Polydimethylsiloxane (PDMS) spreading morphological patterns on silicon wafers in vacuum and in air

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Abstract:

This paper reports the investigation of the morphological patterns and kinetics of polydimethylsiloxane (PDMS) spreading on a silicon wafer using combination of techniques including ellipsometry, atomic force microscope (AFM), scanning electron microscope (SEM) and optical microscopy. A macroscopic silicone oil drops as well as PDMS water based emulsions were studied after deposition on a flat surface of a silicon wafer in air, water and vacuum. Measurements using an imaging ellipsometer clearly show the presence of a precursor film. The diffusion constant of this film, measured with a 60 000 cS PDMS sample spreading on a hydrophilic silicon wafer, is $D_f = 1.4 \times 10^{-11}$ m^2/s. Regardless of their size, density and method of deposition, droplets on both types of wafer (hydrophilic and hydrophobic) flatten out over a period of many hours, up to 3 days. During this process neighbouring droplets may coalesce, but there is strong evidence that some of the PDMS from the droplets migrates into a thin, continuous film that covers the surface between droplets. The thin film appears to be ubiquitous if there has been any deposition of PDMS. However, this statement needs further verification. One question is whether the film forms immediately after forced drying, or whether in some or all cases it only forms by spreading from isolated droplets as they slowly flatten out.

Keywords: polydimethylsiloxane, Silicone oil, Spreading, contact angle.

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1. Introduction

Spreading of silicon oil on various surfaces is of importance to many industrial applications and especially in cosmetic industries where silicon oil is widely used. To study the spreading dynamics, simplified conditions are often used in wetting experiments. Flat and atomically smooth solid surfaces and non-volatile liquids are preferable. A smooth surface is necessary to avoid hysteresis effects and in practice a silicon wafer with highly polished surface (inevitably with a thin layer of oxide) is a convenient choice. Using polydimethylsiloxane (PDMS) as a pure and non-volatile liquid minimises possible Marangoni effects driven by evaporation. PDMS is available with a wide range of molecular weights, giving a wide range of viscosity (η). The silicon wafer/PDMS combination was the popular choice for a range of experimental studies to be described below that were carried out in the late 1980's, with French researchers at the forefront.

Spreading a PDMS droplet onto a solid surface belongs to a "dry" wetting processes because of the non-volatility of the liquid. Because the shape of the droplet deposited on flat surface depends on the droplet size we concentrate here on small droplets where $R<<\kappa^{-1}$ (κ^{-1} is the capillary length), in which regime the effects of gravity are negligible. In such case, the long range capillary forces play the crucial role in determining the contact line between solid and liquid. This force pulls out of the drop a film whose thickness results from a balance between the large capillary term and large disjoining pressure [1], and the extent of the film can be macroscopic. The spreading and thin-film dynamics of the precursor film have been the subject of a number of theoretical [2-3] and experimental [4-10] papers. The profile of the macroscopic droplet is measured using interference microscopy [11] but thickness of the precursor film is experimentally measured using ellipsometry [5, 8]. At equilibrium, the film is a "pancake" [12] of thickness e, with microscopic contact angle $\pi/2$, owing to the thickening influence of the disjoining pressure. According to [1], the width ΔR of the foot can be written as

$$\Delta R = \sqrt{(D_f t)} \qquad (1)$$

where D_f is a diffusion coefficient for the foot and t is time. As long as the volume of the foot is negligible, the central drop and the foot behave independently. The diffusion coefficient for the foot is also found to depend on the roughness amplitude h and on the fluid viscosity η:

$$D_f \sim h/\eta \tag{2}$$

The shape of the macroscopic drop is rather smooth, without steps being observed in the precursor film profile.

The aim of the research described in this paper is to investigate the morphological patterns and kinetics of PDMS spreading on silicon wafer using combination of techniques like ellipsometry, atomic force microscope (AFM), scanning electron microscope (SEM) and optical microscopy. A macroscopic silicone oil drops as well as PDMS water based emulsions were studied after deposition on a flat surface of silicon wafer in air, water and vacuum.

2. EXPERIMENTAL DETAILS

Sample used was bulk silicon oil (Down Corning) of viscosity 60,000 cS used for spreading experiments in an imaging ellipsometer, optical microscopy and scanning electron microscopy (SEM). The others are emulsion samples, one with 10 μm droplets of 60,000 cS PDMS (Unilever sample DC2-1310 BB), and six emulsions with 50% v/v of 1 μm PDMS droplets stabilised by a non-ionic surfactant. The viscosities of the PDMS in these six samples, numbered 1 through 6, are 20, 350, 5000, 60000, 300000 and 600000 cS respectively.

An Imaging Ellipsometer (Beaglehole Instruments, New Zealand) was used to investigate thin films of PDMS on a silicon wafer. The main feature of this particular ellipsometer is that it takes an image, capturing the thickness data over an area of the sample. The incident light beam was filtered by optical 600nm wave length filter. Resolution is ~10 μm in directions parallel to the surface, and ~0.1 nm in the normal (i.e. film thickness) direction.

The SEM studies were carried out using a Philips XL30 field emission gun microscopy operating at 5 kV accelerating voltage. Studied samples were not coated and observe in the vacuum 10^{-5} millibars over 20 hours. A Nanoscope III AFM (Digital Instrument) was used for oil droplet imaging in tapping mode with scan head J(100 x 100 μm) and scan rate 0.5 – 1 Hz.

Imaging ellipsometry images were taken of macroscopic drops of 60,000 cS PDMS deposited on silicon wafers. The wafers were cleaned with chromic acid, distilled water and ethanol, then treated in a water-vapour plasma, which means that their surfaces are hydrophilic with contact angle ~0. Very small drops (>1 mm) were deposited in air by dipping a sharp tweezers tip into PDMS and touching the drop to the wafer surface.

3. Results and discussion

3.1. Imaging ellipsometry of the PDMS precursor film

All AFM, ellipsometer and SEM images show distinctive aurora spreading around macroscopic oil drop but do not directly show the film thickness. Software available on ellipsometer can correctly compute the thickness at a single point in the image, and an alternative software program that uses an analytical expression to compute thicknesses at every point in the image. We also have made a semi-empirical calculation which should be reasonably accurate for films of PDMS that are less than a few nm thick. Applying that to the area maps of (x,y) data produces an area map of the film thickness d. This map shows the extent of spreading of a precursor film, and also delineates the perimeter of the macroscopic drop.

Optical microscopy in monochromatic line shows a series of Newton's rings that can be used to estimate the height and contact angle of the macroscopic drop. Although these methods have not been combined for the drops shown below, in principle such a combination should show the profiles of both the macroscopic drop and the precursor film.

Figure 1 shows the thickness maps for a single drop, taken at various times after deposition. The elapsed time in minutes is shown beside each image. Note that the

images are foreshortened because they are viewed at a large angle of incidence (65° from the perpendicular – this angle gives good resolution in the ellipsometric parameters). Hence the horizontal axis shows a true lateral dimension, but the vertical axis in these figures is not calibrated (the numbers shown are simply camera pixels). Furthermore, due to the high angle of incidence, only the central horizontal region of the sample is in proper focus. Note also that the scale is different for the last two images which were recorded at a lower magnification.

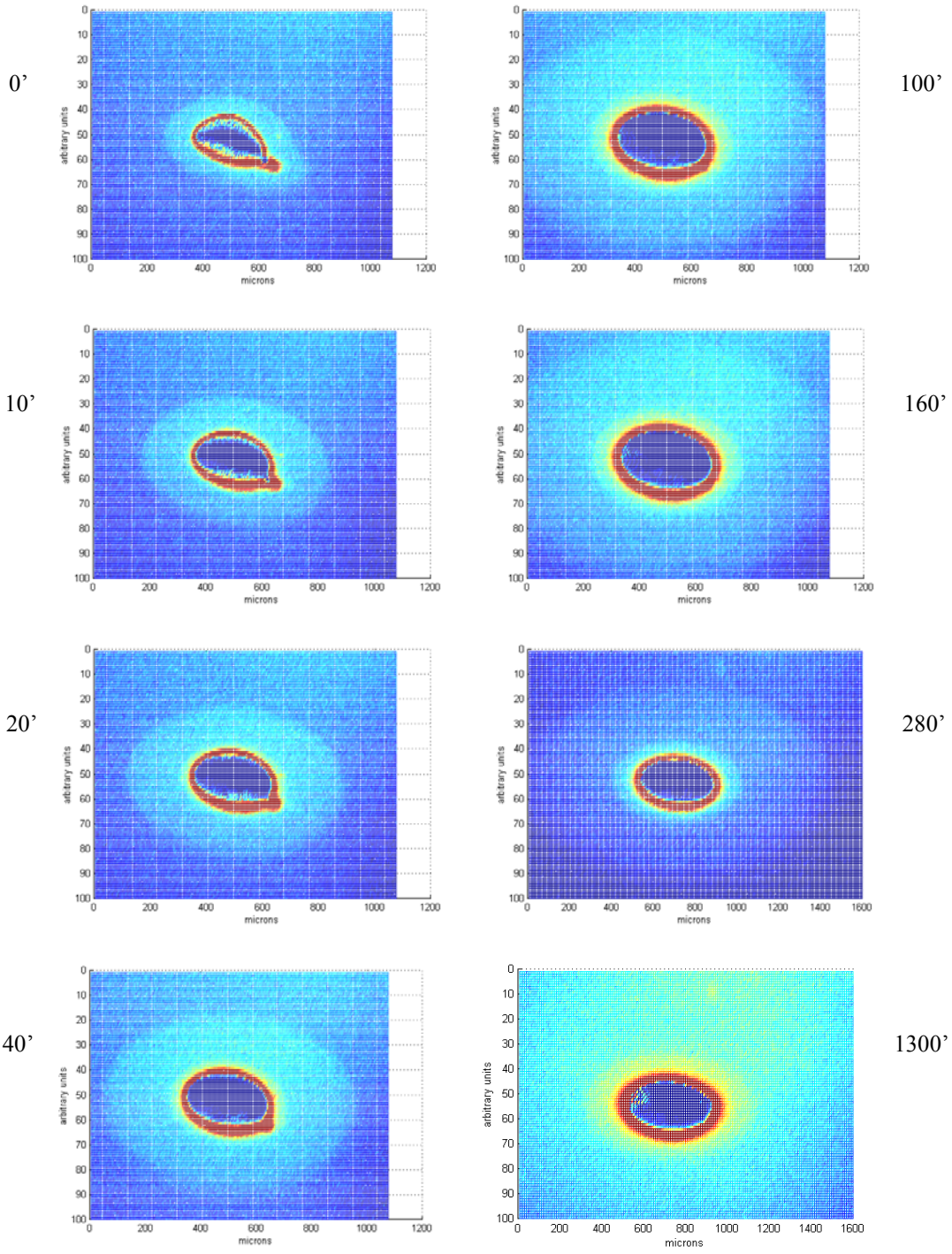


Fig. 1. Thickness maps surrounding a PDMS drop deposited on the plasma cleaned silicon wafer.

Several features are immediately apparent from the series of thickness maps in Fig. 1:

1. There is a precursor film spreading ahead of the drop, which continues to spread over a period of hours. This is seen as the pale blue annulus around the drop, whose macroscopic edge appears as yellow (going to dark red as its thickness increases). Our measurements show that the precursor film thickness

is $d \approx 0.5$ nm. For the first four hours the thickness of the precursor film appears to diminish as it spreads, but it is difficult to be certain about this because the ellipsometer measurements may vary slightly over this period of time, and comparing the calculations between different images may not be precise at the 0.1 nm level.

2. The main drop spreads slightly and slowly, and becomes more circular as it spreads.

3. In the final image taken the following day (after 1300 min), part of the drop appears to have spread into the precursor film, thickening it to 1-2 nm.

The development of precursor layer was also observed on the plasma cleaned (low contact angle) silicon wafer in vacuum chamber of SEM. In SEM micrographs presented in Fig. 2 two different in size droplets have been observed. Larger droplet, 0.6 mm in diameter has very small, only 25 μm in diameter satellite micro-droplet. The precursor layer can be seen on SEM images as distinctive light aurora spreading from both droplets. Because precursor forms immediately after droplet deposition and handling sample into SEM chamber with subsequent air evacuation take few minutes it is impossible to observe development of precursor film layer from the very beginning. In Fig. 2a precursor film already spreads 100 μm from macroscopic droplet foot. Interestingly the width of spreading film seams to be independent of the macroscopic droplet size and is equal in size for larger and smaller droplets. SEM measurements gave possibility to measure the rate of spreading the precursor film but gave no indication about thickness of this film unlike ellipsometry did.

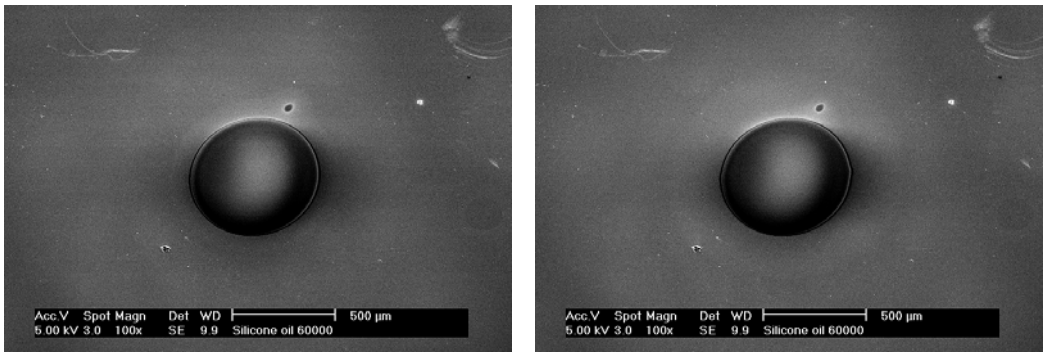


Fig. 2. SEM micrograph of silicon oil drop at the beginning of the experiment and after one hour. Bright ring of precursor film evolve.

Both precursor film widths measured in function of time, spread on plasma cleaned silicon wafer in air (using ellipsometry) and in vacuum (using SEM) are shown in graph Fig. 3. This figure shows the radius of the main drop and width of the precursor film (measured from the edge of the drop to its periphery) as a function of time. From curves in Fig. 3 is clear that spreading rate of the precursor film is similar regardless of hydrophilicity of substrate in air and vacuum which indicate similar slope angle.

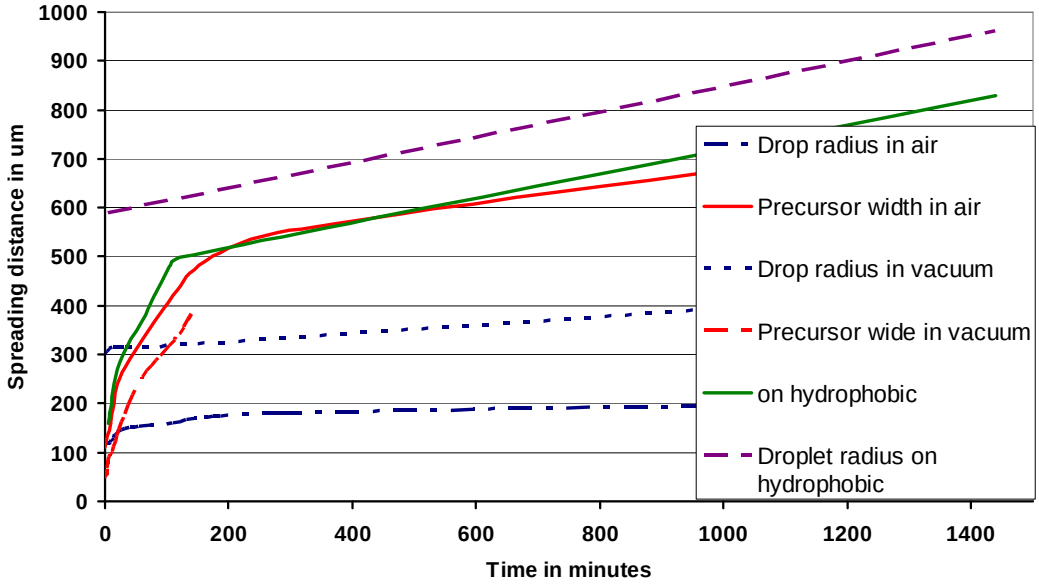


Fig. 3. Increase of drop radius and precursor film width with time, estimated from the images in Figs. 1 & 2. The upper plot has time on a linear scale; the lower one compares precursor film width to √t.

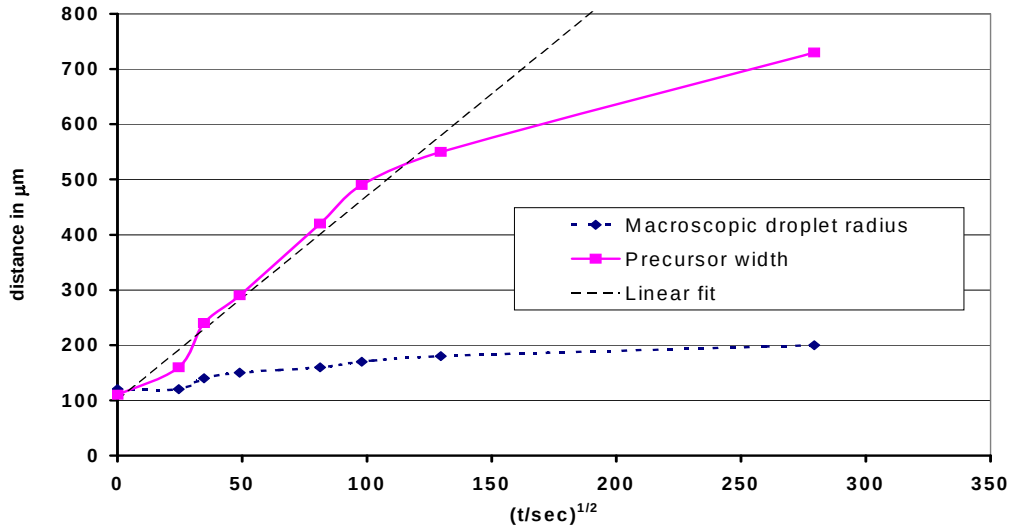


Fig. 4. Increase of drop radius and precursor film width with time, estimated from the images in Fig. 1. The upper plot has time on a linear scale; the lower one compares precursor film width to √t.

