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Application News

SPM-8100FM High Resolution Scanning Probe Microscope (Atomic Force Microscope)

Visualization of Current Distribution by ZXY Measurement: Current Measurement of Graphite Sample

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User Benefits

- Enables measurement of the current of sample surfaces with large and µm order irregularity.
- Possible to acquire current images of composite material samples with solid and liquid components.
- Application to electrode materials for secondary cells can be expected.

■ Introduction

Since conventional current measurements are conducted in the contact mode, measurement of samples with large surface irregularity and samples with high viscosity or a strong meniscus force was difficult due to the large external force in the reverse direction to the probe scanning direction. This report describes visualization of current distribution by ZXY measurement (Application News No. S47), which is relatively unaffected by these external forces. Application of this measurement technique to secondary cell electrodes with large surface irregularity due to carbon particles and additive materials is expected.

■ SPM-8100FM

The instrument used in this measurement technique is the Shimadzu SPM-8100FM high resolution scanning probe microscope (SPM (AFM)).

This instrument has the following three features.

① Adoption of the frequency modulation (FM) method.
② ZXY measurement for acquisition of volume data.
③ Simultaneous acquisition of signals such as magnetic force and electric force in ZXY measurement.

This report describes the establishment and application of ZXY-current measurement, which newly combines measurement of electric current with the measurements in ③.

■ Principle of ZXY Measurement

Fig. 1 shows a schematic illustration of ZXY measurement, which is based on force curve measurement. Force curve measurement is a type of measurement in which the force acting on the probe is measured while the distance (Z) between the probe and the sample is changed greatly in the vertical direction (approach and release). In the current measurement technique described here, the current that flows between the probe and the sample is detected simultaneously with the force curve measurement. A ZX scanning plane is prepared by continuous measurement in the X direction. Next, volume data containing 3-dimensional information for the Z, X, and Y directions is created by continuously measuring this ZX scanning plane in the Y direction. Arbitrary horizontal XY planes and ZX scanning planes can be constructed from the volume data acquired in this manner. For details, please refer to Application News No. S47.

Table 1 shows the measurement conditions used in this experiment.

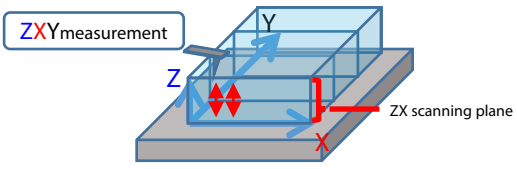

Fig. 1 Schematic Illustration of ZXY Measurement

Table 1 Measurement Conditions

Instruments	:	Scanning probe microscope SPM-8100FM
Scanner	:	Au vapor-deposited film Middle range scanner (XY: 30 µm, Z: 5 µm) Graphite sample Deep type scanner (XY: 55 µm, Z: 13 µm)
Observation mode	:	Contact mode
Current holder	:	Micro current holder Measurement range: ±10 nA
Scanning mode	:	ZXY
Pixel number	:	Au vapor-deposited film Z: 2048 X: 256 Y: 64 Graphite sample Z: 1024 X: 256 Y: 256

■ Au Vapor-Deposited Film on Glass Substrate

An Au vapor-deposited film on a glass substrate was prepared to simulate the Au electrodes generally used in batteries and electronic devices. A ZXY-current measurement was carried out in the boundary region between the glass and the Au film, and a height image and current image were constructed from the volume data, as shown in Fig. 2. A difference in level between the glass and the Au film can be recognized in the height image (a), and the same current as in the conventional method was detected on the Au film, as shown in the current image (b).

