Study of Interactions between Interfacial Nanobubbles and Probes of Different Hydrophobicities

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ABSTRACT: In this study, hydrophilic, medium hydrophobic, and strong hydrophobic probes are obtained via treatment with plasma and octadecyl trichlorosilane. The interaction between the probes and interfacial nanobubbles (INBs) is examined using atomic force microscopy. The results show that a hydrophilic probe can scan the true shape of the INBs, and the distance between the first inflection point and the zero point of the approach force curve is equal to the vertical height of the nanobubble. The medium hydrophobic probe caused severe deformation of INB morphologies in the horizontal direction during scanning; nevertheless, the complete shape of the INB is obtained using this probe by lowering the scanning parameters. However, the characteristic of the approach force curve proves that the size of the nanobubbles is underestimated. The strong hydrophobic probe deforms INB morphologies severely, whose size cannot be obtained. The maximum attractive force in the approach force curve and the adhesive force in the retract force curve obtained using the strong hydrophobic probe are approximately 6 and 12 nN, respectively, which are both higher than those of the hydrophilic and medium hydrophobic probes. It is reasoned that the liquid film is maintained between the hydrophilic probe and the INBs, the medium hydrophobic probe pierces the INBs slightly, while the strong hydrophobic probe punctures the liquid film and demonstrates a pinning effect.

1. INTRODUCTION

Nanobubbles are small bubbles, with the size of several hundred nanometers. The height of an interfacial nanobubble (INB) with a spherical crown shape is less than 100 nm and its transverse radius is 50−500 nm.1 According to the classical thermodynamics theory, bubbles of nanometer scale cannot exist stably, and calculations show that bubbles with a radius of 100 nm can exist in water only for 10 μs.2 However, many experimental studies have shown that nanobubbles may exist at solid−liquid interfaces, and there is an increasing amount of recent evidence supporting the existence of nanobubbles. The proposal that nanobubbles exist at solid−liquid interfaces originated from preliminary research into long-range interaction forces between hydrophobic solids. Blake and Kitchener3 determined the presence of a long-range attractive force, significantly exceeding the intermolecular interaction, between two hydrophobic solids immersed in water. Subsequently, the existence of this long-range force was proved and its range of action was determined to be 10−100 nm.4−6

In 1994, atomic force curves with a step feature were found on the surfaces of two hydrophobic solids, based on which the presence of several bubbles on the solid surfaces was proposed. Parker et al. believed that bubbles, if any, on the surfaces of two solids in proximity to each other fuse and form a "gas bridge", thereby causing a long-range interaction between the two solids.9 Although this mechanism was further confirmed, bubbles were not observed on solid surfaces until 2000, when Lou et al.10 first determined the existence of nanobubbles at the interface of mica and water using atomic force microscopy (AFM). Concurrently, Ishida et al.11 used AFM to directly obtain images of nanobubbles on the surface of silicon modified by octadecyl trichlorosilane (OTS), and this finding strongly supported the existence of nanobubbles.

At present, AFM is the most widely used and effective method in the research of interfacial nanobubbles (INBs). The probe of the AFM instrument comes in contact with the nanobubbles when it scans their morphologies. This is believed to introduce an error between the true morphologies of nanobubbles and those obtained via AFM.12−14 Therefore, significant research has been carried on the interaction between AFM probe tips and INBs. Zhang et al.15 studied the force curve between water and surfactant solution and found that the long-range repulsion in the force curve was not...
2. RESULTS AND DISCUSSION

2.1. Probe Contact Angle Measurements. The surface contact angles of the silicon wafers treated with plasma and OTS were measured using a contact angle meter. The shape of the liquid drop on the surface of each silicon wafer was photographed, as shown in Figure 1. The contact angles of the three types of silicon wafers, as shown in Figure 1a−c, were 2, 65, and 105°, respectively. It was determined that these values corresponded to the probes of different hydrophobicities, which established that the required hydrophilic, medium hydrophobic, and strong hydrophobic probes were successfully prepared.

