



Synthesis of Nanostructure Zinc Oxide Formation from Zinc Acetate and Deposited on Sapphire Substrate using Pulsed Laser Deposition for NO₂ Gas Sensor

Nadheer Jassim Mohammed, Marwa Abdul Muhsien Hassan, Ibrahim R. Agool and Nisreen Zaid
Department of Physics, College of Science, Al-Mustansiriyah University, Baghdad, Iraq.

ARTICLE INFO

Article history:

Received: 8 February 2015;

Received in revised form:

28 March 2015;

Accepted: 13 April 2015;

Keywords

ZnO Nanostructure,
Gas Sensor,
FESEM,
PLD.

ABSTRACT

Zinc oxide nanostructure were successfully synthesized by chemical method and deposited on Al₂O₃ substrate using PLD. XRD analysis demonstrated that the ZnO nanostructure has a wurtzite structure with orientation of (002). SEM results indicated that by increasing the calcined temperature, the dimension of the ZnO nanostructure increases. The optimum temperature for synthesizing high density ZnO nanostructure was determined to be 1250 K. Room temperature PL spectra of the ZnO nanostructure showed a strong UV emission peak located at around 380 nm and a relatively weak green emission at around 540 nm, confirming that the as-grown nanorods possess good optical properties. The sensitivity of zinc oxide NRs films to 50 ppm vapor NO₂ gas as a function of working temperature with different doping.

© 2015 Elixir All rights reserved.

Introduction

Zinc oxide (ZnO), a II-VI compound oxide semiconductor with a direct band gap of 3.37 eV and a high exciton binding energy of 60 meV at room temperature, is an important kind of technological semiconductor due to its distinguished optical, electrical, and piezoelectrical properties, which can be widely used in optoelectronic and photovoltaic devices [1, 2]. Various methods, such as precipitation, sol-gel, vapor-liquid-solid (VLS) growth, chemical vapor deposition (CVD), thermal decomposition, metal organic vapor-phase epitaxy, have been developed for controlling ZnO structures, since its various properties strongly depend on its structures including the crystal size, orientation, morphology, aspect ratio and even crystalline density. Currently, many interesting ZnO nanostructures including nanorods, nanowires, tetrapods, nanocombs, nanotubes, nanopencils and star-like have been successfully synthesized [3-7]. Metal oxide semiconductors such as ZnO, SnO₂, TiO₂, Fe₂O₃, NiO, WO₃, In₂O₃ etc., have been widely used for gas sensors. Among these sensing materials, ZnO has attracted increasing attention and been proven to be a highly useful sensing material for detecting both oxidizing and reducing gases. In recent years, great efforts have been made to fabricate low dimensional ZnO nanostructures, since their gas sensing properties can be efficiently improved in this way. Taking advantage of their small and uniform particle size, high surface-to-volume ratio, specific pore structure, anti-aggregation properties and so on, these low-dimensional nanostructures may exhibit better sensing properties than those of traditional nanoparticles and thin films. Hitherto, low-dimensional ZnO nanostructures with different morphologies including nanobelts, nanotubes, nanorods, nanowires, nanofibers, nanodisks, nanospindles and nanoneedles, have been successfully developed, and many exhibit interesting gas sensing performances towards H₂, CO, NO₂, H₂S, SO₂ and some volatile organic compounds (VOCs). Pawar *et al.* obtained interesting morphological transformations from rod-to-disk-to-spindle-to-flower merely by varying the pH of the growth solution. Pawar and co-workers also synthesized

vertically aligned ZnO nanorods, hexagonal nanorods, faceted microrod rods, nanoneedles and nanotowers assisted with different surfactants (polyetherimide PEI, polyacrylic acid PAA, diammonium phosphate DAP and DAP-PAA). Chai *et al.* reported the synthesis of functionalized individual ZnO microwires prepared by a carbothermal reduction vapor phase transport method and their gas sensing properties for natural gases such as H₂, O₂, CO₂, CO, CH₄ and C₂H₅OH. Hamedani *et al.* applied a fast and facile microwave assisted method to prepare various ZnO nanocrystal morphologies and investigated their response and selectivity for CO, CH₄ and C₂H₅OH [8].

