

FABRICATION AND CHARACTERIZATION OF N-TYPE ZINC OXIDE/P-TYPE BORON DOPED DIAMOND HETEROJUNCTION

Marián Marton^{*} — Miroslav Mikolášek^{*} — Jaroslav Bruncko^{**}
Ivan Novotný^{*} — Tibor Ižák^{***} — Marian Vojs^{*}
Halyna Kozak^{***} — Marián Varga^{***}
Anna Artemenko^{***} — Alexander Kromka^{***}

Diamond and ZnO are very promising wide-bandgap materials for electronic, photovoltaic and sensor applications because of their excellent electrical, optical, physical and electrochemical properties and biocompatibility. In this contribution we show that the combination of these two materials opens up the potential for fabrication of bipolar heterojunctions. Semiconducting boron doped diamond (BDD) thin films were grown on Si and UV grade silica glass substrates by HFCVD method with various boron concentration in the gas mixture. Doped zinc oxide (ZnO:Al, ZnO:Ge) thin layers were deposited by diode sputtering and pulsed laser deposition as the second semiconducting layer on the diamond films. The amount of dopants within the films was varied to obtain optimal semiconducting properties to form a bipolar p-n junction. Finally, different ZnO/BDD heterostructures were prepared and analyzed. Raman spectroscopy, SEM, Hall constant and I-V measurements were used to investigate the quality, structural and electrical properties of deposited heterostructures, respectively. I-V measurements of ZnO/BDD diodes show a rectifying ratio of 55 at ± 4 V. We found that only very low dopant concentrations for both semiconducting materials enabled us to fabricate a functional p-n junction. Obtained results are promising for fabrication of optically transparent ZnO/BDD bipolar heterojunction.

Key words: boron doped diamond, zinc oxide, Raman spectroscopy, bipolar heterostructure, wide-bandgap

1 INTRODUCTION

Doped diamond is a unique material due to its physical and chemical properties. The most significant advantages compared to other semiconductors are: wide-bandgap (5.47 eV), very high breakdown voltage (20 MV/cm) and high charge carrier mobility (4500 and 3800 cm²/Vs for electrons and holes, resp.), low dielectric constant, radiation and chemical resistance, high working temperature and possibility to concentrate large power into small area [1–3]. Technological methods for both types of doping need to be used for application in active electronic devices. While the deposition of p-type diamond requires only a simple addition of boron containing gas (diborane, trimethylborane) into the gas mixture during the CVD growth, deposition of n-type diamond is difficult due to the dimensions of classic donors (P, As) which are not able to effectively be built into the diamond lattice. This is the limiting factor in production of bipolar diamond electronics.

Zinc oxide (ZnO) is also a wide-bandgap (3.37 eV) semiconductor which is electrically similar to diamond, it has high breakdown voltage, low noise, high working temperature and power [4–6]. Alike diamond, ZnO is optically transparent, radiation and chemically resistant and

biocompatible. However, the p-type doping is here the issue and therefore it is not possible to produce bipolar devices based only on ZnO material. A solution of the absence of one type doping in both wide-bandgap semiconductors could be the application of p-type diamond (boron doping) and n-type ZnO (Al, Ga, Sc doping) and thus, producing a transparent wide-bandgap heterostructure (n)ZnO/(p)diamond. Combination of the diamond and ZnO unique properties opens wide range of application in electronics, sensorics, photovoltaics and biotechnology.

2 EXPERIMENTAL PART

The growth of boron doped diamond (BDD) thin films was performed in the HFCVD reactor installed at UEF FEI STU [7]. The BDD films were grown for 3 hours in CH₄/H₂/(H₂ + TMB) gas mixture (1 % of CH₄) at 3 kPa in order to obtain thickness of 300 nm. The H₂ and (H₂ + TMB) flows were set to vary the boron to carbon ratio (B/C) in gas mixture to 500, 1000, 2000, 5000, 10000, and 15000 ppm. The substrate temperature was maintained at 600 °C by 5 hot tungsten filaments (0.7 mm diameter) heated up to 2000 °C. Doped ZnO lay-