2.2. Interaction between the Hydrophilic Probe and INBs. The parameters used were a scanning force of 200 pN, scan rate 0.5 Hz, and scan area 20 μm × 20 μm. The morphology and corresponding profiles of INBs A−E were obtained using the hydrophilic probe with a DNP-A tip, as shown in Figure 2. The height diagram of the INBs is shown in Figure 2a, and the color bar ranges from −15 to +65 nm. The profile diagram is shown in Figure 2b, and the cross-sectional diameter of the nanobubbles is approximately 1.2 ± 0.1 μm. Combining the two figures, it can be concluded that the INBs have a spherical cap shape, which is consistent with other findings reported in the literature.15,21,22,27−29

After the nanobubbles were scanned, INB A in Figure 2a was selected as the research object. At different trig threshold values, the interaction between the hydrophilic tip and nanobubble A was measured by loading the tip from the top center of the bubble. The interaction between the tip and blank substrate was tested using the same parameters. The relationship between the force and separation distance was obtained (Figure 3). The zero position of abscissa represents the peak force corresponding to the different trig threshold values. The first inflection point of the approach force curve is the position where the tip comes in contact with the surface of the nanobubble. In Figure 3a, there is only one inflection point in the force curve when the trig threshold is ≤1500 pN. When a weak attractive force between the hydrophilic tip and nanobubble is produced, the surface tension of the liquid film produces an obvious repulsion to prevent the bubble from deformation. When the trig threshold is ≥2000 pN, a second inflection point appears near the zero point in the force curve. At this time, the probe completely deforms the INB, which is more evident in the retract force curve. This phenomenon does not occur in the interaction between the probe and blank substrate (Figure 3b).

Referring to a previous work,19 in the approach force curve, the distance between the zero point and the point of the horizontal extension of the first inflection point in the approach force curve is the height of the nanobubble, as shown in Figure 4. Therefore, comparing the approach force curve in Figure 3a with the cross section of nanobubble A presented in Figure 2b, it can be seen that the distance from...
point 1 of the approach force curve to the zero point is essentially the same as the vertex value in the cross-sectional view. This indicates that the tip comes in contact with the substrate under the INB at the second inflection point. Thus, the height of the nanobubble can be obtained from the approach force curve. In addition, the interaction forces of attraction and adhesion between the hydrophilic tip and INBs are very low; similar findings have been reported from other studies, and these values are generally less than 1 nN.\textsuperscript{30}

2.3. Interaction between the Medium Hydrophobic Probe and INBs. Using different scanning parameters, the morphologies and profiles of INBs were obtained using the medium hydrophobic probe, as shown in Figure 5. In Figure 5a, the scanning force is 300 pN, scan rate is 0.3 Hz, and scan area is 10 \( \mu m \times 10 \mu m \). The INBs are deformed along the

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**Figure 2.** INBs and the profiles obtained using the hydrophilic probe: (a) height diagram of INBs at a scanning force of 200 pN, scan rate 0.5 Hz, and scan area 20 \( \mu m \times 20 \mu m \) and (b) horizontal profile corresponding to INBs in (a).

**Figure 3.** Interaction between the hydrophilic probe and nanobubbles/blank substrate.
scanning direction of the probe. The nanobubbles A, B, and C marked in Figure 5a are cut vertically and horizontally, and the resultant profile diagrams are shown in Figure 5b and c, respectively. The vertical tangent remains arc-shaped, while the horizontal tangent is no longer arc-shaped. This suggests the presence of an attractive force when the medium hydrophobic probe comes in contact with the INBs under the above conditions such that the probe cannot be effectively and timely separated from the bubble surface. The interaction between the probe and INBs reappears when one line of scan is completed and the probe comes in contact with the INBs in the next line. However, the scan surfaces of the lines do not affect each other, and the nanobubbles are just deformed along the horizontal direction. Even when the parameters are decreased to a scanning force of 150 pN, scan area 5 μm × 5 μm, and scan rate 0.3 Hz, the INB is still severely deformed, as shown in Figure 5d. We continued to scan the INBs using the zoom function of the software by changing the parameters (scan area: 1.5 μm × 1.5 μm, scan rate: 0.3 Hz). However, the morphology obtained was close to that of a spherical cap, as shown in Figure 5e. The results showed that when the scanning force was decreased to 150 pN, as well as the scan area and scan rate were declined, the complete INB morphology was obtained using the medium hydrophobic probe. However, owing to the potential attractive force between the medium hydrophobic probe and INBs, the bubble size might have been underestimated.23

