纳米光子学丛书

The Kelvin Probe Force Microscopy and Its Related Technology with High Sensitivity and High Resolution

高灵敏及高分辨KPFM及其相关技术

马宗敏 著

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前　言

近年来，以扫描探针为代表的超高分辨量子精密测量技术取得了长足进展，是人类认识微观、纳观，甚至原子的“眼睛”，在三维形貌、电荷量、自旋等物理量测量方面，已经达到原子分辨率（小于 10^{-10}m）。盖尔德·宾尼（Gerd Bining）和海因里希·罗雷尔（Heinrich Rohrer）的扫描隧道显微镜（STM），以及赫尔（Stefan Hell）、贝兹（Eric Betzig）等的超分辨荧光显微技术由于实现了对半导体、有机物的原子（纳米）分辨率成像而获得了诺贝尔物理学（化学）奖。因此，谁掌握了精密测量技术，谁就拥有了通向微观世界的钥匙。

高分辨开尔文探针力显微镜（KPFM）是基于原子力显微镜（AFM）的扫描探针技术（SPM），通过测量和改变探针和样品间的局域接触势能差（LCPD），实现了纳米甚至原子尺度的量子材料精确设计和控制，成为“由下而上”制备原子级传感器、原子/分子开关、量子存储器等量子器件最关键的技术之一。

KPFM 通过测量金属 AFM 探针和样品间 LCPD 进行高分辨功函数或材料表面成像。自从 1991 年由非内马赫（Nonnenmacher）等提出以来，KPFM 已经广泛应用于金属纳米材料量子尺寸效应的电学特性表征、半导体纳米材料和表面电学特性分析与表征，以及半导体电子器件高分辨表面势能测量与表征。在材料性能的极限测量与显微方面，目前，已实现半导体、绝缘体及导体材料的表面电荷分布、局域接触势能差、电荷间传输、三维静电力与力谱测量等纳米级或原子级电荷分辨率测量；实现了带电粒子的高精度识别与控制（单电荷），为相关物理现象解析、原子尺度电荷操控提供了新的方法和技术。在纳机电系统测量与构建方面，利用 KPFM 的电荷操控能力可以实现纳机电系统的制备，完成分子/原子级的电子器件功能化设计。KPFM 可以为原子级机电系统（单分子开关）验证及未

来的实用化打下基础。在电子器件表征与测量方面，利用 KPFM 还可以进行绝缘材料(例如电解液氧化聚乙烯，电池或者湿度传感器皿)内部空间电荷的形成、三维测量及移动，这为微纳米能量存储器件开发、纳米级电荷光刻技术等纳电子器件研发提供了新的工具和方法。

作者自 2008 年踏入扫描探针显微镜领域以来，已过去了十几年，期间师从日本大阪大学菅原康弘教授和李艳君教授，主要从事 NC-AFM 及 KPFM 新方法探索与材料测量，在原子分子操纵、表面电荷传输、功函数测量方面进行了一系列研究。近几年，作者充分感受到了日本式严谨、踏实的科研精神；特别是近年来在中日双方合作项目支持下，我们在 AFM、KPFM 领域一直保持着密切的合作和联系；同时，作者也认识到在该领域中国与日本及其他发达国家还有不小的差距，急需在方法、技术及仪器等方面全方位追赶。

在本书撰写过程中，作者有幸得到了多位导师、友人的帮助和支持。首先对菅原康弘教授和李艳君教授多年来的培养及共同合作研究表示深深地感谢，没有他们的帮助，本书不可能完成。感谢课题组张文栋教授、刘俊教授、熊继军教授及薛晨阳教授，没有他们多年来的关心和支持，中北大学在 AFM、KPFM 方向的确立和发展是不可想象的。特别感谢刘俊教授多年来的栽培和指导，刘教授高瞻远瞩，能够把复杂问题简单化，加快了 AFM 在精密测量领域的应用和发展。

