Chapter 1

Introduction

"Nanowires, nanorods or nanowhiskers. It doesn't matter what you call them, they're the hottest property in nanotechnology."

These are the opening sentences of an article published in *Nature* in 2002 [1], where the author[1] attributes the remarkable progress made in the field of nanotechnology in the recent decade to the discovery and controlled synthesis of carbon nanotubes [2] and semiconducting nanowires [3] that can serve as a basis for various device structures. Devices based on nanowires combined with bottom-up (instead of top-down) patterning techniques will not only ensure a further shrinking of the chip dimensions down to nanometer scales, but will also considerably upgrade their performances at a reduced electrical power consumption. Especially semiconducting nanowires seem advantageous for device applications, since they grow in a self-organized process and their chemical composition can be tailored, too.
Today, semiconducting nanowires and nanoparticles, or nanostructures in general, are already employed in various applications. Nanowires are mostly incorporated in electronic devices like nanoscale field effect transistors [4] and logic gates [5] or in optoelectronic devices [6], whereas nanoparticles, because of their enormous surface to volume ratio, are preferentially used as sensing elements in gas or humidity detectors.

Among research on semiconducting nanostructures, especially nanowires based on zinc oxide (ZnO) recently attracted much attention. The II-IV semiconductor has the property of self-organized growth leading to a variety of shapes like nanowires, nanorings, nanobelts and nanoparticles. The resulting structures are of high crystallinity with low defect densities and the dimensions are controllable by adjusting the growth parameters.

[1] D. Appell, freelance science writer.

With a direct band gap of 3.37 eV and an exciton binding energy of 60 meV at room temperature, ZnO is a promising candidate for optoelectronic applications. Additionally, growth may result in ordered and well aligned nanowire arrays building regular block structures that can be used, for instance, as basis for high density pixel arrays in displays and LEDs. Furthermore, the environmentally friendly, long-term stable, radiation and oxidation resistant material is also valued for its piezoelectric features that can be exploited for power generation [7].
Changes in ambient conditions strongly influence the electrical properties of ZnO nanostructures, a property that can be employed for detection of oxidizing and reducing gases. Moreover, besides the use in electronics, optoelectronics and sensorics, ZnO could also form the basis for spintronic devices: Theoretical calculations predict that when doped with transition metal (TM) ions, ZnTMO should exhibit ferromagnetism even at room temperature [8, 9].

ZnO nanostructures have many unique properties; however, in order to fully exploit their functionality, it is important not only to study their electrical transport characteristics in a laboratory environment, but also to thoroughly investigate their behavior upon changing atmospheric and light conditions. Even though many groups have already examined the electrical properties and also the photoresponse of ZnO upon UV illumination, the discrepancies in the reported photocurrent decay times (ranging from nanoseconds [10] up to minutes [11]) reveal that the photocurrent mechanism is very complex and not yet fully understood. One objective of this work is therefore to deliver a complete investigation of the electrical transport properties of ZnO nanostructures and to provide a model describing the observed effects. The analysis is subdivided into the investigation of nanowires grown by vapor phase transport and by aqueous chemical growth. Also layers consisting of ZnO nanopowder particles are examined.

Furthermore, there are still some open questions regarding the applicability of transition metal doped ZnO for spin sensitive devices. The magnetic properties of ZnTMO layers have already been extensively studied; however, due to considerable differences in the observed experimental results, ferromagnetism in ZnTMO is still under debate. While most investigations focus on layers, only few reports deal with research on magnetic ZnO nanowires or nanostructures. The second aim of this thesis is therefore to investigate Mn-, Co- and V-doped ZnO nanostructures concerning their magnetic properties and their applicability as basis for spin-sensitive devices.
Finally, one more goal is to present device structures and concepts based on the obtained results.

The thesis is structured as follows:
Chapter 2 shortly recapitulates the historical development of nanotechnology by presenting some of the major discoveries and findings as well as a number of the technological progresses involved. Furthermore, some semiconducting nanowire based devices are presented.
Chapter 3 introduces the basic properties of the semiconducting material ZnO, the specific characteristics of ZnO nanostructures and the synthesis techniques involved in this work.
Chapter 4 presents the electrical property studies of ZnO nanostructures. The first part deals with the investigation of nanowires grown by vapor phase transport. Additionally, an overview of published data concerning the resistivities of nanowires is given and factors influencing the resistance are discussed. The second part investigates the transport characteristics of nanowires grown in an aqueous chemical process and contacted using various methods. The results concerning the influence of illumination and ambient conditions on the electrical properties of nanopowder layers complete this chapter.
After a short introduction of magnetism in semiconductors, Chap. 5 shows the results from the magnetic property investigations of Mn-, Co- and V- doped ZnO nanostructures.
Chapter 6 presents a few device concepts based on the findings presented in the previous chapters.
A short outlook completes this work.

Furthermore, it should be pointed out that even though quasi zero- and one-dimensional structures (like quantum dots, quantum wells or thin films) are also referred to as nanostructures (by definition, nanostructures have *at least* one dimension on the nanometer scale), in this thesis, the term nanostructures or nanosystems is exclusively used for structures having two or three dimensions on the nanoscale.