RESEARCH PAPER

Synthesis, Characterization, and Gas Sensing Properties of In-doped ZnO Nanopowders

Sanaz Alamdari[1,2], Morteza Sasani Ghamsari[1,*], Majid Jafar Tafreshi[2]

[1] Photonics and Quantum Technologies Research School, NSTRI, Tehran, Iran

[2] School of Physics, Semnan University, Semnan, Iran

ARTICLE INFO

Article History:
Received 15 April 2017
Accepted 29 June 2017
Published 1 July 2017

Keywords:
Acetone
Gas Sensor
Indium Ions
Zinc Oxide

ABSTRACT

Indium (1at %) doped ZnO and ZnO nanoparticles have been synthesized via sol gel method. The structural characters of the synthesized nanoparticles have been studied by X-ray diffraction pattern (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). From synthesized nanopowders a tablet was prepared by using the isostatic pressing and then sintered at 600°C. Then, the gas-sensing properties of ZnO and IZO powder tablets were evaluated with respect to the acetone gas at different temperatures and concentrations. XRD pattern and SEM images showed the prepared samples were crystallized in the wurtzite structure with the average particle size of 32 and 27 nm. The gas sensing measurement results showed that the indium dopant ions improved the gas sensitivity of ZnO for high acetone concentrations effectively. Therefore, it is suggested that the IZO tablet can act as reliable and low cast gas sensor for acetone detection. Sintering temperature strongly increased the grain size and density of samples. EDX analysis confirmed the presence of indium in zinc oxide structure.

How to cite this article
Alamdari S, Sasani Ghamsari M, Jafar Tafreshi M. Synthesis, Characterization, and Gas Sensing Properties of In-doped ZnO Nanopowders. Nanochem Res, 2017; 2(2):198-204. DOI: 10.22036/ncr.2017.02.006

INTRODUCTION

Acetone as one of the hazardous chemical solvent is highly used in industry and laboratory [1]. It is classified as volatile organic compounds (VOCs) and its gas is extremely flammable, explosive and toxic. Thus, for practical applications and in the workplace, the detection of acetone using a fast response/recovery time's gas sensor is important for human safety and health [1]. For instance, the determination of acetone concentration is of great importance for food quality control and its detection is being a significant index of the diagnosis of human diseases. At present, various acetone sensors have been fabricated by using semiconductor oxides that are well known as a good sensor platform due to their remarkable ability for detection of both oxidizing and reducing gases [2-10]. Gas sensing properties of this type of materials are characterized by the distortion of electrical response with respect to the environmental gases [11]. Oxide semiconductor nanostructures have attracted a lot of attention over the last decade owing to the widely use of toxic gas detection due to the low cost, high responsivity, and easy-monitoring of the air pollution [12]. Among them, zinc oxide (ZnO) with unique properties and wide range of applications in various fields such as gas sensors, light emitting devices, solar cells, piezoelectric devices and visitors has considerably noticed [13,14]. Due to high electrochemical stability, chemical sensitivity to different adsorbed gases, non-toxicity, and low cost, ZnO has been

* Corresponding Author Email: *msasani@aeoi.org.ir*

considered a novel material of fast-response and highly sensitive gas sensor devices [15-20]. Zno has also capabilities to detect, identify and display the presence of gases and their concentrations. The performance of ZnO sensor can easily improve by addition of dopants [21,22].

Sadeghian Lemraski and Nadimi [23] performed ab initio density functional theory-based calculations and employed quantum molecular dynamic simulation to investigate the adsorption mechanism of acetone molecule on ZnO based thin film sensors. They have found that the sensitivity of a metal oxide sensor exceedingly depends on molecular oxygen exposure and operating temperature. Their results indicated that at elevated temperatures a competitive process controls the removing of preadsorbed oxygen molecule from the surface and this competition is responsible for the resistive switching behavior in the ZnO-based gas sensors. Gas sensitivity of this kind of materials is affected by the surface states and their morphology. Therefore, an increasing interest in nanomaterials for gas sensing was demonstrated [24]. Recently, Bhoi et al [25] studied the powder size effects and gas sensing properties of Co doped ZnO sample synthesized by sol–gel technique followed by calcinations at 650°C. 10 mm diameter and 2 mm thickness cylindrical pallet has been prepared from the calcined powders by using hydraulic press and then annealed at a temperature of 700°C for 4 hours. They found that at higher temperature nanocrystalline Co doped ZnO shows a better sensitivity to the gases (ethanol and acetone) of less than 100 ppm concentration. In this approach, we try to study the high temperature sintering effect on sensor performance of ZnO and indium doped ZnO nanopowders for detection of the low concentrations of acetone that may cause narcotic effects.

