

## Elucidation of an isopropyl alcohol (IPA) adsorption phenomenon on a wafer surface for achieving an ultra-clean and IPA-saving drying process in the batch cleaning system

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**Abstract.** Displacing the water remaining on a wafer surface by using condensed IPA improves the effectiveness of IPA-based drying techniques. Although this drying technology has been used for years, recent device technologies have needed extremely high-performance drying processes. We characterized an IPA adsorption phenomenon on a wafer surface by using the batch cleaning system and determined the appropriate drying conditions. Our results revealed that the IPA supply rate had a great influence on watermark formation. This can be prevented by increasing the IPA supply rate because the rapid increase of IPA concentration in the remaining water on wafer surface suppresses the dissolution of silicon into water. Through both understanding of an IPA adsorption on a wafer surface and control of the drying condition, an ultra-clean and IPA-saving drying process with a watermark-free performance for future device technologies can be achieved.

### Introduction

The IPA drying process has been widely used in the cleaning systems for semiconductor manufacturing. In the IPA drying process, an effective drying performance is obtained by using condensed IPA to displace water remaining on a wafer surface. Recently, with the scaling down of semiconductor devices, organic contamination such as IPA residue on a wafer surface can cause serious deterioration of device properties [1]. Furthermore, an IPA-saving process is required under the current conditions that call for environmentally-friendly cleaning processes. Developing an ultra-clean and IPA-saving drying process is thus important for future device technologies. To achieve such a drying process with a watermark-free performance, the phenomenon of IPA adsorption on wafer surfaces need to be elucidated. We characterized an IPA adsorption phenomenon using the batch cleaning system and determined the appropriate ultra-clean drying conditions. We will describe the mechanism of an ultra-clean and IPA-saving drying process with a watermark-free performance we developed on the basis of the results.

### Characterization of IPA adsorption on wafer surfaces

**Experimental procedures.** As wafer temperature and IPA concentration are considered crucial effects on IPA adsorption on a wafer surface, we investigated how the amount of IPA residue affects the two. The samples were treated in dilute HF solutions to remove native oxides and dried in different conditions using a batch cleaning system (Figure 1). Wafers were moved to the upper drying chamber just after the dilute HF and rinse treatments were completed. The amount of IPA residue was measured using a wafer-thermal desorption gas chromatography mass spectroscopy (WTD-GC-MS). The relationship between the IPA process time and the amount of IPA residue on the wafer surface is shown in Figure 2. The IPA residue became saturated when the IPA process time was more than 60 seconds, so, this was the IPA process time for our evaluations.

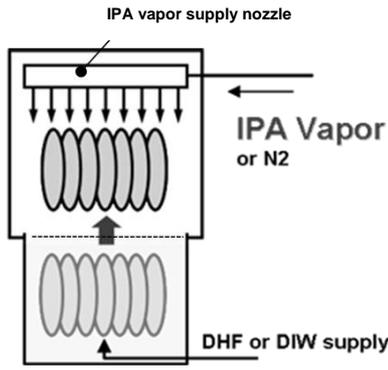


Figure 1: Schematic of wafer treatment.

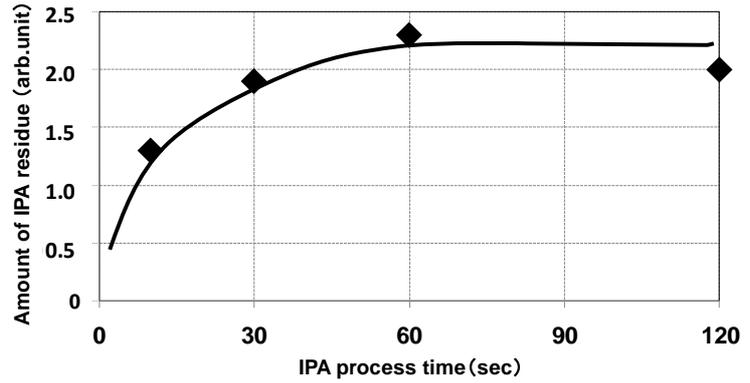


Figure 2: Relationship between IPA process time and amount of IPA residue on wafer surface.