The INB A (Figure 5a) was selected as the research object, and the medium hydrophobic probe approached the center of the nanobubble at different trig threshold values. The interaction between the tip and INB A as well as that between the tip and blank substrate was measured, as shown in Figure 6. In Figure 6a, when the trig threshold is ≥3000 pN, the second inflection point of the approach force curve between the medium hydrophobic tip and INB begins to appear near the zero point. However, the force curve between the tip and blank substrate does not exhibit a similar phenomenon (Figure 6b). According to the approach force curve obtained between the medium hydrophobic probe and INBs, the vertical height of INB A is approximately 50 nm, while those of the INBs in Figure 5b and c are less than 35 nm. This proves that not only are the INBs deformed by the medium hydrophobic probe but also their size is underestimated during the scan. In addition, the maximum attractive force and adhesive force between INBs and the medium hydrophobic probe are 0.42 and 1.30 nN, respectively, which are both greater than those between the substrate and the medium hydrophobic probe. It indicates that the existence of INBs can improve the interaction between the substrate and the medium hydrophobic probe through the bridging function. What is more, comparing Figure 3a with Figure 6a, it can be seen that the attractive and adhesive forces between the medium hydrophobic probe and the INB are greater than those between the hydrophilic probe and the INB.

2.4. Interaction between the Strong Hydrophobic Probe and INBs. Using a scanning force of 100 pN, scan rate of 0.2 Hz, and scan range of 5 μm × 5 μm, the morphologies and profiles of INBs were obtained using the strong hydrophobic probe, as shown in Figure 7. Compared with

Figure 4. Typical approach force—distance curves between the hydrophilic probe and INBs.

Figure 5. INBs and the profiles obtained using the medium hydrophobic probe: (a) height diagram of INBs at a scanning force of 300 pN, scan rate of 0.3 Hz, and scan area of 10 μm × 10 μm; (b) vertical profile corresponding to INBs in (a); (c) horizontal profile corresponding to INBs in (a); (d) height diagram of INBs at a scanning force of 150 pN, scan rate of 0.3 Hz, and scan area of 5 μm × 5 μm; (e) height diagram of INBs at a scanning force of 150 pN, scan rate of 0.2 Hz, and scan area of 1.5 μm × 1.5 μm.
the original morphology of highly oriented pyrolytic graphite (HOPG), some yellow spots were observed in Figure 7a and the color bar ranges from $-5$ to $+20$ nm. The profile obtained by horizontally cutting the most obvious spot is a bending curve composed of several peaks (Figure 7b), among which the maximum and minimum peak heights are approximately 20 and 8 nm, respectively. The results indicate that these yellow spots are INBs generated on the surface of HOPG, which are punctured and deformed by the strong hydrophobic probe. When an INB is punctured, it may move with the probe due to the strong pinning effect of the three-phase contact line on the hydrophobic tip. It is certain that the tip cannot be separated from the surface of the INBs effectively owing to high hydrophobicity. Therefore, the strong hydrophobic probe cannot locate the true initial position of the INB or obtain the true morphology, and the size of the scanned INB is far lower than that obtained using other probes.

