Role of Ambient Composition on the Formation and Shape of Watermarks on a Bare Silicon Substrate

A. H. Tamaddon,a,b* P. W. Mertens,a,† J. Vermant,a G. Vereecke,a,* F. Holsteijns,a,* M. Heyns,a,b and S. De Gendt,a,†

aInec, Leuven B-3001, Belgium
bDepartment of Material Engineering, KU Leuven, Leuven 3001, Belgium
cDepartment of Chemical Engineering, KU Leuven, Leuven 3001, Belgium
dDepartment of Chemistry, KU Leuven, Leuven 3001, Belgium

Wetting and drying in wet cleaning process received a lot of attention to meet the requirements of advanced technology nodes. Drying performance is evaluated by the number of watermarks produced during the rinsing and drying steps. Watermarks appear by evaporation of a very small sized water droplet remaining at the end of the drying step. In this article the influence of relative humidity and oxygen concentration of ambient on formation of different watermark shapes is studied by evaporation of ultra-pure water droplet on HF-last silicon surfaces. A qualitative model is presented taking into account: evaporation and gas-ambient (O2) exchange, chemical reactions forming the residue species starting from dissolved O2 and Si, transport of species by diffusion and evaporation driven convective radial outward flow. The watermarks are subdivided in two components: an outer ring shaped component and a more or less flat residue bed inside the ring. The experimental results showed a transition between ring shape to somehow circular shape of watermark (bed part) by increasing the relative humidity of ambient. The low humidity resulted in the shorter drying time and in the smallest drying residue, consisting mainly of a ring-shaped component, which is in agreement with the model.

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As the semiconductor devices shrink, perfect drying after each wet processing step is mandatory.1,2 The formation of drying defects and watermarks (WM) has been identified as a serious problem.1,3 WM are composed of silica species which form by precipitation of dissolved silica present in rinsing ultra-pure water (UPW).3-6 Different shapes of the WM have been reported in literature.7-9 The formation of so-called coffee ring stains is driven by convective transport of colloidal particles inside an evaporating sessile droplet and has been extensively studied in the literature.10-12 Deegan9 was the first who reported a the ring shape coffee ring stain in relation to a pinned droplet of a colloidal solution. According to his analysis, the evaporation of the water is highest near the contact line. In order to maintain the pinned shape water molecules evaporated at the contact line (CL) are replaced by the water molecules drown from the center of the droplet. This outward radial flow which transports the water molecules also transports all matter dispersed in the liquid to the CL. Deposition of solutes accumulated at the CL causes the coffee ring shape WM.7 These models essentially deal with inert liquid-substrate combinations, where the substance that form the water mark is originally dispersed in the liquid.

In contrast, evaporation of droplets of UPW, i.e. water that contains only very small amounts of non-volatile impurities (less than a few ppb by weight)), has been reported to result in WM formation when present on a base silicon substrate.7,13 In this case chemical reaction(s) between the substrate and the liquid, create non-volatile species that get dispersed in the liquid. In this case, the concentration of non-volatile species in the liquid is determined by the kinetics of the liquid substrate chemical interaction. The drying process of such water droplets on bare silicon consists of three phases starting by a pinned phase then continue to a receding phase, and again a short pinned phase that ends with the total drying of the remaining liquid. Evaporation of a liquid drop (consequently formation of WM) is a simultaneous process of heat and mass transfer. The heat and mass transfer is a function of droplet geometry, temperature, relative humidity (HR) and transport properties of the gas ambient surrounding each droplet. Moreover, HR directly influences the drop evaporation rate, i.e. a drop evaporates faster at lower HR values.14 As such, the interaction time of the liquid to the substrate, and the formation of residues in the liquid will vary in space and with time.

In this paper the effect of the ambient composition on the evaporative drying of ultrapure water (UPW) droplets on a hydrophobic bare Si surface and the corresponding water mark formation will be studied. The ambient was alternated between N2 (with low residual oxygen concentration) and normal air ambient, both with a variable relative humidity level.