**Effect of wafer temperature on IPA residue.** Wafer temperatures can be controlled by the temperature of the rinse water directly before the drying process begins. The relationship between wafer temperature and IPA residue is shown in Figure 3. We found that the amount of IPA residue on the wafer surface decreases as the wafer temperature goes up.

**Effect of IPA concentration on IPA residue.** IPA concentration can be controlled by the IPA supply rates during the drying process. The more the IPA supply rate increases, the higher the concentration of IPA in the process chamber becomes. The relationship between the IPA supply rate and the amount of IPA residue for different wafer temperatures is shown in Figure 4. We found that the amount of IPA residue increases and gradually becomes saturated as the IPA supply rate increases. We also found that the amount of IPA residue decreases as the wafer temperature goes up at the constant IPA supply rates. It is interesting to note that the behavior of the IPA residue is identical to the Langmuir adsorption isotherm.

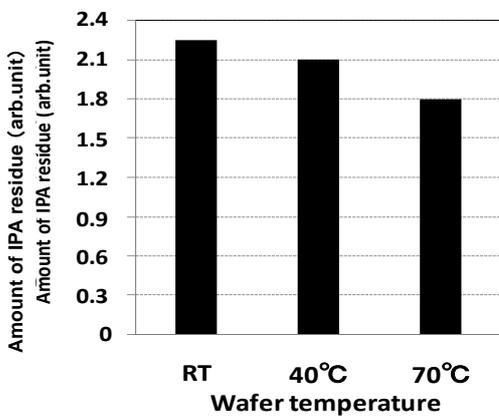


Figure 3: Relationship between wafer temperature and IPA residue.

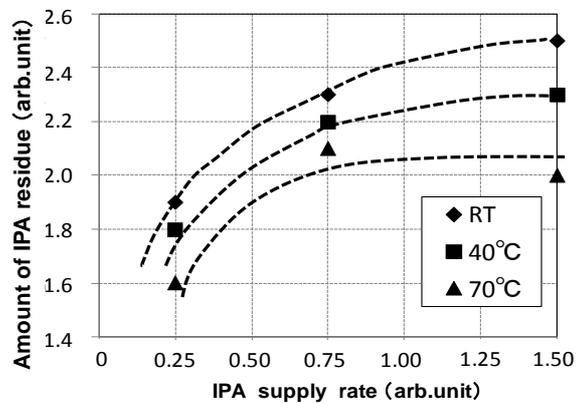


Figure 4: Relationship between IPA supply rate and amount of IPA residue for different wafer temperatures.

**Evaluation of watermark formation for ultra-clean IPA drying conditions**

We determined the following methods of reducing IPA contamination on wafer surfaces, *increasing wafer temperatures, lowering IPA supply rates, and reducing the IPA process time.* We have evaluated the drying process performance using a watermark test element group (TEG) wafer.

**Increasing wafer temperatures.** As mentioned above, wafer temperatures can be controlled by the temperature of the rinse water. The relationship between rinse water temperatures and the formation of watermarks is shown in Figure 5. We have observed that more watermarks were formed at a higher rinse temperature. To prevent the formation of watermarks, wafer temperatures should be kept low.

**Lowering IPA supply rates.** The dependence of watermark formation on the IPA supply rate is shown in Figure 6. Increased watermark formation at a lower IPA supply rate can be observed. We have also determined that the formation of watermarks is unavoidable even though the total amount of the IPA supply increased. The dependence of watermark formation on the total amount of IPA supply, which is controlled by changing IPA process time under the same IPA supply rate is shown in Figure 7. The numbers of watermarks on a wafer are almost the same among three conditions of total amount of IPA supply. These results indicate that it is impossible to prevent the formation of watermarks by lowering the IPA supply rate even with an increase of the total IPA supply.