Plotting the precursor film width against the square root of time (Fig 4, lower part) shows linear behaviour at least for the first four hours. The slope of this line corresponds to a precursor film diffusion constant (from equation (1)) of $D_f = 1.4 \times 10^{-11}$ m^2/s. $t = 0$ was set when the first measurement was taken, not when the drop was deposited. Extrapolating the straight line back to zero precursor film width is consistent with a delay of about 12 minutes between drop deposition and the first recorded image. Ellipsometry measurements for both precursor films formed in air and in vacuum have similar thickness 2.7 nm on top of the oxide layer estimated as 1.4 nm in thickness.

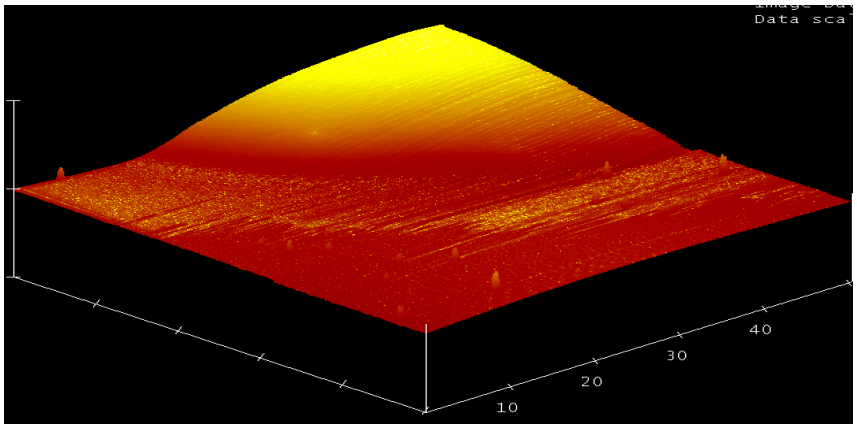


Fig. 5. AFM 3-dimensional image of macroscopic droplet with possible precursor film advancing around its perimeter.

It is very difficult to observe the precursor film development using AFM partly because soft oil droplet surface forms film which is in the same magnitude with silicon wafer roughness. Fig. 5 showing 3-dimensional reconstructions of AFM images, a precursor film extending up to 20 micrometres can be seen. The thickness of this precursor foot measured near the border of a macroscopic droplet, from the section of this droplet is about 13 nm which is many (about 18) times the size of a molecular monolayer. However, the front of the precursor film may be further from what we can observe in AFM micrographs and the real extent may be larger.

In Fig. 6a the edge of the macroscopic silicon oil drop placed in vacuum observed after overnight (18 h since deposition Fig. 2) reach the small droplet perimeter and both droplets are merging. This process also has been observed in optical microscopy in Fig. 6b. Estimating from Newtonian rings in small droplets seen in monochromatic light 589.5 nm on magnified fragment in Fig. 6c the high of this droplet is about 412 nm.

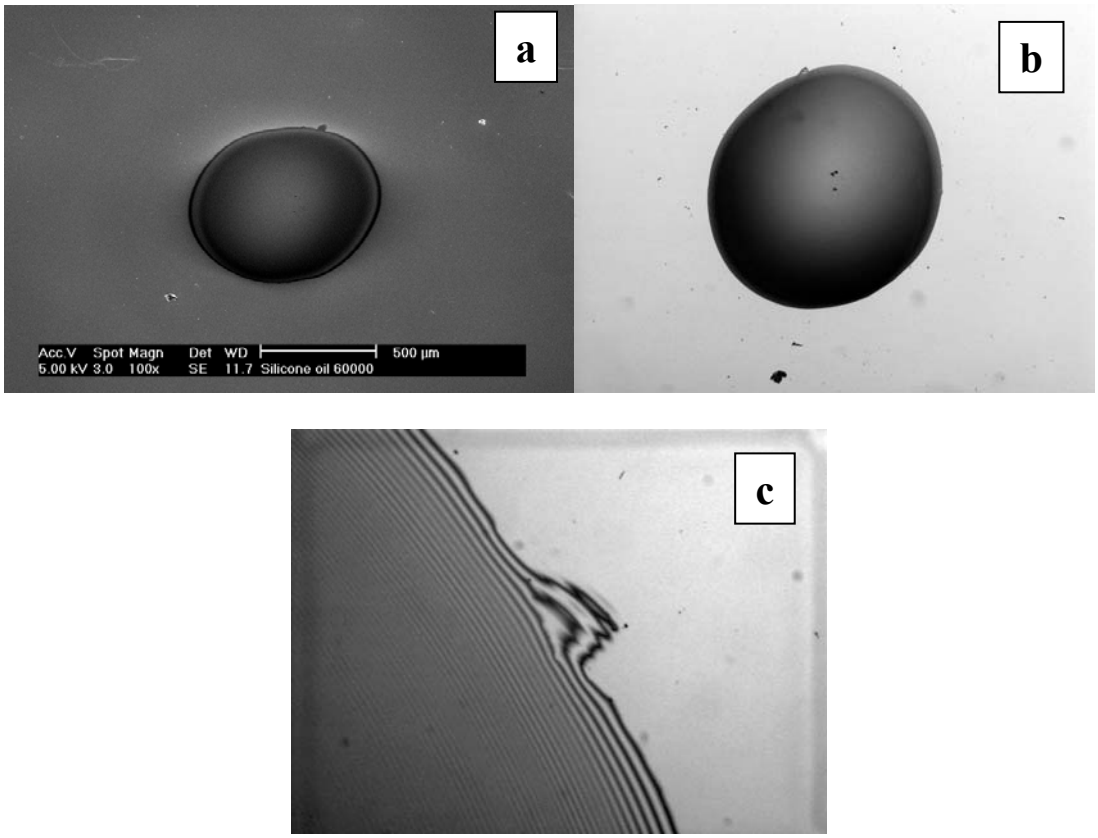


Fig. 6. SEM (a) and optical microscopy observations (b – white light and c- monochromatic light) of merging oil droplets which differ in size.

Merging oil droplets also has been observed using AFM presented in Fig. 7 at the beginning of observation (Fig. 7a) and its final stage after 100 min (Fig. 7b). Also in this occasion droplets largely differ in size. Images from intermediate times in this series were analysed for the dimensions change of the small drop. These parameters are displayed in Fig. 7c and show steady spreading with a slow increase in diameter (less than 0.1 µm per minute) and a progressive decrease in height. The droplet volume, calculated from its dimensions and assuming the shape is a spherical cap, remains steady, while the aspect ratio (the ratio of diameter to height of the spreading drop) increases as the drop flattens. The "spreading ratio" (the ratio of drop diameter

on the surface to the calculated diameter of a spherical drop of the same volume) is about 2 in this case, and increases slowly with time.

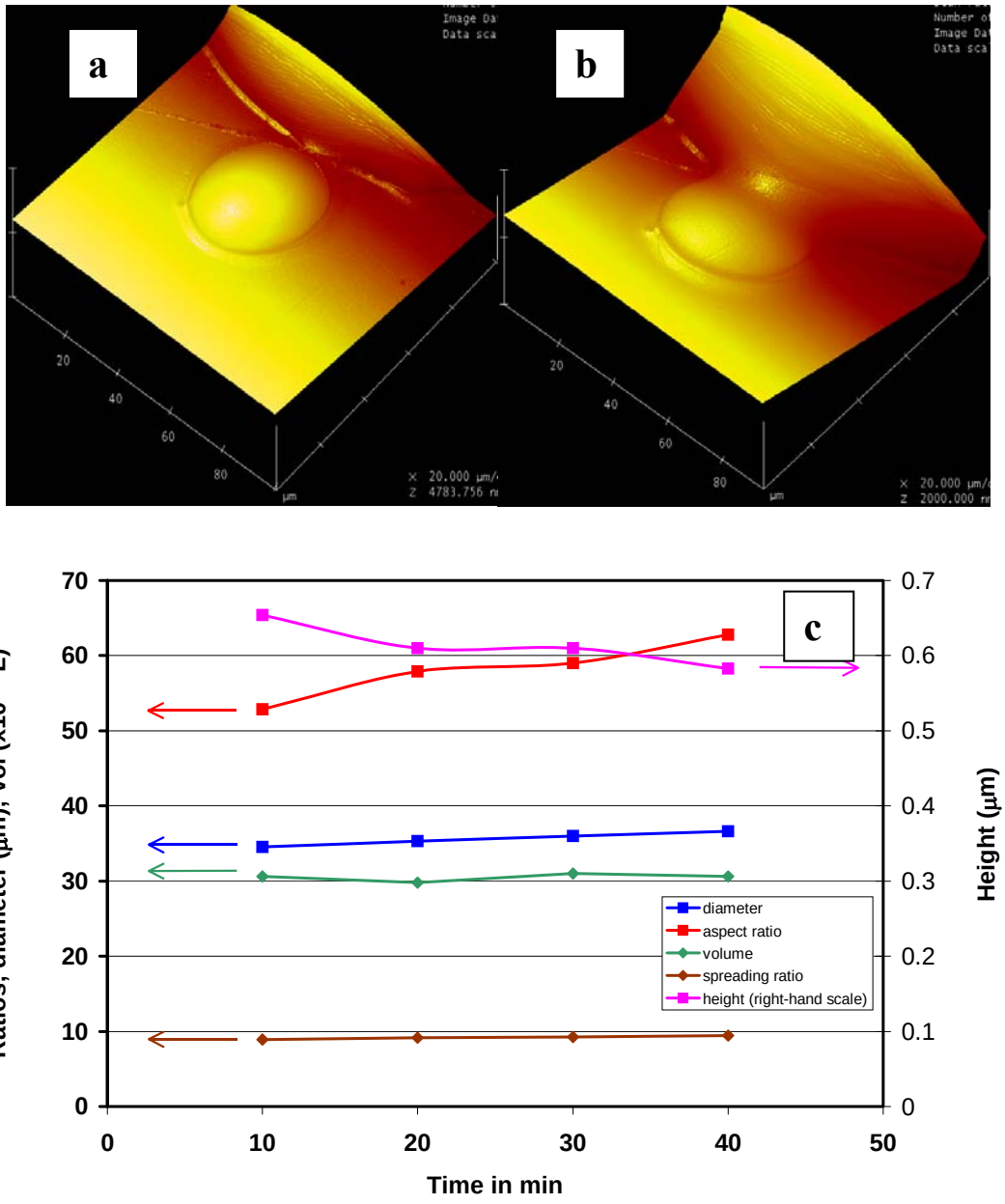


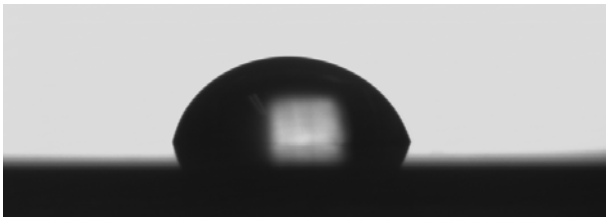
Fig. 7. AFM 3-dimensional images showing the gradual coalescence of a small silicone drop with a large one. Image b was taken 100 minute after image a have been recorded. The area is 100 µm × 100 µm. © The time evolution of shape parameters of the small drop taken from Figure 7c.

OBSERVATIONS USING OPTICAL MICROSCOPY

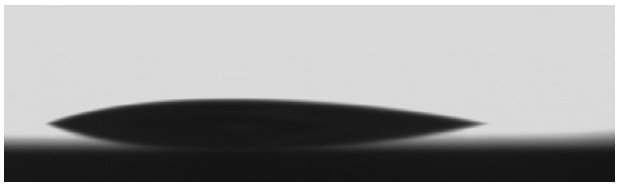
It is simple to observe the spreading of a macroscopic drop using optical microscopy. This can be done with a standard vertically-mounted microscope, in which case the drop can be illuminated with monochromatic light, and Newton's rings

used to determine the drop profile and height. Alternatively, a more direct image of drop profile is obtained using a low-power horizontal microscope designed for measuring contact angles of sessile drops. Drops can be monitored over a period up to many days if necessary, and it is straightforward to make similar observations under water. The precursor film is too thin to be observed by optical microscopy.

Figure 8 presents a series of optical micrographs taken in the horizontal configuration, showing profiles of a PDMS large macroscopic drop during its spreading on a silicon wafer in air. It is clearly seen that the drop spreads, reducing its contact angle and height, over a period of hundreds of minutes. The diameter of the drop at 1 minute (this is the time after deposition of the drop) is 3.3 mm. For clarity of picture we show in Fig. 8 only three photograph of the first, intermediate and last stage of drop spreading.



1 min



36 min

201 min

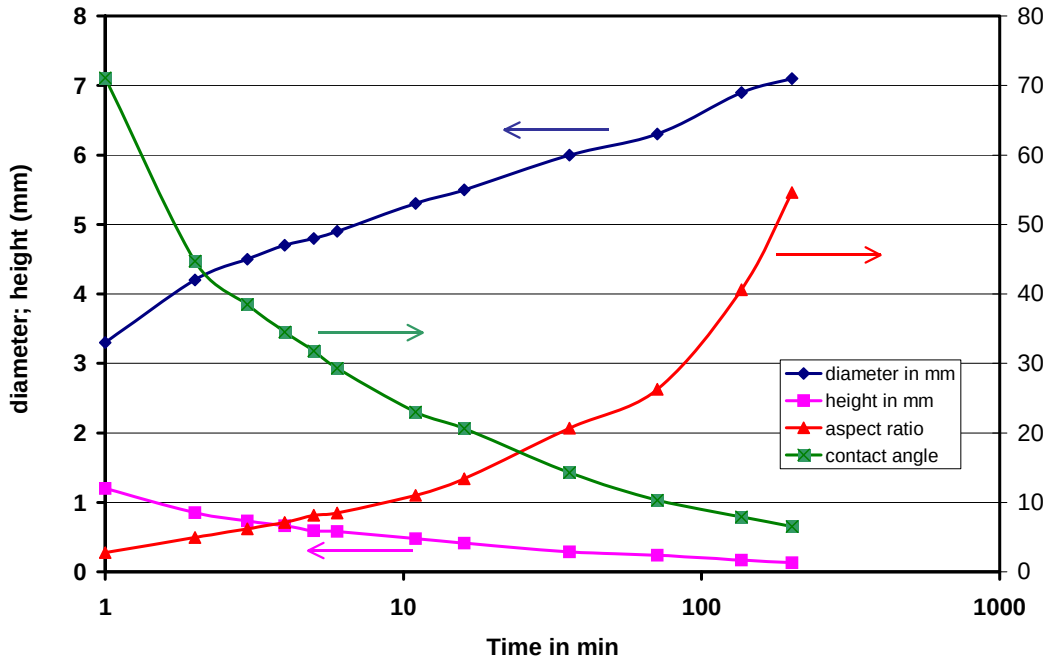


Fig. 8 Optical micrographs of a silicone drop spreading on a silicon wafer in air. Shape analysis of the optical images from, showing the spreading and flattening of the drop. Note the large decrease in contact angle from 70° to less than 10° over 200 minutes for this 60,000 cS silicone on silicon in air.

Figure 8 shows the change in dimensions of the spreading drop illustrated in profiles photographs, i.e. spreading on a silicon wafer in air. The drop diameter on the surface increases while its height decreases, thus the contact angle decreases and the aspect ratio increases quite markedly. The volume is calculated as 6 mL and the spreading factor is 4.

In contrast to this, Fig. 9 shows that a PDMS droplet (0.7mm in diameter) under water does not spread measurably on the silicon wafer over a similar time frame.

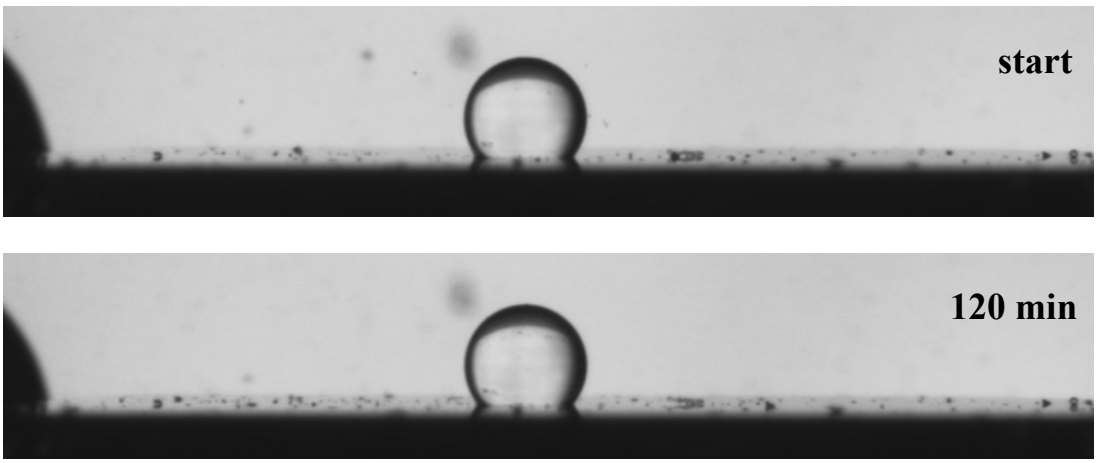


Fig. 9 Optical images of a 0.7 mm diameter silicone drop on a silicon wafer under water, showing that in this environment it does not spread, over a time frame similar to that of Fig. 8.

The advancing and receding contact angles of water on the silicon wafer has been measured using sessile drops apparatus and gives values of 63° and 25° respectively.

