ZnO Growth Technologies:Current Status and Perspectives

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Abstract – **Development of new technologies for ZnO nanomaterials and thin films is of critical importance for further fundamental investigations and practical applications. We discuss on the main technical control of the synthesis of zinc oxide and its properties, which are of significance in understanding the growth mechanism and further developing ZnO-based devices. Next, we present a brief summary of recent research activities, current status and progress in developing improved control of technological processes for zinc oxide as advanced material.**

Index Terms – **ZnO, nanostructures, thin films, synthesis.**

I. INTRODUCTION

Semiconducting metal oxide functional nanomaterials are of potentially broad fundamental and technological interests in science ranging from the quantum physics to optoelectronics [1,2]. Bulk crystals are of importance for making substrates of high quality and for enhanced devices with extended lifetime. However, size reduction to the nanometer range causes quantization of density of states, which alters the intrinsic properties of crystalline materials. Scientific interest for studying the behavior of low-dimensional matter (micro-nano-scale) has accelerated the elaboration of a number of new advanced multifunctional materials with well defined structures, sizes and properties. These novel electronic, magnetic or optical performances of the materials ranging from micro to nano-scale, along with multifunctionality derived from small size effect, have contributed extensively to different fields of device applications, especially for optoelectronics, medical diagnostics, and chemical sensing. Zinc oxide is one of technologically important materials, which presents significant practical and scientific importance for different areas [1-4]. For example, ZnO exhibits various applications in gas sensors, electrodes for dye-sensitized solar cells DSSCs, light-emitting devices, luminescent materials, and thin-film transistors [1-12]. To show potential utilities of zinc oxide material, we noted some typical applications of ZnO low-dimensional structures in Table I (here we present our results only).

TABLE I. OUR RECENT REPORTED APPLICATIONS ON ZNO LOW-DIMENSIONAL STRUCTURES (OUR RESULTS ONLY).

Authors	Year	Application	Refs
Lupan *et al.*	2007	Single Tripod-Nanosensor	[5]
Lupan *et al.*	2008	Nano-photodetector	[6]
Lupan *et al.*	2008	Single Nanorod-sensor	[7]
Lupan *et al.*	2009	Single tetrapod - microsensor	[8]
Lupan *et al.*	2010	Individual Nanowire-nanosensor	[9]
Lupan *et al.*	2010	Nanowire-DSSC	[10]
Lupan *et al.*	2010	Nanowire-LED	[11]
Lupan *et al.*	2011	Tunable-LED	[12]

Thus, understanding its technological aspects is of importance for solving great difficulties in achieving stable doped ZnO due to low-doping efficiency and others.

II. PROBLEMS AND SOLUTIONS

For reliable device applications, a major problem is the lack of reproducible and reliable *n*- and *p*-type conductivity with shallow donor or acceptor states in ZnO, respectively. It is expected that doping low-dimensional crystals will lead to new physics and chemistry as these complex assemblies are investigated [13]. Just like their bulk counterpart, doping of semiconductor nanocrystals by impurity atoms permits tailoring their behavior, which can enable their new application in nano-electronics and nano-optoelectronics [14]. However, multiple previous reports indicated dopant could be difficult for nanocrystals [14]. It has to be mentioned that by a simple addition of a transition metal compounds to the growth solution does not result in incorporation of dopants. These difficulties could be due to the fact that the surface-bound dopants may have different geometries, and exchange coupling interactions with the semiconductor band electrons than substitutionally incorporated dopants have, and the target physical properties of the material may therefore be compromised. Enormous efforts have been directed to this area of research by different research groups worldwide.

