Droplet Evaporation and Watermark Formation on Si Wafers with Various Films

Ayako YANO**, Kenji AMAGAI**, Kazuki MATSUMOTO***, Hirokuni HIYAMA¹, Akira FUKUNAGA¹, Shohei SHIMA³ and Naoyuki HANDA¹

Abstract: The evaporation of droplets from Si wafers coated with low-dielectric-constant (Low-4), Cu, and thermally oxidized (Th-Ox) films was investigated to fundamentally study precision wafer cleaning. Ultrapure water was dropped onto the wafer, and the resulting droplet shapes and watermarks were observed using microscope cameras. These images were then used to measure the droplet’s shape, namely its height and contact area, from which the contact angle and droplet volume were calculated. The watermark size was also measured after the evaporation was completed. Results showed that the droplet evaporation processes can occur in two modes, namely constant contact angle (CCA) and constant contact radius (CCR) modes. The watermark size was strongly affected by the evaporation process: for CCR-type evaporation, the watermark was almost the same size as the initial droplet contact area, whereas the watermarks produced via CCA-type processes were smaller. For the Low-k and Th-Ox films, the evaporation processes changed from CCR to CCA, whereas the droplet on the Cu film showed only CCR-type evaporation. The droplet evaporation process and watermark size were measured for a patterned wafer with a Cu pattern on a Low-k film. Results showed only CCR-type evaporation, similar to that observed in the Cu film.

Keywords: chemical mechanical polishing, wafer cleaning, droplet evaporation, watermark

1. Introduction

Chemical mechanical polishing (CMP) is a key technology used to planarize semiconductor wafer surfaces during manufacturing¹. Nowadays, 300-mm-diameter wafers are used in the mainstream production of semiconductor chips. After CMP, porous brushes are used to clean off slurry particles and other contamination². Spin rinsing is also used to remove any remaining particles, and ultrapure water is used in the final spin cleaning step.

The surface flows observed in thin liquid films on rotating disks³⁴ and the effect of surfactants on the behavior of these flows⁵ were previously investigated. Spin drying was performed after completing these cleaning processes. If any droplets remained on the wafer after cleaning, the Si in the wafer could dissolve and oxidize in them, thereby forming watermarks on the wafer as the water evaporates.

These droplet evaporation phenomena were previously studied⁶⁻¹¹, and numerical simulation studies were conducted¹²⁻¹⁶. In addition, the effect of droplet evaporation on the residue pattern was discussed for droplets with impurities¹⁷⁻²⁰. Watermarks were formed in a similar way to these residue patterns. In the CMP cleaning field, watermark patterns were investigated in terms of the residue patterns caused by droplet evaporation²¹. These watermarks were formed irregularly on the wafer’s surface, adversely affecting its electric characteristics and causing defects in the resulting semiconductor products. To improve semiconductor manufacturing yields, the formation of such watermarks must be prevented, and spin drying technology is one of the important processes to avoid watermark formation. However, the details of the watermark formation mechanism still remain unclear. In particular, the effect of surface properties on these evaporation phenomena must be investigated.

In this study, the fundamental characteristics of droplet evaporation on wafer surfaces coated with various films were experimentally investigated. Low-dielectric-constant (Low-k) and thermally oxidized (Th-Ox) films are used as interlayer dielectric films in semiconductors, and Cu is generally used for the wiring. The experiments therefore consider Low-k, Th-Ox, and Cu films.

Droplet evaporation in the pattern wafers was also observed. Two types of evaporation pattern, namely constant contact angle (CCA) and constant contact radius (CCR) patterns, were reported for various surface properties²²⁻²⁵. The effect of surface roughness was also previously discussed²⁶⁻³². Evaporation process of droplet on poly(methyl methacrylate) (PMMA) substrates with different surface roughness was investigated²⁷. For smoother surface with Rₙ ≤ 19 nm, evaporation process change from CCR to CCA. In contrast, for large roughness with Rₙ ≥ 209 nm, droplet evaporate with CCR all the time. The surface roughness of films used in this paper were several nm. There was no significant difference between surface roughness of three films. Herein, the relation between the film type and the
appearance of CCR and CCA evaporation patterns will be discussed.

2. Experimental Setup

Figure 1 overviews the experimental apparatus. To maintain a clean environment, the high efficiency particulate air (HEPA) filter was attached to an acrylic glove box that was 500-mm deep, 800-mm wide, and 450-mm high. To create conditions similar to those present in the clean rooms used for semiconductor manufacturing, clean air was introduced into the glove box by passing it through the HEPA filter and later expelled from the bottom of the glove box. The temperature and relative humidity were measured by a thermo-hygrometer (TR-77Ui, T&D Corporation, Japan).

