European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

WGs & MC Meeting at SOFIA (BG), 16-18 December 2015

New Sensing Technologies for Indoor Air Quality Monitoring: Trends and Challenges

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GRAPHITE/ZNO NANOROD JUNCTIONS FOR HYDROGEN SENSORS

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cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

EuNetAir European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

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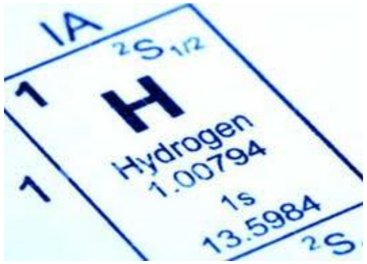
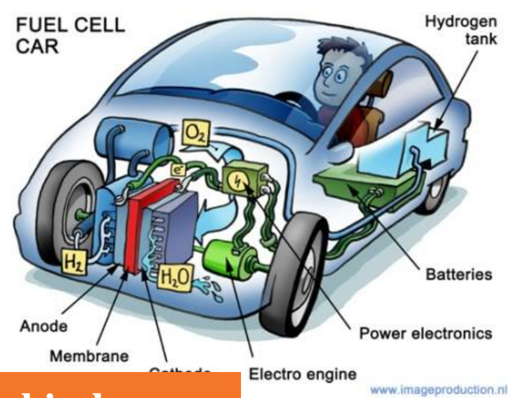
Motivation



Hydrogen-fuelled vehicles



Chemical industry

Medicine

Small leakage of high concentration of hydrogen-containing gases can cause explosion.

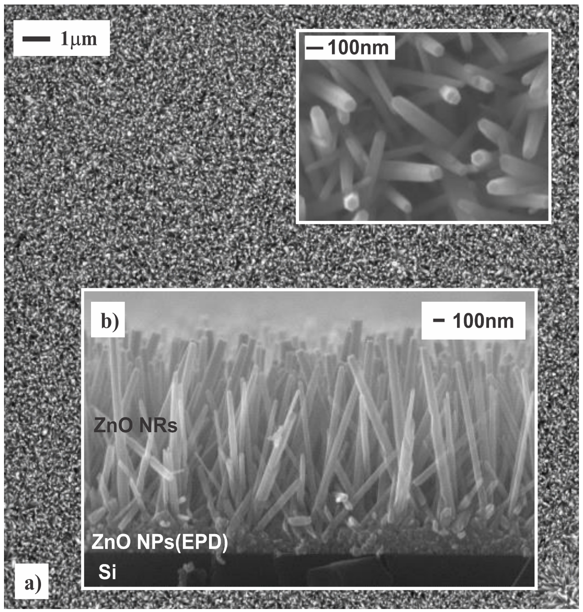
- ✓ high sensitivity,
- ✓ short response time,
- ✓ small size,
- ✓ low cost.

Semiconductor gas sensor

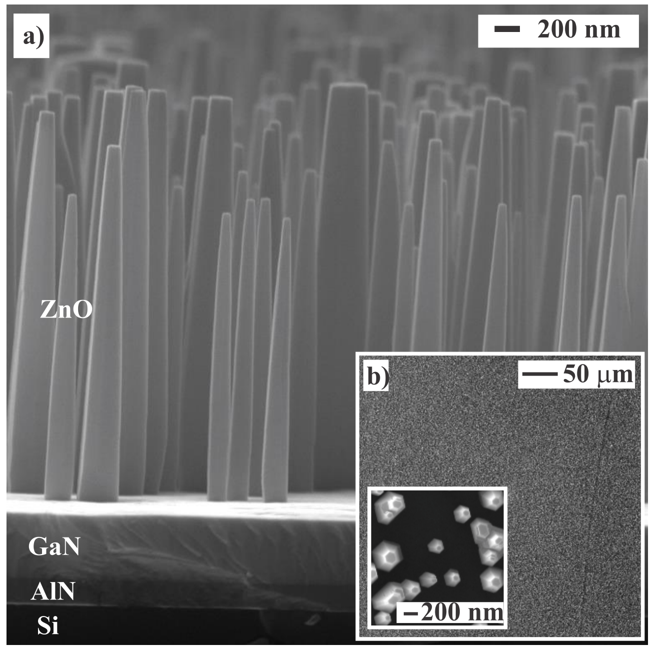
Preparation of the ZnO NRs

Hydrothermal growth (95°C, 3h) Zinc nitrate $\{Zn(NO_3)_2 * 6H_2O(NO_3)\}$ + HMTA $\{C_6H_{12}N_4\}$

