Zinc Oxide – The Material of Future Optoelectronics and Photonics

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***Abstract* — In this review paper we present new possibilities for nanostructuring of ZnO grown by MOCVD, CVD and electrochemical deposition. The prospects for future applications of ZnO are evaluated on the basis of laser developments. We demonstrate, in particular, lasing effects in both individual ZnO nanorods, microtetrapods and various spatial architectures. We show that nanostructuring leads to a considerable enhancement of the radiation hardness of the material. A comparative analysis of the properties of ZnO and GaN is realized and important advantages of ZnO are identified.**

I. INTRODUCTION

Nowadays the electronic circuits are based on silicon, the onchip technologies being mainly limited to electrical interactions. Researchers are looking for the possibility to bring on chip optoelectronic, magnetic and photonic interactions, bio- and piezo-electrical technologies etc. In this connection the humankind needs a material that is cheap and at the same time compatible with semiconductor technologies, optical technologies, biotechnologies and nanotechnologies. The material should be environmentally-friendly and exhibit piezoelectric and magnetic properties, transparency in the visible region, good semiconducting properties (allowing both n- and p-type doping) etc. Is there such a material in nature?

Fortunately, there is a binary compound, namely zinc oxide, that meets all the requirements mentioned above. This compound is actually not new and it has been used in various branches of industry for a dosen of years. In particular, at present it is widely used for medical purposes: anticeptics, rashes, sunscreen lotions, to name a few. Besides, it is used as filler in rubber manufacturing, pigment for paintings and coatings, piezoelectrics, transparent thin film coatings in electronics etc. Note that Zn is relatively abundant and ZnO is inexpensive.

Zinc oxide is a wide band gap semiconductor compound (E_g = 3.37 eV at 300 K), with high melting temperature (1975 °C) and high electron mobility (> 100 cm^2/Vs). There are several reports on p-type conduction and ferromagnetic behavior of ZnO. Zinc oxide is a direct bandgap semiconductor possessing a high exciton binding energy (~ 60 meV) and is considered the most promising material for solid state lighting. It is important to note, in this regard, that an efficient band gap engineering can be accomplished by substituting either Cd or Mg for Zn to provide emission of all visible wavelengths. Lattice-matching and controlled growth is facilitated by the hexagonal (wurtzite) structure. Being synthesized by all vapor phase and a number of solution methods, ZnO is an excellent material for nanotechnological applications, including nanoscale electro-mechanical fabrication. It is characterized by the largest variety of nanostructures such as single-crystalline nanoneedles, nanowires, nanobelts, nanorings, nanohelixes, nanoflowers, nanocombs etc.

Non-toxicity, low production cost and superior optical properties inherent to ZnO may lead to a more efficient solid-state lighting technology and revolutionize the optoelectronics industry in the near future. In particular, nanostructured ZnO may stimulate the development of a number of important fields such as electronic sensors, photovoltaics, nano-bio-medicine, nano-robotics, providing a tremendous economic and social impacts.

II. RESULTS AND DISCUTIONS

Due to the possibility of multiple and switchable growth directions of the wurtzite structure and the high ionicity of its polar surfaces, ZnO provides conditions for the formation of a rich diversity micro/nanostructure.

A multitude of synthesis methods, such as various wet chemical methods [1,2], sol-gel methods [3], metal organic chemical vapour deposition (MOCVD) [4], electrochemical deposition [5] and metal-catalyzed vapour-liquid-solid (VLS) growth [6] has been applied for the fabrication of ZnO micro/nanostructures. Apart from VLS growth, a related thermal chemical vapour transport and condensation method without metal catalysts has been employed [7].

We have grown a variety of ZnO nanostructures such as hexagonal nanorods, cylinders, tetrapods, microtorches and other specific nanostructures as illustrated in Fig. 1 with a carbothermal evaporation process in horizontal or vertical furnaces with an argon/oxygen flow with various technological conditions such as gas flow rates and temperatures regimes.

