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Application News

No. S57

High Resolution Scanning Probe Microscope FM-AFM

Visualization of Distribution of Electrostatic Force in Electrolyte Clarifying Corrosion and Cell Reactions

A. Kogure, K. Yamasaki, T. Fujii

User Benefits

- Enables measurement and visualization of the distribution of electrostatic force in electrolytes, which had been impossible with conventional scanning probe microscopes.
- Can be used in the fields of corrosion protection and batteries, and is expected to be useful in new energy development, beginning with electric vehicle technology.

■ Introduction

Systems that utilize the electric potential of materials and substances, such as batteries, IC chips, and memory devices, support everyday life. The Kelvin probe force microscope (KPFM) method, which measures the potential of the sample surface, is widely used in scanning probe microscopes (SPM/AFM), but cannot be used in electrolytic solutions in which electrochemical reactions occur. As reported here, the authors established a new EFM-Phase-ZXY measurement method applying the electrostatic force microscope (EFM) and successfully visualized the distribution of electrostatic force of samples in electrolytes.

■ Electrostatic Force Distribution of Mica Substrate in Ultrapure Water and NaCl Aqueous Solution

Fig. 1 shows examples of visualization of the electrostatic force at the surface of a mica substrate. The surface of the white mica ($KAl_2SiAl_3O_{10}(OH)_2$) used in this experiment has a minus charge, and it is known that this minus charge is neutralized by ions in a solution. The charge distribution and density of this mica surface was visualized by EFM-Phase-ZX measurement.

Fig. 1 shows an EFM-ZX image of the sample from the cross-sectional direction, where the top part of the image is the space side (ultrapure water or NaCl solution), and the position of the black dotted line is the mica surface.

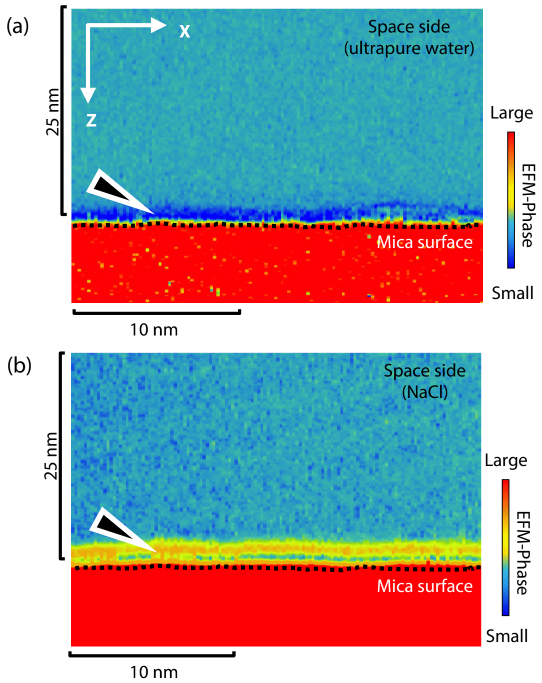

Fig. 1 EFM-ZX Image of Mica Substrate
(a) Ultrapure Water, (b) 1 mol/L NaCl (aq)

In the ultrapure water in Fig. 1(a), a blue layer (arrow) can be observed between the space and the sample surface. However, in the 1 mol/L NaCl aqueous solution in Fig. 1(b), the blue layer in (a) has disappeared, and the existence of two layers (orange and light blue; arrow) can be confirmed. This change in the layers represents the charge distribution of the mica surface, and it is thought that the image visualizes the electric double layer formed by neutralization of the mica surface by the Na^+ ion in the NaCl solution.

■ Electrostatic Force Distribution on Glass and Au Vapor Deposition Film in NaCl Aqueous Solution

Fig. 2 shows the results of EFM-Phase-ZXY measurements of a glass substrate and an Au vapor deposition film in a 50 mmol/L NaCl aqueous solution. Fig. 2(a) is the height image (XY image) obtained simultaneously with the ZXY measurement. Here, a difference in level between the glass and the Au film that was vapor-deposited on the glass surface can be observed. Fig. 2(b) is an EFM-ZX image of the position indicated by the white dotted line in this height image, and Figs. 2(c) and (d) are enlargements of the ZX images of the electrostatic force on the glass substrate and Au film surfaces. Although a yellow layer (arrow) has been obtained on the glass, this cannot be observed on the Au. Thus, the layer indicated by the arrow is considered to originate from the electrostatic charge of the glass.

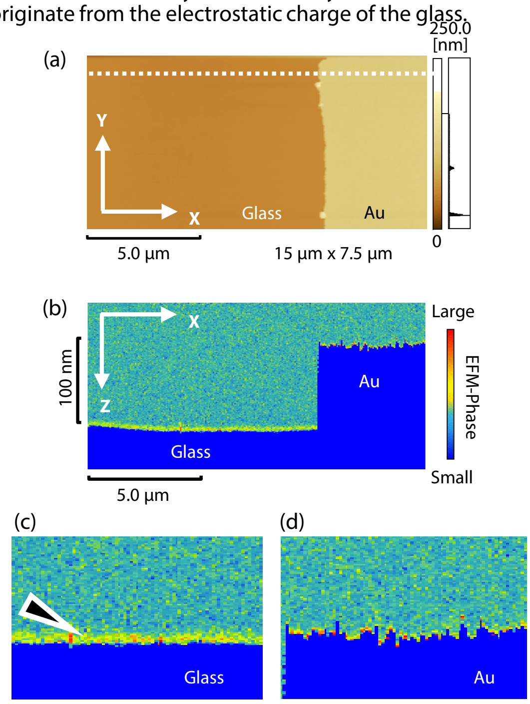

Fig. 2 Visualization of Electrostatic Force on Glass Substrate and Au Vapor Deposition Film
(a) Height image, (b) EFM-ZX Image,
(c) (d) Enlarged Views of EFM-ZX Image

