

A STUDY OF THE FORMATION OF WATER MARKS FROM MEMBRANE-DISTILLED WATER AND ULTRAPURE WATER

HARUMI MATSUZAKI, ISAO OOKOUCHI, HIDEAKI KUROKAWA,
KATSUYA EBARA AND SANKICHI TAKAHASHI

Hitachi Research Laboratory, Hitachi Ltd., Hitachi-shi, 317

Key Words: Water Mark, Evaporation, Ultrapure Water, Silicon Wafer, Organic Matter

Effects of evaporation temperature on the formation of water marks left on a Si wafer were studied using membrane-distilled water and ultrapure water.

The main constituent of water marks from membrane-distilled water was found to be liquid hydrocarbon, with some C=C bonds present, and when evaporation velocity was greater than about $20 \text{ kg}/(\text{m}^2 \cdot \text{h})$ evaporation could take place without marks formation. Water marks from ultrapure water had a higher boiling point than those from membrane-distilled water and were left on a Si wafer even when the water was evaporated at a velocity of about $20 \text{ kg}/(\text{m}^2 \cdot \text{h})$.

Introduction

The quality of ultrapure water used in semiconductor device manufacturing is estimated by resistivity, the number of particles and bacteria, TOC (total organic carbon) and other criteria. This industry has great need of higher-quality ultrapure water due to the increasing degree of integration. It is especially desirable to lower the TOC value, which influences the quality of the SiO_2 film formed on a Si wafer by oxidation. It is the final object of this study to produce the water without water-mark constituents or to evaporate the water without the formation of water marks.

The organic matter in ultrapure water is estimated by the TOC value. For the increasing degree of integration, it is necessary to study TOC constituents in ultrapure water and their effect on semiconductor properties. While studies³⁾ of the effect of TOC on semiconductor properties have been made, no work has examined TOC constituents.

In the present work it was defined that water marks were the resulting residue or spot left on a Si wafer after evaporating a drop of water, and the effect of evaporation temperature on the formation of water marks^{1,2)} was studied, using membrane-distilled water and ultrapure water.

1. Experimental Method

Water marks were left on a Si wafer after evaporating a drop of sample water at a given temperature in a

clean ventilation space. The Si wafer with a drop of sample water was set on a hot plate with a given temperature. The drop of water weighed about 0.1 g and had a diameter, d , of 8–10 mm on a Si wafer. The effect of evaporation temperature on water mark weight was studied by varying wafer temperature. Evaporation velocity of the drop of water was calculated using measured evaporation time and d .

Membrane-distilled water and ultrapure water with the respective water qualities shown in **Table 1** were used. The former was produced in a distillation system using a hydrophobic membrane. This system was composed of a degassing part and a membrane distillation part. In the former part, dissolved gases and volatile matter were removed by heating. In the latter part, the mist accompanying the vapor was filtered by the hydrophobic membrane and membrane-distilled water containing very few impurities was produced, because only pure vapor was condensed here. The ultrapure water was produced in a conventional system using ultrafiltration, ion-exchange resins and so on.

Table 1. Qualities of sample waters

	Membrane-distilled water	Ultrapure water
Resistivity [$\text{M}\Omega\text{-cm}$]	> 18	> 18
Particles [particles/ml]	12 ($0.2 \mu\text{m}$)	< 50 ($0.1 \mu\text{m}$)
Bacteria [units/ml]	Trace	< 0.05
TOC [$\mu\text{g}/\text{l}$]	46	100
Si [$\mu\text{g}/\text{l}$]	Trace	< 5

Received January 4, 1988. Correspondence concerning this article should be addressed to H. Matsuzaki.

Water marks were observed using a photo microscope and a SEM (scanning electronic microscope). The constituents of water marks were analyzed using FT-IR (Fourier transfer infrared) spectroscopy. After making many water mark formations on the same Si wafer, a microcell was prepared using a mixture of KBr powder and the water marks on the wafer.

2. Results

2.1 Form and temperature dependence of water marks

Figure 1 shows photomicrographs of water marks left on a Si wafer after evaporating membrane-distilled water at various temperatures. Figure 1-(a) shows water marks obtained at room temperature. The water marks were small circles or ellipses with diameters of 1–30 μm . **Figure 2** shows a magnification of Fig. 1-(a). Newton rings were observed on respective water marks, indicating that they had a very smooth spherical surface. Also, water marks changed shape from an ellipse to a circle as time elapsed.

From these results, water marks were left by liquids and then organic matter. Also, water marks were from non-ionic species based on a comparison between resistivity and TOC (Table 1).

