radicals are used, the removal rate is reaching a limit. To further enhance, we focused on OH radicals, whose reactivity against unsaturated hydrocarbons is high [8,9].

To produce OH radicals, we examined a way of adding a trace amount of O₂ to the atmosphere in which H radicals are produced from H₂ on metal hot filament surfaces. The removal rate was found to be a few times higher than that in pure H₂ systems [10-14]. Not only OH radicals but also O radicals can be produced in such H₂/O₂ mixed systems [5,15]. According to Umemoto et al., the density of O and OH radicals generated on an Ir filament in the

absence of photoresists is 4.2×10^{11} and 1.6×10^{10} cm^{-3} , respectively, when the filament temperature is 2100 K and O_2 gas pressure is 1.0 Pa [15]. The population of OH radicals is less than a tenth part of that of O radicals. It is not clear which radicals contribute more to the enhancement of the removal rate.

Our earlier study demonstrated that the enhancement has been observed when the gas flow rate of O_2 against that of H_2 is less than 10% [10–14]. This saturation has been ascribed to the decrease in the H radical density. To avoid the complicated interactions between radicals, we used He, instead of H_2 , in this study. Since ionization or electronic excitation is not expected on hot filament surfaces, only ground-state O radicals are expected for active species in He/ O_2 mixed systems. The density of O radicals in the presence of 0.8 Pa of pure O_2 has been measured to be as large as 2×10^{12} cm^{-3} when the Ir filament temperature is 2350 K [16].

2. Experimental

The experiment apparatus and the procedure were similar to those described elsewhere [10–14]. The He gas ($\geq 99.99\%$; Takamatsu Teisan Co.) flow rate was fixed at 100 sccm using a mass flow controller. (PE-D20; HORIBA STEC). The O_2 gas ($\geq 99.5\%$; Iwatani Sangyo Co. Ltd.) flow rate was varied between 0 and 10.0 sccm using another mass flow controller (SEC-400MK3; STEC Inc.): i.e., the amount of added oxygen (flow rate ratio of O_2 to He) was varied between 0 and 10.0%. The typical total pressure under processing was 2.7 kPa, as measured using a vacuum gauge (Baratron 622A12TAE; MKS Instruments Inc.).

As a hot filament catalyst, a resistively heated iridium filament (99.9%, 0.5 mm diameter, 500 mm long; Tanaka Precious Metals) was used: it was coiled with 11 turns, with respective coil length and diameter of 40 mm and 8 mm. The distance between the catalyst and the substrate was 20 mm. A DC power supply (EX-750L2; Takasago Ltd.) was used to heat the catalyst. The catalyst temperature at the central position, which was measured through a quartz window using a two-wavelength (0.80 and 1.05 μm) infrared radiation thermometer, was 1800 ± 10 °C. The input power was 230 W in pure H_2 system. The power in He/ O_2 mixed systems was adjusted from 145 W to 165 W; it increased with increasing the amount of added O_2 .

A positive-tone novolak photoresist (Tokyo Ohka Kogyo OFPR-800) was used in this study. It was

spin-coated onto a Si wafer using a spin coater (Kyowariken K-359 S-1) at 2.6×10^3 rpm for 20 s and was prebaked in an oven (Koyo Thermo Systems CLO-2AH) at 100 °C for 60 s. The initial photoresist film thickness was 1.2 μm , which was measured using a surface texture measuring instrument (Tokyo Seimitsu Surfcom 480A).

Changes in film thickness were evaluated using thin film interference of the photoresist [10]. By thin film interference, the peaks and valleys of the reflected light intensity were observed alternately during changes in film thickness. The film thickness can be calculated from the reflected light intensity. Green laser light from the optical source (520 nm, 150 mW; CivilLaser, Naku Technology Co. Ltd.) entered the center of the stage at an incident angle against the substrate surface of 76°. A Si photodiode (S1787-04; Hamamatsu Photonics K.K.) in reverse bias was used as a photodetector to measure the intensity of light reflected from the substrate. Its cathode was connected to +5 V DC through a 60 k Ω resistor. The reflected light intensity was ascertained by correcting the voltage between both ends of the resistor.

We heated the substrate using a substrate stage heater to evaluate the dependence of the removal rate on the substrate surface temperature. A sheath thermocouple (TK ϕ 1.6 $\times$ L300; As One) was used for the surface temperature measurement. The thermocouple was placed on the substrate surface 20 mm distant from the stage center. The temperature and film thickness were measured simultaneously at 0.2 s intervals. The removal rate was calculated from the average decrease in film thickness during 2 s.