In Figure 10 there is an interesting observation of how water spreads on a wafer that was previously covered in silicone oil. Fig 10A shows the low receding contact angle of water on top of a thin PDMS layer, giving a low value of about 15°. The water droplet shown in Fig. 10B was placed on top of a thick PDMS film, and shows an unusual shape. Close examination shows a slight groove running around the drop at about 1/3 of its height, which may be a PDMS/water/air three-phase line at the top of a PDMS meniscus rising up the water drop, as illustrated schematically in Fig. 10C.

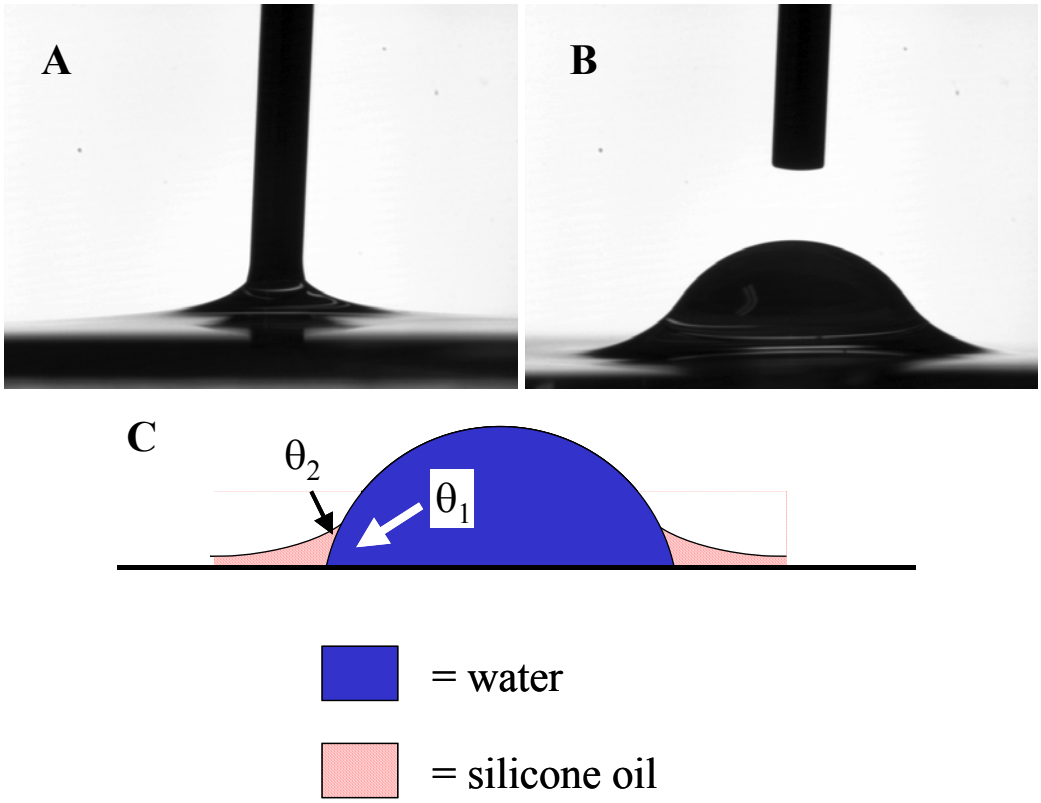


Fig. 10. Optical images of a water drop pressed onto a silicon wafer that was previous covered with a thin (A) or thick (B) layer of silicone oil. The syringe diameter is 1 mm. In (B) a faint, roughly horizontal, line can be seen about 1/3 of the way up the drop on the left-hand side. We think this is a silicone/water/air three-phase line as illustrated schematically in (C), where θ_1 is the contact angle of water on silicon underneath silicone oil, and θ_2 is the contact angle of silicone oil on water in air.

2. METHODS USED TO DEPOSIT PDMS DROPLETS FROM EMULSIONS

Four different methods were used for deposition of PDMS emulsion droplets onto flat solid substrates. They were not all successful, as it was shown below, but the

information gained by trying different methods has proven helpful in understanding how deposition may be achieved using this emulsion.

The various methods are illustrated in Figure 11. The first method is to place a macroscopic drop of the diluted emulsion form concentrated (50%) one by a factor of ~10^3 to 10^4, directly onto a wafer placed horizontally. The drop is then dried on air, or placing in a vacuum chamber. For most of the results shown below, and unless stated otherwise, the vacuum drying method was used since it gave the least amount of mechanical disturbance caused by fluid flow during drying.

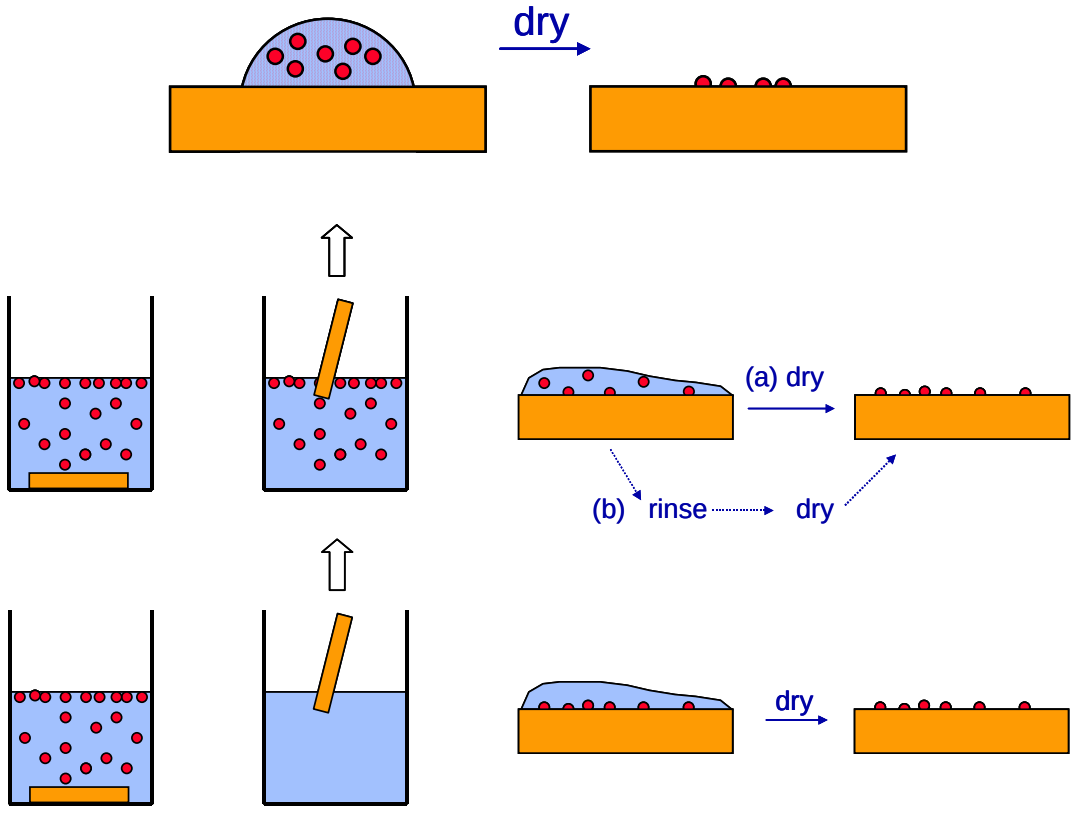


Fig. 11. Illustrating the three methods to test deposition of emulsion drops onto a flat solid substrate. In Method 1 (top) a drop of emulsion is placed on a horizontal substrate and then dried. In Method 2a (middle) the substrate is immersed in the emulsion for several minutes, withdrawn and then dried. A variation (2b) is to rinse the suspension from the wafer after withdrawal and before drying. Method 3 (bottom) is similar to the second, except that substrate is immersed in pure water and subsequently emulsion is produce by addition of concentrated emulsion droplets, latter is diluted by copious amounts of water before withdrawing the substrate and drying it.

The second method (Method 2a) consists of immersing the substrate in a diluted suspension of emulsion drops for about one minute, then withdrawing it and drying it in vacuum. The third method (2b) is a variation on this in which the suspension that is

entrained on withdrawing the substrate is rinsed by water before drying. This is designed to test whether droplet deposition occurs before the drying process.

The final method (Method 3) starts by immersing the substrate in pure water, then produce suspension by addition of concentrated PDMS emulsion to water vessel with substrate lying on the bottom. However, before withdrawing the substrate, the suspension is washed away by repeated replacement by water. This variation is to test whether deposition occurs within the suspension before withdrawal, and/or by a kind of Langmuir-Blodgett effect during withdrawal. Doing so substrate is not driven through water surface on which thin film of silicon oil may be present.

3. RESULTS FROM METHOD 1 – DROP ON SURFACE

Initial trials produced the AFM images shown in Figure 12. Here the undiluted (50%) suspension was placed directly on a natural wafer. The left-hand image shows the result of air drying, compared to vacuum drying on the right. The vacuum-dried sample shows a thick, continuous film with pockmarks that we attribute to pockets of water being evacuated from the film. The air dried sample shows much less coverage and distinctive pools of oil, probably from coalescence of droplets across the surface during drying.

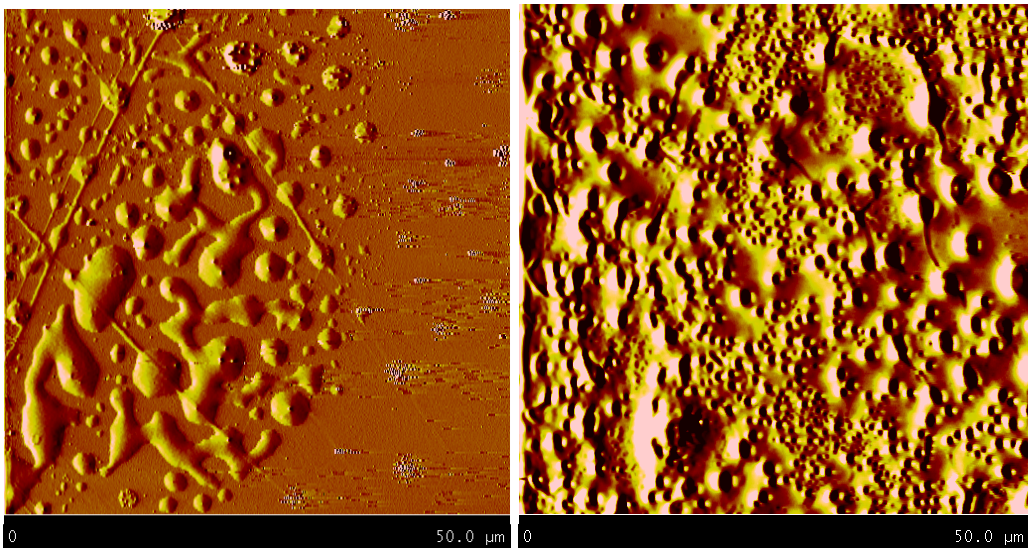


Fig. 12. AFM tapping mode images of PDMS on not treated (high contact angle) silicon wafers, deposited from a drop of concentrated suspension that was subsequently dried. The images are 50 µm frame, and show the result of deposition from an undiluted emulsion drop (50% v/v) followed by air drying (left) and vacuum drying (right).

Subsequently it was found much easier to obtain consistent results by using suspensions that had been diluted by 10^3 to 10^4 times. Using Method 1 gave a suspension drop that did spread differently on the hydrophobic (high contact angle) and hydrophilic (low contact angle) surfaces of mica and silicon wafer. When the drop of dilute PDMS suspension was dried out on the hydrophobic silicon wafer, a "coffee ring" pattern was observed (clearly seen in Figures 13) with deposited oil concentrated around the edge of the original drop, and near the centre of the circumference. Similar results were obtained on hydrophobised mica surface.

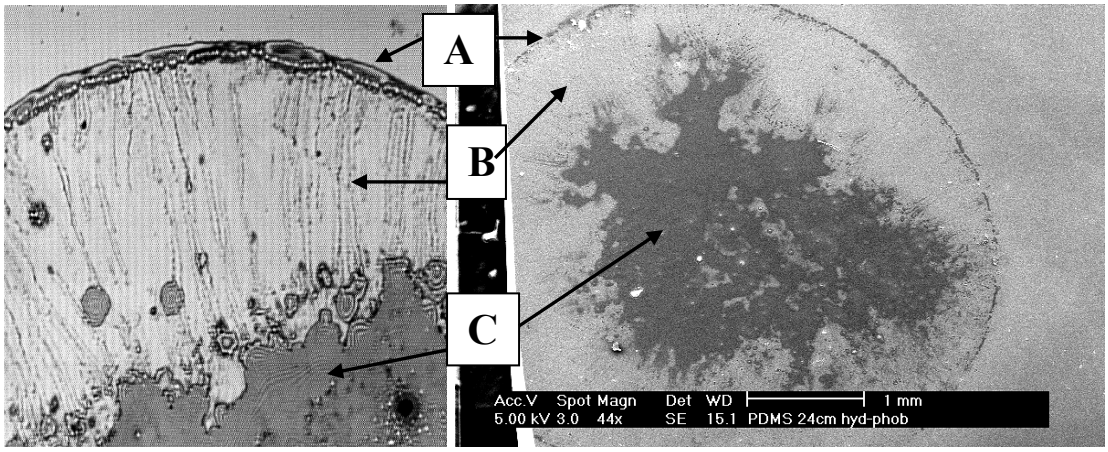


Fig. 13. Optical interference microscope image (left image) of substrate after diluted emulsion drops were vacuum dried on the high contact angle wafer surface. The image, made in reflection using monochromatic light, show constant-thickness interference fringes (Newton's rings) that can be used to measure the height and profile of spread drops. The left-hand image shows the deposition from a drop of emulsion diluted to about 0.025% PDMS. Regions mark respectively the coffee ring (A), a sparse, stringy region(B) and the centre where oil is pooled (C). The right-hand image shows SEM image of similar drop. The scale bars are 1 mm and this image was taken in secondary electron mode.

Both optical microscopy and SEM images show that there is concentration of oil pools on former droplet circumference which developed in to "coffee ring" pattern and in the central part of former droplet. In additional experiments droplets have been observed during drying (Fig. 14). In micrographs obtained from optical microscopy and shown in Fig. 14 can be deducted that because deposited diluted suspension droplet has been anchored to the coffee ring circumference it did not change diameter when drying. When drying it rather shallowing droplet to flatter pancakes like rather than lenses like with significant curvature in central part of this droplet. During drying small oil spheres in suspension were coalesce in many places within coffee ring circumference. This coalescence did not occur in one place in the droplet centre but

randomly spread in island pattern within the circumference. Small oil droplets inside suspension having buoyancy in natural way concentrate away from circumference of the coffee ring pattern where water film is thinner and congregate rather near the central part where thicker water film is still available. In the moment when water evaporates all oil droplets aggregated within islands coalesced and turn into oil pools in result as it is shown in Fig. 14.

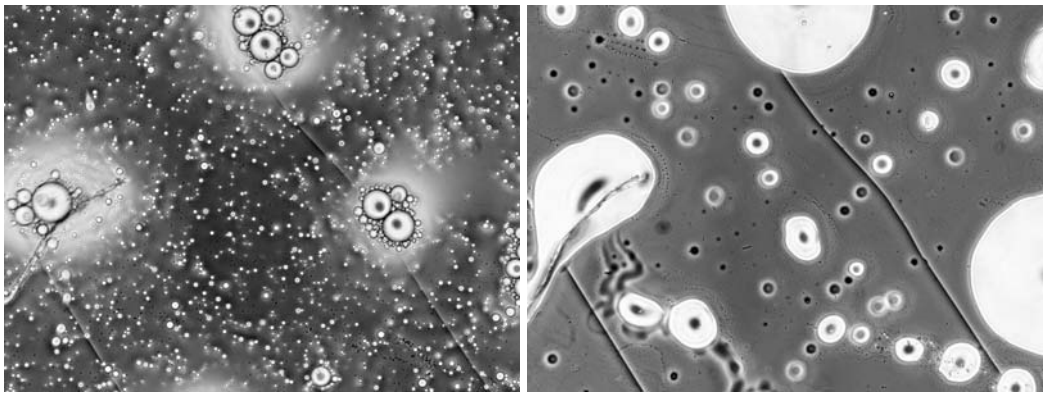


Fig. 14. Droplets of diluted PDMS suspension on hydrophobic substrate when draying show increase larger oil spheres which coalesce in to larger oil pool.

In Fig. 13 it is also visible that between coffee ring structure and the central oil pools island is also very distinctive area where very small oil droplets were stretched into radial oriented fibre like stringy patterns with obvious marks of stress being experience during drying. These strings may be remnants of ruptured oil film which covered whole suspension drop surface. This film could be formed even before suspension droplet deposition onto the substrate.

Figure 15 shows AFM and SEM images of this stringy intermediate region at two magnifications. It is clearly visible that oil was deposited from viscous fibre-like stretched film rather than from spherical droplets. In the central region it appears that a film of PDMS exists in the areas between the deposited droplets, but it is not clear whether such a film exists in the areas between strings from the intermediate region. Figure 15 shows an excellent correlation between SEM and the AFM images taken in the stringy region in small and large magnification. Given their radial orientation, a likely explanation for these strings is that they are formed as a result of the suspension drop's surface PDMS film rupture during the final stages of drying. Figure 15 right images shows similar features obtained with the SEM in secondary electron mode.

