Chapter 3

Kelvin Probe Force Microscopy

3.1 Fundamentals of KPFM

(1) Work function

In solid-state physics, the work-function[1] is the minimum energy (usually measured in electronvolts) needed to remove an electron from a solid to a point immediately outside the solid surface (or the energy needed to move an electron from the Fermi level into vacuum). Here "immediately" means that the final electron position is far from the surface on the atomic scale but still close to the solid on the macroscopic scale. The work function is a characteristic property for any solid phase of a substance with a conduction band (whether empty or partly filled). For a metal, the Fermi level is inside the conduction band, indicating that the band is partly filled. For an insulator, the Fermi level lies within the band gap, indicating an empty conduction band; in this case, the minimum energy to remove an electron is about the sum of half the band gap and the electron affinity, Figure 3-1 give a band diagram of an insulator.

Φ is measured by CPD, V_{AB} exists between the surfaces of two solids A and B of work functions Φ_A and Φ_B, when connected electrically, since

$$\Phi_B - \Phi_A = eV_{AB}. \tag{3.1}$$

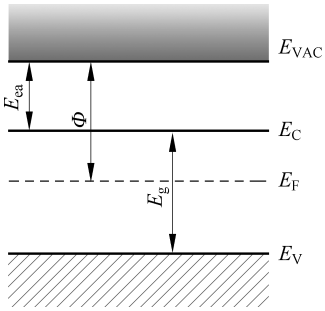

Figure 3-1 Simple band diagram with denoted vacuum energy E_{VAC}, conduction band E_C, Fermi energy E_F, valence band E_V, electron affinity E_{ea}, work function Φ and band gap E_g

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For the two solids at same temperature, the method involves a prior knowledge of the work function of one of the solids if that of the other is to be measured absolutely.

(2) Contact potential difference

Contact potential difference (CPD) is a method of measuring work function changes of a surface. The technique usually involves capacitor plates which are caused to vibrate as the voltage potential on the plates is measured. One capacitor plate is used as a reference which should remain inert to adsorption electrons. The other plate will be altered in some way, such as by the adsorption of electrons on the plate.

KPFM measures CPD between a conducting AFM tip and a sample. The CPD (V_{CPD}) between the tip and the sample is defined as

$$V_{CPD} = \frac{\Phi_{tip} - \Phi_{sample}}{-e}, \tag{3.2}$$

where Φ_{sample} and Φ_{tip} are the work functions of the sample and the tip, and e is electronic charge. When an AFM tip is brought close to the sample surface, an electrical force is generated between the tip and the sample surface, due to the differences in their Fermi energy levels. Figure 3-3 shows the energy level diagram of the tip and the sample surface when Φ_{sample} and Φ_{tip} differ. Figure 3-2 (a) depicts the energy levels of the tip and the sample surface when separated by a

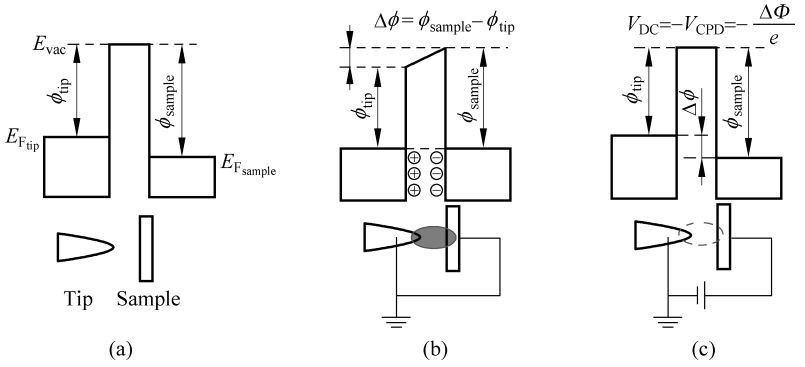

Figure 3-2 Electronic energy levels of the sample and AFM tip for three cases

(a) tip and sample are separated by distance d with no electrical contact; (b) tip and sample are in electrical contact; (c) external bias (V_{DC}) is applied between the tip and the sample to nullify the CPD and, therefore, the tip-sample electrical force. E_{vac} is the vacuum energy level. $E_{Fsample}$ and E_{Ftip} are Fermi energy levels of the sample and the tip respectively