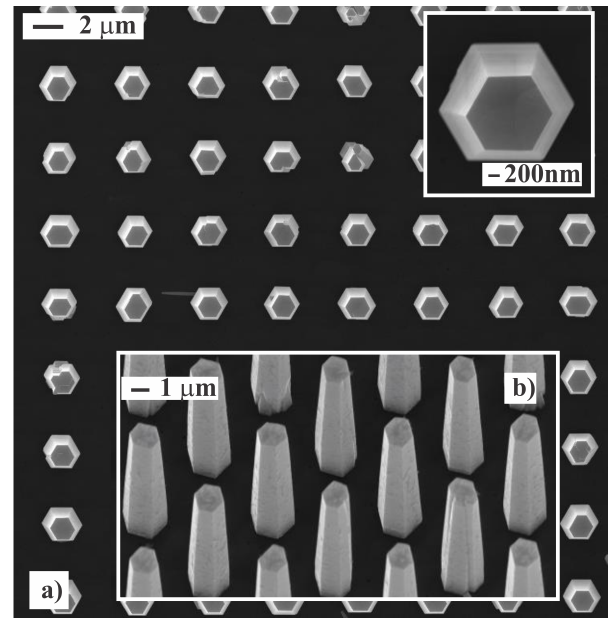
SEM images of ZnO NRS prepared by hydrothermal growth on a ZnO NP seed layer.



SEM image of the ZnO NRs prepared by hydrothermal growth on a GaN substrate



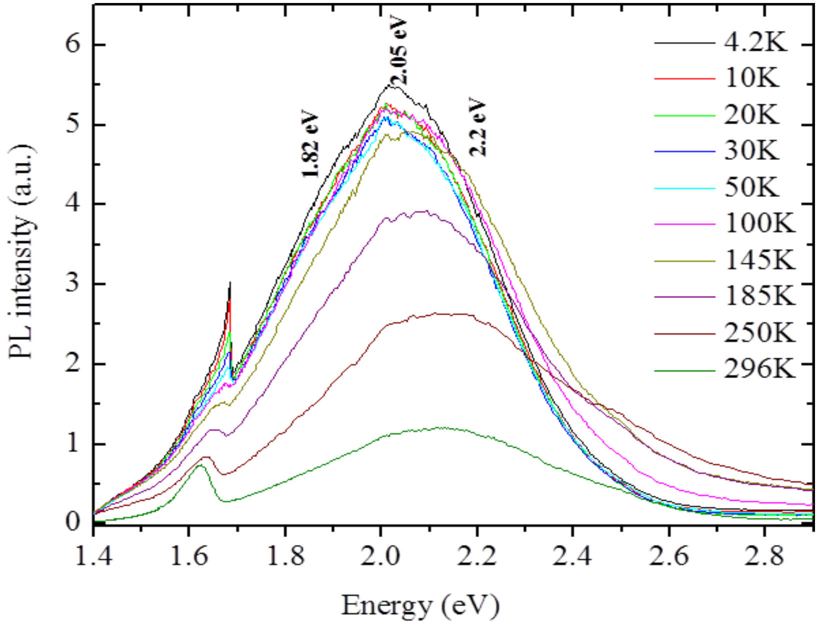
SEM image of the ZnO NRs prepared by hydrothermal growth on a GaN substrate with lithographic patterns:



R. Yatskiv, V. V. Brus, M. Verde, J. Grym and P. Gladkov, Carbon 77, 1011-1019 (2014).
R. Yatskiv, J. Grym and M. Verde, Solid State Electron 105, 70-73 (2015).
R. Yatskiv, J. Grym, P. Gladkov, O.Cernohorsky, J.Vanis, J.Maixner, J.H.Dickerson, Solid State Electron (In Press) doi:10.1016/j.sse.2015.10.011