In this process, the Zn vapour is first generated from a carbothermal reduction of ZnO in the high temperature zone of the furnace. Subsequently it is transported into the lower temperature zone of the furnace, and deposited on the surface of a substrate where Zn is oxidized by reacting with CO/CO_2 and oxygen from the gas flow

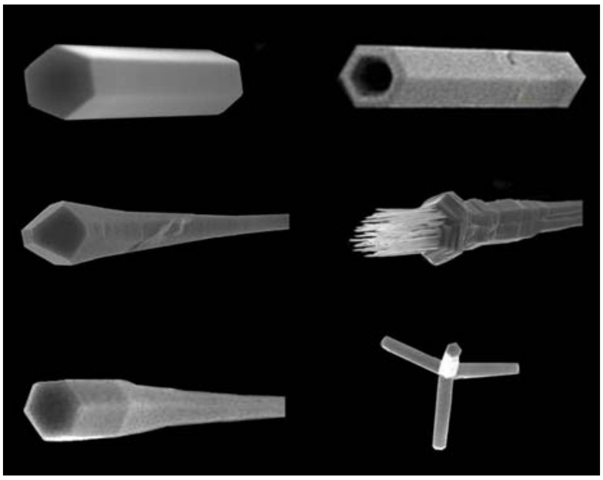

Fig.1. A variety of ZnO nanostructures grown by carbothermal chemical vapor transport.

These nanostructures represent suitable building nano-elements for nanofabrication. A fascinating property of the technology is the possibility of self-assembling of these nanostructures in microstructures like cylindrical, spherical or planar assembly of nanotetrapods as shown in Fig. 2.

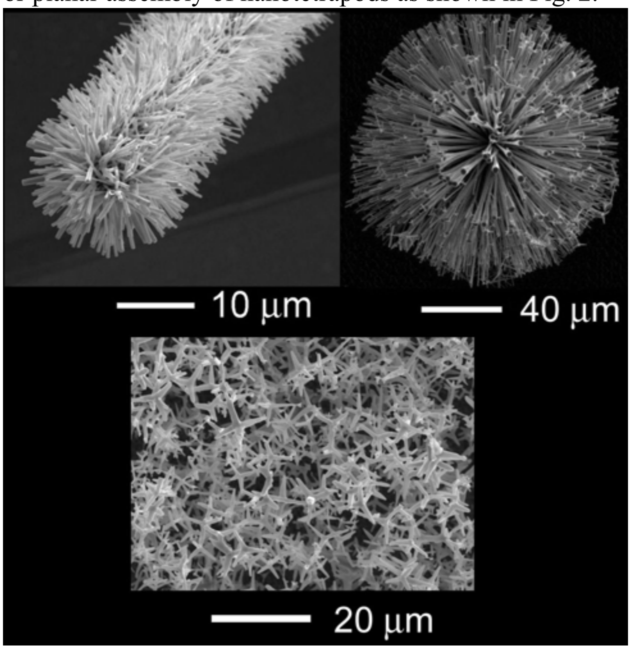

Fig. 2. Self assembled microstructures consisting of ZnO nanostructures.

Another method employed for the growth of nanostructured ZnO layers is metalorganic chemical vapor deposition (MOCVD) in a horizontal set-up consisting of a source furnace and a main furnace as described elsewhere [8]. Zinc acetylacetonate hydrate was used as source material introduced into the source furnace. The vapours were transported into the main furnace by Ar gas flow which was mixed with another flow of Ar and O_2 gases at the entrance of the main furnace. The variation of the gas flow rates results in the growth of layers with different morphologies such as nanodots, arrow-headed nanorods, or nano-carpets as illustrated in Fig. 3.

