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内 容 简 介

本英文专著是国内外第一部介绍硅纳米线的著作。作者论述了硅纳米线的制备、结构、性能和应用；引用了国内外大量的原始文献，结合自己的实验，阐述了硅纳米线的背景、现状和前景。作者还通过 X 射线衍射分析、拉曼光谱、能量色散 X 射线光谱、透射电子显微镜和高分辨透射电子显微镜等设备拍摄了大量硅纳米线及其相关纳米线的照片。本书附有中文译文、参考文献等。该书的主要内容曾获首届香港城市大学优秀博士学位论文奖及 2005 年度的中国国家自然科学二等奖。

图书在版编目(CIP)数据

硅纳米线分析 = Analysis of Silicon Nanowires/唐元洪著 .
—长沙：湖南大学出版社，2006. 3

ISBN 7 -81113 -014 -9

Ⅰ. 硅…　Ⅱ. 唐…　Ⅲ. 硅—纳米材料—分析—英、汉

Ⅳ. TB383

中国版本图书馆 CIP 数据核字(2006)第 012206 号

Analysis of Silicon Nanowires
硅纳米线分析

作　　者：唐元洪　著
责任编辑：严小涛　　**责任印制**：陈燕
装帧设计：吴颖辉
出版发行：湖南大学出版社
社　　址：湖南·长沙·岳麓山　　**邮　　编**：410082
电　　话：0731 -8821691(发行部)，8821334(编辑室)，8821006(出版部)
传　　真：0731 -8649312(发行部)，8822264(总编室)
电子邮箱：yanxiaotao@ hnu. cn
网　　址：http://press. hnu. cn
印　　装：湖南新华精品印务有限公司
开本：880 ×1230　32 开　　**印张**：9. 5　　**字数**：230 千
版次：2006 年 3 月第 1 版　　**印次**：2006 年 3 月第 1 次印刷
印数：1 ~2 000 册
书号：ISBN 7 -81113 -014 -9/TB · 5
定价：48. 00 元

作者简介

唐元洪 1965年1月出生，湖南长沙人。现为湖南大学教授、博士生导师，“岳麓学者”特聘教授，“985”首席科学家（纳米材料分析），湖南大学材料科学与工程学院副院长，湖南大学纳米技术与信息材料研究所所长。同时为教育部首届新世纪优秀人才、湖南省新世纪121人才、教育部高等学校材料物理与材料化学教学指导委员会委员，中国国家同步辐射实验室用户专家委员会委员，于1985年、1988年在湖南大学分别获得学士、硕士学位，然后留校任教。1996年10月进入香港城市大学材料物理系攻读博士学位，并于2000年8月获得博士学位，2000年9月至2002年9月在加拿大西安大略大学化学系做博士后，2002年10月至2003年8月任位于加拿大首都渥太华的加拿大科学院（NRC）客座研究员，获得2002年度加拿大国家自然科学与工程委员会（NSERC）客座研究员奖。2003年9月提前回国加盟母校湖南大学。其从事纳米硅材料研究长达十年，在Phys. Rev. Lett(物理评论快报)，Adv. Mater（先进材料），Appl. Phys. Lett（应用物理快报）等国际著名权威杂志上发表相关论文多篇，总引用次数高达1007次。本英文专著为国际上第一本硅纳米线专著，其主要内容曾获首届香港城市大学优秀博士学位论文奖及2005年中国国家自然科学二等奖。

ABSTRACT

Quasi one-dimensional Si nanowires (SiNWs) have aroused much attention recently since SiNW is one of the most promising candidates for future nanoscale functional semiconductor materials. Many synthesis methods have been developed in order to obtain SiNWs in large scale at low cost. Among these methods, the laser ablation method is the most promising method. It is because this method can produce various free-standing nanoscale materials in high yield and purity with controllable experimental conditions.

More recently, we have achieved large scale synthesis of SiNWs with high purity by the laser ablation method. The yield and linear growth rate could reach 30 mg per hour and 500 microns per hour respectively. The SiNWs deposits were characterized by X-ray diffraction (XRD), Raman, energy dispersive X-ray spectroscopy (EDS),

transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM).

TEM study showed that the SiNWs were extremely long (millimeters in length) and highly curved, with a typical diameter of about 16 nm. Each nanowire consisted of an outer layer of Si oxide and a crystalline Si core. A high density of defects, such as stacking faults and microtwins, has been observed in the crystalline Si core. As identified with selected-area electron diffraction (SAED) and HRTEM, the axes of the nanowires generally lay along <112> directions, and the {111} surfaces of the Si crystalline core were parallel to the axis of the nanowire.

In general, over 95% SiNWs have smooth surfaces and uniform diameters. However, in addition to this normal form of SiNWs, four other different forms of the nanowires, named spring-shaped, fishbone-shaped, frog-egg-shaped, and necklace-shaped SiNWs, were also observed. The morphologies of these nanowires were studies by TEM.