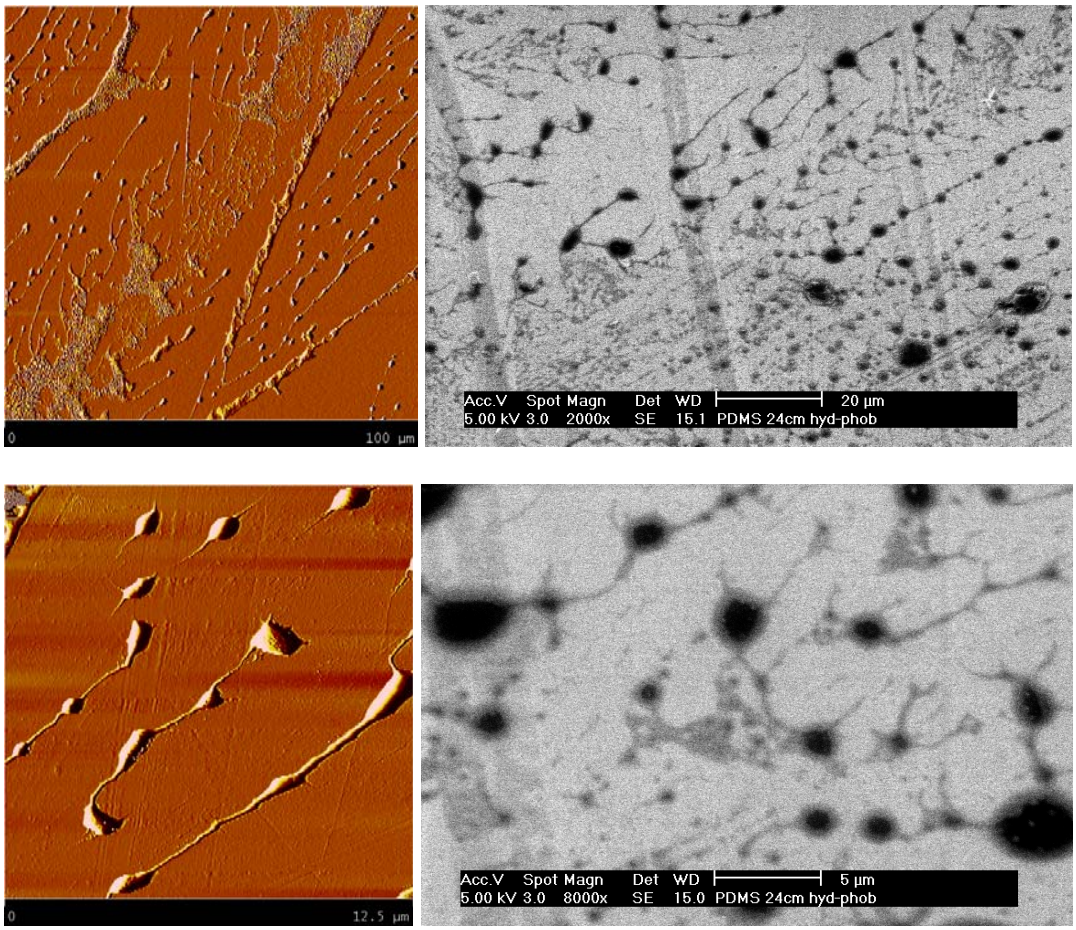


Fig. 15. Comparison between and AFM images (left) SEM images (right) of Region B, showing a clear similarity in the images taken by the different techniques. The scale bars of the secondary electron SEM images are 200 µm (upper right) and 5 µm (lower right), while the AFM images are of 100 µm (upper left) and 12.5 µm (lower left) squares.

In hydrophilic surfaces like on freshly cleaved mica and on plasma treated silicon wafer the dynamic of drying the dilute PDMS suspension is different. There are not coffee rings and because of it droplet is not anchored to the surface which allow the shrink droplet diameter during drying. Fig 16 shows the dynamic of PDMS dilute suspension drying. In this case, the macroscopic drop retracts smoothly as it dries, with no pinning of its perimeter, no accumulation of PDMS drops there, and no resultant coffee ring. Emulsion micro-spheres of PDMS accumulate at the surface of the main drop, forming close-packed arrays with local hexagonal ordering giving a "fly's eye" appearance. The accumulation occurs at the apex of the drop, so it is possible that gravity is having an effect (the buoyancy of PDMS pushing the spheres to the highest part of the drop). This was investigated by placing the main drop underneath as well as no top of the mica. It is also apparent that the PDMS spheres

near the apex of the main drop have a larger size, suggesting that coalescence is occurring. After a fairly short time (a few minutes) the coalescence results in a larger pool of PDMS forming at the apex – this is the phenomenon known as *creaming*. Then, after drying, we observe that the coalesced pool of PDMS is deposited on the substrate.

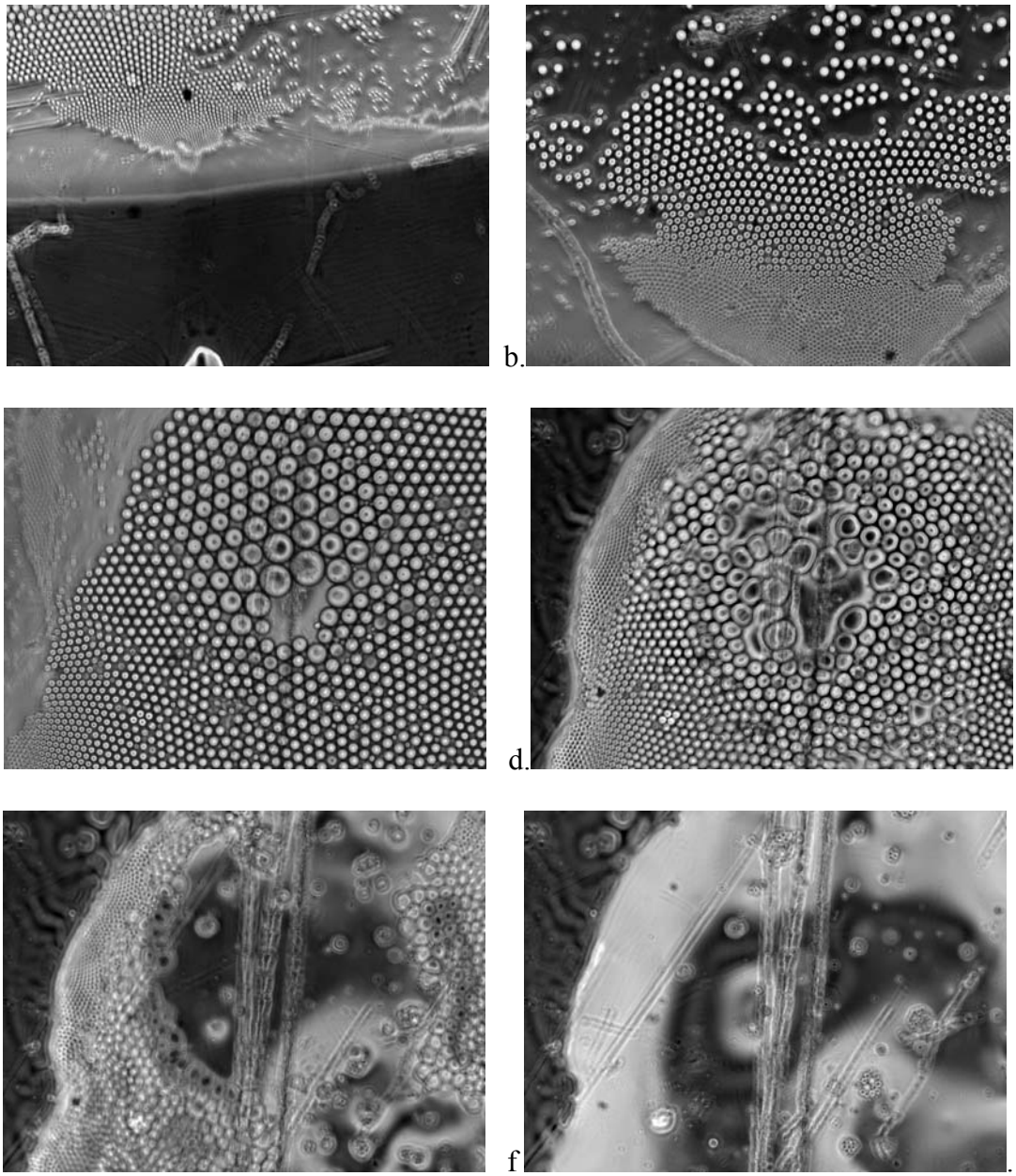


Fig. 16. Optical micrographs of deposition by drying in air of a dilute suspension of 10 μm PDMS emulsion droplets on a hydrophilic surface (freshly-cleaved mica). The width of each image is 220 μm. (a) Near the edge of the main drop which retracts smoothly over the surface as it dries. Emulsion droplets of PDMS are pushed away from the drying edge toward the centre of the main drop. (b) Larger droplets in the distribution are found towards the centre. (c) Large droplets appear at the apex of the drop. It appears that some of the drops must have coalesced, since they are larger than the original 10 μm emulsion droplet size. (d) The large drops at the apex coalesce to form bulk PDMS. (e) A pool of bulk PDMS forms at the apex, and after drying, (f) it is deposited onto the substrate. In this

step, remaining emulsion droplets visible off-centre in (e) also coalesce. The whole process from (a) to (f) occupies a few minutes. The rough vertical lines are scratches on the lower surface of the mica. Focus was changed between images as the drop evaporated.

These observations help us to understand the textures that we have previously observed with a coffee ring formed by forced drying of a suspension. In that case (on a hydrophobic substrate) the perimeter of the main drop remains pinned during drying, and some of the PDMS droplets after coalescence within the ring area are attached to the perimeter and end up being deposited there to form the coffee ring. However, other emulsion droplets probably behave in the same way as shown in Figure 14, so that there are not many of them deposited near the coffee ring, still far from the centre. A larger concentration – and probably a pool of bulk PDMS from coalesced drops – is deposited onto the substrate near the centre of the coffee ring. The two situations are sketched in Figure 17.

The difference in behaviour may or may not be due to the hydrophilicity /hydrophobicity of the substrate. It appears (Figure 16a) that the more important factor is whether or not the perimeter of the main drop can retract freely. Pinning may be associated with surface lipophilicity more than the contact angle.

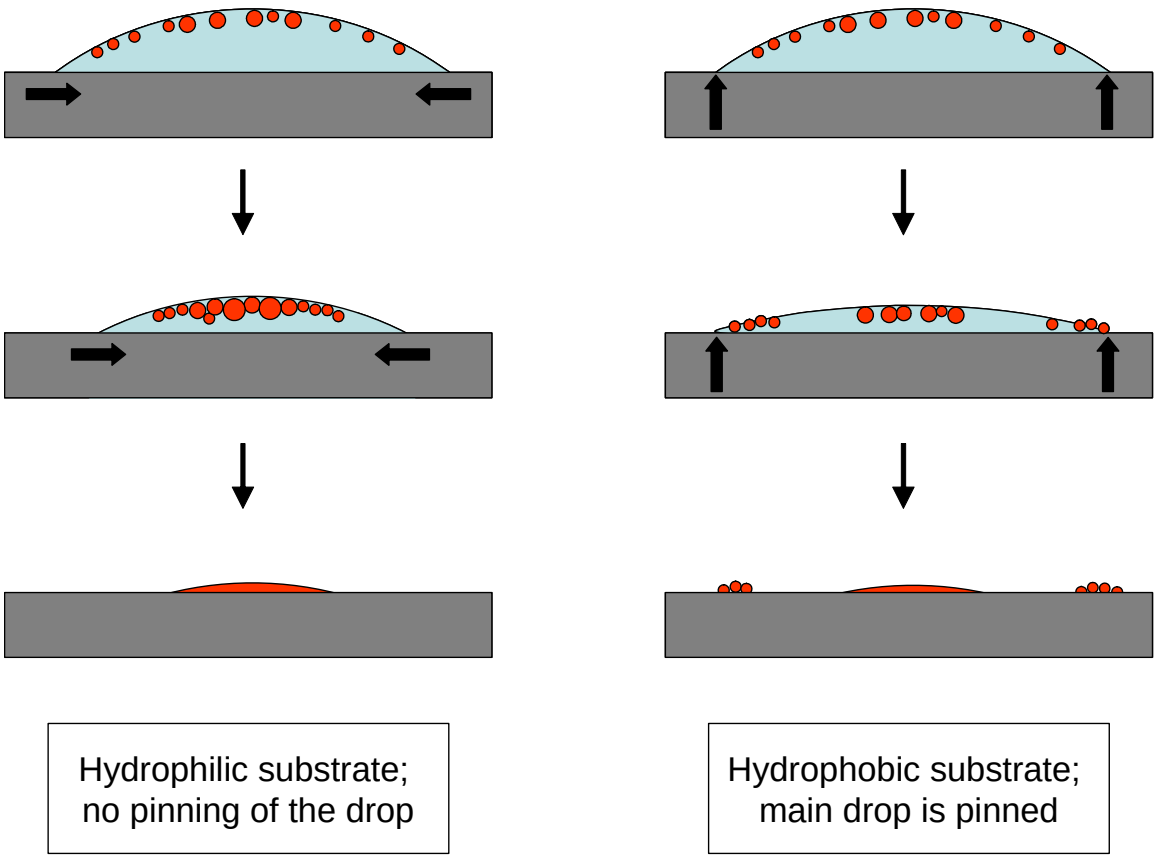


Fig. 17 Schematic illustration of drying of a drop of suspension (blue) containing emulsion droplets of PDMS (red) with two types of behaviour that we have observed.

Statement that emulsion droplet retracts smoothly on the hydrophilic surface is however not entirely correct. Behind the retracting front some small morphological patterns are visible on some micrographs and they are similar to region B patterns from Fig. 13. This may suggests that all droplets may be covered by thin film of oil (probably monolayer) which may be not perfectly spread but rather net like covering the droplet surface. Fragments of this film may adhere to the substrate surface around retracted suspension droplet, but because of its minor quantity, it remains behind the retracting liquid droplet front as fragmented stringy patterns instead massive coffee ring patterns observed on hydrophobic substrate.

The nature of the PDMS deposited by forced drying (with or without the coffee ring caused by pinning of the perimeter) would therefore depend on the relative rate of drop drying compared to the rate of creaming. If the main drop dries quickly before drop coalescence or creaming progresses, the PDMS will be deposited as small emulsion droplets. However, if creaming is rapid, the PDMS will be deposited in the form of drops that are considerably larger than the original emulsion drops. It is also

possible that the droplet coalescence and creaming is forced by the increasing volume fraction of PDMS in the suspension as the water evaporates, in which case it would be an inevitable consequence of drying.

When method 1 is used with a wafer that has been made hydrophilic by plasma treatment, the suspension drop spreads over most or the entire wafer, resulting in no obvious coffee ring after drying, and a more uniform distribution of deposited drops at a lower areal density. As seen in Figure 18, the density is lower when the original drop has a lower concentration of emulsion. The larger droplets present on the surface of the higher-concentration sample are presumably the result of droplet coalescence when the surface density of emulsion droplets is higher.

Although it is not visible from the optical micrographs, there is a thin film covering the wafer between the isolated drops. Ellipsometer measurements made in the regions between the drops give a film thickness of 5.7 nm.

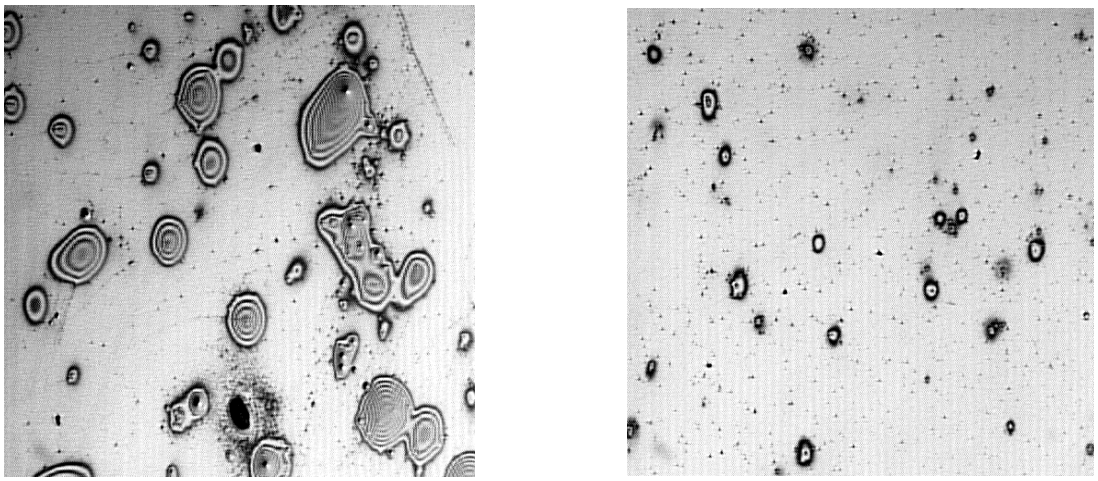


Fig. 18. Optical interference micrographs of 2 mm square regions showing PDMS emulsion droplets deposited on a plasma-treated (hydrophilic) silicon wafer. In this case the suspension wets and spreads over the whole wafer before being vacuum dried. The left-hand images show deposition from the 0.025% suspension and right-hand side from 0.006% suspension.

Images shown in Fig. 18 were taken with a low-resolution camera, and while they are reasonably clear when viewing the electronic version of this document on a computer screen, Moiré effects produce artefacts (regular patterns of lines) that tend to obscure the images in the printed document. The second point is to note that interference fringes are spaced at thickness intervals of $\lambda/2n$ (where n is the refractive index of PDMS), which is about 240 nm. Hence the height of a droplet is about (m/4) μm, where m is the number of fringes seen in the image of the droplet.

The following Figure (19) presents evidence that the PDMS droplets deposited on a surface, either hydrophobic (top) or hydrophilic (bottom), continue to flatten and spread over a long period of time, 3 days or more. The evidence is obtained by observing a reduction in the number of interference fringes associated with each identifiable droplet – think of the fringes as height contours on a map, at intervals of 240 nm.

