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Growth and optical properties of nanowires

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Abstract

The present paper reviews the growth mechanism, processes and optical properties of nanowires with special reference to ZnO. A brief description of free standing vertical nanowires of ZnO grown in our lab is also included.

Keywords: Nanowires, optical properrties, ZnO

INTRODUCTION

The study of inorganic semiconductor nanostructures advanced from quantum wells to (embedded) quantum wires to quantum dots roughly from the 1970s to the 1990s with the development of epitaxial growth and lithographic methods.The increasing degree of quantum confinement had allowed to substantially alter the physical properties leading to fundamentally new physics under reasonable external conditions.Examples include the quantum Hall effect, ballistic and Coulomb blockade.

In turn, this has generally led to improved physical properties such as higher electron mobility for nanowires, reduced nonradiative recombination, and lower lasing threshold as the degree of confinement increases, or the design of new devices such as nanowire solar cells, infrared photodetectors, and field-effect transistors.More recently, however, the development of chemical synthesis and bottom-up methods has expanded the study of free-standing nanowires. The first conceptualization of a quantum wire (QWR) is usually attributed to a 1980 paper by Sakaki.[1]

The potential of these new techniques is that they involve much simpler chemical synthesis methods, are relatively inexpensive, and produce single-crystal nanowires of high quality and purity. A nanowire or quantum wire can be defined as a structure exhibiting quantum confinement effects in the plane perpendicular to the wire axis and free-electron-like behaviour along the latter.Typical geometrical dimensions are 1–100 nm linear lateral dimensions and microns in length.

Growth and Synthesis

In the rest of the article, the term NW's will be restricted to free-standing homogeneous wires with very large aspect ratio (typical experimental length being of the order of microns which is treated theoretically as infinite).Quantum wires (QWR's) will refer to the embedded structures. .One-dimensional (1D) nanostructures have been grown in various shapes and geometries: embedded with square cross-section, T-shaped, strain induced lateral confinement in quantum wells, V-groove shaped, plain free-standing, nanobelts, quantum rods, core–shell, axially modulated, and nanotubes. The variety reflects not only the curiousity in how properties change but also the experimental constraints.For example, core– shell structures protect the inner core from surface effects inherent in a free-standing nanowire.InP-based systems are preferred over AlGaAs due to the ease of oxidation of the latter.CdS nanowires are preferred over GaAs ones for the polarized photoluminescence studies due to the higher emission efficiency of the former.We will now summarize the growth of various types of one-dimensional nanostructures, with emphasis on nanowires.

Growth of Quantum Wires

In1982,one dimensional structures displaying quantum confinement of two dimensions were reported by Petroff et al.[2] Those were GaAs quantum-well wires with submicron dimensions obtained using molecular beam epitaxy(MBE) of GaAs and $Ga_{1-x}Al_xAs$.Transmission electron microscopy (TEM) showed them to be single crystal, defect-free wires, with cross-section dimensions as small as 20×20 nm. Quantum wires can also be formed at the intersection of two quantum wells and have been named T-shaped QWR's. The basic process has been to grow one set of quantum wells (via MBE), then cleave the sample, and finally, grow the second set of intersecting quantum wells.Such QWR's are expected to have high structural quality Nanowires that have been grown or synthesized include AlN,CdS,CdSe,GaAs, GaN,GaP, Ge, InN, InAs, InP, MnS ,Si, SiC, ZnO, ZnS, and ZnSe.These nanowire sizes range from a few hundred to a few nm. Apparently, the ultimately thin wire would be a linear chain of atoms. However, the thinnest known semiconductor wire is perhaps the subnano meter [0001] zigzag atomic chain of wurtzite ZnTe (with only four atoms per period) [3].

Growth mechanism

Several mechanisms behind different growth methods have not been completely understood until recently. For example, the vapor-liquidsolid (VLS) mechanism [4] was first proposed to explain the growth of micrometer diameter whiskers from a liquid droplet. It was the primary mechanism cited to describe the nanowires grown when a particle was observed at one end of the nanowires. However, only recently have real-time observations of the VLS growth stages been demonstrated via in situ TEM. In 2004, the very idea that VLS growth automatically applies to all NW's found with a metal particle at one end has been challenged. Instead, even though metal "seed" particles were involved in the growth, a vapor-solid-solid mechanism was proposed to explain some III–V compound NW's growth by chemical beam epitaxy (CBE). Several growth mechanisms involving liquid phase growth environment have also been explored, e.g., Trentler et al [5] synthesized several III–V compound (InAs, InP andGaAs) nanowires by a solution phase synthesis,i.e., the so-called solution-liquid-solid (SLS) mechanism. Depending upon the solvent, this has also been referred to as the solvothermal or hydrothermal method. The other similar mechanism is called super-critical fluidliquid- solid mechanism, in which a super-critical solution was used to dissolve source materials (precursors and other agents) for subsequent nanowire growth. Among different nanowire growth mechanisms, the VLS growth mechanism is so far the most versatile and extensively used to grow a variety of semiconducting nanowires.VLS was proposed several decades ago by Wagner and Eillis[4] to explain the growth of semiconducting Si whiskers using impurity metal particles, such as Au, Ni, Cu, etc

Morales and Lieber [6] demonstrated that much smaller diameter Si and Ge nanowires (3–20 nm in diameter) and several nm in length could be grown using a pulsed laser to vaporize the semiconductor and Fe needed in the growth seed. This so-called pulsed laser vaporization (PLV) method provides nanometer-sized Fe particles and Si/Ge vapor supply. It was this landmark paper that arouses worldwide research on semiconducting nanowires.