Figure 3 shows photo and SEM micrographs of the same water mark. The former is a magnification of Fig. 1-(b). Water marks in the latter had a pretreatment of Pt physical vapor deposition (0.05 Torr, 0.5 h) before the SEM observation. The latter showed that only a thin film, formed on the surface of water marks, was left on the Si wafer. This thin film with a higher boiling point than the inner matter was formed on the surface by polymerization, etc. The inner matter vaporized under the pressure of 0.05 Torr and broke the thin film.

From these results, water marks were organic matter which polymerized in air at normal temperatures.

Figure 1 showed that water-mark weight decreased with increasing evaporation temperature. **Figure 4** shows the relation between water mark residual ratio, R , and evaporation velocity, v . R is the ratio of water-mark area at a given temperature to that at room temperature. In the case of membrane-distilled water, if v was greater than about $20 \text{ kg}/(\text{m}^2 \cdot \text{h})$, the water could be evaporated without the formation of water marks. The evaporation velocity of $20 \text{ kg}/(\text{m}^2 \cdot \text{h})$ was nearly equal to that in the distillation system using a hydrophobic membrane.

From these results, water marks have a higher boiling point than that of H_2O .

Figure 5 shows photomicrographs of water marks from ultrapure water at room and high temperatures, respectively. Water marks could be observed at both temperatures. Therefore, water marks from ultrapure water had a higher boiling point than those from

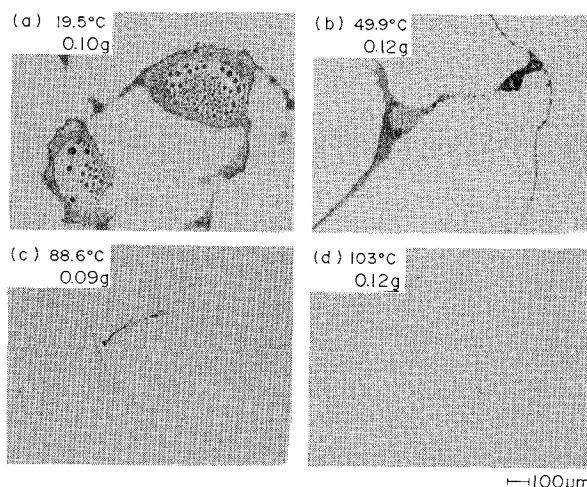


Fig. 1. Effect of evaporation temperature on water-mark weight

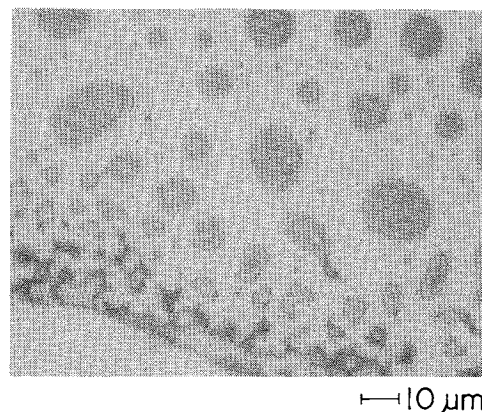


Fig. 2. Magnification of Fig. 1-(a)

