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A Simple and Rugged Home-Built Scanning Tunneling Microscope for Operation in Both Air and Liquid

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A simple, rugged home-built scanning tunneling microscope for operation in both air and liquid that uses a Z-stage micrometer to provide coarse mechanical positioning is described. The construction of this STM was accomplished at low cost without precision machining. The tunneling current is typically acquired within 10—15 minutes. The atomic resolving power of our STM has been demonstrated by a cleaved HOPG at a 15-Hz scanning rate in air. There was no use of plate-stack-type isolators, due to the high rigidness of the tunneling unit. The STM image of a HOPG in ultrapure water was also observed with a glass-coated tip. Images of a pc-Ag electrode in 0.1 mol dm^{-3} KCl demonstrate stable operation in a liquid solution. The lateral drift was shown to be less than 0.13 nm min^{-1} for operation in liquid, estimated by subsequent imaging of the same area. This STM is easy to handle and has a suitable design for in situ electrode surface characterization.

Scanning tunneling microscope (STM) and associated techniques are beginning to be incorporated into the field of electrochemistry. To date, surface chemistry is poorly understood on account of the limited measuring conditions and resolving power of available tools. The currently developing scanning tunneling microscope is a suitable instrument for investigating the surfaces of conducting materials at the nanometer scale under various environments.1) A number of designs for scanning tunneling microscopes (STMs) have been published since the pioneering work of Binnig and Rohrer.2) Among them, Sonnenfeld and Hansma3) have demonstrated that STM could be used to study surfaces immersed in liquid solutions. The investigations of Hansma's group have opened up the field for in situ observations of surface structures at the solid/liquid interface.4) Bard et al.,5) Arvia et al.,6) and Itaya et al.7) were the first groups to apply the STM in the field of electrochemistry. Considerable attention has recently been focused on in situ observations.8) To apply STM to the particular interests of electrochemistry, suitable STM needs to be constructed. Much effort has been expended on ingenious designs of STM. However, the construction of our STM was accomplished at low cost without precision machining. Here, we present the design of a simple, rugged home-built STM for operation in both air and liquid. It has a suitable design for studying electrochemical processes in situ. The emphasis of this paper is on the STM itself.

Experimental

Tunnel Unit Design. The basic principle for construction of a tunneling unit is simplicity and rigidness. Figure 1 shows a schematic illustration of our tunneling unit. The unit comprises essentially two main parts. The lower part is a high-precision, vertical-translation Z-stage (Σ-303-(2), Sigmakohki Co., Ltd., Japan) and a four-legged piezoactuator (Fuji Ceramics, Co., Ltd., Japan) which is attached to a motionless part of the Z-stage. The upper part is a tripod scanner fixed inside a stainless-steel enclosure which is rigidly screwed to the stage. At the top of the unit, a current-sensitive preamplifier is installed so as to decrease electronic noise. Our unit has several advantages: (1) no precision machining is required, (2) unit fabrication can be accomplished at low cost, (3) exchanging both the tip and the sample is facile, (4) different areas can be observed by sliding the enclosure across the stage, and (5) for operation in liquid, the tip approaches the vertical direction from above the sample.

Tunneling Tip and Sample Setting. Commercially available Pt–Ir tips with a diameter 250 µm (Longreach Scientific Resources Co., Ltd., USA) were used. This type tip was slightly bent and mounted within a steatite tip holder by inserting it into a steel tube made from a hypodermic needle. A sample is attached with silver paint to

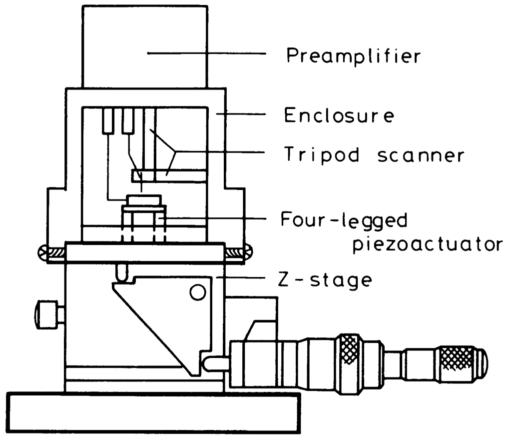

Fig. 1. A schematic cross-sectional view of the tunnel unit.

quartz glass which is glued with epoxy to the top of a four-legged piezoactuator.

