Dissertation

Improvement of stability and speed in liquid-environment atomic force microscopy

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Abstract

Invention of atomic force microscopy (AFM) impressed researchers in various field of nanotechnology such as material science and biological materials. It can be operated in liquid as well as air and vacuum for wide range of samples. AFM has attracted much attention due to its unique capability of visualizing nanoscale structures. Several techniques were developed in visualizing the nanoscale dynamic process and high-speed AFM (HS-AFM) can be one of best candidates. However, in the HS-AFM the usability is limited because of the small size of the sample to be scanned especially in Z direction. To overcome this problem, I propose a design of the cantilever holding mechanism utilizing a precisely-machined plate spring to be fixed with a screw. On the other hand, during the imaging some phenomena such as creeping, non-linearity and hysteresis may affect accuracy of the AFM. So, as a solution crystal oscillator can be used as a part of capacitive sensor to detect amount of unwanted displacement. In addition, sometimes during the imaging we may lose stability and reproducibility. So, I was focused on the tip preparation process to improve imaging conditions.

1. General remarks

There are frictional stories about amazing electro mechanical products in micro or nano scale. The nature surrounds us consists of atoms. Different combinations of these atoms create molecules. Each of them has a specific chemical and physical property. These molecules bond to each other with attractive or repulsive forces caused different physical phase like solid, liquid and gas. These molecular interaction forces keep the materials steady, known as van der Waals force which plays the major role in nanotechnology. The fantasy of engineering in nano scale or atomic level made the scientists to discover molecular space conditions. The physical and mechanical characteristics in nano space must be investigated. This new field of science requires precise metrology, positioning and microscopy methods in atomic level. Human being always wanted to see small features as deep as perceivable. Invention of optical microscope by van Leeuwenhoek in 17^{th} century opened new criteria of knowledge. First optical microscope was a simple hand held glass lens made of silver or copper. Optical high school microscopes which are familiar to all of us can magnify objects around one micron like red blood cells (7 μm). Investigating far through features progressed ceaselessly to obtain more resolution and visibility. Microscopy is categorized in three main branches known as optical, charged particle (electron and ion) and scanning probe microscopy. Optical and charged particle microscopy, as their name proposed, collect data from specimen by diffracting, reflecting, and refraction of electromagnetic wave or electron/ion with sample surface while the scanning probe microscopy investigates by different interaction of scanning probe and sample surface. Scanning probe microscope includes the technologies provides high resolution imaging for not only quantitative measurements but also physical and chemical properties at the nano scale level. This microscopy particularly provides sample morphology so it is playing a main role in thin film physics, nanometrology or any structural base science. The SPM scanning developments provide dominant

achievements in different fields of science and engineering. The system instrumentation based on a sharp tip (about 10 nm) mounted on a flexible cantilever travels across the sample surface. During tip moving over the sample, the intermolecular forces between them effect on cantilever detection. These influenced movements could be detected by various sensors. According to interaction types this microscopy includes three main methods. Atomic force microscopy (AFM), scanning tunneling microscopy (STM) and near field scanning optical microscopy operated based on molecular interaction force, weak electrical current flow and tiny light source respectively. For many AFMs, the cantilever and integrated probe are made by wet etching of silicon. There are many different types of SPMs operated based on various physical phenomena like magnetic, electrostatic, electrical capacitance, optical and thermal interactions, which creates different setups.

