Chapter 1: Introduction

1.1 Background

Nano is a familiar prefix used everywhere these days as public interest in nano materials has grown rapidly. The last forty years people have seen a number of crucial technical developments in field. These developments have initiated changes in human life of an unprecedented kind. This period has simultaneously witnessed other landmark developments. The construction of point contact transistor in 1947 rapidly led to intensive research which ultimately led crystallized in the concept and subsequent realization of the information technology (IT) era. In the 1970's, the information age per se started. We saw step wise appearance of quartz optical fiber, III-V compound semiconductors and gallium arsenide (GaAs) lasers. During the evaluation of the information age, silicon (Si) occupied a dominant place in the commercial market, as it was used to fabricate the discrete devices and integrated circuits needs of for computing, data storage and communication. Zinc oxide (ZnO) is a II–VI compound semiconductor with a wide direct band-gap of 3.3 eV and a hexagonal structure. ZnO is often used in the paint, paper, rubber, food and drug industries. It is also a promising material in nanotechnology applications, for example in nano-electronics and nano-robotic technology. With its wide band-gap, high exciton binding energy and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications. To produce such optoelectronic devices, control of electronic properties, such as the nature of conduction and carrier density, is required.

1.2 Moore's Law

Since Si has an indirect band gap it is not suitable for optoelectronic devices such as light emitting diodes (LED) and laser diodes, GaAs with direct band gap is used instead. Hence the progress is often started by questing the famous Moore's Law. It states that the number of transistors that can be placed on an integrated circuit is doubling every eighteen months, the increasing demands has been the driving force for the semiconductor industry ever since its beginning. Researchers are working hard to find ways to reduce the size of the transistors to squeeze more transistors inexpensively on the same die size. They have been able to keep up with the pace demand by Moore's Law. As a result, the dimension of the transistor has shrunk to almost the minimum possible. Ultimately it is governed by underlying semiconductor physics. Scientists are therefore searching for viable alternatives in order keep pace with Moore's Law and to make new progress possible.

Nanotechnology has recently become a focused research area and has the potential to become one of the key technologies of the new world. Nanotechnology involves the investigation and design of materials or devices close the atomic and molecular levels. One nanometer, a measure equal to one billionth of a meter, spans approximately 10 atoms and one may be able to rearrange matter with atomic precision to an intermediate size. Adopting one of the preceding definitions may however may

ISBN: 978-81-942709-0-4

Series: AIJR Thesis
Thesis DOI: 10.21467/thesis.78

unduly restrictive. In a broad survey it is profitable to include anything and everything that has been described as nanotechnology. One may then evolve a framework for classifying and understanding the different types of nanotechnology.

1.3 The Short Scale Limits

In upcoming years, it may become possible to build any detailed object completely at the atomic level, consistent with the laws of physics and chemistry. It may well be that with new insights much of the existing brilliant predictive thought in chemistry and physics may become redundant. According to Richard Feynman, (a Nobel Laureate in 1959), small scale phenomenon may reveal a large number of extraordinary characteristics. In the 21stcentury, there is global surge in nanotechnology and science. The two main consequences of miniaturizing a material are: 1) the surface area to volume ratio becomes large and 2) Quantum effects become important.

In order to exploit nanotechnology to the full and extent, we must be able to accurately predict the characteristics and properties of materials at the atomic and molecular scale. The nano scale requires a new set of guiding theories and meta principles in order to understand describe and predict phenomenon. To frame such theories, one must investigate measure and build model at this scale. One may then accurately predict the relevant parameters. The present investigation, ZnO nanostructures have been synthesized, characterized and their optical and electrical properties studied.

1.4 ZnO nanostructures

The research interest in ZnO, (one of wide band gap semiconductors,) has increased in recent years. The first enthusiasts who started studies of the lattice parameter were M.L. Fuller in 1929 [1] and C.W. Bunn' in 1935 [2]. During the last decade, the ZnO related research has received an increased impetus. The number of articles published on ZnO has steadily increased every year and in 2007, ZnO became the second most popular semiconductor material (after Si). This popularity, to a large extent, is due to the improvements in growth related techniques of single crystalline ZnO (in both epitaxial layers and bulk form). Another reason is emergence of novel electrical, mechanical, chemical and optical properties with reduction in size. They are largely believed to be the result of surface phenomena and quantum confinement effects. Study of one dimensional (1D) materials has become a frontier area in nano science and technology. Functionally ZnO is a versatile material. 1D ZnO nanostructures such as nanotubes [3], nanowires [4], nanorods [5], nanobelts [6], nanocables [7] and nanoribbons [8] have stimulated considerable interest leading to fundamental physics studies, and also to their potential applications in nanoelectronics, nanomechanics, and flat panel displays. Particularly, the optoelectronic device application of 1D ZnO nanostructure has become one of the major focal points in recent nanoscience researches [9-11]. The main advantages of ZnO are a wide band gap, large refractive indices over the infrared and visible ranges, its large exciton binding energy (60 meV) compared to GaN (25 meV), and the existence of well-developed bulk and epitaxial growth processes. For electronic applications, the attractiveness of ZnO lies in its high breakdown strength and high saturation velocity.

