PROPERTIES OF GaP/ZnO HETEROSTRUCTURES FOR PHOTOVOLTAICS

J. Kováč[1], M. Čaplovičová[2], D.Búc,[1] T.Brath[1], J.Kováč jr [1], P. Eliáš[3], S. Hasenohrl[3] and J. Novák[3]

[1] *Institute of Electronics and Photonics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia*
[2] *Department of Geology of Mineral Deposits, Comenius University, Bratislava, Slovakia*
[3] *Institute of Electrical Engineering, Slovak Academy of Sciences, Bratislava, Slovakia*
E-mail: jaroslav.kovac@stuba.sk

Received 30 April 2012; accepted 09 May 2012.

1. Introduction

Zinc oxide (ZnO) is emerging as a multifunctional material for broad applications in blue and ultraviolet optoelectronic devices because of its direct and wide band gap of 3.4 eV [1,2]. Conductive and transparent *n*-type ZnO thin films have significant commercial impact due to their use as transparent electrodes for solar cells [2], organic light emitting devices and flat panel displays. Nanowire solar cells are promising devices for solar energy conversion. They are inexpensive since of the small amount of material needed and are efficient because of strong light absorption and rapid carrier collection. In the past few years, photovoltaic devices have been reported based on arrays of dye-sensitized ZnO nanowires, nanoflowers, nanotrees, silicon nanowires, nanocones, and multi-layered nanopillars and nanorods. The enhanced optical absorption of these photovoltaic devices compared to planar solar cells can be attributed to three effects [3]. Significant progress has been made in thin film solar cells that have demonstrated efficiency in excess of 30 percent for GaAs based multijunction solar cells, which are being used for space mission [4]. During the last decade, several new concepts for solar-to electric energy conversion have been reported to challenge the traditional photovoltaic devices based on the *p–n* junction diode. The most promising amongst the alternative approaches has been the high efficiency multijunction solar cells using GaN/InGaN, ZnO/MgZnO. We proposed to incorporate wide band-gap pGaP/nZnO nanowires (NWs) junction to increase solar cell efficiency to shift the absorption edge more to the blue part of the solar spectrum (350-480 nm). The GaP/ZnO heterojunction is formed in nanowires (NWs), which allow for an enhanced photon capture at the cell top. Among a variety of techniques for deposition of ZnO thin films on GaP substrate and GaP NWs the pulsed-laser deposition (PLD), metal-organic chemical vapor deposition, radio-frequency (RF) DC and magnetron sputtering is utilized.

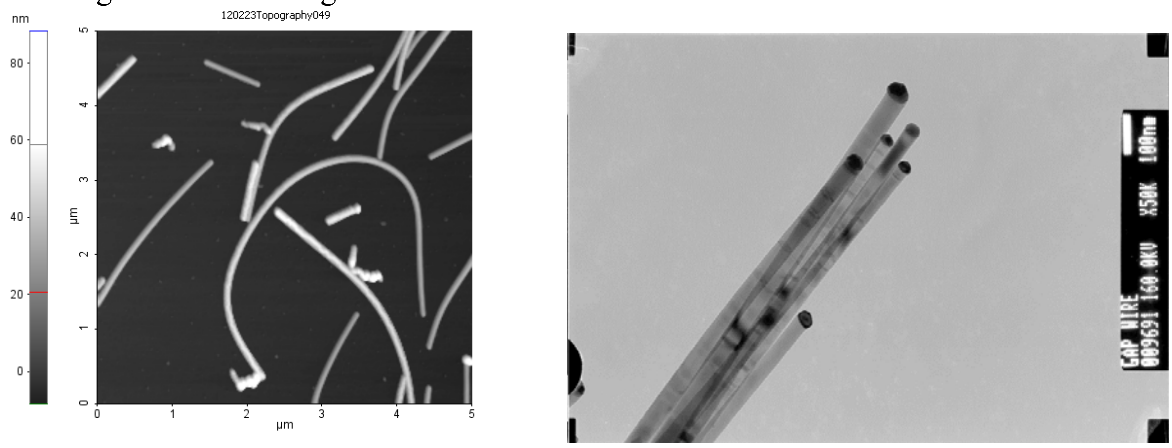
In this paper, we discuss the deposition of ZnO thin layers on GaP substrate and GaP nanowires by RF magnetron sputtering and their influence on the structural properties. The main goal of this work is to find the optimal technology for deposition very thin ZnO layers by RF magnetron sputtering with defined parameters to cover round GaP nanowires surface prepared by MOVPE technology.

