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厦门大学

中美联合培养博士学位论文

不同维度结构材料的构筑及其半导体性质

The growth of different-dimensional structural materials and their semiconducting properties

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摘要

随着信息技术的不断进步，信息表达和处理方式逐渐趋向高速度、高密度、高可靠的方向发展。低维纳米材料作为一种具有全新结构的材料，其微小的尺度正符合了当今信息社会对电子器件集成度日益增长的要求。而当材料进入低维小尺度时，往往表现出许多独特的效应，例如相变特性，电子输运现象，电导涨落和库仑阻塞等，为开发具有新原理、新结构的固态电子、光电子器件提供了广阔的发展空间。近年来，各种制备和表征技术的持续进步，以及组装工艺的日臻完善，推动着低维纳米材料由研发制备向器件应用的方向发展。同时，也对其结构性质、形成机制等方面的研究提出了更高的要求。就目前的发展形势来看，各种类型的低维材料在可控制备、结构表征、器件应用等方面仍存在着一定程度的不足，成为制约其进一步发展的瓶颈。因此，本论文围绕零维、一维、二维等不同维度的典型纳米材料及其异质结构，针对亟待解决的问题，从理论模拟、材料制备、结构表征、性质探索、器件应用几个主要方面展开研究，具体内容包括以下三个部分：

(1) 在 Si(111)-(7×7)表面上制备了零维的全同 Au 团簇，并通过 STM 技术观测其在不同偏压下的电子态形貌。结合第一性原理总能计算和 STM 形貌模拟确认其由 6 个 Au 原子和 3 个 Si 原子组成，为 Au_6Si_3 构型。该结构最大程度地饱和 Si(111)-(7×7)表面悬挂键，使体系的总能大幅度降低，从而具有最强的稳定性。其形成机制可归因于 IB 过渡族金属 Au 的电子价态特性和 Au 和 Si 之间的相互作用。STS 测量结果表明，Si(111)-(7×7)表面 Au_6Si_3 团簇的形成对其所占据的层错半单胞和邻近的无层错半单胞的电子态密度分布均产生重要的影响。首先，Si(111)-(7×7)表面位于-0.6 V 和+1.0 V 处的 Si 中心顶戴原子悬挂键被饱和，从而在费米能级附近产生宽度约为 1.8 V 的禁带，使原先具有金属导电性的 Si(111)-(7×7)表面和 Au 都显示出半导体特性；同时，Au_6Si_3 团簇的形成使邻近无层错半单胞中最近邻的 Si 中心顶戴原子在-0.6 V 处的占据电子转移到团簇中，进一步提高了团簇在 Si(111)-(7×7)表面的稳定性。

(2) 采用微波等离子体 CVD 法生长 ZnO 四脚纳米结构，该结构由一个零维的

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中心体与四根一维纳米棒连接而成。其中纳米棒在 HRTEM 图像中呈显 WZ 晶格构型，而与中心体连接处的原子堆叠次序由 *AB* 转变为 *ABC*，表明了 ZB 结构 ZnO 的出现。拉曼散射光谱结合第一性原理模拟的声子色散曲线首次确认了 ZB 结构 ZnO 的 LO 和 TO 声子模的拉曼频率，且证明 ZnO 四脚纳米结构的中心体和四根纳米棒分别为 ZB 和 WZ 结构。动力学模拟结果显示，当 ZnO 在室温下承受高于 26 GPa 的流体静压强时，ZB 相将转变为稳定结构。据此，分析表明，ZnO 四脚纳米结构晶核生长初期晶粒尺度很小，所受的拉普拉斯应力可高达 25~30 GPa。此时 ZB 比 WZ 结构 ZnO 的吉布斯自由能更低，ZnO 生长优先选择了 ZB 结构；随着晶粒的长大，拉普拉斯应力逐渐减小，并在 ZB 晶粒的四个等价{111}生长前沿将率先超过临界尺寸，使 ZB 结构不再具有稳定存在的低能优势，此后，从 ZB{111}面上生长的四根一维纳米棒为 WZ 结构，于是形成了四脚纳米结构。这一结果揭示了四脚 ZnO 的分级结构，同时澄清了其形成机制。此外，阴极荧光测量结果表明，四脚 ZnO 特殊的结构使其中心体的发光峰较纳米棒而言呈显出略低的峰位和更高的强度。

(3) 采用热壁 CVD 系统，在 Cu-Ni 合金表面制备了二维的石墨烯薄膜。通过碳同位素标定，结合拉曼散射谱像扫描法，揭示了石墨烯在 Cu-Ni 合金表面的生长为溶解析出机制，较高的生长温度、较长的生长时间均产生较高覆盖度的石墨烯薄膜。对比采用 $^{12}CH_4$ 和 $^{13}CH_4$ 气体生长的 ^{12}C-和 ^{13}C-石墨烯发现，即使在相同的生长条件下，^{12}C-石墨烯的覆盖度均明显高于 ^{13}C-石墨烯，表明合金体内碳原子的扩散系数是石墨烯生长的重要参数。冷却速率不仅影响石墨烯薄膜的覆盖度，还可以调控其同位素组分，是碳原子析出过程的关键性因素。除了单层和亚单层石墨烯以外，我们还成功制备了大面积双层石墨烯薄膜，并通过拉曼散射光谱和 TEM 选区衍射图像，证明其为具有强烈层间耦合的 *AB* 堆叠结构。进一步采用第一性原理模拟石墨烯与团簇和薄膜这两种不同形态结构的 Au 接触的宏观平均电势的差别，揭示了两体系电子呈现出相反转移方向的特性。运用表面沉积技术在 CVD 生长的石墨烯表面构建零维 Au 团簇和二维 Au 薄膜，结合拉曼散射光谱和 TEM 形貌观测证实了零维 Au 团簇在石墨烯中引入 *n* 型电导，而二维 Au 薄膜则使其呈现 *p* 型电导的规律。以此为基础制作了石墨烯 FET 器件，通过精确控制沉积 Au 的形态及覆盖度，实现对石墨烯电导类型和载流子浓度的有效地调控，拓展了

