

## ELECTRICAL PROPERTIES OF NANOROD-BASED ZnO/SiC HYBRID HETEROJUNCTIONS

Stanislav TIAGULSKYI, Roman YATSKIV, Hana FAITOVÁ, Šárka KUČEROVÁ, Jan VANIŠ,  
Jan GRYM

*Institute of Photonics and Electronics of the Czech Academy of Sciences, Prague, Czech Republic, EU,*  
[tiagulskyi@ufe.cz](mailto:tiagulskyi@ufe.cz)

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### Abstract

ZnO nanorods have attracted increasing interest in recent years due to their potential in optoelectronic applications. The lack of p-type ZnO emphasizes the importance of rectifying junctions realized on other p-type materials. SiC is a good candidate to create hybrid heterojunctions with ZnO due to its wurtzite crystal structure and a small lattice and thermal mismatch. The ZnO/SiC heterojunctions have a potential to show intense UV electroluminescence. We investigate morphology and electrical properties of a single vertically-oriented ZnO nanorod on a SiC substrate. The current-voltage measurements are performed directly in the vacuum chamber of a scanning electron microscope. The contact to a single nanorod is obtained by a nanoprobe, which allows for the measurement of the current-voltage characteristic of a single nanorod heterojunction of choice. The influence of ZnO growth parameters and post-growth treatment of ZnO/SiC structures are studied with the aim to minimize the density of structural/interfacial defects and to create low-dimensional hybrid heterojunctions with the potential to show intense UV electroluminescence.

**Keywords:** Chemical bath deposition, current-voltage characteristics, SEM, ZnO nanorods, ZnO/SiC heterojunctions

### 1. INTRODUCTION

Zinc oxide (ZnO) with its wide band gap of 3.37 eV and high exciton binding energy of 60 meV is a promising material for electronic and photonic applications. ZnO offers several advantages over other wide-bandgap materials: a low cost and wide availability, environmental safeness, high thermal stability, and possibility to form different kinds of nanostructures by a variety of growth techniques. As-grown ZnO is intrinsically n-type semiconductor and reproducible p-type doping is difficult to be achieved. Therefore, the advantageous properties of ZnO for light-emitting devices are frequently investigated in the form of heterostructures with other materials [1,2].

Silicon carbide (SiC) is another promising wide bandgap semiconductor material with a high thermal conductivity, high breakdown voltage, low response time, excellent mechanical properties, and good chemical stability. SiC is a good candidate to create hybrid heterojunctions with ZnO due to its wurtzite crystal structure and small lattice (~5 %) and thermal (<1 %) mismatch [3,4].

Chen et al. reported ZnO/SiC heterojunctions that were deposited by metal-organic chemical vapor deposition on n-6H-SiC [5]. The isotype heterojunctions showed rectifying characteristics with the reverse current in the picoampere range, the on/off ratio  $\sim 10^7$ , and the ideality factor  $\sim 1.23$ . The native SiO<sub>2</sub> layer on SiC surface was reported to have impact on the morphology of the deposited ZnO and consequently on the electrical properties of ZnO/SiC heterojunctions. Felix et al. reported that the heterojunctions formed by thermally deposited ZnO thin films on n-4H-SiC had excellent electrical properties with the leakage current lower than 1 nA and the rectification ratio  $\approx 10^5$ . The larger than unity ideality factor was ascribed to the thickness and composition variation of interfacial layer [6]. Taube et al. studied the electrical properties of ZnO/SiC heterojunctions created by atomic layer deposition of ZnO layers on n-4H-SiC and p-4H-SiC substrates. The

isotype heterojunction diodes showed better electrical properties than the anisotype diodes. In particular, lower values of ideality factor, series resistance, capacitance and built-in voltage were reported. The lower resistance and capacitance are especially important for the increase of the response time of UV photodetectors. Due to the absence of donor-acceptor pair transitions in n-type 4H-SiC, the isotype ZnO/4H-SiC heterojunctions showed lower response to visible light while keeping UV light response at the same level as observed for anisotype heterojunctions [7]. Rebaoui et al. reported on the effects of polytypes and doping nature on electrical properties of ZnO/SiC heterojunctions. The ZnO/SiC diodes based on n-type 4H-SiC polytype showed the best electrical performance. It was found, that the ZnO/n-4H-SiC heterojunctions had 40 times lower leakage current than the ZnO/p-4H-SiC heterojunctions and two times higher rectifying ratio than the ZnO/n-6H-SiC heterojunctions. The excellent performance of ZnO/n-4H-SiC heterojunctions was ascribed to high vertical a-axis electron mobility, higher heterojunction barrier, and suppressed trap assisted tunneling [8].