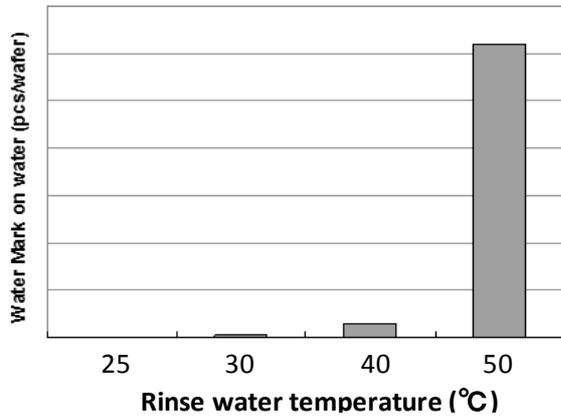


Figure 5: Relationship between rinse water temperature and formation of watermarks.

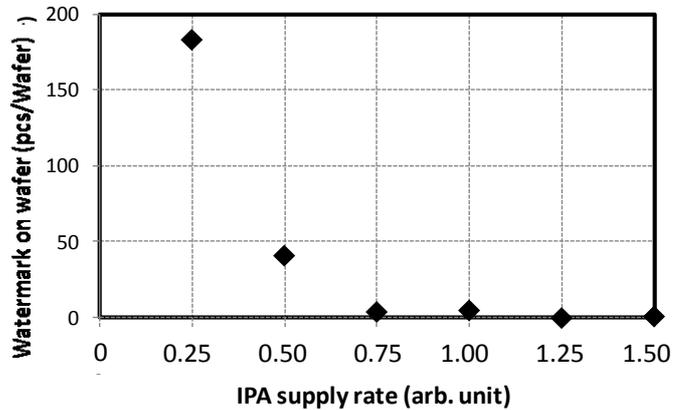


Figure 6: Dependence of watermark formation on IPA supply rate.

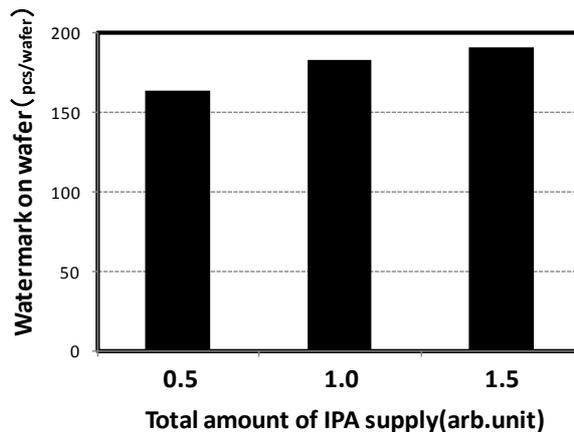


Figure 7: Dependence of watermark formation on total amount of IPA supply.

**Reducing the IPA process time.** It is obvious that merely reducing the IPA process time leads to the increase of watermark formation because there is insufficient IPA for drying. Therefore, we have reduced the IPA process time when there is an increased IPA rate. We investigated the dependence of watermark formation on the IPA process time for several IPA supply rate conditions. As shown in Figure 8, increasing the IPA supply amount by extending the IPA process time does not prevent watermark formation in the lower IPA supply rate. On the other hand, the watermark is not formed even though the IPA process time is very short in the increased IPA supply rate. The relationship between watermark formation and IPA supply rate for three conditions of the total amount of IPA supply is shown in Figure 9. An effective drying performance at a higher IPA supply rate is observed when the total amount of IPA is small, which indicates an ultra-clean and IPA-saving drying process with a watermark-free performance can be achieved. Thus, it can be said that the watermark formation is prevented by the increase in the IPA supply rate rather than the total amount of IPA supply. We now discuss the mechanism of an ultra-clean and IPA-saving drying process with watermark-free performance. Since a watermark is likely to form when the water film or droplets containing more silicon-related material evaporate on the wafer surface, it is important

to prevent the dissolution of silicon into the remaining water just before the drying process. The results of silicon dissolution into an IPA/DIW mixed solution for different temperatures can be seen in Figure 10. Because the rapid increase of IPA concentration in the remaining water on the wafer surface suppresses the dissolution of silicon into the water, the increased IPA supply rate prevents a watermark forming. The results of more silicon dissolution at higher temperature are consistent with the relationship between rinse water temperature and formation of watermarks shown in the previous subsection.