We found that the presence of oxides in the target is an important ingredient for the synthesis. Upon laser ablation, various kinds of semiconductor oxides would be generated. Subsequent decomposition of the vapor-phase oxides at high temperatures plays a crucial role in the nucleation and growth of the nanowires. In the case of pure Si target, SiNWs can also be synthesized from metal-, SiO_2-, Fe_2O_3-containing Si targets or directly from SiO powder. Irrespective of the oxide type contained in the target, the resulting nanowires show no difference in their morphology and microstructure.

This oxide-assisted growth mechanism has been successfully extended to other synthesis methods, such as thermal evaporation, hot-filament chemical vapor deposition (HFCVD), microwave chemical vapor deposition (MWCVD) etc. It can also be used to synthesize other semiconductor nanowires, such as Ge nanowires.

As the SiNWs have ultrafine tips and are promising materials for electronic applications, such as cold-cathode field-emission device, we have also studied its field emission properties. The turn-on field of SiNWs is 15 V/μm which is comparable to those of other field emitters including carbon nanotubes and diamond. It is anticipated that the field-emission characteristics of SiNWs may be improved by oriented growth.

CONTENTS

1

INTRODUCTION

1.1 Silicon and its significance

Silicon (Si) is the most important material in today's information age. The hearts of computers and many other electronic products are integrated circuit (IC) chips made of Si material. Si is one of the most studied elements in the periodic table. Si is the second element to oxygen in abundance and Si compounds comprise 25% of the Earth's crust.[1] So device grade Si costs much less than other semiconductor materials and very-large-scale integration (VLSI) becomes synonymous with well-established Si VLSI technology.[2]

In term of structure, Si is a material where the silicon atoms are bonded with four neighbours and this situation is periodically repeated in exactly the same way. The equilibrium phase of crystalline semiconductor silicon under normal pressure and temperature conditions has the diamond cubic structure as schematically shown in Figure 1. This structure can be viewed as two interpenetrating face-centered cubic (fcc) lattices. The lattice constant "a" is 0.543 106 3 nm.[3] Other forms of silicon which are commonly used during IC processing are amorphous and crystalline and polycrystalline silicon mostly deposited by chemical vapor deposition (CVD) techniques. Under certain conditions small clusters of hexagonal silicon, which is a high pressure phase of silicon, have also been observed in silicon substrates after low temperature processing. A number of other high pressure silicon phases obtained under extreme pressure conditions are also reported in the literature, some of them having metallic or even superconducting properties.[4]

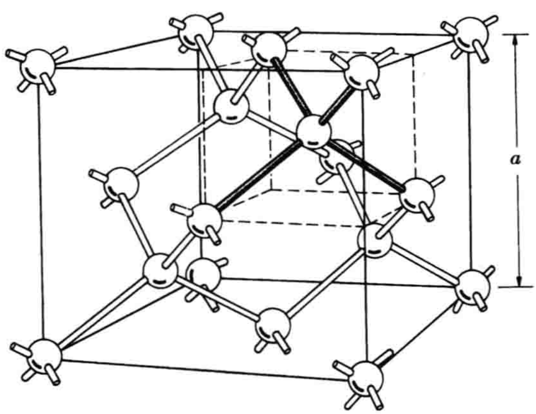

Figure 1 A schematic diagram of silicon lattice

Properties of silicon have been extensively studied. Electronic properties are the most important ones among them. The main properties of intrinsic silicon are listed in Table 1.[5] Other properties including optical and thermal data can be easily found in textbooks.[6] These properties describe the characters of bulk silicon, or three-dimensional silicon. The properties can be accurately determined because large scale synthesis of high purity bulk silicon materials have been achieved. As the base material of nanoelectronics, large scale synthesis of one-dimensional silicon material or Si nanowire (SiNW) has aroused much attention.

Table 1 Properties of intrinsic silicon

Atomic number	14
Atomic weight	28.1
Density/(g/cm^3)	2.33
Relative permittivity	11.9
Atoms/cm^3	5.0×10^{22}
Energy gap E_{G0} at 0 K/eV	1.21
Energy gap E_G at 300 K/eV	1.12
Resistivity at 300 K/$\Omega \cdot cm$	2.30×10^5
Electron mobility μ_n at 300 K/[$cm^2/(V \cdot s)$]	1 500

Continued

Hole mobility μ_p at 300 K/[cm^2/(V · s)]	475
Intrinsic concentration at 300 K/cm^{-3}	1.45×10^{10}
Electron diffusion constant D_n at 300 K/(cm^2/s)	34
Hole diffusion constang D_p at 300 K/(cm^2/s)	13

1.2 Overview of one-dimensional materials

Considerable interest has been aroused recently by the successful synthesis of various nanotubes and nanorods materials. Si nanowires is one of the most important nanorods. The large scale synthesis of Si nanowires in the present work is in fact stimulated by the recent progress in the synthesis of carbon nanotubes. So the progress in the research of carbon nanotubes is briefly reviewed here.