EXPERIMENTAL

ZnO and In doped ZnO (IZO) nanoparticles were synthesized by sol-gel method [26-30]. Analytical grade of zinc acetate dihydrate (99.5%) purchased from Merck, indium nitrate purchased from Sigma Aldrich (98%), triethylamine (99%) purchased from Merck, and absolute ethanol (99.7%) purchased from China have been used as starting materials. First, zinc acetate dehydrate (2 M) was dissolved in 20 cc of absolute ethanol then 2cc TEA as stabilizer was added to the solution at room temperature and stirred by a magnetic stirrer for 20 min, finally (1 at%) indium nitrate was added to precursor solution and stirred again for 30 min. The sol became homogeneous and clear, and allowed to age for 1 week. ZnO and IZO precipitates were dried at 300°C for 1 h, then 0.8 gr of the synthesized nano powders were hydraulic-pressed and sintered at 600°C to be molded into tablets with radius of 12 mm and thickness of 1.5 mm. Electrodes on the prepared powder tablets were placed by silver paste and dried at 150°C for 1 h. Field scanning electron microscopy (FESEM Mira Tescan) was employed to study the morphology and size of particles. X-ray diffraction analysis (XRD, PANalytical PW3050/60 diffractometer) was used to investigate the crystal structure. The elemental compositions of the samples were analyzed by energy dispersion X-ray spectroscopy (EDX, IROST). To study the sensing properties, the resistance changes of tablets in the presence of acetone gas were measured. For connecting the sensor and electric circuit, the conductive silver paste was used with high temperature tolerance. After applying conductive adhesive, samples were dried at 120-150°C, then the sensors were placed in a vacuum chamber on a hot

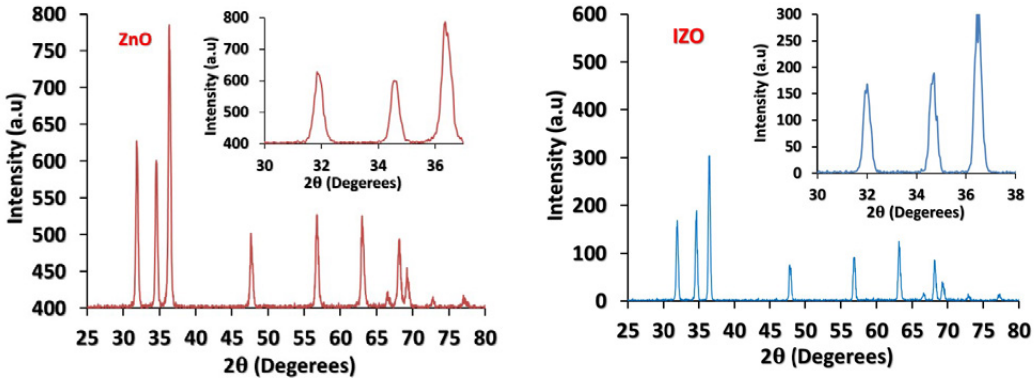

Fig. 1: XRD patterns of ZnO and IZO powders.

plate and the pressure inside the chamber was reduced to about 150 Torr using a vacuum pump. Finally, through a gradual increase in power supply voltage and the resulting increase in temperature of samples, resistance changes of tablets in various concentrations of acetone gas were determined.