Experimental

All experiments are done in a class 1000 clean room of 21 °C and 40% relative humidity. Silicon wafers (with a (100) surface crystal orientation) are cleaned and treated with an HF/HCl mixture (0.1 w/w%), rinsed by UPW and dried with pure nitrogen to target a hydrophobic Si surface and the corresponding water mark formation will be observed. The ambient was alternated between N2 (with low residual oxygen concentration) and normal air ambient, both with a variable relative humidity level.

All experiments were performed with a Sycamore Dri-Test® coating system equipped with a Sycamore Vapor® vapor phase reactor and a Sycamore CO2 laser for moisture detection. The qualitative model was presented taking into account: evaporation and gas-ambient (O2) exchange, chemical reactions forming the residue species starting from dissolved O2 and Si, transport of species by diffusion and evaporation driven convective radial outward flow. The watermarks are subdivided in two components: an outer ring shaped component and a more or less flat residue bed inside the ring. The experimental results showed a transition between ring shape to somehow circular shape of watermark (bed part) by increasing the relative humidity of ambient. The low humidity resulted in the shorter drying time and in the smallest drying residue, consisting mainly of a ring-shaped component, which is in agreement with the model.

The initial volume of UPW droplets was determined by an accurate pipette in the range of 1 to 7 μL. These UPW droplets are deposited by the pipette on a hydrophobic Si wafer placed in a 30 Liter glass box with a clamped lid for sealing. After droplet deposition, the box is closed and evacuated immediately to minimize the time of transient uncontrolled ambient (i.e. clean room air). Upon loading the sample and closing the lid, a procedure is run to replace the air inside the box. The box is evacuated down to a residual pressure of a few mbar and subsequently purged and filled with the controlled ambient gas under study at a flow rate of 25 SLM. This evacuation- gas-purge cycle is performed 3 times in a row and takes about 2 mins in total. Then from the end of this 3-fold purge cycles the ambient in the box stays in a static state without any purging.

Nitrogen gas with a controlled relative humidity concentration (HR range: 20–70%) has been used. The humidity was added using a bubbler with UPW. The residual oxygen concentration in the box after the N2 purging cycles was measured with a digital oxygen analyzer (PLAS-Lab Inc., Model 800 DOI) The measured oxygen concentration was 0.02 to 0.03%. In addition to N2 also “synthetic” air, i.e. a
mixture of (79.5%) N₂ and (20.5%) O₂, was used with variable concentrations of water vapor. The choice of the initial droplet size (in range of 1 to 7 μL) is a compromise between two phenomena. On one hand, to limit the transient effects caused by loading in the uncontrolled ambient, in all experiments, sufficiently large UPW droplets are used, i.e. with an initial volume larger than 1 μL. The evaporation time even for the lowest ambient humidity is then longer than 10 minutes, which is at least 5 times longer than the box loading time. On the other hand the droplets are chosen sufficiently small, in order to limit their contribution to the humidity upon evaporation inside the box. In case of the largest droplet, the HR may increase up to 1.5% and thus can be neglected.

The time evolution of the droplet volume, the base diameter and the contact angle were measured in a small dedicated closed cell (OCA 20, DataPhysics) of a contact angle measurement tool.

After total evaporation of a UPW droplet, the surface profile of the remaining residue is measured by High-Resolution stylus Profilometry (KLA-Tencor, HRP). A typical circular WM has a diameter on the order of 200–500 μm. The HRP produces a 3D profile composed of more than 100 parallel 2D scans of the WM with a lateral spatial resolution between 1–2 μm. The scanning speed of each 2D measurement is 20 μm/s with a sample rate of 200 Hz.

