

EFFECTS OF TEMPERATURE ON OPTICAL PROPERTIES OF ZnO NETWORKS

Rajat NAGPAL^{1,2*}, Cristian LUPAN¹

¹Center for Nanotechnology and Nanosensors, Department MIB, Technical University of Moldova,
168 Stefan cel Mare Av., MD-2004 Chisinau, Republic of Moldova

²Department of Materials Science, Chair for Functional Nanomaterials, Faculty of Engineering,
Kiel University, Kaiserstraße 2, D-24143 Kiel, Germany

*Corresponding author: Rajat Nagpal, rajat@doctorat.utm.md

Coordinator: **Oleg LUPAN**, univ. prof. dr. hab., Center for Nanotechnology and Nanosensors,
Department MIB, Technical University of Moldova, Department of Materials Science, Chair for
Functional Nanomaterials, Faculty of Engineering, Kiel University

Abstract. ZnO tetrapodal (*t*-ZnO) based photodetector has been fabricated for UV applications like wearable sensors, optical communications, pollution monitoring, etc. In this study, influence of operating temperature has been evaluated on *t*-ZnO based UV detectors. The structure and morphology of *t*-ZnO were studied using characterization tools like XRD and SEM. Photo response was evaluated at different operating temperatures from 25 °C up to 100 °C, observing maximum photo response of ~ 7178 for 400 nm wavelength at 25 °C. The rise and fall time have been monotonically reduced ~ 496 seconds to ~ 102 seconds and ~ 1493 seconds to ~ 132 seconds in the respective tested temperature range (25 °C to 100 °C). This decreasing trend of rise/fall time can be attributed to the faster desorption rate at higher temperatures. This work shows UV response decreases by increasing operating temperature in temperature range 25 °C to 100 °C. This work can be extended to lower temperature ranges to evaluate its optical sensing performance in polar regions.

Keywords: photodetection, wavelength, 400 nm, fall time, UV response.

Introduction

Optoelectronic devices are of great significance in different fields like wearable electronics [1], space exploration [2], optical communication [3], etc. The applications like wearable device-based monitoring require moderate operating temperature (~20 °C to 40 °C), but applications like space exploration or other polar region UV monitoring require low temperature (<= 0 °C) operability [2]. It is necessary to study optical properties at high temperatures above 100 °C for industrial monitoring and control applications to ensure their reliable operation at high temperatures. These types of applications require reliable and stable photodetectors which can work under harsh operating conditions.

ZnO is one of the direct wide bandgaps (~3.36 eV) semiconducting material being used for optoelectronic devices. ZnO due to its good thermal stability, optoelectronic properties and its optical bandgap lies in UV regime makes it excellent UV photodetector [4]. ZnO network-based sensors eliminate high temperature operation requirement and can effectively work at room temperature which extends the sensor lifespan [5]. Generally, ZnO based UV detectors shows slow charge carrier dynamics at sensing surface due to charge carrier trapping at oxygen adsorption/desorption sites [6].

This work elucidates on evaluating effect of operating temperature on optical properties of ZnO based photodetector. In case of ZnO based UV detector, the role of oxygen adsorption/desorption was investigated for wide temperature range 25 °C to 100 °C, which can be useful for diverse applications. This thermally stable ZnO based photodetector can be further

tested at other temperature ranges like low temperature range to confirm its thermal stability for space exploration applications.

Experimental section

Tetrapodal networks were obtained using flame transport synthesis method, as reported before in [7,8]. Morphology and structural properties were studied using SEM and XRD, as reported before in [9]. UV sensing properties were evaluated using setup described in [10].

Results and discussion

The morphology and structural investigation were confirmed through SEM and XRD characterization tools.

