Development and Applications of a Frequency Modulation Atomic Force Microscope for High-resolution Imaging in Liquids

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Although dynamic mode atomic force microscopy (AFM) using frequency modulation (FM) detection technique is capable of atomic/molecular-resolution imaging in ultrahigh vacuum (UHV) environments, the imaging resolution of FM-AFM in liquids is extremely reduced by a large decrease in the Q-factor caused by hydrodynamic damping in liquids. We improved a commercial atomic force microscope (AFM) for high-resolution AFM imaging in liquids. The noise density of the improved optical beam deflection sensor was successfully decreased to 29 fm/√Hz at a laser power of 1 mW in liquid. In addition, the noise level and the bandwidth of the FM detector were also improved to 6 mHz/√Hz and 6 kHz, respectively. Thermal drift was reduced to less than 1 nm/min in air for a sufficiently long time without any special air conditioning. As a result, we succeeded in obtaining high-resolution images of a polypropylene sheet, Au thin films in water and DNA molecules in a buffer solution. The results indicated that liquid environments could provide a suitable condition for high-resolution FM-AFM imaging such as UHV environments.

Introduction

The dynamic mode atomic force microscope (AFM) using the frequency modulation (FM) detection technique [1] has been widely used for high-resolution imaging in ultrahigh vacuum (UHV) with the aid of a high Q-factor of the cantilever [2]. In fact AFM imaging in air, where the instrumental setup can be generally much simpler, is more suitable for various, practical applications. However, the true atomic/molecular resolution imaging by AFM in air is extremely difficult. A major difficulty in achieving such resolution in air AFM is that the specimen surface and/or the AFM tip can be damaged by the strong adhesion force acting between the tip and the surface due to a thin water layer of the surface. AFM imaging in liquid is a possible way for avoiding the adhesion problem and for the high-resolution imaging. High-resolution imaging with FM-AFM in liquid is again very difficult because of a large decrease in the Q-factor due to the hydrodynamic damping in liquid. Recently, several high-resolution images of mica surfaces and organic molecules including bio-molecules have been successfully reported using FM-AFM in liquids [3]. The success of high-resolution FM-AFM imaging in liquid encourages us to expand the applications of FM-AFM to new research fields.

In this study we improved a commercial AFM, JSPM-5200, and succeeded in obtaining high-resolution images of polypropylene sheet, Au thin film and DNA molecules in liquids. These results show that our improved FM-AFM has the capability of high-resolution imaging in liquids. This FM-AFM is expected to be used for a wide variety of industrial and scientific applications.

Discussion

A sufficient noise reduction in both cantilever deflection sensor and FM detection circuit is necessary for high-resolution imaging in liquids [4]. A commercial AFM (JSPM-5200) using the optical beam deflection method, as shown in Figure 1, was modified. Figures 2 show photos of the improved AFM. To decrease the mode hop and the interference noises in the optical detection system, the coherence of the laser beam used for the cantilever deflection sensor was suppressed by adding a radio frequency modulation signal to the laser diode. Furthermore, the optical setup of the deflection sensor was also optimized, as shown in Figure 3. As a result, the noise density of the improved deflection sensor was reduced to 29 fm/√Hz in water at a laser power of 1 mW, which is compliant to class II for the classification of performance standard for light-emitting products. This value is much smaller than those obtained with conventional instruments (typically 500-1000 fm/√Hz). In addition, the noise of the phase-locked loop (PLL) circuit in the FM detector was also reduced while the frequency bandwidth was expanded to 6 kHz. As a result, stable FM-AFM imaging in liquids is possible gate array (FPGA), as shown in Figure 4. The FM detector noise was reduced to 6 mHz/√Hz and the frequency bandwidth was expanded to 6 kHz. Moreover, the SPM head was placed in a vacuum thermo-stabilized chamber to reduce the thermal drift as shown in Figure 5. As a result, the thermal drift was kept at less than 1 nm/min in air for a sufficiently long time in an ordinary room where several people were walking around. Thermal drift in liquid was a little larger than in air because of the influence of the liquid evaporation. Consequently, sub-nanometer resolution images of muscovite mica surfaces in a buffer solution were successfully obtained by FM-AFM mode using our improved AFM with a small oscillation amplitude of 0.5 nm, as shown in Figure 6.
Fig. 1 JSPM-5200. The modified part is shown in Fig. 2.

Fig. 2 High-resolution AFM for imaging in liquid.

Fig. 3 Schematic diagram of the AFM head.

Fig. 4 The block diagram of the FM detection electronics.

Fig. 5 Schematic diagram of the vacuum thermo-stabilized chamber.