Electronic and Optical Properties

The most direct way of studying the electronic properties is by making nanowires of different size, shape, and orientation and measuring the optical spectra. The optical spectrum of a nanowire would not only eludicate the physics and provide a characterization of the nanowire, but is also important in designing photonic devices. There have been a few measurements of the size dependence of the band gap. Various measurements (e.g., PL and scanning tunneling spectroscopy) have been reported Si, and size-dependent PL for InP and CdSe nanowires, with a blue shift measured for diameters smaller than 20 nm. Dependence of properties on nanowire morphology is less studied. Examples are for InP, ZnO and CdS. A problem of current interest is the nature of the light polarization emitted or absorbed by quantum rods and Nanowire. The polarization dependence of the photoluminescence excitation (PLE) data was attributed to the different properties of light holes and heavy holes in the quantum-confined regime. The above problem was also studied for free standing nanowires, first of zincblende structure, then also of wurtzite structure. A related study is of the optical polarization for quantumrods.Hu et al.[8] studied CdSe QR's with aspect ratios from 1 to 30 and with radii of 2–3 nm. Their polarized luminescence experiments gave a transition to *z*-polarized optical emission at an aspect ratio of 1.5–2. Similar polarization data were obtained for ZnO QR's.

Characterization Techniques

For completeness, we briefly mention a few characterization techniques that have been used to obtain other properties of nanowires. Current–voltage plots have been used to distinguish between homogeneous InAs and InAs/InP modulated nanowires [9]. Longitudinal photoconductivity has been used on GaAs/AlGaAs V-groove QWR's as a method that combines absorption spectroscopy with carrier transport. Relaxation dynamics in CdSe quantum rods were studied using femtosecond transient absorption spectroscopy.

Wurtzite NWs

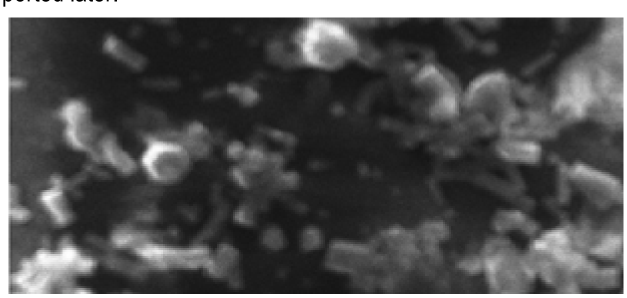
Xiang et al.[10] have calculated the electronic structure of wurtzite ZnO nanowires. In contrast to the Si/Ge system that has relatively small type-II energy alignment; core–shell nanowires based on GaN/GaP or ZnO/ZnSe with large type-II energy alignments have recently been investigated. The central finding is that the electron state at the CBM and the hole state the VBM are, respectively, confined in the core and shell, resulting in an efficient charge separation. Additionally, the band gap is found to be tunable in a much larger range than that defined by the two components. The PL studies of NWs show strong polarization anisotropy. For ZnO NWs the interplay of the dielectric mismatch and band structure to the relative size of the nanostructure and the wavelength of the electromagnetic field is accounted for this anisotropy. Maslov and Ning[11] again found that quantum confinement alone leads to a polarization anisotropy of an GaN nanowire that should decrease as the radius increases and the polarization is predominantly along the axis for a radius near 3.5 nm.

Doped NWs

Highly conductive and transparent impurity-doped ZnO thin films have recently gained much attention because they are composed of inexpensive, abundant materials Highly transparent and conductive ZnO thin film have been prepared by doping with a group III and group IV impurities, using magnetron sputtering and metal organic chemical vapor deposition (MOCVD) methods. From the many reported investigations of the doping effect of impurities on ZnO, it is widely thought that the best dopants for transparent, conducting ZnO flms are Al and Ga. This may be attributable to the fact that the ion radius of Al and Ga is closer to, as well as being smaller than, that of Zn, in comparison to other impurities. Zn^{2+} and RE^{3+} will not favor substitution of Zn^{2+} by RE^{3+}. Still, it is known that RE ions can be incorporated in bulk II-VI semiconductors. Efficient luminescence from intraconfigurational $4f_n$-$4f_n$ transitions has been observed for RE ions in bulk ZnS upon excitation over the band gap. However, high temperatures (900-1200 °C) are needed to accomplish this.

A facile route for preparation of ZnO nanowires:

In our laboratory we were able to prepare free standing nanowires of ZnO. We modified the available processes for good adhesion and high density growth of nanowires. We used a combination of wet chemical methods like CBD, SILAR and sol-gel for a controlled growth of nanowires. The figure below shows the hexagoanal tipped free standing high density nanowires of ZnO. The optical and electronic properties are being studied and will be reported later.



CONCLUSIONS

The present paper reviews the growth mechanism, characterization techniques and optical properties of various NWs. The doping of NWs and their applications are also discussed. This review provides a pathway for future research.

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