最后还要感谢家人多年来的支持和鼓励。感谢我的妻子乌日嘎女士，感谢她多年来对全家的付出和牺牲；感谢儿子的到来，让我体会到作为一个父亲的责任和担当，也让我有幸和他一起成长；感谢我的母亲和离世多年的父亲，他们苦难和坚韧的人生是支撑我走下去的力量源泉。

CONTENTS

Chapter 1
Introduction

1.1 Preface

1.1.1 Nanoscience and Surface

Over the last twenty-five years nanoscience has developed from embryonic beginning to a fully edged cross-disciplinary field of academia, with research now being carried out in fields as diverse as power generation[1], catalysis[2], drug delivery and metamaterials[3]. During this time, developments in optical, electronic, and scanning probe microscope techniques have allowed new and varied insights into the workings of physical world on the sub-micron to atomic level. However, despite recent advances, attempting to understand how physical and chemical forces affect, and operate on, nanometer sized features is still an active area of research with many unanswered questions. Even in tightly controlled ultrahigh vacuum (UHV) conditions at low-temperature, there is still debate as to how some of the most commonly used techniques interact with materials and what the fundamental limits of such techniques actually are. One of the key goals of nanophysics is not only to develop the control of matter on the nanoscale but also to reach a complete understanding of forces, and critically how they interact. With the size of a system varies, the dominant controlling force can often change due to different scaling

behaviors. In general, the observation of unexpected or unexplained behavior in well understood experiments can point the way to new and exciting areas of research, and nanoscience is no exception.

In addition to developing a fundamental understanding of forces on the nanoscale, a primary motivation is using the tools to build structures. The traditional route for manufacturing nanoscale features, optical lithography, is still the most widely used, despite numerous premature predictions of its drawback[4]. The development of increasingly ingenious techniques now show that sub-wavelength features are routinely produced[5] and used around the world. It now appears that the fundamental limit for silicon-based electronics may be the very materials they are created from, rather than the technique used to create features. Despite optical lithography's great success, it still has its acknowledged fundamental limits, and is not suited for general-purpose applications, especially manufacturing outside of clean-room level facilities. Increasingly large investments are required for diminishing returns[6], and, as such, research into alternative techniques that may be applied more cheaply or perhaps more widely in different environments continues a pace.

1.1.2 Surface Charge

Surface charge is the amount of electricity present at an interface or a surface. There are many different processes, which can lead to a surface being charged, including adsorption of ions, protonation/ deprotonation and the application of an external electric field. It is defined as the amount of electric charge q, that is present on a surface of given area A, and $\sigma = q/A$. The relation between the surface charge and the surface potential can be expressed by the Grahame equation, which stated that the total charge of the double layer must be equal to the negative of the surface charge[7]. Surface charge or potential distributions are very significant properties of materials, and they affect various physical and chemical processes on surface, such as surface chemical

reactions, catalyst, electrostatic, dielectric and magnetic properties, contact charging, etc. Figure 1-1 is a typical charge transfer on TiO_2 surface, which states that the surface is always partially reduced after preparation, but soon, even in UHV, ambient water molecules begin to dissociate at the oxygen vacancies resulting in hydroxyl groups. Surface charge distributions are usually measured by using Kelvin probe force microscopy (KPFM)[8-12] and electrostatic force microscopy (EFM)[13] combined with noncontact atomic force microscopy (NC-AFM)[14,15]. NC-AFM gives the topographic information and KPFM (EFM) gives the potential distribution information.