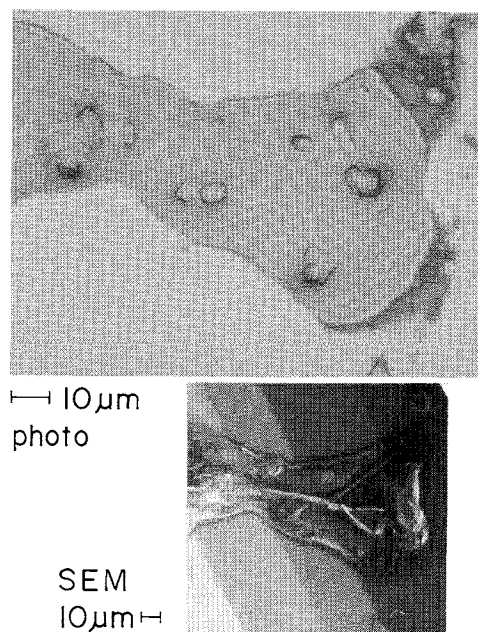


Fig. 3. Photo and SEM micrographs of the same water mark

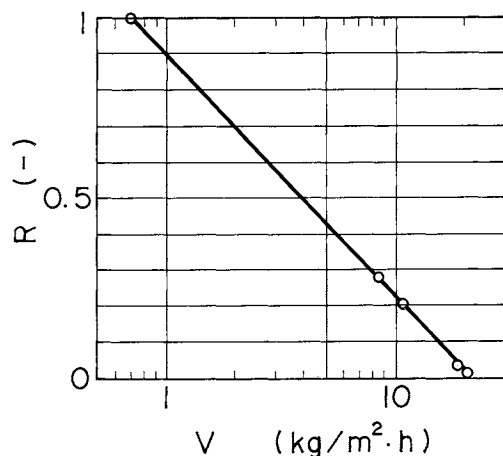


Fig. 4. Relation between R and v

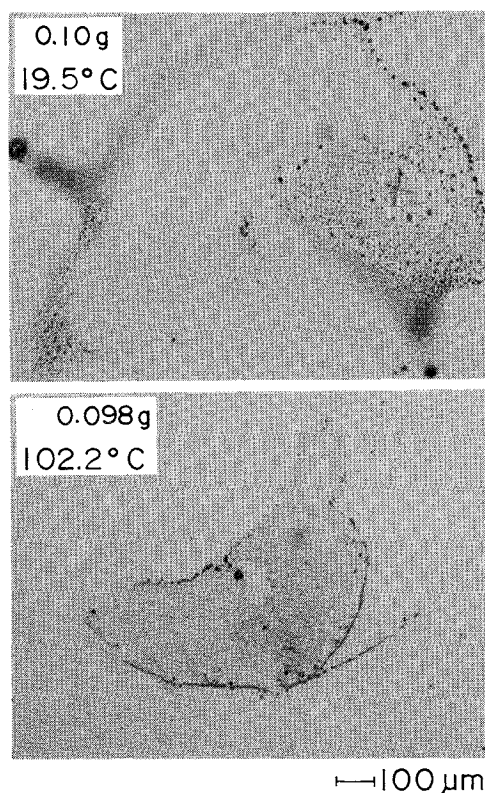


Fig. 5. Water marks from ultrapure water

membrane-distilled water.

2.2 IR spectra for water marks

Figure 6 shows IR spectra for water marks from membrane-distilled water and an SiO_2 sample. The OH peaks at 3430 cm^{-1} and 1630 cm^{-1} resulted from H_2O absorbed by the KBr. The SiO peaks at 1100 cm^{-1} and 800 cm^{-1} resulted from the Si wafer. The peaks in the ranges marked A and C showed C-H bonds and the peaks in the range marked B showed

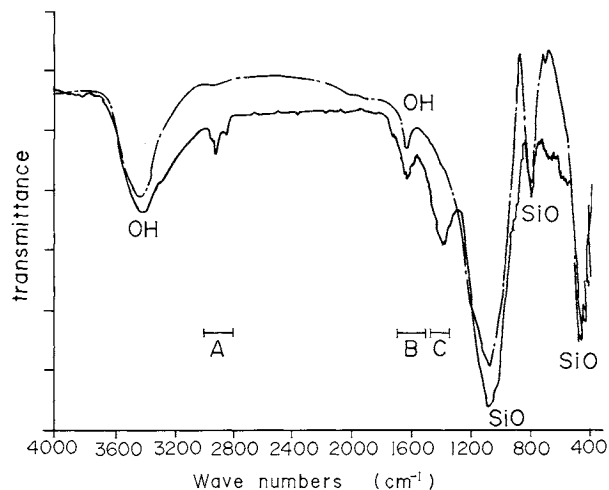


Fig. 6. IR spectra for water marks from membrane-distilled water and SiO_2

C=C bonds. There were no peaks for bonds of C=O and C-O.

Therefore, the main constituent of the water marks was hydrocarbon, containing some C=C bonds.

Conclusion

Effects of evaporation temperature on the formation of water marks was studied using membrane-distilled water and ultrapure water with the respective water qualities shown in Table 1. The following conclusions were obtained.

- (1) The main constituent of the water marks from membrane-distilled water was liquid hydrocarbon, containing some C=C bonds.
- (2) When evaporation velocity was greater than about $20\text{ kg}/(\text{m}^2 \cdot \text{h})$, membrane-distilled water could be evaporated without the formation of water marks.
- (3) Water marks from ultrapure water had a higher boiling point than those from membrane-distilled water. The former were left on the Si wafer, even when the water was evaporated at a velocity of about $20\text{ kg}/(\text{m}^2 \cdot \text{h})$.

Nomenclature

d	= diameter of a drop of water on a Si wafer	[m]
R	= water-mark residual ratio	[—]
v	= evaporation velocity	$[\text{kg}/(\text{m}^2 \cdot \text{h})]$

Literature Cited

- 1) Balazs, M. K.: 4th Annual Semiconductor Pure Water Conference, p. 222 (1985-1).
- 2) Oomi, T. and H. Mishima: ULSI Ultra Clean Technology Symposium, No. 2, p. 399 (1986-3).
- 3) McConnelee, P. A., S. J. Poirier and R. Hanselka: 5th Annual Semiconductor Pure Water Conference, p. 219 (1986-1).