RESULT AND DISCUSSION

XRD spectra of pure ZnO and IZO powders are shown in Fig. 1. All the peaks in the XRD patterns indicate that the samples are crystallized in the hexagonal wurtzite phase. No diffraction peaks of other compounds such as In_2O_3 or secondary phases were detected. As can be found from this figure, the intensity of peaks in the X-ray diffraction pattern of pure ZnO is higher than IZO. It can be attributed to lattice change caused by introduced indium ions. This means that the crystal structure must be under stress, due to the difference in sizes of indium and Zn atoms (the radius of In^{+3} ion =0.092 nm > radius of Zn^{2+} ion =0.074 nm).

It is well known that the decrease in crystal quality of IZO sample is due to the local disorder and lattice distortion resulting from the substitution of Zn^{+2} by In^{+3} ions. The average size of crystallites of the prepared samples, determined by using Debye–Scherrer formula, is equal to 32 and 27 nm for pure ZnO and IZO, respectively. EDX analysis was performed to identify the elemental composition of the samples. Fig. 2 a, shows the EDX analytical results of pure ZnO sample consisting of O and Zn elements. The EDX analytical result of IZO sample

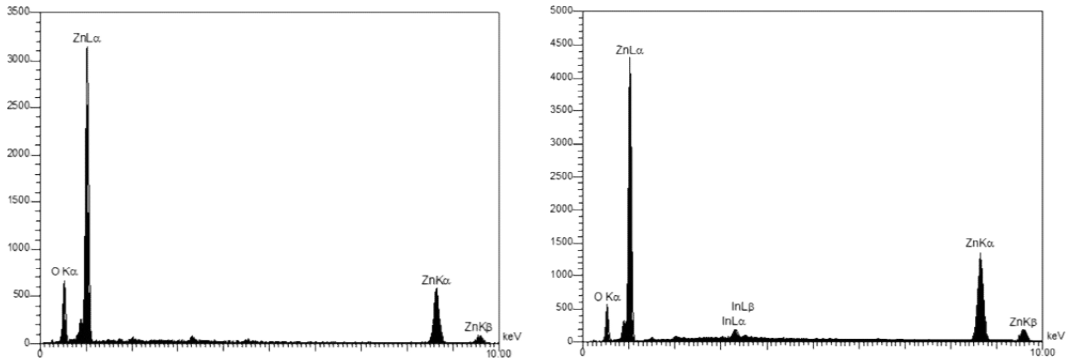

Fig. 2: EDX spectra of (a) pure ZnO (b) In doped ZnO nanoparticles.

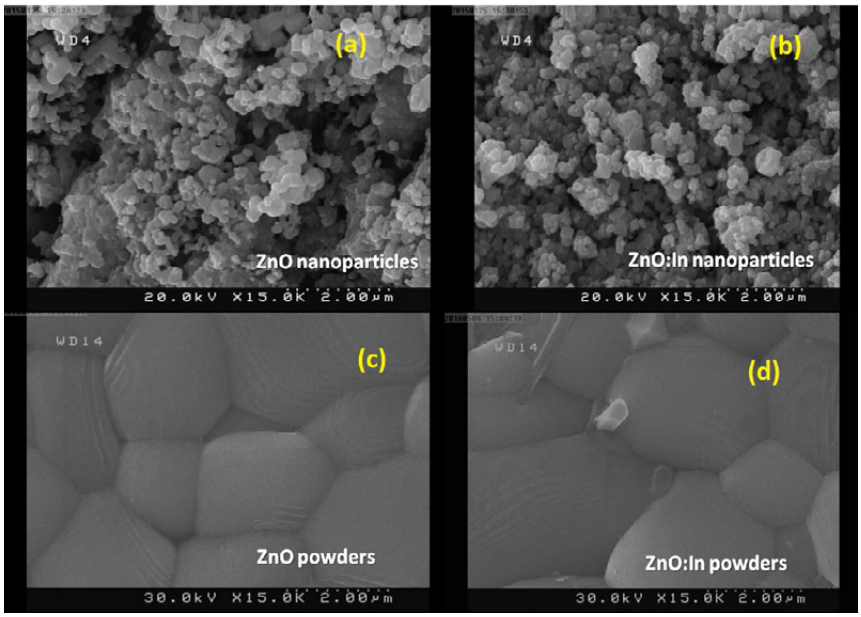

Fig. 3: SEM images of the prepared samples (a) ZnO dried at 300°C (b) IZO nanopowders dried at 300°C (c) ZnO calcined at 600°C and tablet preparation (d) IZO calcined at 600°C and tablet preparation.

confirmed the presence of In ions in the sample (Fig. 2b).

