Surface potential measurement by heterodyne frequency modulation Kelvin probe force microscopy in MHz range

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Abstract
The chemical and physical processes on surfaces are significantly influenced by the surface potential of materials. When using the frequency modulation Kelvin probe force microscopy (FM-KPFM), which has been widely used for measuring the surface potential distribution with high spatial resolution, it is very difficult to distinguish the surface potential due to the surface state from that due to the bulk state, because the charge transfer between the surface and bulk states occurs at a low-frequency ac bias voltage in the kHz range. Here, we propose a heterodyne FM-KPFM method using a high-frequency ac bias voltage in the MHz range to distinguish the surface and bulk states. This method is based on the heterodyne effect between the mechanical cantilever oscillation and the oscillating electrostatic force. For the first time, we succeeded in achieving the atomic-resolution imaging of the surface potential on an O- rich TiO2(110) surface using the electrostatic interaction in the MHz range. Furthermore, we could measure the upward and downward band bending on the surface at the atomic scale.

1. Introduction
Surface potential distributions are very significant properties of materials, and they influence various chemical and physical processes on surfaces. Thus, the surface potential distributions should be characterized to control the catalytic activity [1, 2] and electronic transport process [3, 4]. The surface potential is strongly influenced by the charge states at surfaces, which are determined by whether charges (electrons and holes) transfer from the bulk states to the surface states or from the surface states to the bulk states [3, 4]. The response speed of the charge transfer from the surface state to the bulk state is limited by the time constant of electron emission from the surface state [3, 4]. Thus, it is essential to separate the information of the surface state and that of the bulk state to clarify the electronic properties of the surface.

Kelvin probe force microscopy (KPFM) [5, 6] combined with atomic force microscopy (AFM) [7–9], which is based on the frequency modulation (FM) technique [10] to detect the tip-sample interaction force, has been widely used to image the surface potential and topography with high spatial resolution [11]. In FM-KPFM, the electrostatic force is modulated by applying an ac bias voltage with a frequency (fm) that is lower than the cantilever resonance frequency and higher than the topographic feedback bandwidth (figures 1(a), (b)). The resultant modulated component of the frequency shift (Δf) of the cantilever (figure 1(c)) is detected and used to regulate the dc bias voltage between the tip and the sample. FM-KPFM is sensitive to the electrostatic force gradient, and therefore atomic resolution imaging is achievable [6, 12]. It has also several advantages, namely, a simple implementation to add an FM-AFM, no need to increase the bandwidth of the cantilever deflection sensor, and high detection sensitivity using a cantilever with a weak spring constant at the first resonance. However, in FM-KPFM, the frequency (fm) of an ac bias voltage is limited to be 2 kHz, because a surface potential image is degraded as fm increases [13], in which the charge transfer between the surface and the bulk states easily occurs, and hence the surface potential contains the information of the surface and bulk states [14, 15]. Thus, the development of FM-KPFM that can distinguish the surface state from the bulk state using a high-frequency ac bias voltage in the MHz range [3, 4] is required.
Here, we present a new FM-KPFM method using the electrostatic interaction in the MHz range. This method is based on the heterodyne effect between the mechanical cantilever oscillation and the oscillating electrostatic force \([16-18]\). Hereafter, we refer to this method as 'heterodyne FM-KPFM.' We demonstrated the atomic-resolution imaging of the surface potential on an O-rich TiO\(_2\) (110) surface using the electrostatic interaction in the MHz range. We could measure the upward and downward band bending on the surface at the atomic scale.