Fig. 6 FM-AFM image of a muscovite mica surface in a buffer solution (0.1mol/L KCl). Scan size is $5 \times 5$ nm$^2$. 
Using the improved AFM, we imaged surfaces of a polypropylene sheet and annealed Au thin films on a mica surface in a liquid. A highly doped n-Si cantilever (Nanoworld: NCH) was used as the force sensor. The peak-to-peak amplitude of the cantilever oscillation was set at a value ranging from 0.5 to 1.0 nm. First, the polypropylene sheet was observed in UHV. The results are shown in Figures 7. The polypropylene chains are clearly resolved, as shown in Figure 7(a), on a (110) crystal facet in a magnified image of a fiber circled in Figure 7(b) [5]. Figures 8(a) and (b) show FM-AFM images of the same polypropylene sheet taken in a buffer solution (0.1 mol/L KCl). An island composed of some terraces was observed in tangles of polypropylene fibers (Fig. 8a). The periodic structure corresponding to the molecular array was also observed on a surface of the terrace (Fig. 8b), whose spatial resolution seems to be almost comparable to the one obtained in UHV. As shown in Figure 8(c), a high-resolution image was also obtained in air. However, the cantilever oscillation had to be five times larger than in the liquid to avoid the cantilever adhesion to the surface, which could have disturbed imaging of the fine structures of the sample.

Figures 9(a) and (b) show FM-AFM images of an annealed Au thin film on mica in the buffer solution (0.1 mol/L KCl). Usually, the atomic scale images of the Au thin film surface can be obtained using UHV-STM or Electro-Chemical STM. In this experiment, the herringbone structure on a terrace was successfully observed even in liquid, as shown in Figure 9(a). Furthermore, the periodic structure corresponding to the atomic array could be visualized with the size of 3 × 3 nm² on a flat area of the surface as shown in Figure 9(b).

We also successfully obtained high-resolution images of a highly orientated pyrolytic graphite (HOPG) surface in pure water. While the atomic scale images of the HOPG surface have been obtained using FM-AFM in UHV, it is pointed out that the topographic signal is quite small because of the relatively weak interaction force between the tip and the HOPG surface [6]. Figure 10 shows an FM-AFM image of the HOPG surface taken in pure water. The peak-to-peak amplitude of the cantilever oscillation was set at 0.2 nm. The periodic structure was visualized corresponding to the periodic structure of the surface, as shown in Figure 10. Thus we succeeded in obtaining high-resolution images of HOPG by FM-AFM in liquid as well as in UHV.

With this advanced technique, we also imaged DNA tiles, in which several numbers of DNA strands were self-assembled and packed into two-dimensional patches [7,8]. There have been several studies on high-resolution imaging of DNA molecules in UHV [9]. However, high-resolution imaging of DNA molecules in liquid is strongly required in biological studies. This is because the structure and the properties of the DNA are stable only in physiological solution. The peak-to-peak amplitude of the cantilever oscillation was set at 1.0 nm. Figures 11(a) and 11(b) show a design of a DNA tile used in this experiment and an FM-AFM image of the DNA tiles on mica in a buffer solution, respectively. As shown in Figure 11(b), pairs of double strands aligned in parallel were...
fig. 11 (a) The design of a DNA tile used in this experiment, (b) FM-AFM image of the DNA tile on mica in a buffer solution. Scan size is 38 × 38 nm².

fig. 9 FM-AFM images of a Au thin film on mica in a buffer solution (0.1 mol/L KCl). Scan size of (a) and (b) are 200 × 200 and 3 × 3 nm², respectively.

fig. 10 FM-AFM images of highly orientated pyrolytic graphite (HOPG) surface in pure water. Scan size of (a) and (b) are 5 × 5 and 3 × 3 nm², respectively.

Fig. 11 (a) The design of a DNA tile used in this experiment, (b) FM-AFM image of the DNA tile on mica in a buffer solution. Scan size is 38 × 38 nm².

Imaged as one big strip surrounded by the orange rectangles. A periodic structure with a 3.5 nm pitch, which is consistent to the periodicity of the DNA double helix model, can be clearly seen in the strip. The periodicity of DNA obtained in a previous UHV observation [9] was 4.2 nm. This difference in the periodicity is probably caused by the drying process in the specimen preparation for UHV observation.

Conclusion

We succeeded in improving our commercial AFM for high-resolution imaging of various materials in liquids. With this AFM, high-resolution images of a polypropylene sheet and an Au thin film were reproducibly obtained in liquid. The spatial resolution in these images was comparable to that in the typical images of the same samples taken in UHV. Furthermore, the double strand structure of the DNA double helix was observed in liquid, which had not been obtained in UHV. The present success in obtaining high-resolution images of the several sample surfaces in liquid indicates that the liquid environment is a quite suitable and promising environment to perform high-resolution AFM imaging. Thus it can be the alternative to the UHV environment for high-resolution FM-AFM observation.

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References

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