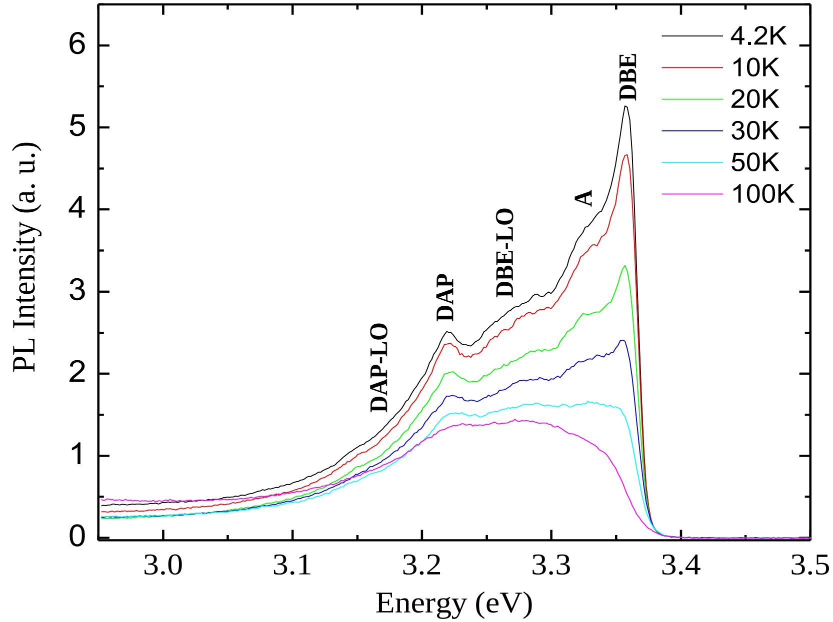
Photoluminescence properties of the ZnO NRs

Temperature dependent PL spectra of the ZnO NRs – the deep level emission.



1.82 eV transition associated with the zinc interstitial,
2.05 eV transition which is typically observed in ZnO nanostructures prepared by chemical methods, is still under discussion; however, it is mostly ascribed to the transition from the conduction band to a specific defect level,
2.2 eV transition due to $Zn(OH)_2$ groups attached to the surface of ZnO NRs.

Temperature dependent PL spectra of the ZnO NRs – the near band edge emission



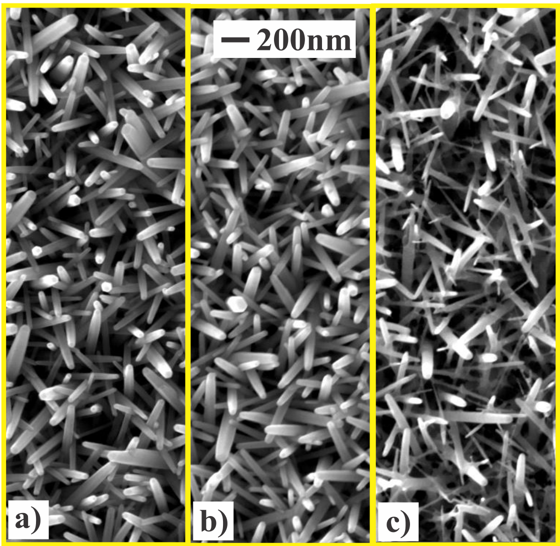
DBE (3.36 eV) exciton bound to neutral shallow donor,
A (3.33 eV) exciton bound to structural defects,
DAP (3.22 eV) shallow donor-shallow acceptor transition.