2. Theoretical consideration

2.1. Relationship between frequency shift and electrostatic force

Here, we consider the operation principle of FM-KPFM and heterodyne FM-KPFM. In the FM detection system, the cantilever vibrating on resonance is used as a frequency determining component of a self-driven oscillator. The frequency shift of oscillating cantilever \((\Delta f)\) is given by \([19-22]\)

\[
\Delta f \approx -\frac{f_m^2}{kA} \int_0^{t_0} F_0(t) \cos(\omega_0 t) dt,
\]

where \(f_0(=\omega_0/2\pi)\), \(k\) and \(A\) are the resonance frequency, effective spring constant, and vibration amplitude of the cantilever, respectively. \(F_0\) is the force between the tip and the sample surface. We assume a harmonic oscillation of the cantilever, such as \(z(t) = z_0 + A \cos(\omega_0 t)\), where \(z_0\) is the mean distance between the tip and the surface. The periodic force \(F_0\) is represented by a Fourier series:

\[
F_0(t) = F_0 + \sum_{n=1}^{\infty} F_{0n}^{(n)} \cos(n\omega_0 t).
\]
By substituting equation (2) into equation (1), \( \Delta f \) is given by [13]
\[
\Delta f = \frac{1}{2} \frac{f_0}{k} F_{tc}^{(1)},
\]
where \( F_{tc}^{(1)} \) is the conservative electrostatic force which changes with the same phase as that of the cantilever vibration (\( \cos(\omega_0 t) \)). The electrostatic force between the conductive tip and the sample surface \( F_{es}(t) \) is given by
\[
F_{es}(t) = \frac{1}{2} \frac{\partial C}{\partial z} V_{ts}^2.
\]
Here, \( C \) and \( V_{ts} \) are the capacitance and bias voltage between the tip and the sample surface, respectively. We introduce the variable \( \alpha(z) \) as
\[
\alpha(z) = \frac{1}{2} \frac{\partial C}{\partial z}(z(t)).
\]
Because \( \alpha(z) \) is a function of the time-dependent tip position \( z(t) \), it is approximated by the first-order Taylor series around the mean distance \( z_0 \)
\[
\alpha(z) \approx \alpha(z_0) + \alpha'(z - z_0) = \alpha_0 + \alpha' \cos(\omega_0 t).
\]
From equations (4)–(6), \( F_{es}(t) \) is given by
\[
F_{es}(t) = \{\alpha_0 + \alpha' \cos(\omega_0 t)\} V_{ts}^2.
\]

### 2.2. FM-KPFM

In FM-KPFM, the electrostatic force between the tip and the sample is induced by applying a dc bias voltage \( V_{dc} \) and an ac bias voltage with frequency \( \omega_m (\omega_m \ll \omega_0) \) (figure 1(a)),
\[
V_{ts} = V_{dc} - V_{cpd} + V_{ac} \cos(\omega_m t).
\]
Here, \( V_{cpd} \) is the contact potential difference (CPD) between the tip and the surface. \( f_m = \omega_m / 2\pi \) is set to be within the bandwidth of the phase-locked loop (PLL) and in practice ranges from 100 Hz to 2000 Hz order. By substituting equations (8) to (7), \( F_{es}(t) \) becomes as follows (figure 1(b)):
\[
F_{es}(t) = \{\alpha_0 + \alpha' \cos(\omega_0 t)\} V_{ts}^2 = \{\alpha_0 + \alpha' \cos(\omega_0 t)\}
\times \left[ \left( V_{dc} - V_{cpd} \right)^2 + \frac{1}{2} V_{ac}^2 \right] + 2(V_{dc} - V_{cpd}) V_{ac} \cos(\omega_m t)
\times V_{ac} \cos(\omega_m t) + \frac{1}{2} V_{ac}^2 \cos(2\omega_m t).
\]

The conservative electrostatic force \( F_{es}(t) \) which changes with the same phase as that of the cantilever vibration \( (A \cos(\omega_0 t)) \) is given by
\[
F_{es}(t) = \alpha' \left[ \left( V_{dc} - V_{cpd} \right)^2 + \frac{1}{2} V_{ac}^2 \right] + 2(V_{dc} - V_{cpd}) V_{ac} \cos(\omega_m t)
\times \frac{1}{2} V_{ac}^2 \cos(2\omega_m t).
\]

