As decreasing device size, probing of nanoscale surface properties becomes more significant. In particular, nanoscale probing of surface potential has paid much attention for understanding various surface phenomena. In this article, we review different atomic force microscopy techniques, including electrostatic force microscopy and Kelvin probe force microscopy, for measuring surface potential at the nanoscale. The review could provide fundamental information on the probing method of surface potential using atomic force microscopy.

**Key Words:** Atomic force microscopy, Electrostatic force microscopy, Kelvin probe force microscopy, Surface potential, Surface charge

**INTRODUCTION**

Surface electrical properties are being interest for many different applications including solar cell (Coffey & Ginger, 2006; Yoo et al., 2014) and information technologies (Vasudevan et al., 2013). Recently, as decreasing device size, nanoscale surface properties become more significant. In particular, since surface potential is directly relevant to work function of materials and/or surface charge, nanoscale probing of surface potential has paid much attention for understanding various surface phenomena such as photovoltaic phenomena, screening behavior of ferroelectric surfaces, and work function and surface states of semiconducting materials (Takahashi et al., 2000; Kalinin & Bonnell, 2001; 2004; Hong et al., 2009).

The nanoscale probing of surface potential is still challengeable. In fact, atomic force microscopy (AFM) is a well know technique which allows exploring nanoscale material properties. Among various AFM modes, electrostatic force microscopy (EFM) and Kelvin probe force microscopy (KPFM) allow us probing surface potential in many different types of materials including metal, ceramic, and organic materials at the nanoscale (Ellison et al., 2011). We review operational mechanisms of EFM and KPFM which allow exploring surface potential at the nanoscale. Also, we discuss advantages and disadvantages of each technique and show some of experimental examples of these AFM modes.

**ELECTROSTATIC FORCE MICROSCOPY**

EFM is based on the non-contact AFM mode for detecting surface electrostatic interaction between a sample and an AFM tip. Fig. 1A depicts a dual-pass scanning method which is used for the EFM operation. Even though a single-pass scan can be used for operating EFM, the dual-pass scan is a more common and accurate approach (Girard, 2001). First, when a conducting tip is close to the sample, surface topography can be obtained since van der Waals force is dominant. Second, the tip scans the same trajectory of the first scan with lifting the tip. In the latter, since the tip is moved away from the sample surface, van der Waals force drastically decreases and an electrostatic force becomes dominant (Gady et al., 1996). Thus, the second scan provides topography free electrostatic information.

Electrostatic force, acting on tip and sample, makes shifting of resonance frequency of the cantilever as depicted in Fig. 1B. Since the cantilever is still driven at the resonance frequency, amplitude and phase can be changed by the electrostatic force.
Probing of Surface Potential Using Atomic Force Microscopy

101

contribution to the resonance frequency. For instance, when positive bias is applied to the tip and, accordingly, positive charges exist on the sample surface, it leads repulsive force between the tip and the sample surface. This situation makes reducing of both oscillation amplitude and phase (Fig. 1B and C).

Electrostatic force in EFM can be described as (Sadewasser, 2012):

$$F_{es} = \frac{dE_{es}}{dz} = \frac{1}{2} \frac{dC}{dz} V^2$$  \hspace{1cm} (1)

Since ac voltages is applied between the tip and the sample, equation (1) can be rewritten as:

$$F_{ac} = -\frac{1}{2} \frac{dC}{dz} \left(V_{cpd} + V_a \sin \omega t\right)$$  \hspace{1cm} (2)

Fig. 2 shows the schematic of EFM setup. Through the ac deflection of cantilever, we can obtain images of surface topography and electrostatic phase and amplitude, respectively.

The benefit of the EFM is no feedback control for the electrostatic signal. Thus, the measurement speed can be relatively fast. However, this technique is a passive method of recording. Hence, electrostatic signal cannot show quantitative contact potential difference or surface potential which is only expressed as an arbitrary unit. To obtain quantitative electrostatic information, an additional voltage control is necessary.