Experimental Method

Zinc acetate [(CH₃COO)₂Zn.H₂O] and sodium dodecyl sulfate (C₁₂H₂₅NaO₃S) were dissolved in deionized water at 0.2 mol/L concentration, respectively

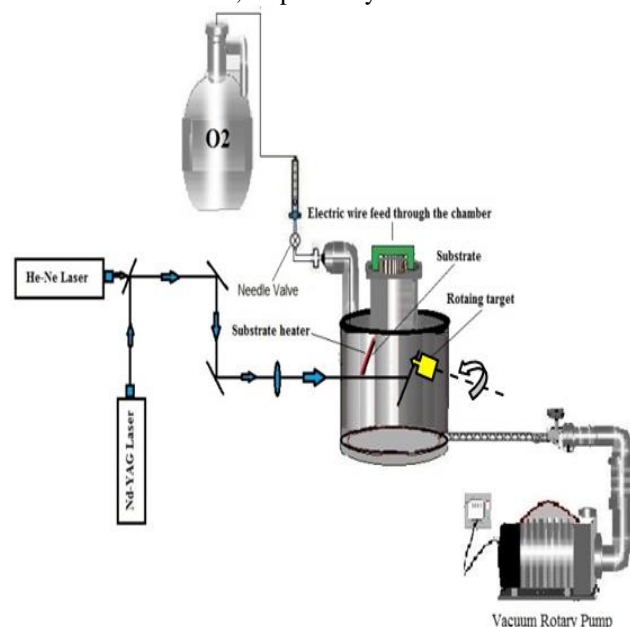


Figure 1. Pulsed laser deposition technique (PLD)

Tele:

E-mail addresses: marwa_alganaby@yahoo.com

© 2015 Elixir All rights reserved

Then, certain volume zinc acetate solution was slowly added to sodium dodecyl sulfate solution under vigorous stirring at room temperature for 25 min. The samples were filtrated and washed with distilled water several times. Finally, the samples were dried in air at 378 K for 4 h. The ZnO samples were obtained by calcined at (1150, 1200 and 1250) K for 6 h in tube furnace.

Zinc oxide and different doping noble metal (Ag and Ni) with high purity (99.999%) at concentrations (4%) mixed with corresponding concentrations in methanol by magnetic blender for 2 hour. After the liquid was dry out, the mixed powder was blended mechanically again so that the mixture is uniformly distributed. The resultant powder was ground again and was pressed under 5 ton to form a target with 2.5 cm diameter and 0.4 cm thickness. The target should be as dense and homogenous as possible to ensure a good quality of the deposit. Thin films from the prepared target were deposited on (α -Al₂O₃ (006)) single crystal sapphire substrate by pulsed laser deposition technique (PLD). The pulsed laser deposition experiment is carried out inside a vacuum chamber generally in (10^{-3} Torr) vacuum conditions, at low pressure of a background gas for specific cases of oxides and nitrides. A schematic diagram of the set-up of laser deposition chamber, given in figure (1), shows the arrangement of the target and substrate holders inside the chamber with respect to the laser beam. The focused Nd:YAG SHG Q-switching laser beam coming through a window is incident on the target surface making an angle of 45° with it. The substrate is placed in front of the target with its surface parallel to that of the target. Sufficient gap is kept between the target and the substrate so that the substrate holder does not obstruct the incident laser beam. Modification of the deposition technique is done by many investigators from time to time with the aim of obtaining better quality films by this process. These include rotation of the target, heating the substrate, positioning of the substrate with respect to the target etc. The oxygen background pressure 5×10^{-2} mbar. ZnO pellets were ablated by a Q-switched Nd: YAG Laser Second Harmonic Generation (SHG) (Huafei Tongda Technology—DIAMOND-288 pattern EPLS, $\lambda = 532$ nm, 5 Hz and 10 ns pulse duration) with a fluence of 2 J/cm². The substrate temperature is maintained at $\sim 450^\circ\text{C}$.