Coarse and Fine Adjustment. The Z-stage micrometer with a 0.5 μm resolution provides a simple coarse adjustment mechanism that brings the tip into the operating range of the four-legged piezoactuator, while being observed by an optical microscope of 100 magnification. After coarse positioning the tip mechanically with the Z-stage micrometer from the sample, the Z-stage is clamped by a screw so as to prevent any backlash. The tunneling current is automatically detected by raising the sample under the control of the four-legged piezoactuator in connection with a personal computer (PC98VX4, NEC, Japan) while operating a feedback control of the Z-piezoactuator. The four-legged piezoactuator provides displacements from $-2.0\ \mu$m to $+2.0\ \mu$m by a stable dc voltage source (M107, Systron Donner, USA) with an accuracy of 0.002%. The feedback voltage applied to the Z-piezoactuator is in the range between +250 V to −250 V, determined by the feedback gain. The full voltage range of the feedback response of the Z-piezoactuator corresponds to a tip motion of 1.0 μm. The tunneling current is typically acquired within 10—15 minutes without crashing the tip into the sample; no additional precision mechanisms are employed.

3-Dimension Scanning. Prototype tripod piezoelectric actuators (three orthogonal piezoelectric rods) are being used for a 3-dimensional scanner. X, Y, and Z PZT-piezoelectric arms ((C-8), Fuji ceramics Co., Ltd., Japan) have the same characteristics with a resonance frequency of 140 kHz, an electrostatic capacity of 180 pF, and a curie temperature of 210 °C. The three (X, Y, Z) piezoelectric arms are attached to a steatite ($MgO\cdot SiO_2$) tip holder with epoxy. Calibration of the piezoelectric sensitivity is performed by the STM image of a highly oriented pyrolytic graphite (HOPG), as described later. Its sensitivity is 2.0 nm V^{-1}.

Vibration Isolation. Vibration isolation is provided by an air-suspension table with a resonance frequency of 1.8 and 2 Hz in the vertical and horizontal directions, respectively. The suitability of vibration isolation for our STM operation was checked with the cooperation of Meiritsuseiki Co., Ltd., Japan using an FFT analyser. A 15-kg circular weight is located on the air-suspension table; the tunneling unit sits on top of it. Neither a plate-stack type isolator nor a coil-spring type isolator was necessary, due to the high rigidness of the tunneling unit. The unit was installed in a shield box in order to avoid any acoustic or electronic noise.

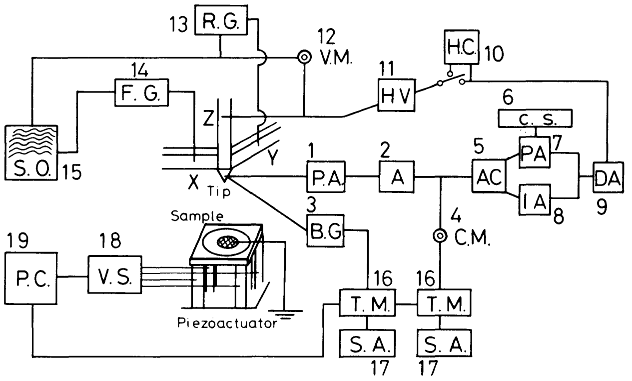

Fig. 2. A block diagram of the electronic setup of STM. 1: preamplifier, 2: amplifier, 3: tunnel bias generator, 4: tunneling current monitor, 5: absolute value circuit, 6: tunnel current setting, 7: proportional amplifier, 8: integrated amplifier, 9: differential amplifier, 10: feedback hold circuit, 11: high voltage source, 12: feedback voltage monitor, 13: ramp generator, 14: function generator, 15: storage oscilloscope, 16: transient memory, 17: signal averager, 18: stable DC voltage source, 19: personal computer.