2. Purpose

There are some potential research areas in AFM, in which we can classify in 3 groups. First group is new technologies that cover 3D-AFM and surface potential measurements. Second group is improvement of performance including the high-speed AFM, high sensitivity and mechanical design of AFM. The last group covers applications of AFM in biology, chemistry, industry and so on. Our aim through this research is to improve the mechanical design of AFM. In order to do, I will focus on improving accuracy, usability and stability of AFM. During this study, I introduced new designs for advancing the imaging speed. I introduced two type of precisely machined plate with screw holding mechanism Z tip scanner and its performance by imaging of the calcite crystal. In addition, counterbalance Z tip scanner with two arrangements and those performance and effect of them on the imaging speed was admitted. There are three parameters that affect the accuracy of scanner. First of all non-linearity of our system; second, hysteresis, and the last one is creeping. To solving these problems, we have to use closed-loop feedback controller. Although there are several types of closed-loop feedback controller, but I want to use capacitive detection system. On the other hand, in recent years, one of the main major improvements of atomic force microscopy in aqueous environments has been achieving of high atomic scale resolution in various interfacial phenomena studies. During this analysis, instabilities and poor data reproducibility made systematic studies impossible. To solve this problem, the effect of various tip treatment methods for atomic scale imaging and force measurements in liquid environments is investigated during the following research. The tested methods, examined in Si coating, Ar plasma, Ar sputtering and UV/O_3 cleaning tips. The experiments demonstrated that, all of these methods provide remarkable progress in both the imaging and force measurements even though the tip is transferred through the air.

3. High-speed Z tip scanner for atomic-resolution atomic force microscopy

3.1 Introduction

In 1986, invention of atomic force microscopy (AFM) impressed researchers in various field of nanotechnology such as material science, biological materials, physics and chemistry. Atomic force

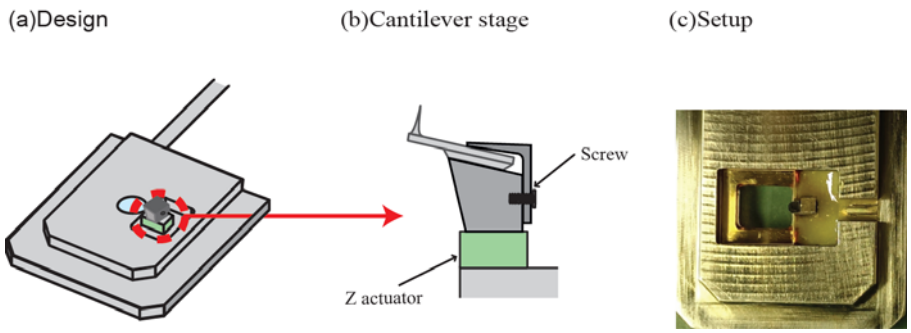

Figure 1: High-speed Z tip scanner with vertical arrangement screw cantilever holding mechanism ; (a)Design (b)Cantilever Stage (c)Setup

microscopy can be operated not only in liquid but also in air and vacuum. Moreover, it can be used for samples from organic to mineral, from insulated material to conductive one and from very soft material to harder ones. Owning to these unique capabilities, AFM can be used for wide range of samples. In contrast, AFM has a large room for further improvements. Typically the scan rate of AFM is approximately 1 Hz and for having of image by dimension of 10 nm ×10 nm takes 1 min for every frame. It would be advantageous to have an AFM with a higher scan rate to image dynamic processes at solid/liquid interfaces. High-speed AFM requires creating the mechanical controlling system which has high first resonance frequency. Scan rate is limited by parameters such as: (1) first resonance frequency of XY scanner, (2) force sensing system, (3) bandwidth of feedback control and (4) first resonance of the Z tip scanner. Scan rate is determined by the slowest responsiveness of these issues. Therefore, researchers focus on the enhancement of the resonance frequency of scanners and reducing the cross talk between XY and Z scanner. Based on the previous works, high-speed AFM has been developed. Tabak et al. introduce the micro electro mechanical system (MEMS) as a high-speed Z scanner to provide high-speed scanning motion. The introduced Z scanner has low mass (about 10^{-11} Kg) and high resonance frequency (in order of several MHz). On the other hand, they used separated XY and Z scanner to avoid the cross talk. Ando et al. developed high-speed scanner by using the counterbalance structure. This improvement was done by decreasing the cross talk of scanners. Fukuma et al. developed resonance frequency of Z axis by inertia balance support and can get 540 kHz resonance frequency in Z axis. They supported cubic actuator at 4 sides perpendicular to excitation axis. Hansma et al. represented scanning unit for AFM system 3 times faster than the conventional AFM. They used the parallel flexure stage for this purpose. Their design was developed more by other researchers. Miyata et al. presented a design of separate-type high-speed scanner that consists of XY sample and Z tip scanners. In addition, they presented the design of a wide bandband low noise HVAMP to achieve sufficient noise performance to allow high-speed and high- resolution imaging. So, improving the first resonance frequency of Z tip scanner is one of the most important part that strongly influence the operation speed and usability of AFM. I focus on the improvement of the Z tip scanner and for this purpose I will introduce two kinds of developed Z tip scanner by the name of precisely machined plate with screw holding mechanism Z tip scanner and counterbalance Z tip scanner. Some experiment will be done to demonstrate the improvement on the following methods.

