Pressure Dependence of Photoresist Removal Rate Using Hydrogen Radicals

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Photoresists play a key role in lithography processes for the fabrication of electronic devices, but must be removed after processing. The removal method using hydrogen radicals, which are produced on a tungsten hot-wire catalyst, is effective to resolve some environmental and industrial problems in usual methods. However, the removal rate is not as good as that of the usual methods. We have previously described that the removal rate is enhanced just by decreasing Hydrogen pressure but the rate limitations not clarified. In present study, we examined the removal rate dependence on the pressure and revealed that the upper limitation of the enhancement is achieved at 0.50 Pa. The removal rate at 0.50 Pa was 8.3 times higher than that at 20 Pa when the surface temperature was 250 °C.

Keywords: Photoresist, Removal, Hydrogen radical, Hydrogen pressure, Environment

1. Introduction

Lithography processes using photoresists are indispensable for the fabrication of electronic devices. Roles of photoresists include protection of substrate surfaces from etching, thin-film deposition, and ion-implantation. Moreover, photoresists must be removed after processing. Actually, photoresist removal presents several problems such as environmental impacts and costs of chemicals because large amounts of hazardous chemicals are usually necessary [1-3].

One removal method to remove photoresists in some cases uses no such chemicals: removal method by ashing, in which the photoresist is decomposed to oxide–carbon compounds using oxygen plasma [4-6]. However, device performance might be destabilized by charged particles in the plasma. Instead of ashing, photoresist removal methods that do not use chemicals and plasma are sought to resolve these problems.

Some findings related to the use of hydrogen radicals produced on a tungsten hot-wire catalyst for photoresist removal have already been reported [7-12]. In general, the catalyst and the substrate are heated to enhance the removal rate, but limitations do exist. When heating the catalyst, metal contaminants from the catalyst become a major issue [8]. When heating the substrate, thermal damage to the substrate is another issue [9]. Thermal damage to the substrate is also induced by radiation heat from
A report of an earlier study described that the removal rate is enhanced by using hydrogen radicals produced under a low-pressure condition [12]. Decreasing the pressure is an effective way of removal rate enhancement without heating the catalyst and the substrate. However, the density of hydrogen radical decreases concomitantly with decreasing pressure because the density decreases in proportion to the square root of hydrogen pressure [13]. Furthermore, the removal rate increases proportionally to the density [10]. Therefore, the removal rate is expected to increase concomitantly with decreasing pressure, but it attains the upper limit and then decreases. However, no such phenomenon has ever been reported in the literature. This paper presents description of an investigation of removal rate dependence on pressure to clarify the rate limitations due to decreasing the pressure.

2. Experimental

The experimental apparatus and the procedure were similar to those described elsewhere [12, 14, 15]. In the stainless steel cylindrical chamber, 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.). An oil-sealed rotary vacuum pump was used to draw a vacuum on the chamber. The hydrogen pressure under processing was between 0.36 and 40 Pa, adjusted using the evacuation valve. The pressure became the lowest (0.36 Pa) when the valve was fully opened. The pressure was measured using a vacuum gauge (Baratron 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; the coil length and the diameter were, respectively, 40 mm and 8 mm. The distance between the catalyst and the substrate was 100 mm to prevent the substrate from heating by thermal radiation from the catalyst. A DC power supply (EX-750L2; Takasago Ltd.) was used to heat the catalyst. The catalyst temperature was 2.0×10³ °C. The output power was adjusted to 340–430 W.

A positive-tone novolak photoresist (OFPR-800; Tokyo Ohka Kogyo Co. Ltd.) was used. It was spin-coated onto a Si-wafer using a spin coater (Spinner-1H-III; Kyoei Sangyo Co. Ltd.) at 2.60×10³ rpm for 24 s and was pre-baked in an oven (CLO-2AH; Koyo Thermo Systems Co., Ltd.) at 100 °C for 60 s. Additionally, the substrate was baked at 300 °C for 5 min after pre-baking. The film thickness was decreased by thermal shrinkage during 5-min baking at temperatures below 300 °C. We excluded film shrinkage in advance before hydrogen radical irradiation by additional baking. The rate of removal by hydrogen radicals can be obtained by keeping the substrate temperatures below 300 °C while the photoresist is removed. The photoresist film thickness was found using a surface-texture measuring instrument (Surfcom 480A; Tokyo Seimitsu Co. Ltd.). The photoresist film thickness was about 0.8 μm after additional baking.

Changes in the photoresist film thickness were measured using thin film interference of photoresist film. The optical source was a green laser (520 nm, 150 mW; CivilLaser, Naku Technology Co. Ltd.). The laser light entered the center of the stage. The incidence angle against the substrate surface was 76°. A phototransistor (NJL7502L; New Japan Radio Co. Ltd.) was used as a photodetector. The emitter side of the phototransistor was connected to ground. Its collector was connected to +5 V DC through a pull-up resistor (1 kΩ).

For thin film interference, peaks and valleys of reflected light intensity can be alternately observed while changing the film thickness [14]. The reflected light intensity becomes maximum and constant when the photoresists are removed completely in the laser irradiated area. It is possible to ascertain the endpoint from the intensity. Then we stopped heating the filament immediately.

