
PHD theses

Synthesis and characterisation of zinc-oxide thin films and nanostructures for optoelectrical purposes

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BACKGROUND

Semiconducting ZnO is an actively researched material of the past few decades. Among others, its piezoelectricity and photoconductivity make it a highly appealing material for sensorics. As a wide band-gap semiconductor it can be applied in UV/blue light emitting devices, transparent electrodes, or even for spintronics. It can be deposited on cheap substrates in high quality with low temperature methods. One of the most important applications is as a substitute for indium tin oxide as the transparent oxide of a number of optoelectronic devices, such as silicon based solar cells, as it is considerably cheaper and easier to synthesise. The study of ZnO nanostructures began in MFA in 2008 under the supervision of János Volk. Thin film ZnO and Al:ZnO prepared by magnetron sputtering had been studied earlier, and we started investigating atomic layer deposition (ALD) in 2010, since then, ALD ZnO, Ga, Al and Ti doped ZnO films have been in the focus of our work. I have been working with ZnO since 2009, first as a diploma work, then as my doctoral work.

AIMS

The aim of the present work was to deposit ZnO thin films, and grow nanostructures on top of them, which can later be applied in optical and optoelectronic devices. My work focused on the preparation and characterisation of nanostructures that could be applied for such purposes.

One of the focuses of my research was to investigate if the commonly used ITO transparent electrodes in GaN based LEDs could be replaced by doped ZnO. Ga doped ZnO seemed to be the most promising candidate for this purpose, but first, the optimal doping concentration had to be found to achieve films with the required crystallinity and electrical properties, and at the same time the possible problems arising during LED manufacturing had to be addressed. These thin films were deposited with ALD.

The second aim of my work was to prepare micro- and nanostructured ZnO architectures and examine their optical properties. This required

finding the appropriate seed layer and the optimal growth parameters. I prepared micrometre sized ZnO columns, wires and whiskers by a cheap and simple wet chemical method at a low temperature. The ZnO columns were grown perpendicular to the substrate surface into well-defined locations prepared by e-beam lithography. As one of the focuses of my research was to apply these structures in optical devices (e.g. to increase the light extraction of LEDs), therefore I also examined their optical behaviour with simulations and compared the results with experiments.

Due to their high specific surface, hierarchical ZnO structures grown in several deposition steps may have a significant application as active semiconducting components of in dye sensitized solar cells. The base of these structures was a conductive, doped ZnO film and the ordered ZnO nanocolumns grown on top of that. The specific surface was increased with a second seed layer and a consequent growth of side branches. The aim was to prove the active role of the side branches in increasing the efficiency of the solar cells. The deposition of the secondary seed layer was attempted with sol-gel technique, and also with ALD, which offers a much more conformal coverage.

Finally, as the disadvantage of e-beam lithography is that it can only access a limited area, and photolithography could not ensure the required resolution, I developed a new patterning procedure to grow ZnO columns organised in a hexagonal pattern. I used self-assembled silica nanospheres to achieve a large area high resolution photolithographic technique.

THESES

1. TWO STEP METHOD TO PREPARE GZO FILMS FOR LED PURPOSES

I applied rapid thermal annealing between two ALD steps in the case of Ga doped ZnO films, thus ensuring the small contact resistance of the p-GaN/GZO interface ($1,33 \times 10^{-2} \Omega \text{cm}^2$) and the high conductivity of the GZO film ($5,2 \times 10^{-4} \Omega \text{cm}$). I showed that the Ga dopant is incorporated into the ZnO matrix, and acts as a donor, thus increasing the carrier concentration and the conductivity of the films. I showed that the GZO layers prepared this way can be applied as transparent conductive oxides in LEDs and their thickness, composition and electrical properties are homogeneous in 4" wafer size as well. [A]