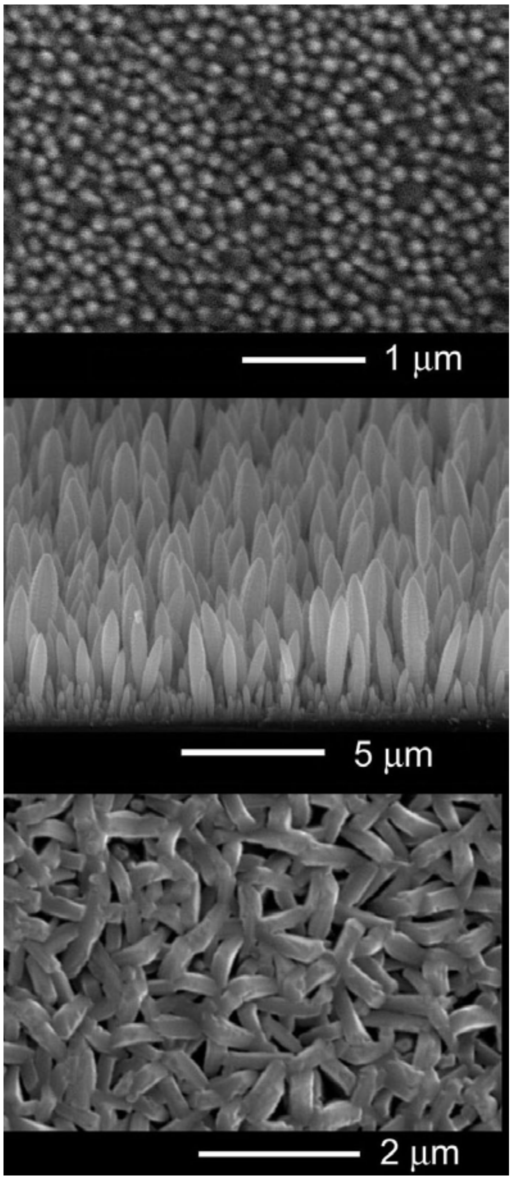

Fig. 3. Nanostructured ZnO layers with different morphologies grown by MOCVD.

One of the advantages of carbothermal CVD and MOCVD growth is the very high optical quality of the produced ZnO nanostructures. However, these methods require relatively high growth temperatures which make the technology expensive.

In contrast to this, electrochemical deposition is a cost-effective and versatile method for the preparation of a variety of morphologies ranging from nanorods, as shown in Fig. 4 (upper section), to complex assemblies as demonstrated in the middle and lower sections of Fig. 4. The electrochemical deposition was performed from an electrochemical solution consisting of ($Zn(NO_3)_2$) and (H_2O_2) with an Ag/AgCl reference electrode, a Pt counter electrode and a metallic Zn plate as a substrate working electrode. Zinc hydroxide ($Zn(OH)_2$) is formed as result of chemical reactions after the application of a cathodic potential. The hydroxide is transformed into zinc oxide which is deposited onto the cathode at temperatures above 60 °C.

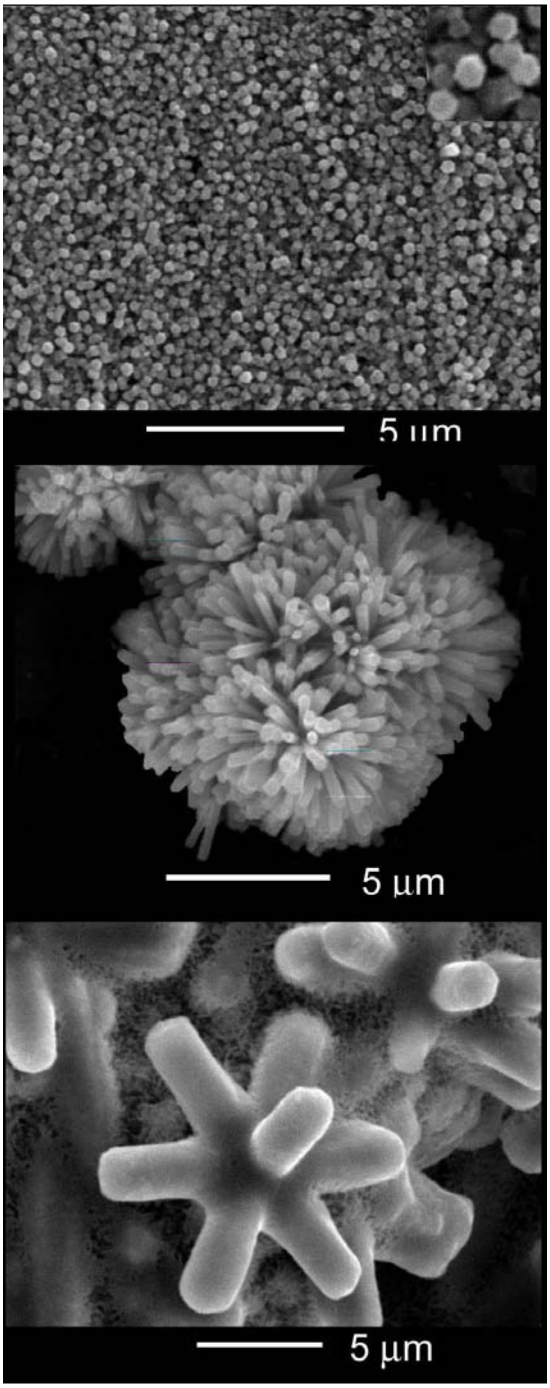

Fig. 4. Layers of ZnO nanorods and assemblies prepared by electrochemical deposition.