2. Experimental

The GaP NWs were prepared in an AIX 200 MOVPE low-pressure reactor by a vapour-liquid-solid (VLS) method from 30 nm BBI colloidal gold particles. Zn-doped GaP(111)B substrate was deposited with Au particles (30 ± 1) nm in diameter from a water-based colloidal solution. The Au particles were randomly distributed over the substrate at a density of ~ 2 × 10^8 cm^{-2}. Nanowires deposition was performed in palladium purified H_2 carrier gas from phosphine (PH_3) and trimethylgallium (TMGa) used as the phosphorus and gallium sources, respectively [5]. ZnO thin films were deposited on GaP substrate and GaP substrate covered by NWs by using RF reactive magnetron sputtering at room temperature (RT). ZnO n-type conductivity is relatively easy to realize via excess Zn or with Al or Ga doping. A sintered disk of ZnO:Al (99.99% purity for both ZnO and Al_2O_3) with 2 at. % Al_2O_3 was used as the target. The diameter and the thickness of the target were 76 and 5 mm, respectively. The distance of substrate and target centres was fixed at 60 mm and central axes of the sample and target was tilted under 85 degrees. Prior deposition, the rinsed substrates were placed on the rotating substrate holder. The vacuum chamber was evacuated to a base pressure of 2.10^{-3} Pa before sputtering and then high-purity Ar and O_2 (99.99% for both cases) were introduced as sputtering gas and reactive species, respectively. The total pressure was fixed at 0.3 Pa. The Ar/O_2 partial pressure ratio was set to the desired value equal to 100:1. Prior to film deposition, the target was pre-sputtered for about 10 minutes to remove the surface contaminants. ZnO films were sputtered at room temperature for 20 minutes at RF power of 125 W. The surface morphologies of ZnO films and core-shell GaP-ZnO NWs were examined by SEM and AFM. The nanostructures were examined using transmission electron microscopes JEOL JEM 2000 FX equipped with the ASID20 scanning unit and JEOL JEM 200CX, working at accelerating voltages of 160 and 200 kV, respectively. Energy dispersive spectrometer (EDS) Noran Explorer was used for determination of the chemical composition of the nanostructures.

3. Results and discussion

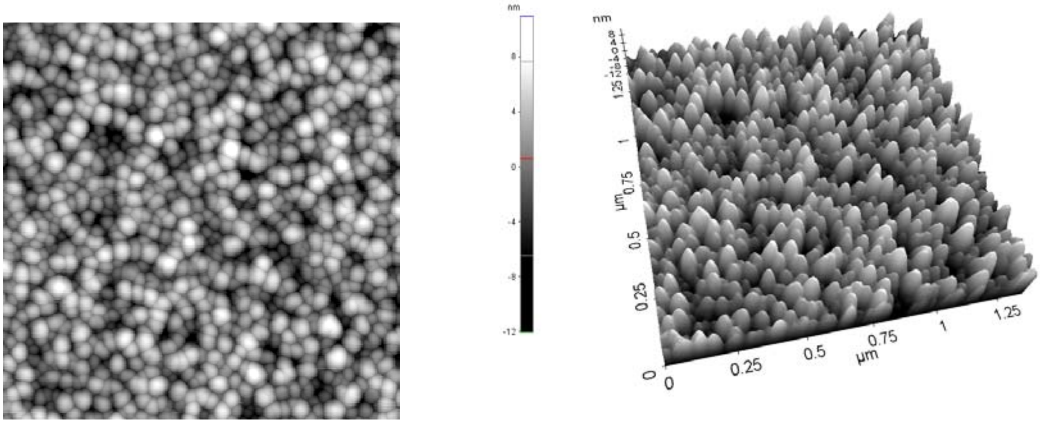
After growth of GaP NWs on GaP substrate the nanowires were removed from GaP on Si substrate for AFM investigation. In Fig.1a are depicted the different shapes of GaP NWs with revealed base and end of nanowires during growth. The as-grown wires are typically ~ 4- 6 μm long and 50–80 nm in diameter which was confirmed by the detail TEM image as shown in Fig.1b.