Currently several dopants are considered as the most promising dopant for *p*-type ZnO, like Sb, Ag, P, Li, Cu. Another approach is co-doping of elements, which can enhance the solubility of the doping atoms and produce shallower defect levels. At the same time it is still controversial about co-doping, since it requires a complex decision on multiple aspects related to the impurity impact on the crystal structure or the formation of possible secondary phase in the doped region, and the uniformity in distribution for the dopant. Extensive research efforts have been made for the design and control of ZnO crystals with low-dimensions via innovative strategies. Zinc oxide one-dimensional (1D) nano-structures are important due to their conduction behavior of quantum particles and large aspect ratio which permits for distinct structural performance as well as greater chemical reactivity. It is reported that different ZnO nanowires/nanorods can be synthesized easily by using a pattern on any kind of substrate. However, for the monocrystalline-based optoelectronic device fabrications, it is important to control the growth of ZnO single crystalline nanowires directly on film in order to eliminate the strain effect derived from lattice mismatch between mono-crystalline substrates and ZnO single crystalline low-dimensional structures. In this way, the film may serve as a convenient pathway for the transport of electrons, phonons, and photons. Another significant problem is defect chemistry or possibility to control defects in ZnO material. By solving it, it will be possible to tune the functional properties. The most abundant point defects in ZnO are interstitial zinc atom (Zn_i) or oxygen vacancy (V_O). Therefore, it is of importance to carry out more comprehensive study of the technically control over the synthesis technique in order to allow exact control over the defects, the type conduction and the emission properties with the possibility to elaborate and fabricate nano-ZnO -based electrical, magnetic and optical nanodevices.

III. GROWTH OF ZNO

Zinc oxide material posses several types of fastest growth directions [1]. The preferred crystallization could be understood by considering that ZnO wurtzite crystals have different growth rates for different planes too: $V_{(0001)} > V_{(10\bar{1}1)} > V_{(10\bar{1}0)}$ [1,15]. Due to different growth rates, the controlled synthesis of preferred nanoarchitecture for specific applications can be realized by a well control of the synthesis process [15]. The crystal synthesis on a specific surface in the aqueous solution is based on heterogeneous nucleation and subsequent growth. Considering these directions and the polar surfaces due to atomic terminations, zinc oxide exhibits a variety of nanostructures that can be synthesized by controlling the growth rates along these directions. It is well known that a crystal posses different kinetic parameters for different crystal planes, which are emphasized under controlled growth conditions. Thus, synthesis techniques and regimes are very important for synthesis of a specific structure.

The growth techniques for zinc oxide nanostructures can broadly be classified as:

1. solution phase synthesis and
2. gas phase synthesis.

In the solution growth procedures, the synthesis of the material is carried out in a liquid. In most of reports they are in aqueous solutions and the process is referred to as hydrothermal synthesis. Due to the fact that the heterogeneous nucleation takes place at a low level of supersaturation of the complex solution, we can grow different ZnO nanoarchitectures by controlling the reactant concentration, process temperature, and pH value [15]. This technique can be represented by: template assisted growth; spray pyrolysis for growth of thin films; electrophoresis; electrodeposition; sol-gel route; hydrothermal [1,15].

In the gas phase growth procedures: gas phase synthesis is realized in the gaseous environment in a closed chamber. In most of the reports such kind of growth is carried out at elevated temperatures from 450 °C to 1450 °C. The following gas phase methods has been reported: physical vapor deposition; vapor phase transport, which includes vapor solid (VS) and vapor liquid solid (VLS) growth; metal organic chemical vapor deposition (MOCVD); chemical vapor deposition; thermal oxidation of pure Zn and condensation; field assisted thermal decomposition [1]. In Appendixes A-M - some morphological and structural properties of the ZnO low-dimensional structures have been shown. Detailed technological description for these low-dimensional structures and their characteristics has been reported in our works [15-30].

These new developments of the technological methods are believed to offer new perspectives for zinc oxide crystal and nanostructures growth by well established techniques.

IV. CONCLUSION

ZnO low-dimensional structures are attractive building-blocks for applications in a micro-nano- devices like sensors, photodetectors, energy generators, solar cells, light-emitting devices as well as artificial structures for tissue engineering. Within the next decade, zinc oxide nanostructures will move into industrial applications, if its growth and performances can be well controlled. Also, if synthesized low-dimensional structures will be integrated in devices by using different approaches, e.g. focused ion beam nanoliphography [29], self-assembly, electric-field assisted assembly, etc.

Aligning of the grown nanorods and nanowires can be realized using a specific template. Simplest way used to make ordered nanowire arrays during of growth is ZnO film grown on substrate is to create on the surface equal conditions to form seeds and grow to form uniformly distributed nucleus and finally nanorods [15]. It is anticipated that the ZnO branched rods will find many applications in novel nanodevices and are expected to promote synthesis of nanorod *p-n* junctions.

