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ZNO NANORODS FOR GAS SENSORS

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Outline

- ✓ Introduction
- ✓ Experimental result and discusion
  - Preparation of ZnO nanorods
  - Optical characterization of ZnO nanorods
  - Electrical characterization of ZnO nanorods
  - Graphite/ ZnO NRs heterojunction for hydrogen sensors.
- ✓ Conclusion

Acknowledgment

Introduction

ZnO is semiconductor and piezoelectric material with:

- *direct wide bandgap (~3.37eV at 300K),*
- *large exciton binding energy (~60 meV),*
- *good optical transmittance in visible region (90%),*
- *very resistive to high-energy radiation, etc.*

Possible applications

Photovoltaics
(nanostructured solar cells, dye-sensitized solar cells)

Sensors
(gas sensor,biosensors)

Metrology
(AFM cantilever)

Energy production
(nano-generator)

Optoelectronics
(emission devices such as LEDs, laser diodes; Non linear optical devices).

Introduction

In recent years the use of one-dimensional ZnO nanostructures, and more specifically nanorods, in applications such as gas sensors, dye sensitized solar cells, field effect transistors have attracted increasing interest.

Methods for preparation 1D ZnO nanostructure

Gas phase method
(physical vapor deposition, molecular beam epitaxy, pulsed laser deposition, etc.)

disadvantages:
- ✓*high temperature,*
- ✓*sophisticated instrumentation,*
- ✓*high cost,*
- ✓*poor sample uniformity, etc.*

advantage:
- ✓*high quality*

Chemical or solution-base method
(sol gel, electrodeposition or hydrothermal growth.)

advantages:
- ✓*low growth temperature,*
- ✓*allow large scale production,*
- ✓*low cost,*
- ✓*flexibility in the selection of the substrate, etc.*

disadvantages:
- ✓*low quality*

Experimental result and discussion

Preparation of ZnO nanorods

In our experiments ZnO NRs were synthesized by hydrothermal method from aqueous solution at 95 °C [1]. The chemical mechanism for growth of the ZnO NRs can be summarized by the following equations:

$$(CH_2)_6\ N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3$$

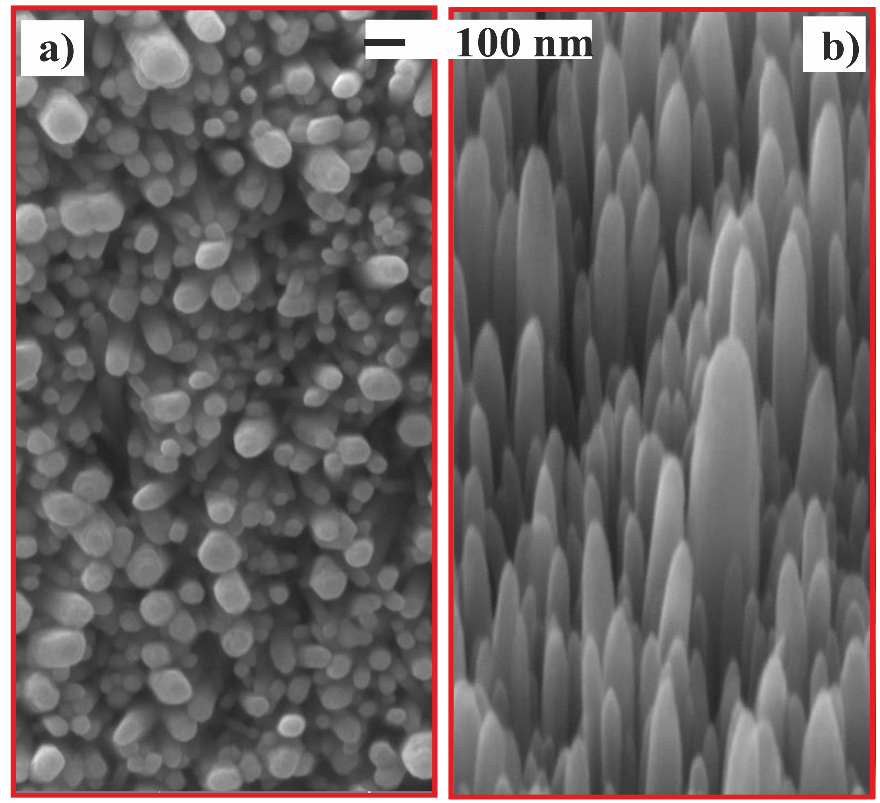
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$$Zn(NO_3)_2 \cdot 6H_2O \rightarrow Zn^{2+} + 2NO_3^- + 6H_2O$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$