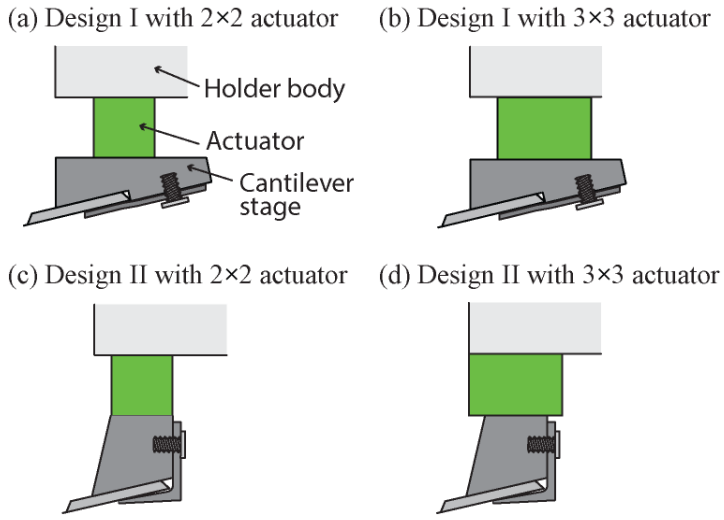

Figure 2: Schematic models of the Z tip scanners with different designs of a cantilever screw holding mechanism

3.2 Basic Designs of screw type Z tip scanner

In the previous works, different cantilever holding mechanisms using a screw, a plate spring and glue was compared. The result showed that the screw holding mechanism gives the best balance between the performance and the usability. However, the design for the Z tip scanner with a screw holding mechanism was not optimized for achieving the best performance. For example, the dependence of the performance on actuator size and screw arrangement has not been investigated. In figure 1, I introduce the new precisely machined plate with screw cantilever holding mechanism. I compare it with different cantilever holding mechanism (Figure 2). These designs are different in actuator size and screw arrangement. The screw is laterally displaced from the cantilever position in Figs. 2(a) and 2(b) while vertically displaced in Figs. 2(c) and (d). Here I refer to the former as Design I and the latter as Design II. The actuator in Figs. 3.2(a) and 2(b) has a smaller size ($2 \times 2 \times 2$ mm^3) while the one in Figs. 2(c) and (d) has a larger size ($3 \times 3 \times 2$ mm^3). An actuator is fixed to a holder body with glue. Then, a cantilever stage is fixed on the actuator. A cantilever is sandwiched between the cantilever stage and a metal plate spring. The plate spring is fixed with a screw to the cantilever stage. All the metal parts are made of stainless steel (SS316).

3.3 Experimental details

FEA software (COMSOL Metaphysics, COMSOL) was used for theoretical analysis of the frequency response and vibration modes of the scanner. I used Young's Modulus of 193 GPa, Poisson's ratio of 0.25 and density of 7970 kg/m^3 for modeling the scanner bodies made of SS316. For modeling the stack piezo actuators, I used density of 7500 kg/m^3.