Future work: Our future research efforts will be directed towards synthesizing oriented one – dimensional nanorods, which will facilitate construction of semiconductor oxide-based nanodevices with well-ordered alignment, which are extremely important for scientific, technological and industrial application. Development of single doped ZnO nanorod LED for light emission sources. Also, high sensitivity and selective nanosensors as well.

APPENDIX A

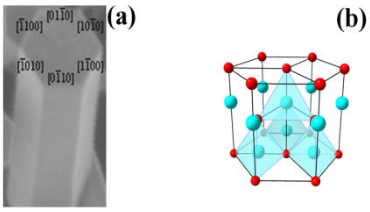

Fig. A. (a) SEM image of the single ZnO Nanorod grown by an aqueous technique at 97 °C from $ZnSO_4$ and NaOH solution. Also directions are indicated on SEM image. (b) Stick-and-ball representation of zinc oxide crystal structures.

APPENDIX B

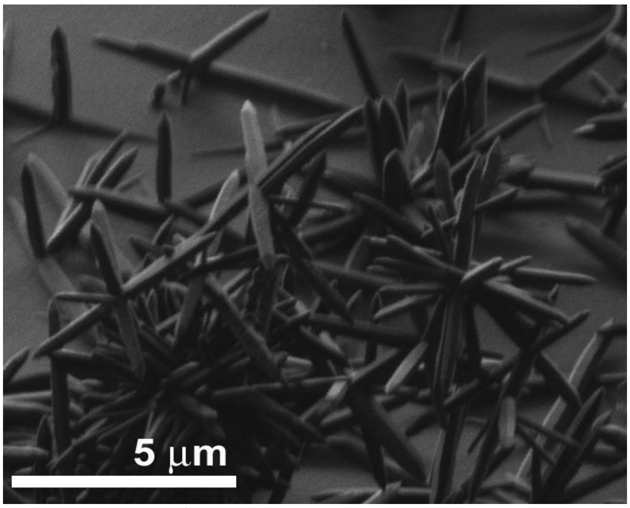

Fig. B. SEM image of the ZnO Nanowires branched in complex structures grown by an aqueous technique at 97 °C from $ZnSO_4$ and NaOH solution.

APPENDIX C

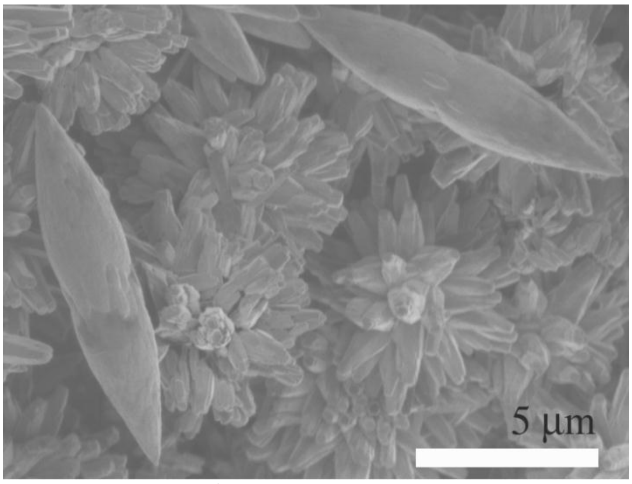

Fig. C. SEM image of the ZnO branched needles synthesized in a hydrothermal process at 77 °C from $ZnSO_4$ and NH_4OH solution.

APPENDIX D

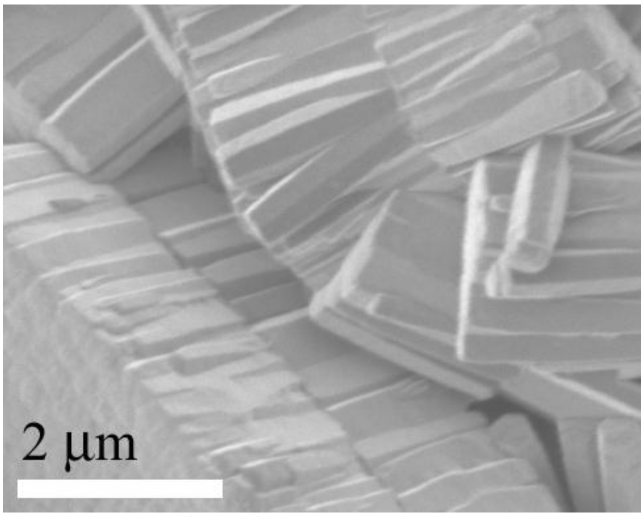

Fig. D. SEM image of the self-assembled nanorods grown by hydrothermal technique.