A droplet of pure water was then applied to a Si wafer placed in the glove box, and droplet evaporation was observed using a digital single-lens reflex camera. Specifically, K-5 and K-7 cameras (PENTAX, RICOH) were placed vertically above the wafer, whereas a K-r camera (PENTAX, RICOH) was placed horizontally to the side of the wafer. To observe the droplet in three dimensions, still images were simultaneously captured at certain time intervals by all cameras. Magnified images of the droplet were captured by microscopes mounted on both cameras.

Light from a halogen lamp was projected onto a screen set behind the droplet to observe its outline clearly in the horizontal direction. In the vertical direction, light from a second halogen lamp was projected via a ring-type light guide onto a screen set in front of the microscope lens. The droplet temperature was measured using a radiation thermometer.

3. Experimental Results

3.1 Effect of wafer film on droplet evaporation

Evaporation occurs via CCA and CCR modes, as shown in Fig. 2. CCA evaporation processes maintain a constant contact angle, whereas CCR processes maintain a constant contact radius.

Figures 3–5 show the photographs of droplets evaporating from the Low-k, Cu, and Th-Ox films, respectively. Ultrapure water (1 μL) was dropped on the wafer at $t = 0$ s (the initial volume condition), and images were captured at regular time intervals in the vertical and horizontal directions using a digital camera. At the final terms of the evaporation process, we were able to observe the various sizes of watermarks. In this paper, we state about only visible watermarks to evaluate the fundamental characteristics. The chemical compositions of watermarks were analyzed by scanning electron microscope / energy dispersive X-ray spectroscopy (SU-70, Hitachi high-technologies Co.). However, the film-derived component was mainly detected, and some oxygen and carbon were also detected. It is assumed that oxygen is from oxidation products, and that carbon is from organic substance on the wafer surface. Furthermore, the difference of the chemical composition of watermark area and other area was not elucidated, and then the specific chemical compositions of watermarks were not detected.

Figure 3 shows the photographs of the droplet on the Low-k film captured at $t = 20$, 520, and 1020 s. In this experiment, ambient temperature was 296 K, relative humidity was 42 %, and droplet temperature was 294 K. Figure 4 shows the droplet on the Cu film at $t = 20$, 420, and 780 s. In this experiment, ambient temperature was 297 K, relative humidity was 41 %, and droplet temperature was 295 K. Fig. 5 shows the droplet on the Th-Ox film at $t = 20$, 420, and 840 s. In this experiment, ambient temperature was 297 K, relative humidity was 42 %, and droplet temperature was 295 K. With the Low-k and Th-Ox films, the droplets shrank over time while maintaining their shape. In contrast, the droplet on the Cu film simply decreased in height as it evaporated. Watermarks formed on the wafers after evaporation in all cases. The watermarks on the Low-k and Th-Ox films had smaller diameters than the initial droplet, whereas the watermark on the Cu film had approximately the same diameter as the initial droplet. These results therefore confirm that the evaporation processes of droplets on Si wafers can be different when using different films.

For a detailed investigation of the evaporation process, the contact angles and contact areas were then calculated from these results. Although the droplet's shape was in principle determined by the surface tension and gravity, the droplet's vanishingly
Droplet Evaporation and Watermark Formation on Si Wafers with Various Films

\[ V_d = \frac{\pi r^3}{3 \sin \gamma} \left(2 - 3 \cos \theta + \cos^3 \theta \right). \]  

Due to uncontrollable contamination of the wafer surface, the contact angle with each film was different from that with the clean surface of a new wafer. Temporal change of contact angle was measured under the condition of releasing into the atmosphere after washing of wafer surface. Then the contact angle increases gradually. An example of Cu film, it changed from 20 degrees to more than 60 degrees in the cases where change is relatively great. However, the CCA or CCR mode for evaporation behavior was not influenced by the effect of the change for contact angle. Figures 6-8 show the changes in each droplet’s volume \( V_d \), contact angle \( \theta \), and contact area \( S_c \) over time for the three film types. Each droplet’s initial volume was 1.0 \( \mu \)l. The horizontal axes show the elapsed time \( t \), the vertical axes show the droplet volume \( V_d \), contact angle \( \theta \), and contact area \( S_c \). Figures 6-8 show representative results of the changes of \( V_d \), \( \theta \), and \( S_c \), because repeatability of experiments were confirmed.

Figure 6 shows that the droplet volume linearly decreases for the Cu film but follows a curve for the Low-k and Th-Ox films. Figures 7 and 8 show that for the Low-k film, the droplet’s contact angle initially decreased and the contact area remained constant. Then, after \( \sim 200 \) s, the contact area began decreasing linearly, whereas the contact angle became constant. During the final stages of evaporation, the contact angle and contact area decreased. The pattern was similar for the Th-Ox film; however, the contact angle steadily decreased for the Cu film while the contact area remained constant.