The excellent rectifying properties of isotype ZnO/SiC heterojunctions considered above were explained in detail by Zhang et al. using x-ray photoelectron and Auger electron spectroscopies of ZnO layers deposited on 6H-SiC substrates by molecular beam epitaxy from which the band alignment for the isotype ZnO/SiC interface was calculated. Significant band offsets were suggested to be the reason for high rectification ratios of isotype ZnO/SiC structures. Together with the significant band offsets, the absence of chemical interactions and additional interfacial layers on the abrupt MBE-ZnO/SiC interface was considered as the reason for highly rectifying isotype ZnO/SiC structures [9]. On the other hand, Mu et al. reported the presence of the zinc silicate species at the ZnO/SiC interface prepared by the radiofrequency magnetron sputtering. He suggested, that the interface species significantly affect the electronic structure of the ZnO/SiC interface [10].

To summarize, the 4H polytype of SiC is more attractive for the device application due to its wider bandgap and higher mobility than other polytypes. Moreover, it is widely believed that the isotype n-ZnO/n-SiC heterojunctions are more suitable for optoelectronic devices than the anisotype n-ZnO/p-SiC heterojunctions.

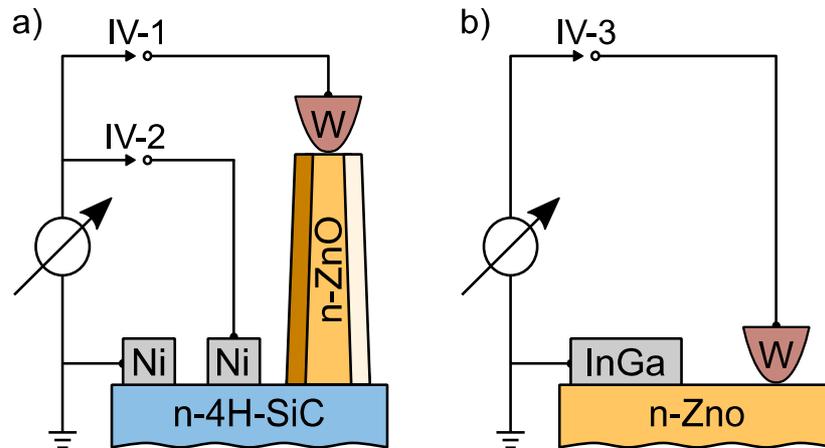
As was mentioned above, ZnO easily forms several types of nanostructures that are suitable for the manufacturing of vertically stacked devices (e.g. ZnO nanorods/SiC LEDs). However, further downscaling to nanoelectronic devices requires a deep understanding of electrical properties of nanoscale heterojunctions below a single nanorod. In this work, electrical properties of a single ZnO nanorod on n-4H-SiC substrates are investigated by measuring the current-voltage (I-V) characteristics. The contact to a single nanorod is obtained by a nanoprobe in the chamber of a scanning electron microscope (SEM), which allows for the measurement of the current-voltage characteristic of a single nanorod heterojunction of choice.

## 2. EXPERIMENTAL METHODS

Conventional chemical bath deposition (CBD) method was used to synthesize ZnO nanorods on n-4H-SiC substrates [11]. Commercially available nitrogen doped 4H-SiC substrates with a thickness of 350 nm and an electron concentration of  $n=10^{17} \text{ cm}^{-3}$  were used for the fabrication of the ZnO/SiC junctions. The substrate was sequentially cleaned in  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ ,  $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  (1:1:5) at 70 °C,  $\text{HF}:\text{H}_2\text{O}$  (1:20) and  $\text{H}_2\text{O}:\text{HCl}:\text{H}_2\text{O}_2$  (6:1:1) at 70 °C. After each step, the substrate was rinsed in deionized water and dried with nitrogen. A backside ohmic contact was created by thermal evaporation of 150 nm of Ni and subsequently annealed at 950 °C for 10 min in Ar atmosphere [12].