^{*} FEI STU, Ilkovičova 3, 812 19 Bratislava, Slovakia, marian.marton@stuba.sk ^{**} International Laser Center, Ilkovičova 3, 841 04 Bratislava, Slovakia; ^{***} Institute of Physics, ASCR, Cukrovarnická 10, 162 00 Prague 6, Czech Republic

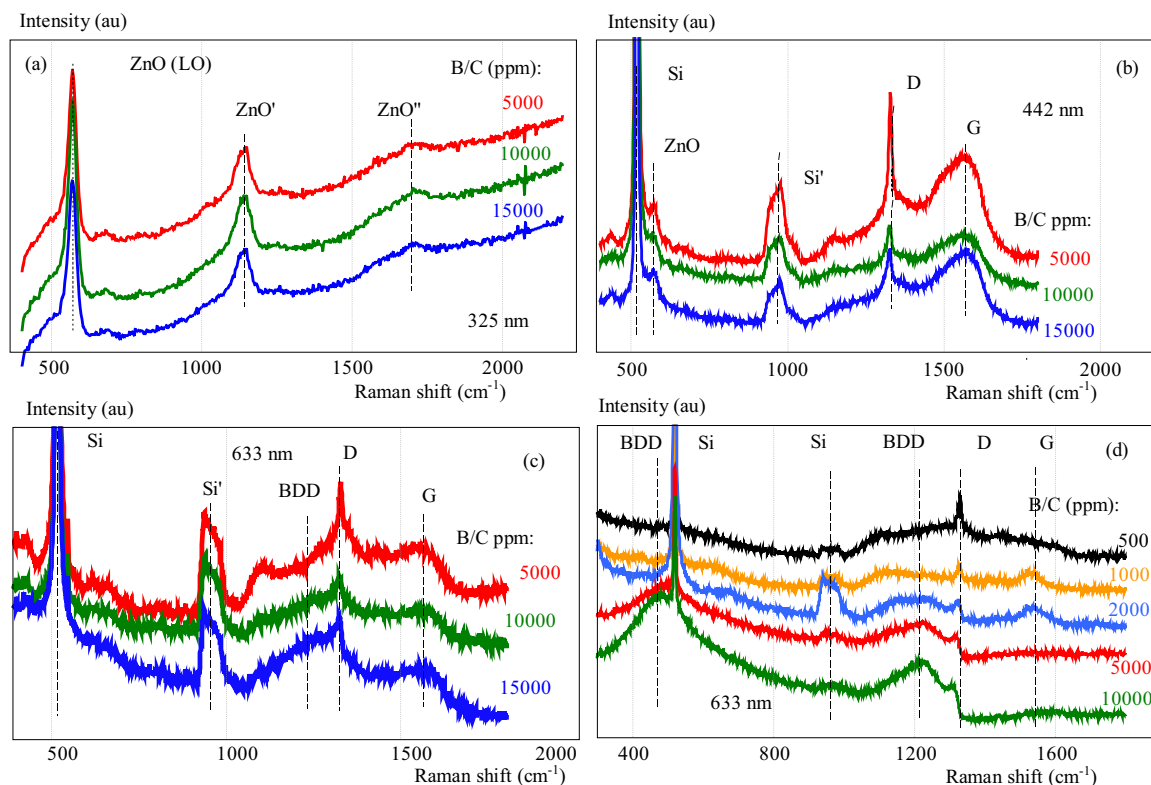


Fig. 1. Raman spectra of the ZnO:Al/BDD heterostructures measured with (a) — 325, (b) — 442, (c) — 633 nm laser excitations, (d) — Individual BDD layers with 500–10000 ppm B/C ratio in the gas mixture

