Removal of Polymers for KrF and ArF Photoresist Using Hydrogen Radicals Containing a Small Amount of Oxidizing Radicals

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Photoresist removal method using hydrogen radicals, which are produced on a tungsten hot-wire catalyst, is effective to resolve some environmental and industrial problems in conventional methods for the fabrication of electronic devices. However, its removal rate is not as good as that of the conventional ones. We have previously described that the removal rate of a positive-tone novolac photoresist is enhanced by the addition of a small amount of oxygen gas to the atmosphere, in which hydrogen radicals are produced. Oxidizing radicals, such as OH and O radicals, can be produced together with H radicals. In present study, we examined the effects of oxygen addition on base polymers of KrF and ArF photoresists: the former is poly(vinyl phenol) (PVP), and the latter is poly(methyl methacrylate) (PMMA). Effects of oxygen addition on PVP was confirmed, as was found for the novolac photoresist. On the other hand, the effects on PMMA were different from the cases of the novolac photoresist and PVP. Results were ascribed to the presence or absence of benzene rings, the properties of polymers and the reactivity of oxidizing radicals.

Keywords: Photoresist, Removal, Hydrogen radical, Oxygen addition, Environment

1. Introduction

Photoresists, which are important materials supporting photolithography processes used for electronic device fabrication, are used to protect substrate surfaces from etching, thin-film deposition, and ion-implantation. Photoresists must be removed for subsequent processes. Most commonly, that is done with chemicals [1,2]. Although such chemicals are harmful, large amounts are unfortunately used in the processes. Actually, photoresist removal presents several difficulties that include adverse environmental effects and costs of chemicals. Oxygen plasma ashing [3-6] is one removal method that uses no chemicals, but the ashing engenders the possibility of destabilizing the device performance because of charged particles in the plasma.

To alleviate the difficulties described above, we have studied removal methods using hydrogen radicals [7-12]. Hydrogen radicals are produced by decomposing molecular hydrogen on a metal hot-wire catalyst [13,14]. A major issue related to removal using hydrogen radicals is the lower removal rate than that of the chemicals. From an earlier study, we reported that the removal rate of a positive-tone novolac photoresist is enhanced by the addition of a small amount of oxygen gas to the atmosphere, in which hydrogen radicals are produced [15-17].

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In actual photolithography processing, novolac photoresists (i/g-line) are used, but also KrF and ArF photoresists are usually used. Poly(vinyl phenol) (PVP), which is protected by the tert-butoxycarbonyl group, is used as a base polymer of a KrF photoresist. Poly(methyl methacrylate) (PMMA), of which the side-chain end is replaced by an adamantyl group, is used as the base polymer of a ArF photoresist. In this study, we examined the removal performance of PVP and PMMA using hydrogen radicals containing a small amount of oxidizing radicals.

2. Experimental

The experimental apparatus and the procedure were similar to those described elsewhere [12, 15-17]. The flow rate of hydrogen gas (≥99.99%; Air Liquide Japan Ltd.) was fixed at 100 sccm using a mass flow controller (SEC-400MK2; STEC Inc.). The oxygen gas (≥99.5%; Iwatani Sangoy Co. Ltd.) flow rate was varied between 0 and 2.0 sccm using another mass flow controller (SEC-400MK3; STEC Inc.). In other words, the amount of oxygen addition, the flow rate ratio of O₂ to H₂, was varied between 0 and 2.0%. The typical total pressure under processing was 20 Pa, as measured using a vacuum gauge (Baratoron 622A12TAE; MKS Instruments Inc.). A resistively heated tungsten wire (99.95%, 0.5 mm diameter, 500 mm long; The Nilaco Corp.) was used as a hot-wire catalyst. This wire was coiled with 11 turns; its respective coil length and diameter were 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 temperature of the catalyst at the central position was measured through a quartz window using a two-wavelength (0.80 and 1.05 μm) infrared radiation thermometer (ISR12-L0; Impac Electronic GmbH). It was 1.6 × 10³ °C when the input power was 1.9 × 10² W.