The 5mM aqueous solution of zinc nitrate hexahydrate, which is a source of  $\text{Zn}^{2+}$  ions, and hexamethylenetetramine, which is a source of  $\text{OH}^-$  ions, was used for the CBD of ZnO nanorods. To activate the reaction, the temperature of the solution was elevated to 95 °C for 2 hours.

The morphology of ZnO nanorods was observed using Tescan Lyra 3 GM FIB/SEM system. The I-V characteristics of the nanoscale heterojunction formed by a single ZnO nanorod on SiC substrate were measured in the chamber of the same FIB/SEM system (**Figure 1**).

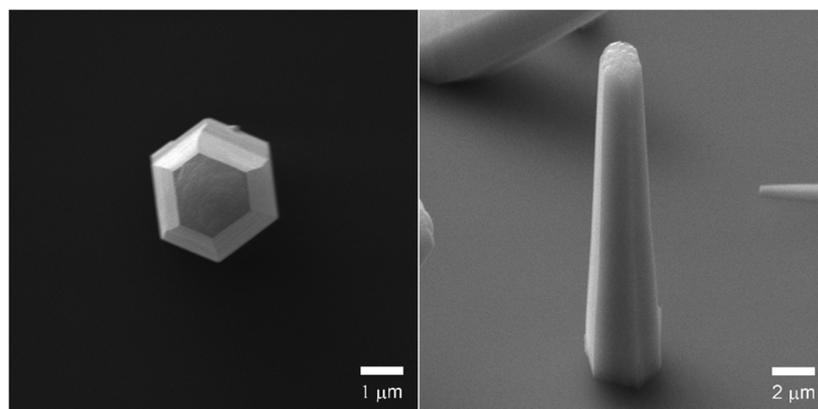


**Figure 1** Schematic illustrations of the current-voltage measurements of: (a) freestanding ZnO nanorods on n-4H-SiC substrate and Ni/n-SiC contacts; (b) W-probe on a reference n-type ZnO bulk substrate

A tungsten needle of a SmarAct nanoprobe served as a top ohmic contact. The tip of the needle was cleaned using the focused ion beam to remove native tungsten oxide. The bottom metal contact was deposited on pre-cleaned SiC substrate by vacuum evaporation of a 150nm layer of Ni with subsequent annealing of the substrates. The I-V characteristics were measured by applying a linear voltage sweep to the top needle contact while the bottom contact was grounded. The ohmic behavior of the metal contacts was confirmed by additional measurements (electrical circuits “IV-2” in **Figure 1a** for the bottom contact, electrical circuit “IV-3” in **Figure 1b** for the top contact).