This indicates that the \( \omega_m \) and \( 2\omega_m \) components of the conservative electrostatic force are induced (figure 1(b)). Assuming \( F_{es}(t) = F_{es}(t) \), from equations (3) and (10), the \( \omega_m \) component of the frequency shift \( \Delta f_m \) induced by the modulation of the electrostatic interaction is given by (figure 1(c))
\[
\Delta f_m = -\frac{f_0}{k} \alpha' (V_{dc} - V_{cpd}) V_{ac}.
\]

### 2.3. Heterodyne FM-KPFM

In order to enhance the modulation frequency of the electrostatic interaction, we propose a heterodyne FM-KPFM. This method is based on the heterodyne effect between the mechanical cantilever oscillation and the oscillating electrostatic force; frequency conversion is used according to the equation \( \cos(\omega t) \cos(2\omega t) = (1/2) \{ \cos(3\omega t) + \cos(\omega t) \} \). The use of the ac bias voltage with twice the resonance frequency of cantilever was proposed by our group for the dissipative electrostatic force interaction [16]. In heterodyne FM-KPFM, the electrostatic force between the tip and the sample is induced by applying a dc bias voltage \( V_{dc} \) and an ac bias voltage with frequency \( 2\omega_0 + \omega_m (\omega_m \ll \omega_0) \) (figure 2(a)),
Note that $f_{m}$ is set to be within the bandwidth of the PLL. From equations (7) and (12), the conservative electrostatic force ($F_{esc}(t)$), which changes with the same phase as that of the cantilever oscillation, becomes as follows: (figure 2(b))

$$F_{esc}(t) = \alpha' A \left\{ \left( V_{dc} - V_{pd} \right)^2 + \frac{1}{2} V_{ac}^2 \right\} + \left( V_{dc} - V_{pd} \right) V_{ac} \cos(\omega_{m} t).$$

(13)

Note that the $\omega_{m}$ component of the frequency shift is induced, but the $2\omega_{m}$ component is not induced unlike FM-KPFM (figure 2(b)). Assuming $F_{esc}(t) = F_{esc}(t)$, the $\omega_{m}$ component of the frequency shift ($\Delta f_{m}$) is given by (figure 2(c))

$$\Delta f_{m} = -\frac{f_{0}}{2k} \alpha' (V_{dc} - V_{pd}) V_{ac}.$$

(14)

Compared with equation (11) for $\Delta f_{m}$ in FM-KPFM, equation (14) for that in heterodyne FM-KPFM has a factor $1/2$ [12, 13]. $V_{cpd}$ is measured by adjusting $V_{dc}$ to nullify $\Delta f_{m}$.

The most important advantage of heterodyne FM-KPFM is that the frequency of the ac bias voltage can be increased to $2f_{0} + f_{m}$. Now, conductive cantilevers with $f_{0}$ in the MHz range are commercially available. This indicates that the surface potential measurement using ac bias voltage in the MHz range is possible by using heterodyne FM-KPFM.

3. Experimental method

Figure 3 represents the block diagram of FM-KPFM and heterodyne FM-KPFM combined with FM-AFM. The frequency shift $\Delta f$ of the oscillating cantilever was detected with PLL. The vibration amplitude $A$ was kept constant with the automatic gain control (AGC). AFM images are obtained by regulating the tip-sample distance at constant $\Delta f$. In FM-KPFM, an ac bias signal of $\cos(\omega_{m} t)$ is generated by the oscillator. In heterodyne FM-KPFM, an ac signal of $\cos(2\omega_{0} t)$ is generated by PLL under the second harmonic mode ($n = 2$) synchronized with
the cantilever oscillation. An ac bias signal of $\cos(2\omega_0 + \omega_m)t$ is generated by mixing the signal of $\cos(2\omega_0)t$ with that of $\cos(\omega_m)t$ using a single sideband (SSB) modulator. In both FM-KPFM and heterodyne FM-KPFM, the $\omega_m$ component of the frequency shift $\Delta f_m$ is measured with a lock-in amplifier and used to regulate the dc bias voltage $V_{dc}$. KPFM images are obtained by regulating $V_{dc}$ to nullify $\Delta f_m$. Experiments were performed using FM-AFM with the optical beam deflection method under ultrahigh vacuum (UHV) condition at a low temperature (80 K) [23].

