

纳米科学与纳米技术学瞻

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内 容 简 介

本书为 2001 年 7 月在北京举办的第一届国际华人科学家纳米科学技术研讨会的论文集。其中有近 30 位国际知名学者撰写的论文,内容包括纳米材料的制备、纳米结构的设计与控制、纳米尺寸范围的新奇的光、电、磁、化学特性的研究以及在材料、生物、化学等工业领域的应用前景。每篇论文都附有大量的参考文献供读者进一步查阅。

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FOREWORD

Over the next several years, Tsinghua University Press will publish a series of books addressing progress in basic sciences and innovations in technology . We have made no attempt to pursue a comprehensive coverage of all disciplines of science and technology . Rather, topics for this series were selected with an emphasis on the currently active forefront of science and technology that will be contemporary in the next century . Most books in this series will deal with subjects of cross disciplines and newly emerging fields . Each book will be completed by individual authors or in a collaborative effort managed by an editor (s) , and will be self-consistent, with contents systematically focused on review of the most recent advances and description of current progresses in the field . Sufficient introduction and references will be provided for readers with varying backgrounds . We have realized clearly the challenge of encompassing the diverse subjects of science and technology in one series . However, we hope that, through intensive collaboration between the authors and editors, high standards in editorial quality and scientific merit will be maintained for the entire series .

The international collaboration on this series has been coordinated by the Association of Chinese Scientists and Engineers-USA (ACSE) . In the science community, authors voluntarily publish their results and discoveries in the full conviction that science should serve human society . The editors and authors of this series share this academic tradition, and many of them are fulfilling a spiritual commitment as well . For our editors and authors who were graduated from universities in China and further educated abroad in science and engineering, this is an opportunity to dedicate their work to the international

education community and to commemorate the historical open-door movement that began in China two decades ago . When the human society enters the information age, there is no geographic boundary for science . The Editorial committee hopes that this series will promote further international collaboration in scientific research and education at the dawn of the new century .

The Editorial Committee

1999 .6

《21 世纪科技前沿》 丛 书 序 言

由清华大学出版社出版的这套丛书是基础科学和应用科学领域内的专门著作。除了可作为研究生教材外,也可作为科研和工程技术人员的参考书。在丛书的题材选择中,着重考虑目前比较活跃而且具有发展前景的新兴学科。因此,这套丛书大都涉及交叉和新兴学科的内容。编写的方式大多由主编策划并组织本学科有影响的专家共同执笔完成,从而使每一本书的系统性和各章节内容的连贯性得到了充分的兼顾。丛书涵盖学科的最新学术进展,兼顾到基本理论和新技术、新方法的介绍,并引入必要的导论和充分的参考文献以适应具有不同学术背景的读者。编撰一套容纳多学科的科技丛书是一项浩繁的工作,我们希望通过主编和作者的集体努力和精诚协作,使整套丛书的学术水准能够保持在较高的水平上。

编辑《21 世纪科技前沿》丛书是由“旅美中国科学家工程师协会”发起的一项国际科技界的合作。传递信息,加强交流,促进新世纪的科技繁荣是编著者们参与此项工作的共同信念。此外,这套丛书还具有特别的纪念意义。20年前,历史的进程使成千上万的中国学生、学者有机会走出国门,到世界各地学习和从事科学研究。今天,活跃在世界科技前沿领域的中华学子们没有忘记振兴祖国科技教育事业的责任和推动国际学术交流与合作的义务。正是基于这一共同的心愿,大家积极参与这套系列丛书的撰写、组稿和编辑工作。为此,我们愿以这套丛书来纪念中国改革开放 20 周年。

编 委 会
1999 .6

International Workshop on Nanoscience and Nanotechnology

Sponsored by:

Chinese Academe of Science
National Nature Science Foundation of China
China Ministry of Science and Technology
Chunghui Project of China Ministry of Education

Preface

The first International Workshop of Chinese Scientists on Nanoscience and Nanotechnology (IWCSNN) was held in Beijing at the China-German Conference Center, July 16-18, 2001. There were a total of 190 participants. 56 were invited speakers, and among them 28 were overseas Chinese scientists from the United States, Japan, and Australia. The workshop was co-sponsored by Chinese Academy of Science, National Nature Science Foundation of China, and the Ministry of Science and Technology. In addition, the Ministry of Education provided support thorough its "Chunhui" Project to a number of overseas participants to cover partial international travel expenses. The Institute of Physics of Chinese Academy of Science and the Association of Chinese Scientists and Engineers (ACSE) in the United States co-organized the workshop.