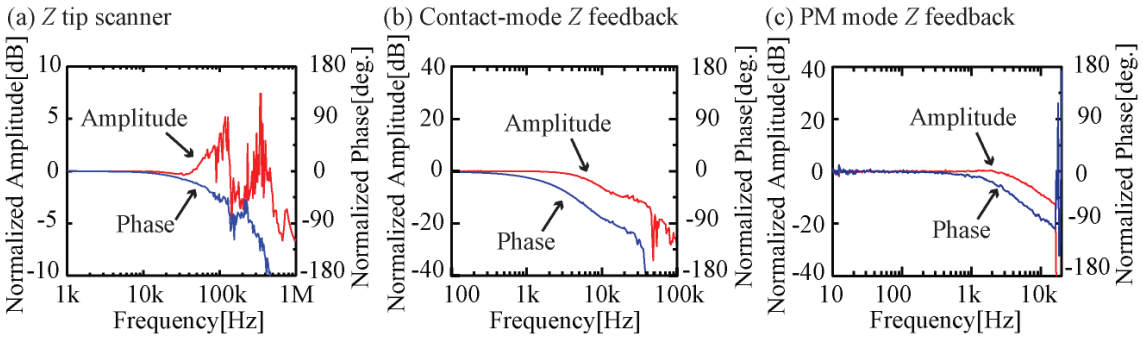

Figure 3: Frequency response of (a) the developed Z tip scanner; (b) Z feedback regulation measured in contact-mode AFM ;(c) Z feedback regulation measured in PM mode AFM.

I measured frequency response of the developed scanner by frequency response analyzer (FRA5097, NF). I measured displacement of the Z scanner by detecting the vibration of cantilever body attached to the cantilever stage using a heterodyne laser displacement sensor (ST-3761, IWATSU).For AFM imaging, I used a home-built AFM system with an ultralow noise cantilever detection sensor. To demonstrate the ability of new developed Z tip scanner to image in atomic resolution, I image the cleaved surface of the mica disc(≈ 12mm,Furuuchi chemical) by a cantilever with spring constant of ~ 85 N/m (AC55) in phosphate buffered saline(PBS)solution and frequency mode AFM. For this experiment, I used a commercially available AFM controller (ARC2,Asylum Research).

I performed contact-mode AFM imaging of a cleaved surface of a calcite crystal (Furuuchi Chemical) using a cantilever with a spring constant of ~2 N/m (AC240, Olympus). I used the XY sample scanner and the HVAMP that previously developed. This experiment was performed at room temperature in water.

3.4 Results and Discussions

Based on the analysis presented above, I have developed a Z tip scanner with Design II and a 3×3 actuator. Figure 3(a) shows frequency response of the developed Z tip scanner. The amplitude

curve shows a broad peak from 40 kHz to 130 kHz. This frequency range agrees with the frequencies of Modes 1-4.

Figure 3 (b) shows frequency response of the tip-sample distance regulation measured by contact-mode AFM with AC240 cantilever. The feedback gains are adjusted such that the bandwidth is maximized. The amplitude curve shows that ~3 dB bandwidth of the feedback regulation is ~6 kHz. This is sufficient for performing high-speed AFM imaging at a few seconds per frame as demonstrated below. Figure 3(c) shows frequency response of the tip-sample distance regulation