**KELVIN PROBE FORCE MICROSCOPY**

To overcome the previous issue on the EFM, Kelvin method has been suggested for the application of AFM. KPFM combines of the non-contact AFM and Kelvin method which is a vibrating capacitor method of non-contact mode. Kelvin method was developed in 1898 by Lord Kelvin (Kelvin, 1898). It is a measurement method of surface potential using two parallel materials. If there are different two materials which are composed of capacitor and electrically connected together, electrons will flow from the material with low work function, here the tip, to the material with high work function, here the sample (Fig. 3B). It generates opposite charges on the capacitors and a contact potential difference between the two materials. External dc voltage $V_{dc}$ can be applied to nullify this potential difference. When $V_{dc}$ is the same with the contact potential difference $V_{cpd}$, electrostatic contribution becomes zero (Fig. 3C). Then, the contact potential difference $V_{cpd}$ or surface potential can be defined by the $V_{dc}$ (Palermo et al., 2006; Wu & Shannon, 2006). Since the work function of commercially available tips is well known, the work function of the sample can be readily obtained from the Kelvin method. Thus, quantitative electrostatic information can be obtained from KPFM. Indeed, the surface (Takahashi et al., 2000) Fermi levels on GaAs substrates were reported from the evaluation of the KPFM data.

For the actual operation of KPFM, contact potential difference or surface potential can be obtained from the above background with two different scanning modes, i.e., single- and dual-pass scans (Jacobs et al., 1999; Li et al., 2012). Although a typical scanning mode even for the KPFM is single-pass scan, the KPFM was first invented as a single-pass scan mode in which two feedback systems are used (Nonnenmacher et al., 1991). One of them is used to

![Fig. 1. (A) Schematic of a dual-pass scanning technique. (B) Attractive and repulsive force on cantilever affects amplitude and phase of the cantilever vibration.](image)

![Fig. 2. Schematic of electrostatic force microscopy (EFM).](image)
measure the contact potential difference or surface potential, and another is used to measure the surface topography. Both information can be simultaneously obtained using a single-pass KPFM. However, topographical errors can be caused by electrostatic forces, the contact potential difference or surface potential can be less reliable. Thus, as similar to the EFM, the dual-pass scan is more commonly used even for the KPFM. In KPFM, dc voltage $V_{dc}$ is applied to compensate the contact potential difference between the AFM tip and the sample (Fig. 4). The fundamentals of KPFM is similar to that of EFM shown in Fig. 1. The only difference is on the dc voltage feedback. Since dc and ac voltages are applied between the tip and the sample for the operation of the KPFM, the electrostatic force can be written as:

$$ F_{ac} = \frac{\partial C}{\partial z} (V_{ac} - V_{CPD}) \sin(\omega t) $$

From equation (3), first harmonic component of the electrostatic force, $F_{ac}$, can be written as:

$$ F_{ac} = \frac{\partial C}{\partial z} (V_{ac} - V_{CPD}) \sin(\omega t) $$

If dc voltage $V_{dc}$ equals to contact potential difference $V_{CPD}$, the first harmonic electrostatic force can be nullified as shown in Fig. 3C. In such a case, contact potential difference or surface potential can be quantitatively obtained from dc voltage $V_{dc}$. In order to show some of experimental examples of EFM and KPFM measurements, each measurement was carried out in the ferroelectric Pb(Zr0.35Ti0.65)O3 (PZT) film. Since the ferroelectric film shows two different states of surface charges, it can be a good model system for demonstrating EFM and KPFM. In order to show some of experimental examples of EFM and KPFM measurements, each measurement was carried out in the ferroelectric Pb(Zr0.35Ti0.65)O3 (PZT) film. Since the ferroelectric film shows two different states of surface charges, it can be a good model system for demonstrating EFM and KPFM.

Fig. 3 shows EFM and KPFM images of the PZT thin film. A positive voltage of +13 V is applied to the Pt/Cr coated conductive tip for switching the film as downwards, then a negative voltage of −13 V is applied to the conductive tip for generating opposite polarization states inside the previously poled area. Finally, these areas were scanned by EFM and KPFM modes. When bias voltage, which is larger than coercive voltage of the ferroelectric films, is applied to the ferroelectric surface, the applied bias voltage can switch ferroelectric polarization states and, as a result, surface charges can be determined by the polarization states. However, the measured surface potential is dominantly originated from the injected charge during the switching (Kim et al., 2010). Since KPFM image depicts quantitative value of surface potential, these charge behavior can be quantitatively visualized by KPFM. As expected, positive (negative) biased region shows higher absolute value of surface potential which is originated from positive (negative) injected charges (Fig.