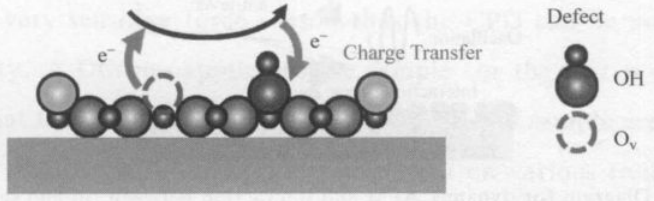

Figure 1-1 Surface charge of charge transfer on TiO_2 surface

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1.1.3 Scanning Probe Microscopy

Surface science was revolutionized in 1982 by the invention of the scanning tunneling microscope by Binnig and Rohrer[16,17]. In 1986 the invention of the atomic force microscope widened the range of samples from conductive to non-conductive ones[18]. Further research develop the non-contact (or dynamical) mode of the atomic force microscopy (AFM)[19,20], where a cantilever supporting a sharp tip at its end is vibrated close to its resonance frequency and changes in the vibration because the tip-sample interaction is employed to maintain a constant distance to the sample surface while scanning across the sample, as shown in Figure 1-2. Forces exerted by the tip on the sample are minimal in non-contact mode. In this case, the elastic force on the cantilever overcomes the van der Waals attraction of a tip to a surface and prevents the so called "jump-to-contact"[21]. Since the tip is not then in permanent direct

hard contact with the surface. By using NC-AFM, surface topography, atomic structure and film growth, the measurements of adhesion and the strength of individual chemical bonds, friction and lubrication, atom/molecular manipulation, and many others from the micrometer to the sub-nanometer scale have been achieved by extracting the interaction force from the frequency shift or amplitude variation. Figure 1-3 show the frequency shift (amplitude variation) as a function of tip-sample distance.

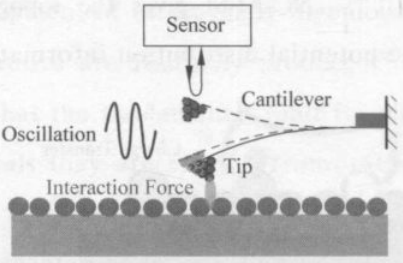

Figure 1-2 Diagram for dynamic AFM and interaction between tip and sample surface

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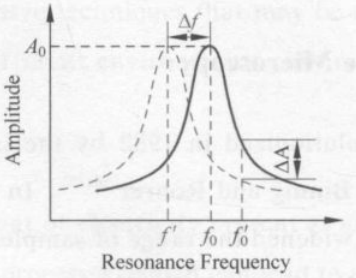

Figure 1-3 Resonance variation induced by the interaction force

the resonance frequency f_0 was shift to f_0', amplitude variation was ΔA

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A wide field of applications has been opened by the combination of the AFM[14,15] with other measurement methods, thus providing additional sample properties on a lateral scale in the nanometer range, such as the large family of electrostatic force spectroscopy (EFS) and electrostatic force microscopy (EFM)[13]. Inspired by classical Kelvin probe, KPFM is probably one of the

most important types of electrostatic AFM. Nonnenmacher et al[8,9] first developed KPFM and it allows to plot surface electronic properties, namely the contact potential difference (CPD). The name "KPFM" originates from the macroscopic method developed by Lord Kelvin in 1898 using a vibrating parallel plate capacitor arrangement, where a voltage applied to one vibrating plate is controlled such that no current is induced by the vibration. The reduction of this exact principle to the microscopic scale, however, results in a poor sensitivity, since the size of the plates is too small to generate a sufficient current. Therefore, in KPFM the electrostatic force is used. The cantilever in an AFM is a very sensitive force sensor, thus the CPD can be measured with high sensitivity. A DC-bias applied to the sample (or the tip) is controlled in such a way that the electrostatic forces between tip and sample are minimized. For KPFM, it has reached atomic-scale resolution on various conductive[22-24], semiconductor[25,26], insulating surfaces[27-29] and even on a single molecule[30] since last two decade years, just as shown in Figure 1-4, Figure 1-5 and Figure 1-6.