Electronics. Figure 2 shows a block diagram of the electronic setup of STM and tunneling spectroscopy. Our electronic setup differs from the commonly used types mainly regarding three aspects: (1) the sample is a ground for all the electronics, (2) the tunneling bias is applied to the tip, and (3) the tunneling current is detected from the tip. The scanning rate in the X-direction can be changed from 0.1 Hz to 100 Hz by a function generator (FG-143, NF Electronic Instruments INC., Japan). A ramp generator was used for Y-scanning. Our STM is operated in an analog mode and images are monitored on a storage oscilloscope. It also has a computerized arrangement for tunneling spectroscopy, using a feedback hold mode at a point (Fig. 2). The tunneling current and bias are monitored by two transient memories (S210, Autonics, Japan); each is averaged by an averager (F601, Autonics, Japan). The digital data is transferred to a personal computer and can be calculated numerically. The surface density of states of a $TiO_2(110)$ single crystal obtained by tunneling spectroscopy using our STM setup is discussed elsewhere.[9]

Sample. As a standard sample for STM study,[10] a cleaved HOPG single crystal (Nippon Carbon, Co., Ltd., Japan) was used to examine the resolving power of our STM.

Results and Discussion

STM Images in Air. In Figs. 3(a) and (c) we display images of a HOPG in air at a frequency of 5 and 15 Hz in the X-direction, respectively. These images were taken with a constant current mode over an area of $1.4\times1.4\ nm^2$. The tunneling bias and current were set at +10 mV (tip positive) and 1 nA, respectively. The STM image (Fig. 3(a)) shows the atomic structure of graphite. It coincides with the surface crystallographic structure[11] in the same area depicted in Fig. 3(b). The geometrical configuration of the carbon atoms of graphite have three sites (Fig. 3(b)). At site A (•) the atoms in the two uppermost layers are atop. At site B (●) there is only an atom in the upper layer; at site C (○) the atom is only in the underneath layer.[10,11] The STM images in Figs. 3(a) and (c) show the atomic configuration of B site of graphite.[12] Therefore, our STM has a resolving power better than 0.25 nm in the lateral direction and 0.10 nm in the vertical direction, respectively. The STM has an atomic resolving power at a high X scanning rate (15 Hz) due to the rigidness of the tunneling unit (Fig. 3(c)). The time required for imaging was only 5 seconds. To observe the atomic corrugation, the rigid setting of the tunneling tip was a dominant factor. It is noteworthy that any dust attached to the tip of the needle or a sample can be stripped by flowing N_2 before imaging. We also in-