These results indicate that the droplets on the Low-k and Th-Ox films initially evaporated via CCR; however, the evaporation process switched to CCA after the contact angle decreased to a certain critical angle. In contrast, the droplet on the Cu film evaporated via CCR during the entire process. Table 1 summarizes these changes during evaporation.

---

\[ \theta = 2 \tan^{-1} \frac{h}{r}, \]  

small volume implied that any deformation by gravity was negligible; hence, this was ignored. The contact diameter \( r \) and droplet height \( h \) were measured from the droplet photographs. The droplets were assumed to be spherical caps, and their volume \( V_d \), contact angle \( \theta \), and contact area \( S_c \) were calculated based on the measured \( r \) and \( h \) values as follows:

---

Fig. 6 Changes in droplet volume \( V_d \) over time for the Cu, Low-k, and Th-Ox films.
Therefore, the contact angle is considered to be advancing. Then, evaporation via CCR reduces the contact angle to a critical angle, at which point the process switches to CCA and the contact line begins to recede. Thus, the contact angle during the CCA process is considered to be receding. These changes are also confirmed by the results for the Low-k and Th-Ox films shown in Fig. 7. This change from advancing to receding contact angles is known as contact angle hysteresis.

On the other hand, a droplet on the Cu film shows different evaporation process. The surface roughness of watermark was measured by scanning probe microscope (SPA-400, EKO Instruments) after the finish of evaporation for each film type. As a result, some chemical composition deposited at the edge of the watermark. It seems that the contact line is fixed by the deposition being formed. These deposits are considered to be formed by film component dissolved in the droplet. Therefore, dissolution rate of film component has a direct influence on deposition forming speed.

Dissolution rate of Cu and Si films in the ultrapure water were estimated experimentally. The dissolution rates were 669 pg/s/cm² (average during 300 s) and 0.25 pg/s/cm² (average during 360 s) in the case of Cu film and Si film, respectively. According to these results, Cu dissolved in droplet very quickly,
and oxidation products were formed near the contact line. Then, contact line is fixed at the initial position. In the case of Low-\textit{k} and Th-Ox films, Si dissolves in droplet slowly. It is considered that the contact line was not fixed because oxidation products were not formed before the evaporation process switched to CCA.

3.2 Droplet evaporation from a pattern wafer

Evaporation phenomena were also observed on a Cu/Low-\textit{k} patterned wafer. In this experiment, the droplet diameter was chosen to be larger than the Cu pattern printed on the Low-\textit{k} film so that the droplet covered several repetitions of the Cu pattern.

Figure 10 shows photographs of the droplet and watermark. Herein, the droplet appeared to evaporate without changing its contact line; thus, the watermark formed on the patterned wafer had almost the same shape as the droplet's initial contact area. The droplet's evaporation process changed from CCR to CCA on the Low-\textit{k} film; however, no observable reduction in the contact area was observed in this case. This result caused by the difference between dissolution rate of Cu and Si. Dissolution rate of Cu is very first compared with that of Si. The oxidation products derived from Cu film were deposited near the contact line, and fix it at initial contact line.

Figure 11 shows the areas of the watermarks left on the different types of film after evaporation. Here, the horizontal axis shows the film type, whereas the vertical axis shows the watermark area on a logarithmic scale. Low-\textit{k} and Th-Ox films are used as interlayer dielectric films in semiconductors. The evaporation processes for a porous Low-\textit{k} film and boron-doped polycrystalline silicon (P-Si), which have both been used in recent years to obtain lower dielectric constants, were also measured. For all these films, the watermark area was smaller than the droplet's initial contact area. The watermark area of the Th-Ox film was larger than that of the Low-\textit{k} film probably because of the smaller contact angle yielding a larger contact area. The watermark area of the Cu film was larger than that of the dielectric film because of the CCA evaporation process involved. The evaporation process was also measured for the Cu/Low-\textit{k} patterned wafer, wherein the droplet left a watermark similar to that observed for the Cu film. From these results, it was confirmed that the relationship between the film type and areas of the watermarks.

4. Conclusion

Herein, the droplet evaporation and watermark formation processes were observed for various types of wafer films. Results confirmed that the evaporation pattern depends on the film type. Droplets evaporate according to either CCA-type or CCR-type processes. For the Low-\textit{k} and Th-Ox films, the evaporation process changed from CCR to CCA. The droplet on the Cu film evaporated via a purely CCR-type process although the reason for this was not investigated. In this case, the watermark was larger than that seen for CCA evaporation, which produced smaller watermarks because of the decrease in the droplet radius during evaporation. A Cu/Low-\textit{k} patterned wafer exhibited similar droplet evaporation characteristics to the Cu film. Our future study will focus on explaining these phenomena via modeling and other theoretical investigations.

References