APPENDIX E

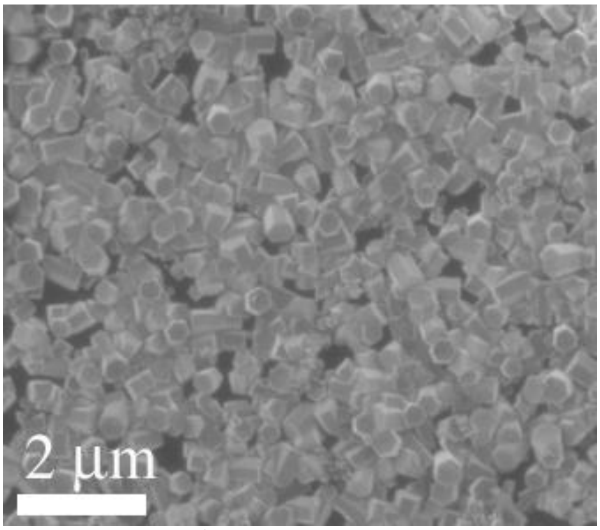

Fig. E. SEM image of the Mn-doped ZnO nanorods synthesized in a hydrothermal process at 97 °C aqueous solutions.

APPENDIX F

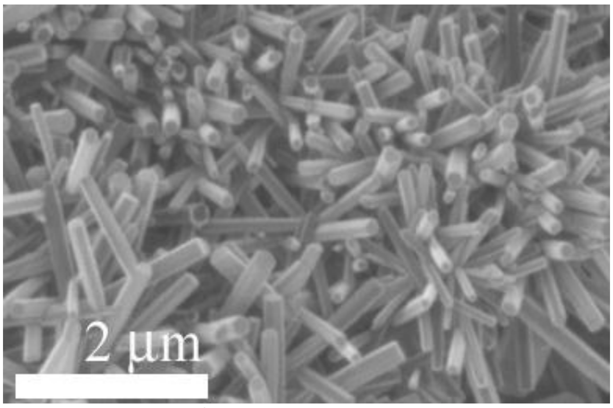

Fig. F. SEM image of the Ag-doped ZnO nanorods synthesized in a hydrothermal process at 95 °C from $ZnSO_4$, $AgNO_3$ and NH_4OH solution.

APPENDIX G

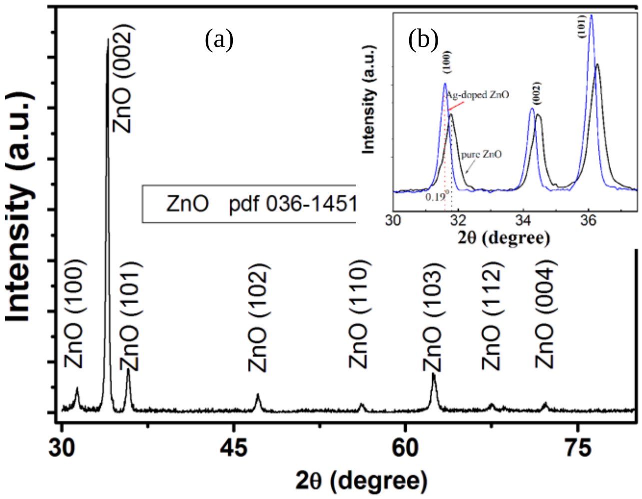

Fig. G. (a) XRD pattern of ZnO nanorod arrays as-prepared on glass synthesized by the aqueous-solution method. (b) XRD pattern of doped ZnO nanorod arrays on glass synthesized by the aqueous-solution method showing shift of the peaks due to lattice parameters changes.