In order to characterize the size and morphology of the synthesized samples, field emission scanning electron microscopy (FESEM) was used. FESEM image of the synthesized pure and In doped ZnO particles before and after tablet preparation are shown in Figs. 3. As can be found from this figure, the average particle sizes of ZnO and IZO nanopowders (dried at 300°C and before tablet preparation) were about 45 and 65 nm. The average particle size of samples after sintering at 600°C and tablet preparation was changed to 0.84 and 1.001 µm, respectively. It seems that the sintering temperature strongly leads to increase in the grain size and density of the IZO sample. The hexagonal structure of ZnO can be seen clearly in the sample images that confirms the crystalline structure of zinc oxide in synthesized tablets. With the presence of indium as dopant, in ZnO network, some nanometer-sized rod-shaped grains have grown on ZnO surface. To investigate the gas sensing properties, tablets of ZnO and IZO were exposed to acetone gas with concentration of 500 to 1500 ppm under different temperatures varied from 100 to 250°C. Brief schematic of the gas sensing procedure and sensor fabrication can be found in Fig. 4. To evaluate the sensing performance, three important parameters such as sensitivity, response and recovery time of the sensor needed to be measured. The response time is commonly defined as the time it takes the sensor to reach 90% of the final signal for a given concentration of gas [31]. However, the recovery time is usually expressed as the time for the signal to fall below 10% of the maximum response [31]. The sensitivity of the sensors was determined as $S= R_a/R_g$, where R_a and R_g are the resistances of the sensor in air and desired gas, respectively [31]. The response and recovery times of ZnO and IZO gas sensor at 250°C for 1500 ppm acetone concentration are shown in Fig. 5.

Experimental results showed that the response time of IZO sensor was less than about 12 s and its recovery time was about 17 s. Both of the response and recovery time are much less than the pure ZnO sample. Fig. 6a presents the sensitivity of ZnO and

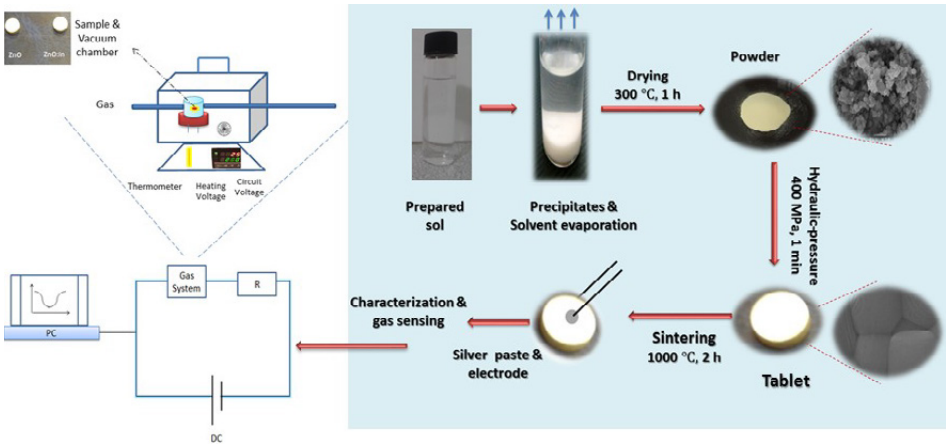

Fig. 4: Brief schematic of the gas sensing device and sensor fabrication.