The workshop achieved its objectives in promoting information exchange and international collaboration in the newly merging field of nanoscience and nanotechnology with a comprehensive program that covers synthesis, nanostructure design and control, structure and property characterization and simulation, and materials and technology applications. Emphasis was given to basic research and innovative technology and materials development. Despite only a half of the invited speakers submitted their manuscripts to the IWCSNN proceedings, we found that the scope and quality of these papers warrant the proceedings to be published as a volume of the international series of Frontiers of Science and Technology for the 21st Century, which is being published by Tsinghua University Press in collaboration with Springer-Verlag and other international publishers. Each paper included in the proceedings was peer reviewed and revised before submission for publishing.

The benefit of the workshop was recognized by many participants and the

sponsors . In addition to the presentations that are informative and of relatively high-level of scientific merit, individual discussions, and especially, the sessions of panel discussion on future R&D directions made the workshop a great success . Many suggestions were made for improving government guidance as well as for optimizing collaboration within the science community . As editors and members of the Program Committee, also on behalf of the overseas participants, we thank the Conference Secretariat and other local organizers, especially, Mr . Jinghua Cao of Chinese Academy of Science . Without his enthusiastic support and personal involvement, this workshop could not be possible .

Guokui Liu

Argonne National Laboratory

USA

Zhong Lin Wang

Georgia Institute of Technology

USA

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Nanowires and Nanobelts of Semiconductive Ceramics-Potential and prospects

Zhong Lin Wang^{*}, Zhengwei Pan and Zurong Dai

Center for Nanoscience and Nanotechnology

School of Materials Science and Engineering

Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

^{*} E-mail: zhong.wang@mse.gatech.edu

Index words: nanobelt, nanowires, nanotubes, carbon nanotubes, semiconductive ceramics, morphology, functional oxides, quantum wires, dislocations, melting point, synthesis, characterization, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray spectroscopy, structural transformation, functional oxide nanowires, evaporation, amorphous phase, structural control, crystal structure

Abstract

One-dimensional nanobelt structures have been successfully synthesized for ZnO, SnO₂, In₂O₃, CdO, Ga₂O₃ and PbO₂ by simply evaporating the desired commercial metal oxide powders at high temperatures. The as-synthesized oxide nanobelts are pure, structurally uniform, single crystalline and most of them free from dislocations; they have a rectangular-like cross-section with typical widths of 30—300 nanometers, width-to-thickness ratios of 5—10 and lengths of up to a few millimeters. The belt-like morphology appears to be a unique and common structural characteristic for the family of semiconducting oxides with cations of different valence states and materials of distinct crystallographic structures. The nanobelts are structurally controlled and they are intrinsic semiconductors, providing a new system after carbon nanotubes for a systematic understanding on dimensionally confined transport phenomena in functional oxides. They are also ideal building blocks for fabrication of nano-scale devices based on the integrity of individual nanobelts.

1 Introduction

One-dimensional quantum wires are of fundamental importance to the study of size-dependent chemical and physical phenomena. With a reduction in

size, unique electrical, mechanical, chemical and optical properties are introduced, which are largely believed to be the result of surface and/or quantum confinement effects. The most important challenges for the future nanoelectronics are interconnects and the integration between interconnects and devices. Nanowire-like structures are an ideal system for studying the transport process in the one-dimensionally confined objects, which are potential candidates for understanding the quantum phenomena in interconnects. As the size of the devices shrinks below 100 nm, searching and building three-dimensional interconnects become crucial. It is natural to explore the possibility of building functional devices in the wires, so that the interconnects and devices are conjunctive and inseparable.

Much of the studies of one-dimensional like structures have been focused on carbon nanotubes [1], silicon nanowires [2, 3] and compound semiconductor nanowires [4], such as InP. Our research has taken a slightly different approach with an emphasis on functional oxides. Some of the transition and rare earth metal oxides are semiconductive and they are the fundamental to the development of the smart and function devices, which have key applications in electro-mechanical, electro-optical, electro-chemical and opto-thermal applications. The metal oxides will have two important characteristics including 1) cations with mixed valences and 2) significant oxygen vacancies. The oxides are usually made into single crystals, dispersive nanoparticles, or condensed films. This paper reviews our most recent advances in the synthesis and characterization of semiconductive oxide nanowires and nanobelts.