As a sample surface, a rutile O-rich TiO$_2$ (110) surface was used, where oxygen adatoms (O$_{ad}$) were dissociatively adsorbed on five-fold Ti rows [24, 25]. An O-rich TiO$_2$(110) surface was prepared as follows. First, a TiO$_2$(110) surface was prepared by cyclic Ar-ion sputtering (0.9 keV, $1 \times 10^{-6}$ Torr) and annealing (900 K, 30 min). Then, oxygen molecules were exposed on the reduced TiO$_2$(110) surface at room temperature for 15 Langmuir ($5 \times 10^{-9}$ Torr, 5 min) to obtain an O-rich TiO$_2$(110) surface. As a force sensor, we used an Ir-coated Si cantilever (SD-T10L100x10, Nanosensors) with $k = 1500$ N m$^{-1}$ and $f_0 = 1.128$ MHz. The use of a cantilever with high $k$ and $f_0$ provides the small-amplitude operation that not only enhances the force sensitivity [26] but also reduces the contribution of unwanted long-range force and hence enhances the contribution of the short-range force associated with the atomic-scale information on the surface [27]. The stiffness, resonance frequency, and quality factor of the Ir-coated Si cantilever were

Figure 3. Block diagram of FM-KPFM and heterodyne FM-KPFM. The frequency shift $\Delta f$ of the oscillating cantilever is detected under a constant vibration of amplitude $A$ with PLL. In FM-KPFM, an ac bias signal of $\cos(2\omega_0)t$ is generated by the oscillator. In heterodyne FM-KPFM, an ac signal of $\cos(n\omega_0)t$ is generated by PLL under the second harmonic mode ($n = 2$). An ac bias signal of $\cos(2\omega_0 + \omega_m)t$ is generated by an SSB modulator. The $\omega_m$ component of the frequency shift $\Delta f_m$ is measured with a lock-in amplifier and used to regulate the dc bias voltage $V_{dc}$.

Figure 4. Structural model of O-rich TiO$_2$(110) surface. (a) Top view and (b) side view. Oxygen adatoms (O$_{ad}$) were dissociatively adsorbed on five-fold Ti rows.
4. Results and discussion

Figures 5(a) and (b) represent the spectrum of \( \Delta f \) as a function of the frequency measured on the TiO\(_2\)(110) surface at \( V_{dc} = -0.2 \) V (without KPFM feedback) by FM-KPFM with \( f_m = 200 \) Hz and heterodyne FM-KPFM with \( 2f_0 + f_m \approx 2.3 \) MHz, respectively. Peaks of the spectrum appear at \( f_m = 200 \) Hz in FM-KPFM and heterodyne FM-KPFM. A peak of the amplitude spectrum appears at \( 2f_m = 400 \) Hz in FM-KPFM, while no peak appears at \( 2f_m = 400 \) Hz in heterodyne FM-KPFM, which agrees with the theoretical result. These results demonstrate that the conservative electrostatic force synchronized with the cantilever oscillation is generated by the heterodyne effect between the mechanical cantilever oscillation and the oscillating electrostatic force. Note that the spectrum (~0.55 [Hz]) at \( f_m = 200 \) Hz in heterodyne FM-KPFM is less than 1/2 of that (~1.62 [Hz]) in FM-KPFM. This suggests that the surface potential and the capacitance gradient (\( \alpha \)) between the tip and the surface depends on the frequency of the electrostatic interaction.