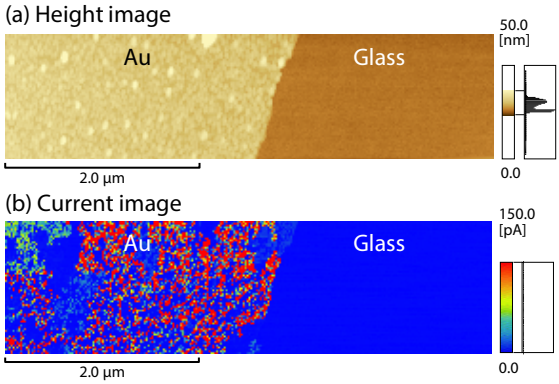

Fig. 2 Au Vapor-Deposited Film on Glass Substrate

■ Graphite Sample Simulating Battery Electrode

A cross section of a graphite sample simulating a battery electrode was prepared. This sample was a composite material prepared by heating and molding a graphite and a resin and finally impregnating the sample with oil. The scale-like structure of the graphite can be seen in the height image in Fig. 3 (a), and a current following the shape of the graphite has been detected in the current image in (b).

In the height image, spiky graphite with surface irregularity of about 1.5 µm can be observed. In operation in the conventional contact mode, it was difficult to measure the height and current if the surface irregularity of a sample exceeded approximately 1 µm, but satisfactory measurement was possible with the ZXY-current measurement method.

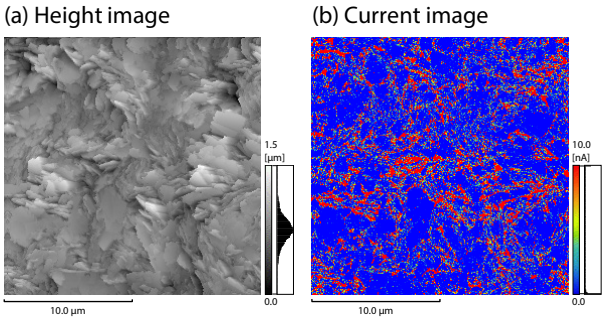

Fig. 3 Graphite Sample Simulating Battery Electrode

■ Image Construction of Graphite Sample

ZXY measurement of the graphite sample was carried out in a 5 µm area, and the images shown in Fig. 4 (a) to (h) were constructed.

The ZX images of the positions indicated by the yellow dotted lines in the height image and the current image are shown in (e) and (f), respectively. Since the ZX images are images in which the sample is seen from the cross-sectional direction, the upper part of the figures is the space above the sample, and the white dotted line in the lower part represents the graphite surface on the sample side. In (e), the height image at the position of the blue dotted line corresponds to (a) and the height image at the position of the white dotted line corresponds to (b).

The force curve at the positions of the downward-pointing black arrows in (e) and (f) of the ZX images is shown in (g), and the current-Z curve is shown in (h).

■ Discussion

(1) Fig. 4 Height image, current image, and adsorption force image

- In height image (a), the concave parts of the shape and the outline of the graphite are blurred.
- In height image (b), the shape of the graphite is clear.
- In the current image (c), a current was detected in the spaces between graphite particles and in the depression indicated by the arrows in height images (a) and (b).
- In the adsorption force image (d), large adsorption force was measured at the areas where a current was detected.

(2) Fig. 4 Height ZX image (e)

- Regions of attractive force existed in areas with a concave shape.
- If a liquid component exists on a sample surface, it is known that the probe will be drawn into the liquid (attractive force) by the meniscus force of that liquid.
- The constituent components of the sample included oil.

(3) Fig. 4 Current distribution

- In the current distribution in the current ZX image (f), a correlation with the distribution of the attractive force region in the height ZX image (e) was recognized.
- A correlation can be seen between the attractive force detection positions and the current detection positions in the force curve (g) and current-Z curve (h).
- The current distribution in the current image (c) and the distribution of the adsorption force image (d) show good agreement.

Based on these points, the generation of attractive force and detection of a current are considered to be caused by the oil content of the sample. Reconsidering the images in Fig. 4 (a) to (d), the shape of the oil film on the graphite surface can be observed in (a), and (b) is the result of observation of the shape of the graphite under the oil film. The fact that large current values and adsorption force were measured in the spaces between graphite particles and in depressions, as indicated by the arrows, can be explained by the presence of larger amounts of oil, which is a liquid, in those areas.

Although a current was not detected on the graphite surface, it can be inferred that this was because the electrical conductivity of the graphite was reduced by impregnation with an additive resin, and the current flowed in the oily parts, as oil has relatively small electrical resistance.