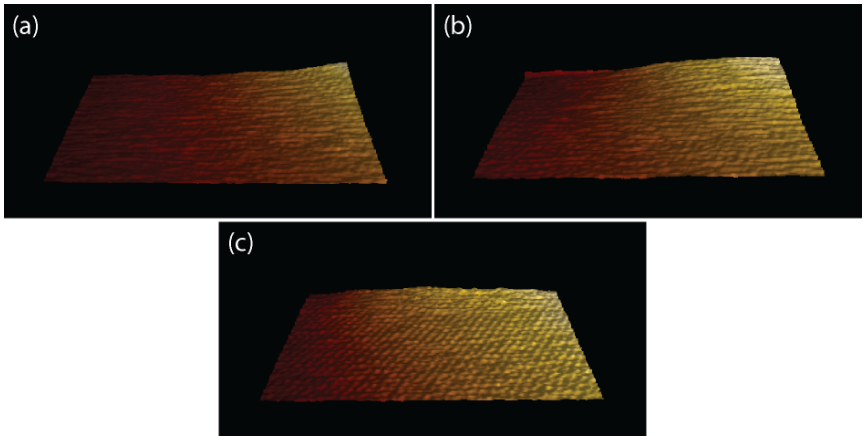

Figure 4: Snapshots of 44 successive contact-mode AFM images of calcite crystal dissolution process in water. (a) 0 s. (b) 40 s. (c) 80 s. Scan size: 20 × 10 nm^2.Scan rate: 50 Hz. Imaging speed: 2 s/frame. Pixel size: 200 × 100 pix2. Tip velocity: 4 μm/s. f_{cr} = 5-8 kHz.

measured by PM-AFM. In this experiment I used phase detector system with AC55 cantilever. In this condition, by ~5 dB Amplitude the bandwidth of feedback is ~4.3 kHz.

Figure 4 shows snapshots of successive AFM images of calcite crystal dissolution process. The imaging was performed at 2 s/frame in water using contact-mode AFM. In spite of the fast scanning speed, the images show atomic scale contrasts separated by ~0.5 nm. The images also show that the movement of the upper terrace edge from the top right to the bottom left of the image.

The atomic-scale corrugation period is 0.5-0.8 nm while the tip velocity was 4 μm/s. Thus, frequency (f_{cr}) of the corrugations that tip-sample distance regulation should follow is 4-8 kHz. This is close to the feedback bandwidth estimated from the frequency response curve shown in

Fig. 3(b). The result demonstrates that the developed scanner is applicable to atomic-scale high-speed AFM imaging in liquid.

4. Stability and reproducibility improvement of atomic force microscopy in liquid

4.1 Introduction

There are lots of efforts on improving the specific resolution and force sensitivity to provide atomic resolution of dynamic mode AFM. However stability and reproducibility of these methods are not adequate for practical experiments. The obtained scanning image contrast, usually changes overall one frame scan even when scanning applied over a standard sample like cleaved mica layer. Besides, atomic scale contrasts in one image is not repeated in another one necessarily.

Such these weaknesses like instabilities and uncertain reproducibility block systematic research on interfacial phenomena. These troubles derive from instability and poor reproducibility of the tip apex situations. A suitable solution method is a tip cleaning when scanning is done in vacuum for instance in FM-AFM by ion beam sputtering.

For liquid environment scanning, the condition is a little different somehow the cleaned tip should enter to an aqueous surface through the air so keeping the clean tip apex, during the oscillation, seems difficult. Previous studies demonstrate that surface treatment methods using plasma, UV/O3, piranha solution (mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) to solve and clean organic contamination) are enhanced at least for nanoscale measurements. This research is going to propose an enhanced tip cleanliness and hydrophilicity effects on AFM measurements. However it could not generally conclude that these methods are also effective to atomic scale AFM measurements especially where atom to atom interactions predominantly play a major contributed role in image contrast. The examined methods contain silicon (Si) coating, Ar plasma, Ar sputtering and UV/O3 cleaning steps. The results show the best method from performance aspect in atomic scale AFM measurements. Additionally the tip surface properties before and after treatments by X ray photoelectron spectroscopy (XPS) and contact angle measurements (CA) are compared and probed. The variety of methods with different performance and basis are studied and the cleaning mechanism is clarified.