In 1991, Iijima of NEC corporation published a paper in *Nature* magazine entitled "Helical microtubules of graphite carbon".[7] Carbon nanotubes ranging from 4 to 30 nm in diameter and up to 1 μm in length were synthesized by an d. c. arc-discharge evaporation method similar to that used for C_{60}.[8~10] Nanotubes appeared perfectly graphitized and capped at both ends with pentagons, just like the fullerene molecules. Most important of all, Iijima noticed that the carbon atoms in each nanotube's closed shells were arranged with various degrees of helicity, i. e. the path of carbon bonds formed a spiral around the tube.

This discovery excited the whole science community. From a material point of view, carbon nanotubes were seen as the ultimate fiber with an exceptional strength-to-weight ratio. Theoretical scientists revealed that the nanotube would be either a metal or a semiconductor, depending not only on the diameter but also on the helicity.[11~13] As with carbon fibers, perhaps the most important potential application of carbon nanotubes is based on the use of their mechanical properties, in particular their high strength-to-weight ratio. Nevertheless, nanotube can offer intriguing possibilities for materials science. Its inner hollow cavity can serve as a nanoscale test tube or mold, while the outer shell could be decorated to yield catalysts with unique properties due to the high curvature.[14] Capillarity work on metal oxide has been done by Ajayan et al.[15~17] At the same time, organic solvents wetting experiment was completed by Tsang et al.[18] They used nitric acid HNO_3 to open the nanotube tips by oxidation and fill the nanotube with a metallic compound dissolved in an acid. In other words, the nitric acid acts first as a tube opener and then as a low surface tension carrier to introduce material inside the nanotube that otherwise would not have gone in spontaneously. This technique should be very useful for filling nanotubes with a variety of materials. Besides nanotubes can also have applications in other areas. Experiments indicate that nanotubes can be used as atomic-scale field emitters,[19,20] pinning material in high-T_c superconductors,[21] nanoprobes in scanning probe microscopy[22] and coherent electron source[23].

Therefore, low cost methods for producing large quantities of perfectly graphitized nanotubes are needed for such applications. Responding to the need, Ebbesen and Ajayan in the same laboratory of Iijima presented a paper entitled "Large-scale synthesis of carbon nanotubes" in *Nature* magazine.[24] They use a variant of the standard arc-discharge technique for fullerene synthesis under helium atmosphere. Discharge occurs between two graphite rods of different diameters. On the large graphite rod, a rod-shaped deposit formed and it contained nanotubes in gram quantities. The diameter of the nanotubes ranges from 2 to 20 nm, whereas the lengths are several microns. The tips of the tubes are capped with pentagons as reported by Iijima.[25] This large scale synthesis of nanometer fibrous materials with large aspect ratios of length/diameter, such as the carbon nanotubes, is of importance in materials science.[26] Large quantities of carbon nanotubes can also be produced by another methods, such as thermal deposition of hydrocarbon or CVD.[27,28]

A few years after discovery of carbon nanotubes, a paper entitled "Large scale synthesis of aligned carbon nanotubes" appeared in *Science* magazine at the end of 1996.[29] In this paper, Li et al. reported the large quantities synthesis of aligned carbon nanotubes using a method based on thermal deposition of hydrocarbons catalyzed by iron nanoparticles embedded in mesoporous silica. SEM images show that the nanotubes are approximately perpendicular to the surface of the substrate with spacing between the nanotubes of about 100 nm. The nanotubes are up to about 50 μm long and well graphitized. Except arc-discharge and thermal deposition methods, laser ablation of graphite can also produce carbon nanotubes.[30~32] The advantage of this method is that high quality carbon nanotubes can be produced in higher yield. This is the reason why this method is used here to synthesize Si nanowires.

Success in carbon nanotube research led to discoveries of other kinds of nanotubes and nanorods. BN[33,34] and BCN[35] nanotubes have been synthesized by arc-discharge method while MoS_2[36] nanotubes have been produced by CVD method of the gas-phase reaction between MoO_{3-x} and H_2S in a reducing atmosphere at elevated temperatures. Carbide nanorods including TiC, NbC, Fe_3C, SiC and BC_x have been produced by converting carbon nanotubes into carbide nanorods by reaction with volatile oxide and/or halide species.[37]

1. 3 From three-dimensional to one-dimensional silicon

As a kind of nanorods, researchers also believe large scale synthesis of Si nanowires is possible and success in this field may change our life. Microelectronics, which change our life from TV to computer, is so-called because it is based on device dimensions of a few microns. Nanoelectronics will become the successor of microelectronics when dimensions of future generation electronic devices can be greatly reduced into size of nanometers.

From the view point of materials, the base materials of microelectronics is three-dimensional silicon, i. e. bulk silicon. The base materials of nanoelectronics may be one-dimensional silicon. Hence, studies on the optical and electronic properties of semiconductor nanocrystallites, have attracted much attention. Recently, the discovery of efficient visible luminescence in Si[40], Ge[41] and SiC[42] nanocrystallites has stimulated considerable efforts in understanding the optical properties of semiconductor nanocrystallites. In particular, the room-temperature photoluminescence of porous silicon[43] aroused a great interest. Porous silicon obtained by anodic etching of monocrystalline silicon in hydrofluoric (HF) acid,[44] show strong luminescence in the visible range at room temperature. This character is different from bulk silicon which emits only ex-