![Fig. 3. Schematic diagrams of the electronic band structure when we assume that two materials are tip and sample, respectively, and work function of tip is larger than that of sample. (A) Two different materials of tip and samples without contact between tip and sample. $\phi_{tip}$ and $\phi_{sample}$ represent work functions of tip and sample, respectively. (B) When two materials of tip and sample are electrically contacted, electrons flow from tip to sample until Fermi levels of both sides become the same. (C) When electric field between two materials shown in Fig. 3B is eliminated by an application of dc voltage $V_{dc}$, the dc voltage $V_{dc}$ becomes the same with contact potential difference, $V_{CPD}$, between two materials.](image1)

![Fig. 4. Schematic of Kelvin probe force microscopy (KPFM). While the black colored components are for both electrostatic force microscopy and KPFM, the blue colored components are for only for KPFM.](image2)
Probing of Surface Potential Using Atomic Force Microscopy

Furthermore, it shows that negative biased region shows higher magnitude of surface potential. Even though EFM cannot provide quantitative value of electrostatic response, it still can provide electrostatic information on the sample surface. In the EFM images of Fig. 5B and C, it can be found that obtained behavior on the EFM amplitude and phase images are consistent with KPFM image.

OPEN-LOOP KELVIN PROBE FORCE MICROSCOPY

KPFM can be operated in open-loop (OL) feedback system as well. Fig. 6 shows schematic of OL-KPFM. This technique takes a dual lock-in amplifier for removing voltage feedback control. By comparison of OL technique with conventional KPFM, there are several advantages in the OL techniques (Collins et al., 2013). First, OL method is suitable for the measurement of voltage sensitive materials like semiconductors, insulators and organic and inorganic photovoltaic materials. Second, since instability of voltage-feedback system in the conventional KPFM makes its gain low, it causes a long time measurement. However, the OL-KPFM takes an additional lock-in amplifier for measuring harmonic component (Takeuchi et al., 2007).

In a close-loop KPFM, first derivative of \( \Delta f(V_{dc}) \), which is detected by a first lock-in amplifier, is written as:

\[
\Delta f'(V_{dc}) = \frac{d^2 C}{dz^2}(V_{dc} - V_{cpd})
\]

However, this first derivative force cannot show quantitative surface potential measurements. The signal of second harmonic gives second-order derivative of frequency shift, \( \Delta f''(V_{dc}) \), which can be written as:

\[
\Delta f''(V_{dc}) \propto \frac{d^2 C}{dz^2} = \text{const.}
\]

If \( \Delta f' \) and \( \Delta f'' \) are measured at a certain bias voltage, \( V_{cpd} \) can be written:

\[
V_{cpd} = V_{dc} - \Delta f'(V_{dc})/\Delta f''(V_{dc})
\]

Since this technique does not need bias-voltage feedback, it

Fig. 5. Topographic (A), electrostatic force microscopy (EFM) amplitude (B), EFM phase (C), and surface potential (D), measured by Kelvin probe force microscopy, images in the Pb(Zr0.35Ti0.65)O3 thin film. All the images were taken in the same position. The white (blue) area in Fig. 5A represents poled area by +13 V (−13 V). Scale bar=2 \( \mu m \).

Fig. 6. Schematic of open-loop Kelvin probe force microscopy. To obtain contact potential, numerical calculation is performed instead of bias-voltage feedback.
ensures stability of surface potential images.

**CONCLUSIONS**

In conclusion, here we review AFM techniques for probing surface potential at the nanoscale. EFM allows exploring electrostatic information, however it can be limited for measuring quantitative electrostatic interaction. To achieve quantitative electrostatic interaction, i.e., surface potential, KPFM has been suggested based on Kelvin method. We also show how the obtained results by EFM and KPFM can be interpreted. From this review, we could provide fundamental information on the probing method of surface potential using AFM. Furthermore, we believe that AFM would be a greatly useful and a most suitable technique for exploring electrostatic information at the nanoscale.

**CONFLICT OF INTEREST**

No potential conflict of interest relevant to this article was reported.

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