R. Yatskiv, J. Grym: *Luminescence properties of hydrothermally grown ZnO nanorods*, submitted to Superlattices and Microstructures

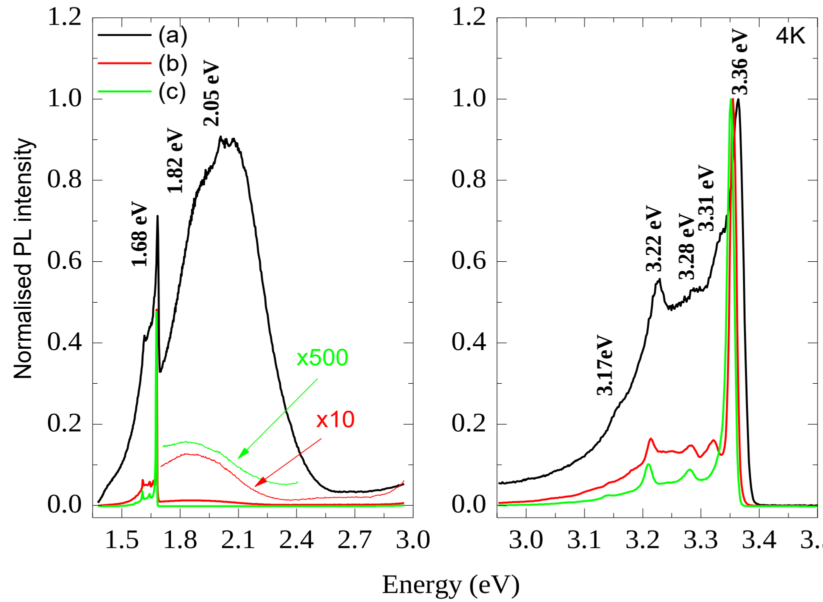
Photoluminescence properties of the ZnO NRs

To obtain more information about the nature of defects in the ZnO NRs, a series of annealing experiments in different ambient atmospheres (air, N_2, vacuum) were applied. The best optical quality of the ZnO NRs was obtained after annealing in N_2.

SEM images of the as grown ZnO NRs (a), and annealed in nitrogen at 700°C (b) and 800°C (c).



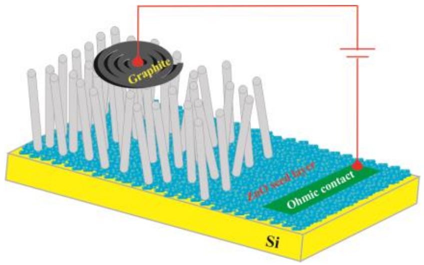
4K PL spectra of the as grown ZnO NRs (a), and annealed in nitrogen at 700°C (b) and 800°C (b).



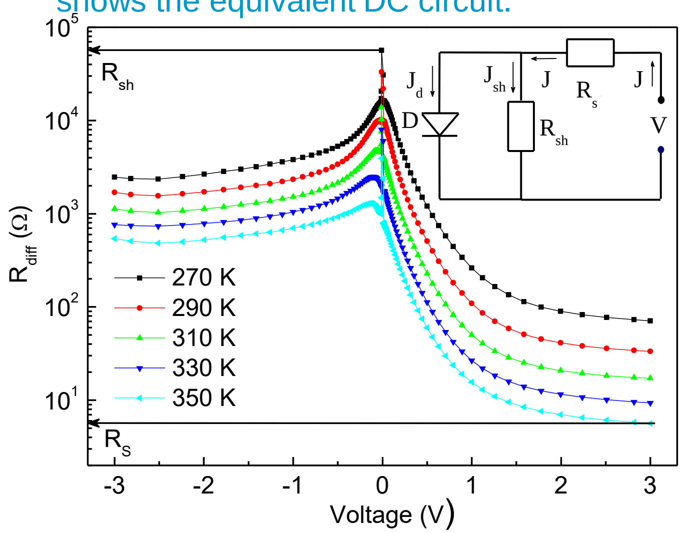
R. Yatskiv, J. Grym: *Luminescence properties of hydrothermally grown ZnO nanorods*, submitted to Superlattices and Microstructures