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石墨烯在微电子领域的应用。

关键词：Au 团簇；ZnO 四脚纳米结构；石墨烯；原子构型；形成机制；电子结构；化学气相沉积；电导调制；第一性原理计算。

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Abstract

As the development of information technology, the information expression and process tend gradually to high speed and reliability. Low-dimensional materials with their novel structures are consistent with the increasing integrity requirements of electronic devices in current information society. Moreover, as the materials reduce into low-dimensional region, many unique effects emerge, involving phase transition, electron transport, conductance fluctuations and Coulomb blockade, which provide a broad developing space for photoelectric devices. However, the controlled-synthesis, characterization, and applications are still challenging for various low-dimensional materials, which strongly restrict its further development. To cover these critical issues, the thesis mainly focuses on the aspects of theoretical simulation, material preparation, properties characterization, and devices applications, to study the typical zero-, one-, two-dimensional materials. The major results are as follows:

We successfully fabricated zero-dimensional Au clusters with identical size on Si(111)-(7×7) surface. The topographical images obtained by *in situ* (STM) show a bias-dependent feature. According to counting statistics, the adsorption of Au clusters displays a preference for the faulted half unit cells (FHUCs). The first-principles adsorption energy calculations, combined with the STM images indicate a Au_6Si_3 geometrical cluster structure with the fully saturated surface dangling bonds. The formation mechanism of this atomic configuration is intimately associated with the complicated chemical valences of Au and the interaction between Au and Si(111)-(7×7) surface. *In situ* STM was used to characterize the current-voltage properties, and the results suggest that adsorption of Au_6Si_3 cluster significantly influences the electronic structures of both the unfaulted and faulted half unit cells. First, the saturation of metallic Si adatom dangling bond states at about -0.6 V and +1.0 V lead to the semiconducting characteristics of cluster adsorbed Si(111)-(7×7) surface. Moreover, the surface dangling bond state at about -0.6 V transfers from the the closest Si center

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adatom in neighboring unfaulted half unit cells to the cluster, which further stabilizes the cluster structure.

ZnO nano-tetrapods were synthesized by the microwave plasma method. The hierarchical lattice structure of ZnO nano-tetrapods with ZB core and WZ legs is demonstrated by means of microscopical analysis, Raman spectroscopy and theoretical calculations. Crystal orientation or structure of the legs is imaged to be different from that of the core in dark-field transmission electron microscopy(TEM). The stacking sequence change during the phase transformation could be clearly observed in the boundary of the core and legs in HRTEM images. Raman spectroscopy was employed to study large number of ZnO nano-tetrapods. To our knowledeg, it is the first time to detect the ZB phase in ZnO nano-tetrapods by Raman spectra, and determined by the first principles calculated phonon dispersion relations. Based on these results and the considered lattice symmetry, the atomic configuration of ZnO nano-tetrapods is constructed with one ZB core connecting to four WZ legs, which is coincident with the HRTEM images. First-principles molecular-dynamics simulations suggests that as the hydrostatic pressure reaches to about 26GPa, ZB structure of ZnO can be stabilized with lower Gibbs free energies than that of WZ structure. Accordingly, the formation mechanism induced by Laplace pressure in the initial growth stage of ZnO nano-tetrapods is proposed.

A hot wall chemical vapor deposition system was used to synthesize two-dimensional graphene films on Cu-Ni alloy foils. Carbon isotope labeling in conjunction with Raman spectroscopic mapping reveals a surface precipitation mechanism of graphene growth. The growth parameters were modulated to investigate their effect on graphene coverage and isotopic composition. It was found that higher carbon deposition temperature, longer deposition time, higher diffusion coefficient, and slower cooling rate all produced higher graphene coverage on Cu-Ni alloy foil. The isotopic composition in graphene could also be modified by adjusting the cooling rate. Based on the understanding of the growth mechanism and the effects of growth parameters, large area, uniform bilayer graphene was obtained, with the Raman spectrum and TEM selected

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area electron diffraction measurements suggesting an AB-stacked structure. Furthermore, using the first-principles calculations, the conductivity type of Au-graphene system was found to be tunable due to the charge transfer between graphene and different Au configurations. To verify the theoretical results, Au nanoparticles and films were deposited onto clean graphene surfaces to examine the effect of interactions. Micro-Raman spectra show that both the conductivity type and carrier density of graphene can be tuned by fine control of the Au deposition. The morphological structures of Au on graphene are imaged by TEM, which indicate a size-dependent electrical characteristic: isolated Au nanoparticles produce *n*-type doping of graphene, while continuous Au films produce *p*-type doping. Accordingly, graphene field effect transistors were fabricated, with the *in situ* measurements suggesting the tunable conductivity type and level by contacting with different Au configurations.

Keywords: Au clusters; ZnO nano-tetrapods; Graphene; Atomic configuration; Growth mechanism; Electrical properties; Conductivity modulation; The first-principles calculation.

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