Effects of Nitrogen Dilution on the Photoresist Removal Rate by Hydrogen Radicals

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We have previously demonstrated that photoresist removal rate comparable to oxygen plasma is accomplished by optimizing the removal conditions with H radicals produced on hot metal filament surfaces from H₂/N₂ mixtures (H₂:N₂ = 10:90 vol%). N₂ gas was used to dilute the concentration of the H₂ gas and to reduce the risk of explosion. However, it is not clear how the dilution of H₂ by N₂ affects the removal rate. In this paper, we examined the relationship between the removal rate and the H₂ content; the flow rate ratio of H₂ to H₂+N₂. The removal rate increased with increasing the H₂ content. In addition, the removal rate increased with increasing the substrate temperature according to an Arrhenius equation, when the H₂ content was over 90%. However, below 60%, the removal rate decreased with increasing the temperature over 230 ± 5 °C. Denaturation of photoresist, e.g. hardening and/or crosslinking, may be induced by substrate heating when the H-radical density is low. The removal rate decreases not only by the deficiency of H radicals but also by the denaturation of films in H₂/N₂ mixed systems.

Keywords: Photoresist, Decomposition, H Radical, H₂/N₂ mixture

1. Introduction

Photoresists are indispensable materials for fabricating fine patterns on the substrate in micro- and nano-electronics device manufacturing. The role of photoresist is to protect the predetermined area from some processes, e.g. deposition, etching, and ion implantation. In general, photoresists must be removed for the next step. Chemicals, which are hazardous to humans and the environment, are often used to remove photoresists [1,2]. There are several problems such as environmental impacts and costs of chemicals in photoresist removal, because an enormous amount of chemicals is necessary to shorten the batch process times.

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

molecular H₂ on metal hot filament surfaces [5-7]. Our earlier study demonstrated that the removal rate comparable to oxygen plasma is accomplished by optimizing the removal conditions in H₂/N₂ mixed systems (H₂:N₂ = 10:90 vol%) [3]. N₂ gas was used to dilute the concentration of the H₂ gas and to reduce the risk of explosion. However, the relationship between the removal rate and the dilution ratio has not been examined enough. In this paper, we show the effect of the dilution on the removal rate in H₂/N₂ mixed systems.

2. Experimental

The experiment apparatus and the procedure were similar to those described elsewhere [8-12]. The H₂ gas (≥99.99%; Takamatsu Teisan Co.) flow rate was varied between 0 and 50 sccm using a mass

flow controller (PE-D20; HORIBA STEC). The N_2 gas ($\geq 99.995\%$; Takamatsu Teisan Co.) flow rate was also varied between 0 and 50 sccm using another mass flow controller (PE-D20; HORIBA STEC). The H_2 content, the dilution ratio by N_2 , was calculated by dividing H_2 flow rate by H_2+N_2 flow rate. This content was varied between 0 and 100%. 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 wire (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 (T_C) 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 $1670 \pm 10^\circ\text{C}$. Table 1 shows the relationship between DC power and T_C in various H_2 content atmosphere.

Table 1. The relationship between DC power and T_C in various H_2 content atmosphere.

H_2 content [%]	DC power [W]	T_C [$^\circ\text{C}$]
100	169	1669
90	163	1669
80	150	1670
60	130	1670
40	116	1672
20	100	1670
10	96	1671
0	91	1670

A positive-tone novolak photoresist (OFPR-800; Tokyo Ohka Kogyo) was used in this study. It was spin-coated onto a Si wafer using a spin coater (K-359 S-1; Kyowariken) at 2.6×10^3 rpm for 20 s and was prebaked in an oven (CLO-2AH; Koyo Thermo Systems) at 100°C for 60 s. The initial photoresist film thickness was 1.2 μm , which was measured using a surface texture measuring instrument (Surfcom 480A; Tokyo Seimitsu).

Changes in film thickness were evaluated using thin film interference of the photoresist [8]. 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; CiviLaser, 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 whether or not 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 calibrating 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 (T_{surf}). 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. Initial T_{surf} was 25°C . Averaged rate of T_{surf} increase was $8.2^\circ\text{C}/\text{min}$. T_{surf} must be determined by some factors, such as not only the stage heater but also the radiation heat, when the Ir filament is heated. The temperature and film thickness were measured simultaneously at 0.2 s intervals. The removal rate was calculated from the average 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 pure H_2 or N_2 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 heating the filament in H_2 atmosphere, the removal rate increased drastically. This can easily be attributed to the removal by H radicals produced from H_2 . The

Fig. 1. Removal rate of novolak photoresist as a function of the substrate surface temperature in H_2 or N_2 atmosphere.

substrate temperature dependence was Arrhenius-like, which is consistent with our former observation [13,14]. In N₂ atmosphere, on the other hand, the substrate temperature dependence is less remarkable. The production of N radicals on hot filament surfaces is inefficient, as will be discussed below [15,16]. The decomposition of polymers by N radicals cannot be expected.