It is not surprising that Zinc oxide has received a vast amount of attention in the last few years. This material is both transparent and conductive with a wide variety of applications in both industry and research [Hartnagel et al*,* 1995]. An important aspect of these is the utilization of ZnO thin films for solar cell applications. Interesting aspects of ZnO include the anisotropy in crystal structure, a wide band gap the optical transparency in the visible range, it's fairly high refractive index, and its large piezoelectric constant.

1.5 Applications

The applications of nanomaterials are based on the properties of these materials such as (i) peculiar physical properties of nano sized materials, (ii) the huge surface area and (iii) the small size that offers extra possibilities for manipulation and room for accommodating multiple functionalities. Since nanomaterials possess unique, beneficial chemical, physical, and mechanical properties, they can be used for a wide variety of applications. Due to the nanometer size, many of the mechanical properties of the nanomaterials are modified from the bulk materials including the hardness, elastic modulus, fracture toughness, scratch resistance and fatigue strength etc. ZnO is often used in paint, paper, rubber, food and drug industries. It is also a promising material in nanotechnology applications, for example in nano-electronics and nano-robotic technology. With its wide band-gap, high exciton binding energy and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications. To produce such optoelectronic devices, control of electronic properties, (such as the nature and magnitude carrier density), is required. A few applications of ZnO are mentioned below.

ZnO nanostructures are used for sensing applications because of their high sensitivity to the chemical environment. Nanostructures have the advantage of a high surface area, and electronic processes are strongly influenced by surface processes. ZnO nanowires have demonstrated high sensitivity even at room temperature, whereas thin-film gas sensors often need to be operated at elevated temperatures. The sensing process is governed by oxygen vacancies on the surface that influence the electronic properties of ZnO. Upon oxidation, (via adsorption of molecules such as NO2 at vacancy sites that accept electrons), electrons are withdrawn and effectively depleted from the conduction band, leading to a reduction of conductivity. On the other hand, reducing molecules (such as those of H2) can react with surface-adsorbed oxygen, leaving behind an electron and a higher conductivity. The challenge is to sense certain gases selectively. A ZnO nanorods H2 sensor has now been developed [12]. The sensitivity of this sensor was improved by sputter deposition of Pd clusters on the ZnO rod surface. The addition of Pd appears to be effective in the catalytic dissociation of H2 into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 ppm (in N2 at room temperature), whereas there is no response to O2. By exposing the sensor to air or O2, the conductance recovers up to 95% after 20 s. The same investigation has also shown H2 sensitivity for Pt-coated ZnO nanorods [13]. A different group used a thick film of ZnO nanoparticles for H2 sensing [14]. A sensitivity of 10-1000 ppm H2 was achieved for a Pt-impregnated, 3% Co-

doped ZnO nanoparticles film at a working temperature of 125°C or lower. O2, NO2, and NH3 oxidizing sensors in field – effect transistor geometry of single nanowires has also been demonstrated. The oxygen sensitivity is higher for smaller diameter nanowires and can be modulated by the gate voltage. Distortion of adsorbed NO2 molecules is observed when a large negative gate voltage is applied. This can be used as a method to store the sensor to its original level. An ethanol sensor with good sensitivity and fast response at 300°C has been demonstrated using Pt inter dictating electrodes. Tetrapod-films prepared in a flow of humidified Ar show excellent performance in sensing ethanol with a short response time. A photo current gas sensor made of Ru-sensitized ZnO nano particles has been shown to be highly influenced by the gas molecules adsorbed on the surface. Presence of CO molecule increases the number of electrons on the surface of ZnO and, therefore, leads to an increase in photoconductivity. On the contrary, O2 can capture electrons directly on the surface and lower the concentration of charge carriers in the ZnO conduction band and, therefore, the photoconductivity. A glucose sensor based on ZnO nanorods has also been reported. The negatively charged glucose oxides (GOx) enzyme is immobilized on positively charged ZnO through electrostatic forces. At an applied potential of +0.8 V versus an Ag/AgCl reference electrode, the glucose biosensor shows a linear response from 0.01-3.45 mM and experiment limit of detection of 0.01 mM. The response time was less than 5 s.