Results and Discussion

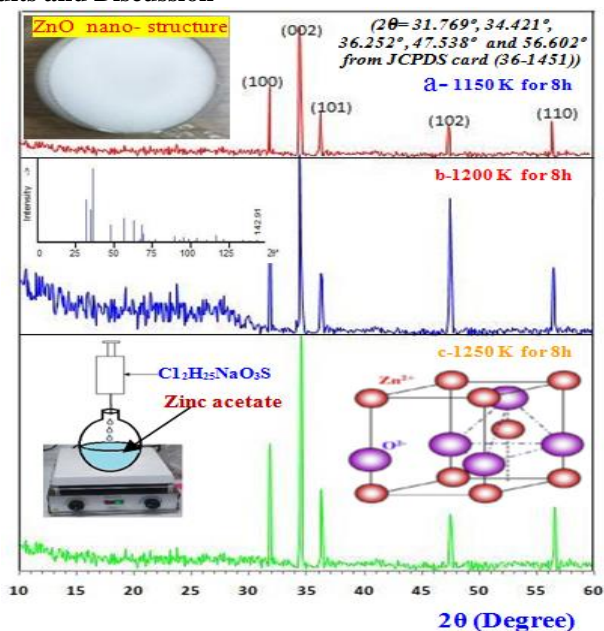


Figure 2. XRD of ZnO powder calcined at (a) 1150 K, (b) 1200 K and (c) 1250 K for 6 h.

Structural Characterization. XRD pattern of ZnO powder nanorods obtained via the chemical method only consist of a pure phase of ZnO nanomaterial is shown in figure (2) (a, b, c). The unit cell of the ZnO crystal was found to be hexagonal structure with the presence of the peak (002) plane, compared with the card number (JCPDS 36-1451) and measured lattice constants of a and c of 3.25 and 5.21 Å (c/a) 1.60, respectively. The crystallite size was calculated using the Scherer's formula at highest intensity (002) peak was analysed and considered it to be Gaussian. The crystallite size was found to be 35 nm. Besides, no impurity peaks were detected which indicates that the construction ZnO powder is highly pure nanomaterials. EDX spectrum curve of figure (3) (a, b) shows that only O and Zn elements, the atom ratio of Zn to O is quantitatively calculated found to be 70:30 besides the carbon.

Figure 3. EDX of ZnO powder calcined at (a) 1200 K and (b) 1250 K for 6 h

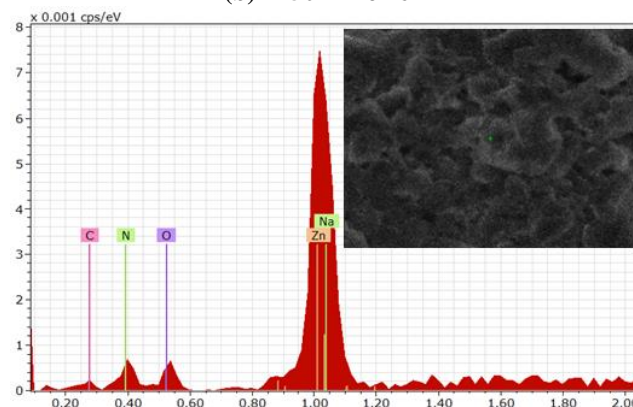
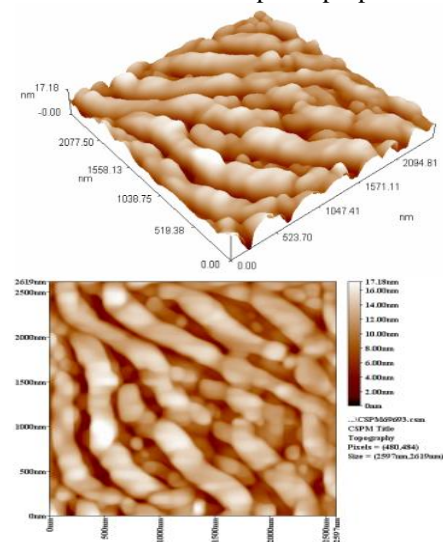


Figure (4) show FESEM images with different magnifications of the as-prepared zinc oxide powder calcined at 1200 and 1250 K for 6 h. The ZnO surface morphology nanostructures are randomly distributed in the powdered ZnO sample. The ZnO powder contains nanoneedles and nanorods with average diameter found to be ~ 35 -60 nm and length $\sim (250$ -300) nm. The software used in calculation of this work was MBF_Image J. program. We have taken the FESEM images from different point region of the distributed powder sample. The surface nanorod was characterized using AFM micrographs. It shows a change in roughness of the oxide surface with calcined temperature as shown in figure (5). It is known that the increase in surface roughness may cause deterioration of the electrical and optical properties.