A positive-tone novolac photoresist (OFPR-800; Tokyo Ohka Kogyo Co. Ltd.) was used as an i/g-line photoresist. It was spin-coated onto a Si-wafer using a spin coater (Spinner-1H-III; Kyoei Sangoy Co. Ltd.) at 2.60 × 10³ rpm for 24 s. As base polymers of the KrF and ArF photoresists, PVP (341584, Mw=89,000–98,000; Sigma-Aldrich Corp. LLC) and PMMA (200336, average Mw=15,000; Sigma-Aldrich Corp. LLC) were used, respectively. The PVP and PMMA were dissolved in ethyl lactate (Wako first Grade; Wako Pure Chemical Inds., Ltd.). The solid content concentration of PVP was 12 wt%; that of PMMA was 10 wt%. The PVP solution was spin-coated at 2.00 × 10³ rpm for 24 s. The PMMA solution was spin-coated at 1.00 × 10³ rpm for 24 s. These substrates were then pre-baked in an oven (CLO-2AH; Koyo Thermo Systems Co., Ltd.) at 100 °C for 60 s. Each film thickness was measured using a surface-texture measuring instrument (Surfcom 480A; Tokyo Seimitsu Co. Ltd.).

Changes in the film thickness were evaluated using an optical interferotype film thickness measurement system, which utilizes the thin film interference of polymer film [12,15-17]. In the thin film interference, peaks and valleys of the reflected light intensity were observed alternately while changing the film thickness [15,17]. Green laser light from the optical source (520 nm, 150 mW; CivilLaser, Naku Technology Co. Ltd.) entered the center of the stage. The incident angle against the substrate surface was 76°. A Si photodiode (S1787-04; Hamamatsu Photonics K.K.) in reverse bias was used as a photodetector to measure reflected light from the substrate. Its cathode was connected to +5 V DC through a 60 kΩ resistor. The reflected light intensity was determined by correcting voltage between both ends of the resistor. The film thickness was calculated from the reflected light intensity.

To investigate the relation between the removal rate and the temperature, we heated the substrate using a substrate stage heater. The substrate stage temperature was measured using a K-type thermocouple placed on the stage edge. The temperature and the film thickness were measured simultaneously every 0.5 seconds. The removal rate was calculated from the decrease in the film thickness with respect to the time at intervals of a few seconds [15,17]. Similarly to studies [12, 15-17] described in earlier reports of the literature, the substrate temperature was evaluated using the time-averaged value at intervals of a few seconds.

3. Results and discussion

In Fig. 1, the removal rate (v rmv) of the novolac photoresist is depicted against the substrate stage temperature. The increase in v rmv at temperatures of 60–130 °C is presumably induced by thermal shrinking by vaporization of residual solvent in the photoresist film [9,17]. The rate v rmv increased...
almost exponentially against temperature when the added amounts of O₂ were 0.0% and 1.0% after shrinking. Effects of oxygen addition can be confirmed at temperatures higher than 140 °C. Results show that vₘᵋ decreased when O₂ was added. Actually, vₘᵋ at 2.0% was slightly higher than that at 1.0% until 175 °C, but it was lower and also its increment decreased thereafter. In a pure hydrogen system, vₘᵋ was higher than that at 2.0% when the temperature exceeded 200°C.

In Fig. 2, the removal rate (vₘᵋ) of PVP is shown against the substrate stage temperature. The increase in vₘᵋ by thermal shrinking of the PVP film is confirmed at temperatures of 100–160 °C. vₘᵋ increased almost exponentially against temperature in all cases after shrinking, although each increment was different. Effects of oxygen addition can be confirmed at temperatures exceeding 210 °C. Results show that vₘᵋ with an added oxygen amount of 1.0% was higher than others, as was found for the novolac photoresist. A decrease in the increment of vₘᵋ at 2.0% was not confirmed; vₘᵋ at 2.0% was higher than in a pure hydrogen system for temperatures higher than 210 °C, which is unlike the case of the novolac photoresist.