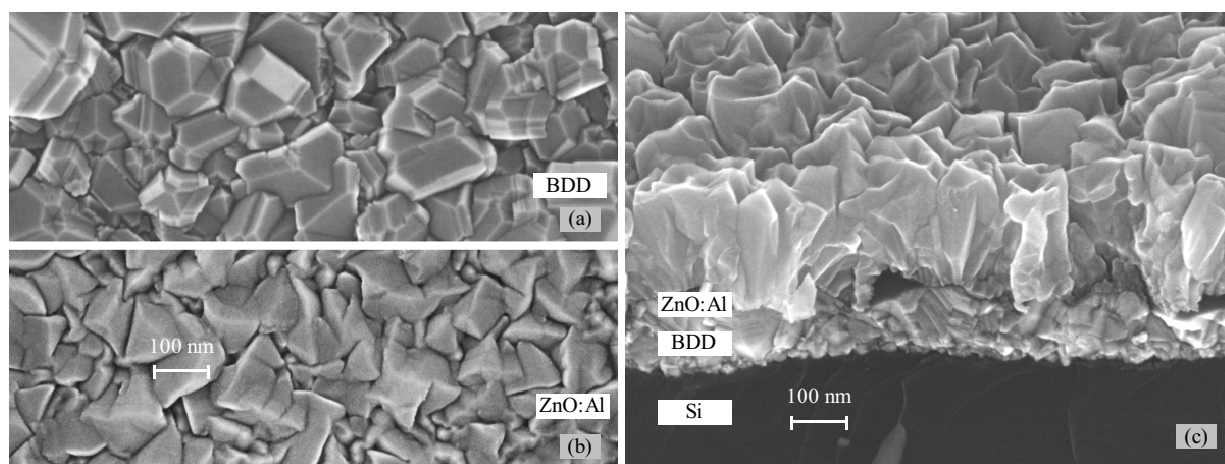


Fig. 2. SEM images of (a) — prepared BDD and (b) — ZnO:Al layers (both viewed from top) and (c) — cross section of the final ZnO:Al/BDD heterostructure

ers were prepared by RF and PLD sputtering methods. ZnO:Al(2% Al_2O_3) target was used for RF sputtering for 20 min at temperature 100 °C and 1.33 Pa Ar pressure. RF source power was 800 W and substrate holder diameter was 6 inch. For PLD sputtering, ZnO:Al(1% Al_2O_3) and ZnO:Ga(0.15% Ga_2O_3) targets were used in 5 Pa O_2 pressure, temperatures 20 (room temperature), 200 and 400 °C for 10 min. BDD and ZnO layers were both deposited on Si, Si/SiO₂ (2 μm CVD SiO₂) and UV grade silica glass substrates in terms of electrical characterization of each film independently.

Morphology and structure of prepared samples were characterized by SEM JEOL 7500F and Raman spectroscopy (Renishaw InVia Reflex Raman spectrometer with the excitation wavelength of 325 and 442 nm and ISA Dilor-Jobin Yvon-Spex Labram confocal system with the excitation wavelength of 633 nm). Electrical properties were determined using 4-point resistivity and Hall method measurements described elsewhere [8]. To form ohmic contacts, BDD thin films were contacted with a 10 min vacuum annealed (10^{-3} Pa, 425 °C) Ni/Au (10/50 nm) double-layer and ZnO with a 100 nm Al layer.