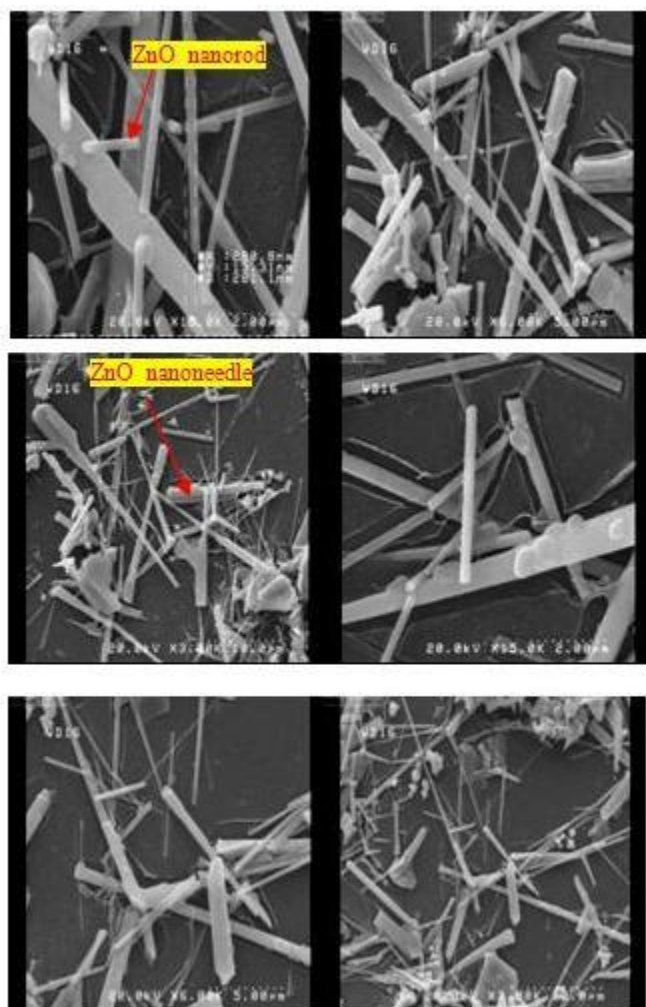


Figure 4. FESEM of ZnO powder calcined at (a) 1200 K and (b) 1250 K for 6 h

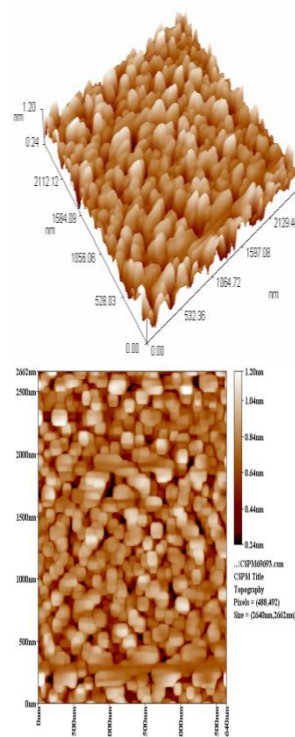


Figure 5. AFM f ZnO powder calcined at (a) 1150 K, (b) 1200 K and (c) 1250 K for 6 h.