In Fig. 3, the removal rate (vₘᵋ) of PMMA is shown against the substrate stage temperature. The increase in vₘᵋ by thermal shrinkage of the PMMA film is indeterminate, unlike the case of the novolac photoresist and PVP. This must be because the removal of PMMA is too rapid to make apparent the thermal shrinking. The rate of thermal shrinking is not greater than several tens of nanometers per minute, while vₘᵋ of PMMA is over 300 nm/min even at 100 °C. Results show that vₘᵋ increased almost exponentially against the temperature in all cases, as found also for PVP. Effects of oxygen addition were confirmed for temperatures higher than 60 °C. vₘᵋ at 2.0% was higher than others, unlike the cases of the novolac photoresist and PVP. Plots of vₘᵋ at 0.0% and 1.0% were very similar. This effect for PMMA must be different from that for the novolac photoresist and PVP. As a side note, the decrease in vₘᵋ by the addition of O₂ over 2.0% may be able to be observed even in PMMA for temperatures higher than 200 °C, but vₘᵋ of PMMA would be too high to evaluate the effects at high temperatures.

As demonstrated in our earlier work [15,16], vₘᵋ of the novolac photoresist increased along with the amount of oxygen addition up to 1.0–1.5%, after which it decreased. The increased vₘᵋ should be ascribed to removal by OH radicals,
which are produced together with H and O radicals [18]. According to some findings [19-23], OH radicals actually have higher reactivity to benzene rings than either H or O radicals. The decrease over 1.5% might be attributable to the decreased production rate of H radicals by the catalytic poisoning of the catalyst surface by O atoms.

In general, polymers would be finally decomposed by hydrogen radicals to volatile low-molecular-weight products, such as CH₄, CH₃OH and CO₂ [7,24]. The bonds of main chains should be broken in end-stage process of the decomposition. Figure 1 shows that \( v_{\text{rmv}} \) of the novolac photoresist at 1.0% was about 1.5 times higher than that in a pure hydrogen system when the temperature was 210 °C. As presented in Fig. 2, \( v_{\text{rmv}} \) of PVP at 1.0% was about 1.2 times higher. This difference might be ascribed to the benzene ring position. The base material of the novolac photoresist is \( m \), \( p \)-cresol type novolac resin. Both novolac resin and PVP have benzene rings in their respective chemical structures: novolac resin has the rings in its main chain; PVP has the rings in its side chain. According to experiments by Goto et al., the removal rate of the novolac photoresist and novolac resin were higher than that of PVP when using a wet ozone, which is mixture of ozone gas and a small amount of water vapor [25,26]. Ozone preferentially attacks easily ortho position of OH group in benzene rings for novolac resin [27,28], because ozone reaction must be an electrophilic reaction [25]. Novolac photoresist alters to hydrosoluble low-molecular compounds by decomposition of the benzene rings in its main chains. PVP may alter to not only low-molecular compounds but also hydrosoluble polymer (e.g. poly(acrylic acid)) by decomposition of the benzene rings in its side chains [25]. The difference in the removal rate would be ascribed to low solubility of polymer compared with low-molecular compounds, although both products are hydrosoluble. A water rinse is indispensable for enhancement of the removal rate of PVP. OH radicals, which have high reactivity to benzene rings as well as O₃, may decompose main chains in novolac photoresist, although decomposing side chains in PVP. Therefore, the novolac photoresist might decompose more readily than PVP when comparing 0.0% and 1.0%. When the amount of added oxygen was 2.0%, production rate of H radicals would decrease drastically. Figure 1 shows that \( v_{\text{rmv}} \), of the novolac photoresist at 2.0% was lower than that in a pure hydrogen system when the temperatures were higher than 200°C although \( v_{\text{rmv}} \) at 2.0% was slightly higher than that at 1.0% when the temperatures were lower than 175 °C. As presented in Fig. 2, \( v_{\text{rmv}} \) of PVP at 2.0% was higher than that in a pure hydrogen system at the temperatures higher than 210 °C although \( v_{\text{rmv}} \) at 2.0% was very similar to that at 0.0% when the temperatures were lower than 210 °C. The decrease in \( v_{\text{rmv}} \) of novolac photoresist was significant although \( v_{\text{rmv}} \) of both polymers decreased when increasing amount of oxygen from 1.0% to 2.0%. Thermophysical property of novolac photoresist may be ascribed to this reason. Novolac photoresist, which is thermoset polymer [29], starts to harden by crosslinking when baking at the temperature higher than about 200 °C [9, 29]. Polymer surface attained a temperature of 260°C by radiation heat from a hot filament when the substrate temperature was 180 °C in this experimental system. Not only decomposition by radicals but also thermal hardening should be proceeded simultaneously on the surface. The hardening may be induced by not only thermosetting property of novolac resin but also thermally altered photoactive compounds (PACs) based on diazonaphthoquinone (DNQ). In any case, \( v_{\text{rmv}} \) of novolac photoresist may be considered to be influenced by trade-off between the decomposition and the hardening: \( v_{\text{rmv}} \) decreases because the hardening is dominant when the H-radical density is low; the decrease of \( v_{\text{rmv}} \) is not observed because the decomposition is dominant rather than the hardening when the density is high. The film thickness of novolac photoresist, after heating only the substrate up to 430 °C at a rate of 13 °C/min in this experimental system, was 0.5 µm, when the initial film thickness was 1.2 µm. In contrast to the photoresist, the film thickness of PVP, after heating up to 320 °C, was 0 nm, even though the initial film thickness was 1.1 µm. Novolac photoresist must be hardenable by heat treatment compared with PVP. The decrease in \( v_{\text{rmv}} \) of PVP, when oxygen additive amount was 2.0%, would be caused by the decrease in H-radical density because PVP has little ability to harden thermally.