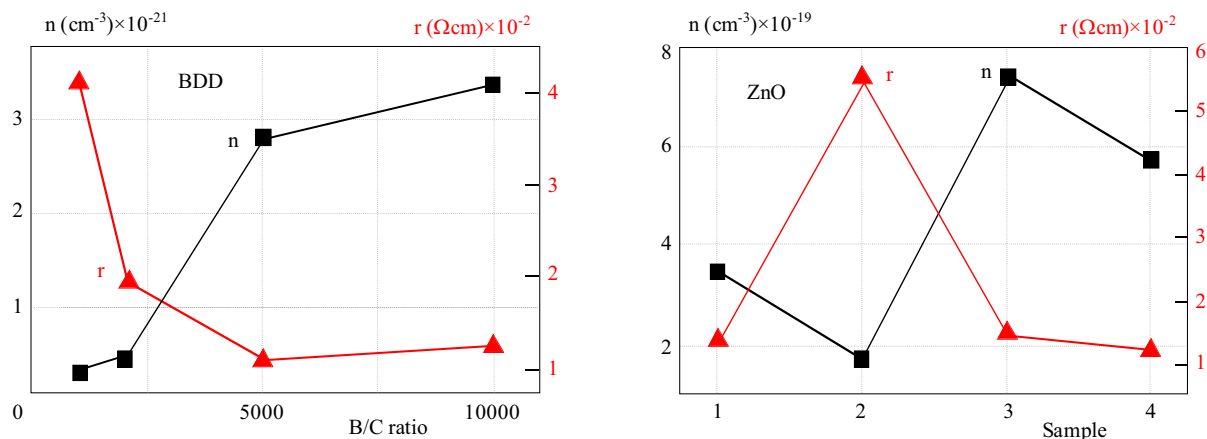


Fig. 3. Charge carrier concentrations and resistivity of BDD and ZnO layers obtained by Hall method. The x -axis represents different samples: for BDD (left) the samples differ in B/C ratio, for ZnO layers (right) the samples differ in target material and deposition temperature, i.e. 1-ZnO:Ga 400 °C, 2-ZnO:Ga 200 °C, 3-ZnO:Al 200 °C, 4-ZnO:Al 400 °C

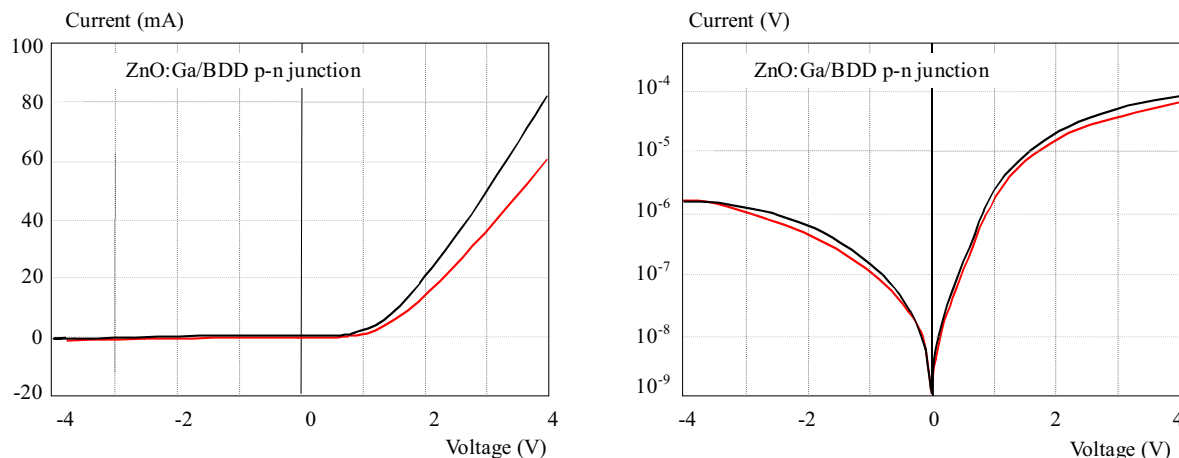


Fig. 4. I-V curves of ZnO:Ga/BDD p-n heterojunctions in linear (left) and logarithmic (right) scale. (ZnO:Ga was deposited at temperature of 20 °C and the B/C ratio of BDD was 500 ppm)

3 RESULTS AND DISCUSSION

3.1 STRUCTURE AND MORPHOLOGY CHARACTERIZATION

Raman spectra of the ZnO films deposited on BDD layers recorded at 325, 442 and 633 nm laser excitation wavelengths are shown in Fig. 1a, b and c, respectively. Since the 325 nm laser excitation wavelength is close to the ZnO band gap (350 nm), only spectra measured by this excitation wavelength showed clearly recognized ZnO Raman lines. The spectra of ZnO films are dominated by the same maxima with similar intensities independently on the boron doping in the BDD film (Fig. 1a). The presented LO (longitudinal) mode at 568 cm^{-1} , of E_1 symmetry, and its overtones (1145 and 1709 cm^{-1}), are typical for c -axis aligned ZnO crystals [9]. For other laser wavelengths the Raman lines of the ZnO films were hardly detectable due to decreased absorption, i.e. in Raman spectra the signals from BDD and Si were dominating.