Bao et al [14] have constructed a single nanowires light-emitting diode. They disperse ZnO nanowires on a Si substrate and then a poly (methyl methacrylate), or PMMA, thin film is spin-coated onto the substrate. The wire is imaged in a focus ion beam (FIB) system and a pattern for e-beam exposure of the PMMA is defined. The unexposed and partially exposed PMMA is removed and then a metallic contact is deposited onto the top surface of a single nanowires. In this way, the researchers are able to measure the current-voltage characteristics, photoluminescence, and electroluminescence of a single nanowires. Lee et al [15] have proposed the use of well-aligned single-crystalline nanowires to be used as sharp Atomic Force Microscopy (AFM) tips. They predict that ZnO nanowires are structurally compatible with AFM cantilevers under typical operating conditions and are promising candidates for high-aspect-ratio probes for AFM. Huang et al [16] have characterized the mechanical resonances of a single nanowire using an alternating electric field. They have monitored the flexural mode of the nanowires in situ in a Transmission Electron Microscope (TEM). With an elastic bending modulus of ~58 GPa and a damping time constant of ~14 ms for the resonance in vacuum, the investigators conclude that a single ZnO nano wire can be used as a nano resonator and a nanoscale cantilever.

Recently, ZnO has been used in dye-sensitized solar cells as an electrode material [17-20]. Investigations of nano porous dye-sensitized ZnO films have shown that ultrafast electron injection from the dye into the conduction band of the ZnO particles takes place [21-24] comparable to the time scale of electron injection into TiO_2 layers, which has been the subject of investigation for a long time [25].

Semiconductors should have a wide band gap, high charge carrier mobility, and films fabricated from the material need to deliver a high surface area for efficient dye-sensitization and light harvesting, which

can only be achieved by a nanostructure film. Therefore, ZnO seems to be a promising material for this type of solar cell and has the advantage over other metal oxides of easy synthesis of controlled nanostructures. Dye-sensitized solar cells usually have an electrolyte (redox system) to regenerate the dye by electron donation to its ground state after excitation.

1.6 Zinc Oxide Synthesis Techniques

ZnO can be deposited by a variety of techniques such as physical vapor condensation method, radio frequency sputtering [Igasaki et al, 1991], direct current magnetron sputtering [Meng et al, 1995], spray pyrolysis [Song et al, 1994], and chemical vapor phase deposition [Manimi et al, 1997].The material properties (i.e. optical and electrical properties) of the ZnO thin film is critically related to the specific growth technique employed and to the growth parameters used.

There are many methods to synthesize ZnO but the method which is used mostly is vapor transport process. In this process Zn and Oxygen are transported and due to a reaction nanostructure ZnO is formed. The decomposition of ZnO is a very simple and direct method and it is applicable up to very high temperature ~1400 ^{0}C. The second method is to heat up Zn Powder under Oxygen flow. The temperature required for this method is smaller (around 500 ^{0}C to 700 ^{0}C). The vapor transport process is divided in two categories; Vapor Solid (VS) and Vapor Liquid Solid (VLS) process, depending upon the nano structure formed. ZnO nanostructures and nanobelts were synthesized by kong et al In other vapor transport condensation process reported by Ren et al nanostructures were grown.

To achieve nanowires, nanostructures, and nanorods, Yao et al have reported a process in which Zn powder was mixed with graphite and heated to 1100 ^{0}C. The growth of nano tetrpod was found in catalyst free process. There was a report by Wat et al for the rapid heating of Zn pellet at 900 ^{0}C in the presence of ambient air. There is other method of synthesis (though vapor transport is dominant) such as electro deposition, solution gel, and polymer assisted growth. These methods operate at low temperature. A variety of methods exist for ZnO deposition and growth. For consolidation, methods have been categorized as either physical vapor deposition (PVD), chemical vapor deposition (CVD), or solution-based chemistry (SBC) [26].