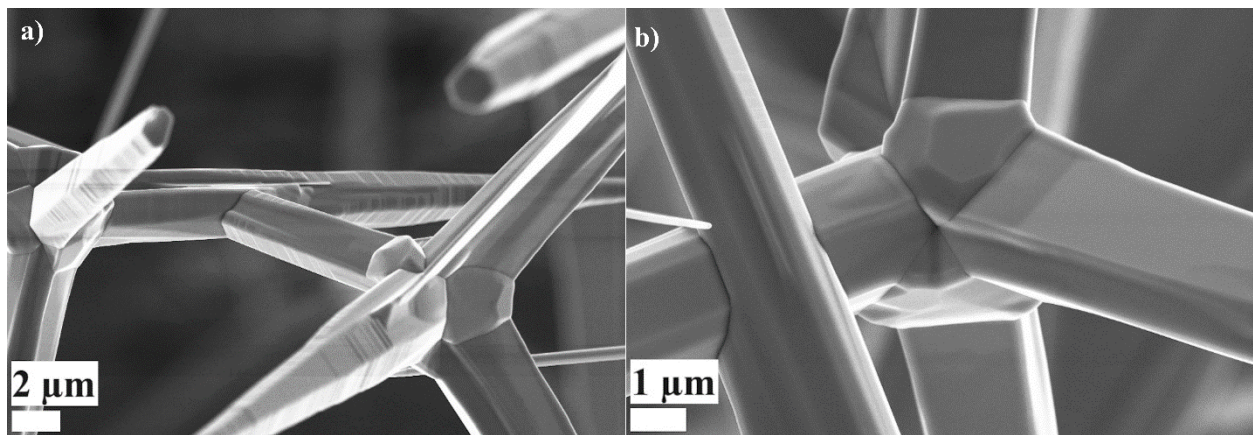


Figure 1. SEM images of ZnO networks at different magnifications: (a) 4000; (b) 9500.

In Fig. 1 we observed that nanostructures have tetrapodal morphology and are interconnected. At higher magnification we noticed that tetrapod arms have columnar form, with a diameter of approximately 2 μm . The interconnected tetrapod networks have great advantage for multiple applications, including UV sensing [11].

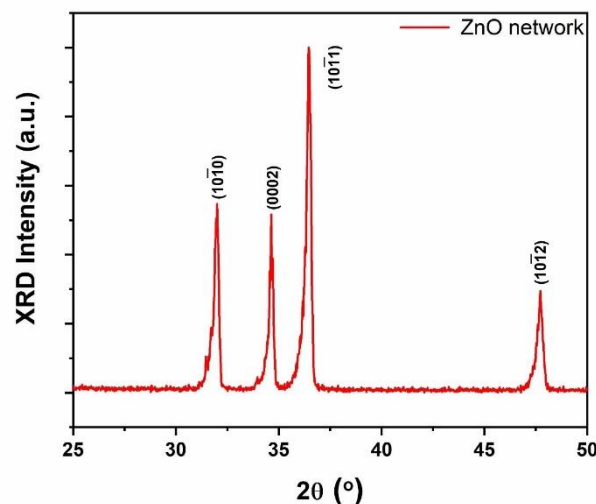


Figure 2. XRD pattern of ZnO networks.

In Fig. 2 is presented XRD pattern of ZnO network used in our study in the 25-50° 2 θ range. Typical ZnO peaks were detected according to PDF 036-1451 at 32°, 34.64°, 36.46° and 47.72°. Highest intensity was observed for 10 $\bar{1}$ 1 peak.

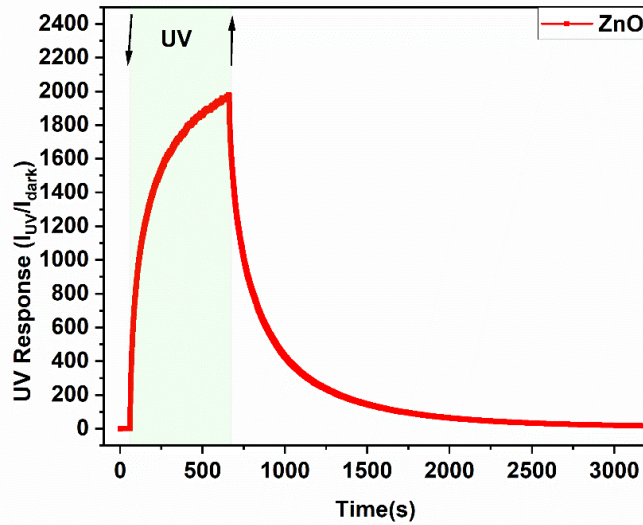


Figure 3. Dynamic UV response for 400 nm UV illumination at 50 °C.

In this study, UV photodetection for 400 nm wavelength has been tested at different temperatures to evaluate the effect of change in temperature on UV response of prepared ZnO networks. Figure 3 shows the transient UV response at 50 °C for 400 nm UV illumination on ZnO networks. It can be observed that UV response at 50 °C is ~1993 for 400 nm tested wavelength. UV response can be calculated by using Eq. (1):

$$UV \text{ response} = \frac{I_{UV}}{I_{dark}} \quad (1)$$

where I_{UV} , I_{dark} denotes photocurrent and dark current, respectively.