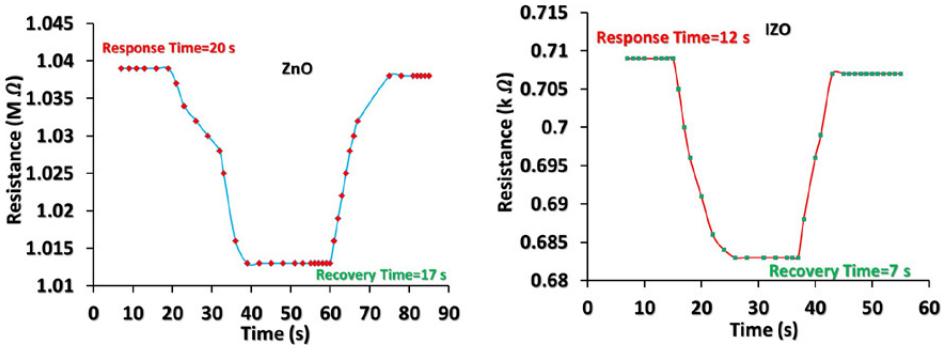

Fig. 5: Response and recovery curves of the samples for 1500 ppm acetone at 250°C.

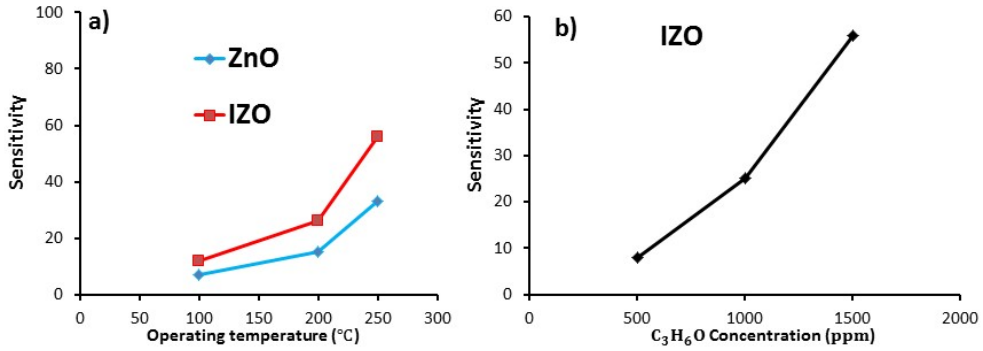

Fig. 6: (a) Sensitivity variation as a function of temperature (b) Sensitivity variation as a function of acetone concentration for ZnO:In sample at 250°C.

IZO samples for 1500 ppm concentration of acetone gas at different operating temperatures. Sensitivity increases with increasing in temperature from 100 to 250°C, due to the chemical adsorption of oxygen at higher temperature on the surface of the sensor [31]. Sensitivity reaches a maximum value of ~55 at 250°C for IZO sample. These results indicate that indium doped ZnO sensor has more rapid response and recovery time and can successfully be used for the detection of acetone and improve the sensing properties of ZnO gas sensors. Fig. 6b shows the sensitivity of IZO sample at different concentrations of acetone at 250°C.

With the increase of acetone concentration, the gas sensitivity of IZO sensor is enhanced. Doping of In^{+3} ion into the ZnO powder can produce more electrons that provide more gas molecules which strike the surface of sensor and finally gas sensitivity improvements. Indium acts as a donor and changes the oxygen vacancy characteristics of ZnO resulting the increase in charge carrier concentration and conductivity. In semiconducting oxide gas sensors, gas sensing mechanism is due to the interaction of the selected gas with the surface of the sensor and adsorbed oxygen. This reaction can be influenced by different factors, including internal and external causes, such as natural properties of base materials, surface area and microstructure of sensing layers, surface additives, temperature and humidity, etc [32]. When ZnO sensor is exposed to the air, it adsorbs oxygen molecules at the grain boundaries and captures electrons from the conduction band (O^{-n} ions forms) [33]. As a result, an electron-depleted space-charge layer in the surface region of the grain will be formed. When the sensor is placed in acetone gas environment, it reacts with the O^{-n} ions [34]. As shown in equation (1-4), the trapped