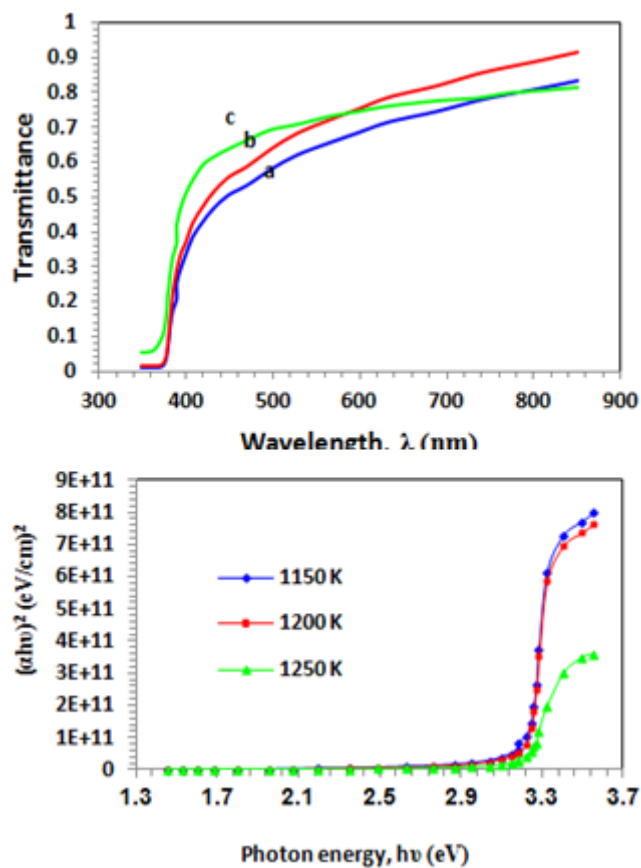
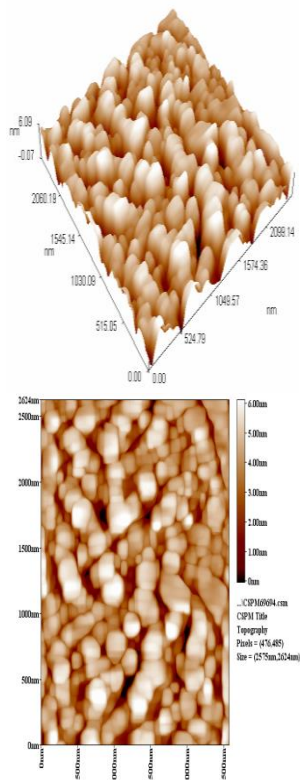


Figure 6. Transmittance with wavelength f ZnO powder calcined at (a) 1150 K, (b) 1200 K and (c) 1250 K for 6 h.

Figure 6 shows the transmittance spectra curve of ZnO powder calcined at (a) 1150 K, (b) 1200 K and (c) 1250 K for 6 h in the wavelengths range of 300-800 nm at room temperature. As can be seen, the average optical transmittance of the ZnO samples in the visible range is amount 80%, leading to a good optical quality of the produced ZnO nano-materials. The direct

allowed band gap semiconductors calculated using the following equation (1) for $n = 1/2$ [4].

$$ahv = A(hv - E_g)^{1/2} \tag{1}$$

The absorption coefficient α could be calculated from the following equation [20]:

$$\alpha = \ln(1/T)/d \tag{2}$$

where T is the transmittance and d is the thickness of the film. The plot of the graph $(ahv)^2$ vs hv (see inset Figure 6) by using equation (1). The optical band gap value of the ZnO powder, determined by the optical method, is obtained by extrapolating the linear portion of this graph to $(ahv)^2 = 0$ and optical band gap is found equal range to be $E_g=3.2-3.3$ eV.

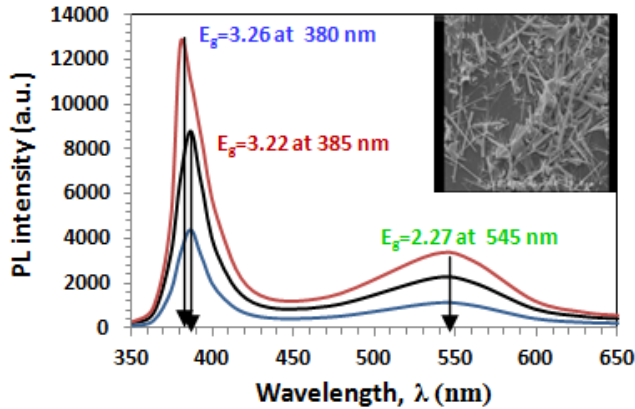
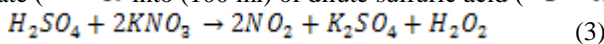


Figure 7. PL with wavelength f ZnO powder calcined at (a) 1150 K, (b) 1200 K and (c) 1250 K for 6 h.

The PL spectrum is recognized of an ultraviolet (UV) emission located at about 380 nm and a broad green emission position at about 540 nm. The UV emission band can be explained by the near band-edge transition of the wide band gap ZnO nanorods, the recombination of free excitons through an exciton-exciton collision process, whereas the peak at 545 nm is due to the deep-level emission (DLE) related to the defects such as oxygen vacancies and Zn interstitials. It has been suggested that the DLE corresponds to the singly ionized oxygen vacancy in ZnO and results from the recombination of a photo-generated hole with the singly ionized charge state of this defect. Strong UV emission and relatively weak green emission from the ZnO nanorods confirm that the grown nanorods possess good optical properties with less structural defects and impurities [9]. NO₂ gas was prepared in laboratory by adding three gm of potassium nitrate (KNO_3) into (100 ml) of dilute sulfuric acid (H_2SO_4)



Metal oxides semiconductors, such as ZnO, SnO₂, In₂O₃, CdO and TiO₂, can be exercised to gases sensors which are mainly based on the current change responses to the target gases. The sensing mechanism of metal oxide semiconductor gas sensors based ultimately on trapping of electrons at adsorbed molecules and band bending induced by these charged molecules are answerable for a change in conductivity.