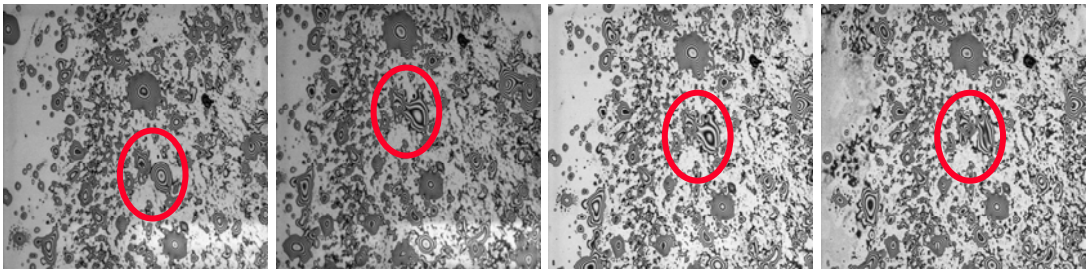


Fig. 19 Optical interference images, each 0.85 mm on the long side, taken at (left to right) 10, 60, 150 and 3600 minutes after drying a 0.025% drop. The upper series shows PDMS on a normal (hydrophobic) wafer and the lower set is for a plasma-treated (hydrophilic) one. Each fringe represents a constant-thickness contour, with contour intervals of $\lambda/2n \approx 240$ nm. Hence the reduction with time of the number of fringes in the same feature of the image shows progressive thinning of PDMS droplets on the surface. Locating the same features in the lower series is not so evident except in the central two images, but the thickness reduction is clear even from these two.

The AFM images in Fig. 20 show continuous (though not smooth) films on both the hydrophobic and hydrophilic surfaces 60 hours after deposition.

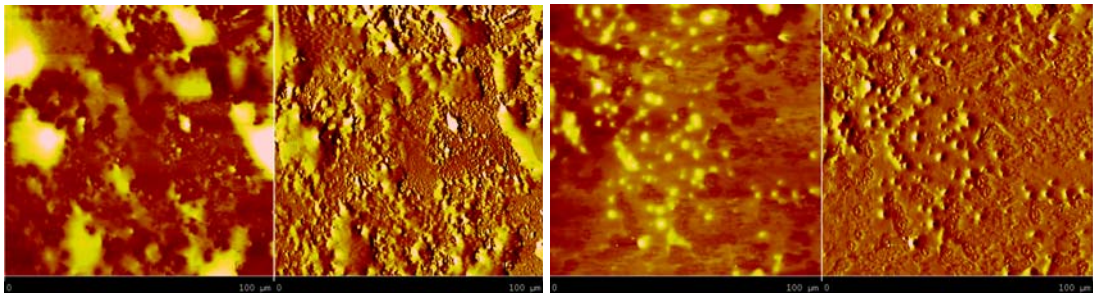


Fig. 20. AFM images of the same samples as in Fig. 21 after 3600 minutes (60 hours). The left-hand pair is for the hydrophobic wafer and the right-hand pair is for the hydrophilic one. An uneven but apparently continuous film is evident on both surfaces.

4. RESULTS FROM METHOD 2 – AFTER IMMERSION IN EMULSION

Optical interference micrographs of a plasma-treated silicon wafer that has been immersed in the suspension then withdrawn and vacuum dried are shown in Fig. 21. The wafer is withdrawn more or less vertically, and since it is hydrophilic a water

film coats it, with an excess of water hanging from the bottom edge. When the wafer is placed horizontally prior to drying, this drop spreads back over the wafer, forming a thick film over part of the surface while the remainder is covered by a thinner film. The left-hand image in Fig. 21 shows the PDMS deposited in the thick-film region (on the left site of the image and the thin-film region is on right site of the thin dividing line. The AFM image show also the dividing line and the thick (upper part of this image) and thin (lower part of this image) film regions. There appears to be a continuous film of PDMS with a scaly appearance in both regions, but it looks thicker on the top of this image. This is confirmed by ellipsometry measurements (made between drops), which give thicknesses of 11.7 nm and 4.1 nm for the thick and thin film regions respectively.

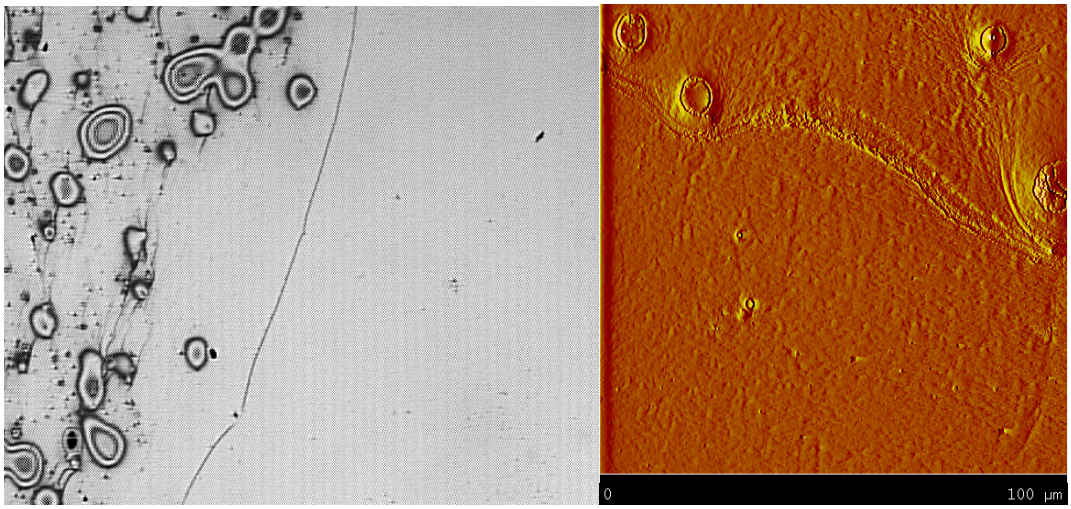


Fig. 21. Optical interference (2 mm square) and AFM images (100 µm square) of PDMS deposited on hydrophilic silicon wafer by immersion in and withdrawal from a diluted emulsion, then vacuum drying. The left-hand images show deposition from a thick film and the right-hand side from a thin film region (see text).

A much reduced amount of PDMS is deposited if the suspension in which a wafer is immersed is greatly diluted before the wafer is withdrawn and dried. This supports the evidence from Method 2b (Fig. 19) and demonstrates that little or no deposition occurs while the wafer is immersed in the suspension. The small amount that does adsorb is probably present in the highly diluted suspension that is entrained with the wafer on withdrawal, and deposited during drying.

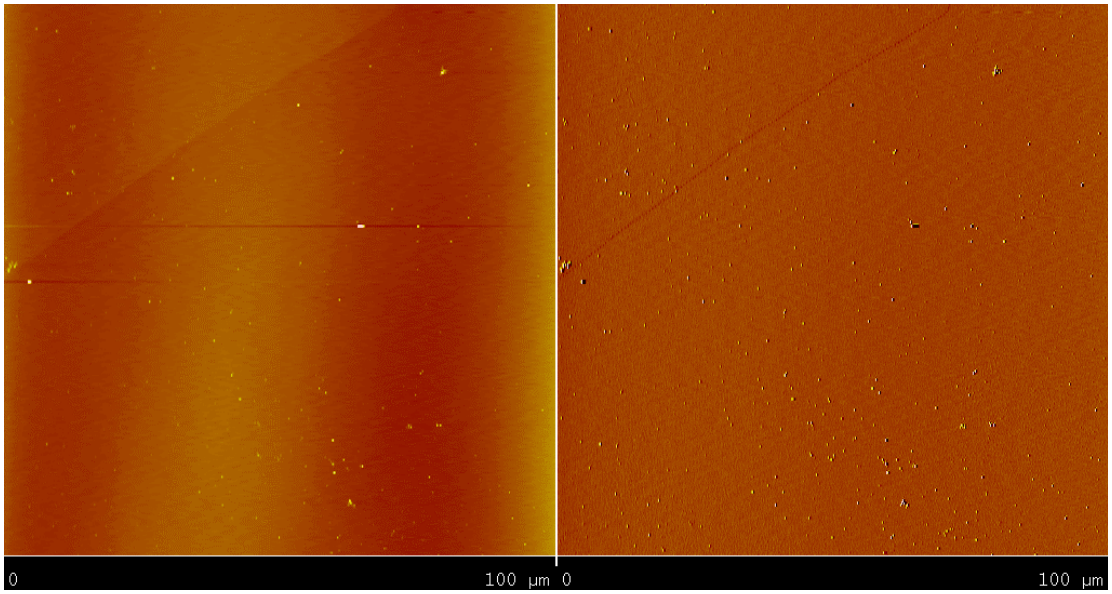


Fig. 22 AFM images (100 µm square) showing two regions of the Method 3 sample. Droplet deposition is sparse.

The AFM images in Fig 22, while unable to show large areas of the surface, indicate that deposited droplets are few and far between. Ellipsometry measurements also suggest that there is little or no film present between the drops, although the result for film thickness could be between 0 and 2.5 nm depending on the assumptions made about the optical properties of the substrate and in particular, whether the ubiquitous thin oxide layer on the silicon wafer is removed by the plasma treatment.

The droplets do not appear to increase in their diameter on the surface, and they are too far apart to coalesce with each other. These facts suggest that the droplet volumes decrease as they flatten, and (apart from the unlikely occurrence of evaporation) the only place for the PDMS to go is into a thin film between the visible drops.

4. SUMMARY

In this paper a brief review has been presented of previous observations of spreading of PDMS drops on silicon wafers. The literature includes a number of experiments which have used ellipsometry techniques to observe the presence and measure the dimensions of a precursor film spreading ahead of, and faster than, the main drop.

We have presented our own measurements using an imaging ellipsometer, which also clearly shows the presence of a precursor film. The diffusion constant of this film, measured with a 60 000 cS PDMS sample spreading on a hydrophilic silicon wafer, is $D_f = 1.4 \times 10^{-11}$ m^2/s.

Series of investigations has been also conducted on the morphological patterns of PDMS diluted emulsion spreading on hydrophobic and hydrophilic surface of silicon wafer and mica. A qualitative rather than quantitative investigation of droplet size, shape, coverage and spreading were resulted from this study. It was intended mainly to show what is possible with the different observation techniques for future investigations of deposition of PDMS emulsion droplets.

Scanning Electron Microscopy can produce good images over a wide range of magnifications, correlating well with optical micrographs at low magnification and AFM images at high magnification. However, since it does not add significantly to what can be observed with optical microscopy and AFM and it is more tedious to use, SEM will probably not be used for the further studies.

AFM and optical interference microscopy can both give good measurements of drop shapes (heights and diameters). Furthermore, they can both be used to monitor changes with time of the deposited drop dimensions. Optical microscopy would be more convenient for following changes that occur over a long time (more than several hours, say) but can only be used for larger drops, whose spread diameter is ~10 μm or more.

None of the microscopies can give accurate measurements of the thickness of nanometric films that are often found around or between droplets deposited on surfaces. For this, ellipsometry is ideal, and the imaging ellipsometer is particularly useful because the measurements can be made in the regions between droplets only, as long as the latter are reasonably spaced.

The qualitative observations made include the fact that droplets from this PDMS emulsion (10 μm droplets stabilized by a nonionic surfactant) are only deposited by forced drying of the suspension.

A “coffee ring” effect is observed on hydrophobic wafers, on which the aqueous suspension drop beads up and emulsion droplets concentrate at the perimeter of the drop as it dries, and are deposited there. However, there is evidence suggesting that in the final stages of drying the main drop does not remain pinned at its perimeter, but

ruptures, dragging emulsion drops with it and depositing the majority of the PDMS near the centre and leaving radially oriented stringy region in between.

Deposition by forced drying occurs on both hydrophobic and hydrophilic wafers, with the main difference being that in the latter case there is no coffee ring effect because the suspension spreads is not pinned in to the wafer surface and retracts is more uniform and forms in effect central oil pool from PDMS micro-spheres coalescence.

Regardless of their size, density and method of deposition, droplets on both types of wafer (hydrophilic and hydrophobic) flatten out over a period of many hours, up to 3 days. During this process neighbouring droplets may coalesce, but there is strong evidence that some of the PDMS from the droplets migrates into a thin, continuous film that covers the surface in between droplets.

The thin film appears to be ubiquitous if there has been any deposition of PDMS. However, this statement needs further verification. One question is whether the film forms immediately after forced drying, or whether in some or all cases it only forms by spreading from isolated droplets as they slowly flatten out.

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Figure captions

Fig. 1 Thickness maps surrounding a PDMS drop deposited on the plasma cleaned silicon wafer.

Fig. 2 SEM micrograph of silicon oil drop at the beginning of the experiment and after one hour. Bright ring of precursor film evolve.

Fig. 3 Increase of drop radius and precursor film width with time, estimated from the images in Figs. 1 & 2. The upper plot has time on a linear scale; the lower one compares precursor film width to $\sqrt{t}$.

Fig. 4 Increase of drop radius and precursor film width with time, estimated from the images in Fig. 1. The upper plot has time on a linear scale; the lower one compares precursor film width to $\sqrt{t}$.

Fig. 5 AFM 3-dimensional image of macroscopic droplet with possible precursor film advancing around its perimeter.

Fig. 6 SEM (a) and optical microscopy observations (b – white light and c-monochromatic light) of merging oil droplets which differ in size.

Fig. 7 AFM 3-dimensional images showing the gradual coalescence of a small silicone drop with a large one. Image b was taken 100 minute after image a have been recorded. The area is 100 μm × 100 μm. © The time evolution of shape parameters of the small drop taken from Figure 7c.

Fig. 8 Optical micrographs of a silicone drop spreading on a silicon wafer in air. Shape analysis of the optical images from, showing the spreading and flattening of the drop. Note the large decrease in contact angle from 70° to less than 10° over 200 minutes for this 60,000 cS silicone on silicon in air.

Fig. 9 Optical images of a 0.7 mm diameter silicone drop on a silicon wafer under water, showing that in this environment it does not spread, over a time frame similar to that of Fig. 8.

Fig. 10. Optical images of a water drop pressed onto a silicon wafer that was previous covered with a thin (A) or thick (B) layer of silicone oil. The syringe diameter is 1 mm. In (B) a faint, roughly horizontal, line can be seen about 1/3 of the way up the drop on the left-hand side. We think this is a silicone/water/air three-phase line as illustrated schematically in (C), where θ_1 is the contact angle of water on silicon underneath silicone oil, and θ_2 is the contact angle of silicone oil on water in air.

Fig. 11. Illustrating the three methods to test deposition of emulsion drops onto a flat solid substrate. In Method 1 (top) a drop of emulsion is placed on a horizontal substrate and then dried. In Method 2a (middle) the substrate is immersed in the emulsion for several minutes, withdrawn and then dried. A variation (2b) is to rinse the suspension from the wafer after withdrawal and before drying. Method 3 (bottom) is similar to the second, except that substrate is immersed in pure water and subsequently emulsion is produce by addition of concentrated emulsion droplets, latter is diluted by copious amounts of water before withdrawing the substrate and drying it.

Fig. 12. AFM tapping mode images of PDMS on not treated (high contact angle) silicon wafers, deposited from a drop of concentrated suspension that was subsequently dried. The images are 50 μm frame, and show the result of deposition from an undiluted emulsion drop (50% v/v) followed by air drying (left) and vacuum drying (right).

Fig. 13. Optical interference microscope image (left image) of substrate after diluted emulsion drops were vacuum dried on the high contact angle wafer surface. The image, made in reflection using monochromatic light, show constant-thickness interference fringes (Newton's rings) that can be used to measure the height and profile of spread drops. The left-hand image shows the deposition from a drop of emulsion diluted to about 0.025% PDMS. Regions mark respectively the coffee ring (A), a sparse, stringy region(B) and the centre where oil is pooled (C). The right-hand image shows SEM image of similar drop. The scale bars are 1 mm and this image was taken in secondary electron mode.