APPENDIX h

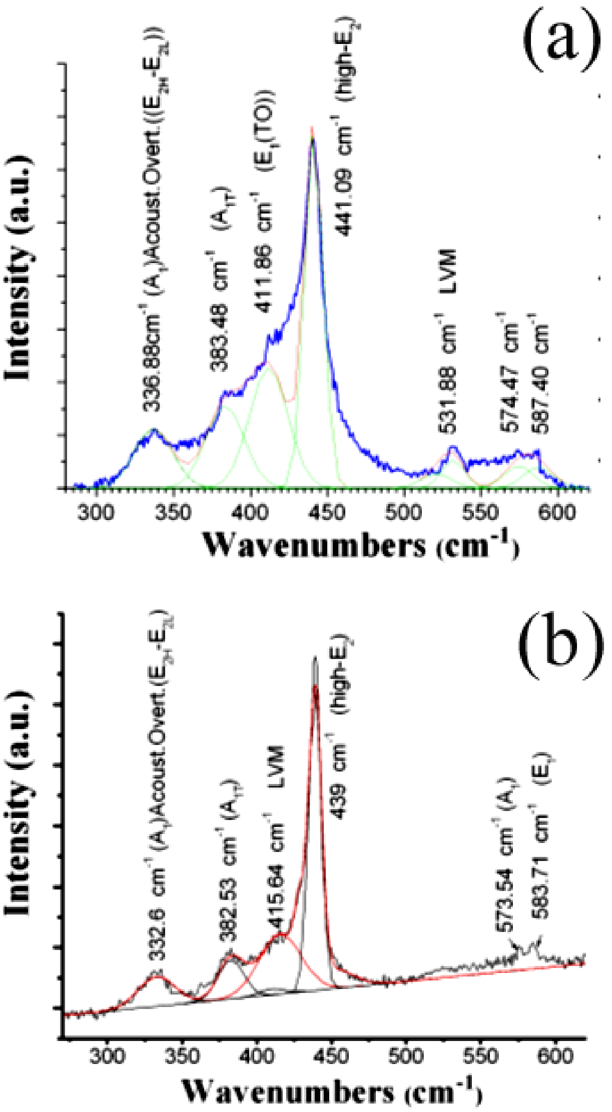

Fig. H. Deconvolution of the 300-600 cm-1 region with Raman peaks using Gaussian fit of Micro-Raman scattering spectra of: (a) Sb-doped ZnO nanorods and (b) Ag-doped ZnO nanorods.

APPENDIX I

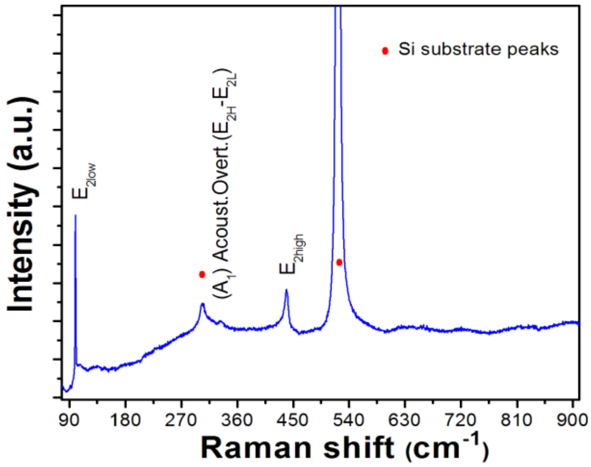

Fig. I. Raman shift of ZnO nanorod arrays on Si substrate synthesized by the hydrothermal method showing the good crystalline quality of the material to be used in a nano *p-n* junction applications.