■ Electrostatic Force Distribution on Copper Plate in NaCl Aqueous Solution

Fig. 3 shows the results of an EFM-Phase-ZXY measurement of a commercially-available copper plate in a 50 mmol/L NaCl aqueous solution, which simulates a sample system closer to corrosion and cell reactions. Fig. 3(a) is the height image of the copper plate, Fig. 3(b) is an EFM-XY image at the Z position separated from the copper plate surface by 25 nm to the space side, and Fig. 3(c) is an EFM-ZX image at the position indicated by the white dotted line shown in Fig. 3(b). In the height image, a hole that appears to be a corrosion pit can be observed, as shown by the arrow, and areas with different electrostatic forces from the surrounding portion originating from this hole were measured in Fig. 3(b). Moreover, similar electrostatic force distributions can also be confirmed in areas where no clear holes exist. Fig. 3(c) shows a condition in which the electrostatic force has an effect extending about 20 to 40 nm from the sample surface toward the space side of the sample. The electrostatic force distribution obtained in these images is thought to show the reaction field in corrosion or electrical cell reactions.

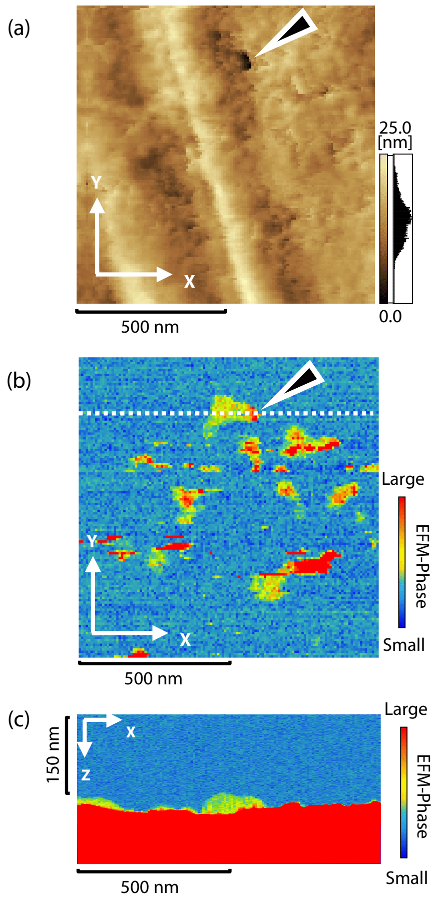

Fig. 3 Shape of Copper Plate and Visualization of Electrostatic Force
(a) Height image, (b) EFM-XY Image, (c) EFM-ZX Image

■ EFM-Phase-ZXY

The KPFM method is a well-known technique for measuring the electric potential of sample surfaces in SPM/AFM. However, this method could not be used in electrolytic solutions in which electrochemical reactions occur, as the principle of measurement requires impressing a direct-current (DC) potential difference between the probe and the sample.

Therefore, in this work, the authors established the new EFM-Phase-ZXY measurement method in order to visualize the electrostatic force distribution in electrolytic solutions. Applying the principle of EFM in SPM/AFM, in the new method, the phase delay ("Phase") of the cantilever caused by electrostatic force is detected. Table 1 shows a comparison of the features of KPFM and EFM-Phase measurement methods. As an advantage of EFM-Phase measurement, the environments in which measurement is possible are not limited, and three-dimensional measurement in the ZXY directions is possible. However, it should be noted that, unlike KPFM, the obtained values are a relative comparison within the image concerned. Details of the ZXY measurement method and visualization of the spatial distribution obtained thereby may be found in Application News No. S47 and No. S49.

Table 1 Features of KPFM and EFM-Phase Measurement Methods

	Applicable environments	Measured value	Dimensions
KPFM	Vacuum Atmosphere	Surface potential	XY
EFM-Phase	Vacuum Atmosphere Nonpolar solvents Polar solvents Electrolytes	Phase delay caused by electrostatic force (EFM-Phase) Relative comparison	ZXY

Patent pending: Patent application 2020-171569, in Japan

■ System Configuration

Fig. 4 shows the system configuration and connection diagram of the measurements in this article. A high performance wideband digital lock-in amplifier (LI5660, NF Corporation) is connected externally to a Shimadzu SPM-8100FM high resolution scanning probe microscope.

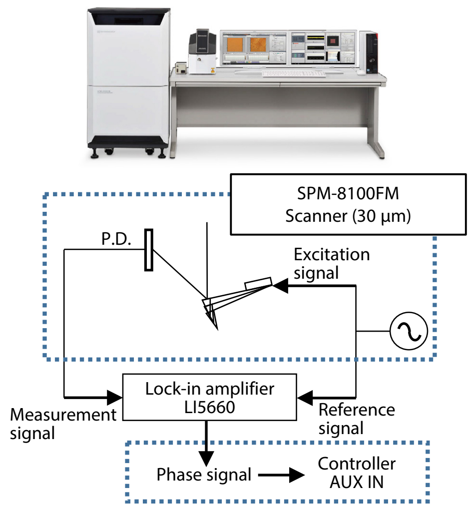

Fig. 4 Connection Diagram of SPM-8100FM and Lock-In Amplifier
(Portions Enclosed in Dotted Lines: Standard Configuration of SPM-8100FM)

■ Conclusion

The EFM-Phase-ZXY measurement method was established as a technique that enables measurement and visualization of the distribution of electrostatic force, even in polar solvents. This measurement method can be used in the corrosion protection and battery fields, and is expected to be useful in new energy development, beginning with electric vehicle technology.

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First Edition: Feb. 2021