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厦门大学

硕 士 学 位 论 文

一维硅纳米材料的制备、表征及作为锂离子电池负极材料的研究

Synthesis and Characterization of One-dimensional Si Nanomaterials and their Applications as Negative Electrodes in Lithium Ion Batteries

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目　录

Table of Content

摘　要

一维硅纳米材料，以硅纳米线和硅纳米管为代表，具有易与当前成熟的集成电路工艺相兼容的特征，又可在纳米限域效应方面发挥其独特的性能，因此成为目前科学研究的热点和前沿。本文采用化学气相沉积的方法制备了硅纳米线和不同形貌的硅纳米管，并对材料进行了详细地形貌和结构表征，结合大量的实验证据，提出了这些材料可能的生长模式。考察了硅纳米线和竹节状硅纳米管的发光特性和一级 Raman 散射光谱。同时，对硅纳米线作为锂离子电池负极材料的应用进行了初步的研究。本论文的主要研究结果如下：

1. 以金纳米颗粒为催化剂，硅烷为硅源，氢气为载气，通过调节硅烷的流量制备出硅纳米线和硅纳米管，同时在不同的温度 400°C、480°C 和 600 °C 下制备了不同形貌的硅纳米管，包括金填充的竹节状硅纳米管、竹节状硅纳米管和中空的硅纳米管。通过扫描电子显微镜（SEM）和透射电子显微镜（TEM）分析，硅纳米线是单晶的结构，直径为 50nm 左右，沿[111]方向生长。三种硅纳米管均为非晶态结构，但形貌存在差异：①竹节状硅纳米管的直径约为 70-100nm，内部周期性且沿轴排列着类似于钟形屋顶的空心，外壁呈波浪型；②金填充的硅纳米管，直径大概为 50nm，催化剂金间歇性地沿轴向填充在竹节状硅纳米管的实心部位，空心的尖端更尖，纵横比更大，类似于三角锥型，填充的金颗粒为单晶颗粒，呈拉长的椭圆形状，通过电子能谱点扫描及线扫描分析，进一步确定了该材料的成分和金填充的竹节状结构；③中空的硅纳米管，直径为 80nm～150nm 左右，内部每个屋顶型空心单元完全连通，形貌类似于通常的硅纳米管，外壁光滑，内壁却是凹凸曲折的。

2. 基于前人对竹节状硅纳米管生长模型的研究，我们综合考虑了流量和温度等因素，并在实验的基础上，对不同形貌硅纳米管的生长模型进行了完善和深化。材料成核和生长主要由硅沿液滴合金表面扩散控制。在温度较高条件下，硅析出时曲率半径增加，致使合金液滴表面产生附加压力，这种随曲率半径逐渐增加的异向作用力挤压合金液滴，达到临界值时将液滴挤向另一端，留下空心。如果该推挤的时间大于硅沿催化剂上部扩散到底部的时间，则在空心的底部会形成

实心的间隔层。挤压的过程反复进行，最终形成周期性排列的竹节空心结构即竹节状硅纳米管。温度的升高，会致使推挤速度和扩散速度均变快，如果此时推挤时间小于扩散的时间，则空心的底部未完全被硅包覆，空心单元之间呈连通状态，最终形成中空的硅纳米管。而在温度较低时，硅烷的分解速度和硅的扩散速度均降低，导致附加压力无法将液滴挤向另一端，而是在附加压力作用下被拉长，并收缩成两个催化剂颗粒和一个空心的间隔层。

3. 考察了硅纳米线（SiNWs）和竹节状硅纳米管（SiNTs）光致发光和阴极荧光特性，SiNTs 室温 PL 谱的中心在 455 和 500 nm 位置，而 SiNWs 在 455 和 530 nm，SiNTs 的发光强度比 SiNWs 高一个数量级。随着温度的降低，两者的发光强度皆逐渐增强，当温度低于 200 K 左右，两种硅纳米材料在 417 和 440 nm 均出现了两个新峰，这是由过剩硅纳米晶粒形成的含有硅空位缺陷引发的。SiNTs 有两个阴极发光带，分别是 470 和 630 nm，这与 SiNWs 的发光带相同。