1.7 Characterization Techniques

After the preparation of the samples, different characterization techniques were used to investigate their structure and optical properties. Scanning Electron Microscope (SEM) was used to get the morphology of the samples. An Atomic Force Microscope (AFM) was utilized to detect the morphology of pretreated substrates. The detailed information about the structure of the samples can be obtained from XRD measurement. The optical properties were investigated by UV spectrometer by absorption and transmission spectra.

1.7.1 Scanning Electron Microscope

The Scanning Electron Microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons

interact with the atoms to make the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. The types of signals produced by a SEM; include secondary electrons, back scattered electrons (BSE), characteristic x-rays, light (cathode luminescence), specimen current and transmitted electrons. These types of signal all require specialized detectors for their detection that are not usually all present on a single machine.

1.7.2 Transmission Electron Microscope (TEM)

Transmission Electron Microscope has been used traditionally as a tool for characterizing local atomic structures of material objects since the information obtained does not require the objects being periodic such as crystal. In the characterization of ZnO nanostructures, TEM is one of the most powerful instruments available due to its excellent imaging and analytical capabilities. TEM imaging allows both the imaging of relatively large areas and the precise measurement of nanostructures diameters.

The TEM has a very high magnification and can give detailed information about the structure of even a single nanostructure. The nanostructures appear 'transparent' in the TEM pictures, which enables the measurement of both inner and outer diameter. It is also possible to determine the number of layers in a nanostructures tube wall and whether it contains any type of structural damage or irregularities. Another type of interesting observation permitted by the TEM is the shape and location of any residual catalyst that may be incorporated in the tube.

One disadvantage with the TEM is that it has to be manually calibrated by taking pictures of special calibration particles several times during each experimental session. The beads have a known size, which is used to compare and calculate the measurements of the particles in the sample. It can also be argued that the TEM is too powerful to generate a fair interpretation of a nanostructures sample. It is far too tempting to concentrate on details rather than on the general picture. Therefore, a SEM or an optical microscope is likely to give a more accurate overall view than a TEM, except when very short (<100 nm) nanostructures are present. The inner structure of the as prepared ZnO nanostructures synthesized by LPCVD was confirmed by TEM.

1.8 Optical properties of ZnO

In condensed matter physics a band gap, also called an energy gap or band gap, is an energy range in a solid where no electron states exist. It is the amount of energy required to free an outer shell electron from its orbit about the nucleus to a free state. The term "band gap" refers to the energy difference between the top of the valence band and the bottom of the conduction band; electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition. The required energy differs for different materials. Electrons can gain enough energy to jump to the conduction band by absorbing either a phonon or a photon. The band gap energy of semiconductors tends to decrease with increasing temperature. When temperature increases, the amplitude of atomic vibrations increased, leading to

larger inter atomic spacing. The interaction between the lattice phonons and the free electrons and holes will also affect the band gap to a smaller extent.

The optical properties of a semiconductor have their genesis in both intrinsic and extrinsic effects. Intrinsic optical transitions take place between the electrons in the conduction band and holes in the valence band, including excitonic effects due to the Coulomb interaction. Excitons are classified into free and bound excitons. In high quality samples with low impurity concentrations, the free excitons can also exhibit excited states, in addition to their ground-state transitions. Extrinsic properties are related to dopants/impurities or point defects and complexes, which usually create electronic states in the band gap, and therefore influence both optical absorption and emission processes. The electronic states of the bound excitons, which may be bound to neutral or charged donors and acceptors, depend strongly on the semiconductor material, in particular the band structure. For a shallow neutral donor bound exciton, for example, the two electrons in the bound exciton state are assumed to pair off into a two-electron state with zero spin. The additional hole is then weakly bound in the net hole-attractive Coulomb potential set up by this bound two-electron aggregate. Similarly, neutral shallow acceptor bound excitons are expected to have a two-hole state derived from the topmost valence band and one electron interaction. Other extrinsic transitions could be seen in optical spectra such as free-to-bound (electron acceptor) and bound-to-bound (donor-acceptor).

Optical properties and processes in ZnO as well as its refractive index were extensively studied many decades ago. The renewed interest in ZnO is fuelled and fanned by its prospects in optoelectronics applications owing to its direct wide band gap of 3.37 eV at room temperature with large exciton energy of 60 meV and efficient radioactive recombination. The strong exciton binding energy, which is much larger than that of GaN (25 meV), and the thermal energy at room temperature (25 meV) can ensure an efficient exciton emission at room temperature under low excitation energy. As a consequence, ZnO is recognized as a promising photonic material in the blue- UV region. Optical properties and processes in ZnO as well as its refractive index were extensively studied many decades ago. The renewed interest in ZnO is fuelled and fanned by its prospects in optoelectronics applications owing to its direct wide band gap of 3.37 eV at room temperature with large exciton energy of 60 meV and efficient radiative recombination. The strong exciton binding energy, which is much larger than that of GaN (25 meV), and the thermal energy at room temperature (25 meV) can ensure an efficient exciton emission at room temperature under low excitation energy. As a consequence, ZnO is recognized as a promising photonic material in the blue- UV region.

