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NANOBUBBLES AT THE LIQUID/SOLID INTERFACE STUDIED BY ATOMIC FORCE MICROSCOPY *

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Bubbles on the nanometer scale were produced by a special method on solid surfaces. Atomic Force Microscopy (AFM) was used to detect these bubbles. It shows that nanobubbles can be seen clearly in the interfaces of liquid/graphite and liquid/mica. In AFM images, the nanobubbles appeared like bright spheres. Some of the bubbles kept stable for hours during the experiments. The bubbles were disturbed under high load during AFM imaging. The conformation of the bubbles is influenced by the atomic steps on the graphite substrate. In addition, a shadow was found around the bubbles, which was due to the interactions between a bubble adhered to the tip and a bubble on the substrate.

Keywords: nanobubble, AFM, mica, graphite
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I. INTRODUCTION

Water films, droplets and bubbles are three kinds of typical phenomena of liquid water. Recently, studies on the properties of water on the nanometer scale attracted considerable interest in the scientific community.[1,2] Methods and techniques have been developed to detect the water films and droplets with nanometer resolution and systematic studies are performed.[1−3] However, properties of bubbles on the nanometer scale are still unclear. There are some difficulties in the investigation of nanobubbles, mainly because of the lack of controlled production of nanobubbles and detection of high spatial resolution.[4−7]

Bubble is playing a crucial role in current industrial processes and taking detrimental effects on the integrated circuit industry, especially.[5−7] For example, during bonding process of a SOI (Silicon-On-Insulator) chip, a small bubble may be deadly to the fabrication of a chip.[8,9] Small bubles on the surface of a DNA chip will largely retard the hybridization process and lower the precision of the DNA tests. However, only a few reports discussed the properties of nanobubbles.[5,7,9]

According to macroscopic thermodynamics, bubbles will be very unstable on the submicron scale.[10,11] The Laplace equation predicts a high internal gas pressure for nanobubbles that should make them dissolve quickly at room temperature.[7] However, some researches suggest nanobubbles to be the origin of the long distance force between two macroscopic hydrophobic surfaces.[7,12] Nanobubbles are situated at the interface of liquid/solid and very few nanometer resolution devices can be used under this condition. The atomic force microscope (AFM) is a powerful tool to study materials under varied environmental conditions with nanometer resolution.[13−16] A recent report proved the existence of long-lived submicron bubbles by measuring the force curve with AFM between a hydrophobic tip and a hydrophobic surface.[17] In our previous work, nanobubbles could be imaged by AFM.[18]

In this report, water bubbles on the nanometer scale were produced by a special method on solid surfaces and measured with an AFM instrument. The

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production mechanism of these bubbles and their behavior on mica and graphite substrates were investigated.

II. EXPERIMENTS

Normally, the nanobubbles were produced by mixing two liquids in an AFM liquid cell. Briefly, one liquid were injected into the cell and then it was replaced by another. During these processes, many bubbles could be produced on mica or graphite surfaces.[18] The samples discussed in this paper were prepared as follows.

First, highly oriented pyrolytic graphite (HOPG) and mica were used as the substrates. Pure ethanol was injected into a liquid cell. Then, the solution of water and ethanol was injected into the cell to replace pure ethanol after several minutes. The volume concentration of ethanol ranged from 0% to 20%. An AFM instrument (Nanoscope IIIa from Digital Instrument, Santa Barbara, CA) was used to image the sample with a normal contact tip in the liquid at a force constant of 0.38 N/m in the tapping mode.

III. RESULTS AND DISCUSSION

The bubbles observed in the experiments were produced by mixing water with ethanol. It can be considered that the solubility of the gas in ethanol is larger than that in water. During the process, when ethanol was first mixed with water, molecules of the gas diffused out and bubbles formed. After the ethanol was fully replaced by water, nanobubbles were produced on the solid surface because of their lower solubility in water.

Bubbles on mica or HOPG could be imaged clearly by AFM in the tapping mode. Normally, bubbles on mica were smaller than those on HOPG under the same conditions, and they showed a spherical shape in our experiments. The apparent sizes of the bubbles were in the range of tens of nanometers. The tips we used had an angle of 70° at the apex and they would widen the sizes of the objects on the surface. Those tips always gave out several times the size of the real diameter of a hard sphere in the AFM image. The smallest bubbles observed in our experiments had an apparent diameter of about 20nm. Its real size, we believe, was around 10nm or less. The apparent heights of those bubbles were from several nanometers to tens of nanometer. It should be pointed out that the height was determined by the load. Higher load usually results in smaller heights. In our experiments, load was often kept as small as possible by adjusting the amplitude of the vibration to the minimum.