In figure 6, we show AFM and surface potential images of the O-rich TiO\(_2\)(110) surface measured by FM-KPFM and heterodyne FM-KPFM. In AFM images (figures 6(b), (d)), the bright and dark rows correspond to bridging oxygen atom and five-fold Ti atom rows, respectively. The large and small bright spots are oxygen adatom pairs with two negative electrons (O\(_{ad}^2^-\) - O\(_{ad}^2^-\)) and oxygen adatoms with two negative electrons (O\(_{ad}^{2-}\)) dissociated and adsorbed on five-fold Ti atom rows, respectively [28, 29]. In the surface potential images (figures 6(c), (e)), bridging oxygen atom rows and five-fold Ti atom rows show high and low \( V_{cpd} \). Both O\(_{ad}^{2-}\) - O\(_{ad}^{2-}\) and O\(_{ad}^{2-}\) represent high and low \( V_{cpd} \). Thus, atomic-resolution imaging of the surface potential

\( k = 1500 \text{ N m}^{-1}, f_0 = 1.128 \text{ MHz}, \) and \( Q = 15 \) 205, respectively. The tip apex was cleaned via Ar-ion sputtering in situ.

In the measurement of the power spectrum density (PSD) of \( \Delta f \) as a function of frequency on the TiO\(_2\)(110) surface, the tip-sample distance was fixed at an average frequency shift of \( \langle \Delta f \rangle = -40 \) Hz, a vibration amplitude of \( A = 500 \) pm, and a dc bias voltage of \( V_{dc} = -0.2 \) V (without KPFM feedback). An ac bias voltage with \( V_{ac} = 0.7 \) V and \( f_m = 200 \) Hz was used in FM-KPFM, while that with \( V_{ac} = 0.7 \) V and \( 2f_0 + f_m = 2 \times (1128-40) + 200 = 2256 \) 120 Hz was used in heterodyne FM-KPFM. In heterodyne FM-KPFM, the conservative electrostatic force synchronized with the cantilever oscillation is generated by the heterodyne effect between the mechanical cantilever oscillation and the oscillating electrostatic force.
is realized not only by FM-KPFM but also by heterodyne FM-KPFM, because the heterodyne FM-KPFM is sensitive to the electrostatic force gradient.

From the cross-sectional profiles along black lines in the AFM and KPFM images (figures 6(b)–(e)), the line profiles of AFM images are almost equal for FM-KPFM and heterodyne FM-KPFM (figure 6(f)), while the line profile of the surface potential image for heterodyne FM-KPFM is different from that for FM-KPFM (figure 6(g)). For the first time, we successfully measured the surface potential at the atomic scale, which changes depending on the modulation frequency of the ac bias voltage in KPFM. This surface potential change can be explained as follows: When an ac bias voltage is applied between the tip and the surface in KPFM, the Fermi level of the tip moves up or down with respect to the surface-state level. There is a limit of the response speed of electron emission from the surface state to the bulk state \([3, 4]\). As a result, the electron transfer between the surface state and the bulk state is strongly influenced by the modulation frequency of ac bias voltage. Namely, at frequencies lower than the cutoff frequency \((f_c) (<100 \text{ kHz})\), which is determined by the rate of charge capture and emission at surface states \([3, 4]\), the charge transfer between the surface states and bulk states occurs, and hence the band bending changes upwardly and downwardly. In contrast, at frequencies higher than \(f_c\) (>several 100 kHz), the charge transfer between the surface states and the bulk states does not occur, and hence the band bending does not change owing to the slow response of the surface state.

Interestingly, in figure 6(f), at the oxygen adatom site, the surface potential is higher for FM-KPFM than for heterodyne FM-KPFM. In contrast, at the five-fold Ti atom site, the surface potential is lower for FM-KPFM than for heterodyne FM-KPFM. Note that there are two types of surface states: acceptor- and donor-like. On the O-rich TiO\(_2\) (110) surface, oxygen adatoms and five-fold Ti atoms act as acceptor- and donor-like surface states, respectively. These experimental results suggest that excess electrons that are accepted cause the upward band bending at the oxygen adatom site, while those that are donated cause the downward band bending at the five-fold Ti atom site \([30]\). This is the first measurement of the band bending at the atomic scale using KPFM.

5. Conclusion

We proposed a heterodyne FM-KPFM using the electrostatic interaction in the MHz range. We demonstrated the atomic-resolution imaging of the surface potential on an O-rich TiO\(_2\) (110) surface using the electrostatic interaction in the MHz range. We could measure the upward and downward band bending on the surface at the atomic scale.
The performance of wide bandgap semiconductors is limited by high trap state densities and hence trap states at interfaces such as oxide/semiconductor interfaces are of great importance for technical applications. We expect to be able to identify trap states or determine the life time of trap states by measuring the frequency dependence of ac bias voltage.

