Effects of Oxygen Microbubbles on Photoresist Layers under Hot Water Conditions


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1. Introduction
Tiny bubbles are a promising candidate for an environmentally friendly method of photoresist removal. It has been demonstrated that ozone microbubbles remove photoresist on a silicon wafer, even after the photoresist have been damaged by a high-dose ion-implantation [1]. But significant challenges are still remained, partly because the removing rate is not enough first for the usage of microbubbles in the semiconductor manufacturing industry. Therefore, we need to enhance the removing ability of microbubbles through the clear understanding of the functional mechanisms of microbubbles for the removal of photoresist layers. The purpose of the present study is to clarify the effect of microbubble on the surface of photoresist layers.

2. Characteristic of microbubbles relating to photoresist removal
Microbubbles are tiny bubbles in aqueous solutions and their diameter may be less than 50 micrometer. The bubbles gradually decrease in size due to the dissolution of interior gases to the surrounding water and eventually disappear under water. This character enables the tiny bubbles to acquire promising functions, such as the increase of interior gas pressure and the accumulation of surface electricity during the collapsing process of tiny bubbles [2-6]. Figure 1 shows photographs of a high-dose ion-implanted photoresist wafer before, during and after the ozone microbubble treatment. The wafer was treated through a single wafer spin cleaning method, and the ozone microbubble water was poured on the center of the wafer held on a spin table. Considering the treatment condition it might have been reasonable to anticipate that the cleaning process would start at the center of wafer and extend to outer part, such as the case of a mere baked photoresist shown in Fig. 2. But the result indicated the contradict pattern for the high-dose ion-implanted photoresist, and the layer of photoresist was stripped, instead of dissolution, from the outer edge to the center of the wafer. These results enable us to obtain an important information considering the practical usage of microbubble in photoresist removals.

Fig. 1. Removal of high-dose ion-implanted photoresist by ozone microbubbles on a spin table.
3. Experimental procedure

Figure 3 shows a schematic of the microbubble generation system used in the present study, and all parts of the system in contact with water are made of metal-free Teflon materials. It was a depressurizing type of microbubble generator (SHIGEN-KAIHATU CO., INC.). A diaphragm pump introduced both of water and gas through its intake line, and discharged them through a dissolution tank in which the gas was effectively dissolved in water under a pressure of approximately 0.4 MPa. The water containing the dissolved gas was then released by a dispersing nozzle. Turbulent flow in the nozzle caused the generation of microbubbles through bubble nucleation under a supersaturated condition produced by the rapid pressure reduction to the ambient. Figure 4 shows the bubble size distribution of generated oxygen microbubbles in super-purified water at around 20ºC in a clean room. And it was observed that the size distribution changed according to the temperature of water.

As the samples for the present experimental study, high-dose ion-implanted photoresists were used as one of the most challengeable targets in the semiconductor manufacturing [7, 8]. Silicon wafers spin-coated with a high-resolution positive type photoresist for KrF excimer laser (TDUR-P3116EM 15cp, TOKYO OHKA KOGYA CO., LTD.) and patterned by an exposure tool. Wafers were implanted with arsenic ion at doses of 1E15/cm2 and an energy of 55keV, and were also implanted with boron ion at doses of 1E15/cm2 and an energy of 11keV. The wafers were diced into samples with a size of 20*20mm2, and a diced sample was placed on a spin table by a stick tape in-between the center and the edge of the table.

The tests were conducted by pouring water with oxygen microbubbles onto the center of the rotating spin table. The water flow rate was around 1 L/min, and the temperature was controlled at approximately 70 ºC by a heating system.

4. Results

Figure 5 shows the results of microscopic observation of the samples after oxygen microbubble treatment under hot water condition for 30 minutes. As clearly shown in these photographs, ion-implanted patterned photoresist layers were invaded and a part of the layer was peeling from the edges by the effect of poured water with microbubbles. And the photographs also indicated that the direction of water flow strongly affected the invasion of the aqueous liquid into the photoresist layers. We can recognize the change of the layers more clearly by cross-sectional SEM images as shown in Figure 6.
Inner part of the layers, a part of the bulk resist was removed, and the top and the side walls of crust layers were remained. Hot water without oxygen microbubble was also evaluated by the same method at the temperature of around 70 °C, and we could not observe such a significant damage on the photoresist layers.

5. Discussion

Considering the oxidation ability of the gas of oxygen, the results informed us several important aspects of the usage of microbubble for photoresist removal. The change in the photoresist layer suggested us the presence of any strong oxidant in the system, but oxygen dissolved in hot water could not be enough strong to invade into the bulk photoresist through the crust wall. Therefore, for the evaluation of the effect of microbubble, it is significantly meaningful to examine the generation of oxygen centered radicals from microbubbles, because it has been demonstrated that microbubbles in acidic water cause the generation of hydroxyl radicals during their collapsing process. So we also conducted the experimental study of the measurement of the radicals by using Electron Spin Resonance (ESR). 5,5-Dimethyl-1-pyrroline N-Oxide (DMPO) was used as the spin-trap reagent, because it is a very useful agent for the detection of the oxygen centered radicals. But as the results of the test we did not observe any significant signals relating to the radical generation under ambient and hot water conditions. The experimental results suggest us the presence of any physical properties of microbubbles affecting on the surface of photoresist layers. Since the direction of water flow had an important meaning for the stripping of the photoresist layers and microbubbles more likely contacted with the upstream side of photoresist layers, the interaction between the bubbles and the photoresist layers could cause a trigger of the phenomena of photoresist stripping. And we also conducted an experimental study about the effect of microbubble on high-dose ion-implanted photoresists, which was a joint research with Industrial Technology Institutes of Ibaraki Prefecture. Air microbubbles generated in strong alkaline waters were used for the test at an ambient temperature, and 5% Tetramethylammonium hydroxide (TMAH) almost completely stripped the patterned photoresists, except larger patterned layers, in around 10 minutes (Figure 7). Considering the fundamental properties of microbubbles in aqueous solutions, the strong stripping effects under alkaline condition might be caused by the surface electricity of the gas-water interface of the tiny bubbles.

Fig. 7. Microscopic observation of photoresist before (a) and after (b) air microbubble treatment dispersed in 5% TMAH.

Under hot water conditions of around 70 °C the size distributions of the generated oxygen microbubbles are different from that at an ambient temperature, and the extremely smaller bubbles are likely increasing in number. Unfortunately it is very difficult to observe the electrical properties of these tiny bubbles in hot water conditions by an electrophoresis method, but the increasing number might be relating to the change in the electrical properties of gas-water interface [3,4,9].

At present we don’t have enough information to discuss in more detail the mechanism of the enhanced ability of microbubble under hot water conditions, but the surface properties of gas-water interface must be the key factor for the acceleration of the stripping rate of photoresist layers. Thus, for the further development of the microbubble
technology in the photoresist removal, we are planning to clarify the mutual effect of the collapsing microbubbles and the surface of photoresist layers under ambient and hot water conditions.

References