

论文中英文摘要

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论文题目：分子尺度量子态探测与调控的扫描隧道显微学研究

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中文摘要

在物质科学研究中，人们一直在寻求各种方法以便能更直观地揭示物质的微观性质，并期望能按照特定的目的和意愿利用和控制微观物质的属性，实现特定的功能。原子和分子是构成物质世界的最基本单元，在这一尺度上对物质的研究成为整个物质科学研究的基础，具有重要而深远的意义。同时，从实际应用的角度来看，随着微电子技术的飞速发展，目前微电子器件的尺寸已经进入深亚微米量级，即100纳米量级，然而由于尺度、维度的减小和量子效应的凸现，以及微纳加工技术的限制，再进一步减小器件尺寸已十分艰难。而单个原子和分子尺度上的物质的性质及相互作用其本质上是量子力学的。因此探测与研究单个分子、原子和团簇各种量子性质，并进一步实现原子分子尺度上的量子态调控，“从下而上”地（“bottom-up”）改变和调控物质的形态和性质，将有希望构造各种特殊的物质和功能器件，并对量子信息、材料科学、生命科学等诸多领域产生深远的影响。扫描隧道显微镜（STM）作为一种极为重要的科学研究工具，在物理、化学、材料、生物等学科领域中有非常广泛的应用。本论文中，我们利用低温超高真空STM研究了表面吸附的单个分子、原子与团簇的量子态（如电子态和自旋态）的探测与调控。

在论文的第一章中，我们首先介绍了扫描隧道显微学的基本理论和论文实验部分所使用的低温超高真空STM的结构、工作原理以及相应的样品制备、数据采集与分析等实验方法，并以单分子物理化学性质研究为例，从单分子表征与探测和单分子操纵两方面系统地归纳和总结了近年来使用扫描隧道显微学对表面吸附体系的各种分析方法和研究手段。

在第二章的工作中，我们利用UHV LT-STM对吸附于Au(111)表面的CoPc分子的物理和化学性质进行了仔细的研究，并通过对单个分子配体（Pc）的操纵来调节和改变其中心磁性离子（ Co^{2+} ）的化学环境，从而实现对单个分子电子态和自旋态的调控。

近藤效应（Kondo effect）来源于凝聚态体系中局域自旋和传导电子的耦合相互作用。其表现为足够低的温度下，在体系的输运性质中出现由于传导电子与局域磁矩作用所导致的散射与共振效应。过去对近藤效应的研究都集中在宏观体材料中。近年来纳米科技的发展，尤其是STM的发明，使得人们从实空间探测和调控单个磁性杂质的自旋及其近藤效应成为可能。金属酞菁和卟啉类的平面大环配合物分子由于其中心可以内嵌带有确定自旋的磁性原子，可以作为单个局域自旋的良好载体。因此我们选择了钴酞菁这一带有单个磁性离子的平面大环配合物分子，对其吸附到表面的单分子体系进行了仔细的研究。

自由的 CoPc 分子中 Co^{2+} 离子中含有未成对电子, 因此存在局域磁矩; 然而当 CoPc 分子吸附到 Au(111) 表面后, 由于分子与衬底的相互作用 (主要通过 Co 离子 d 轨道与 Au 衬底的轴向耦合) Co 离子中局域磁矩完全淬灭。如何通过 STM 操纵来调控其中心 Co 离子的电子态和自旋态成为这项研究中的一个关键难题。我们利用单分子选键化学的方法, 通过针尖施加特定能量的隧道电流激发分子配体外围苯环顶端的 C-H 键, 使苯环脱氢并使脱去 H 原子的苯炔基团与金属表面形成强化学键。在脱去所有 4 个瓣上 8 个氢原子后的 d-CoPc 分子中 Co 离子费米面上出现了强烈的近藤共振峰, 表明 Co 离子的局域磁矩得到了恢复。测量得到的近藤温度 T_K 超过 200 K, 远高于过去实验得到的单原子和单分子体系中的 T_K 。基于第一性原理的理论计算分析和 STM 图像模拟验证了 d-CoPc 局域自旋的存在并重现了实验的结果。我们还对不同吸附环境下的 CoPc 的脱氢及其近藤效应进行了研究, 通过对台阶下分子配体外围苯环的脱氢可以导致整个分子发生剧烈的变化并导致近藤效应的出现, 而台阶处多样的吸附环境和结合方式可以非常有效地调节近藤温度从约 100 K 至 500 K 左右。这一结果表明单个局域磁矩所导致的近藤效应可以通过调控其与周围传导电子的耦合相互作用来任意控制。