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distance and not electrically connected (note that, the vacuum levels are aligned but Fermi energy levels are different). Equilibrium requires Fermi levels to line-up at steady state, if the tip and the sample surface are close enough for electron tunneling. Upon electrical contact, the Fermi levels will align through electron current flow, and the system will reach an equilibrium state, as in Figure 3-3 (b). The tip and the sample surface will be charged, and an apparent V_{CPD} will be formed (note, the Fermi energy levels are aligned but vacuum energy levels are no longer the same, and a V_{CPD} between the tip and the sample is formed). An electrical force acts on the contact area, due to the V_{CPD}. As shown in Figure 3-2 (c), this force can be nullified, if an applied external bias (V_{DC}) has the same magnitude as the V_{CPD} with opposite direction, and the applied voltage eliminates the surface charge in the contact area. The amount of applied external bias (V_{DC}) that nullifies the electrical force due to the V_{CPD} is equal to the work function difference between the tip and the sample; therefore, the work function of the sample can be calculated when the tip work function is known[2].

(3) KPFM methods

By applying an AC voltage (V_{AC}) plus a DC voltage (V_{DC}) to the AFM tip, KPFM measures the work function of the sample. V_{AC} generates oscillating electrical forces between the AFM tip and the sample surface, and V_{DC} nullifies the oscillating electrical forces that originated from CPD between the tip and the sample surface. The electrostatic force (F_{es}) between AFM tip and the sample is given by

$$F_{es}(z) = -\frac{1}{2}\Delta V^2 \frac{dC(z)}{dz}, \tag{3.3}$$

where z is the direction normal to sample surface, V is the potential difference between V_{CPD} and the voltage applied to the AFM tip, and dC/dz is the gradient of capacitance between the tip and the sample surface. When $V_{DC} + V_{AC}\sin(\omega t)$ is applied to AFM tip, the voltage difference will be

$$\Delta V = V_{tip} \pm V_{CPD} = (V_{DC} \pm V_{CPD}) + V_{AC}\sin(\omega t) \tag{3.4}$$

Note that the $\pm$ sign depends on whether the bias (V_{DC}) is applied to sample (+) or tip (−)[3]. Substituting Equation (3.4) in Equation (3.3) gives the expression of the electrostatic force applied to the AFM tip:

$$F_{es}(z,t) = -\frac{1}{2}\frac{\partial C(z)}{\partial z}[(V_{DC} \pm V_{CPD}) + V_{AC}\sin(\omega t)]^2 \tag{3.5}$$

This equation can be divided into three parts:

$$F_{DC} = \frac{\partial C(z)}{\partial z}\left[\frac{1}{2}(V_{DC} \mp V_{CPD})^2\right], \tag{3.6}$$

$$F_{\omega} = -\frac{\partial C(z)}{\partial z}(V_{DC} \pm V_{CPD})V_{AC}\sin(\omega t), \tag{3.7}$$

$$F_{2\omega} = -\frac{\partial C(z)}{\partial z}\frac{1}{4}V_{AC}^2[\cos(2\omega t) - 1]. \tag{3.8}$$

Here, F_{DC} (Equation(3.6)) results in a static deflection of the AFM tip. F_{ω} with frequency ω (Equation(3.7)) is used to measure the V_{CPD}, which shows a parabolic form as a function of V_{DC}, just as shown in Figure 3-3 (a), and $F_{2\omega}$ (Equation (3.8)) can be used for capacitance microscopy[4]. When electrostatic forces are applied to the tip by V_{AC} with V_{DC}, additional

oscillating components (due to the electrical force) will be superimposed to the mechanical oscillation of the AFM tip. A lock-in amplifier is employed to measure the V_{CPD}, by extracting the electrical force component with frequency $\omega(F_\omega)$, which is a function of V_{CPD} and V_{AC}. The output signal of the lock-in amplifier is directly proportional to the difference between V_{CPD} and V_{DC}, just as shown in Figure 3-3 (b). The V_{CPD} value can be measured by applying V_{DC} to the AFM tip, such that the output signal of the lock-in amplifier is nullified and F_ω equals zero. Subsequently, the value of V_{DC} is acquired for each point on the sample surface, composing a map of the work function or surface potential of the whole sample surface area.