**Results**

The evaporation of a droplet with a contact angle of around 70° as it is illustrated in Figure 1a, starts immediately by a pinned phase. When the droplet is in its pinned phase, the volume and the contact angle of the droplet shrink with time until the contact angle reaches its receding value. Figure 1b shows droplet volume shrinkage as a function of time for two values of the relative humidity of ambient. The receding phase begins at a point where the slope of volume evaporation is changed from low evaporation rate in the pinned phase to a higher rate in the receding phase. The switch to the receding regime can be observed as a kink in the curve and is indicated by dashed lines. At this time, the receding phase starts by further shrinkage of the radius of the droplet (higher evaporation rate). At the end of the receding phase again there is a relatively short pinned phase where the final watermark is formed at the footprint of droplet. The droplet stays in the pinned phase (the residues deposited at the contact line enhance the pinning) till the height of the droplet become so thin that the droplet shape becomes unstable and all liquid completely evaporates. The final pinned phase is not visible in Fig. 1b because it is too close to the horizontal axis. Figure 2a shows a 3D profile of a typical WM. The measured 3D profile can be numerically integrated over the entire area to obtain the total volume of the WM. The volume is converted to mass by assuming the density of the residue to be that of silica - i.e. 2.65 kg/dm³. In the WM two main components can be discriminated: an outer ring-component and a central rather flatbed component inside the ring. In a 2D slice of the WM, shown in Figure 2b, the rather flat but extended residue bed inside the ring of the WM is clearly visible. A dedicated algorithm is implemented in MATLAB to separate the volume of the two components of the drying residue. The algorithm works on each 2D profile of the watermark. In the first step the maximum height of the ring is determined. Then, the border between the ring and the bed-component is established, by starting from the ring peak, finding the location where the slope becomes horizontal or changes sign. By a numerical integration we can estimate the volume of the ring and of the central bed, separately.

**Effect of relative humidity in nitrogen and air ambient.**—The WM formation from droplets on a hydrophobic silicon surface in nitrogen ambient for different values of relative humidity is evaluated. Figure 3a shows the total mass of the WMs formed from droplets of 3 different sizes, as a function of the time required for complete...
Figure 3. a) Residue mass as a function of the drying time for different UPW droplet volume (mass) in N2 + H2O ambient. For each droplet volume drying time for the ambient humidity varies from 23% to 70% (left to right). b) Total residue mass and contribution of ring and bed part of the WM formed by evaporation of 5.5 μL UPW droplets in different relative humidities in N2 ambient. c) Residue mass normalized by droplet initial mass vs. time in N2 + H2O ambient.

drying by varying the relative humidity in the N2 ambient. As can be expected, the drying time increases with increasing HR and also with increasing initial droplet volume. The total residue mass increases with increasing evaporation time and increases with increasing initial droplet volume. The initially wetted area increases from 26 to 41 mm² for a droplet size increase from 4 to 7.5 μL (CA = 70°).

Figure 3b shows the two individual components i.e. the ring and bed parts, of a WM evaporated from a 5.5 μL UPW droplet as a function of relative humidity in nitrogen ambient. The ring component is dominant at low HR and increases only weakly with increasing HR, on the other hand, the bed component is very small at low HR but increases strongly with increasing HR. In low humidity ambient the ring is the largest fraction while in high humid ambient the WM is composed of 50% ring and 50% bed. This reveals the importance of the evaporation as the driving force for the ring-shape residue formation in analogy to the coffee-stain phenomenon reported in literature.7 While for the bed component simply the total drying time (i.e. time for liquid-substrate interaction) is more important.

The residue mass can be normalized to the initial droplet mass (see Fig. 3c). For low HR of 23% it can be seen that the values are approximately 5 ppm, independent of the initial droplet size. This means that the absolute residue mass is proportional to the initial droplet mass. As the HR increases gradually a weak dependency on the initial droplet size develops. Larger initial droplets result in a smaller normalized residue mass.

To study the effect of ambient oxygen concentration on WM formation, experimental results at low oxygen concentration are compared to evaporation of UPW droplets in synthetic air with 20% oxygen.

Figure 4a shows the total mass as well as ring and bed contribution for a 1.5 μL UPW droplet evaporated in different humidity conditions (O2 concentration: 20%). Comparing Fig. 4a with Fig. 3b shows that the relative fraction of the bed component is somewhat higher in case of the synthetic air ambient. The main trends observed with respect to the effect of humidity and time are similar to those observed under N2 (in Fig. 3b). However the effect of increasing relative humidity on increasing the bed contribution is more significant in 20% oxygen concentration than in pure N2.