Figure 4 shows comparative UV response study for 400 nm illumination at different temperatures. This study clearly depicts that the UV response monotonically decreases from ~7178 to ~295 by increasing operating temperature from 25 °C to 100 °C. This can be ascribed as due to faster desorption rate at higher temperature leads to faster de-trapping of oxygen molecules. The error bar for Fig. 4 is taken as 10% of respective UV response at different temperatures.

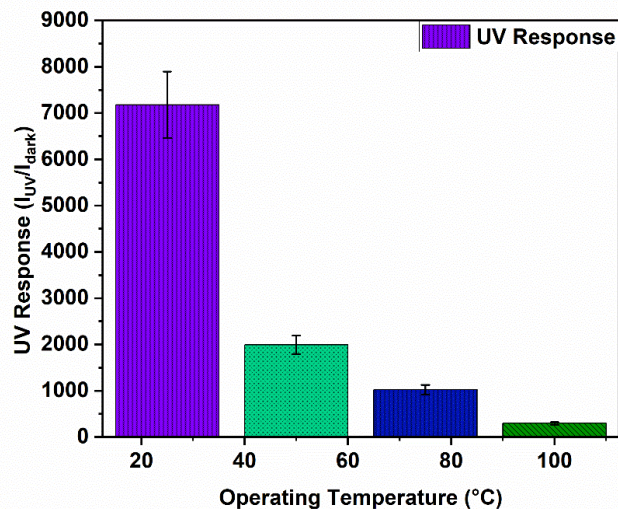


Figure 4. Dependence of UV response for 400 nm UV illumination at different operating temperatures

The effect of operating temperature on rise/fall time has been evaluated. Tab. 1 shows the rise/fall time for 400 nm UV illumination at different operating temperatures. The rise/fall time was calculated as time taken by the sensor to reach 10%/90% and 90%/10%, respectively of maximum response value in a cycle.

Table 1

Effect of temperature on rise/fall time of ZnO networks

Operating temperature (°C)	Rise time (sec)	Fall time (sec)
25	496	1493
50	343	658
75	220	266
100	102	132

The evaluation of rise/fall time trend in Table 1 clearly shows by increase in operating temperature, rise/fall time decreases. This confirms the above explained mechanism of faster de-trapping of adsorbed molecules at higher temperatures. These obtained results can be explained well through oxygen adsorption/desorption mechanism in the absence/presence of UV illumination, respectively.

After UV illumination on ZnO networks, electron-hole pairs generated as shown in Eq. (2).



Before UV illumination, oxygen adsorption occurs on ZnO networks surface as shown in Eq. (3). After UV illumination, oxygen desorption occurs from ZnO networks surface as shown in Eq. (4). This oxygen molecule's adsorption/desorption lead to change in conductivity of ZnO network surface.



where h , ν , e^{-} , h^{+} , $O_{2(gas)}$, $O_{2(ads)}^{-}$ and $O_{2(des)}$ represents Planck's constant, frequency of photon, electron generated, hole generated, oxygen gas molecule, adsorbed oxygen ion and desorbed oxygen molecule, respectively.

Conclusions

In this work, we observed the effect of operating temperature on UV response and rise/fall time for 400 nm UV illumination on ZnO networks. The morphology and structure of ZnO networks were investigated through SEM and XRD showed typical ZnO peaks and tetrapodal morphology, with diameter of ~2 μm . The effect of operating temperature on UV response of ZnO networks showed maximum response ~7178 for 400 nm illumination at 25 °C which monotonically decreases by increase in operating temperatures among all tested temperatures. The rise/fall time also reduces from ~496/1493 sec to ~102/132 sec by increasing temperature from 25 °C to 100 °C. This study exhibits effect of operating temperature on surface properties of photodetector which can be attributed to enhancement in oxygen gas molecule's desorption rate with temperature. This study may contribute to the progress of wearable sensors and this study can further extended in future to lower temperature regime to find further applications in polar regions.

Acknowledgments. Author acknowledges Mr. Erik Greve for his synthesis contribution of ZnO networks. This paper was partially supported by the Technical University of Moldova and by the project EU-project SENNET "Porous Networks for Gas Sensing", which runs under the Marie Skłodowska-Curie Actions funded by the European Union, under the number 101072845.