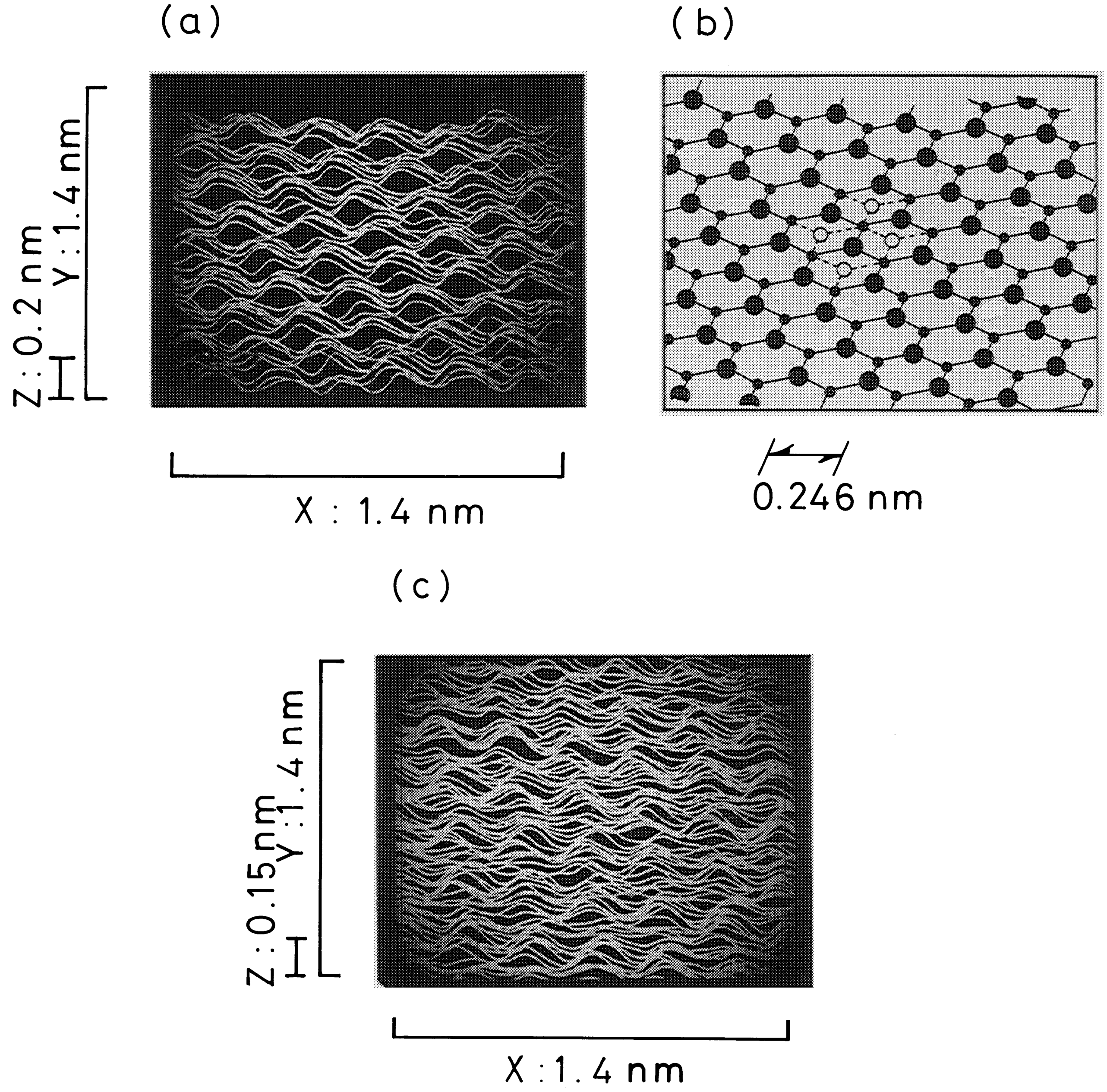

Fig. 3. Constant current images of a HOPG in air observed at a frequency of 5 Hz (a) and 15 Hz (c), respectively. Measuring conditions (1 nA, +10 mV (tip positive)). (b) is the surface crystallographic structure of graphite. A, B and C site are denoted •, ●, and ○, respectively.

vestigated the surface morphology of a polycrysalline (pc-) Ag (99.88%, The Japan Lamp Industies Co., Ltd.) in air. It is difficult to mechanically polish a soft metal like Ag with a SiO_2 powder because the SiO_2 abrasive sticks to the surface. In this work mechanical polishing was accomplished with wet lapping films containing alumina powder (9, 3, 1, 0.3 μm grain size) using Newdaiyalap (ML-451) with the cooperation of Maruto Co., Ltd., Japan. Figures 4(a) and (b) are STM images of pc-Ag in air at ambient pressure. Figure 4(b) was obtained by sliding the enclosure across the Z-stage after the observation of Fig. 4(a). A shallow surface was captured in the STM image (Fig. 4(a)); the surface was nearly flat over an area of 25×20 nm^2. At different regions of the same sample (Fig. 4(b)), a 2-nm step as well as a tableland structure can be seen. Under air and ambient pressure, our STM draws the same profile of the surface during about 20 minutes.