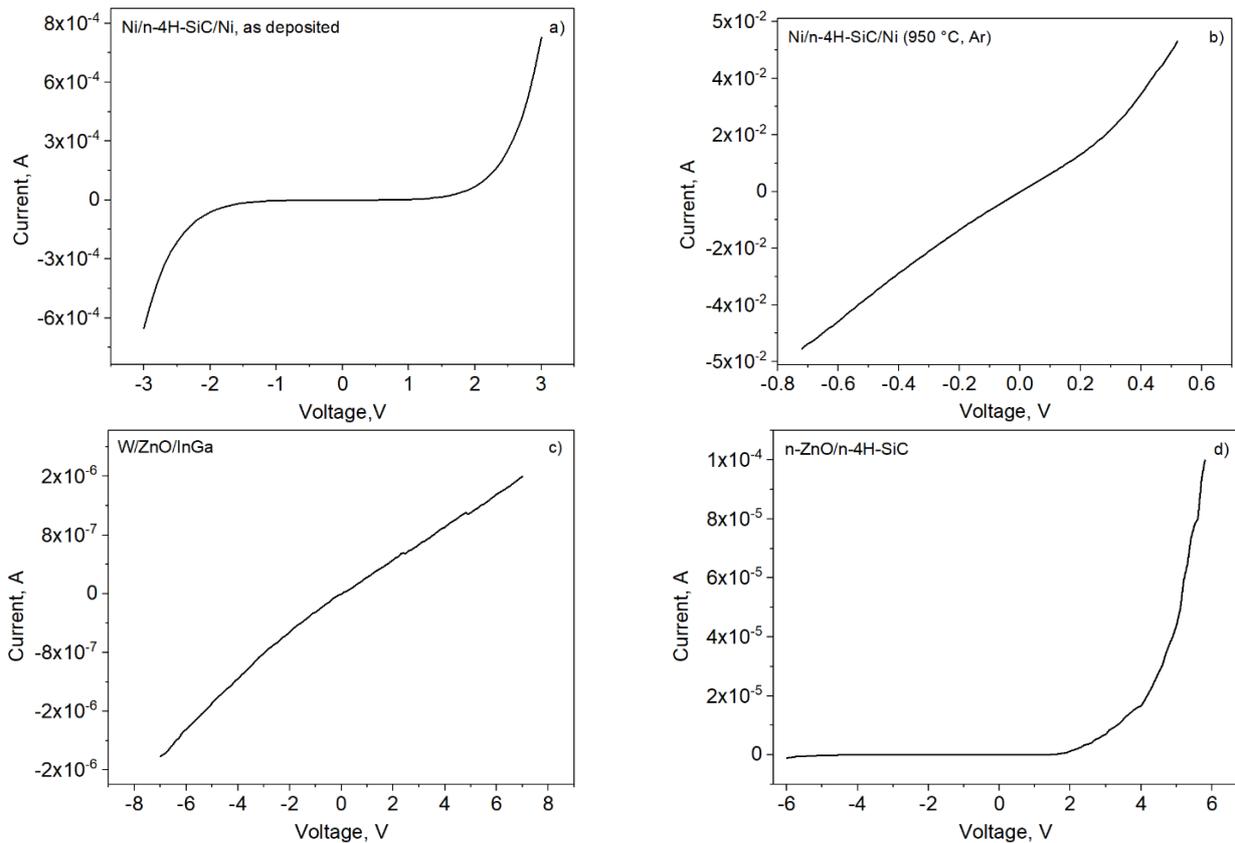
### 3. RESULTS AND DISCUSSION

**Figure 2** shows SEM images of individual nanorods grown on the n-4H-SiC substrates. The nanorods were grown randomly and their lengths and diameters had a significant dispersion. Before the electrical characterization, the samples were carefully examined in SEM to select the nanorods with equal dimensions: typical values of the length and diameter of ZnO nanorods were  $L = 14 \mu\text{m}$ ,  $d = 1.8/3.5 \mu\text{m}$  (top/bottom), respectively.



**Figure 2** Top view and 55° tilted view SEM images of a single ZnO nanorod grown on n-4H-SiC substrate

**Figure 3** shows representative current-voltage characteristics (i) of the bottom Ni/SiC contact before and after thermal annealing, (ii) of the top W/ZnO contact measured on the reference bulk hydrothermally grown ZnO substrate, and (iii) of the single n-ZnO nanorod/n-4H-SiC heterojunction.