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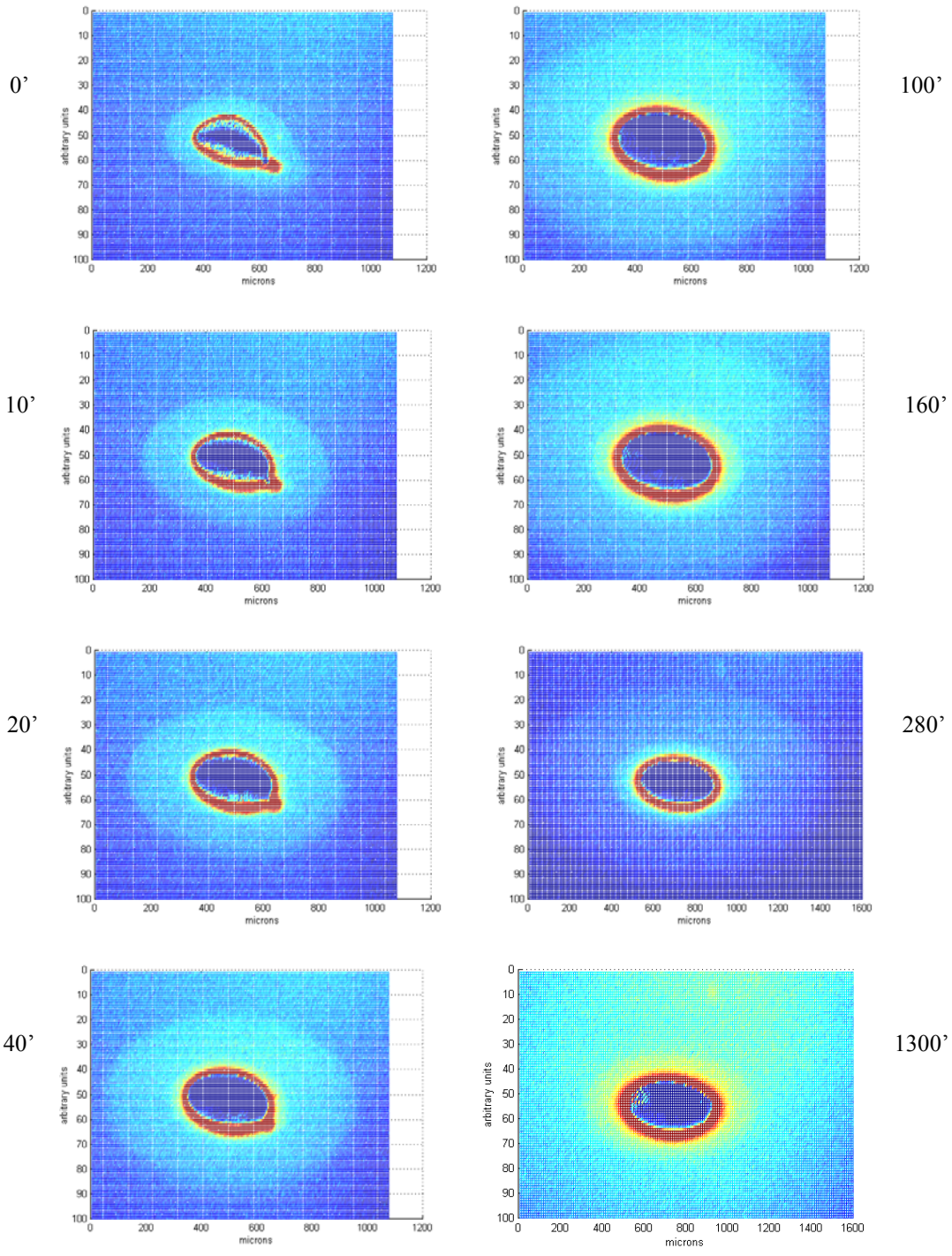

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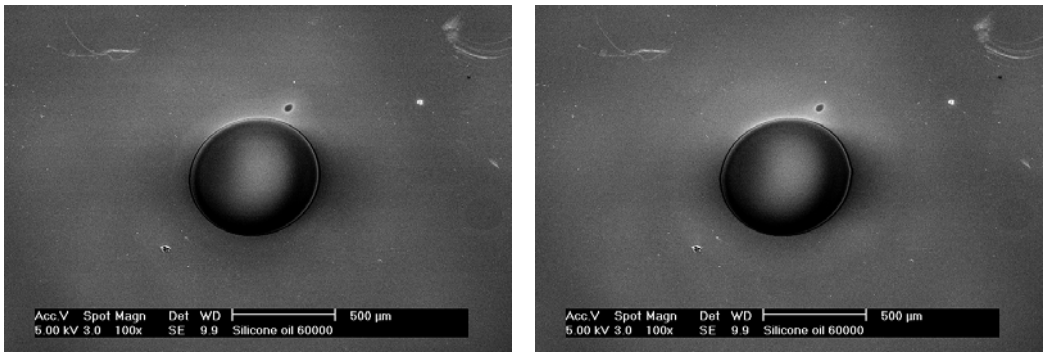

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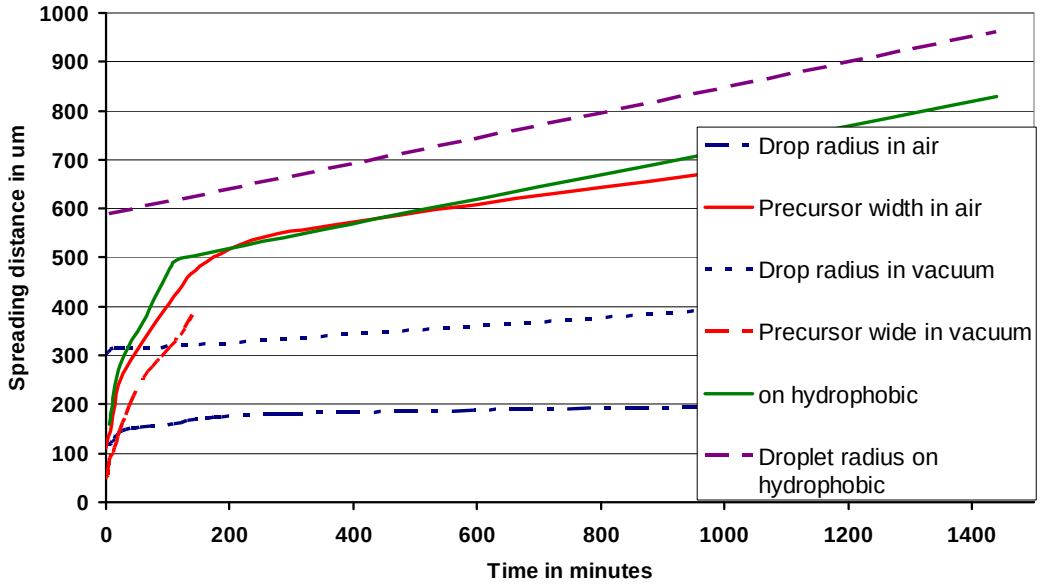

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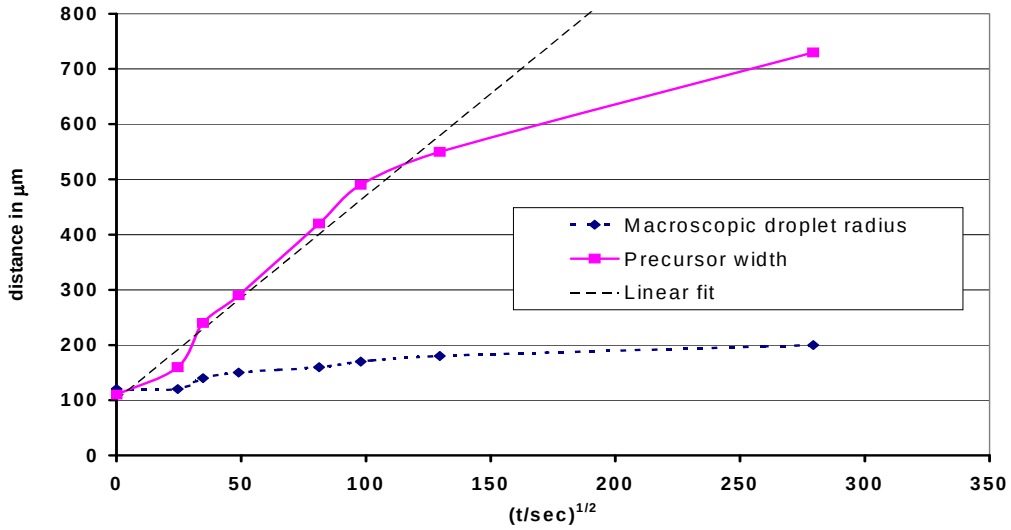

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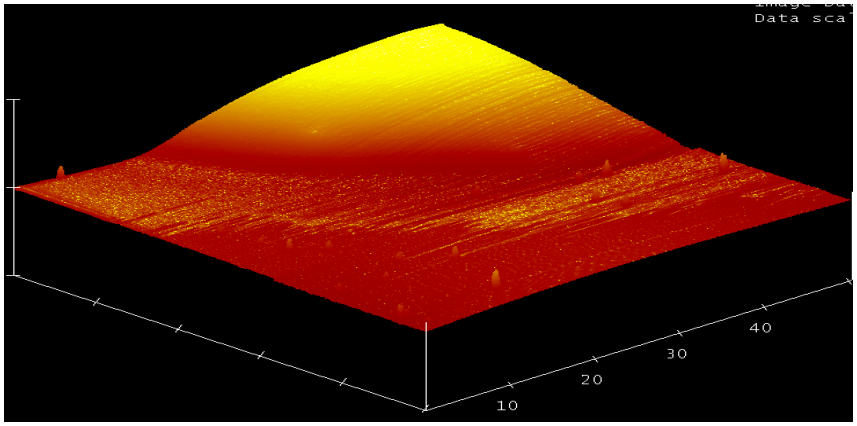

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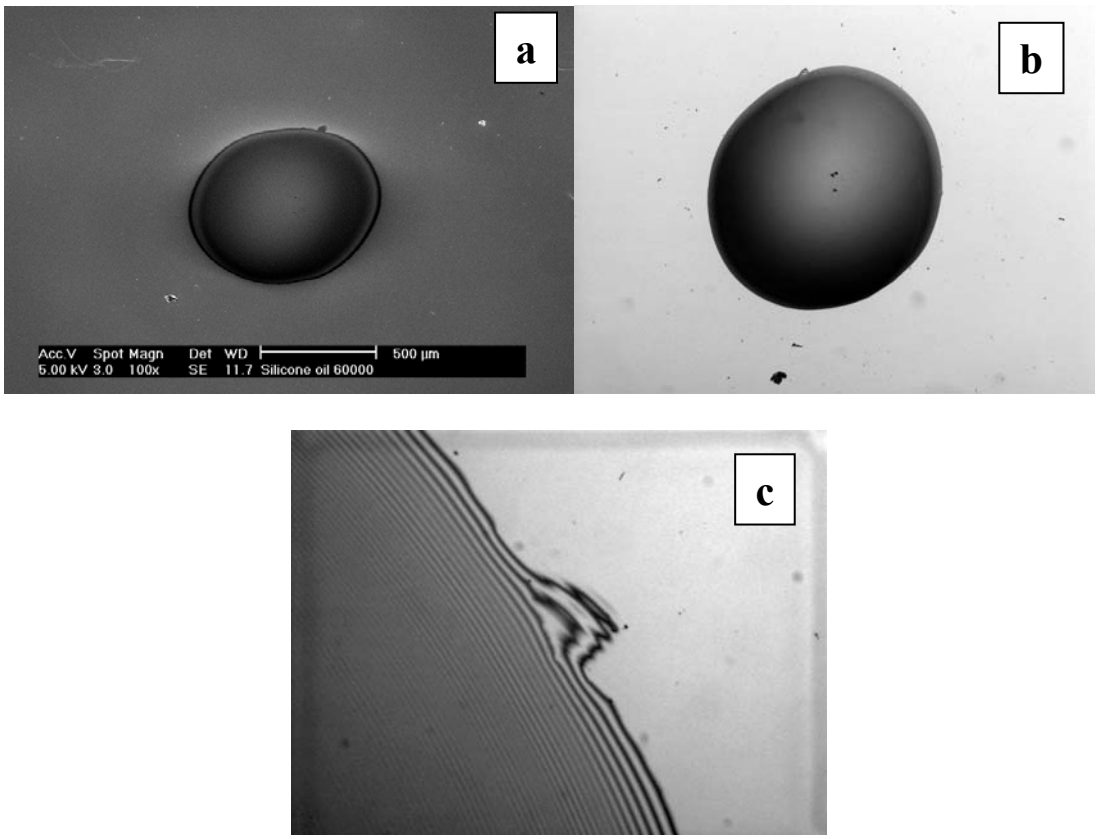

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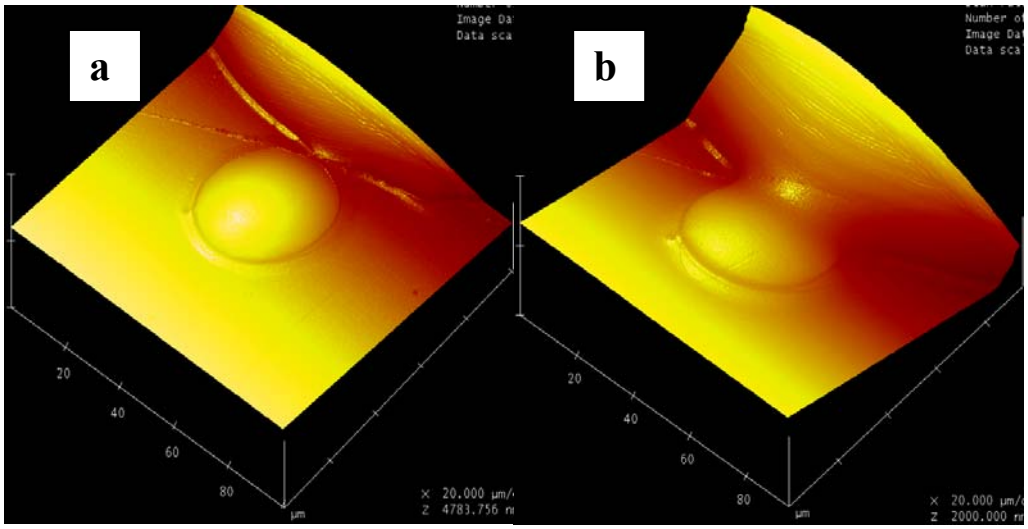


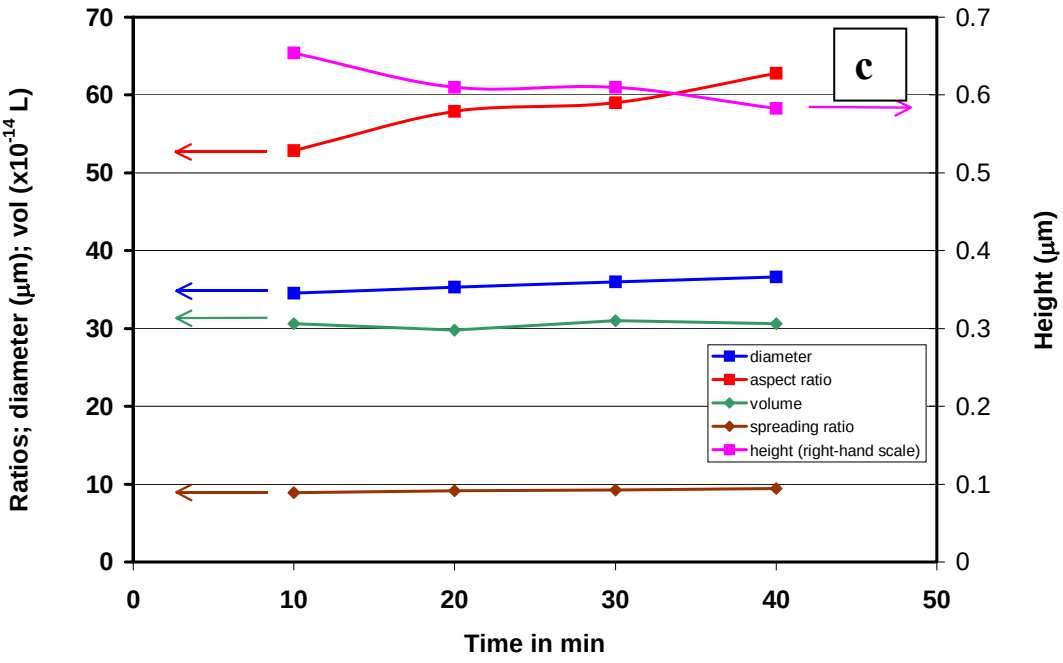
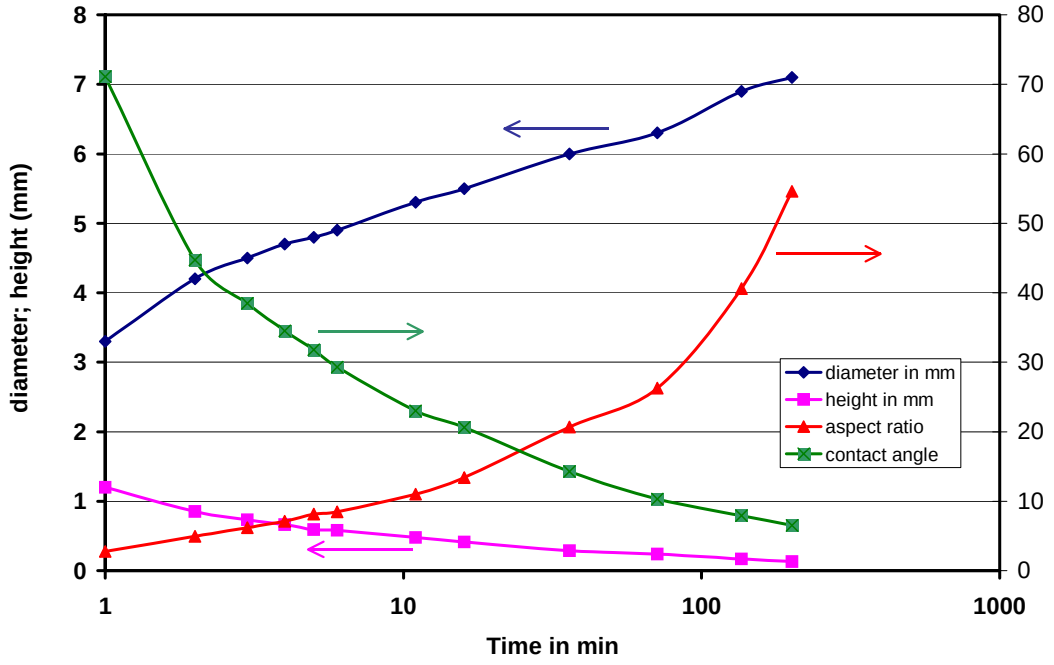
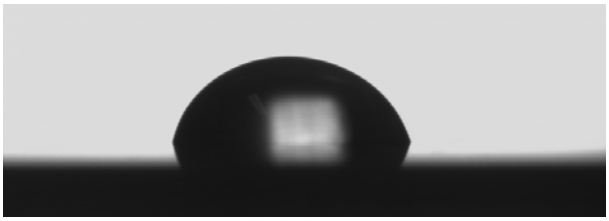
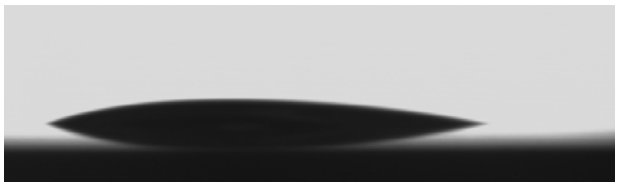


Fig. 7. AFM 3-dimensional images showing the gradual coalescence of a small silicone drop with a large one. Image b was taken 100 minute after image a have been recorded. The area is 100 µm × 100 µm. © The time evolution of shape parameters of the small drop taken from Figure 7c.