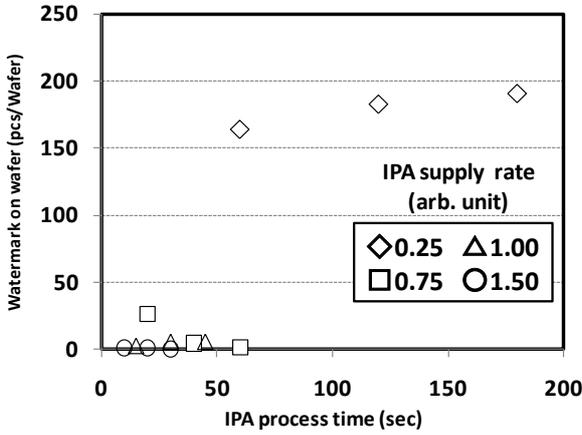


Figure 8: Dependence of watermark formation on IPA process time for several IPA supply rate conditions.

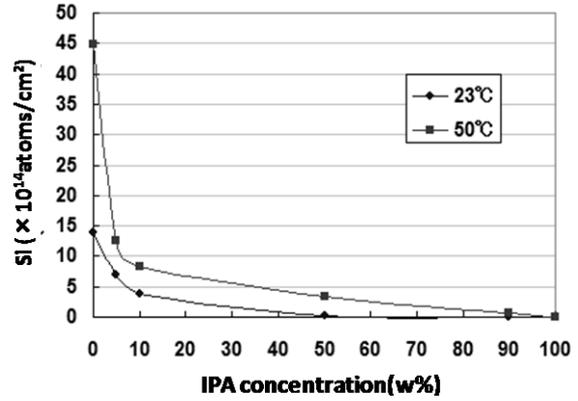


Figure 10: Silicon dissolution into IPA/DIW mixed solution for different temperature.

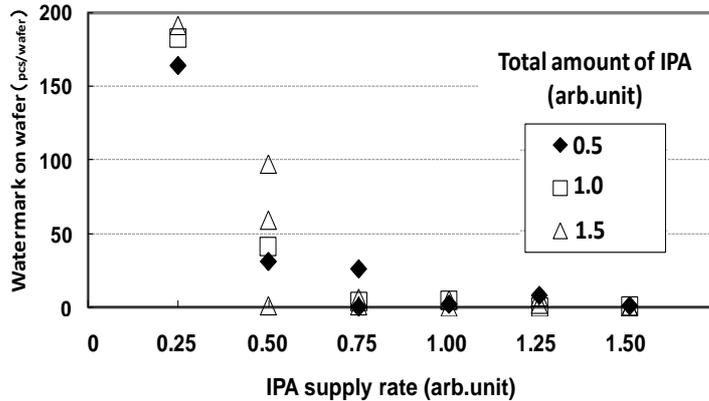


Figure 9: Relationship between watermark formation and IPA supply rate for three conditions of the total amount of IPA supply.

**Summary**

We have demonstrated that the behavior of IPA residue on wafer surfaces is identical to the Langmuir adsorption isotherm. We evaluated the drying process performance for ultra-clean conditions and found that the IPA supply rate had a great influence on watermark formation. This can be prevented by using an increased IPA supply rate because the subsequent rapid increase of IPA concentration in the remaining water on wafer surface suppresses the dissolution of silicon into water. An ultra-clean and IPA-saving drying process that is both watermark-free and that can be applied to future device technology is thus possible.

**References**

[1] K. Motai et al., Extended Abstracts of the 1997 International Conference on Solid State Devices and Materials, pg.24 (1997).

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