To assess the relation between the removal rate and the surface temperature, we heated the substrate from 20 °C to 300 °C using a substrate stage heater. The substrate was also heated by radiation heat from the hot catalyst. The temperatures of the substrate and its surface were measured using two K-type thermocouples. 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 substrate temperature and the film thickness were measured simultaneously at a 0.2 s interval. The removal rate was calculated from the decrease in the film thickness with respect to the time between the neighboring peak and valley. The surface temperature was also estimated using the time-averaged value of the peak and valley, according to an earlier report of the literature [14].

3. Results and discussion

In Fig. 1, the photoresist removal rate is plotted against the time-averaged substrate surface temperature. The removal rate, which increased almost exponentially against the temperature at each H₂ pressure, was remarkably enhanced under low-pressure conditions. At pressure lower than 0.50 Pa, the plots were almost identical. At temperatures less than 150 °C, it was difficult to discriminate differences of the removal rate at each H₂ pressure. We examined differences at 200, 230 and 250 °C.

Figure 2 portrays the dependence of the photoresist removal rate on H₂ pressure when the respective time-averaged substrate surface temperatures ($T_{AvgSurf}$) were 200, 230, and 250 °C. Results showed that the removal rate was almost constant even with the increase in H₂ pressure up to 0.50 Pa. It then decreased in inverse proportion to the pressure.

In this study, results show the upper limitation of the removal rate enhancement. The limitation was achieved at 0.50 Pa when decreasing the pressure. In general, the pressure for the ashing is a few tens of Pascals, except for plasma at atmospheric pressure. When $T_{AvgSurf}$ was 200 °C, the removal rate at 0.50 Pa was 5.1 times faster than that at 20 Pa. When $T_{AvgSurf}$ was 250 °C, the removal rate at 0.50 Pa was 8.3 times higher than that at 20 Pa. In our previous study, we achieved a removal rate of about 1.0 μm/min when the catalyst temperature, $T_{AvgSurf}$, the distance, and the pressure were, respectively, 2000 °C, 280 °C, 20 mm and 20 Pa [14]. If the distance was 20 mm, then the removal rate might increase further, becoming comparable to that achieved using conventional methods.

The removal rate decreased when the pressure was higher than 0.50 Pa. This pressure dependence might be explained by the pressure dependence of the kinetic energy of hydrogen radical. Hydrogen radical right after production on the catalyst surfaces may have a high kinetic energy (translational temperature) corresponding to “the catalyst temperature - 1000 K” [16], but it should be relaxed to ambient temperature by collisions of about one hundred times in the gas phase [17]. The mean-free-path decreases in inverse proportion to the pressure. It is not easy to estimate the mean-free-path under the present conditions, but it must be less than a few tens of millimeters at pressures exceeding 1.0 Pa. In our previous study, when the distance between the catalyst and the substrate was 20 mm and the
pressure was higher than 5.0 Pa, we explained the reason for the pressure dependence as the change in the kinetic energy caused by the collision in the gas phase because hydrogen radicals are probably not thermalized [12]. The removal rate is obtained from the change in the film thickness per unit time. The removal rate increases in proportion to the density when the pressure is constant [10]. According to Umemoto et al. [13], the density of hydrogen radical increases proportionally to the square root of H$_2$ pressure. For this study, we adjusted the output power to maintain the filament temperature as 2.0×10$^3$ °C. The density in this study must have similarly increased. However, the velocity of hydrogen radical decreases in inverse proportion to the pressure. At high pressures, the collisional thermalization must be fast because the mean-free-path is small. In other words, a repetition frequency of hydrogen radical irradiation must have decreased because of the thermalization. The decrease in the removal rate would be a reasonable result because the decrease in the irradiated hydrogen radicals per unit time has a dominant influence on the removal rate, even if the density increases with increase in the pressure.

Pressure dependence at pressures below 0.50 Pa might be explained by both the hydrogen radical density and the kinetic energy influence. The density of hydrogen radical would decrease with decreasing H$_2$ pressure [13]. However, hydrogen radicals have high kinetic energy because the mean-free-path is large under low-pressure conditions. Hydrogen radicals are probably not thermalized because no more than half a dozen collisions would occur until hydrogen radicals arrive to the photoresist surface, even if the distance was 100 mm. There might be a tradeoff between the density decrease and the kinetic energy increase. Consequently, the removal rate might become almost constant even with a decrease in pressure to lower than 0.50 Pa. We may be able to observe the decrease in the removal rate caused by the density-limiting if producing the pressures below 0.36 Pa by using a vacuum system consisting of a series connection of the rotary pump and a turbo-molecular pump.

Instead of conventional photoresist removal methods, we investigated a novel environmentally friendly removal method using hydrogen radicals generated on a tungsten hot-wire catalyst. We examined the removal rate dependence on H$_2$ pressure. Results showed that the upper limitation of the enhancement of the removal rate is achieved at 0.50 Pa when decreasing the pressure. The removal rate at 0.50 Pa was 8.3 times higher than that at 20 Pa when the surface temperature was 250 °C. This enhancement might be ascribed to the high repetition frequency of hydrogen radical irradiation. Optimization of the removal conditions might produce a removal rate comparable to that achieved when using chemicals and ashing.

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