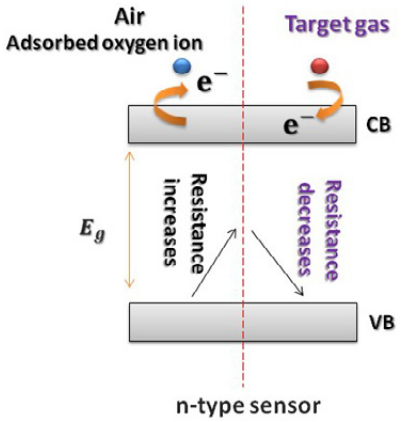

Fig. 7: Schematic diagram for changing the resistance of sensor in the presence of the target gas.

electrons are given back to the surface reducing the thickness of the electron depletion layer on the surface of the sensor [34]:

$$O_2(gas) \rightarrow O_2(ads) \quad (1)$$

$$O_2(gas) + e^- \rightarrow 2O_2^{-n}(ads) \quad (2)$$

$$2O_2^{-n}(ads) + e^- \rightarrow 2O^-(ads) \quad (3)$$

$$CH_3COCH_3\,(gas) + 8O^- \rightarrow 3CO_2\,(gas) + 3H_2O\,(gas) + 8e^- \quad (4)$$

Hence, the carrier concentration will tend to increase and the sensor resistance will tend to decrease (see Fig. 7) [35].

With the gas withdrawal, the process repeats and the resistance of sensor increases and finally reaches saturation value. Generally there are few reports on the gas sensing of indium doped ZnO ceramics or bulk sensors compared with thin film materials. In similar studies the rapid response

and recovery time and high sensitivity values of In doped ZnO were reported but these results were corresponded to thin film gas sensors [36]. For Mn doped ZnO tablets the response time of 240 s, and recovery times of 6630 s for high concentration and various gas concentrations have been reported [37]. For the ZnO sensors, In as an additive leads to the introduction of more oxygen vacancies defects in ZnO structure. Therefore, more adsorption sites for gas molecules are provided by these oxygen vacancies causing the surface to become highly active for reaction, so that the sensing properties are improved [36].

CONCLUSION

In this paper, pure ZnO and ZnO:In samples with hexagonal crystal structure have been synthesized by the simple sol-gel method. The gas sensing measurement results showed that the In dopant effectively improves the gas sensitivity ZnO sensor for high acetone concentrations. Indium doped ZnO tablet showed good sensitivity and fast response/recovery time to acetone gas, which has not been reported before. Therefore, it is suggested that the IZO ceramic sensor can act as an economically and simple gas sensor to detect acetone. Sintering temperature strongly increased the grain size and density of particles. EDX analyses also confirmed the presence of Indium and zinc in structure.