The optical properties of ZnO, such as photoluminescence, photoconductivity and absorption, reflectance the intrinsic direct band gap, a strongly-bound exciton state, and gap states due to point defects .A strong room temperature near band-edge UV photo luminescent peak at ~3.2 eV is attributed to an exciton state, as the excitation binding energy is of the order of 60 meV. Optical transitions in ZnO have been studied by a variety of experimental techniques such as optical absorption, transmission, reflection, photo reflection, spectroscopic ellipsometry, photoluminescence, cathode luminescence and calorimetric spectroscopy.

1.9 Electrical Properties of ZnO

Electrical conductivity is a measure of a material's ability to conduct an electric current. When an electrical potential difference is applied across a conductor its movable charges flow, giving rise to an electric current. Due to its physical properties (e.g., high excitonic binding energy, high saturation velocity, high piezoelectric constant) the wide-band-gap semiconductor ZnO is a very promising material for electronic and optoelectronic devices. Such devices include high power, high speed electronics, chemical sensors and blue or UV light emitters. However, most of these applications are currently hampered by the lack of control over the electrical conductivity. A conductor such as a metal has high conductivity and a low resistivity. An inductor like glass or a vacuum has low conductivity and a high resistivity. The conductivity of a semiconductor is generally intermediate, but varies widely under different conditions, such as exposure of the material to electric fields or specific frequencies of light, and, most important, with temperature and composition of the semiconductor material. The degree of doping in solid state semiconductors makes a large difference in conductivity. More doping leads to higher conductivity. The conductivity of a solution of water is highly dependent on its concentration of dissolved salts and sometimes other chemical species which tend to ionize in the solution. Electrical conductivity of water samples is used as an indicator of how salt-free, ion-free, or impurity-free the sample is; the purer the water, the lower the conductivity. Electrical conductivity is strongly dependent on temperature. In metals, electrical conductivity decreases with increasing temperature, whereas in semiconductors, electrical conductivity increases with increasing temperature. Over a limited temperature range, the electrical conductivity can be approximated as being directly proportional to temperature. In order to compare electrical conductivity measurements at different temperatures, they need to be standardized to a common temperature.

It is well known that there is a strong correlation between structural characteristics of the thin films and their electronic transport properties. On the other hand, a heat treatment of the films may modify these structural characteristics. Consequently, in situ measurement of some electrical properties such as the electrical resistivity of thin films during their heat treatment may offer very useful information about possible changes in the film structure determined by the heating process. Keeping in mind this assumption, the temperature dependence of the electrical resistivity, ϱ, during heating of the Zn films was measured in the temperature range 290–660 K to emphasize the oxidation process.

The degree of doping in solid state semiconductors makes a large difference in conductivity. Electrical conductivity is strongly dependent on temperature. In metals, electrical conductivity decreases with increasing temperature, whereas in semiconductors, electrical conductivity increases with increasing temperature. Over a limited temperature range, the electrical conductivity can be approximated as being directly proportional to temperature. (In order to compare electrical conductivity measurements at different temperatures, they need to be standardized to a common temperature). This dependence is often expressed as a slope in the conductivity vs temperature graph.

1.10 About this Book

The main objective for this book is to successfully synthesis of ZnO nanostructures with investigation of the electrical and optical properties in detail by the methods of Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Field Emission Scanning Electron Microscope (FESEM) etc. In this book, physical vapor deposition is used to grow ZnO nanostructures on glass substrates. One the other hand, the electrical and optical properties of ZnO nanostructures were investigated in detail. This book not only provides the effective way to synthesize, but also obtains some beneficial results in aspects of their optical properties and electrical optical properties with experimental foundation for much better and broader applications of ZnO nanostructures.