■ Conclusion

This experiment demonstrated the possibility of applying the ZXY-current measurement method established here to samples with large surface irregularity and measurement of the height image and current distribution not only of solids, but also that caused by liquid components. Application of this measurement technique to electrode materials for secondary cells is expected.

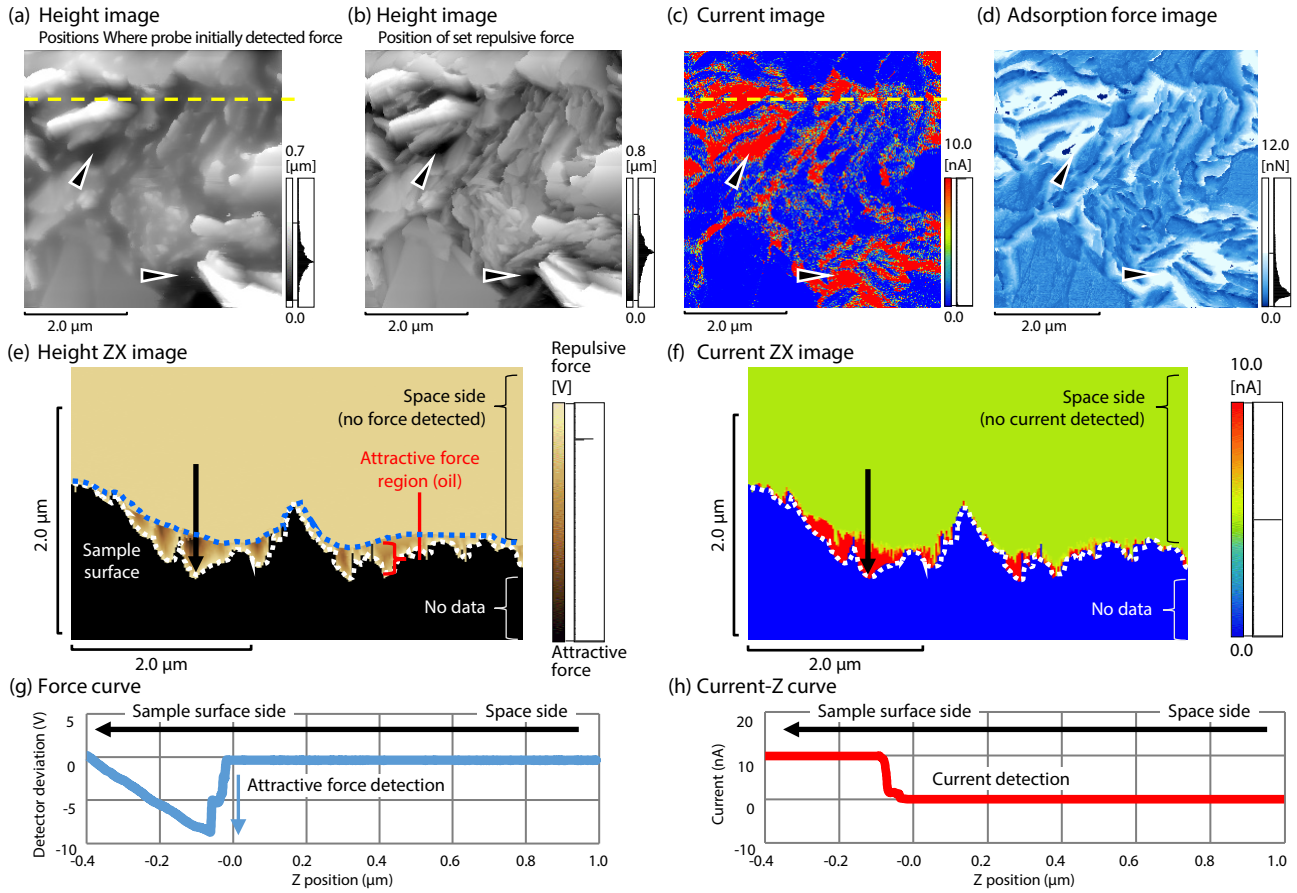

Fig. 4 Construction of Image of Graphite Sample

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