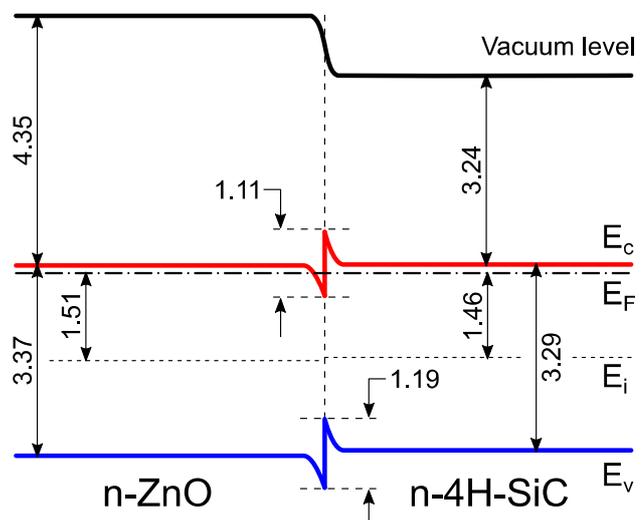
**Figure 3** Experimental current-voltage characteristics. (a, b) Ni contact on SiC before/after annealing, (c) tungsten probe on the surface of the bulk ZnO, (d) a single nanorod ZnO/n-4H-SiC heterojunction

**Table 1** The parameters extracted from the experimental current-voltage measurements

$I_{on}/I_{off}$ at $\pm 2V$ (unitless)	$V_{on}$ (forward) (V)	$R_{W/ZnO}$ , (Ohm)	$R_{Ni/SiC}$ , (Ohm)
$\approx 40 \cdot 10^3$	1.6	$\approx 10^6$	$\approx 20$

The I-V measurements between two as-deposited Ni contacts show the presence of two back-to-back Schottky diodes. However, after the thermal annealing, a clear ohmic behavior of Ni/SiC contact was observed. The top W/ZnO contact also demonstrates almost linear behavior. Therefore, we can suggest that the diode-like I-V characteristics of n-ZnO nanorod/n-4H-SiC heterostructures are determined by the charge transport through the ZnO/SiC interface rather than by the metal contacts. The parameters extracted from the current-voltage measurements are summarized in **Table 1**.

**Figure 4** Schematic energy band diagram for the n-ZnO/n-4H-SiC heterojunction. The unit is eV in all cases



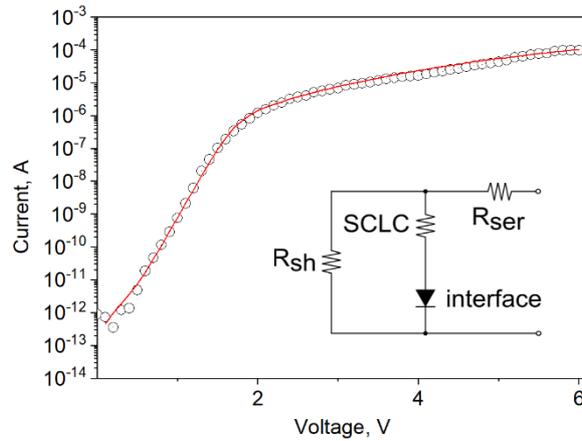
To explain the rectifying behavior of n-ZnO/n-4H-SiC heterojunctions, in the first approach, the Anderson model was used to construct the n-ZnO/n-4H-SiC heterojunction band diagram (**Figure 4**). The electron affinities of ZnO and of 4H-SiC were taken as  $X_{ZnO} = 4.35$  eV and  $X_{SiC} = 3.24$  eV, and the bandgap energies of ZnO and SiC as  $E_{g, ZnO} = 3.37$  eV and  $E_{g, SiC} = 3.29$  eV, respectively.

The conduction band offset is therefore  $\Delta E_C = X_{ZnO} - X_{SiC} = 1.1$  eV, while the valence band offset is  $\Delta E_V = (X_{ZnO} + E_{g, ZnO}) - (X_{SiC} + E_{g, SiC}) = 1.19$  eV. Adjustment can be made to account for the position of the Fermi level relative to the conduction band in each material. The positions of Fermi level below the conduction band edge  $E_C - E_F$  is taken from the Boltzmann's statistics assuming that all dopants are fully ionized:

$$E_C - E_F = -kT \ln \frac{N_D}{N_C}, \quad (1)$$

where,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $N_D$  is the donor concentration and  $N_C$  is the effective density of states in the conduction band [13].