3. Results and discussion

Figure 1 shows the removal rate of novolak photoresist as a function of the substrate surface temperature in H_2 or He atmosphere. Strictly speaking, the vertical axis of Fig. 1 is the decrease rate in film thickness, which includes the rates of not only removal by decomposition but also thermal shrinkage. However, just for simplicity, we would like to call removal rate. When the Ir filament was unheated, we can determine the removal (shrinkage) rate of photoresist. Pyrolysis must be minor below 350 °C because of the heat resistance of photoresist, which is mainly composed of a phenol resin [17]. When the filament was heated, the rate increased with increasing the temperature, although the rate in He is much smaller than that in H_2 . The increase in the removal rate when the filament is heated in the

presence of He cannot be ascribed to metastable He atoms because its energy is too high to be excited on hot filament surfaces.

It should be remembered that some volatiles are effused from photoresist films, when the film is heated by stage heater and/or radiation from the hot filament. One of the major volatiles must be propyleneglycol monomethyl ether acetate (PGMEA), which is commonly used for the solvent of photoresist, remaining in the film. These volatiles can be decomposed on hot filament surfaces to produce radical species, including H radicals, which may decompose polymer films.

In order to evaluate the effect of oxygen addition on removal of photoresist in He/O₂ mixtures, we analyzed the removal property using peak separation. Figure 2 shows the results in He and He/O₂ mixtures and peak-fitting analysis. Here, as is the case for Fig. 1, removal is used to present both decomposition and shrinkage. The filament was not heated in these cases. It is found that the removal curve is separated into 5 peaks. Magnitude of peaks 1 and 3 increased with increasing the oxygen additive amount. On the other hand, magnitude of peaks 2, 4, and 5 stayed unchanged against the oxygen addition. The increase in the magnitude of peaks 1 and 3 might be ascribed to thermo-oxidative degradation by O₂. These peaks are independent of each other, as described below.

Figure 3 shows removal rate of novolak photoresist as a function of the substrate surface temperature in He/O₂ mixtures when the filament was heated. To our surprise, the removal rate decreased significantly when oxygen was added. The cause of this decrease is probably the thermal

(a) 100 sccm He

(b) 100 sccm He, 10.0 sccm O₂

Fig. 2. The removal of novolak photoresist in He/O₂ mixtures and peak-fitting analysis. The filament is unheated. The center of peak 1 is 123 °C; peak 2 is 172 °C; peak 3 is 220 °C; peak 4 is 250 °C; peak 5 is 292 °C. The sum from peak 1 to peak 5 is also illustrated.

Fig. 1. Removal rate of novolak photoresist as a function of the substrate surface temperature in H₂ or He atmosphere.

Fig. 3. Removal rate of novolak photoresist as a function of the substrate surface temperature in He/O₂ mixtures. The filament is heated to 1800 ± 10 °C.

hardening and crosslinking. Our earlier study suggests that the photoresist is hardened thermally and its removal rate decreases with increasing the baking temperature in the air [18]. Some hardening layers might be produced on the film surfaces. The layers can prevent not only the removal of photoresist but also volatilization of the solvent. The peak at the temperature of 100-150 °C should represent the shrinkage by volatilization of the solvent. When the photoresist with surface-hardened layer is heated, the layer explodes by increasing the internal pressure induced by escaped gas from the lower layer [19]. This phenomenon is named as “popping”, which is famous problem in the removal of ion-implanted photoresist. We confirmed an alligatoring on the surface of retrieved samples from the chamber in such hydrogen-free systems, and it looked like popping. In addition, radical species produced from effused volatiles might be deactivated by added oxygen.

Umemoto et al. have measured the absolute O-radical densities not only in H₂/O₂ mixed systems but also in pure O₂ systems when the Ir catalyst temperature was less than 2350 K [15,16]. In both systems, the densities of O-radicals increase with increasing the filament temperature and the oxygen amount. The density in the present system is estimated to be about 10¹² cm⁻³. In Fig. 3, the removal rate increased slightly at 100-200 °C when the O₂ amount was 10.0 sccm. This slight increase may be ascribed to decomposition by O radicals. In any case, however, the photoresist must be decomposed little by O radicals.

When the filament was not heated, five peaks could be identified, as is shown in Fig. 2. On the other hand, when the filament was heated with an O₂ flow, particular peaks are remarkable. When the oxygen additive amount is 0.5 sccm, peaks 1 and 3 are observed. The removal rate at the temperature range of peak 1 is as large as that of pure He, while the rate depends little on the substrate temperature over 170 °C. In the case of 3.0 sccm, peak 1 becomes absent and peak 3 stands out. In the case of 10.0 sccm, peak 3 is absent but peak 5 is more remarkable. Additionally, the rate increased slightly at temperature range of 100-200 °C. The decomposition reaction at lower temperatures might play no role in reaction at higher temperatures; e.g. only peak 5 is observed despite the absence of peaks 1 and 3 when the oxygen additive amount is 10.0 sccm. Therefore, the removal mechanisms corresponding to these peaks are independent of each other.

Fig. 4. Magnitude of each peak as a function of the oxygen additive amount in He/O₂ mixtures.