In N₂ atmospheres, although small, decrease in film thickness could be observed even when the filament was not heated. This should be attributed to the shrinkage 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]. The shrinkage at the temperature of 100-150 °C must be caused by volatilization of the solvent, which is remaining in the photoresist film. Boiling point of propylene glycol monomethyl ether acetate, which is commonly used for the solvent, is 146 °C under standard atmospheric pressure. This boiling point, of course, decreases under low pressures. Shrinkage may also be caused by the thermal hardening and crosslinking. Our earlier study shows that the photoresist is hardened thermally and its removal rate decreases with increasing baking temperature in air [18]. The hardening and/or crosslinking may take place.

From the data when the Ir filament was unheated, we can determine the shrinkage rate. Our earlier study shows that the shrinkage almost saturates within 1 min at temperatures lower than 250 °C and increases with increasing the baking temperature in air [3]. The decrease in the film thickness for 1 min at 250 °C was 0.24 μm (decrease ratio 20%) and then the film remained constant in thickness even when baking for 60 min. When the temperature reached 250 °C under N₂ atmosphere (Fig. 1), the decrease without a hot filament was 0.18 μm (18%). Therefore, the decrease must be ascribed to the shrinkage of the photoresist film since the decrease ratio was similar.

Although minor, the decrease rate in thickness is larger when the filament is heated in N₂ atmosphere. It is possible to produce N radicals from N₂ on a hot catalyst without coproducing other active species. The density has been measured to be $1.2 \times 10^{11} \text{ cm}^{-3}$ when the W filament temperature is $2.8 \times 10^3 \text{ K}$ and the N₂ pressure is 100 Pa [15,16]. At $2.0 \times 10^3 \text{ K}$, the density is estimated to be $3 \times 10^7 \text{ cm}^{-3}$. This value is negligibly small compared to the typical density of H radicals, 10^{14} cm^{-3} at $2.0 \times 10^3 \text{ K}$ [19]. The situation must be similar when Ir is used instead of W. N radicals (N•) cannot be obtained by the gas-

phase reaction between N₂ and an H radical (H•); N₂ + H• → NH + N•, either. This reaction is too endothermic to take place [20]. Therefore, we may conclude that N radicals cannot influence on the photoresist removal.

Even in pure N₂ atmosphere, when the filament is heated, photoresist may be decomposed by radicals, including H radicals, which are produced by catalytic decomposition of volatiles effused from photoresists. One of the candidates of such volatiles is the solvent for polymers. Another possibility is the shrinkage of photoresist film induced by heat radiation from the hot filament. These can be regarded as the factor of the increase in the removal rate. Incidentally, in air, the decrease for 1 min at 350 °C was 0.35 μm (decrease ratio 29%) and then the film thickness decreased at the rate of about 20 nm/min for 9 min (45%) [3]. The thickness decreased at the rate of about 4 nm/min from 10 min to at least 60 min (60% at 60 min). This rate was probably caused by the decomposition but very small. This small rate should be ascribed to the enhancement of the heat resistance on photoresist by the thermal hardening and crosslinking [18]. In Fig. 1, the decrease in the film thickness, when the temperature reached 350 °C using heated Ir under N₂ atmosphere, was 0.64 μm; the decrease ratio of the film thickness was 66%. The time the temperature takes to reach that temperature was 32.8 min. The decrease ratio in Ref [3] corresponding to this condition is about 52% and is 14% lower than that using heated Ir. On the other hand, when using unheated Ir, the temperature reached 340 °C at 38.1 min. The decrease in the film thickness was 0.27 μm (27%). Even if the temperature was 350 °C, the decrease must not be too different. The decrease ratio in Ref [3] is about 57% and is 30% larger than that using unheated Ir. The thermal hardening and crosslinking should be regarded as the factor of the decrease in the removal rate since they can cause this small decrease ratio. The decomposition and the hardening can simultaneously take place when using a hot filament. All of them are fortuitously balanced, so the removal rate might become constant against the substrate surface temperature. We will discuss this possibility later.