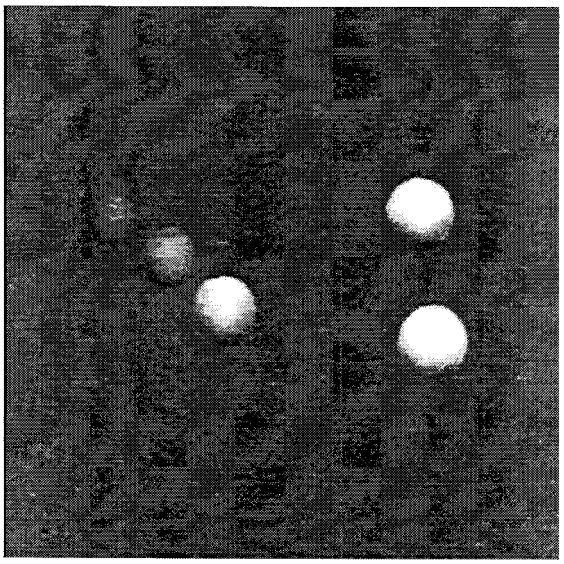


Fig.1. AFM image of bubbles on mica surface in water in tapping mode, with normal contact cantilever of force constant 0.38N/m from Digital Instruments. Image size: 1μm×1μm. These bubbles were quite stable.

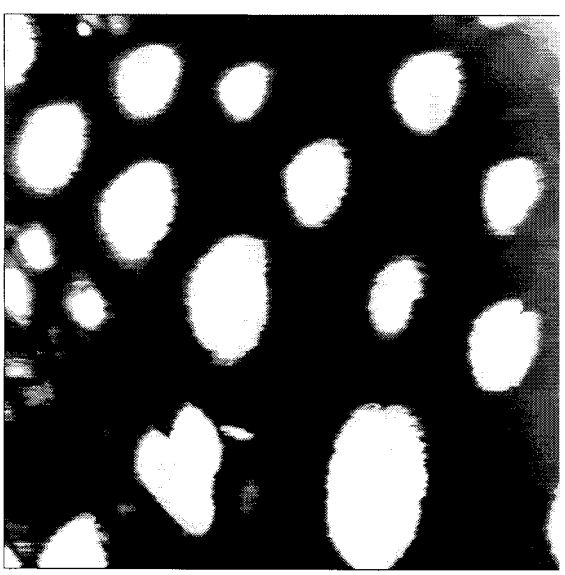


Fig.2. AFM image of bubbles on HOPG surface in water in tapping mode, with normal contact cantilever of force constant 0.38N/m from Digital Instruments. Image size: 4μm×4μm.

Apart from the careful preparation of water and ethanol, there are several reasons why we are sure of having detected bubbles, not contamination. First, when the solution of water and ethanol was treated with an ultrasonic generator before it was injected

into a liquid cell, the density of bubbles on the substrate was lower than that without treatment. Second, those bubbles became smaller when the concentration of ethanol was increased in the cell, and they usually disappeared when the ethanol concentration was beyond 70%, in agreement with the decreasing surface tension of the solution. Finally, similar bubble phenomena were found by mixing other liquids such as water and salt solutions.[17] It does not make sense that contamination is produced when diluting water solutions of salt with water itself.

Sometimes, very interesting images were found. There were some shadows around the bubbles. The force curve showed that there was a very soft stuff on the tip. It was assumed that a bubble adhered to the tip and behaved as a pseudo tip. The shadow means that the contrast is low. This is due to the attraction force between the bubble on the tip and the bubble on the substrate. It is well known that the attraction force will give a negative contribution to the contrast in the tapping mode. In pure water, we found that the tip easily picked up bubbles during scanning. It is interesting that the bubble on the tip was still very stable after it got in touch with the bubbles on the substrate. This offers us a way to detect the interactions between two nanobubbles, which is very important in bubble study.

IV. CONCLUSION

In summary, nanobubbles have been successfully produced on solid surfaces by a controlled method. AFM was used to detect these bubbles. It is shown that nanobubbles can be stably seen on liquid/graphite and liquid/mica interfaces. The conformation of the bubbles is influenced by the atomic steps on the graphite substrate. In addition, shadows around the bubbles were found, which were due to the interactions between a bubble adhered to the tip and a bubble on the substrate.

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