在第三章中, 我们用 STM 图像和 $I-t$ 谱研究并澄清了衬底温度为室温以及 420 K 下单个 Ge 原子在 Si(111)-(7×7) 表面的初期吸附形态。

Si 是一种重要的半导体材料, Ge 在 Si 表面的生长在半导体异质结、微纳电子学、光电器件等领域中有着重要的潜在应用。Si(111) 表面存在形式多样、具有复杂周期性结构的多种表面重构, 为各种纳米结构的表面生长和制备提供了良好的基础。单个 Ge 原子与 Si(111)-(7×7) 的相互作用研究对于理解和认识 Ge/Si 半导体界面的微观结构和研究各种 Ge/Si 纳米结构的形成具有重要的意义。虽然 Ge 纳米结构在 Si 表面的生长与吸附得到了广泛的研究, 但长期以来, 对于单个 Ge 原子在 Si(111)-(7×7) 表面的吸附态仍然存在很大的争议。早期的实验与理论研究认为 Ge 原子倾向于吸附在顶戴原子和静止原子的正上端, 然而其他的一些实验却得出了完全不同的结论。透射电子衍射的实验结果表明较高温度下 Ge 原子将随机地取代表面的 Si 原子; 光电子能谱测量则发现了在吸附了 Ge 的表面经过退火后 Ge 取代 Si 原子的证据。然而由第一性原理给出的理论计算结果却又与上面的两种结论截然不同。

为了澄清这一问题, 利用低温 STM, 我们仔细地研究了衬底温度为室温以及 420 K 下 Ge 在 Si(111)-(7×7) 表面的初期吸附形态。我们发现 Ge 原子的吸附在这两种条件下有着显著的区别。衬底温度为 420 K 时, 沉积到表面的单个 Ge 原子随机地取代 Si 表面的顶戴原子。当衬底温度为室温时, 沉积到表面的 Ge 原子并不取代 Si 顶戴原子, 而是在表面扩散。我们通过第一性原理仔细地研究了 Ge 的各种可能吸附位的能量, 并通过与实验 STM 图像的对比确定 Ge 的最稳定吸附位为高配合 G' 位, 其次为 G 位。室温下的 STM 图像表明 Ge 原子在表面 (7×7) 重构的半元胞内快速扩散。78 K 下 STM 图像表明室温沉积 Ge 原子的吸附存在两种状态: 一种状态下, 由于与邻近的 $G(G')$ 之间的跳跃势垒较高, Ge 稳定吸附于顶角顶戴原子附近的 G 位; 另一种状态下, 由于 G' 位之间的跳跃势垒较低, Ge 原子在中间顶戴原子附近的 G' 位之间扩散。同时我们的研究清楚地阐明了热力学上的稳定态是 Ge 原子取代 Si 顶戴原子, 尽管需要在一定的温度下才能有足够的热能量使 Ge 原子到达这一稳定态。如果衬底温度为室温, 则可以存在亚稳的吸附态。基于第一性原理的理论计算和模拟很好地再现了全部的实验现象并验证了 Ge 吸附于 $G(G')$ 位的基本结论。

在论文第四章, 我们通过 STM 并结合第一性原理研究了自组装在 Si(111)-(7×7) 表面的

Ag 纳米团簇的电子态及其输运性质，并发现了一种新颖的整流效应。

纳米团簇仅由非常少的原子构成，其电子态本质上是量子力学的，在量子点器件、生物荧光标记等领域具有非常广阔和重要的用途。研究半导体表面自组装金属团簇的电子态和电子输运性质，将有可能自下而上地构建电子学器件，极大地提高电子器件的集成度，并且能够与目前传统的基于半导体的微电子学很好地兼容，因此具有重要的研究意义。我们以 Si(111)-(7×7) 表面半元胞为模板通过自组装的方法制备出直径仅 1.3nm 的 Ag 纳米团簇，并使用 STM 研究了其电子态和输运性质。