ZnO assemblies similar to those presented in the left and middle sections of Fig. 2 are perspective structures for lasing devices due to the high optical quality of the material produced by CVD [9]. Each of the nanostructures constituting the assembly may represent an individual laser, and the emission from these lasers is superimposed in the assembly. Figure 5 demonstrates lasing from an individual ZnO nanorod and an individual microtetrapod.

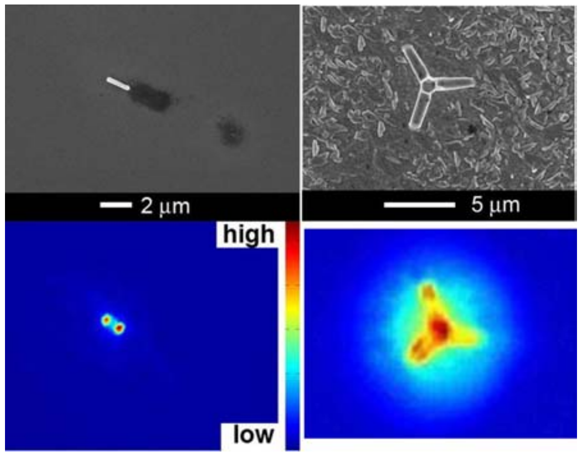

Fig. 5. The SEM images (upper row) and the CCD images of a ZnO nanorod and a microtetrapod at lasing conditions (lower row).

The spectral characteristics of these nanolasers are presented in Fig. 6.

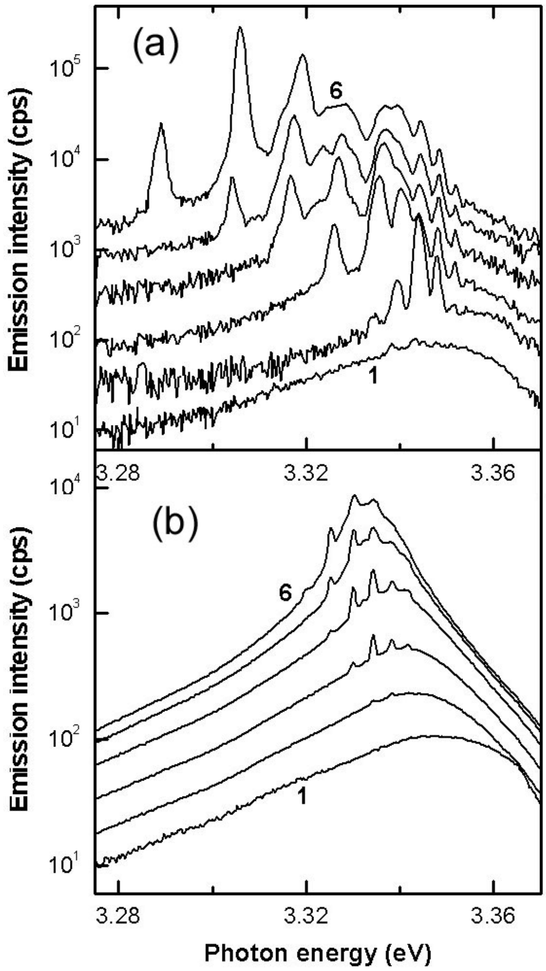

Fig. 6. (a) Lasing in a single nanorod with the length of 1.5 μm and the diameter of 300 nm measured with different excitation power densities: 1 – 115; 2 – 150; 3 – 310; 4 – 580; 5 – 760; 6 – 1400 kW/cm^2; (b) Lasing in a single ZnO tetrapod with the leg length of 12 μm measured with different excitation power densities: 1 – 100; 2 – 150; 3 – 275; 4 – 500; 5 – 800; 6 – 1100. The spectra are excited by 10 nsec laser pulses at 10 K.

