# Watermark formation mechanism by evaporation of ultra-pure water: Study the effect of ambient

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Abstract

The watermark (WM) formation process has been reported in literature for many years [1]. Evaporation of ultra-pure water (UPW) from Si surfaces is more complicated than the well-known coffee ring phenomenon due to the kinetics of chemical interactions between oxygen containing UPW and silicon surface [2-3]. The resulting watermarks are composed of a flat "bed" inside a rather narrow ring of residue [2]. In this paper the dynamics of the evaporative drying of UPW-droplets on a hydrophobic Si surface in a controlled ambient is studied. A quantitative study of the WM residue volume and mass as well as topological distribution of residue is performed from low to high ambient humidity. The effects of oxygen in the gas phase and dissolved $O_2$ concentration in UPW are investigated for different levels of ambient humidity.

Experiment & Measurement

Unless otherwise stated, tests are performed in a 30 Liter glass box that is purged with nitrogen with a controlled concentration of water vapor in the RH range of 20–70 %. UPW droplets (with a volume of 1 to 8 µL) are deposited on ultra clean dilute-HF-last silicon wafers placed in the box . The box is then closed immediately to minimize the time of transient poorly uncontrolled ambient (clean room air). As a result of the loading procedure some oxygen is expected to remain in the ambient. The oxygen concentration was below 1%, which is the sensitivity limit of the measurement tool. The RH increase due to evaporation of the droplet can be neglected: even the largest droplet result in an increase in RH < 1.5 %. The evaporation of the droplet is monitored visually. After total evaporation of the UPW droplet, the geometry of the remaining residue is measured by a High-Resolution Profilometry (HRP) (KLA-Tencor). A mathematical algorithm is developed to calculate the volume of the WM, based on the HRP profile: the volume of the ring-component is extracted separately from the central bed-volume (inside Fig.1). The volume is converted to mass by assuming a silica-density of 2.65 kg/cm$^3$.

Result and discussion

On all of our samples clear residues could be detected. The formation of the residue is due to a chemical reaction between the oxygen dissolving from ambient into the droplet and the substrate. In figure 1 the drying residue mass of a 3µL size UPW droplet is plotted for different ambient humidity. It can be observed that the longer evaporation time for high ambient humidity resulted in more residues. The constant droplet size resulted into the same initial wetting area with a diameter of around 3 mm for all RHs. This increase in residue mass is affected mostly by the longer evaporation time in case of high ambient humidity.

Figure 2 shows drying residue mass as a function of the initial UPW droplet volume for different levels of ambient humidity. It is clear that residue mass increases linearly with the initial droplet volume. A larger initial droplet volume results in a larger wetting area but also in a longer drying time. A bigger wetting area leads to a larger interaction area with the substrate and thus production of a larger residue. The increase in residue volume can be attributed to both an increase in wetting area as well as in drying time.

Figure 3 exhibits the effect of oxygen concentration on the residue mass as a function of the initial droplet volume at 42% relative humidity of clean room air. The mass of the residue formed in air ambient is only 2-3 times higher than in nitrogen ambient containing less than 1% $O_2$. This relatively small difference is less than the difference in the oxygen concentration. Further study on how oxygen dissolved in the contact line of the different droplet shape is ongoing. Also the separation of the residue topography into a ring-part and a flat "bed" will be further explained.

Conclusion

This quantitative study on WM formation in different ambient humidity showed indeed linearly increase of the drying residue mass as a function of UPW droplet volume. The ambient oxygen diffusion at the contact line is the key factor to develop a model for predicting the amount of final residue of WMs.

References

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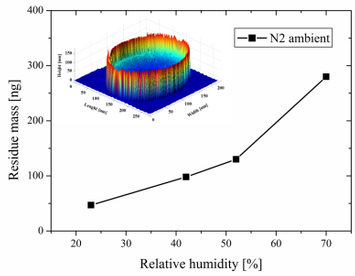


Figure 1. Drying residue of a 3µL UPW droplet as a function of relative humidity in N2 ambient. Inside figure: a 3D HRP shape of WM.

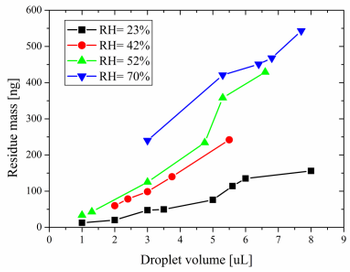


Figure 2. Residue mass as a function of the initial UPW droplet volume and for different $N_2$ ambient with different relative humidity. Effect of both wetting area and evaporation time are combined for large UPW droplets.

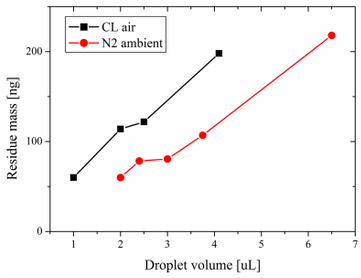


Figure 3. Drying residue in less than 1% $O_2$ and 20% $O_2$ concentration at 42% relative humidity.