**Figure 5** shows the experimental and theoretically fitted forward bias I-V characteristic of a single nanorod n-ZnO/n-4H-SiC isotype heterojunction in semilogarithmic scale. The proposed equivalent circuit of the nanoscale heterojunction (the inset in **Figure 5**) takes into account the current flow through the potential barrier at the n-ZnO/n-4H-SiC interface; the current limited by the space charge region; the leakage current that bypasses the junction region; and the excessive serial resistance of the contacts and neutral regions of the semiconductors.



**Figure 5** Experimental and theoretically fitted forward bias I-V characteristics of a single nanorod n-ZnO/n-4H-SiC isotype heterojunction

In the frame of the proposed model, the current flowing through the potential barrier is given by:

$$I_1 = I_0 (e^{\frac{q}{nkT}(V - I_1 R_{ser})} - 1) \quad (2)$$

where  $I_0$  is the reverse bias saturation current of the junction,  $n$  is the ideality factor of the junction,  $q$  is the electron charge,  $k$  is the Boltzmann's constant,  $T$  is the temperature and  $R_{ser}$  is the serial resistance [13].

At higher biases, when the impact of potential barrier is negligible, the current is limited by the conductance of the space charge region. In general case the space charge limited current (SCLC) is given by:

$$I_2 = A(V - I_2 R_{ser})^\beta \quad (3)$$

where  $A$  is a coefficient that is related to the length and conductivity of the current flow path and  $\beta$  is a scaling exponent of the power-law current-voltage dependence, which should be equal to 2 in the case of trap-free space charge limited current, or  $>2$  in the case of traps distributed over the bandgap [14].

The leakage current that bypassed the heterojunction follows the Ohm's law:

$$I_3 = (V - I_3 R_{ser}) / R_{sh} \quad (4)$$

where  $R_{sh}$  is the shunt resistance of the leakage path.

According to the Kirchhoff's rule, the total current injected to a single nanorod n-ZnO/n-4H-SiC heterojunction is:

$$I = \frac{I_1 I_2}{I_1 + I_2} + I_3 \quad (5)$$

The I-V curve modelled using **Equations (2) - (5)** fits well experimental I-V characteristics of the single nanorod n-ZnO/n-4H-SiC heterojunction. The fitting variables are summarized in **Table 2**.

**Table 2** The parameters extracted from the fitting of the forward bias I-V curves for the single nanorod n-ZnO/n-4H-SiC heterojunction

n (unitless)	$I_0$ (A)	$\beta$ (unitless)	Rsh (Ohm)	Rser (Ohm)
3.9	$4 \cdot 10^{-14}$	4	$2.5 \cdot 10^{12}$	$4 \cdot 10^4$

The ideality factor larger than unity, relatively high saturation current  $I_0$ , and the power law exponent larger than two allow us to consider the trap assisted tunneling process through the interface states distributed over the band gap as the main transport mechanism for the single nanorod n-ZnO/n-4H-SiC heterojunction. The leakage current determined by the shunt resistance is on the order of 1 pA, which is the noise level of our measurement setup. Taking into account the experimental I-V characteristics measured on the reference bulk ZnO substrate (**Figure 3c**), a large serial resistance is ascribed to the resistance of the top W/ZnO contact and of the ZnO nanorod.

#### 4. CONCLUSIONS

In summary, nanoscale heterojunctions between a single free-standing *n*-type ZnO nanorod grown on n-4H-SiC substrate were obtained by chemical bath deposition. Using the nanomanipulator mounted in the scanning electron microscope, the current-voltage characteristics of individual n-ZnO nanorod/n-4H-SiC heterojunctions were measured. Heterojunctions showed diode-like characteristics with a high rectification ratio and low leakage current. The equivalent circuit of the isotype n-ZnO/n-4H-SiC heterojunction was proposed. The parameters of the heterojunctions were extracted from the experimental current-voltage characteristics using a proposed fitting model. We believe that the method of characterization of a single nanorod-based heterojunction proposed in this paper opens door for a detailed analysis of charge transport in a variety of nanoscaled optoelectronic devices.