4. SiNTs的Raman光谱存在 488 cm^{-1}和 520 cm^{-1}两个峰，分别对应SiNTs主体部分的非晶态硅和过剩硅晶粒的晶态硅的谱峰。晶态SiNWs的Raman谱峰向低频方向发生了不对称宽化，同时可在 494 cm^{-1}观察到一肩峰。随着激光功率的降低，SiNWs在 494 cm^{-1}处的肩峰逐渐变得尖锐可见，且不随激光功率的变化而发生频移；而 508 cm^{-1}谱峰，峰形对称，随激光功率的降低谱峰强度相应降低，并有逐渐蓝移倾向。

5. 采用两种方法制备电极：一种是采用涂膜法，将制备的硅纳米线与导电剂及粘合剂混均后涂膜并压制在导电基底上，制成电极；另一种是直接生长成膜法，即在导电基底上直接生长硅纳米线，形成电极。涂膜法制备的硅纳米线电极循环性能差，而直接生长纳米线制备的硅纳米线电极具有良好的循环特性，容量保持率较优异。随着充放电电流的增加，这种硅纳米线仍表现出较高的充放电容量，同时也展现出良好的循环稳定性。采用X射线衍射（XRD）表征了硅纳米线电极在首次放电过程中不同截止电压的结构，表明晶态硅随着嵌锂的进行逐渐转变为非晶态，并且这种非晶状态在随后的脱嵌锂过程中始终保持；同时，在不同的嵌锂状态下均没有检测到新的晶相物质生成，这表明锂嵌入硅后生成的物质为非晶态Li_xSi。对比未经放电的硅纳米线电极和不同嵌锂状态对应的电极的表面形貌，发现随着嵌锂过程的进行，硅纳米线的直径逐渐地增大，但硅纳米线的线状

结构仍保持完好，没有出现粉末化和破碎现象。这与硅纳米线的一维结构密切相关，一方面一维结构可以沿横向（直径）和纵向（长度）膨胀，有效的缓冲了体积效应；另一方面，每根纳米线之间都有效地提供了空隙，这些空隙有利于缓冲硅体积膨胀导致的粉末化，使硅纳米线保持完好的一维结构。

关键词： 硅；纳米线；纳米管；锂离子电池；负极材料；光学性质

Abstract

One-dimensional silicon-based nanoscale materials have attracted great interest in the last few years owing to the excellent compatibility with the present silicon technology, and the superior and unique properties of quantum confinement effect and small size effects. Silicon nanowires (SiNWs) and silicon nanotubes (SiNTs) with various morphologies were successfully fabricated by using chemical vapor deposition method. The morphologies, structures and compositions of these nanomaterials were investigated in detail. Furthermore, the optical properties of SiNWs and SiNTs were analyzed though Raman, PL (Photoluminescence) and CL (Cathodoluminescence) spectrum. The application of SiNWs as anode materials in lithium ion batteries was also studied.

The main results are summarized as follows:

1. Different one-dimensional silicon nanomaterials, i.e., SiNWs and SiNTs, were synthesized by chemical vapor deposition of SiH_4 at 480 ^oC through controlling the flow rate of SiH_4 at 10 sccm and 5 sccm. By increasing the growth temperature from 400 °C to 600 °C, the transition from gold-encapsulated, bamboo-like SiNTs of smaller diameters (400 °C) to bamboo-like SiNTs (480 °C), and eventually to completely hollow SiNTs of larger diameters (600 °C) was observed. For the samples grown at 400 °C, the nanostructures have diameters of around 50~70 nm. As the growth temperature increases, the diameters of the products increase to 70~100 nm at 480 °C and 80~150nm at 600 °C. All the three samples are amorphous, while the morphology are different from each other. ①The products obtained at 480 °C are bamboo-like SiNTs, which are composed of a series of periodic dome-shaped hollow compartments. In addition, we found that the encapsulated catalytic particles are located at the tips of the SiNTs, and the nanotubes have a wave-shaped outer surface. ②Compared to the bamboo-like SiNTs with dome-shaped interior grown at 480 °C, the products grown at 400 °C reveal that gold nanoparticles are encapsulated along the bamboo-like SiNTs, which we called gold-encapsulated SiNTs with dome-shaped

interior. ③The hollow interiors along the tubular structures synthesized at 600 °C tend to connect with each other, and the products are inclined to form completely hollow SiNTs. No crystal lattice stripes were observed in the HRTEM (High resolution Transmission Electron Microscopy) images, suggesting that all the three samples are amorphous, which were further confirmed by selected area electron diffraction.