Electrical characterization of the graphite/ZnO NRs junction

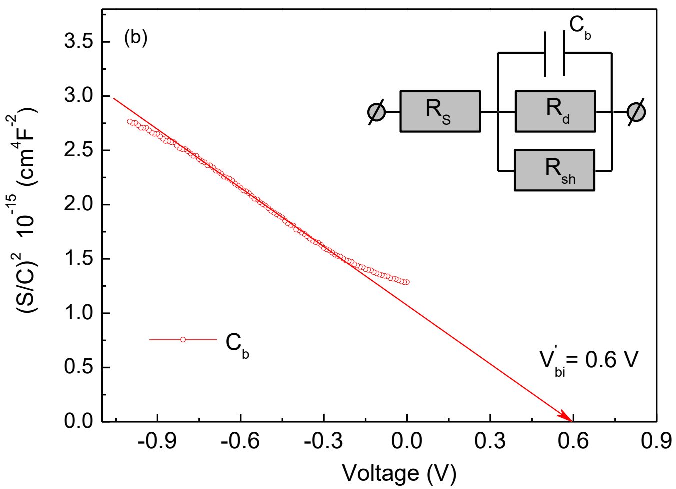
Schematic cross section of the graphite/ZnO NRs junction.



Differential resistance Rdiff of the graphite/ ZnO NRs junctions vs. voltage. The inset shows the equivalent DC circuit.



C-V characteristics of the graphite/ZnO NRs junctions. The inset shows the considered AC equivalent circuit.



The concentration of donors N = 1.24×10^{16} cm^{-3} in the ZnO NRs was calculated from C-V characteristics by using the following equation:

$$N = -\frac{2}{q\varepsilon_{ZnO}\varepsilon_0}\frac{\Delta V}{\Delta\left(\frac{S}{C_b}\right)^2}$$

The density of the charged uncompensated donor-type surface states N_{ass}= 6.9×10^{13} cm^{-2} at the graphite/ZnO NRs interface was calculated by :

$$N_{ss}^{a} = \frac{Q_{ss}}{qS} = \frac{1}{qS}\sqrt{2\varepsilon_0\varepsilon_{ZnO}qN(V_{bi} - V'_{bi})}$$

The high density of the interface states and barrier inhomogeneities at the graphite/ZnO NRs junction interface provide evidence of the predominance of the tunnel-recombination current transport mechanism via interface states. I-V characteristics graphite / ZnO NRs can by described by equation:

$$J = J_0^t \exp[\beta T]\exp[\alpha(V - JR_s)] = J_{00}^t \exp[\alpha(V - JR_s)]$$

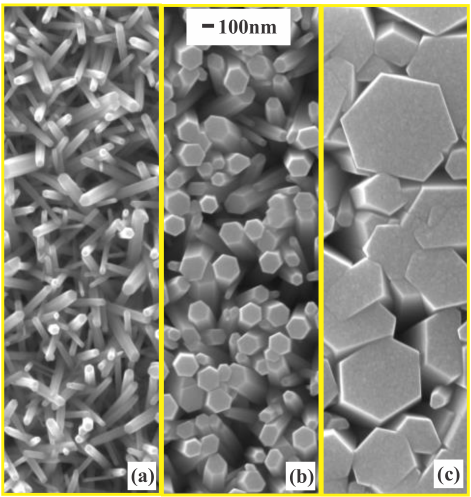
The reverse J-V characteristic of an abrupt junction in the case of the tunneling at reverse bias is governed by the following equation :

$$J_{rev}^{c} = a_0 V \exp\left(-\frac{b_0}{\sqrt{\varphi_b + V_{rev}}}\right)$$

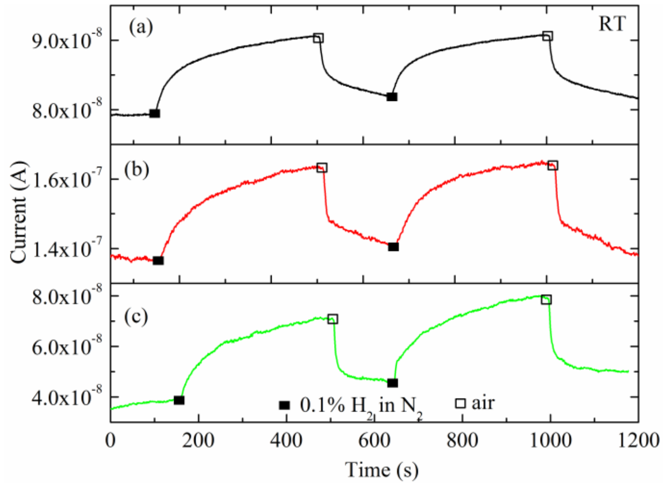
R. Yatskiv, V. V. Brus, M. Verde, J. Grym and P. Gladkov, Carbon 77, 1011-1019 (2014).