APPENDIX J

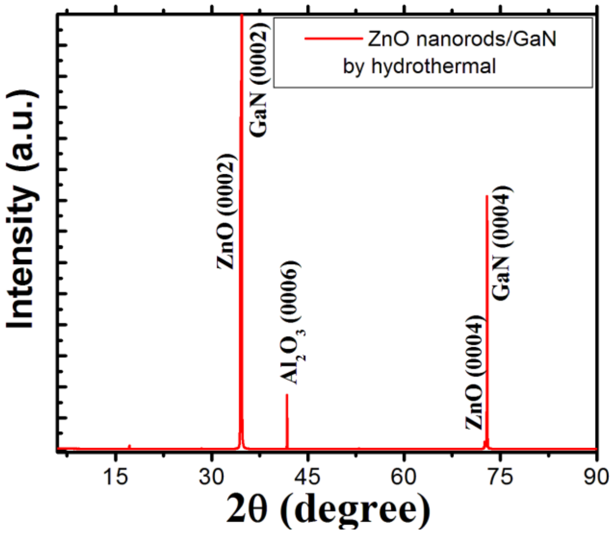

Fig. J. X-ray diffraction θ-2θ scan of the ZnO nanorods grown on GaN/sapphire (0001) substrate by hydrothermal technique.

APPENDIX K

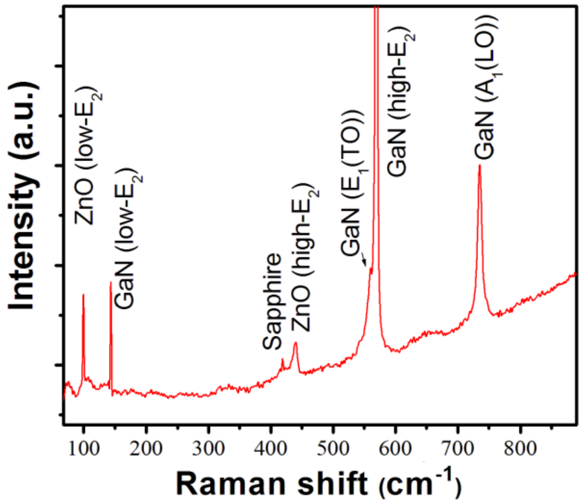

Fig. K. Room-temperature Raman spectra of ZnO nanorods hydrothermally grown on GaN substrate.

APPENDIX L

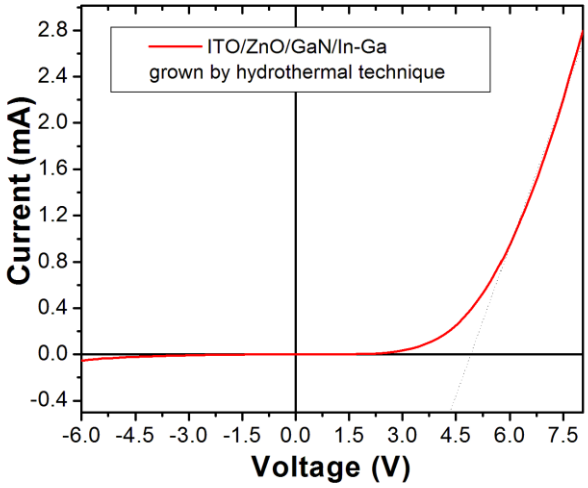

Fig. L. *I-V* characteristics of the ZnO nanorods/*p*-GaN heterojunction in the dark measured at 300 K.

APPENDIX M

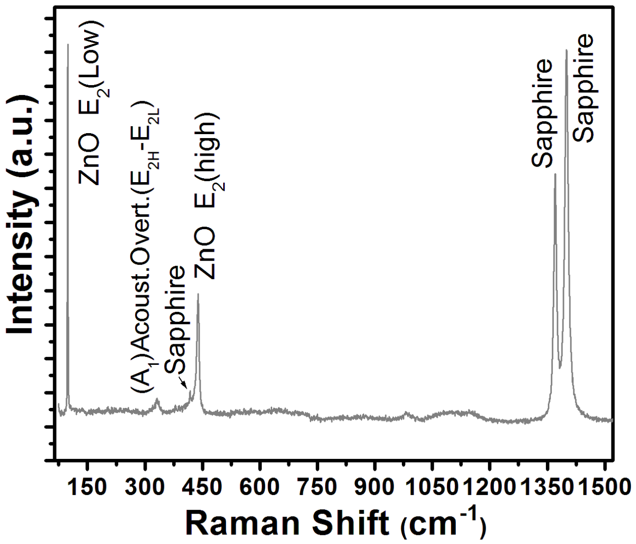

Fig. M. Room-temperature Micro-Raman scattering spectrum of the zinc oxide nanorods grown by hydrothermal technique on sapphire substrate with single crystal structure.

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