CITY UNIVERSITY OF HONG KONG

香港城市大学

Synthesis and Characterization of GaN/ZnS Nanomaterials

氮化镓和硫化锌纳米材料的制备和性能

Submitted to

Department of Physics and Material Science

物理及材料科学系

in Partial Fulfillment of Requirements

for the Degree of Master of Philosophy

哲学硕士学位

by

Liu Ji

刘佶

March 2004

二零零四年三月

Abstract

Low-dimensional semiconductor compound nanomaterials, such as III-V group GaN and II-VI group ZnS, have attained much interest over the last decade because of their novel properties and expected diverse applications particularly in nanotechnology and optoelectronics. Therefore it is not surprising that nanoscience and nanotechnology are hot topics. Studying nanomaterials is essential for understanding the behavior of these low-dimensional nanomaterials and utilizing their outstanding properties.

This work presents the approaches in synthesis of intrinsic GaN nanowires, GaN nanowires doped with silicon, GaN nanoflakes, ZnS nanoribbons and nanowires. This work is also dedicated to the study of these structures and their properties on nano and atomic levels, and discussion of the relevant growth mechanisms.

Hot-filament chemical vapor deposition (HFCVD) was used to grow III-V group GaN nanowires. Different morphologies of the GaN nanostructures were obtained by synthesis at various temperatures. The GaN nanowires grew optimally on graphite substrates at temperature of 900 °C. Bulk quantities of GaN nanowires doped with silicon grew on Au-coated Si (100) wafers using similar procedure as applied to GaN nanowires prepared on graphite substrates. The GaN nanowires doped with silicon were systematically characterized by scanning electron microscopy, transmission electron microscopy, x-ray diffraction, Raman spectroscopy, and photoluminescence (PL). The analysis shows diameters of nanowires mostly smaller than 10 nm and lengths up to several hundreds micrometers. Since the wire diameters is smaller than the Bohr exciton radius of GaN in most of cases, the quantum confinement effect is evident in the optical and Raman properties of the GaN nanowires. EDX and EELS integrated in a TEM

instrument reveal that the doping level of silicon is 3% and it is uniformly distributed over the whole bulk of GaN nanowires. The GaN nanowires doped with silicon exhibit intense emission peak at 344 nm, which is blue shifted from the peak corresponding to the GaN bulk emission. The blue shift designates the quantum confinement effect. The detailed TEM analysis discloses that the GaN nanowires grow along the [001] crystallographic directions. For this particular case, a possible growth model based on the oxide-assisted metal-catalyst VLS (vapor-liquid-solid) growth of the nanowires is proposed. GaN nanoflakes were fabricated too. Their field emission properties were comparable with the field emission performance of materials traditionally used for electron field emission.

The second scope of this work is synthesis and characterization of ZnS (II-VI semiconductor compound) nanoribbons and nanowires. The ZnS nanoribbons were synthesized in bulk quantities using hydrogen-assisted thermal evaporation at 1100°C. The prepared ZnS nanoribbons are single crystals with uniform and flat morphology. The width and length of the nanoribbons are sensitive to the duration of the deposition process and deposition temperature. Most ZnS nanoribbons are wurtzite structures and have a [120] growth direction. The strong green emission of the nanoribbons, centered at 534.5 nm implies possible exploitation of these nanostructures in nanoscale optoelectronic devices.

This work also claims the first synthesis of ultrafine zinc sulfide (ZnS) nanowires with a sphalerite structure. The ZnS nanowires were synthesized over large areas on Au-coated silicon substrates with high density. The ZnS nanowires prepared at 1050 ^{o}C have diameters of 10-20 nm and lengths of several micrometers. These nanowires with a sphalerite structure grow in the [111] direction. Their growth is explained by the VLS (vapor-liquid-solid) model, in which the deposition temperature is a very important factor for controlling the nanostructures of final products.

CONTENTS

List of Figures

Figure 11 (a) TEM image of silicon doped GaN nanowires; (b) HRTEM image of a silicon doped nanowire grown along the [001] growth direction. The inset is the SAED pattern with [100] axis zone; (c) HRTEM image of a silicon doped nanowire with [021] growth direction. The inset is the SAED pattern with [100] axis zone; (d) EDX of a single GaN nanowire doped with silicon. The inset is the EELS mapping of silicon taken from GaN nanowires. The mapping shows uniform distribution of silicon over the bulk of the silicon nanowire.

Figure 12 Photoluminescence (PL) spectrum of GaN nanowires doped with silicon; the PL spectrum was obtained at the 235 nm photo-excitation.

Figure 13 The model of growing GaN nanowires doped with silicon with assistance of Au catalyst.

Figure 14 SEM image of GaN nanoflake (a) low magnification image; (b) high magnification image.

Figure 15 Field emission *J-E* data taken from the GaN nanoflakes film.

Figure 16 SEM images of the ZnS nanoribbons synthesized at 1100 °C. A bulk quantity of the nanoribbons were collected from the quartz wall of the furnace tube (a) low magnification image; (b) high magnification image.

Figure 17 XRD patterns of (a) synthesized ZnS nanoribbons with wurtzite structure (b) the ZnS source with sphalerite structure.

Figure 18 (a) TEM bright-field image of ZnS nanoribbons and in-situ EDX spectrum (inset); (b) a typical HRTEM image and SAED pattern of the [001] zone axis (inset) of a nanoribbon with wurtzite structure and [120] growth direction.

Figure 19 Room-temperature photoluminescence spectra (a) excitation spectrum; (b) spectrum of the ZnS nanoribbons; (c) spectrum of ZnS source powder.

Figure 20 (a) A typical SEM image of the deposited ZnS nanowires; (b) a lower magnification image showing the uniform distribution of ZnS nanowires over a large area on the Au-coated silicon substrate.

Figure 21 XRD spectrum collected from ZnS nanowires revealing sphalerite fcc structure.

Figure 22 TEM bright field image of the ZnS nanowires showing ZnS nanowires a fair uniformity in diameter (10-20 nm) and smooth surface.

Figure 23 (a) a bright field TEM image of ZnS nanowires; (b) a HRTEM image of one nanowires; inset is the corresponding transmission electron diffraction; the arrow ‘c’ indicates the ZnS interface with a spherical Au particle at the tip of the ZnS nanowires.

Figure 24 Photoluminescence (PL) spectrum collected from the synthesized ZnS nanowires.