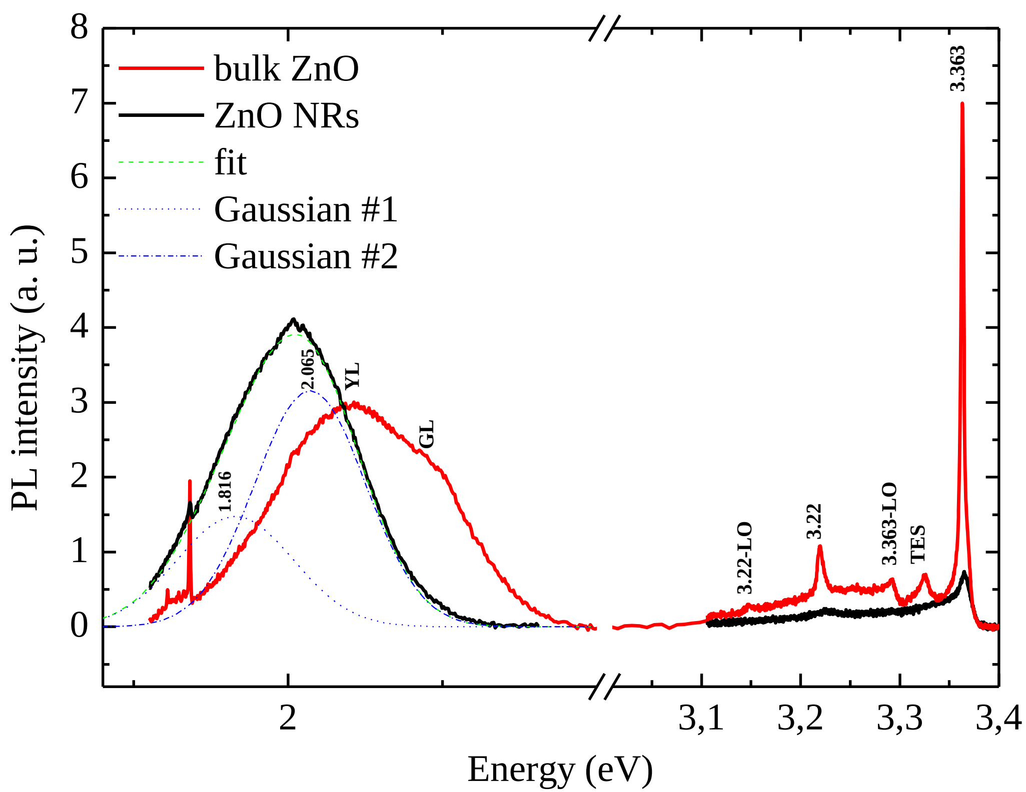
[1] Vayssieres L ***Adv. Mater.* 2003**; 15: 464.