a) b)

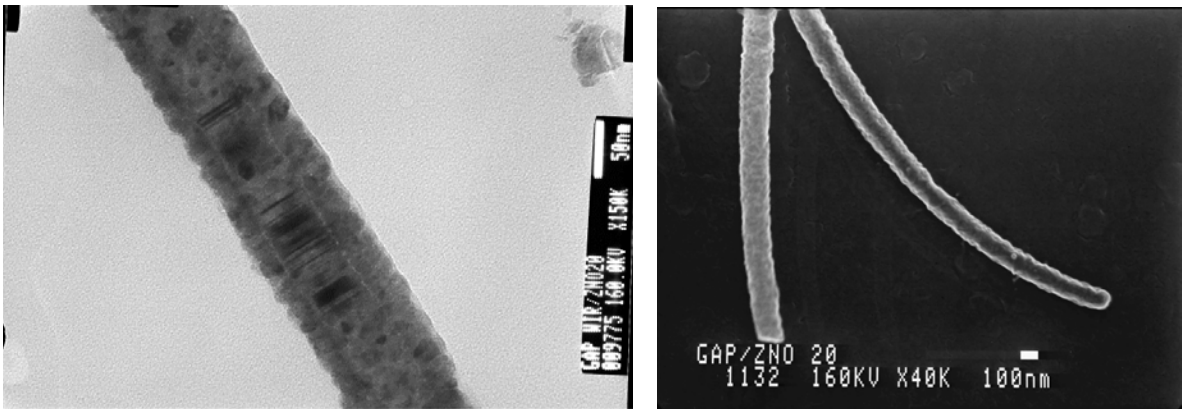
Fig. 1 a) AFM image of different broken GaP NWs and b) TEM image of GaP nanowires cluster after their MOCVD growth

GaP nanowires were stuck on TEM Cu-grid covered by collodium and carbon layers and then examined under transmission electron microscope. The 2D and 3D surface morphology AFM image of ZnO layer deposited on GaP reference substrate is shown in Fig.2a,b. The polycrystalline ZnO layers show good homogeneity of the grains ordering with ~10 nm grain height and ~50-80 nm grain diameter. The ZnO layers show n-type conductivity with concentration in the range of $6.10^{16} – 1.10^{18}$ cm^{-3} and resistivity 0.46 –19 Ωcm.



a) b)

Fig. 2 a) 2D and b) 3D AFM image of as deposited ZnO layer surface morphology



a) b)

Fig. 3 a) Detailed bright field TEM image of GaP nanowire covered with ZnO:Al film and b) SEM image of GaP NW with deposited ZnO:Al layer