The current of the film was measured before and after exposure to gas.

$$Sensitivity (\%) = (I_{gas} - I_{air})/I_{air} \times 100 \tag{4}$$

where I_a is the current in air and I_{gas} is the current in a sample gas. In general, intrinsic ZnO nanorod behaved as an N-type semiconductor and has many oxygen vacancies, thus, its gas sensitive effect is obvious and is generally considered a surface adsorption-controlled mechanism as shown in figure (8). Its response to the measured gas is caused by the chemisorption reaction between oxygen in the air and the ZnO NRs sensor

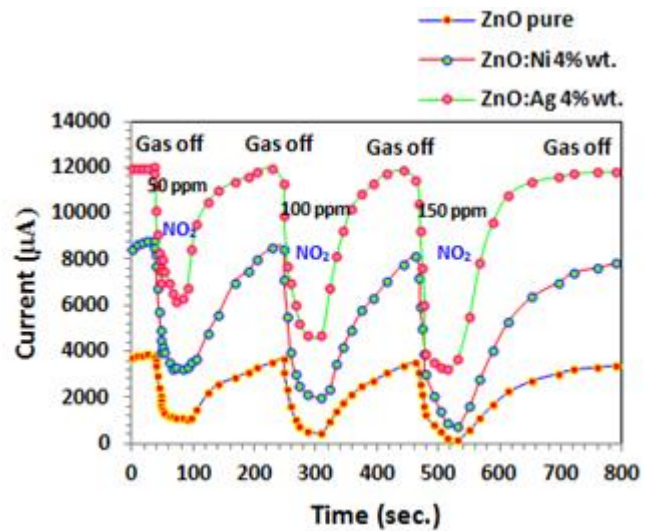


Figure 8. Relation between current and time of zinc oxide NRs film deposited on Al₂O₃ with different doping. Oxygen ions exist in the grain boundaries between grains, thereby causing the grain boundary barrier to become higher, thus, the resistance of the ZnO NRs sensor increases, blocking the transfer of the carriers. When meeting the reducing gas or the electron supply gas, an oxidation reduction occurs between the surface adsorbed oxygen ions and the reducing gas. The number of adsorbed oxygen ions decreases sharply, the sensor surface potential barrier is reduced, carrier shifting is promoted, ZnO resistance is reduced, and the gas sensing response is finally achieved [10, 11]. The interpretation of metal oxide semiconductor gas-sensitive materials is extremely influenced by the working temperature. Figure (9) shows the response curve (sensitivity) of ZnO nanorod gas sensor semiconductor at different working temperatures (*i.e.*, surface temperature) at 50 ppm vapor NO₂ gas. As obvious, the sensitivity increases with the temperature and reaches a maximum value in identification of work temperature T= 200-300 °C. If the temperature increases again, the sensitivity decreases.

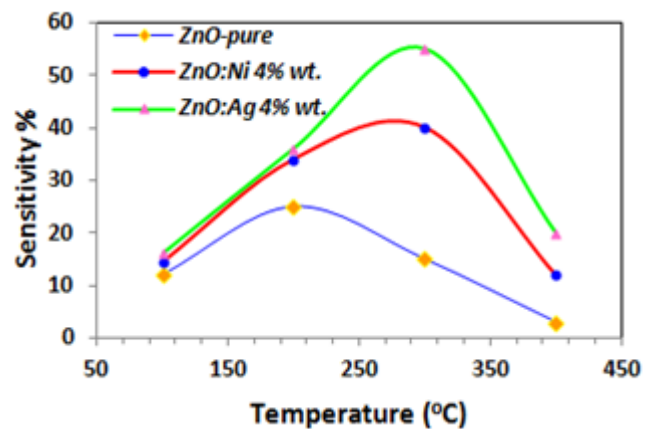


Figure 9. Relation between sensitivity and temperature of zinc oxide NRs film on Al₂O₃ with different doping