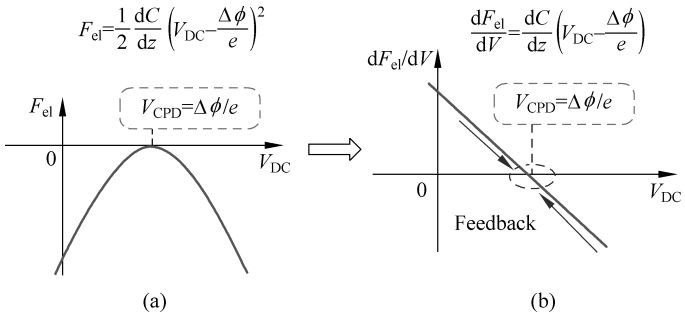

Figure 3-3 Working principle of KPFM

(a) shows the electrostatic force in KPFM is a parabolic form as a function of V_{DC}; (b) shows that output signal of the lock-in amplifier is directly proportional to the difference between V_{CPD} and V_{DC}

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3.2 Amplitude Modulation and Frequency Modulation Modes in KPFM

As previously described, AFM can detect atomic forces by AM or FM mode. The electrostatic force F_ω can also be detected either by AM or FM mode in KPFM. In AM mode, KPFM measures F_ω directly from the amplitude of cantilever oscillation at ω_2 induced by V_{CPD} and V_{AC}. V_{DC} is applied to AFM tip to nullify the measured amplitude, thereby measuring V_{CPD}. In FM mode, F_ω is detected by the frequency shift at ω, and V_{DC} is applied to AFM tip to

nullify the frequency shift, thereby measuring V_{CPD}[5].

KPFM measures the topography concurrently with V_{cpd}, using an AFM tip. A method to separate the topographical signal from the V_{cpd} measurement is required. In KPFM experimental setup, the V_{ac} is usually modulated at a frequency higher than the bandwidth of topography feedback system to prevent cross-talk between the topography and the CPD measurement. In AM-KPFM, the topography is measured by the oscillation at the first resonance frequency of AFM tip, and V_{cpd} is measured by the amplitude of oscillation at the second resonance frequency of AFM tip. A mechanically vibrated cantilever generally has several resonance peaks in the oscillation amplitude-frequency spectrum. The second resonance frequency normally has a broader peak than the first. The amplitude of the second resonance frequency peak is usually less than one-third of the first, and the frequency of the second resonance peak is typically 6.27 times higher than the first[6]. V_{ac} is tuned to the second resonance frequency to excite the AFM tip by electrical force, while the first resonance frequency is assigned for the tip height control. Using these techniques, topography and V_{cpd} signal can be separated. Conversely, in FM-KPFM, the AFM tip is mechanically excited at the first resonance frequency. V_{ac} induces a modulation of electrostatic force, which is detected by superimposed oscillation at the frequency variation of mechanical oscillation of AFM tip, leading to the separation of the topography and the V_{cpd} signal. Atomic resolutions on various surfaces have been obtained up to now, here, in Figure 3-4, we give the simultaneous measurement of topographic and LCPD images on Ge(001) surface on atomic scale by AM- and FM-KPFMs, we also give the line profiles of topographies and LCPDs in both methods, which show different patterns and vales in topography and LCPD images using the two methods.