In the recorded Raman spectra, BDD films are represented by several characteristic bands. The broad maxima at approximately 500 cm^{-1} and 1220 cm^{-1} are associated with incorporation of boron into the diamond lattice [10]. The increase in its intensity follows the increase in B/C ratio. As the boron concentration in gas mixture raised, the peaks became more visible and finally dominate the spectrum for the highest boron concentrations. The 500 cm^{-1} maximum is attributed to the local vibrational modes of the boron pairs [10] and the small shoulder at 1320 cm^{-1} is associated with polycrystalline diamond in highly boron doped films. A peak at 1332 cm^{-1} (D) corresponding to the polycrystalline diamond was also recorded in spectra of the films with lower and no (residual) boron concentrations. The maximum at 1580 cm^{-1} (G) is due to the sp^2 bonded carbon located mainly at grain boundaries, inter- and intra-granular defects. The small bands at 1140 cm^{-1} and 1430 cm^{-1} are associated with transpolyacetylene at grain boundaries [11]. Figure 1d shows the continuous change in Raman spectra related to the change of B/C ratio in the gas

mixture during the CVD deposition process of the BDD layers. The sharp peak at 521 cm^{-1} and the broad one at 950 cm^{-1} belong to the Si substrate.

SEM images (Fig. 2) show the surface of BDD (a), ZnO (b) and cross-section of the deposited heterostructure ZnO/BDD (c). Both BDD and ZnO layers were homogeneously deposited over the whole substrate. The grain size of BDD films was in the submicron scale ($< 400\text{ nm}$) and the sputtered ZnO films overgrown its surface copying its morphology with the characteristic columnar structure. The thickness of the individual layers was around 300 nm and thus, the whole ZnO/BDD hetero-structure reached $600 \div 700\text{ nm}$ in thickness.

3.2 ELECTRICAL CHARACTERIZATION

In order to prepare a properly operating p-n heterojunction, both of the used wide-bandgap materials need to exhibit good enough semiconducting properties. However, BDD as well as ZnO are known as semimetals if the doping level is higher than a so-called transition value ($2\text{--}3 \times 10^{20}\text{ cm}^{-3}$ for BDD) [5, 12]. Therefore, layers of both materials with different dopant concentrations were prepared and examined in this study. Figure 3 shows charge carriers concentrations and resistivity of different BDD or ZnO layers as measured by Hall method for various doping concentrations. As expected, the higher B/C ratio in the gas mixture resulted in higher boron concentration in the diamond films and the resistivity decreased down from 4.11×10^{-2} to $1.06 \times 10^{-2}\Omega\text{cm}$. Similarly, the higher substrate temperature during ZnO depositions leads in higher charge carrier concentrations and lower resistivity from 4.53×10^{-2} to $1.2 \times 10^{-2}\Omega^{-2}\text{cm}$.

After analyzing individual layers, we have fabricated ZnO/BDD heterostructures by depositing ZnO on BDD layers. Although we have used only layers with low doping concentrations, only few structures were properly operating as a bipolar heterojunction. If the doping level was too high, only ohmic like character was observed. For the BDD layers, the doping level was limited to 500 ppm of B/C gas mixture ratio, combined with room temperature deposited ZnO:Ga layers. Similar limitation with highly doped BDD layers was observed also by Hikavyy *et al* [13] who prepared a heterojunction using hydrothermally deposited ZnO films and boron doped nanocrystalline diamond. Other works of Wang *et al* [14, 15] presented a p-n heterojunction prepared from ZnO and highly doped BDD deposited on single crystal diamond. They did not observe ohmic like behavior of the investigated structures, nevertheless, only ZnO layers without dopants were used in the published studies. Hence, we can suppose that the use of non-doped ZnO layers might be a good option which allows application of highly doped BDD layers for fabrication of p-n junction as well.

Representative current-voltage characteristics ($\pm 4\text{ V}$) of ZnO/BDD p-n heterojunction are shown in Fig. 4. Up to three areas with nearly linear character can be seen in the logarithmic scale of I-V curves, what together with a rectifying ratio of 55 at $\pm 4\text{ V}$ confirm the diode like

functionality of the p-n heterojunction. In the works of Wang *et al* [14, 15] slightly higher rectifying ratio was observed (*ie* 120), which is most probably due to the non-doped ZnO layers used. Although these values are relatively small in comparison with currently used diodes with values in order of thousands, the other advantages of ZnO/BDD p-n junctions together with the possibility of its further research-based improvement make it a very promising solution for wide range of applications.