For low humidity ambient the ring formation is the dominant process for both oxygen concentrations while in the high humidity ambient the bed formation is the dominant process for the 20% oxygen concentration, with bed contributions up to 70%. The drastic difference in overall shape and appearance of the watermarks formed under synthetic air is worth noting. For relative humidity of 70% in
Effect of relative humidity on the size of watermarks.— Another effect of relative humidity is observed on the final footprint of WMs. The footprint of WM corresponds to the diameter of the droplet where the receding phase ends and the droplet gets pinned again. As a result of pinning the height of the droplet starts to decrease until a very thin layer of liquid remains. This very thin layer of liquid becomes unstable and finally completely evaporates.

The result of 2D HRP across the center of the final footprint for two droplets are plotted in Figure 5. The final footprint of the WM increased by increasing the relative humidity of ambient. Increased HR results in longer drying times, and therefore more time for chemical reactions (oxidation of silicon surface and dissolution of silica into the UPW droplet) generate the ingredients for the watermarks. From these results already important practical conclusions can be drawn. For a given initial droplet size, the overall volume of a watermark residue resulting from evaporative drying is smallest when operating in low oxygen concentration and low relative humidity (corresponding to shorter evaporation time).

The dissolved species will diffuse away from the substrate/water interface into the water droplet. As in the chemical reactions with the substrate O₂ is consumed, in general O₂ from the ambient will dissolve in the droplet, at its free surface and O₂ will be transported toward the substrate by diffusion. A two-step chemical process takes place. At first, at the silicon surface silica is generated, hydrated, and dissolved in the water. The second step is a polymerization of the dissolved mono silicic acid. In the first step the hydroxyl ions break the silicon bond of the surface and make Si-OH bond. When all four bonds of the silicon are replaced by Si-OH bonds, a soluble silicate (like H₂SiO₃) is formed. The amount of silica formed by this reaction depends on the wetted area underneath the droplet and also the oxygen concentration. Since the silica produced by chemical oxidation can dissolve into the water, new silicon hydrogen bonds underneath are exposed to water molecules, then the process of chemical oxidation can continue. The second step is a polymerization of mono silicic acid when its solubility limit is reached.

Because of the “discontinuity” at the border of the droplet and the resulting diffusion divergence in the ambient, the rate of exchange of O₂ between the droplet and the ambient will be highest close to the contact line. Because the diffusion path is shortest close to the contact line, the rate of diffusion is also expected to be highest close to the contact line. Due to these combined effects the rate of the above mentioned reaction will be strongly increased close to the CL.

At the free surface, evaporation of water takes place. The evaporation rate is non-uniform. It is highest close to the contact line, the rate of diffusion is also expected to be highest close to the contact line. As such the non-uniform evaporation in itself will lead to an increased concentration of dissolved species close to the contact line. This effect is nicely illustrated by the formation of salt-scales on the surface of an evaporating salty droplet as reported in ref. 13. By increasing the relative humidity in the experiment the evaporation rate and all related phenomena can be slowed down (without introducing other effects). As such more time is given to other phenomena to take place.

Secondly, while in the pinned state, the evaporation of the droplet drives a radial outward flow. Based on literature the internal flow inside on evaporative droplet during the pinned phase is primarily determined by a capillary outward radial flow driven by the enhanced evaporation near the CL (replacing the evaporated water at the contact line). Theoretically there is also a thermal Marangoni effect that would generate an inward flow due to a surface tension gradient (liquid/substrate temperature difference). Since this effect is estimated to

Figure 5. 2D profile of WM in air ambient for initial droplet volume of 3 μL for relative humidity of 40% and 70%.

Figure 6. Schematic of WM creation model, with silicon surface chemical oxidation process by diffused oxygen from the contact line (left part). Radial outward flow of fluid toward the contact line (right part) induced by evaporation hydrodynamics.

O₂ with its ambient. A chemical surface reaction converts silicon into dissolved silicic–acid. A simple representation of the chemical reactions is:

\[
\text{Si} + O_2 \rightarrow SiO_2 \tag{1}
\]

\[
SiO_2 + H_2O \rightarrow H_2SiO_3 \tag{2}
\]

In literature related to semiconductor processing, it has been postulated that the presence of oxygen and the contact of water with silicon play a key role in the WM formation. The droplet will exchange

Chemical oxidation

Silica
O₂

Radial outward flow

O₂ dissolution flux

\(j_r\) evaporation flux
be very small it will be neglected in this analysis. The convective flow of water will also carry dissolved silica.