The effect of surface morphology of ZnO NRs on sensing properties of the graphite/ZnO nanorod junction.

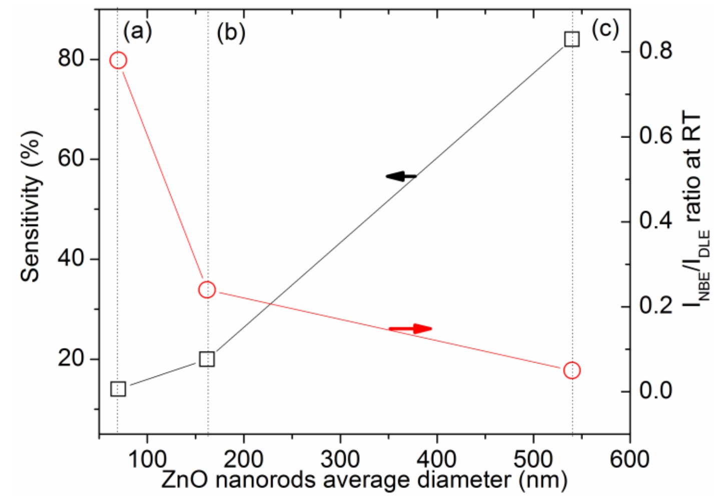
Top view SEM images of the ZnO nanorods prepared by hydrothermal growth with different precursor concentrations.



Current transient characteristics of the graphite/ZnO NRs junctions measured at -0.1 V.



Ratio of I_{NBE}/I_{DLE} (calculated from PL) and sensitivity of graphite/ZnO NRs hydrogen sensor as a function of the diameter of the ZnO NRs.



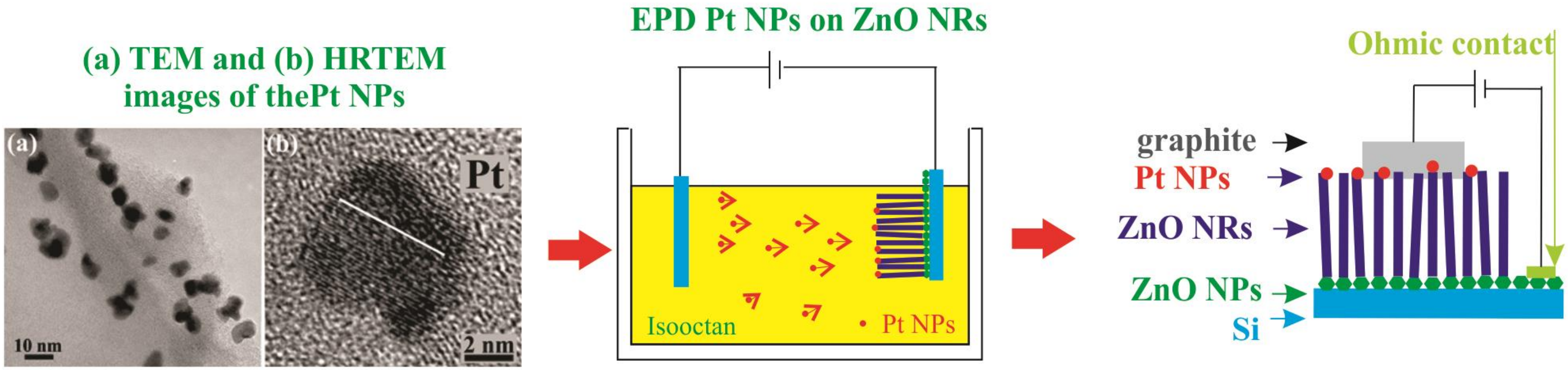
The sensor response and response time parameters of the graphite/ZnO NRs junctions with different sizes of ZnO NRs