2. SIMULATION AND DIFFRACTION MEASUREMENT OF COLUMNAR ZNO STRUCTURES

I prepared ordered epitaxial ZnO nanowires on the surface of traditional, InGaN/GaN based blue LED structures. The two dimensional columnar photonic crystal yielded a 17%, 19%, and 32% integral light extraction efficiency growth measured in 0° , 30° , and 60° angles to the surface normal in the case of a 500 nm lattice constant. I measured the transmission and the first order diffraction peak corresponding to a given wavelength, in the case of ordered nanostructures grown on sapphire. The transmission curve defined with the finite difference time domain method and the experimental curve agreed well. [B]

3. GROWTH OF ZNO NANOCOLUMNS WITH A SELF-ASSEMBLED PHOTOLITHOGRAPHIC MASK

I developed a new method to grow ordered ZnO nanocolumns on a large area using a self-assembled photolithographic mask layer. The wet chemical growth took place from the hexagonally ordered holes defined in photoresist by the illumination of silica or polystyrene spheres applied on the surface by the Langmuir-Blodgett technique. The advantage of this procedure is its speed compared to other methods, and that it does not require the preparation of a mask, and has a high resolution: The distance between the holes can be reduced to as low as 400 nm. Using the finite-difference time-domain method I showed that the limit of the resolution is 400 nm using 200 nm thick photoresist. [C]-[D]

4. PREPARATION AND EXAMINATION OF HIERARCHICAL ZNO STRUCTURES

I developed a new method to prepare hierarchical ZnO structures with a two step method consisting of the deposition of an unordered nanocrystalline seed layer with sol-gel technique or atomic layer deposition followed by a wet chemical growth. Using the adsorption and dissolution of D149 dye, I established the relative specific surface of the nanostructures, which showed an as high as two orders of magnitude growth compared to the flat reference. The dye sensitized solar cells using these hierarchical ZnO nanostructures showed a significantly higher short circuit current than the columnar reference. [E]

PUBLICATIONS CONNECTED TO THE THESES

[A] Szabó Z, Baji Z, Basa P, Czigány Z, Bársony I, Wang H-Y, Volk J Homogeneous transparent conductive ZnO:Ga by ALD for large LED wafers **APPLIED SURFACE SCIENCE 379**: pp. 304-308. (2016), *IF: 3.15*

[B] Szabó Z, Erdélyi R, Makai J, Balázs J, Volk J Highly ordered three-dimensional ZnO nanorods for novel photonic devices **PHYSICA STATUS SOLIDI C-CURRENT TOPICS IN SOLID STATE PHYSICS 8**:(9) pp. 2895-2898. (2011), *Conference proceeding*

[C] Szabó Z, Volk J, Fülöp E, Deák A, Bársony I Regular ZnO nanopillar arrays by nanosphere photolithography **PHOTONICS AND NANOSTRUCTURES 11**:(1) pp. 1-7. (2013), *IF: 1.792*

[D] Volk J, Szabó Z, Erdélyi R, Khánh NQ Engineered ZnO nanowire arrays using different nanopatterning techniques **PROCEEDINGS OF SPIE - THE INTERNATIONAL SOCIETY FOR OPTICAL ENGINEERING 8263**: Paper 82631L. 6 p. (2012), *Conference proceeding*

[E] Szabó Z, Fülöp E, Erdélyi R, Volk J Hierarchical ZnO nanostructure based solid-state dye-sensitized solar cell, **Solar Energy for World Peace**, August 17-19, 2013, Istanbul, Turkey, *poster (Best poster award)*

FURTHER PUBLICATIONS

[F] Erdélyi R, Halász V, Szabó Z, Lukács I E, Volk J Mechanical characterization of epitaxially grown zinc oxide nanorods **PHYSICA E-LOW-DIMENSIONAL SYSTEMS & NANOSTRUCTURES 44**:(6) pp. 1050-1053. (2012)

[G] Zolnai Z, Toporkov M, Volk J, Demchenko DO, Okur S, Szabó Z, Özgür Ü, Morkoç H, Avrutin V, Kótai E Nondestructive atomic compositional analysis of BeMgZnO quaternary alloys using ion beam analytical techniques **APPLIED SURFACE SCIENCE 327**: pp. 43-50. (2015)