Figure 2 shows the removal rate of novolak photoresist as a function of the substrate surface temperature in H₂/N₂ mixtures. Here, as is the case for Fig. 1, *removal* is used to present both *decomposition* and *shrinkage*. H₂ content is the flow rate ratio of H₂ to H₂+N₂. The removal rate

decreased with decreasing in H_2 content, as expected, but the removal rate at H_2 content of 90% was very similar to that in the pure H_2 system. Both removal rates increased with increasing the substrate temperature, according to an Arrhenius equation. Therefore, the dilution by N_2 might not influence on the photoresist removal at these contents. Remarkably, when H_2 content was between 10 and 60%, the removal rates increased with increasing the temperature up to $230 \pm 5^\circ\text{C}$, but decreased over that temperature.

The decrease in removal rate is to be expected when decreasing H_2 content, because the population of H radicals must decrease with decreasing that of H_2 . The problem is the substrate surface temperature dependence at low H_2 contents. The temperature of $230 \pm 5^\circ\text{C}$, at which the change in slope of the plot is observed, may be related to hardening and/or crosslinking onset temperature of photoresist polymer. Base polymer of novolak photoresists has benzene rings in its main chain. The reaction between benzene rings and H radicals must be the rate-determining step in the removal processes [13, 14]. According to the theoretical approach by Umemoto et al. [21], at least two H radicals must be involved in the decomposition of novolak. After the addition of two H radicals to the benzene ring, the ring opening becomes energetically possible. Polymer chains can be decomposed continuously rather than hardening and crosslinking if the population of H radical is enough. However, if H radical is deficient, polymer is activated insufficiently to produce some active sites, which cannot be starting points of decomposition. These

active sites may be able to bind each other at high substrate temperatures and the decomposition is prevented.

Figure 3 shows the removal rate of novolak photoresist as a function of the square root of the partial pressure of H_2 . The removal rate increases in direct proportion to the H-radical density and its density increases in direct proportion to the square root of H_2 pressure [13,19]. Namely, the removal rate must bear a direct relation to the square root of H_2 pressure. At the temperature of 200°C and 225°C , we confirmed the proportional relationship between the removal rate and the square root of the H_2 pressure, predictably. The H radical density would be enough to decompose photoresist at these temperatures. However, at 250°C , the removal rate bore a non-linear relationship with the square root of H_2 pressure. As shown in Fig. 2, the proportional relationship should be true at H_2 content of 90 and 100% because these removal rates obeyed the Arrhenius equation. Accordingly, we consider that the dashed line connecting the plots (a), (b), and (c), shown in Fig. 3, is proper relationship. The removal rate becomes smaller than the expected when the square root of H_2 pressure is between 0.51 and $1.46\text{ kPa}^{1/2}$. This decrease may be ascribed not only to the decrease in H radical density but also to the denaturation of photoresist.

4. Conclusion

In this study, we examined the relationship between the removal rate and the H_2 content, which is the flow rate ratio of H_2 to H_2+N_2 . The removal rate increased with increasing in the H_2 content. The

Fig. 2. Removal rate of novolak photoresist as a function of the substrate surface temperature in H_2/N_2 mixtures. H_2 content is the flow rate ratio of H_2 to H_2+N_2 . T_C was heated to $1670 \pm 10^\circ\text{C}$.

Fig. 3. Removal rate of novolak photoresist as a function of the square root of partial pressure of H_2 . T_C was $1670 \pm 10^\circ\text{C}$. The partial pressure was calculated by multiplying H_2 content by the typical total pressure.

removal rate in pure N₂ systems was much smaller than that in pure H₂ systems, when using a hot filament. We confirmed that N radicals do not influence on the photoresist removal.

The removal rate saturated when the H₂ content was more than 90%. The H radical density would be enough to decompose photoresist at these contents. Under such conditions, the removal rates increased with increasing the substrate temperature, according to an Arrhenius equation.

When H₂ content was between 10 and 60%, the removal rate decreased with the increase in the substrate surface temperature over 230 ± 5 °C. H radicals must become deficient due to the decrease in the H₂ content. Denaturation of photoresist, e.g. hardening and/or crosslinking, may perhaps be induced by the increase in the temperature and the deficiency in H radicals.

We have previously accomplished the removal rate comparable to oxygen plasma in H₂/N₂ mixed systems, with the H₂ content of 10%. The removal rate may increase more at higher H₂ contents, such as more than 90%. On the other hand, content below 10% is desired to reduce the risk of explosion of exhaust gas. Both requirements, high removal rate and safety, can be satisfied by keeping the low pressure and high contents in the process chamber and by diluting the exhaust gas at the exit-side.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number 19K04543.

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