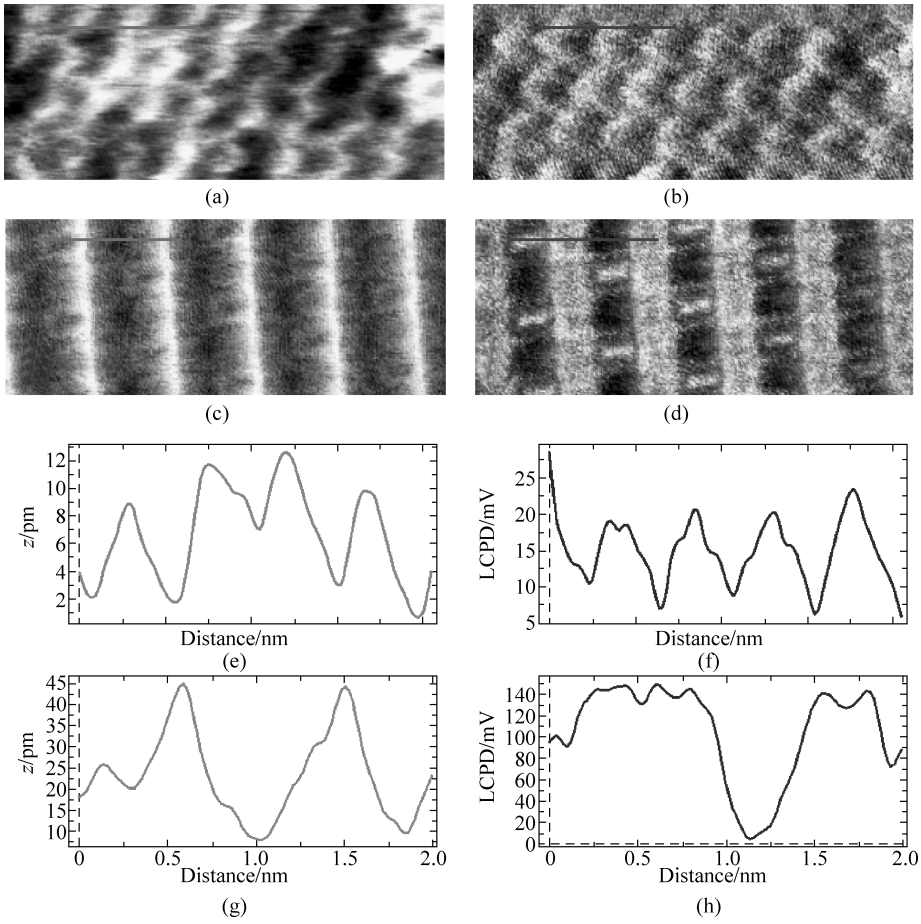

Figure 3-4 Atomic resolution of topographic and potential images on Ge(001) surface in (a)and (b), and topographic and potential line profiles in (e) and (f) in FM-KPFM respectively; topographic and potential images on Ge(001) surface in (c)and (d), topographic and potential line profiles in (g) and (h) in AM-KPFM

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3.3 Minimum Detectable Contact Potential Difference in AM- and FM-KPFMs

In NC-AFM, the frequency shift (Δf) of the cantilever vibration and the energy dissipation results in an amplitude variation (ΔA) of cantilever

oscillation, given by $\Delta f = -f_0 F_c/(2kA)$, $\Delta A = -QF_d/k$. Here f_0, k, Q and A are the resonance frequency, the mode spring constant, the quality factor and the amplitude of cantilever respectively. F_c and F_d are the tip-sample conservative interactions and dissipative interactions respectively.

Therefore, the minimum detectable force for conservative interaction and that for dissipative interaction are given by $\delta F_c = -2kA\delta f/f_0$ and $\delta F_d = k\delta f/Q$. Here, δf and δA are the minimum detectable frequency and amplitude respectively.

For typical NC-AFM measurements in UHV, the deflection sensor noise (n_{ds}) is much larger than the thermal noise $\left(n_{th} = \sqrt{\frac{k_B T f_0}{2\pi k Q f_m^2}}\right)$ of the cantilever. Therefore, δf and δA are given by $\delta f = \sqrt{12}\, f_m n_{ds} \sqrt{B}/\pi A$, $\delta A = n_{ds}\sqrt{B}$. Here B and f_m are the bandwidth of lock-in amplifier and modulation frequency respectively. Therefore, δF_c and δF_d are obtained by[7-11]

$$\delta F_c = \frac{4\sqrt{3}\, k f_m}{\pi f_1} n_{ds} \sqrt{B}, \tag{3.9}$$

$$\delta F_d = \frac{k}{Q} n_{ds} \sqrt{B}, \tag{3.10}$$

the conservative electrostatic force (F_{esc}) is given by

$$F_{esc} = \frac{\pi \varepsilon_0 RA}{z_{t0}^2} V_{ts}^2, \tag{3.11}$$

while the dissipative electrostatic force (F_{esc}) is zero.