在针尖样品距离 z 较大的情况下，Ag 团簇中心处的 $I-V$ 特性表现出非常强的整流效应，导通电压位于 +0.7 V 左右，整流比 R_R 达到近 40 倍；而减小 z 则整流效应逐渐减弱，在针尖接近样品表面的时候原先的整流效应消失， $I-V$ 特性出现新的整流现象，其起源可能是针尖逼近 Si 衬底时 Schottky 势垒所导致的整流效应。在 $I-z$ 谱中对应于整流效应逐渐减弱的针尖位置区域内出现了表观势垒高度 ϕ_{ABH} 的急剧减小；同时不同隧道结参数下的恒流模式与恒高模式的 STM 图像都表现出与整流效应消除以及 ϕ_{ABH} 的反常减小相关的变化，其中恒高模式 STM 图像中 Ag 团簇的电子态表现出明显的核心-壳层结构，该结构及其空间分布有可能是导致不同 z 下 Ag 团簇输运性质显著不同的原因。我们使用第一性原理对于这一 Ag 团簇进行了初步的理论模拟与分析研究。这一研究结果展示了 Si(111)-(7×7) 表面自组装金属团簇作为纳米电子学器件的潜在应用价值，对于研究其他金属团簇的电子输运性质及电子态调控也具有参考意义。

关键词： 扫描隧道显微镜，单分子，近藤效应，酞菁，半导体表面，纳米团簇，整流效应

Quantum states on the Molecular Scale

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ABSTRACT

The properties of matters in the single-atom and single-molecule regime and the interactions among them are quantum mechanical in nature. Detecting and manipulating the quantum states on the molecular scale are important and essential for future applications in designing and constructing novel artificial structures and functional nanodevices in the “bottom-up” scheme. On the other hand, the recent rapid advances in nanotechnology, especially those based on molecules, are due in large part to our newly acquired abilities to measure and manipulate individual structures at the atomic scale. The scanning probe microscopy and the high resolution electron microscopy have become the powerful techniques with atomic resolution in the study of nanometer-scaled structures, their physical and chemical properties, and in exploration of their applications. Among these microscopes, the STM has shown the most fascinating and useful abilities for directly “seeing” and “touching” matters on the atomic level since its invention by Binnig and Rohrer in 1982. As a local probe, STM is particularly good at directly detecting and manipulating single atoms and single molecules with subatomic precision owing to its very high spatial resolution. Studying single atoms and molecules is of great importance and has attracted much attention in recent years because they have numbers of advantages as basic building blocks of matter and serve as good candidates for conceptually new device components when traditional microelectronics reaches the physical limit. With an STM, we are able to investigate the intrinsic properties of single molecules and their interactions with metallic electrodes, which are fundamental issues of molecule based nanotechnology. The STM also allows us to perform a diversity of single-molecule manipulations using the STM tip to create novel artificial molecular structures mechanically or chemically. In the last decade, scientists have made great efforts in these fascinating subjects and revealed a splendid landscape of material sciences on the atomic and molecular level.

In this dissertation, we demonstrate the scanning tunnelling microscopy study for detecting and manipulating the quantum properties (e. g. electronic properties, spin properties) at the single-molecule scale.

In Chapter I, we briefly introduce the fundamental principles and methods of STM in both experimental and theoretical aspects. In the following part, the working mechanism, data analysis, and sample preparation of the work in the thesis are introduced. We also discuss recent progresses on single-molecule characterization and manipulation with STM as well as the STM techniques employed.

In Chapter II, we studied the physical and chemical properties of single cobalt phthalocyanine

(CoPc) molecules adsorbed on Au(111) surfaces using UHV LT-STM and demonstrated how to manipulate the magnetism and Kondo effect of the cobalt ion in individual CoPc molecules through single-molecule bond-selective chemistry.