1 min



36 min

201 min

Fig. 8 **Optical micrographs of a silicone drop spreading on a silicon wafer in air. Shape analysis of the optical images from, showing the spreading and flattening of the drop. Note the large decrease in contact angle from 70° to less than 10° over 200 minutes for this 60,000 cS silicone on silicon in air.**

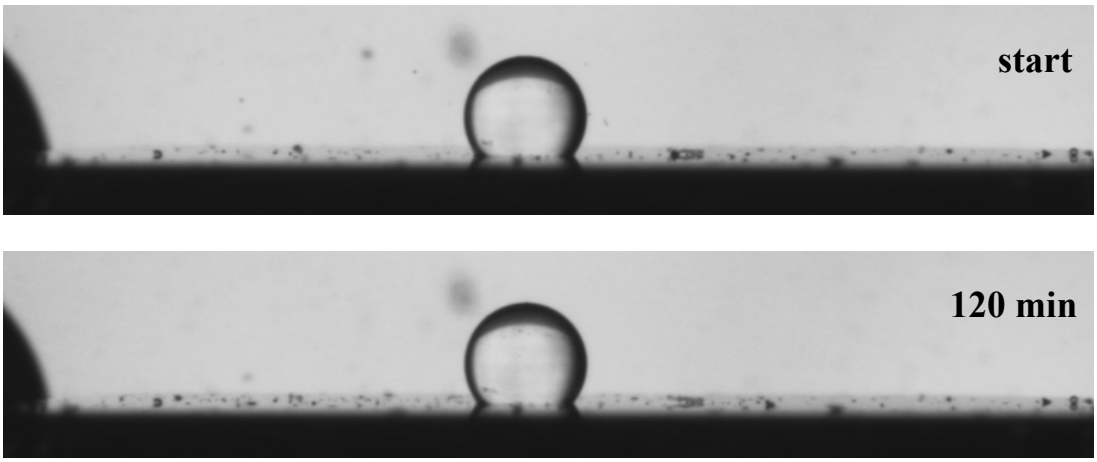


Fig. 9 Optical images of a 0.7 mm diameter silicone drop on a silicon wafer under water, showing that in this environment it does not spread, over a time frame similar to that of Fig. 8.

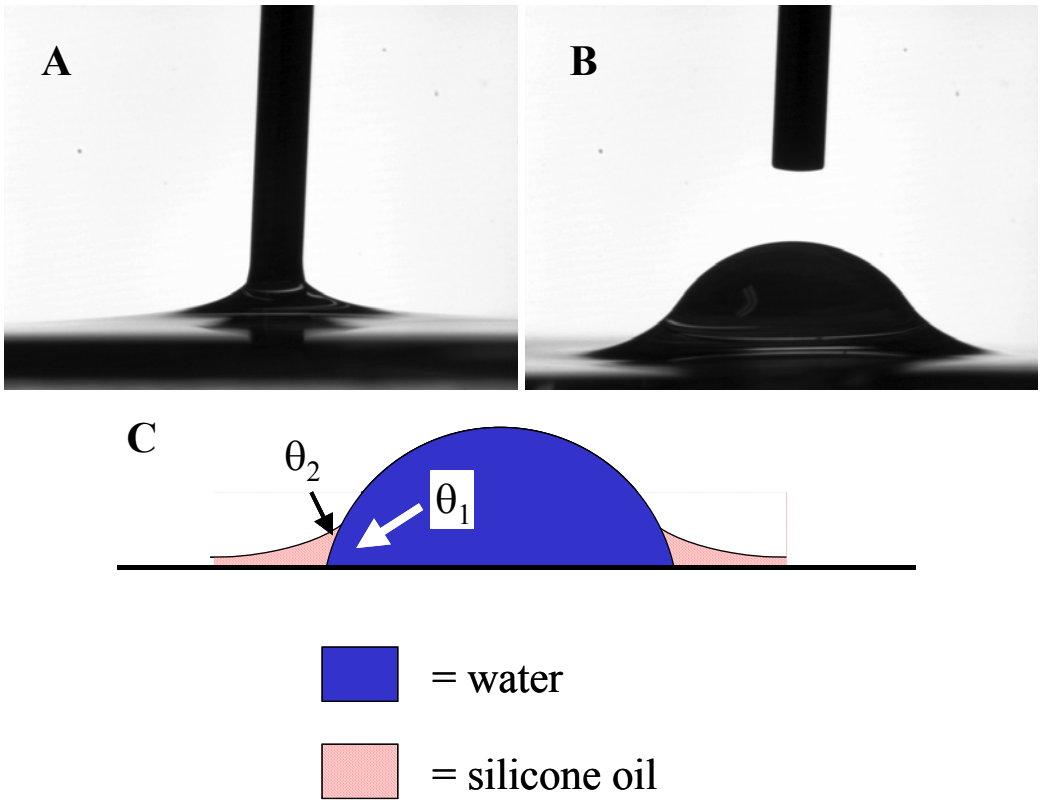


Fig. 10. **Optical images of a water drop pressed onto a silicon wafer that was previous covered with a thin (A) or thick (B) layer of silicone oil. The syringe diameter is 1 mm. In (B) a faint, roughly horizontal, line can be seen about 1/3 of the way up the drop on the left-hand side. We think this is a silicone/water/air three-phase line as illustrated schematically in (C), where θ_1 is the contact angle of water on silicon underneath silicone oil, and θ_2 is the contact angle of silicone oil on water in air.**

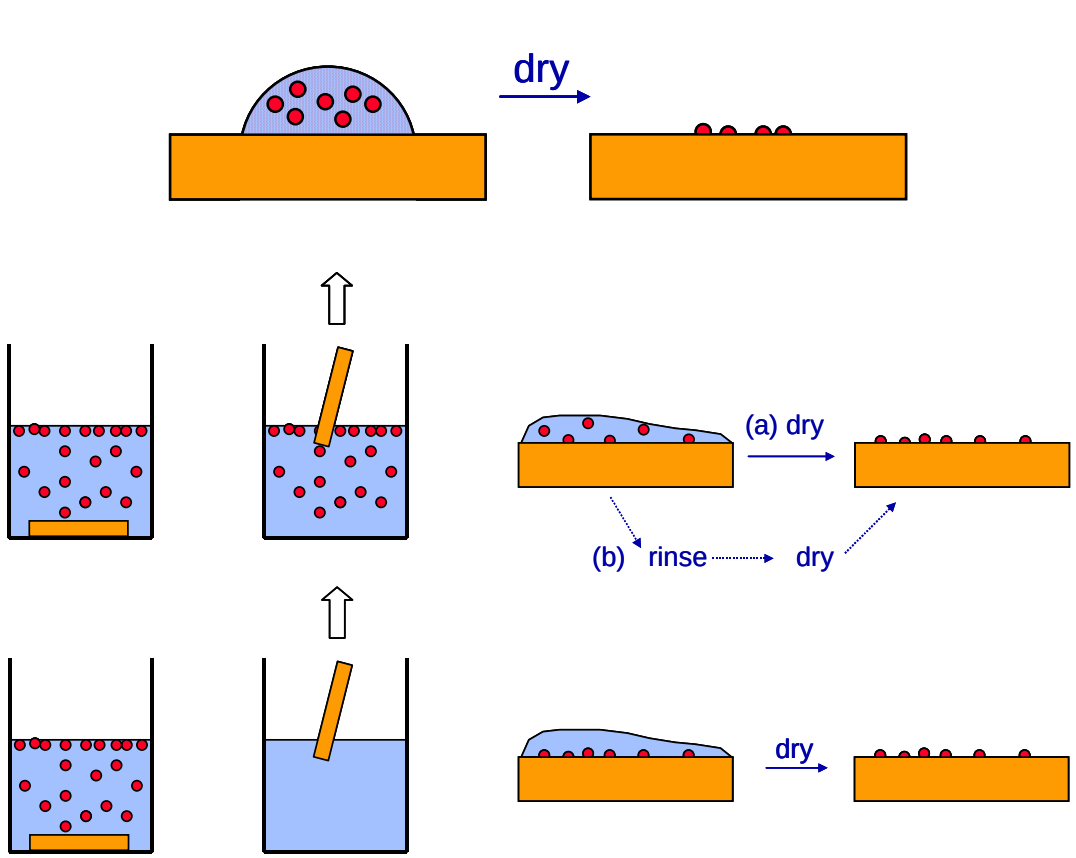


Fig. 11. Illustrating the three methods to test deposition of emulsion drops onto a flat solid substrate. In Method 1 (top) a drop of emulsion is placed on a horizontal substrate and then dried. In Method 2a (middle) the substrate is immersed in the emulsion for several minutes, withdrawn and then dried. A variation (2b) is to rinse the suspension from the wafer after withdrawal and before drying. Method 3 (bottom) is similar to the second, except that substrate is immersed in pure water and subsequently emulsion is produce by addition of concentrated emulsion droplets, latter is diluted by copious amounts of water before withdrawing the substrate and drying it.

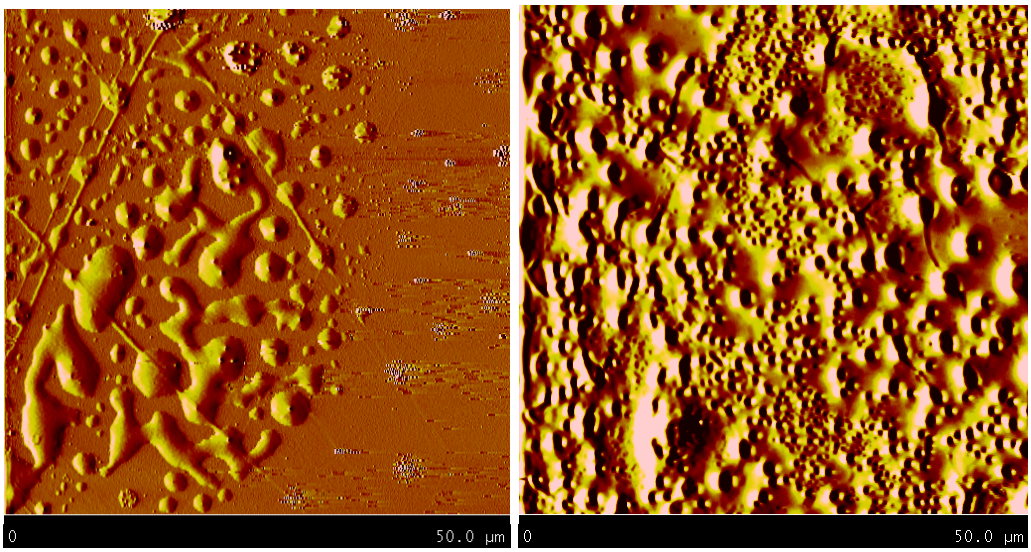


Fig. 12. **AFM tapping mode images of PDMS on not treated (high contact angle) silicon wafers, deposited from a drop of concentrated suspension that was subsequently dried. The images are 50 µm frame, and show the result of deposition from an undiluted emulsion drop (50% v/v) followed by air drying (left) and vacuum drying (right).**

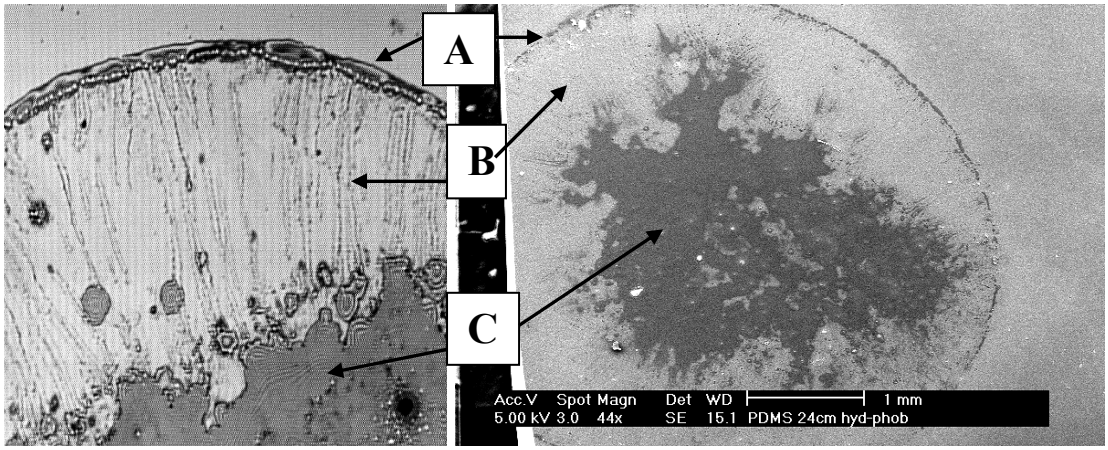


Fig. 13. Optical interference microscope image (left image) of substrate after diluted emulsion drops were vacuum dried on the high contact angle wafer surface. The image, made in reflection using monochromatic light, show constant-thickness interference fringes (Newton's rings) that can be used to measure the height and profile of spread drops. The left-hand image shows the deposition from a drop of emulsion diluted to about 0.025% PDMS. Regions mark respectively the coffee ring (A), a sparse, stringy region(B) and the centre where oil is pooled (C). The right-hand image shows SEM image of similar drop. The scale bars are 1 mm and this image was taken in secondary electron mode.

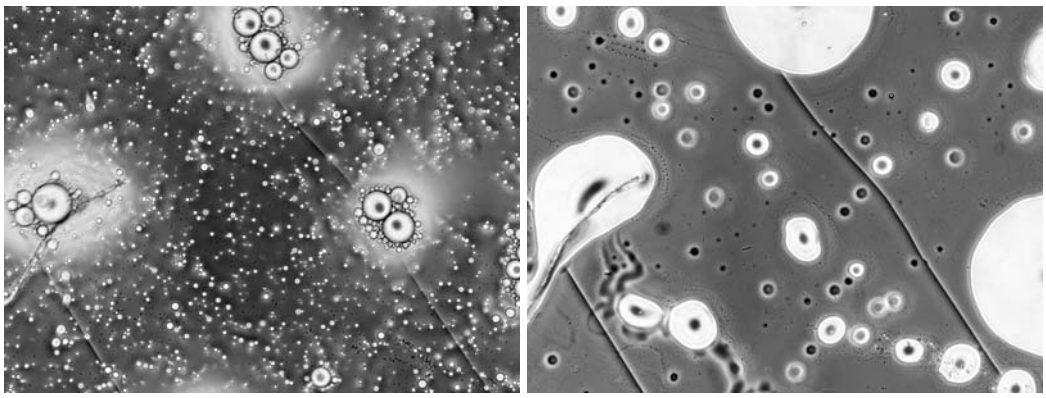


Fig. 14. Droplets of diluted PDMS suspension on hydrophobic substrate when draying show increase larger oil spheres which coalesce in to larger oil pool.

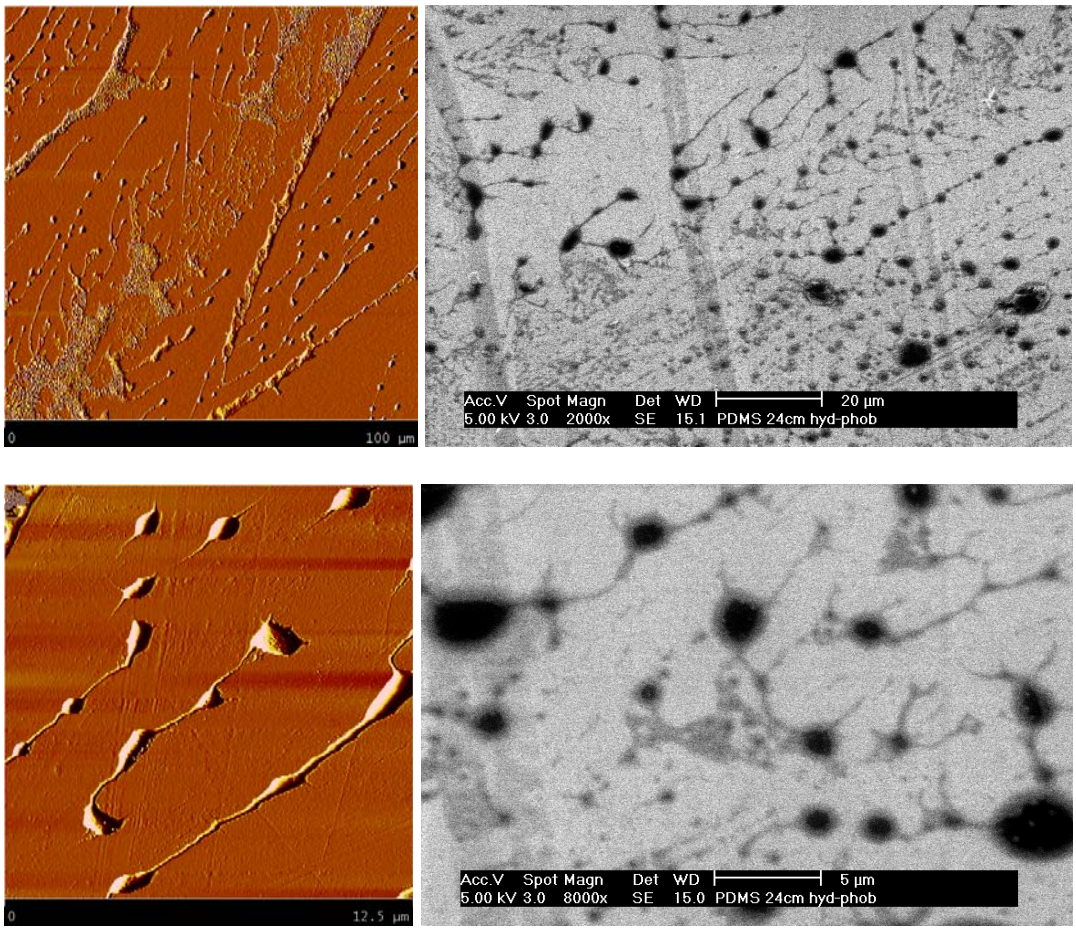


Fig. 15. Comparison between and AFM images (left) SEM images (right) of Region B, showing a clear similarity in the images taken by the different techniques. The scale bars of the secondary electron SEM images are 200 µm (upper right) and 5 µm (lower right), while the AFM images are of 100 µm (upper left) and 12.5 µm (lower left) squares.