4.2 Tip treatment methods

In this study Si coating cantilever with backside Au layer coating (PPP-NCHAuD, Nanoworld) is used. The nominal cantilever spring constant (k) is 42 N/m with typical resonance frequency and Q factor in liquid are 140 KHz and 8, respectively. The nominal tip apex radius (R_t) is less than 8 nm. Silicon coating step is applied on the tip by dc sputter coater (K575XD, Emitech). Silicon deposited layer was set at 30 nm. This thickness is chosen to assure the tip completely covered and protected by silicon thin film. In Ar plasma cleaning step, plasma cleaner from Sanyu Electronics (SC-701) has been used. The examination shows that Ar plasma cleaning with ordinary operation conditions can seriously damage the cantilever surface. Thus, the bias voltage and the inlet gas pressure have been adjusted just as high as required for the plasma remaining. Also the cantilever is covered by tantalum (Ta) plate to suppress the electric field applied over its surface. These conditions make the cleaning damage negligible. In the Ar sputtering method, an ion source from SPECS (IQE 11/35) is applied by custom built vacuum chamber. In this operation the cantilever plays the substrate role placed in 5 cm distance of ion gun. The initial base pressure of chamber before sputtering was 5×10^{-6} pa. Ar gas was injected into the chamber to raise the pressure to 1.3×10^{-4} pa value.
The sputtering operation was done for 5 min with acceleration voltage of 0.6 kV. In UV/O3 cleaning step, UV/O3 cleaner from BioForce Nanoscience (ProCleaner Plus) was used. The cantilever was placed on a piece of large quartz crystal processed in about 5 min. After sputtering process, the cantilever immediately was immersed into water to discharge for a few seconds. This immersion avoided the cantilever contaminant absorption during the moving through the air. In previous studies, tip treatment and cleaning methods was done by acidic solution of piranha which has a successful effect on organic contaminations. Prior experiments show that acidic solution can damage Au backside coating of the cantilever. Despite there must be an effective safe cleaning method to eliminate surface contamination, some of the major dry processing operations have been used for tip treatments.

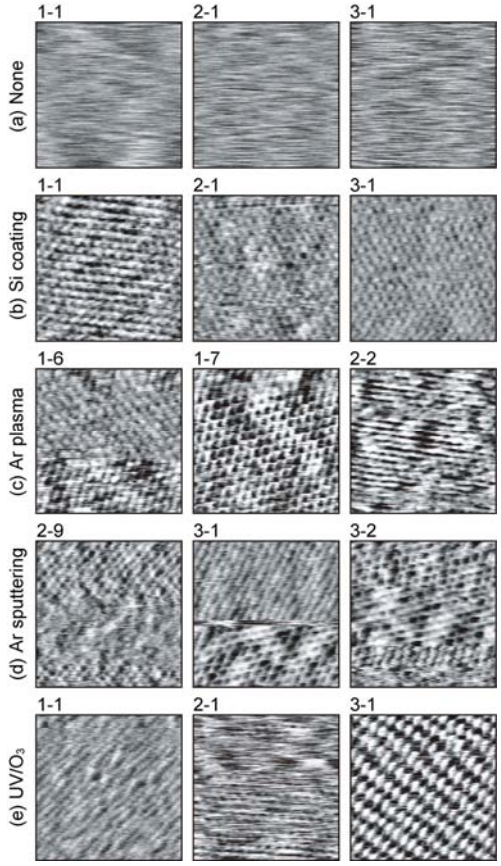

Figure 5: FM-AFM images of a cleaved mica surface obtained in PBS solution. (a) None. (b) Si coating. (c) Ar plasma. (d) Ar sputtering. (e) UV/O3. The numbers n-m indicated in each image shows that the image corresponds to the m-th image obtained in the n-th experiment. Scan size: 8×8 nm^2. Tip velocity: 223 nm/s. A = 0.25 nm. $\Delta f = 800$ Hz.