STM Images in Liquids. To test the operation

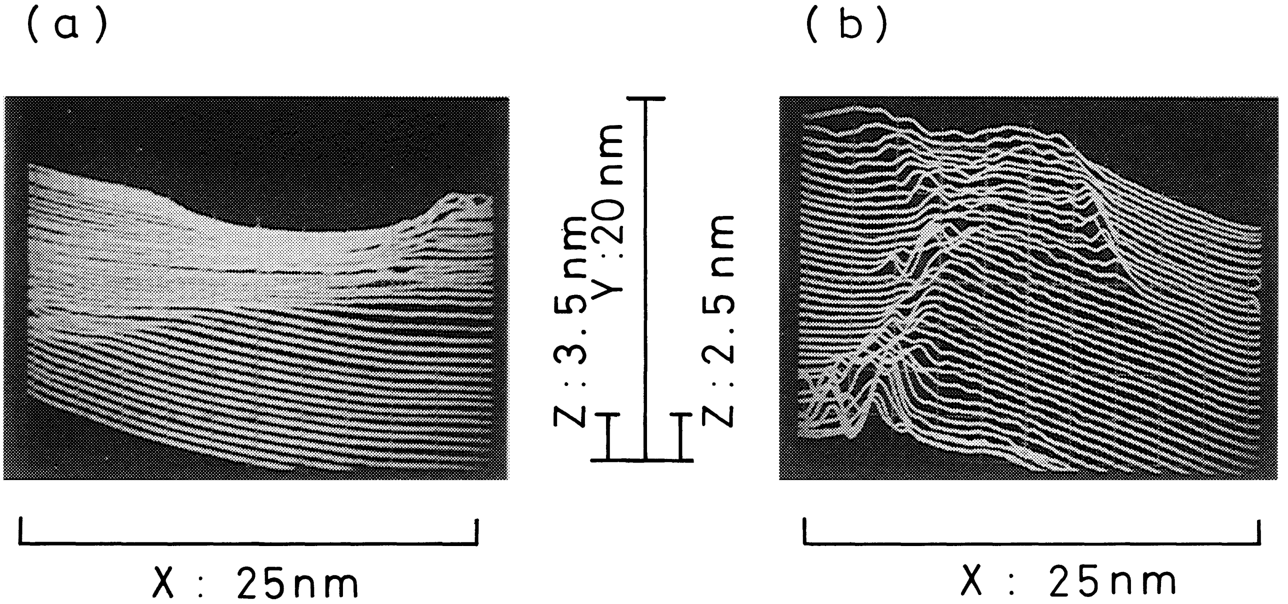

Fig. 4. STM images of a mechanically polished pc-Ag electrode in air. Measuring conditions 1 nA, +200 mV (tip positive), scan rate: 2 Hz). (a) and (b) were observed at different area.

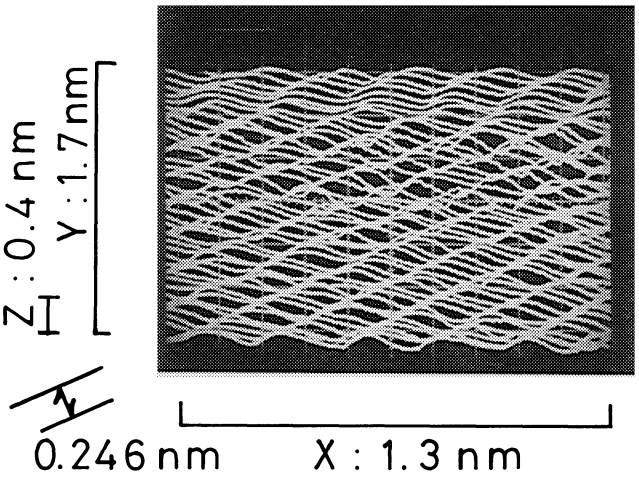

Fig. 5. STM image of a HOPG in ultra water. Measuring conditions (8 nA, +10 mV (tip positive), scan rate: 0.35 Hz).

in liquid we examined the HOPG sample in ultrapure water (UHQ, ELGA). Glass-coated Pt–Ir tips (Longreach Scientific Resources, USA) were used for measurements in liquid solutions. The exposed tip areas were determined by an electrochemical method[13] with an oxidation-limiting current of 1 m mol dm^{-3} of ferrocene in acetonitrile containing 0.2 m mol dm^{-3} TBAP. The exposed areas ranged typically between about 80 and 2 μm^2.[14] The glass-coated tip was rinsed in concd H_2SO_4 for 1 hour and ultra-pure water before use. The cleaved HOPG plate (5 mm×5 mm×1 mm thick) was attached to a Cu plate with silver paint. The exposed area of the Cu plate was covered with epoxy. A Teflon sheet (10 mm×10 mm×4 mm thick) with a hole of 8 mm diameter was attached above sample with epoxy. After the cell was carefully rinsed in 0.1 mol dm^{-3} H_2SO_4 and ultra-pure water, it was set on the four-logged piezoactuator with silver paint. Figure 5 shows the STM image (constant current mode) of the HOPG in the area of 1.3×1.7 nm^2 in ultrapure water. The tunneling current and bias were set at 8 nA and +10 mV (tip positive), respectively. The *X* scan rate (0.35 Hz) was reduced compared to the measuring condition under air in order to avoid any sway of water during tip scanning. The atomic corrugation of the HOPG was slightly distorted. The main reason of this distortion is the surface tension of water. The grass-coated tip was pulled by this force in the direction to the sample surface. A firm setting of the glass-coated tip is necessary in order to gain a good STM image under liquid with respect to the measurements under air. Following the above experiment, we examined a pc-Ag surface in 0.1 mol dm^{-3} KCl. An Ag electrode cell was made with Teflon sheet. The cell was carefully rinsed in acetone and distilled water. Any electrochemical current was less than 100 pA in 0.1 mol dm^{-3} KCl and was suppressed by a factor of 50 under the tunneling current (5 nA) and the tunnel bias (+200 mV: tip positive). Figures 6(a) and (b) are STM images of a pc-Ag in 0.1 mol dm^{-3} KCl. Figure 6(b) was observed 10 minutes after the observation of Fig. 6(a). About a 2.5 nm "mountain range" structure in the top left-side and a small "hill" in the bottom right-side were found in both STM images. The long-term