The INBs marked with red circles in Figure 7a were selected as the research objects. The strong hydrophobic probe was driven from the black mark at different trig threshold values to

![Figure 6. Interactions between the medium hydrophobic probe and INBs (a) and the blank substrate (b).](image)

![Figure 7. INBs and profiles obtained using the strong hydrophobic probe: (a) height diagram of INBs at a scanning force of 100 pN, scan rate of 0.2 Hz, and scan area of 5 $\mu$m x 5 $\mu$m; (b) horizontal profile corresponding to INBs in (a).](image)
test its interaction with the INBs as well as the blank substrate (Figure 8). Figure 8a shows that the approach and retract force curves obtained using the strong hydrophobic probe do not exhibit trends similar to those obtained with the use of hydrophilic and medium hydrophobic probes, although the trig threshold values are changed in the range 30–3000 pN, the tip of the strong hydrophobic probe approaches an INB, the attractive force gradually increases to its maximum value and then decreases to 0 nN rapidly. The repulsive force subsequently emerges and increases to its peak value. When the tip is retracted from the surface, the repulsive force decreases to 0 nN, and the adhesive force increases rapidly to its maximum value and then decreases gradually to 0 nN with the increase of the separation distance. The maximum attractive force in the approach force curve and the maximum adhesive force in the retract force curve obtained between the strong hydrophobic probe and INBs are approximately 6 and 12 nN, respectively, which are both greater than the interaction of the hydrophilic probe and the medium hydrophobic probe with the INBs. In some studies, it has been pointed out that the long-range attractive force was very small on the interaction between the probe and the nanobubbles, and hydrophobicity was the main factor for the generation of attractive force. Therefore, one of the reasons that the attraction and adhesion between the tip and the INBs improved is the increase of the probe hydrophobicity.

On the other hand, the maximum attractive force and adhesive force between the strong hydrophobic probe and blank substrate are approximately 0.5 and 8 nN (Figure 8b), respectively, which are smaller than the interaction between the strong hydrophobic probe and INBs. Furthermore, the interaction range between the strong hydrophobic probe and blank substrate without INBs is evidently shorter than that with INBs. Therefore, it indicates that the INBs significantly enhance the interaction between hydrophobic surfaces through the bridging role. This result is consistent with the theory that nanobubbles are the source of the long-range hydrophobic force, which can be traced back to the bridge capillary force of nanobubbles that was first proposed in 1994.9 Attard et al.33,34 successively researched the mechanism of nanobubbles bridging between hydrophobic surfaces. They pointed out that long-lifetime nanobubble bridging is the cause of long-range attraction on macrohydrophobic surfaces. After the

![Figure 8. Interactions between the strong hydrophobic probe and INBs (a) and the blank substrate (b).](https://dx.doi.org/10.1021/acsomega.0c02327)
morphology of INBs being captured by AFM, Tyrrell and Attard\textsuperscript{35,36} measured the force curves between the hydrophobic colloid probe and the substrate by AFM. They connected the jumping distance of the force curve with the typical height of the INBs. Therefore, INBs play a great enhancing effect on the interaction between solid surfaces. In addition, the adhesive forces in the blank area gradually increase with the number of approach and retract, and this may be caused by the formation of small nanobubbles at the point of contact after multiple contacts. This phenomenon has been speculated in some studies on the sources of the hydrophobic force\textsuperscript{37,38}. 

2.5. Discussion. The effects of probe hydrophobicity on both the morphologies of INBs and the interaction of the INBs with probes are different.