2. A modified vapor-liquid-solid (VLS) mechanism was proposed to explain the formation of different morphologies of SiNTs. When the liquid droplet becomes supersaturated, silicon growth begins at some nucleation site. At this time, the radius of curvature of one side on the droplet becomes smaller than the other side, which leads to the formation of the additional pressure on the gold surfaces. Thus the liquid droplets are squeezed away by these anisotropic pressures, leaving a dome-shaped (similar to geometry of Au particles) void. If the surface diffusion at 480 °C is quick enough to completely wrap the liquid droplet before the additional force to reach a critical point, a solid part will be formed between two dome-shape voids and lead to the obtain of bamboo-like SiNTs. Otherwise, defects will be formed between the two adjacent hollow parts and the formation of silicon nanotubes with completely hollow interior is preferred. At lower temperature (e.g., 400 °C), the liquid droplet will be elongated, instead of being squeezed away suddenly. Driven by the decrease of the surface free energy, the two parts of the elongated particle will separate suddenly, subject to the formation of two individual gold nanoparticles and compartment with dome-shaped void.

3. Photoluminescence spectroscopy (PL) and cathodoluminescence spectroscopy and imaging (CL) was used to investigate the optical properties of SiNWs and SiNTs. Two major broad bands were found around 455 and 500 nm for SiNTs, and 455 and 530 nm for SiNWs, respectively; however, the PL intensity of SiNTs was much higher than that of SiNWs. As temperature decreased, both the PL intensity of SiNWs and SiNTs increased gradually. When the temperature was lower than 200 K, these materials appeared two blue emission bands which were attributed to the excess Si atoms in Si nanostructures. The CL spectrum of bamboo-like SiNTs, which is the

same as that of SiNWs, has two major bands 470 and 630 nm.

4. The SiNTs were observed at about 420 and 520 cm^{-1} by Raman scattering measurements which were attributed to amorphous SiNTs and excess Si atom in the nanostructures, respectively. Raman spectroscopy of crystalline SiNWs showed a downshift and asymmetric broadening of the Raman first order TO (First-order transverse optical phonon mode，1TO) phonon peak when compared with the bulk mode, and a shoulder peak at 494 cm^{-1} was also observed. As the decrease of the laser power, the shoulder peak became clear, while did not shift with the changes of the laser power. The 1TO phonon peak shifted from 508 cm^{-1} to lower wave number as the decreasing laser power.

5. SiNWs electrodes were fabricated by two methods. Method I is to spread as-synthesized SiNWs slurry on current collector; Method II is to directly synthesize SiNWs on a substrate of stainless steel. The electrodes prepared by Method I have shown capacity fading and short battery lifetime, while the other one has a stable capacity over many cycles. The SiNWs prepared by Method II also displayed high capacities at higher currents. In addition, the cyclability of the SiNWs at the faster rates was also excellent. X-ray diffraction (XRD) patterns of SiNWs electrodes (Method II) at open circus potential and various cut-off potentials during the initial discharging process reveal the disappearance of the initial crystalline Si and the start of the formation of amorphous Li_xSi. The structural features of SiNWs during the initial Li insertion process were studied by SEM (Scanning electron microscopy) and TEM (Tranmission electron microscopy) to understand the high capacity and good cyclability of our SiNWs electrodes. SiNWs before electrochemical reaction were crystalline. However, after charging with Li, the SiNWs had roughly textured sidewalls, and the average diameter increased. Despite the large volume change, the SiNWs remained intact and did not break into smaller particles which are closely related to the 1D structure. Facile strain relaxation in the SiNWs allows them to increase in diameter and length without breaking. Furthermore, the space between each SiNWs allows for better accommodation of the large volume changes without the initiation of fracture that can occur in bulk or micron-sized materials.

Key words： silicon, nanowires, nanotubes, Li-ion batteries, anode materials, optical properties