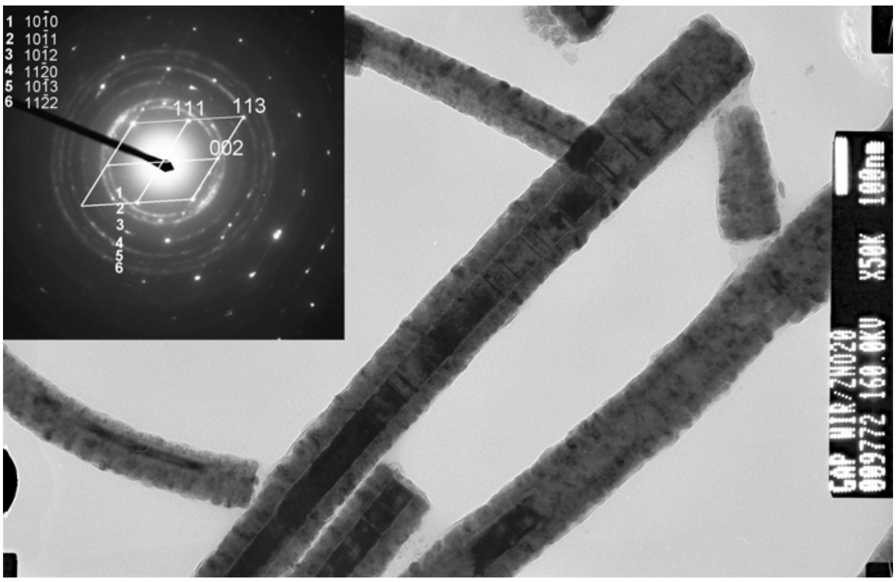


Fig. 4 GaP nanowires covered with nanocrystalline ZnO layer. The presence of GaP and ZnO is evidenced by SAED pattern

The core-shell GaP/ZnO NWs were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As can be seen in detailed bright field TEM image Fig. 3a the ZnO shells were deposited on the nanowire surface with the different side thickness ~20-40 nm. The surface morphology of ZnO layer is in Fig. 3b. By evaluation of spot SAED pattern in Fig. 4 it was determined that GaP nanowire has zinc blende crystal structure and growth axis [111] (Fig. 3a). The ZnO layer exhibited nanocrystalline character and the rings in SAED pattern denoted as 1, 2, 3, 4, 5, and 6 belong to most intense reflections of ZnO according to ICCD 36-1451. The spots in SEAD pattern in Fig. 4 spots are assigned to GaP nanowire (in the centre of image) according to ICCD 12-191.

4. Conclusions

Significant research effort is underway on ZnO nanostructures due to their unique properties for application in transparent electronics, photovoltaics, ultraviolet light emitters, piezoelectric devices, chemical sensors and spin electronics. In this paper, we have discussed growth and characterization of ZnO polycrystalline layers and core-shell GaP/ZnO nanowires examined by AFM, SEM and TEM. TEM images of a GaP/ZnO nanowires revealed that GaP nanowire has zinc blende crystal structure and growth axis [111]. On the other hand ZnO polycrystalline layer formed nano-crystals grains with wurtzite structure and columnar structure. The results revealed the ability to utilize n-ZnO/p-GaP core-shell nanowires for application in the solar cells development and will be subjected for future electrical and optical properties investigation.

Acknowledgement

The work is supported by grant of Science and Technology Assistance Agency "GRONA", no. APVV-0301-10 and VEGA projects 1/1106/12 and 1/0689/09

References:

[1] D. P. Norton, Y. W. Heo, M. P. Ivill, K. Ip, S. J. Pearton, M.F. Chisholm, T. Steiner. *Materials Today*, **7**, 34, (2004)

[2] A. Strohm, L. Eisenmann, R. K. Gebhardt, A. Harding, T. Schlftzer, D. Abou-Ras, H. W. Schock, *Thin Solid Films*, 480–481, **162** (2005).

[3] Marijn A. M. Versteegh, Ruben E. C. van der Wel, and Jaap I. Dijkhuis, *Applied Physics Letters* **100**, 101108 (2012)

[4] Tatsuya Takamoto, Eiji Ikeda, Hiroshi Kurita, and Masamichi Ohmori, *Appl. Phys. Lett.,* **70**, 381 (1997)

[5] S. Hasenöhrl, P. Eliáš, I. Vávra, I. Novotný, J. Kováč, J. Novák, XIV European Workshop on Metalorganic Vapor Phase Epitaxy EW-MOVPE 2011, June 5-8, Wrocław, Poland, p.259-262