SEM image of the ZnO NRs (a) - top view and (b) – images taken at a 55° tilt



Experimental results and discussion

Optical characterization of ZnO nanorods



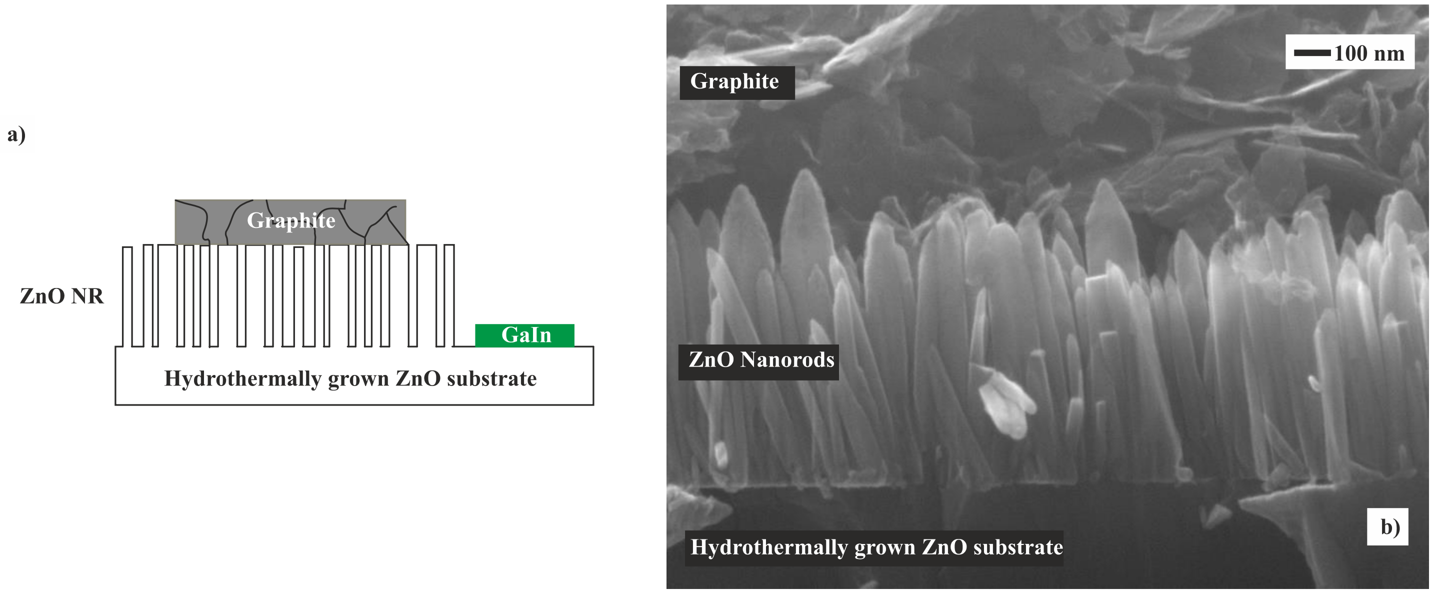
4K PL spectra obtained in one experiment and equal condition from ZnO NRs and bulk hydrothermal ZnO.

Experimental results and discussion

Electrical characterization of ZnO nanorods

Preparation of graphite / ZnO NRs heterojuctions

Recently, we demonstrated that highly rectifying and thermally stable junction can be created by depositing of colloidal graphite on different bulk semiconductor materials [1-4].



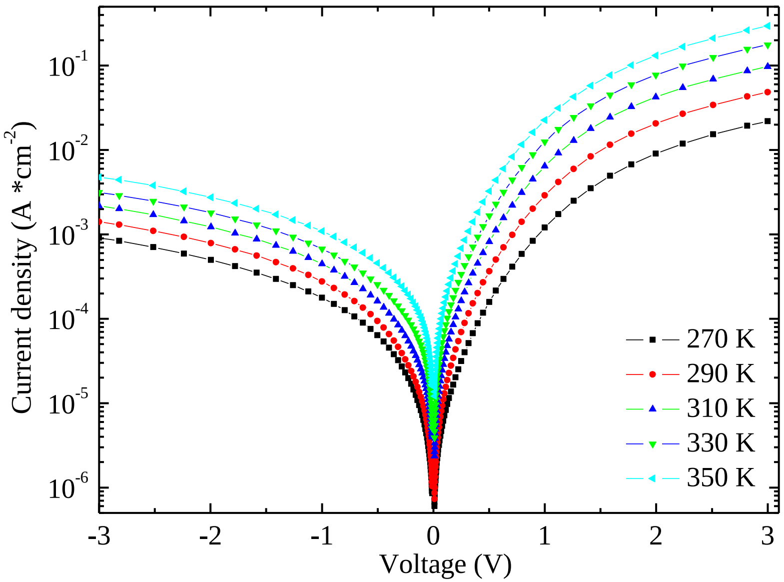
(a) Schematic diagram and (b) cross section of graphite/ZnO NRs junction.