The complete morphology of an INB can be obtained using the hydrophilic probe, as the liquid film always exists at the gas–liquid interface between the probe tip and the nanobubble\textsuperscript{19,23}. Furthermore, the hydrophilic tip cannot puncture an INB, and hence, the real vertical height of an INB can be calculated from the probe-to-nanobubble approach force curve. The advance of the hydrophilic tip can only deform the bubble, while the repulsive force produced by the surface tension of the liquid film hinders bubble deformation. The small force of attraction, which appears when the hydrophobic probe is close to the INB, swiftly becomes a repulsive force. Even when the tip comes in contact with the blank substrate below the INB, it cannot pierce the nanobubble. Once the tip is away from the bubble surface, the bubble returns to its original appearance. In the case of the medium hydrophobic probe, when the tip is close to the INB, there is an obvious attraction between the two owing to the weak hydrophobicity of the tip. Hence, the tip can adhere to the top of the bubble during the scan and a deformed morphology of the nanobubble is obtained. As the attractive force is weak, a repulsive force appears when the tip approaches and is also dominated by the surface tension of the liquid film, which maintains the bubble shape. It is speculated that the medium hydrophobic probe, except for the small point of its tip, does not pierce the liquid bubble film completely to enter the bubble. This explains why the complete INB morphology can be obtained using a medium hydrophobic probe by reducing the scanning force and scan size. When the strong hydrophobic probe is used, there are strong forces of attraction and adhesion in its interaction with the INB. The interaction between macrobubbles and particles is mainly dominated by the capillary force related to the particle hydrophobicity, and hence, it is deduced that the mutual attraction and adhesion between the INBs and the probe are related to the hydrophobicity of the latter\textsuperscript{52}. Besides, the bridging effect of nanobubbles is considered as a representative source mechanism of the long-range hydrophobic force, and the relationship between the long-range hydrophobic force and the properties of INBs has been studied continuously. Therefore, INB bridging is the other reason for the increase of attraction and adhesion between hydrophobic surfaces. Owing to the strong hydrophobicity of its surface, the tip can puncture the liquid film at the gas–liquid interface as it approaches INBs, resulting in a pinning effect. Therefore, despite changes to the process parameters, the complete morphology of the INBs cannot be obtained and even deformed severely. With an increase in the penetration depth, the needle tip enters the interior of the nanobubbles and then comes in contact with the blank substrate underneath, and the three-phase contact line extends along the tip of the probe. However, the morphology of INBs may still be in good shape when the hydrophobic tips leave their surface due to their superstability\textsuperscript{71,39}.

3. CONCLUSIONS

In this study, hydrophilic, medium hydrophobic, and strong hydrophobic probes were obtained following treatment with plasma and OTS. The interaction between the probes with different hydrophobicities and INBs was studied via AFM. The following conclusions are drawn.

1. Using the hydrophilic probe, the true spherical cap morphology of the INBs can be obtained, and the vertical height of the bubble vertex can be calculated from the distance between the first inflection point and the zero point of the approach force curve. The INBs scanned by the medium hydrophobic probe are severely deformed in the horizontal direction, but the complete INB morphology can be obtained using appropriate parameters. However, the distance between the first inflection point and the zero point is greater than the vertical height of the scanned nanobubble, indicating that the medium hydrophobic probe underestimates the real size of the INBs. The strong hydrophobic probe can neither determine the real position of INBs nor scan their morphologies. It also cannot get the relationship between the vertical height of the INBs and the approach force curve.

2. Compared with that between the probes and blank substrate, the interaction between the probes and INBs is obviously stronger, especially in the case of the strong hydrophobic probe. The maximum attractive force in the approach force curve and adhesive force in the retract force curve obtained from the interaction between the strong hydrophobic probe and INBs are 6 and 12 nN, respectively. This indicates that the existence of INBs improves the interaction between the tip and substrate through bridging.

3. A liquid film always exists between a hydrophilic probe and an INB. The medium hydrophobic probe cannot pierce the liquid film at the gas–liquid interface completely despite a weak attraction between them. In the case of the strong hydrophobic probe, the liquid film is punctured and a pinning effect appears, which deforms the INB severely.

4. MATERIALS AND METHODS

4.1. Experimental Materials. Two types of AFM probes with different cantilevers were selected for this experiment, and the parameters are shown in detail in Table 1. A DNP-A tip with an elastic coefficient of 0.35 N/m was treated as the hydrophilic probe, and RFESPA-75 probes with an elastic coefficient of 3 N/m were treated as medium hydrophobic and strong hydrophobic probes.

| Table 1. Probe of the AFM Instrument for the Experiment |
| --- |
| Probe name | Tip radius (nm) | Elasticity coefficient (N/m) | Resonance frequency (kHz) | Needle tip material |
| DNP-A | 20 | 0.35 | 65 | SiN |
| RFESPA-75 | 12 | 3 | 75 | Si |
strong hydrophobic probes. New silicon wafers were selected as contrast-modified samples.