In the present work, the electrical conductivity and optical properties of ZnO nanostructures have been studied. For electrical measurements, we have measured conductivity in a certain temperature range. It is observed that the conductivity increases with the increase in temperature. There are several models available in the literature to explain this type of behavior. The optical properties of nano crystalline materials have been found to be exciting from both the scientific and technological point of view. The optical band gap of semiconductors and the optical transparency behavior of materials could be altered by controlling the grain and/or pore size in the nano crystalline state. For example, the band gap in CdSe semiconductor could be changed from 3.0 eV for clusters of 1.2¡1.5 nm to 2.3 eV for cluster sizes of 3.0¡3.5 nm due to quantum confinement effects; the bulk material has a band gap of 1.8 eV. The reduction of material dimensions has pronounced effect on the optical properties. The objectives of this investigation are synthesis, characterization, and study of optical & electrical properties of ZnO thin films. SEM was used to examine surface morphology, especially the influence of annealing. X-Ray Diffraction (XRD) was used to identify the crystal phases and lattice parameters. We have used inert gas condensation method. In this method, Zn is evaporated in the presence of oxygen and inert gas (Ar) and the resulting nanorods and nano particles of ZnO are collected on the Glass substrate. This Glass substrate is cooled with the help of liquid Nitrogen. After successful synthesis of these nanostructures, we have studied the electrical and optical properties of ZnO nanostructure. In electrical properties the temperature dependence of dc conductivity is studied to understand the conduction mechanism in these nanostructures. As for optical properties, the optical absorption is studied with the help of absorption spectra. We have calculated the optical band gap of these nanostructures. In the subsequent chapters the details of experimental procedure, literature review measurements of optical and electrical properties and conclusion will be presented.

1.11 References

[1] M. Fuller, Science 70, 196 (1929).

[2] C. Bunn, Proc. Phys. Soc 47, 835 (1935)

[3] S. Iijima, Nature 354, 56 (1991).

[4] M. H. Huang, S. Mao, H. Feick, H. G. Yan, Y.Y. Wu, H. Kind, E. Weber, R. Russo, P. D. Yang, Science 292, 1897 (2001).

[5] J. Y. Li, X. L. Chen, H. Li, M. He, Z. Y. Qiao, J. Crys. Growth 233, 5 (2001).

[6] Z. W. Pan, Z. R. Dai, Z. L. Wang, Science 291, 1947 (2001).

[7] J. J. Wu, S. C. Liu, C. T. Wu, K. H. Chen, L. C. Chen, Appl. Phys. Lett. 81, 1312 (2002).

[8] B. D. Yao, Y. F. Chan, N. Wang, Appl. Phys. Lett. 81,757 (2002).

[9] M.J. Zheng, L.D. Zhang, G.H. Li and W. Z. Shen, Chem. Phys. Lett. 363(2002) 123-128

[10] C. H. Liu, J. A. Zapien, Y. Yao, X. M. Meng, C. S. Lee, S. S. Fan, Y. Lifshitz and S. T. Lee, Adv. Mater. 15(2003) 838-841

[11] P. X. Gao and Z. L. Wang, J. Phys. Chem. B, 108 (2004) 7534-7537

[12] Wang, H. T., et al., Appl. Phys. Lett. (2005) 86, 243503

[13] Tien, L. C., et al., Appl. Phys. Lett. (2005) 87, 222106]

[14] Rout, C. S., et al., Solid State Commun. (2006) 138, 136

[15] Lee, W., et al., Acta Mater. (2004) 52, 3949]

[16] Huang, Y., et al., J. Phys.: Condens. Matter (2006) 18, L179

[17] Bedja, I., et al., Langmuir (1997) 13, 2398

[18] Keis, K., et al., J. Photochem. Photobiol. A (2002) 148, 57

[19] Keis, K., et al., Sol. Energy Mater. Sol. Cells (2002) 73, 51

[20] Keis, K., et al., J. Electrochem. Soc. (2001) 148, A149

[21] Katoh, R., et al., J. Photochem. Photobiol. A (2004) 166, 69

[22] Katoh, R., et al., J. Phys. Chem. B (2004) 108, 4818

[23] Furube, A., et al., J. Phys. Chem. B (2003) 107, 4162

[24] Horiuchi, T., et al., J. Phys. Chem. B (2003) 107, 2570

[25] O'Regan, B., and Grätzel, M., Nature (1991) 353, 737

[26] P. Gao, "Piezoelectric Nanostructures of Zinc Oxide: Synthesis, Characterization, and Devices," in School of Materials Science and Engineering, vol. Ph.D. Atlanta: Georgia Institute of Technology, 2005, pp. 269.