PMMA, which is vinyl-type polymer, is a main chain scission polymer [30]. In general, by absorbing external energy (e.g. charged particle beams and radioactive rays), CH₃ at \( \alpha \)-position in
vinyl-type polymers becomes CH$_2^*$. Main chain of the polymers is broken by CH$_2^*$, which takes a bonding electron out of the main chain. $v_{rmv}$ of PMMA was much lower than that of novolac photoresist and PVP when using wet ozone, because of no carbon-carbon double bonds in PMMA [25,26]. However, as presented in Fig. 3, $v_{rmv}$ of PMMA was significantly high rather than that of novolac photoresist and PVP when using hydrogen radicals. PMMA will be removed by main chain scission which is easily induced by CH$_2^*$ produced by radicals. Perhaps for those reasons, $v_{rmv}$ of PMMA is much higher than other polymers. Additionally, OH radicals must be ineffective for the decomposition of PMMA because of no benzene ring in its chemical structure. Major radical would be H radical, because the density of H radical is much larger than that of OH and O radical [18]. Therefore, it might be difficult to observe the effects of oxygen addition at a 1.0% added amount. However, $v_{rmv}$ increased at 2.0%. Figure 3 shows that $v_{rmv}$ of PMMA at 2.0% was about 1.5 times higher than that at 0.0% and 1.0% when the temperature was 100°C. According to measurements by Umemoto and Moridera [18], OH radical density was about one-fiftieth of H radical density and O radical density was about one-twentieth of that when additive oxygen amount was 1.0%. The density of OH and O radical, when the amount is 2.0%, can be inferred from their measurements to be about one-fortieth and one-tenth of H-radical density, respectively. The density ratio of the oxidizing radicals to H-radical will increase with increase in the oxygen amount, although the density of the oxidizing radicals was less than one-tenth of H-radical density. Most of CH$_2^*$ must be produced by H radical, but some of it may be produced by OH and O radical when the density ratio increases. The contribution of oxidizing radicals for hydrogen abstraction may be large, even though their absolute density must be low.

4. Conclusion
The removal performances of PVP and PMMA, which are base polymers of KrF and ArF photoresists, were examined using hydrogen radicals containing a small amount of oxidizing radicals. Oxidizing radicals, such as OH and O radicals, can be produced by the addition of a small amount of oxygen gas to the atmosphere, in which hydrogen radicals are produced. The following results were obtained.

(1) Effects of oxygen addition on PVP removal could be confirmed, as was found for the novolac photoresist. The removal rate of PVP with an added oxygen amount of 1.0% was higher than that with 0.0% and 2.0%. The increase in the removal rate at 1.0% is ascribed to OH radicals, which have high reactivity to benzene rings. The oxygen addition to PVP removal was a little ineffective in the enhancement of its removal rate compared with novolac photoresist.

(2) Effects on PMMA removal could be confirmed, unlike the case of the novolac photoresist and PVP. The removal rate of PMMA at 0.0% and 1.0% were very similar. The removal rate at 2.0% was higher than others. OH radicals must be ineffective for the decomposition of PMMA, which has no benzene rings. In any case, their removal rate was significantly higher than that of novolac photoresist and PVP because PMMA is a main chain scission polymer.

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