The ω_m component of the frequency shift (Δf_m) induced by the electrostatic interaction is given by

$$\Delta f_m = \frac{\pi \varepsilon_0 R f_0 V_{AC}}{k z_{t0}^2} V_{AC} V_{DC}. \tag{3.12}$$

From equation $\Delta f = -f_0 F_{esc}/(2kA)$, the minimum detectable CPD in FM-KPFM can be described[12] as:

$$\delta V_{CPD\text{-}FM} = \frac{2\sqrt{6}\, k_1 z_{t0}^2}{\pi^2 \varepsilon_0 RAV_{AC}} \frac{f_m}{f_{01}} n_{ds} \sqrt{B}. \tag{3.13}$$

In AM-KPFM, the electrostatic force at frequency ω_2 and the CPD between the tip and the sample can be obtained by regulating the V_{DC} to make F_{HAM} equal to zero:

$$F_{\mathrm{FM}} \approx -\frac{2\pi\varepsilon_0 R}{z_{t0}} V_{\mathrm{AC}} V_{\mathrm{DC}} \tag{3.14}$$

Amplitude variation induced by the electrostatic force at frequency ω_2 is described by

$$\Delta A_{\mathrm{AM}} = -\frac{2Q\pi\varepsilon_0 R}{kz_{t0}} V_{\mathrm{DC}} V_{\mathrm{AC}}. \tag{3.15}$$

The minimum detectable CPD in AM-KPFM is given by[57]

$$\delta V_{\mathrm{CPD\text{-}AM}} = \frac{kz_{t0}}{\sqrt{2}\pi\varepsilon_0 QRV_{\mathrm{AC}}} n_{\mathrm{ds}} \sqrt{B}. \tag{3.16}$$

It is demonstrated that the minimum detectable CPD in AM-KPFM is higher than that in FM-KPFM by comparing Equation(3.15) to Equation(3.16)[12,13], and we can achieve a sufficient potential resolution with smaller V_{AC} values than those required for FM-KPFM.

3.4 KPFM in Electrostatic Force Measurements

Kelvin probe force microscopy(KPFM), was introduced as a tool to measure the local contact potential difference between the AFM tip and the sample, thereby high spatial resolution was needed when mapping the work function or surface potential of the sample. Since the first introduction by Nonnenmacher et al in 1991, KPFM has been used extensively as a unique method to characterize the nano-scale electronic/electrical properties of metal/semiconductor surfaces and semiconductor devices. Recently, KPFM has also been used to study the electrical properties of organic materials/devices and biological materials[14]. It can be explained below.

(1) Measurements and imaging with high resolution on various materials

The application of high-resolution KPFM to characterize the electrical properties of metallic/semiconductor/insulator nanostructures and semiconductor surfaces and devices. Since the work function or surface potential strongly affect the chemical and physical phenomena taking place at the surface, KPFM

reveals critical information on the physical and chemical changes of the surface condition, which is needed for understanding physical and chemical phenomena on metal/semiconductor surfaces.

Leo Gross et al have been successfully observed the charge of a gold adatom by one electron charge increased the force on AFM tip by a few pico-newtons, indicating a higher attractive force above a negatively charged Au atom (Au^-) than above a neutral one (Au^0) by using KPFM combined AFM, as shown in Figure 3-5 (a) and (b). Density function theory reveals that the large ionic polarizability of the NaCl film is responsible for the stability of two different charge states. An additional electron on the gold atom forces the Cl^- ion underneath an Au atom to move downward, whereas the surrounding Na^+ ions move upward. This relaxation pattern creates an attractive potential for the additional charge on the Au atom, which is consistent with increase in the absolute value of frequency shift. This work showed a very high sensitivity for detecting the single electron charge. The high sensitivity was achieved by using very small oscillation amplitude (typically 40 pm) and low temperature (5 K) imaging.

Figure 3-6 (a) and (b) shows the frequency shift (Δf) measured as a function of the voltage above Au^- and Au^0. By determining the peak position (Δf^*) of the parabolic curve obtained in a Δf (V) measurement above Au atoms, LCPD is obtained. Witching from a neutral charge state to a negative charge state results in a Δf^* shift of (-0.11 ± 0.03) Hz and a LCPD shift of ($+27 \pm 8$) mV. The same method was used to investigate Ag atoms with Au atoms on bilayer NaCl on a Cu(111) substrate to show that the positive, neutral, and negative charge states can be distinguished and determined with NC-AFM/KPFM, since both neutral Ag^0 and positively charged Ag^+ adatoms are stable on bilayer NaCl on a Cu(111) substrate. KPFM techniques illustrate the discrimination of positively charged, neutral, and negatively charged atoms based on the LCPD shift measured[15,16].

(2) Reconstruction of nanoelectronic mechanical system

KPFM can also be used as the tools to form a nanoelectronic mechanical