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論 文 内 容 の 要 旨

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論文題名	Theoretical and Experimental Study on Surface Potential Measurement Method at the Atomic Level (原子レベルの表面電位測定法に関する理論的と実験的研究)

論文内容の要旨

Atomic force microscopy (AFM) has become a powerful tool for imaging surface structures with atomic resolution, especially on insulator surfaces. Among the AFM imaging modes, frequency-modulation AFM (FM-AFM) is the most widely used because of its extremely high spatial resolution. In FM-AFM, a cantilever is oscillated close to the resonance frequency f_0 under a constant amplitude. The frequency shift of the cantilever due to the tip-sample interaction is detected, which is used as a feedback signal to image the surface structure. FM-AFM has been widely used on semiconductor, metallic, and insulating surfaces.

Kelvin probe force microscopy (KPFM), which is based on AFM, is a method of mapping the contact potential difference (CPD) induced by the difference in the work function between the tip and the sample surface. The CPD can be compensated by applying a dc bias voltage. Depending on the detection mode, KPFM can be divided into FM-KPFM, amplitude modulation (AM)-KPFM, and heterodyne AM-KPFM. In FM-KPFM, the electrostatic force is derived from Δf. An ac bias voltage with a modulated frequency f_m plus a dc bias voltage are applied between the tip and sample, and f_m should be lower than f_0 and higher than the topographic feedback bandwidth. In AM-KPFM, the electrostatic force is derived from the amplitude variation ΔA of the cantilever oscillation at the second resonance frequency f_2, and f_m is set to f_2. In heterodyne AM-KPFM, the electrostatic interaction force is detected from ΔA for the cantilever oscillation at f_2, and f_m is tuned to the frequency difference. In AM-KPFM, the distance dependence of the modulated electrostatic force between the tip and sample is weaker ($1/z$), where z is the tip-sample distance. The surface potential measurement is significantly affected by the stray capacitance between the cantilever and the surface, which induces an artifact in KPFM images. In contrast, FM- and heterodyne AM-KPFMs are sensitive to the short-range force due to the strong distance dependence of $1/z^2$. Actually, the measurement system of heterodyne AM-KPFM is complicated and its application is retained. The three types of KPFM have bias feedback loops, which probably involve instability due to the oscillation of the feedback loop. Although the use of a low feedback gain can prevent such instability, the imaging takes a relatively long time. In addition, the applied dc bias voltage may induce band bending or even a current, which induces a phantom force and affects the KPFM measurement. CPD measurement by FM-KPFM without bias voltage feedback has been proposed. In this method, an ac bias voltage ($V_{ac}\cos 2\pi f_m t$) is applied between the tip and sample, and the f_m and f_{2m} components of Δf are used to calculate the CPD, where the bias feedback loop is removed. The bandwidth of the phase-locked loop used to measure Δf should be at least f_{2m}. This method has several advantages: it avoids the instability of the bias feedback circuit and has a high speed owing to the non-use of a feedback loop. The disadvantage is the reduced signal-to-noise ratio owing to the setting of a wider bandwidth. Using this method, the detection of the CPD on an Au/Si(111) surface has been studied, and surface steps and Au islands were observed in topographic and CPD images, although atomic resolution images have not been realized.

In this research, we investigated the capability of obtaining atomic resolution surface potential images by frequency-modulation Kelvin probe force microscopy (FM-KPFM) without bias voltage feedback. We theoretically derived equations representing the relationship between the contact potential difference and the frequency shift (Δf) of an oscillating cantilever. For the first time, we obtained atomic resolution images and site-dependent spectroscopic curves for Δf and V_{LCPD} on a Si(111) surface. FM-KPFM without bias voltage feedback does not involve the influence of the FM-KPFM controller because it has no deviation from a parabolic dependence of Δf on the dc bias voltage.

The dissertation has seven chapters.

Chapter 1 Introduction

We begin this chapter by introducing surface science and surface analysis methods. Next, we describe the history of AFM and KPFM, and compare the advantages and disadvantages of KPFM. Finally, focusing on unsolved questions of KPFM, we present the motivation of this theoretical and experimental study of surface potential measurement method at the atomic level, and end with an outline of the chapters.

Chapter 2 Principles of FM-AFM and FM-KPFM

This chapter begins with an introduction to the interaction forces between the oscillating cantilever in FM-AFM and the sample surface. In our research, the main interaction forces can be classified into three types: long-range van der Waals force, long-range electrostatic force, and short-range chemical forces. Next, we describe the theoretical relationship between the frequency shift and interaction forces, and clarify the noise that always appears in measurements. In Section 2.3, we explain the theory of FM-KPFM. We introduce the basic physical quantities related to KPFM and explain the relationship between the electrostatic force and CPD.