2 Experimental Method

Our synthesis is based on thermal evaporation of oxide powders under controlled conditions without the presence of catalyst [5]. The desired oxide powders were placed at the center of an alumina tube that was inserted in a horizontal tube furnace (Fig. 1), where the temperature, pressure and evaporation time were controlled. At one end of the furnace, argon or nitrogen flows over a crucible containing the raw powder of interest. The total tube pressure in the inner tube can be made to range from 200 to 650 Torr. This pressure is controlled by a mechanical pump attached to the inner alumina tube through the downstream stainless steel end piece. This end piece is mechanically attached to a "water cooled" cold plate. In our experiments, except for the evaporation temperature that was determined based on the melting point of the oxides to be used, we kept following parameters to be constant: evaporation time, 2 hours; chamber pressure,

300 Torr; and Ar flowing rate, 50 standard cubic centimeter per minute (sccm) . During evaporation, the products were deposited onto an alumina plate placed at the downstream end of the alumina tube .

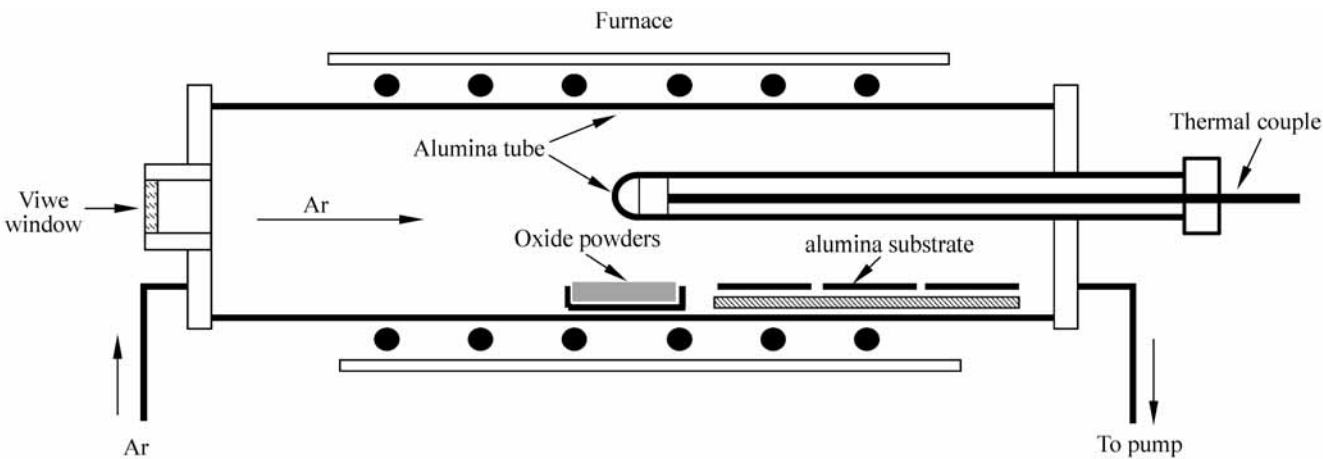


Fig. 1 Experimental set up for the synthesis of nanowire structures .

The as-deposited products were characterized and analyzed by X-ray diffraction (XRD) (Philips PW 1800 with Cu K α radiation), scanning electron microscopy (SEM) (Hitachi S800 FEG), transmission electron microscopy (TEM) (Hitachi HF-2000 FEG at 200 kV and JEOL 4000EX high resolution TEM (HRTEM) at 400 kV), and energy dispersive X-ray spectroscopy (EDS) .

3 Experimental Results

3 .1 Growth of SiC-SiO₂ Biaxial Nanowires

Silicon carbide is a wide bandgap semiconducting material used for high-temperature, high-frequency, and high-power applications . We have applied elevated temperature synthesis to form bulk quantities of biaxially structured silicon carbide-silica nanowires composed of side-by-side sub-nanowires [6] . Key to the experiments is that amorphous SiO is brought into intimate contact with carbon/ graphite in an appropriate mix at elevated temperatures for an extended time period . The process is facilitated as SiO and carbon are located into a low porosity carbon crucible placed at the center of a temperature controlled tube furnace . Figure 2 (a) depicts a low-magnification transmission electron microscopy (TEM) image of the nanowires dispersed on a carbon film . The nanowires are uniform with diameter 50—80 nm, and a length that can be as long as 100 μ m . The as-synthesized materials are grouped into three basic nanowire structures: pure SiO_x nanowires, coaxially SiO_x sheathed β -SiC nanowires (Fig . 3 (b))

(~ 50% of material), and biaxial β -SiC-SiO_x nanowires (Fig . 2 (c)) (~ 30% of material) . The coaxial SiC-SiO_x nanowires have been extensively studied, and have a $\langle 111 \rangle$ growth direction with a high density of twins and stacking faults perpendicular to the growth direction . From the cross-sectional TEM images of the as-synthesized nanowires, the geometrical shapes of the coaxial SiC-SiO_x (Fig . 2 (d)) and the biaxial SiC-SiO_x nanowires (Figs . 2 (e) and (f)) are unambiguously revealed . The SiC nanowires have faceted shapes, as one type of facet corresponds to $\{111\}$, identified from the presence of stacking faults and twins in the image .