[1] R. Yatskiv, J. Grym, ***Appl. Phys. Lett. 2012***;*101(16)*:162106.
[2] R. Yatskiv, J. Grym, K. Zdansky, K. Piksova, ***Carbon 2012***; 50(10):3928–3933.
[3] R. Yatskiv, J. Grym, ***Semicond. Sci. Technol. 2013***; 28: 055009
[4] L. Kosyachenko, R. Yatskiv, N.S. Yurtsenyuk, O.L. Maslyanchuk, J. Grym, ***Semicond. Sci. Technol. 2014*** ; 29: 015006

Experimental results and discussion

Electrical characterization of ZnO nanorods

I-V characteristics of the graphite/ZnO NRs heterojunctions measured at different temperatures.



The graphite/ZnO NRs structures show a rectifying behaviour at different temperatures, which confirms the formation of the electric junction between the graphite film and the ZnO NRs.

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 $\mathbf{N^a_{ss}}$**= 6.9×10^{13} cm**$^{-2}$ at the graphite/ZnO NRs interface was calculated by :

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

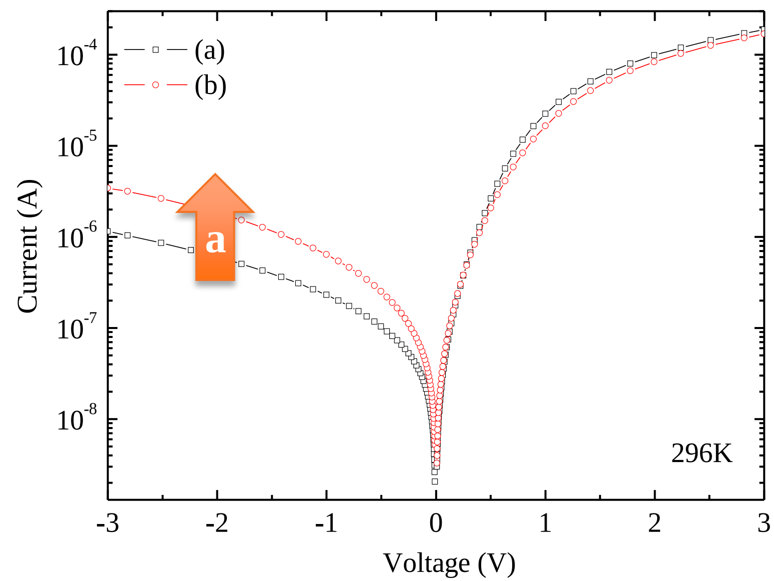
The high density of the interface states and barrier inhomogeneities at the graphite/ZnO NRs heterojunction interface provide evidence of the predominance of the tunnel-recombination current transport mechanism via interface states. I-V characteristics graphite / ZnO NRs can by described by equation:

$$J = J^t_0\exp[\beta T]\exp[\alpha(V - JR_s)] = J^t_{00}\exp[\alpha(V - JR_s)]$$

Experimental results and discussion

Graphite/ ZnO NRs heterojunction for hydrogen sensors.

Current-voltage characteristics of the graphite/ZnO NRs Schottky diode. (a) in air, (b) under exposure to 0.1% H_2 in N_2.



a:

✓Oxygen molecules adsorbed on the surface extract electrons from the conduction band of ZnO to form O^- and O^{2-} anions. This process leads to the formation of a depletion region with reduced carrier concentration near the sample surface.

✓When the sample is exposed to hydrogen, chemisorbed oxygen species react with hydrogen, the extracted electrons are released to the conduction band, and resistivity is decreased.

Conclusion

✓We demonstrated formation of the electric junction between the graphite film and the ZnO NRs.

✓The I-V characteristics of graphite/ZnO nanorods heterojunctions can be well described by a tunnel-recombination current transport mechanism via interface states.

✓The nanostructured heterojunctions showed promising rectifying and gas sensing parameters. The obtained results represent a good starting point for the further development of the nanostructured heterojunction diodes and gas sensors.

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