4.3 Atomic-resolution imaging

FM-AFM imaging of a cleaved mica surface in PBS solution with different tip treatment methods was performed. As explained before for each tip treatment methods three experiments were donewhile 10 images were taken from each of them. Therefore, 150 images were obtained totally in this test. Figure 5 shows some of the example images randomly. Without a tip treatment, obtaining image with atomic resolution is hardly possible. (Figure 5(a)) In contrary, with every tip treatment methods, an atomic resolution image have been obtained from the first scan of the tip approaching. Since the apex of the as-purchased tip is covered by different contaminations, achieving atomic resolution imaging in liquid is impossible. These contaminations should be removed by tip treatment methods, to create an atomic resolution imaging. For the silicon coating method, the images always show a similar atomic-scale contrast. For example the first scan images of the three experiments show similar contrasts (figure 5(b)).However the images obtained by the other methods usually show a discontinuous contrast change due to tip altering (figure 5(c)-(e)). Additionally this is clear that, the

atomic scale contrasts observed in one test are different from those in the other tests (figure 5(c)-(e)). The results significantly proved that the tip apex condition after treatments is not stable and reproducible. Thus, as an outcome, it could be suggested that, silicon coating supplies the best quality and reproducibility in an atomic-resolution imaging.

In conclusion, The tested methods, examined in Si coating, Ar plasma, Ar sputtering and V/O3 cleaning tips. The experiments demonstrated that, all of these methods provide remarkable progress in both the imaging and force measurement even though the tip oscillates through the air. Among these methods silicon coating tips provide the best stability and reproducibility in the measurements. To recognize anti-fouling effect basis of the cleaned tip surface and the comparison of different cleaning methods, the tip surface characteristics have been investigated by x-ray photoelectron spectroscopy and contact angle measurements. The results show that the contaminations adsorbed on the tip during oscillation through the air should be discarded from the tip surface by aqueous solution immersion which is because of the enhanced hydrophilicity by the tip treatments. The prepared silicon coated tip is oxidized by aqueous solution immersion and water absorption. This oxidation creates local spots where stable hydration structures are formed. In other methods there is no active mechanism to create these local hydration sites. Basically these hydration structures are not steady under the tip apex. These results demonstrate the desirable tip characteristics atomic scale AFM in aqueous measurements creates a new guideline for further improvements of the tip treatment methods.

平成２７年１月３０日

学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Improvement of stability and speed in liquid-environment atomic force microscopy（液中原子間力顕微鏡の安定性および動作速度の改善）

２．論文提出者　(1) 所　　属　電子情報科学　専攻

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３．審査結果の要旨（600～650 字）

平成 27 年 1 月 30 日に第 1 回学位審査委員会、口頭発表、および第 2 回学位論文審査会を開催し、慎重審議の結果、以下のとおり判定した。なお、口頭発表における質疑応答を最終試験に代えるものとした。

周波数変調原子間力顕微鏡（FM-AFM）は液中で原子分解能観察が可能なため、様々な固液界面現象の計測分析への応用が期待されている。しかし、従来の FM-AFM では動作速度や安定性の問題で、計測できない構造や現象も多かった。本論文は、AFM の動作速度を制限する主たる要因の一つであるスキャナの高速化を、実用性を維持したまま実現する方法を提案した。特に、カンチレバーや試料の保持機構に関して、有限要素法解析と実験を相補的に利用することで、最適な設計指針を提案した。また、AFM 探針の表面処理方法として、プラズマ、イオンビーム、UV/オゾン、Si コートなどの手法を詳細に比較検討し、Si コートの有効性を初めて見出した。さらに、これらの手法の効果に違いが生じる原因を、X 線光電子分光法や接触角測定を用いて解明した。

以上の研究成果は、液中 FM-AFM の高速化・高安定化技術に関する重要な知見を与えるものであり、本論文は博士（工学）に値すると判定した。

４．審査結果　(1) 判　　定（いずれかに○印）（合　格）・　不合格

(2) 授与学位　　博　士（工学）