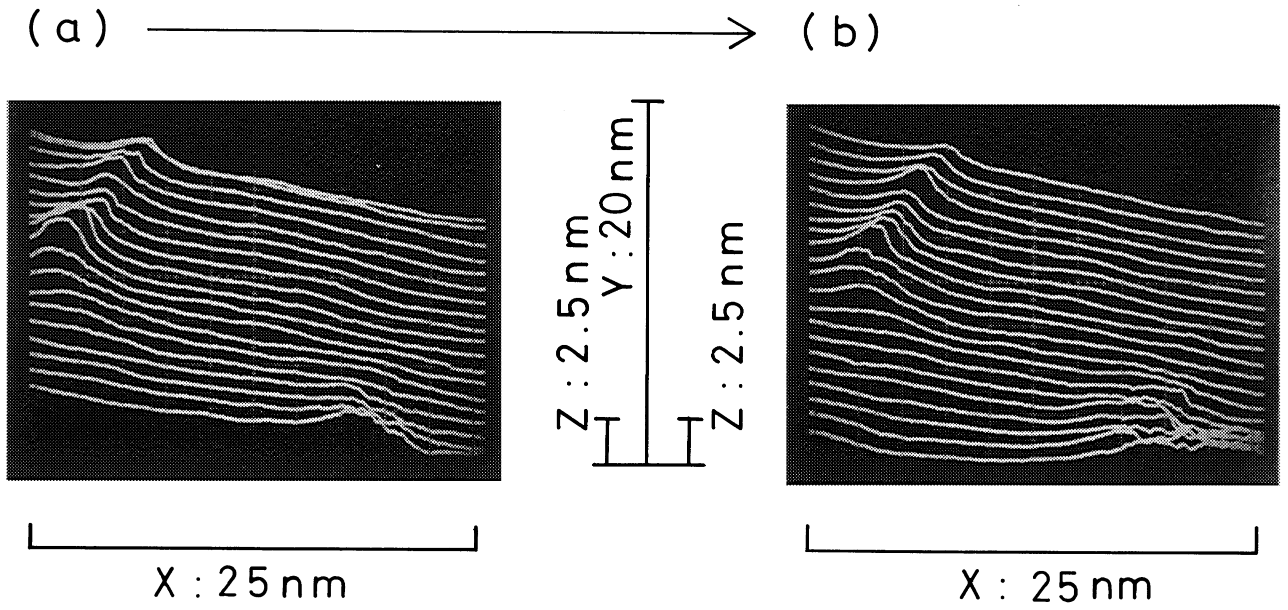

Fig. 6. STM images of a mechanically polished pc-Ag electrode in 0.1 mol dm^{-3} KCl. (b) was observed 10 minutes after the observation of (a). Measuring conditions (5 nA, +200 mV (tip positive), scan rate: 1 Hz).