The Kondo effect arises from the coupling between localized spins and conduction electrons, and at sufficiently low temperatures, it can lead to change in the transport properties through scattering or resonance effects in nanostructures. Although there have been lots of studies on the Kondo effect of macroscale bulk materials in last century, to study and even to control the Kondo effect of single individual magnetic impurities is still not easy. On the other hand, the Kondo effect is usually studied in systems where spins are permanently introduced into the sample through magnetic ions. For example, recently the Kondo effect has been controlled in quantum dot systems by changing their charging and hence the spin state of the dots. Now we show here that the Kondo effect arising from magnetic ions on the surface of a nonmagnetic conductor can be controlled by changing their chemical environment.

Particularly, we chose metallophthalocyanine in our study because coordination compound molecules with planar macrocycle ligand like phthalocyanines and porphyrins serve as good carriers for metal ions. We show that Co ions, when adsorbed on a gold surface as cobalt phthalocyanine (CoPc), do not interact strongly with conduction electrons and exhibit no Kondo effect. However, after dehydrogenation of the ligand by voltage pulses from a scanning tunneling microscope (STM) tip, the Kondo effect is recovered.

In a free CoPc molecule there is an unpaired electron in the central Co^{2+} ion; but when the molecule is adsorbed on a Au(111) surface, the localized spin is totally quenched due to the strong interaction between the cobalt ion and the gold substrate (mainly through axial coupling of the d orbitals to the Au host). Cutting away eight hydrogen atoms from the molecule with STM allowed the four lobes of this molecule to chemically bond to the substrate. The localized spin was recovered in this artificial molecular structure (dehydrogenated CoPc, d-CoPc) and resulted in a clear Kondo resonance indicating a recovery of the localized magnetic moment of the cobalt ion. The Kondo temperature (higher than 200 Kelvin) derived from the experimental data is much higher than any previous Kondo systems of surface impurities or single molecules. Both variable-temperature STM measurements and comparative experiments using CuPc supported our conclusion that the observed Kondo resonances. First-principles theoretical calculations and simulations agreed well with the experimental results and gave a qualitative explanation to the observed Kondo effect. The high Kondo temperature (more than 200 kelvin) is attributed to the small on-site Coulomb repulsion and the large half-width of the hybridized d-level.

We also find that the Kondo effect of the dehydrogenated CoPc can be tuned by its chemical environment. The Kondo temperatures of different single CoPc molecules adsorbed on Au(111) monoatomic steps were found to be varying from ~ 100 K to 500 K due to the diversity and complexity of the adsorbing and bonding configuration. This result implies that the Kondo effect of a given localized spin can be arbitrarily manipulated by changing its coupling to the host substrate.

In Chapter III, using scanning tunneling microscopy and first-principles density functional calculations, we investigated systematically the initial stages of single Ge atoms adsorbed on a

Si(111)-(7×7) surface.

The growth of germanium on silicon surfaces has received much attention in recent years due to its important potential applications in hetero-semiconductor micro/nanoelectronic and photonic devices. Because of its complex periodic structure and diverse bonding configurations, a Si(111)-(7×7) surface serves as a good substrate for growing various Ge nanostructures such as nanoislands and reconstructed Si(111)-(7×7)-Ge and Si(111)-(5×5)-Ge surfaces. The exact nature of the bonding between Ge atoms and Si(111)-(7×7) surface at the initial stage of adsorption is particularly important for understanding the interactions between Ge and Si, but it is still under dispute both experimentally and theoretically. Early experimental and theoretical works suggested that Ge atoms prefer to occupy the on-top sites of Si adatoms and rest atoms, but these results were not confirmed by later experimental observations. Comprehensive transmission electron diffraction investigations, however, suggested that Ge atoms randomly substitute for Si atoms in the Si(111)-(7×7)-Ge interface at elevated temperature. Evidence was also found in core-level photoemission spectroscopy measurements that there is some preference for Ge atoms to substitute for Si adatoms in annealed samples of Ge deposited on a Si(111)-(7×7) surface. A recent STM study with first principles calculations showed that Ge atoms must substitute for Si adatoms during the initial stage of adsorption at an elevated temperature (420 K). All the above results seem to consistently support the conclusion that Ge atoms substitute for Si adatoms on Si(111)-(7×7) surfaces. This conclusion is in strong contrast with the calculation results in an earlier theoretical study of the adsorption of Ge atoms on Si(111)-(7×7), using a 4×4 unit cell with density functional-total-energy calculations, found that high-coordination bridge (B_2) sites are the most stable adsorption sites for Ge. The difference between the two calculations is in the initial configurations. The former assumed that a single Si adatom diffused away from the unit cell while the latter retained all Si adatoms in position. Thus, one might ask whether the latter configuration can be experimentally achieved.