The radial velocity of the liquid and therefore of all non-volatile species inside the droplet has been extracted from the work of Popov.12 He used lubrication theory where the dimensions of the droplet are smaller than the capillary height (approximately 2.2 mm for water). So it is possible to find out a close equation for fluid flow velocity, \( u \), time, \( t \), and the distance from the center of the droplet, \( r \), by solving Navier-Stokes equation.

\[
u(r, t) = \frac{2\sqrt{2}D_{wa}}{\theta(t)} \cdot C_s(1 - H_R) \cdot \frac{1}{\sqrt{R(R - r)}}\]

Here \( D_{wa} \) is the diffusion constant of water vapor in air, \( \theta(t) \) is the contact angle of the droplet, \( R \) is the droplet radius, \( \rho \) is the density of water and \( C_s(1 - H_R) \) is the vapor concentration difference between the droplet surface and the surrounding. Evolution of contact angle as a function of time, \( \theta(t) \), can be achieved by data processing on recorded images of contact angle measurement during evaporation of droplets. As a result of this outward flow all species present inside of the droplet will move to the contact line with a velocity of \( u(r, t) \). The velocity will be relatively low in the center of the droplet but as \( r \) approaches \( R \), the velocity increases asymptotically to an infinite value.

Figure 7 shows calculated (using Eq. 3) internal radial flow velocity at 50 \( \mu \)m from the contact line inside a 1.5 \( \mu \)L size droplet (CA = 70°) as a function of the drying time for different values of ambient relative humidity. As long as the calculated radial velocity is smaller than 1 \( \mu \)m/s it can be neglected with respect to the Brownian motion. In the beginning of evaporation of the pinned droplet, the fluid velocity is low till the droplet reaches its receding contact angle, then the velocity rapidly increases. From Fig. 7 it becomes clear that the radial velocity strongly increases and supersedes the Brownian motion only toward the end of the drying time. This phenomenon has been reported earlier and was referred to as the “Rush hour”.23 It is in this phase that a lot of residues get further deposited at the contact line to contribute to the ring-shaped residue. Figure 7 shows that the relative importance of this “Rush hour” effect decreases as \( H_R \) increases.

As the concentration of silicic acid increases over time it will reach the level of equilibrium with its solid phase and will start to precipitate. This precipitation will take place at the location where the Brownian motion is dominant. The total evaporation time for 20%, 40% and 75% relative humidity are 530s, 760s and 2030s respectively.

Discussion

The velocity of fluid close to the contact line have an impact on how non-volatile species contribute to a ring shape WM. From Fig. 7 it can be seen that the radial flow velocity becomes significant only in the final stage (i.e. approximately last few hundreds of sec) of the drying. For low \( H_R \) this takes almost the entire drying time, while for high \( H_R \), this is a relatively small portion of the entire drying time. This means that the radial flow will contribute more to the ring residue for low \( H_R \) as compared to high \( H_R \) ambient. This is in agreement with the experimental findings presented in Fig. 3b and Fig. 4a.

In the same time the concentration of dissolved silica in the center of the droplet, and more particularly near the top surface of the droplet, increases continuously and eventually reaches the solubility limit and precipitation of silica will contribute to the residue bed.

The normalized residue mass values for drying in \( \text{N}_2 \) with low \( H_R \) of 23% (Fig. 3c) are independent of the initial droplet size and range around 5 ppm. This 5 ppm is approximately equal to the concentration of \( \text{O}_2 \) present in the initial droplet in equilibrium with air, as can be expected by extensive exposure to ambient air prior to loading it into the glass container and starting the evacuation cycles. Thus we can conclude that the oxygen used to form these residues is primarily the oxygen that was initially dissolved in the droplets as they were loaded in the chamber.