Note that heterodyne FM-KPFM can be extended to pump-probe KPFM to determine the time scales of charging and uncharging of the surface states [31, 32]. Moreover, note that the heterodyne method is applicable to not only the FM detection system but also amplitude modulation (AM) and phase modulation (PM) detection systems. Furthermore, note that the heterodyne method is applicable to other types of scanning probe microscopy, such as magnetic force microscopy, magnetic exchange force microscopy, magnetic resonance force microscopy, photoinduced force microscopy [18], and force modulation microscopy. This success is a promising development in the exploration of atomic-scale physical and chemical interactions between atoms/molecules and surfaces and provides deeper insight into the various chemical processes and functions on surfaces.

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References

[1] Diebold U 2003 Surf. Sci. Reports 48 53
[2] Setvin M et al 2013 Science 341 988
[3] Shockley W and Read T 1952 Phys. Rev. 87 835
[4] Sze S M 1981 *Physics of Semiconductor Devices* (New York: A Weley-interscience Publication) 2
[5] Nonnenmacher M, O’Boyle M P and Wickramasinghe H K 1991 Appl. Phys. Lett. 58 2921
[6] Kitamura S and Iwatsuki M 1998 Appl. Phys. Lett. 72 3154
[7] Binnig G, Quate C F and Gerber C 1986 Phys. Rev. Lett. 56 930
[8] Giessibl F J 1995 Science 267 68
[9] Sugawara Y, Ohta M, Ueyama H and Morita S 1995 Science 270 1646
[10] Albrecht T R, Grütter P, Horne D and Rugar D 1991 J. Appl. Phys. 69 668
[11] Sadewasser S and Glazte T 2018 *Kelvin Probe Force Microscopy From Single Charge Detection to Device Characterization* (Springer Series in Surface Science vol 65 (Berlin: Springer)
[12] Ma Z M, Kou L, Naitoh Y, Li Y J and Sugawara Y 2013 Nanotechnol. 24 225701
[13] Fukuma T, Kobayashi K, Yamada H and Matsushige K 2004 Rev. Sci. Instrum. 75 4589
[14] Arita M et al 2014 Appl. Phys. Lett. 104 132103
[15] Polak L and Wijngaarden R J 2016 Phys. Rev. B 93 195320
[16] Nomura H et al 2007 Appl. Phys. Lett. 90 033118
[17] Sugawara Y et al 2012 Appl. Phys. Lett. 100 223104
[18] Yamanishi J, Naitoh Y, Li Y J and Sugawara Y 2018 Phys. Rev. Appl. 9 024031
[19] Giessibl F J 1997 Phys. Rev. B 56 16010
[20] Sasaki N and Tsukada M 1998 *Jpn. J. Appl. Phys.* 37 L533
[21] Dürrig U 1999 Appl. Phys. Lett. 75 433
[22] Livshits A I et al 1999 Phys. Rev. B 59 2436
[23] Arima E, Wen H F, Naitoh Y, Li Y J and Sugawara Y 2016 Rev. Sci. Instrum. 87 093113
[24] Wendt S et al 2008 Science 320 1755
[25] Du Y et al 2010 Phys. Chem. Chem. Phys. 12 6337
[26] Giessibl F J, Biedfeldt H, Hembacher S and Mannhart J 1999 Appl. Surf. Sci. 140 352
[27] Giessibl F J et al 2011 Phys. Rev. B 84 125409
[28] Zhang Q et al 2018 J. Am. Chem. Soc. 140 15668
[29] Adachi Y et al 2019 ACS Nano 13 6917
[30] Zhang Z and Yates J T 2012 Chem. Rev. 112 3520
[31] Murawski J et al 2015 J. Appl. Phys. 118 154302
[32] Schumacher Z et al 2016 Phys. Rev. Appl. 3 044018