We examined an environmentally friendly photoresist removal method using radicals produced by decomposing mixtures of hydrogen and oxygen on a hot iridium catalyst. We earlier reported that the decomposition of photoresists was hastened by adding oxygen gas to a hydrogen flow using a tungsten hot-wire catalyst. The rate increased with the oxygen additive amount up to about 1.0% and then decreased gradually. The decrease is caused by the catalytic poisoning of O atoms on the catalyst surface because of its poor oxidation resistance. In present study, we show that oxygen addition without catalytic poisoning is effective to increase the decomposition rate. The poisoning can be avoided by using an Ir catalyst. The decomposition rate increased with the substrate temperature. The rate also increased rapidly with increasing amounts of added oxygen to 1.0% and then the increase became more gradual. OH radicals must play an important role to hasten the decomposition reactions.

**Keywords:** Photoresist, Removal, Radical, Oxygen addition, Ir hot-wire catalyst

1. Introduction

Photoresists play an important role in photolithography processes for manufacturing electronic devices. Photoresists must eventually be removed. Conventional methods use chemicals or oxygen plasma to remove photoresists [1-6]. Chemicals are not only environmentally unfriendly but also expensive. Additionally, they require a massive cost for disposal. Oxygen plasma might degrade device performance because of charged particles in the plasma.

Our earlier study demonstrated that a positive-tone novolak photoresist was removed by using H radicals, which are generated by decomposing molecular hydrogen on metal hot-wire catalysts, as fast as oxygen plasma [7,8]. This removal method is effective to resolve some environmental and industrial difficulties associated with conventional methods. However, a major issue related to the method is its smaller removal rate than chemicals. As far as H radicals are used, there are limitations on improvement of the rate.

To overcome the limitation, we examined a way of adding a trace amount of oxygen gas to the atmosphere in which H radicals are produced. According to Umemoto and Moridera [9], not only H radicals but also O and OH radicals can be produced by activating mixtures of hydrogen and oxygen on a tungsten hot-wire surfaces in the absence of photoresists. Generally speaking, OH radicals are highly reactive and thereby may improve the rate [10,11]. However, the population of O and OH radicals generated on a hot wire is one-hundredth that of H radicals. It was unclear if such
a trace amount of radicals can increase photoresist removal rate. We earlier reported that the decomposition of photoresists and some polymers was hastened by the way of adding oxygen gas using a tungsten hot-wire catalyst [12-14]. The rate increased with the oxygen additive amount up to an optimal amount (about 1.0%: the flow rate ratio of oxygen to hydrogen) and then decreased gradually. When exceeding 2.2%, the rate was smaller than that in the pure hydrogen system. This increase can easily be explained by the removal by OH radicals. This decrease may be due to the decrease in the production rate of H radicals by the catalytic poisoning of O atoms on the catalyst surface [9]. The added oxygen amount is limited to a small amount when using a W catalyst because of its poor oxidation resistance.

Umemoto et al. reported that OH radicals can be produced without decreasing H-radical density, since the poisoning can be avoided by using an Ir catalyst [15]. However, oxygen additive amounts were limited to a small range of 0-1.2% in their study. Our earlier study demonstrated that the rate at the oxygen amount of 10.0% can be larger than that without oxygen using an Ir catalyst [16]. In pure hydrogen system, the removal rate using an Ir catalyst was comparable to that using W. However, these results contain not only rate of decomposition by radicals but also rates induced by thermal shrinking, cross-linking, and thermal decomposition. In present study, we demonstrate that oxygen addition is effective to increase the decomposition rate without catalytic poisoning by radicals produced on a hot Ir catalyst.

2. Experimental

The experiment apparatus and the procedure were similar to those described elsewhere [8,12-14,16]. The hydrogen gas (≥99.99%; Air Liquide Japan) flow rate was fixed at 100 sccm using a mass flow controller (SEC-400MK2; STEC Inc.). The oxygen gas (≥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 O2 to H2) 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-wire 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 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 fixed at 1.6 × 10³ °C when the input power was 1.7 × 10² W.

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 × 10³ 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 [8,12-14,16]. 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 kΩ 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 (Tsurf). For surface temperature measurements, a small thermocouple (ST-56 K-CA 0200 N-N; RKC Instrument Inc.) was used to avoid disturbing the measurements. The thermocouple was placed on the substrate surface 5 mm distant from the stage center. The temperature and film thickness were measured simultaneously at 0.5 s intervals. The removal rate was calculated from the average decrease in film thickness during 5 s.

3. Results and discussion

Figure 1 presents the removal rate in hydrogen and hydrogen-oxygen mixture system against the substrate surface temperature. The increase in the
rate at temperatures of 120-210 °C presumably reflects a decrease in film thickness induced by thermal shrinking and cross-linking of the photoresist film whether the catalyst was heated or not. The rate when the catalyst was not heated was nearly constant at temperatures of 210-300 °C: it was about 20-30 nm/min. Tendency of the decrease was nearly independent of the added oxygen amount. The cause of this decrease will be discussed later. The rate when using a hot catalyst increases against temperature after shrinking in all cases, although each increment differed. As is distinctively shown at temperatures over 125 °C in the figures, the rate increased with increase in the oxygen additive amount.