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#### REFERENCES

- [1] OZGUR, U., ALIVOV, Y. I., LIU, C., TEKE, A., RESHCHIKOV, M. A., DOGAN, S., AVRUTIN, V., CHO, S. J. and MORKOC, H. A comprehensive review of zno materials and devices. *Journal of Applied Physics*, 2005, vol. 98, no. 4, p. 041301.
- [2] JANOTTI, A. and VAN DE WALLE, C. G. Fundamentals of zinc oxide as a semiconductor. *Reports on Progress in Physics*, 2009, vol. 72, no. 12, p. 126501.

- [3] MORKOC, H., STRITE, S., GAO, G. B., LIN, M. E., SVERDLOV, B. and BURNS, M. Large-band-gap sic, iii-v nitride, and ii-vi znse-based semiconductor-device technologies. *Journal of Applied Physics*, 1994, vol. 76, no. 3, pp. 1363-1398.
- [4] CASADY, J. B. and JOHNSON, R. W. Status of silicon carbide (sic) as a wide-bandgap semiconductor for high-temperature applications: A review. *Solid-State Electronics*, 1996, vol. 39, no. 10, pp. 1409-1422.
- [5] CHEN, Y., SARAF, G., REYES, P. I., DUAN, Z. Q., ZHONG, J. and LU, Y. C. Structural, electrical, and piezoelectric properties of zno films on sic-6h substrates. *Journal of Vacuum Science & Technology B*, 2009, vol. 27, no. 3, pp. 1631-1634.
- [6] FELIX, J. F., AZIZ, M., DE ARAUJO, C. I. L., DE AZEVEDO, W. M., ANJOS, V., DA SILVA, E. F. and HENINI, M. Zinc oxide thin films on silicon carbide substrates (zno/sic): Electro-optical properties and electrically active defects. *Semiconductor Science and Technology*, 2014, vol. 29, no. 4.
- [7] TAUBE, A., SOCHACKI, M., KWIETNIEWSKI, N., WERBOWY, A., GIERALTOWSKA, S., WACHNICKI, L., GODLEWSKI, M. and SZMIDT, J. Electrical properties of isotype and anisotype zno/4h-sic heterojunction diodes. *Applied Physics Letters*, 2017, vol. 110, no. 14.
- [8] REBAOUI, Z., BOUIAJRA, W. B., ABID, M. A., SAIDANE, A., JAMMEL, D., HENINI, M. and FELIX, J. F. Sic polytypes and doping nature effects on electrical properties of zno-sic schottky diodes. *Microelectronic Engineering*, 2017, vol. 171, pp. 11-19.
- [9] ZHANG, Y. F., LIN, N. Y., LI, Y. P., WANG, X. D., WANG, H. Q., KANG, J. Y., WILKS, R., BAR, M. and MU, R. The isotype zno/sic heterojunction prepared by molecular beam epitaxy-a chemical inert interface with significant band discontinuities. *Scientific Reports*, 2016, vol. 6.
- [10] MU, R., STEIGERT, A., LIN, N. Y., WILKS, R., BAR, M. and ZHANG, Y. F. The chemical structure of the zno/sic heterointerface as revealed by electron spectroscopies. *Journal of Physics D-Applied Physics*, 2015, vol. 48, no. 30.
- [11] YATSKIV, R. and GRYM, J. Luminescence properties of hydrothermally grown zno nanorods. *Superlattices and Microstructures*, 2016, vol. 99, pp. 214-220.
- [12] YATSKIV, R. and GRYM, J. Graphite/sic junctions and their electrical characteristics. *Physica Status Solidi a-Applications and Materials Science*, 2017, vol. 214, no. 9.
- [13] SZE, S. M. *Physics of semiconductor devices*, 3rd ed. Hoboken, NJ: John Wiley and Sons, 2007, pp. 815.
- [14] TALIN, A. A., LÉONARD, F., KATZENMEYER, A. M., SWARTZENTRUBER, B. S., PICRAUX, S. T., TOIMIL-MOLARES, M. E., CEDERBERG, J. G., WANG, X., HERSEE, S. D. and RISHINARAMANGALUM, A. Transport characterization in nanowires using an electrical nanoprobe. *Semiconductor Science and Technology*, 2010, vol. 25, no. 2, p. 024015.