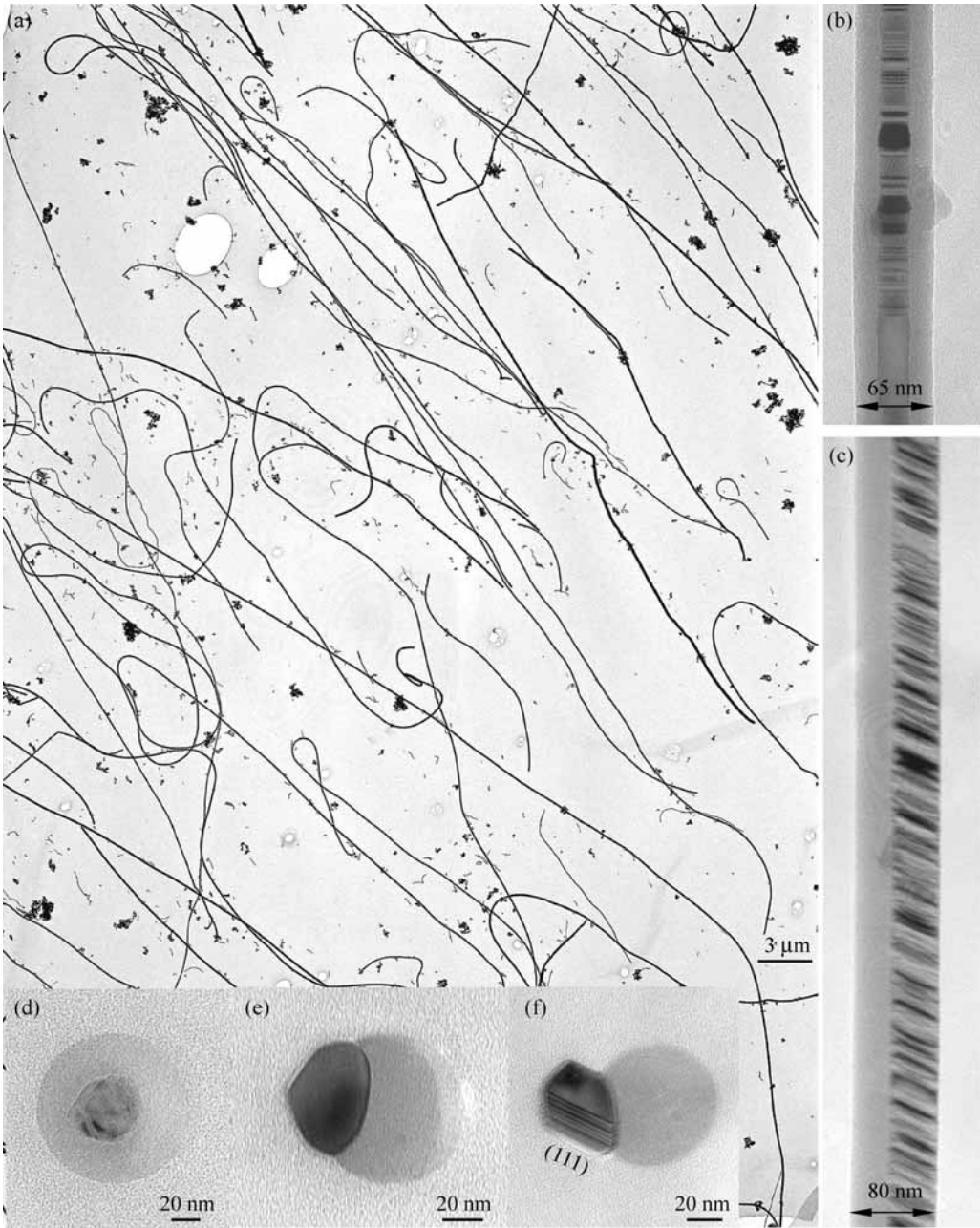


Fig 2 Low-magnification TEM image of the as-synthesized nanowires supported by a carbon film, showing their ultra-long length and uniformity in diameter . Side views of a (b) coaxially and (c) biaxially structured SiC-SiO_x nanowire . Both types of nanowire have different growth directions, but exhibit similar stacking and twin structures in the $\{111\}$ plane . (d) and (e, f) Cross-sectional TEM images of coaxially structured SiC-SiO_x and biaxially structured SiC-SiO_x nanowires, respectively . The SiC sub-nanowire has a faceted shape .