stability of our STM in liquid is demonstrated as shown in Fig. 6. A lateral drift of less than ca. 0.13 nm min^{-1} in a salt water solution was estimated by subsequent imaging of the same area. For operation in liquid, it is necessary to rinse both the sample and the glass-coated tip carefully. In order to compare STM images observed in air and liquid, the following experiment was carried out. First, the surface of a pc-Ag electrode was imaged in air (Fig. 7(a)). After imaging in air, the tip was raised above the sample. A solution of 0.1 mol dm^{-3} KCl was carefully poured into the cell with Microsyringe (HAMILTON). The surface in the same area was then imaged in 0.1 mol dm^{-3} KCl (Fig. 7(b)). The X scan frequency of Figs. 7(a) and (b) were 2 and 1 Hz, respectively. The other measuring conditions were the same. A "mountain range" structure can be seen in both images (Figs. 7(a) and (b)). Both images draw the same surface profile, except for the offset. The appearance of a "hillock" in the top left-side in Fig. 7(b) was caused by drift when the liquid was poured into the cell. However, the "mountain range" in 0.1 mol dm^{-3} KCl (Fig. 7(b)) was higher than that in air (Fig. 7(a)) due to a current without a tunneling current. It seems that the more the exposed tip area is decreased, the greater does the resolving power of STM in the liquid solution increase. In addition, the large-area STM images of a pc-Ag have "island-like" structures.15,16) The characterization of an electrochemically modified (ORC treatment) pc-Ag electrode with or without pyridine molecules in connection with surface-enhanced Raman scattering (SERS) has been discussed elsewhere.15,16)

In conclusion, the rigid construction of an STM unit has demonstrated the atomic resolving power in both air and liquid solutions without additional precision mechanisms and careful vibration isolation. The STM is easy to handle and has a suitable design for in situ electrode surface characterization.

One part of this work was presented at the STM(II) meeting under Thin Film and Surface Physics of the Japan Society of Applied Physics, Dec., 12—14, 1988 at Atagawa, Japan.

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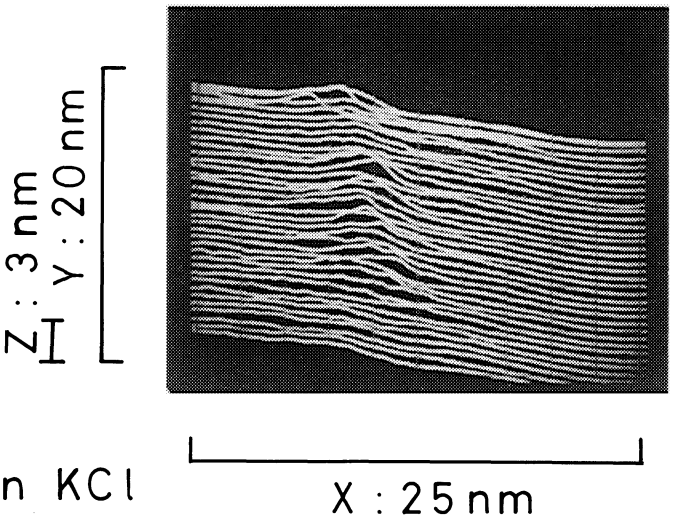
(a) in air



(b) in KCl

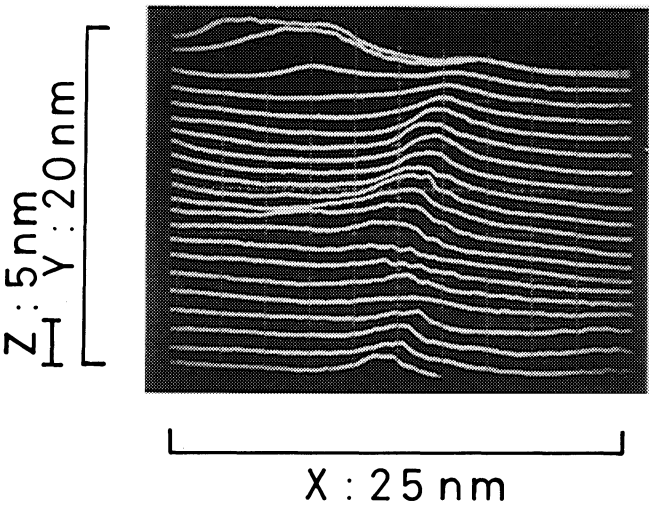


Fig. 7. STM images of a pc-Ag in air (a) and in 0.1 mol dm^{-3} KCl (b) in the same area. Measuring conditions (5 nA, +200 mV (tip positive), scan rate: 2 Hz (a), 1 Hz (b)).

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