References

- [1] M. Ku, J. C. Hwang, B. Oh, and J.-U. Park, "Smart Sensing Systems Using Wearable Optoelectronics," *Advanced Intelligent Systems*, vol. 2, no. 3, p. 1900144, 2020, doi: <https://doi.org/10.1002/aisy.201900144>.
- [2] J. Peng, L. Hou, D. Liu, Z. Zhao, J. Zhang, Z. Qiu, and B.Z. Zhang, "Organic Optoelectronic Devices Based on Through-Space Interaction," *ACS Applied Optical Materials*, vol. 2, no. 1, pp. 15–27, Jan. 2024, doi: 10.1021/acsaom.3c00370.
- [3] O. Wada, "Femtosecond semiconductor-based optoelectronic devices for optical-communication systems," *Opt Quantum Electron*, vol. 32, no. 4, pp. 453–471, 2000, doi: 10.1023/A:1007002408115.
- [4] X. Liao, Q. Liao, Z. Zhang, X. Yan, Q. Liang, Q. Wang, M. Li, and Y. Zhang, "A Highly Stretchable ZnO@Fiber-Based Multifunctional Nanosensor for Strain/Temperature/UV Detection," *Adv Funct Mater*, vol. 26, no. 18, pp. 3074–3081, 2016, doi: 10.1002/adfm.201505223.
- [5] J. Hu, H. Ma, Y. Zhou, L. Ma, S. Zhao, S. Shi, J. Li, and Y. Chang, "Gas-Sensing Properties and Mechanisms of 3D Networks Composed of ZnO Tetrapod Micro-Nano Structures at Room Temperature," *Materials*, vol. 17, no. 1, 2024, doi: 10.3390/ma17010203.
- [6] Y. Yang, Y. Zhang, S. Fernandez-Alberti, and R. Long, "Resolving the Puzzle of Charge Carrier Lifetime in ZnO by Revisiting the Role of Oxygen Vacancy," *J Phys Chem Lett*, vol. 15, no. 1, pp. 1–8, Jan. 2024, doi: 10.1021/acs.jpcclett.3c03195.
- [7] T. Reimer, I. Paulowicz, R. Roder, S. Kaps, O. Lupan, S. Chemnitz, W. Benecke, C. Ronning, R. Adelung, and Y.K. Mishra, "Single Step Integration of ZnO Nano- and Microneedles in Si Trenches by Novel Flame Transport Approach: Whispering Gallery Modes and Photocatalytic Properties," *ACS Appl Mater Interfaces*, vol. 6, no. 10, pp. 7806–7815, May 2014, doi: 10.1021/am5010877.
- [8] Y. K. Mishra, A. Schuchardt, I. Paulowicz, X. Jin, D. Gedamu, S. Wille, O. Lupan, and R. Adelung, "Versatile Fabrication of Complex Shaped Metal Oxide Nano-Microstructures and Their Interconnected Networks for Multifunctional Applications," *KONA Powder and Particle Journal*, vol. 31, pp. 92–110, 2014, doi: 10.14356/kona.2014015.
- [9] C. Lupan, R. Khaledialidusti, A.K. Mishra, V. Postica, M.I. Terasa, N. Magariu, T. Pauporte, B. Viana, J. Drewes, A. Vahl, F. Faupel, and R. Adelung, "Pd-Functionalized ZnO:Eu Columnar Films for Room-Temperature Hydrogen Gas Sensing: A Combined Experimental and Computational Approach," *ACS Appl Mater Interfaces*, vol. 12, no. 22, pp. 24951–24964, Jun. 2020, doi: 10.1021/acsaami.0c02103.
- [10] R. Nagpal, M. Chiriac, A. Sereacov, A. Birnaz, N. Ababii, C. Lupan, A. Buzdugan, I. Sandu, L. Siebert, T. Pauporte, O. Lupan, "ANNEALING EFFECT ON UV DETECTION PROPERTIES OF ZnO:Al STRUCTURES," *JOURNAL OF ENGINEERING SCIENCE*, vol. 30, pp. 45–62, Jan. 2024, doi: 10.52326/jes.utm.2023.30(4).04.
- [11] Y. K. Mishra and R. Adelung, "ZnO tetrapod materials for functional applications," *Materials Today*, vol. 21, no. 6, pp. 631–651, 2018, doi: 10.1016/j.mattod.2017.11.003.