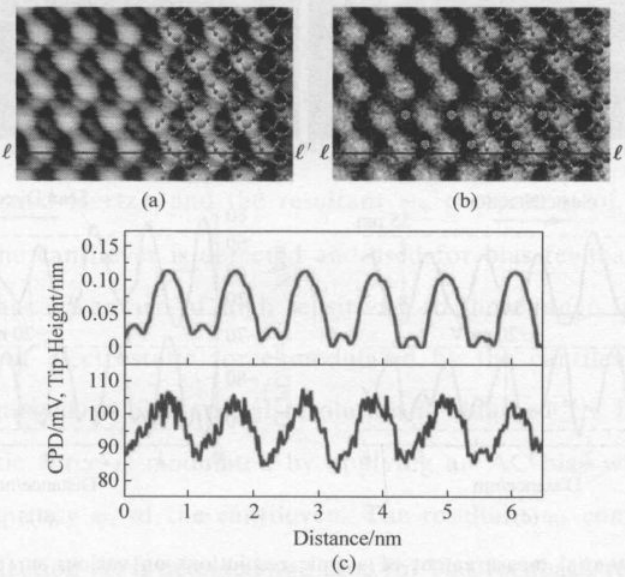

Figure1-4 Potential measurement of atomic resolutions on various surfaces all dangling bonds by KPFM

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Although the interpretation of KPFM contrast on the atomic-scale is under dispute[31-37], the detection of KPFM images is definitely closely related to the charge distribution on the sample surface. Basic principle of the KPFM is: by applying AC bias voltage which modulates the electrostatic interaction between tip and sample, CPD can be detected from the resultant shifts of amplitude or the resonance frequency of cantilever. The DC bias voltage is used to nullify the detected oscillating electrical forces, which originated from CPD between the tip and sample surface. Recently, potential measurement in liquid[38] and without the bias voltage[39] was introduced to broaden KPFM application and to avoid the unstable of system. In particular, current status and many prospects of KPFM for applications in applied sciences have been reported by Barth et al[40].

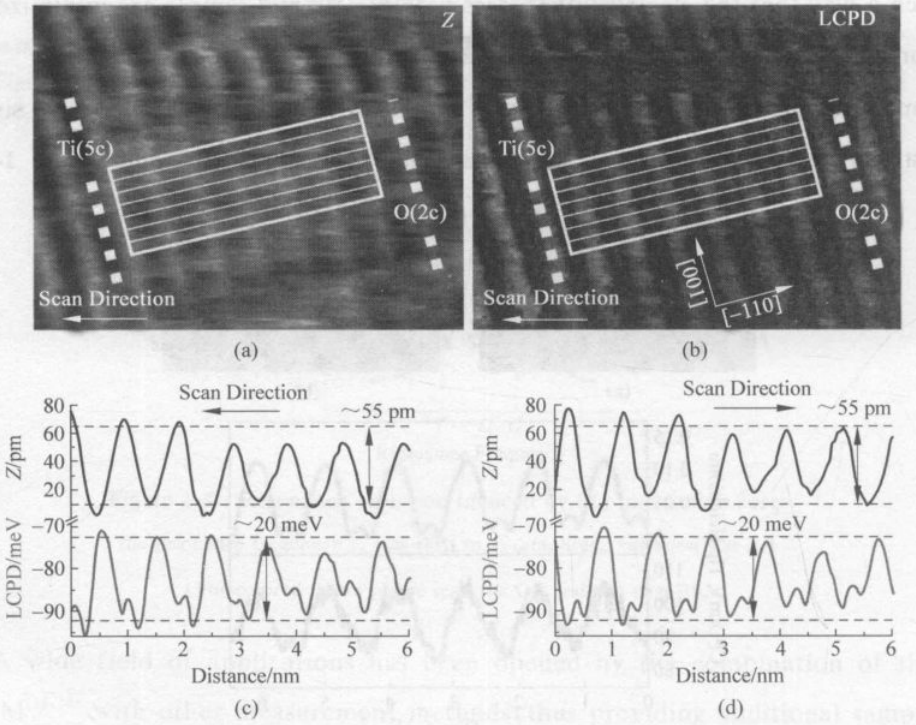

Figure1-5 Potential measurement of atomic resolutions on various surfaces of atomic contrast of geometry and charge by KPFM

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