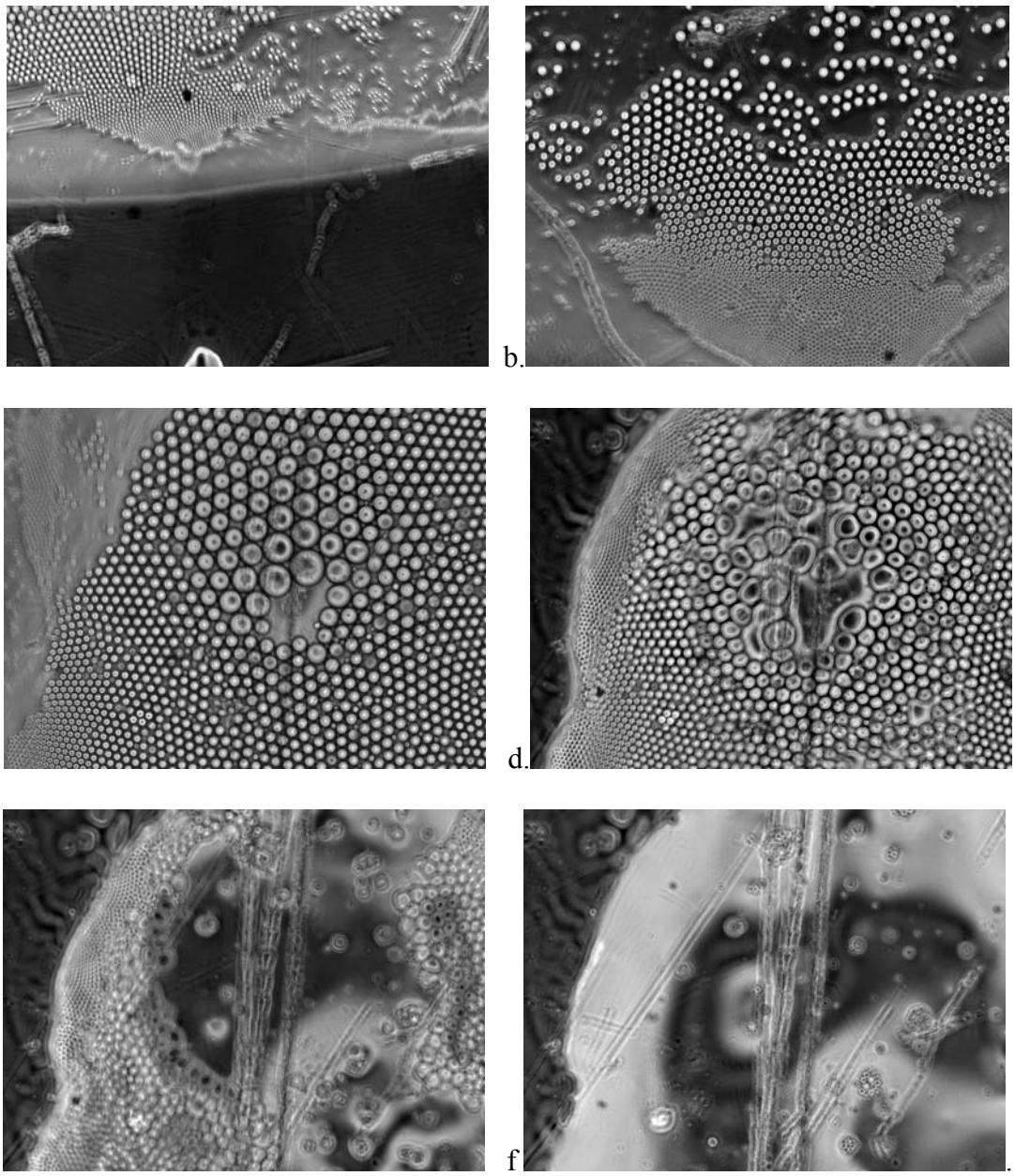


Fig. 16. Optical micrographs of deposition by drying in air of a dilute suspension of 10 μm PDMS emulsion droplets on a hydrophilic surface (freshly-cleaved mica). The width of each image is 220 μm. (a) Near the edge of the main drop which retracts smoothly over the surface as it dries. Emulsion droplets of PDMS are pushed away from the drying edge toward the centre of the main drop. (b) Larger droplets in the distribution are found towards the centre. (c) Large droplets appear at the apex of the drop. It appears that some of the drops must have coalesced, since they are larger than the original 10 μm emulsion droplet size. (d) The large drops at the apex coalesce to form bulk PDMS. (e) A pool of bulk PDMS forms at the apex, and after drying, (f) it is deposited onto the substrate. In this step, remaining emulsion

droplets visible off-centre in (e) also coalesce. The whole process from (a) to (f) occupies a few minutes. The rough vertical lines are scratches on the lower surface of the mica. Focus was changed between images as the drop evaporated.

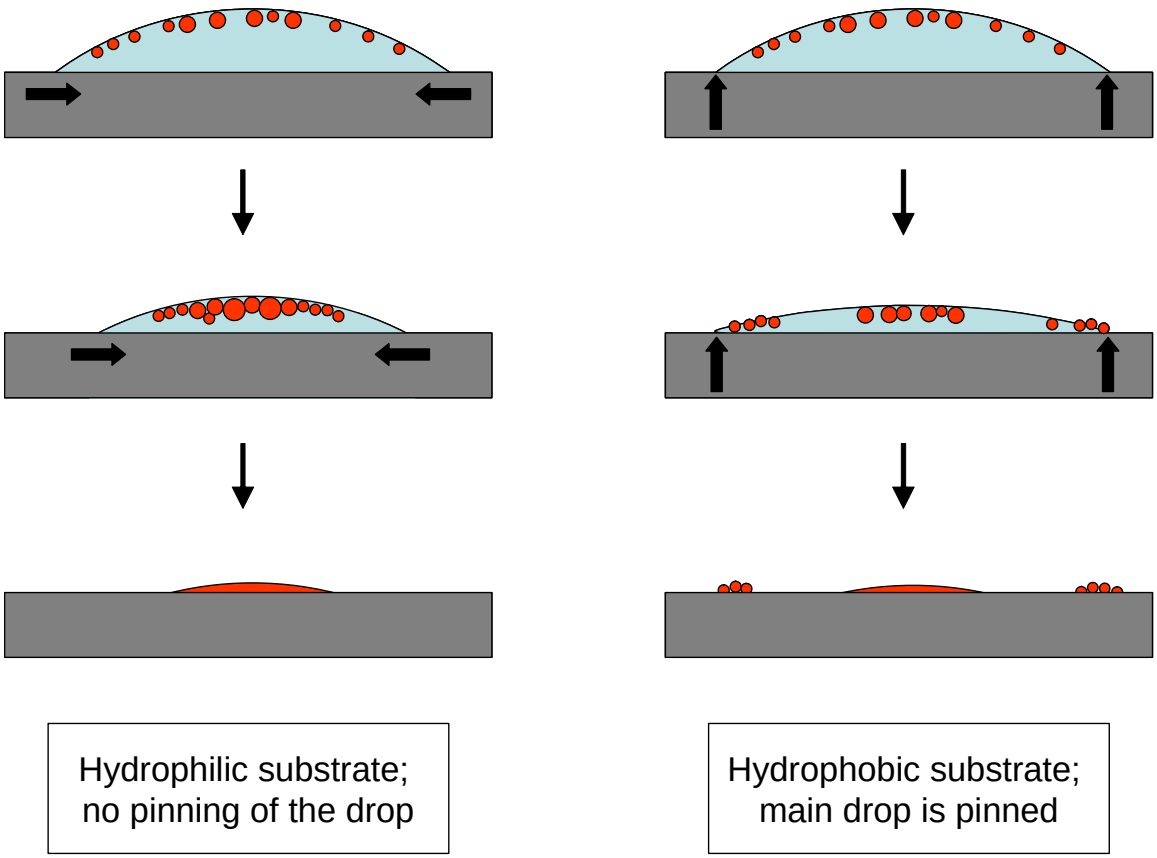


Fig. 17 Schematic illustration of drying of a drop of suspension (blue) containing emulsion droplets of PDMS (red) with two types of behaviour that we have observed.

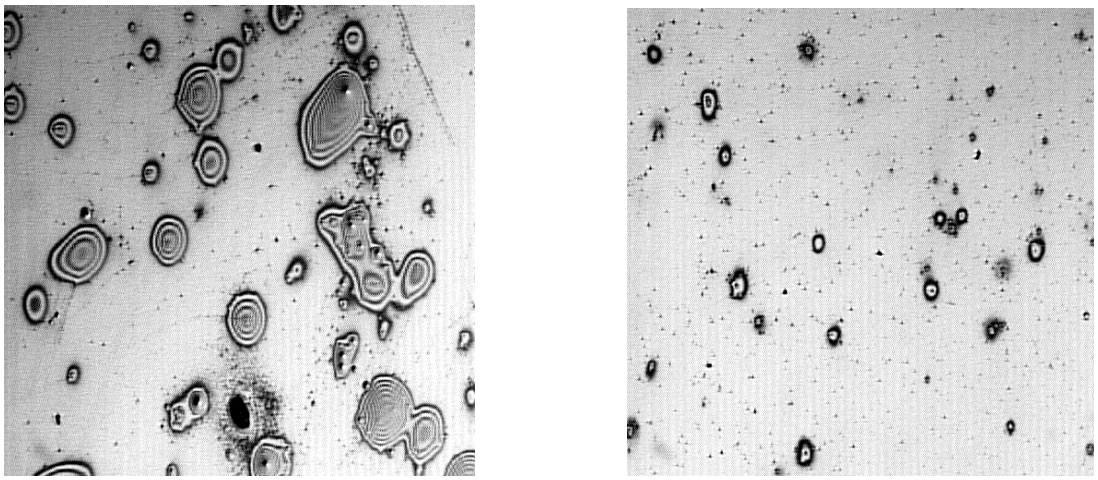


Fig. 18. Optical interference micrographs of 2 mm square regions showing PDMS emulsion droplets deposited on a plasma-treated (hydrophilic) silicon wafer. In this case the suspension wets and spreads over the whole wafer before being vacuum dried. The left-hand images shows deposition from the 0.025% suspension and right-hand side from 0.006% suspension.

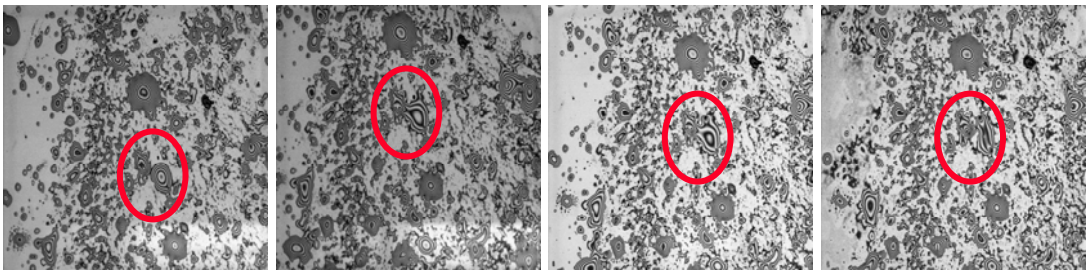


Fig. 19 Optical interference images, each 0.85 mm on the long side, taken at (left to right) 10, 60, 150 and 3600 minutes after drying a 0.025% drop. The upper series shows PDMS on a normal (hydrophobic) wafer and the lower set is for a plasma-treated (hydrophilic) one. Each fringe represents a constant-thickness contour, with contour intervals of $\lambda/2n \approx 240$ nm. Hence the reduction with time of the number of fringes in the same feature of the image shows progressive thinning of PDMS droplets on the surface. Locating the same features in the lower series is not so evident except in the central two images, but the thickness reduction is clear even from these two.

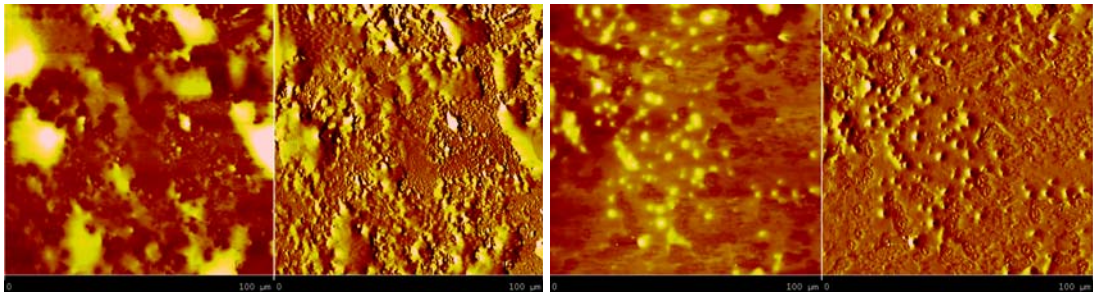


Fig. 20. AFM images of the same samples as in Fig. 21 after 3600 minutes (60 hours). The left-hand pair is for the hydrophobic wafer and the right-hand pair is for the hydrophilic one. An uneven but apparently continuous film is evident on both surfaces.

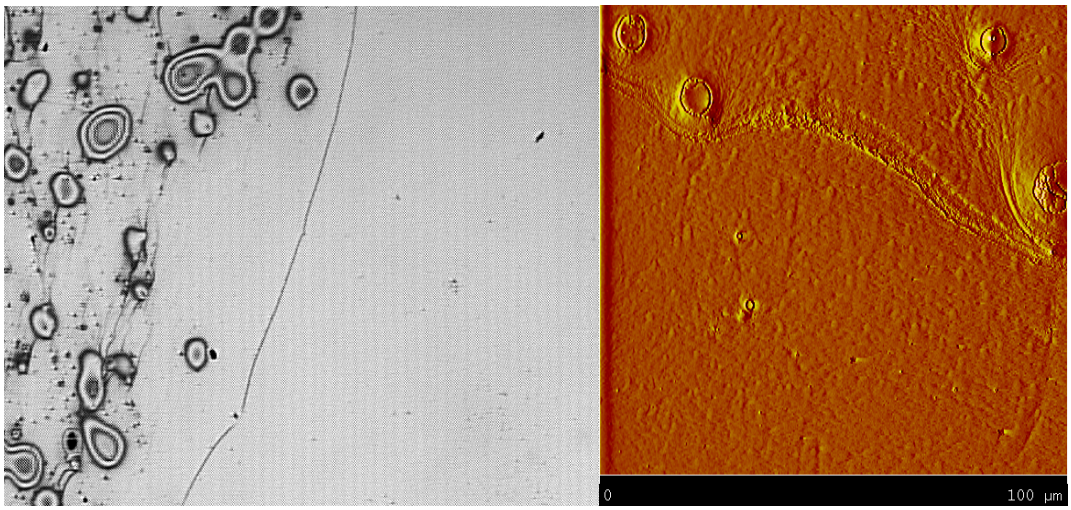


Fig. 21. Optical interference (2 mm square) and AFM images (100 µm square) of PDMS deposited on a hydrophilic silicon wafer by immersion in and withdrawal from a diluted emulsion, then vacuum drying. The left-hand images show deposition from a thick film and the right-hand side from a thin film region (see text).

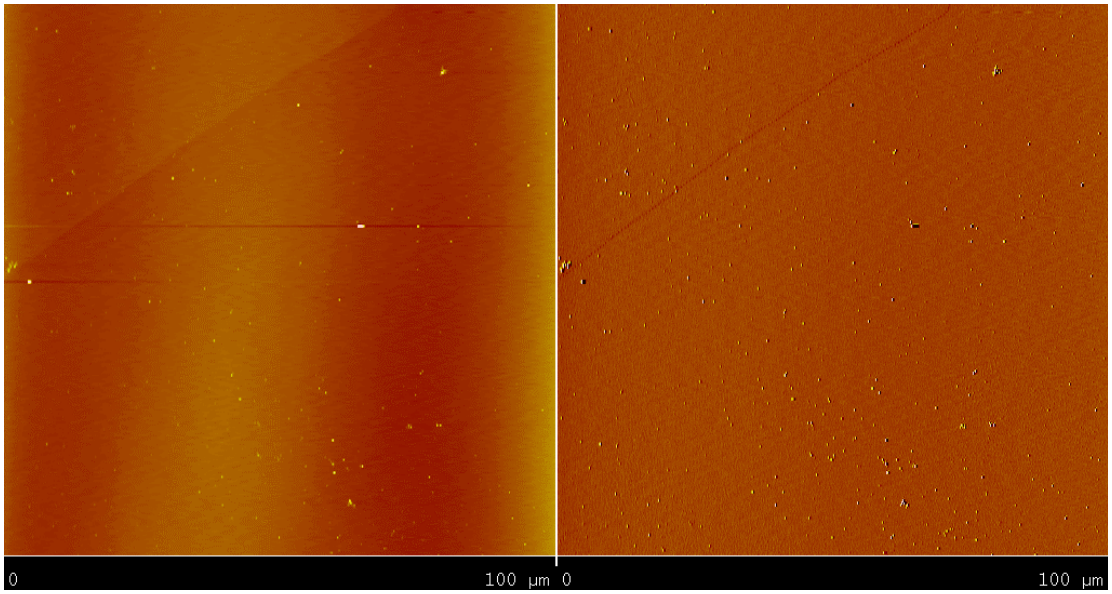


Fig. 22 AFM images (100 µm square) showing two regions of the Method 3 sample. Droplet deposition is sparse.