Figure 4 shows the magnitude of each peak as a function of the oxygen additive amount in He/O₂ mixtures. The magnitude of peak 1 decreased at 0.5-3.0 sccm, and then increased gradually. The magnitude of peak 2 increased at 0.5-3.0 sccm, and then remained almost constant around 10 nm/min. The magnitude of peak 3 increased at 0.5-3.0 sccm, and then decreased gradually. The peak 4 remained almost constant and was a few nm/min. The magnitude of peak 5 is almost flat at 0.5-5.0 sccm, and then increased rapidly. The peaks shown in Fig. 2 were singly observed in Fig. 3. These independent behaviors suggest that the removal mechanisms of these peaks are different. Each peak would exist as a result of an independent hardening and/or crosslinking mode. The mode may be determined by a wide variety of factors, such as the substrate temperatures, including that caused by radiation heat, and the density of radicals.

4. Conclusion

Photoresist removal rate is enhanced by adding a trace amount of O₂ to the atmosphere in which H radicals are produced from H₂ on a hot metal filament. To investigate into the cause of this enhancement, we examined the relationship between O₂ additive amount and the removal performance in He/O₂ mixed systems. The removal rate increased slightly with increasing the O₂ additive amount when the filament was unheated. On the other hand, when the filament was heated, the removal rate decreased by the addition of O₂. The enhancement of removal rate in the H₂/O₂ system cannot be attributed to the removal by O radicals, but should only be caused by OH radicals.

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References

1. H. Morinaga, T. Futatsuki, T. Ohmi, E. Fuchita, M. Oda, and C. Hayashi, *J. Electrochem. Soc.*, **142** (1995) 966.
2. K. Hirose, H. Shimada, S. Shimomura, M. Onodera, and T. Ohmi, *J. Electrochem. Soc.*, **141** (1994) 192.
3. M. Yamamoto, H. Horibe, H. Umemoto, K. Takao, E. Kusano, M. Kase, and S. Tagawa, *Jpn. J. Appl. Phys.*, **48** (2009) 026503.
4. M. Yamamoto, H. Umemoto, K. Ohdaira, S. Nagaoka, T. Shikama, T. Nishiyama, and H. Horibe, *J. Photopolym. Sci. Technol.*, **28** (2015) 303.
5. H. Umemoto and M. Moridera, *J. Appl. Phys.*, **103** (2008) 034905.
6. T. W. Hickmott, *J. Chem. Phys.*, **32** (1960) 810.
7. J. N. Smith, Jr. and W. L. Fite, *J. Chem. Phys.*, **37** (1962) 898.
8. H. Sugimitsu, "Ozone no Kiso to Oyo (Basis and Application of Ozone)", Korin, Tokyo (1996) 20 (in Japanese).
9. S. Fujimura, K. Shinagawa, M. T. Suzuki, and M. Nakamura, *J. Vac. Sci. Technol. B*, **9** (1991) 357.
10. M. Yamamoto, H. Umemoto, K. Ohdaira, T. Shikama, T. Nishiyama, and H. Horibe, *Jpn. J. Appl. Phys.*, **55** (2016) 076503.
11. M. Yamamoto, K. Maejima, H. Umemoto, K. Ohdaira, T. Shikama, T. Nishiyama, and H. Horibe, *J. Photopolym. Sci. Technol.*, **29** (2016) 639.
12. M. Yamamoto, T. Taki, T. Sunada, T. Shikama, S. Nagaoka, H. Umemoto, and H. Horibe, *J. Photopolym. Sci. Technol.*, **31** (2018) 419.
13. M. Yamamoto, T. Shiroy, T. Shikama, S. Nagaoka, H. Umemoto, and H. Horibe, *J. Photopolym. Sci. Technol.*, **32** (2019) 609.
14. M. Yamamoto, S. Nagaoka, H. Umemoto, K. Ohdaira, T. Nishiyama, and H. Horibe, *Int. J. Polym. Sci.*, **2017** (2017) 2983042.
15. H. Umemoto, H. Kusanagi, K. Nishimura, and M. Ushijima, *Thin Solid Films*, **517** (2009) 3446.
16. H. Umemoto and H. Kusanagi, *J. Phys. D: Appl. Phys.*, **41** (2008) 225505.
17. Ed. Osaka Municipal Technical Research Institute and Japan Society of Plastics Technology, "Plastic Dokuhon", Plastic Age, Tokyo, 1985, 14th ed (in Japanese).
18. T. Maruoka, Y. Goto, M. Yamamoto, H. Horibe, E. Kusano, K. Takao, and S. Tagawa, *J. Photopolym. Sci. Technol.*, **22** (2009) 325.
19. T. Miura, M. Kekura, H. Horibe, and M. Yamamoto, *J. Photopolym. Sci. Technol.*, **21** (2008) 311.