The hydrophobicity of the probes was modified using OTS purchased from Aladdin Reagent (Shanghai) Co., Ltd. Ultrapure water with a resistivity of 18.2 MΩ cm was purchased from Shanghai Suitian Environmental Protection Technology Co., Ltd. The water was sealed in a beaker with a preservative film on the surface of which 10 holes were drilled. It was stored in a refrigerator at 4 °C for more than 72 h to prepare freezing water.40

Highly oriented pyrolytic graphite (HOPG, ZYH grade, 12 mm × 12 mm) was used as the substrate for scanning INBs. The macromorphology of HOPG is shown in Figure 9a, and the local morphology of its newly exposed surface as scanned via AFM is shown in Figure 9b. The average roughness of the scanned HOPG surface was 0.422 nm.

4.2. Probe Surface Modifications and Contact Angle Measurements. The hydrophilic probe was prepared by washing a new probe with plasma for 3 min. The medium hydrophobic probe was prepared by first cleaning a new probe with plasma and then modifying it using the OTS agent in the gaseous phase. After more than 12 h, the probe was taken out and dried in a vacuum drying oven at 120 °C for 5 min to obtain a medium hydrophobic probe. The strong hydrophobic probe was obtained by first cleaning a new probe in plasma and then immersing it in 1 vol % OTS toluene solution for approximately 5 min. It was then cleaned with acetone, ethanol, and ultrapure water, purged using nitrogen after being removed from the modified solution, and then dried in a vacuum drying oven at 120 °C for 5 min.27

While the probes were being modified, new silicon wafers were cleaned by plasma and modified with OTS surfaces by the corresponding methods, and the modification effect was characterized via contact angle measurements to represent the hydrophobicity of the probes. A drop of ultrapure water (approximately 8 μL) was deposited on the wafer surface using the drop method. The surface contact angle was measured using a contact angle measuring instrument (DSA100, A.Kruß, Germany).

4.3. AFM Experiments. To study the morphologies of the INBs scanned using the probes of different hydrophobicities and their interaction, freshly cleaved HOPG was fixed to a Petri dish (Φ = 40 mm), into which freezing water was injected using a glass syringe until the surface of HOPG was submerged. The AFM test was carried out after maintaining static mode for 20 min at room temperature, 25 ± 1 °C. To produce large INBs quickly to facilitate the research, the Petri dish with HOPG was heated for 5 min at 45 °C in a vacuum drying oven prior to the injection of chilled water.

A BioScope Catalyst atomic force microscope (Bruker) was used to scan the morphologies of INBs and study the interaction between the nanobubbles and probe tips. Based on peak force values, ScanAsyst in fluid mode was selected for the experimental study. ScanAsyst is an AFM scanning mode developed based on peakforce tapping mode, which can optimize the imaging parameters automatically and continuously. It adopts the intelligent algorithm method to monitor the image quality and makes the corresponding parameter adjustment timely. ScanAsyst can precisely control the force between the tip and the sample, which is far lower than the force required by tapping mode, reduce the impact of the tip on the surface morphology of the sample, and ensure the high-resolution image without damage because the force exerted by the tip alters the apparent nanobubble dimensions to such an extent that it cannot be neglected. Unfortunately, tapping mode does not allow direct control of the force exerted.14,15,18,41 With the ScanAsyst in fluid mode, the interaction between INBs and probes can be researched accurately under different applied forces. After the probe being mounted on the AFM instrument, its reflection sensitivity was calibrated in the liquid phase and the elastic constant of the probe cantilever was then calibrated using Thermal Tune. The scanning force, scan rate, and scan area were adjusted to scan the surface morphology of HOPG. After the nanobubble morphologies were obtained, the force curves between the probes and the designated INBs were determined using the shoot function. The images and force curves were processed using NanoScope Analysis software for subsequent analysis.

Nanobubbles are generated by temperature differences.26,40 During heating, the solubility of air in freezing water decreases, causing supersaturation of gas in the aqueous solution. The excess gas cannot be released owing to obstruction by water and forms nanobubbles on the solid surface. This method of temperature difference is the simplest and most convenient for the preparation of nanobubbles, and no other solvents or impurities are introduced into the ultrapure water in this process.

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Figure 9. (a) Macromorphology of HOPG and (b) AFM micrograph of HOPG.
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Notes

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