The lasing emission lines of the nanorod are defined by the guided modes. The number and the spectrum of lasing modes fit well the expected resonance spectrum of a 1.5 µm long nanorod with a diameter of 300 nm calculated by solving numerically the Helmholtz equation taking into account the anisotropy of both index of refraction and gain as well as the material dispersion [10]. In the microtetrapod the laser emission lines are well explained by longitudinal Fabry-Perot modes generated in cavities formed by individual tetrapod legs.

Nanostructured layers grown by MOCVD with morphologies illustrated in Fig. 3 have been recently demonstrated to be especially suitable for the elaboration of random lasers [11]. On the other hand, these layers as well as assemblies of nanotetrapods and microtetrapods similar to that illustrated in the lower section of Fig. 2 present especial interest for photovoltaic (PV) cells. PV Solar Energy conversion is increasingly being recognized as a key renewable energy source for the future. There are essentially two concepts that could potentially revolutionize PV technology: the first is the use of nanostructured devices which allows independent optimization of the contact interfacial area and transportation pathways of excitons, electrons, holes and/or ions; the second is the use of cheap and abundant materials in a nanostructured configuration. Electrochemical deposition of ZnO is a most suitable technology satisfying the second concept, since it is non-expensive from one side and ensures preparation of ZnO nanostructures with controlled morphology, as illustrated in Fig. 4.

Another major advantage of ZnO nanostructures is their superior optical characteristics and enhanced radiation hardness as compared to GaN which is the second material considered actually promising for solid state lighting, high-frequency and high-power electronics.

The luminescence spectra (Fig. 7) have been used for the investigation of radiation hardness and the impact of nanostructuring upon the radiation hardness in GaN [12] and ZnO [8].

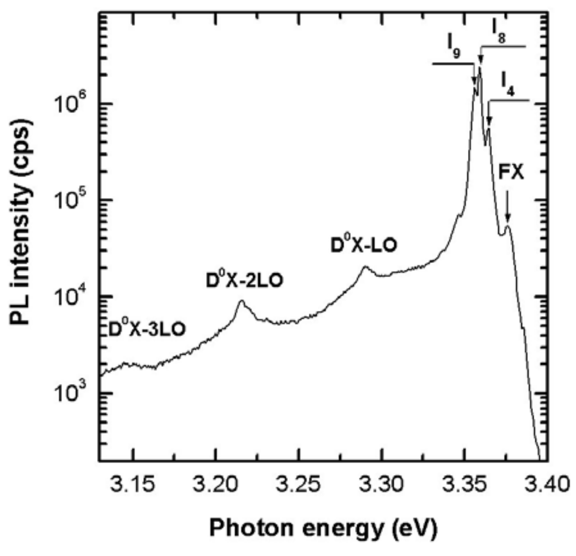

Fig. 7. Typical cw low temperature (10 K) PL spectrum of the ZnO material produced by carbothermal CVD.

The analysis of Fig. 8 demonstrates that nanostructuring of both GaN and ZnO leads to the enhanced radiation hardness, while the radiation hardness of ZnO is considerably higher than that of GaN.

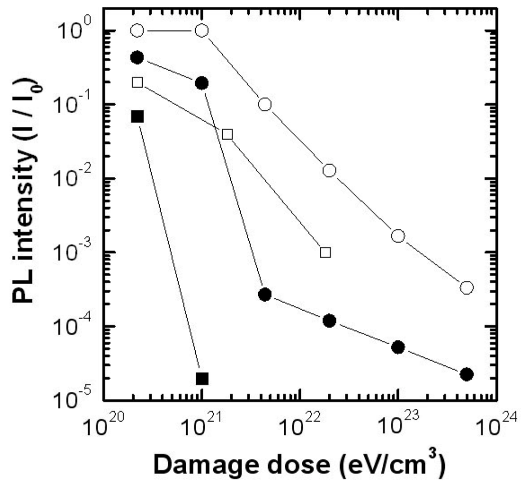

Fig. 8. Dependence of the integral PL intensity upon the irradiation damage dose in bulk (open symbols) and nanostructured (full symbols) GaN (squares) and ZnO (circles) layers grown by MOCVD. The PL intensity (I) is normalized to the intensity in non-irradiated samples (I_0).

III. CONCLUSION

The presented data demonstrate possibilities for nanostructuring of ZnO and the prospects for future applications of ZnO in lasers, photovoltaic cells, and other radiation hard devices.

ACKNOWLEDGMENTS

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