	Sensitivity, S (%)	Response time, t_a (s)	Recovery time, t_b(s)
(a)	14	82	30
(b)	20	109	24
(c)	84	101	14

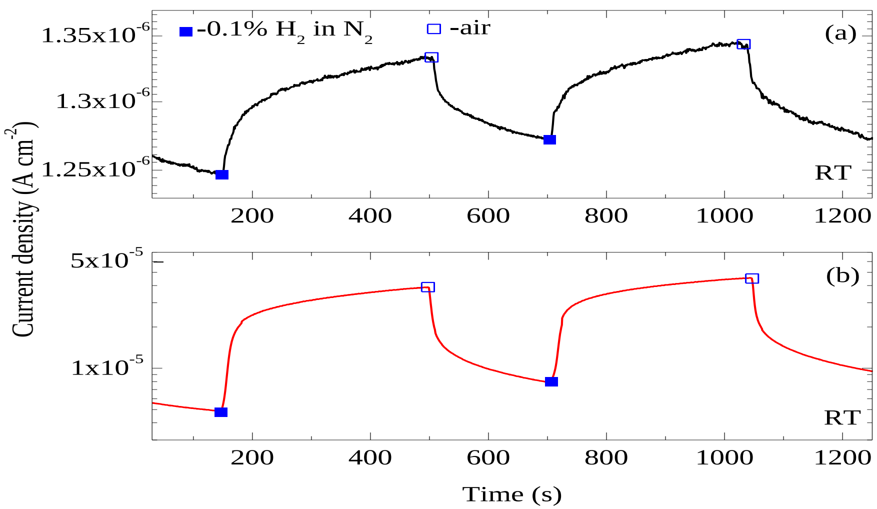
R. Yatskiv, J. Grym, The effect of surface morphology of ZnO nanorods on the sensing response of graphite/ZnO nanorod junctions, in: IEEE SENSORS 2015 - Proceedings, 2015, pp. 150-153.

Hydrogen sensing with the graphite/ZnO nanorod junctions decorated with Pt nanoparticles

Schematic diagrams of the fabrication process of graphite Pt NPs/ZnO NRs junction.



Current transient characteristics of (a) the graphite/ZnO NRs junction, and (b) the graphite Pt NPs/ZnO NRs junction measured at -0.1 V.



The sensor response and response time parameters

	Sensitivity, S (%)	Response time, t_a (s)	Recovery time, t_b(s)
(a)	14	82	30
(b)	700	68	22

- ✓ R. Yatskiv, J. Grym, P. Gladkov, O.Cernohorsky, J.Vanis, J.Maixner, J.H.Dickerson, Solid State Electron (In Press) doi:10.1016/j.sse.2015.10.011
- ✓ R. Yatskiv, J. Grym, V. V. Brus, O. Cernohorsky, P. D. Maryanchuk, C. Bazioti, G. P. Dimitrakopulos and P. Komninou, Semicond Sci Tech 29 (4), 045017 (2014).
- ✓ J. Grym, R. Yatskiv, O. Cernohorský, M. Verde, J. Lorincík, V. H. Pham, T. Gebre and J. H. Dickerson, in Key Engineering Materials (2015), Vol. 654, pp. 213-217.

Conclusions:

- ✓ Optical and electrical properties of the ZnO NRs prepared by hydrothermal method were presented.
- ✓ We investigated the effect of the morphology and point defect concentration in hydrothermally grown ZnO NRs on the sensing properties of the graphite/ZnO NR junctions. A strong correlation between the concentration of point defects in ZnO NRs and the sensing properties of the graphite/ZnO NR junctions was observed.
- ✓ The hydrogen sensing properties were further improved when the graphite/ZnO nanorod interface was decorated with Pt nanoparticles. The sensing response was enhanced by a factor of 50, and shorter recovery and response times were achieved.

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