In this work, we employed scanning tunneling microscopy and spectroscopy techniques combined with full Si(111)-(7×7) unit cell firstprinciples calculations to examine the initial stages and diffusion of single Ge adsorption on a Si(111)-(7×7) surface. We deposited Ge atoms onto the Si surface at different substrate temperatures, namely, at room temperature (RT) and an elevated temperature, to investigate whether metastable states of adsorption exist. There is a strong contrast in the behavior of Ge atoms on the two samples. When the deposition is at a high temperature, Ge atoms do not diffuse but randomly substitute for Si adatoms, which is in agreement with previous works. At RT deposition, there is no evidence showing substitutions of Ge atoms for Si adatoms. Both theory and experiment indicate that G' is the most stable adsorption site and G is the secondary stable adsorption site. During RT imaging, single Ge atoms are found to rapidly diffuse in the half-unit cell of the reconstructed surface. When the imaging temperature is reduced to 78 K, these Ge atoms are found to reside at the G sites near the corner Si adatoms or still hop among the G' sites near the center Si adatoms. The stationary image for Ge at G site is caused by a high diffusion barrier that limits its diffusion to nearby adsorption sites. The fuzzy image for Ge at G' sites is due to fast diffusion over the low barriers among them. Our results also clearly demonstrate that thermodynamically stable states is for Ge atoms to substitute for Si adatoms on Si(111)-(7×7)

surfaces, although sufficient thermal energy is required for the system to reach this stable state. Metastable states can exist if Ge is deposited at RT. The predictions of theoretical calculations, either earlier ones or the present ones, with B_2 or $G(G')$ agree quite well with the experiments.

In Chapter IV, we studied the electronic structure and transport properties of self-assembly Ag nanoclusters on Si(111)-(7×7) surface and found a novel rectification effect.

Rectifier is the basic functional unit in electronic devices. To design or realize a smaller nano rectifier is important for nano-scale electronics. Nanoclusters consist of very few atoms and thus are quantum mechanical in nature. Recent years, the nanoclusters have demonstrated potential applications in various regions including nanoelectronics, medicine, optoelectronics, etc. One of the most feasible methods to prepare identical nanoclusters is using a periodically-structured surface such as Si(111)-(7×7).

In this work, we prepared self-assembly Ag nanoclusters of 1.3 nm in diameter on Si(111)-(7×7) surface and showed clearly rectification effect in the transport properties. The Constant current and constant height STM images, I - V spectra and I - z spectra were measured for understanding the rectification mechanism. Strong rectifying behavior was observed on the Ag nanocluster for larger tip-sample distance, with a rectification ratio close to 40 and an ON voltage of +0.7 V. This rectification decreases with decreasing tip-sample distance, and a new rectification behavior can be observed when the tip approaching to the mechanical contact point, which was considered to be a Schottky barrier effect. An analysis to the z dependence of the apparent barrier height of the system was performed in order to understand the rectification mechanism. We also performed some first-principles theoretical calculations and simulations to the geometric and electronic structure of the Ag nanocluster. Some tentative results were obtained for further analyses. This study demonstrates the potential application of single metallic nanoclusters in nanoscale electronics.

Key words: STM, single molecule, Kondo effect, phthalocyanine, semiconductor surface, nanocluster, rectification