The shrinking when the wire is not heated can consist of at least two parts. One might be caused by vaporization of residual solvent in the film. This shrinking must finish at about 150 °C because the boiling point of propylene glycol monomethyl ether acetate, which is often used as a solvent for general photoresist, is 146 °C. The other might be caused by the cross-linking of the neighboring chain of novolak resin because it is categorized as a main chain cross-linking polymer [17]. We reported that the hardness of the film increased at temperatures over 150 °C and that the thickness significantly decreased at temperatures over 300 °C under one-atmospheric air [7,18]. Additionally, the decrease in the film thickness by shrinking was saturated within 1 min at temperatures less than 250 °C, but the decrease by thermal decomposition continued at temperatures exceeding 300 °C [7]. Thermal decomposition by molecular oxygen starts at about 300 °C and the film carbonizes. Polymers are pyrolyzed even in the absence of oxygen. In present study, fortunately, the decomposition by radicals is major rather than those thermal decomposition. The removal rate with heated Ir is much larger than that with unheated Ir at temperatures over 150 °C, as shown in Fig. 1.

In the case of using the unheated catalyst, the rates of thermal shrinking, cross-linking, and decomposition under hydrogen or hydrogen-oxygen mixtures can be evaluated because of the absence of radicals. These rates are contained in the rates when using a hot catalyst. As will be shown later, the data in Figs. 1(a)-1(c) show that the decomposition rate by radicals can be obtained by subtracting the removal rate when the catalyst is not heated.

We use Fig. 1(c) as an example to explain calculation procedure of the decomposition rate. In Fig. 2, curves approximated to a set of data points
(1) Generate numerical data for fitting curve to data points when the catalyst is not heated; (2) Generate numerical data for fitting curve to data points when the catalyst is heated; (3) Subtract the curve (1) from the curve (2). Results show more clearly that the decomposition rate (curve (3)) increases against temperature.

Figure 3 presents the dependence of the decomposition rate on the amount of added oxygen at temperatures ($T_{surf}$) of 150, 200, and 250 °C. The rate increased with increasing amounts of added oxygen to 1.0%; it then increased more gradually, unlike the case of a W catalyst. The maximum rate at 250 °C was 0.22 μm/min, which is 1.5 times higher than that in the pure hydrogen system; that at 200 °C was 0.092 μm/min, which is 2.6 times higher. The increment rate at 150 °C cannot be calculated because the rate is nearly zero under pure hydrogen system; i.e., the increment rate is infinity. We found that the oxygen addition results in a clear increase in the rate at low temperatures rather than high temperatures.

In the case of a W catalyst, we reported that removal rate increased with the oxygen additive amount up to about 1.0% and then decreased gradually [12-14]. Our earlier report demonstrated that the removal rate of a novolak photoresist increases in proportion to the H-radical density [19]. The rate of removal by H radicals at 1.0% must be much smaller than that in the pure hydrogen system because the H-radical density was reduced to less than one-half that without oxygen [9]. However, O and OH radicals are also produced with H radicals when oxygen is added. The densities of O and OH radicals were infinitesimal and about one-hundredth that of H radicals. Contribution of O radicals to the removal processes must be minor because they are not only less abundant, but also less reactive than H radicals [4,20]. The reactivity of OH radicals, on the other hand, is much higher [10,11]. Although the population of OH radicals is also small, the contribution must be as large as that for H radicals. Therefore, this increase in the decomposition rate can be explained by the decomposition by OH radicals. The decrease at higher oxygen amounts may be due to the decrease in the H-radical density by the catalytic poisoning of O atoms on the catalyst surface [9].

Umemoto et al. have measured the absolute radical densities in hydrogen/oxygen mixed systems when the Ir catalyst temperature was less than 2200 K [15]. Oxygen additive amounts examined in their study were varied within a narrow range of 0-1.2%, while the H$_2$ pressure was kept at 17 Pa. The H-radical density was independent of the added oxygen amount, and its absolute value was comparable to that for tungsten in the absence of oxygen. Both the O- and OH-radical densities increased with increasing oxygen additive amount at least up to 1.2%. Both densities were about one-hundredth of that of H radicals. In their measurements, since the conditions were different from present study (e.g., pressures, oxygen amounts and presence of photoresist substrate), quantitative analyses are difficult, but qualitative discussion may still be possible.

The H-radical density generated on an Ir catalyst may not decrease at the added oxygen amounts from 1.2 to 10.0% because no peaks of the rate are observed in Fig. 3, unlike the case of a W catalyst [12-14]. The O-radical density may still increase.
with the oxygen amount over 1.2%. However, the O radicals may have little influence on the decomposition because of its low reactivity. The density of OH radicals may increase with the added oxygen amounts over 1.2% because the decomposition rate shown in Fig. 3 still increases over 1.0%.

We earlier reported the removal rates by H radicals of polymers with different structures [21, 22]. These results showed that the rates of polymers with benzene rings are small. Novolak photoresists are mainly composed of \( mp \)-cresol resin, which 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. According to Umemoto et al. [23], at least two H atoms must be involved in the decomposition of novolak theoretically. After the addition of two H atoms to the benzene ring, the ring opening becomes energetically possible. We infer that OH radicals must play more important role than H radicals in the decomposition reactions to produce sites for the radical addition.

The density of OH-radicals is probably one or two orders of magnitude smaller than that of H-radicals, nonetheless, we found an astonishing fact that the rate with this small amount of OH radicals is a few times higher than that in pure hydrogen system. Production of highly dense OH radicals may bring about a drastic improvement in decomposition rate.

4. Conclusion
The relations between the degradability and the amounts of added oxygen for novolak photoresist were examined in oxygen-hydrogen mixtures without catalytic poisoning by using a hot Ir catalyst. We evaluated oxygen addition effectiveness for increasing the decomposition rate excluding thermal shrinking, cross-linking, and thermal decomposition of photoresist.

The decomposition rate by radicals increases against substrate temperature. The rate increased rapidly with increasing amounts of added oxygen to 1.0%; it then increased gradually, unlike the case of a W catalyst. The oxygen addition results in a clear increase in the rate at low substrate temperatures rather than high temperatures. The increase might be ascribed to decomposition hastened by OH radicals.

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