With an increase in \( H_R \) the drying time increases. According to Fig. 3c this leads to an increasing normalized residue weight, beyond 25 ppm. For forming such large residues more oxygen than initially dissolved in the droplet is needed. This additional \( \text{O}_2 \) is expected to originate from the ambient (\( \text{N}_2 \) with 0.02% \( \text{O}_2 \)). With increasing ambient, \( H_R \), the normalized residue weight develops a small droplet-size dependence: the larger the droplet produces relatively less residue. This reduction in normalized residue weight can be attributed to the increased droplet size leading to longer transport distances (e.g. diffusion of \( \text{O}_2 \) through the droplet) and thus slower transport. This proves that for this low \( \text{O}_2 \) ambient and for these longer time conditions transport through the droplet (thickness) plays an important role.

The effect of \( H_R \) humidity can be reviewed based on Fig. 3b and Fig. 4a. It is clear that increasing the relative humidity results in a weak increase in ring-residue and a strong increase in bed residue. This confirms that the ring-residue is very much driven by evaporation-related phenomena, in agreement with the above mentioned model. For the bed component simply the total drying time is more important. In case of low humidity, (i.e. fast evaporation), the evaporation related phenomena are most outspoken. This will lead to super saturation being reached first near the CL. In those conditions an outspoken ring-shaped residue is formed at the contact line. This is in agreement with the model: The increase of the total and bed-residue with increasing \( H_R \) is attributed to the increased time available for the watermark formation reactions to take place.

Fig. 4b shows the normalized residue mass for the \( \text{N}_2 \) ambient and for the air ambient. The normalized residue weight shows little dependence on the initial droplet volume (in agreement with Fig. 3c). The normalized residue weight for air ambient is about twice larger than that in \( \text{N}_2 \) ambient, despite the fact that the \( \text{O}_2 \) in the ambient is a factor of 1000 higher. It shows that the effect of the \( \text{O}_2 \) concentration in the ambient is rather weak. It may be attributed to silicon oxidation by water molecules. In the case of \( \text{N}_2 \) ambient, even though there may be some oxygen exchange from the water droplet into the ambient, the result shows the residual amount of dissolved oxygen is still very effective for the WM process to take place.

Conclusions

The evaporation of sessile water droplets on bare Si surfaces was studied. The evaporation of sessile water droplets on bare Si surfaces occurs first in a pinned regime and consecutively proceeds to a hanced droplet pinning as described earlier. As such the formation of the ring-shape residue is expected to occur first, while the bed-residue forms later at the final evaporation of the unstable droplet.
receding regime. Towards the end of the receding regime a short pinned phase is observed. When all liquid finally evaporates a residue (WM) is found on the surface.

In particular the ambient was controlled and varied. 3D profiling was applied to measure the topography and shape of the resulting WM. In general the residue increases almost linearly with the initial droplet volume. Typically the water marks can be split up in two components: A outer ring part and a more flat component (referred to as “bed”) inside this ring shaped residue.

Towards the end of the receding regime a short pinned state occurs during which the outer-ring part of the drying mark is formed and that further stabilizes the pining for a short time while the remainder of the droplet quickly dries completely and leaves an extended rather flat residue bed on the surface.

A qualitative model is presented taking into account: evaporation and gas-ambient ($O_2$) exchange, chemical reactions forming the residue species starting from dissolved $O_2$ and Si, transport of species longer reaction time for residue formation.

The radial outward flow plays a more important role for short drying times (low $H_R$). It explains that evaporation related phenomena contribute particularly to the formation of the ring residue component. The ambient consisted of 0.02% or 21% $O_2$ in N$_2$, with variable concentration of water vapor. A factor of 1000 reduction in ambient oxygen concentration resulted in only a limited reduction of the WM size. As expected, the relative humidity determines the time needed for complete drying. For a given initial droplet size, the overall volume of a watermark residue resulting from evaporative drying is smallest when operating in low relative humidity, resulting in shorter evaporation times. The relative humidity of the ambient was proven to have a different effect on the two residue components. The relative humidity determines the time needed for complete drying. It was found that the low humidity resulted in shorter drying time and in the smallest drying residue, primarily consisting of a ring-shaped component, in agreement with the model. For increasing humidity particularly an increase of the flat “bed” component was observed, attributed to the longer reaction time for residue formation.

Acknowledgments

The authors thank Dr. Naser Belmiloud of Dainippon Screen, he has provided insightful discussions about this research. We also acknowledge Dr. Dennis van Dorp of Imec for his ideas for further scientific research.

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