Chapter 3 Low-temperature UHV FM-AFM and FM-KPFM equipment

The equipment and the control circuits for FM-AFM and FM-KPFM systems are described in this chapter. We first describe a UHV system. Next, we show the cryogenic and vibration isolation system, which maintains the AFM unit at a low temperature with high mechanical stability. Then, we explain the mechanical components and the working mechanism of the AFM unit. Finally, we present the FM-AFM and FM-KPFM control systems. They send out driving signals, control the operations of the AFM units and collect information about the topography and potential of the surfaces.

Chapter 4 Investigation of the surface potential on $TiO_2(110)$-1 × 1 surface by FM-KPFM

Chapter 4 is devoted to the investigation of the surface potential on a rutile $TiO_2(110)$-1 × 1 surface, particularly the surface defects. We first give a concise introduction of the physical structure of the surface. Next, we introduce the experimental details, which include the preparation of the $TiO_2(110)$-1 × 1 surface and the iridium-coated Si cantilever, and the three-dimensional bias spectroscopic mapping method. The latter can avoid unstable noise that occurs in FM-KPFM. In Section 4.4, we give the experimental result. Two typical surface AFM contrasts (hole-mode and protrusion-mode) of $TiO_2(110)$ are shown. A surface potential image in hole-mode and an atomic-specific three-dimensional bias-z-spectroscopic mapping are shown. We suggest the origins of the surface potential for a metal oxide surface. Finally, we point out the limits of FM-KPFM, and state why further research into FM-KPFM without bias voltage feedback is necessary.

Chapter 5 Investigation of the surface potential by FM-KPFM without bias voltage feedback

We prove the capability for resolving surface potential images at atomic resolution using FM-KPFM without bias voltage feedback. In Section 5.2, we describe the theory of FM-KPFM without bias voltage feedback. Next, we explain the experimental methods. Then, we show V_{LCPD} images and the V_{LCPD} spectroscopic curves for FM-KPFM without bias voltage feedback. Lastly, we demonstrate that this method reduces the ohmic voltage drop near the tip-sample junction.

Chapter 6 Development of heterodyne FM-KPFM without bias voltage feedback

Based on FM-KPFM without bias voltage feedback, we propose heterodyne FM-KPFM without bias voltage feedback. In Section 6.2, we introduce the basic principles. In Section 6.3, we explain the experimental set-up and the two-dimensional spectroscopic mapping method. Then, we prove its capability by measuring the surface contrast in topography mode and constant height mode. Additionally, we discuss the two-dimensional force and charge polarization mapping on a semiconductor surface. This chapter ends with a discussion of the origin of the atomic resolution contrast of the surface potential.

Chapter 7 Conclusion and outlook

We give a summary, and describe the future directions in this subject.

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論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

試料の表面電位（あるいは表面電荷）は、多くの物理化学過程を左右する重要な物理量である。表面電位の空間分布を高感度・高分解能にマッピングするツールとして、探針・表面間の静電気的相互作用を検出するケルビンプローブ力顕微鏡が用いられている。従来のケルビンプローブ力顕微鏡では、探針・試料間に直流バイアス電圧を印加するため、半導体などの導電性試料表面に対しては、表面のバンドの曲がりの大きさが直流バイアス電圧によって変化したり、トンネル電流が流れるため試料表面近傍で電圧降下が生じたりする。高感度・高精度に表面電位を測定するためには、これらのバンドの曲がりの影響や電圧降下の影響を除去する必要がある。

本研究では、上記の問題点を解決するため、新しい原子レベルの表面電位測定法を理論的・実験的に研究することを目的とした。具体的には、以下の３つの成果を得た。

(1) 周波数変調方式のケルビンプローブ力顕微鏡において、直流バイアス電圧を印加せずに表面電位を測定するための理論的関係式を導出した。具体的には、カンチレバーの周波数シフトに現れる静電気力の変調成分と２倍の周波数成分から表面電位を測定できることを示した。直流バイアス電圧のフィードバック制御が不要なため、表面電位測定の速度が向上することが期待される。

(2) 試料表面として Si(111)表面を取り上げ、直流バイアス電圧を印加しないケルビンプローブ力顕微鏡を用いて、表面電位を測定できることを実験的に検証した。原子レベルで表面電位を測定することに初めて成功した。本手法により、バンドの曲がりや電圧降下の影響を抑えた表面電位測定が可能であることを実証した。この方法は、直流バイアス電圧を印加していないため、試料表面の化学反応を抑えられることも期待される。

(3) 直流バイアス電圧を印加することなく、試料表面上に働く力と表面電位を同時測定できる分光法を開発した。開発した分光を用いて、原子スケールの力と表面電位の探針・試料間距離依存性を測定し、表面電位のイメージング機構を考察した。

以上のように、本学位申請論文は、ケルビンプローブ力顕微鏡によるナノメートルスケールの表面電位測定法に関して研究したものであり、基礎的な面のみならず、応用の面でも有益な知見を得ており、応用物理学、特にナノ計測学に寄与するところが大きい。よって本論文は博士論文として評価あるものと認める。