4 CONCLUSION

Boron doped diamond and ZnO thin films with various concentrations of dopants were prepared by HFCVD and sputtering methods, respectively. Raman spectroscopy confirmed the growth of ZnO and diamond phase. It was found that UV laser excitation (*ie* 325 nm) is required to measure the ZnO Raman lines in ZnO/BDD heterostructure, while in VIS Raman spectra (*ie* $> 442\text{ nm}$) the signals from diamond films are dominating which strongly suppress the ZnO Raman lines. This effect is also related to absorption properties of ZnO. SEM measurements revealed continuous films for both materials. Carrier concentrations, *ie* the doping, was influenced by the growth conditions (gas mixture and used process). Electrically functional ZnO/BDD heterojunctions were successfully fabricated, as confirmed by Hall and I-V measurements. The current-voltage characteristics have shown a rectifying ratio of 55 at $\pm 4\text{ V}$. Obtained results seem to be perspective for fabrication of optically transparent bipolar heterojunctions combining these two wide-bandgap semiconducting materials.

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Marián Marton (MSc, PhD) graduated in electronics in 2004 and in 2008 he received his PhD in electronics and vacuum technology, both at STU. Currently his research deals with carbon nanomaterials, *eg* diamond, CNTs, CNWs and DLC.

Miroslav Mikolášek (MSc, PhD) was born in Myjava (Slovakia), in 1983. He carried out research in the area of microfluidic circuits at the Johannes Kepler University in Linz, Austria, and received his Master degree in electronics from the Slovak University of Technology, Bratislava, in 2007. In 2011 he received PhD degree in Electronics from STU, Bratislava. At present he works at the Institute of Electronics and Photonics, Slovak Technical University in Bratislava. Main interests of his research include simulation and diagnostics in the field of solar cells based on amorphous silicon.

Jaroslav Bruncko (MSc, PhD) graduated in material engineering in 1990 and received the PhD degree in laser technology treatment of materials at Slovak University of Technology in 1997. His research interest is focused on laser based technologies such thin films growth by Pulsed Laser Deposition.

Ivan Novotný (MSc) finished the university in electrical engineering in 1969 at the Slovak University of Technology,

Bratislava. There he continued his study in the domain of computer science and in 1983 he received Dipl. Ing. Actually, he works as a senior researcher at the Institute of electronics and photonics, FEI STU Bratislava. His research activities are in the field of: thin film technology, thin-film sensors, modelling and simulations of technological processes.

Tibor Izák (MSc, PhD) graduated in microelectronics in 2006 and in 2012 he received his PhD in the same field at Slovak University of Technology in Bratislava. From 2008 he is a researcher at Institute of Physics, Czech Academy of Sciences in Prague. His research topics include mainly material science (thin films & carbon technology), sensorics, and impedance spectroscopy.

Marian Vojts (MSc, PhD) received his MSc in Electronics from the Slovak University of Technology in Bratislava in 2002 and his PhD in Electronics from the Slovak University of Technology in 2009. He is working from 2009 as researcher at UEF FEI STU. Main interests include deposition of diamond, carbon structures, DLC and characterization of morphology, electrical and electrochemical properties and Raman spectroscopy.

Halyna Kozak (MSc, PhD) graduated in Mathematical and Physical Engineering at Czech Technical University in Prague in 2008. She is an associated scientist at Institute of Physics ASCR, v.v.i. She is a specialist in the field of electrical and optical properties of nanocrystalline diamond films for bioelectronics and sensor applications.

Marián Varga (MSc, PhD) graduated in microelectronics in 2008 and received his PhD in 2013, both at Slovak University of Technology. He is engaged in CVD technology focused on fabrication of carbon materials/composites, and analyses such as SEM, Raman and optical measurements.

Anna Artemenko (PhD received in Biophysics, Chemical and Macromolecular physics at Charles University in Prague in 2013). Currently she is a research worker in Institute of Physics, Academy of Sciences of the Czech Republic. Her work is generally focused on XPS surface analysis of carbon nanomaterials (NCD, CNTs, graphene *etc*).

Alexander Kromka (MSc, PhD), born in Nitra in 1971. He received his MSc degree in electronic engineering from the Slovak Technical University, Bratislava, in 1995. He has been a PhD student at the Department of Microelectronics of the Faculty of Electrical Engineering and Information Technology, and received the doctoral degree in 2001. His research interests include diamond thin films deposition techniques and applications.