Conclusion
High quality zinc oxide nanostructure were successfully synthesized by chemical method and deposited on Al₂O₃ substrate using PLD. XRD analysis demonstrated that the ZnO nanostructure has a wurtzite structure with orientation of (002). SEM results indicated that by increasing the calcined temperature, the dimension of the ZnO nanostructure increases. The optimum temperature for synthesizing high density ZnO

nanostructure was determined to be 1250 K. Room temperature PL spectra of the ZnO nanostructure showed a strong UV emission peak located at around 380 nm and a relatively weak green emission at around 540 nm, confirming that the as-grown nanorods possess good optical properties. The sensitivity of zinc oxide NRs films to 50 ppm vapor NO₂ gas as a function of working temperature. As evident, the sensitivity increases with the temperature and reaches a maximum value in correspondence of T = 200-300 °C. If the temperature increases again, the sensitivity decreases.

References

- [1] Bingqiang Cao and Weiping Cai, " From ZnO Nanorods to Nanoplates: Chemical Bath Deposition Growth and Surface-Related Emissions", *J. Phys. Chem. C* 2008, 112, 680-685.
- [2] Pijus Kanti Samanta and Ashok Kumar Bandyopadhyay, " Chemical growth of hexagonal zinc oxide nanorods and their optical properties", *Appl Nanosci* (2012) 2:111–117 DOI 10.1007/s13204-011-0038-8
- [3] Jin Chu , Xiaoyan Peng , Zhenbo Wang , Peter Feng," Sensing performances of ZnO nanostructures grown under different oxygen pressures to hydrogen", *Materials Research Bulletin* 47 (2012) 4420–4426.
- [4] Adel Taabouche1, Abderrahmane Bouabellou, Fouad Kermiche, Faouzi Hanini, Sarah Menakh, Yacine Bouachiba, Tahar Kerdja, Chawki Benazzouz, Mohamed Bouafia, Saad Amara, " Effect of Substrates on the Properties of ZnO Thin Films Grown by Pulsed Laser Deposition", *Advances in Materials Physics and Chemistry*, 2013, 3, 209-213 <http://dx.doi.org/10.4236/ampc.2013.34031> Published Online August 2013 (<http://www.scirp.org/journal/ampc>).
- [5] Wei Feng, Jie Chen and Chun-yan Hou," Growth and characterization of ZnO needles", *Appl Nanosci* DOI 10.1007/s13204-012-0174-9.
- [6] P. K. Samanta, S. K. Patra, A. Ghosh and P. Roy Chaudhuri, "Visible Emission from ZnO Nanorods Synthesized by a Simple Wet Chemical Method", *International Journal of NanoScience and Nanotechnology* ISSN 0974– 3081 Volume 1, Number 1-2 (2009), pp.81-90 © International Research Publications House <http://www.irphouse.com/sci/ijnn.htm>.
- [7] A. George, P. Kumari, N. Soin, S.S. Roy, J.A. McLaughlin, " Microstructure and field emission characteristics of ZnO nanoneedles grown by physical vapor deposition", *Materials Chemistry and Physics* 123 (2010) 634–638.
- [8] Qu Zhou, Weigen Chen, Lingna Xu and Shudi Peng," Hydrothermal Synthesis of Various Hierarchical ZnO Nanostructures and Their Methane Sensing Properties", *Sensors* 2013, 13, 6171-6182; doi:10.3390/s130506171.
- [9] Mohammad Reza Khanlary, Vahid Vahedi and Ali Reyhani," Synthesis and Characterization of ZnO Nanowires by Thermal Oxidation of Zn Thin Films at Various Temperatures", *Molecules* 2012, 17, 5021-5029; doi:10.3390/molecules17055021.
- [10] Xiaoxing Zhang , Jinbin Zhang , YichaoJia , Peng Xiao and Ju Tang” TiO₂ Nanotube Array Sensor for Detecting the SF₆Decomposition Product SO₂ “*journal of sensors* ,Vol. 12,PP. 3302-3313,(2012).
- [11] Zhaohui Li, Dongyan Ding, Qiang Liu and Congqin Ning, "Hydrogen Sensing with Ni-Doped TiO₂ Nanotubes", *Sensors* 2013, 13, 8393-8402; doi:10.3390/s130708393.