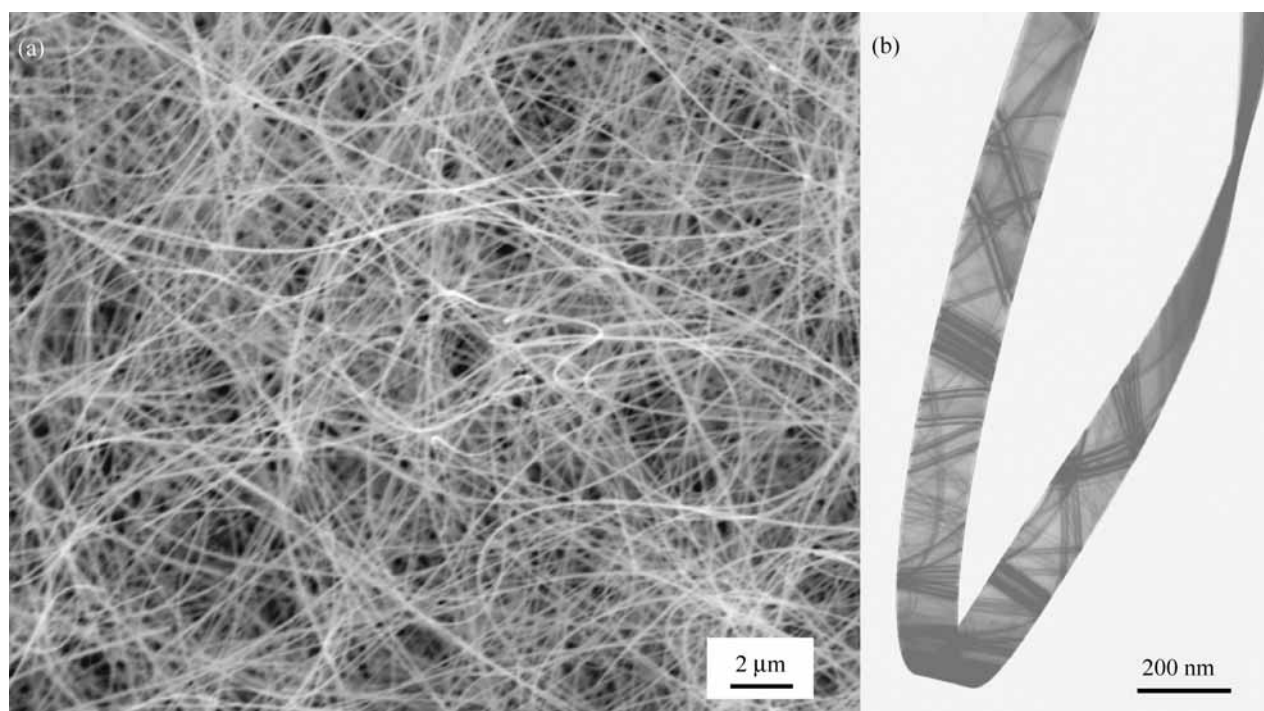


Fig 3 Ultra-long nanobelt structure of ZnO (a) SEM image of the as-synthesized ZnO nanobelts with high purity and crystallinity; (b) Bright-field TEM image showing the bent belt shape . The contrast observed in TEM image is due to bending strain .

We have found that a structural transformation between biaxial and co-axial nanowires can occur along the same nanowire [6], thus providing an ideal system for studying the physics of interface-junctions in one-dimensionally structured nanomaterials . The non-uniform passivation of the silica onto the SiC sub-nanowire suggests that it may be possible to create p-n junctions across the SiC nanowire using a thickness-controlled diffusion of dopants (such as phosphorous or boron) through the silica barrier . This may lead to a possible channel for fabricating functional devices in nanowires by lithographic patterning .

3.2 Growth of Functional Oxide Nanowires

Wide bandgap binary semiconducting oxides, such as ZnO, SnO_2 , In_2O_3 and CdO, are now widely used as transparent conducting oxide (TCO) materials [7] and gas sensors [8] due to their various unique properties . For example, fluorine-doped SnO_2 film is widely used in architectural glass applications because of its low emissivity for thermal infrared heat [7]; SnO_2 nanoparticles are regarded as one of the most important sensor materials for detecting leakage of several inflammable gases owing to its high sensitivity to low gas concentrations [7]; tin-doped indium oxide ($\text{In}_2\text{O}_3:\text{Sn}$, ITO) film is an ideal material for flat panel displays (FPDs) due to its high electrical conductivity and high optical transparency [7]; ZnO is regarded as an ideal alternative material for ITO in some future display applications