ACKNOWLEDGMENT

The authors gratefully acknowledge Dr. Omid Mirzaee and Dr. Davoud Sanavi Khoshnoud, for their technical support of Semnan University.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Wang C, Zhu J, Liang S, Bi H, Han Q, Liu X, et al. Reduced graphene oxide decorated with CuO–ZnO hetero-junctions: towards high selective gas-sensing property to acetone. J Mater Chem A. 2014;2(43):18635-43.
2. Epifani M, Comini E, Díaz R, Genç A, Andreu T, Siciliano P, et al. Acetone sensors based on TiO2 nanocrystals modified with tungsten oxide species. Journal of Alloys and Compounds. 2016;665:345-51.
3. Liang S, Li J, Wang F, Qin J, Lai X, Jiang X. Highly sensitive acetone gas sensor based on ultrafine α-Fe 2 O 3 nanoparticles. Sensors and Actuators B: Chemical. 2017;238:923-7.
4. Zhang Z, Zhu L, Wen Z, Ye Z. Controllable synthesis of Co 3 O 4 crossed nanosheet arrays toward an acetone gas sensor. Sensors and Actuators B: Chemical. 2017;238:1052-9.
5. Park S. Acetone gas detection using TiO2 nanoparticles functionalized In2O3 nanowires for diagnosis of diabetes. Journal of Alloys and Compounds. 2017;696:655-62.
6. Yin M, Yu L, Liu S. Synthesis of thickness-controlled cuboid WO3 nanosheets and their exposed facets-dependent acetone sensing properties. Journal of Alloys and Compounds. 2017;696:490-7.
7. Lee I, Choi S-J, Park K-M, Lee SS, Choi S, Kim I-D, et al. The stability, sensitivity and response transients of ZnO, SnO2 and WO3 sensors under acetone, toluene and H2S environments. Sensors and Actuators B: Chemical. 2014;197:300-7.
8. Dankeaw A, Poungchan G, Panapoy M, Ksapabutr B. In-situ one-step method for fabricating three-dimensional grass-like carbon-doped ZrO2 films for room temperature alcohol and acetone sensors. Sensors and Actuators B: Chemical. 2017;242:202-14.
9. Shen J-Y, Zhang L, Ren J, Wang J-C, Yao H-C, Li Z-J. Highly enhanced acetone sensing performance of porous C-doped WO 3 hollow spheres by carbon spheres as templates. Sensors and Actuators B: Chemical. 2017;239:597-607.
10. Wang C, Liu J, Yang Q, Sun P, Gao Y, Liu F, et al. Ultrasensitive and low detection limit of acetone gas sensor based on W-doped NiO hierarchical nanostructure. Sensors and Actuators B: Chemical. 2015;220:59-67.
11. Radecka M, Kusior A, Lacz A, Trenczek-Zajac A, Lyson-Sypien B, Zakrzewska K. Nanocrystalline TiO2/SnO2 composites for gas sensors. Journal of Thermal Analysis and Calorimetry. 2011;108(3):1079-84.
12. Zhang J, Qin Z, Zeng D, Xie C. Metal-oxide-semiconductor based gas sensors: screening, preparation, and integration. Physical Chemistry Chemical Physics. 2017;19(9):6313-29.
13. Moezzi A, McDonagh AM, Cortie MB. Zinc oxide particles: Synthesis, properties and applications. Chemical Engineering Journal. 2012;185-186:1-22.
14. Özgür Ü, Hofstetter D, Morkoç H. ZnO Devices and Applications: A Review of Current Status and Future Prospects. Proceedings of the IEEE. 2010;98(7):1255-68.
15. Karimi M, Saydi J, Mahmoodi M, Seidi J, Ezzati M, Shamsi Anari S, et al. A comparative study on ethanol gas sensing properties of ZnO and Zn0.94Cd0.06O nanoparticles. Journal of Physics and Chemistry of Solids. 2013;74(10):1392-8.
16. Cardoza-Contreras M, Romo-Herrera J, Ríos L, García-Gutiérrez R, Zepeda T, Contreras O. Single ZnO Nanowire-Based Gas Sensors to Detect Low Concentrations of Hydrogen. Sensors. 2015;15(12):30539-44.
17. Ge M, Xuan T, Yin G, Lu J, He D. Controllable synthesis of hierarchical assembled porous ZnO microspheres for acetone gas sensor. Sensors and Actuators B: Chemical. 2015;220:356-61.
18. Bian H, Ma S, Sun A, Xu X, Yang G, Yan S, et al. Improvement of acetone gas sensing performance of ZnO nanoparticles. Journal of Alloys and Compounds. 2016;658:629-35.
19. Guo W. One-pot synthesis of urchin-like ZnO nanostructure and its enhanced acetone gas sensing properties. Journal of Materials Science: Materials in Electronics. 2016;28(1):963-72.
20. Zhang X, Dong Z, Liu S, Shi Y, Dong Y, Feng W. Maize straw-templated hierarchical porous ZnO:Ni with enhanced acetone gas sensing properties. Sensors and Actuators B: Chemical. 2017;243:1224-30.
21. Qi J, Zhang H, Lu S, Li X, Xu M, Zhang Y. High Performance Indium-Doped ZnO Gas Sensor. Journal of Nanomaterials. 2015;2015:1-6.

22. Al-Hadeethi Y, Umar A, Al-Heniti SH, Kumar R, Kim SH, Zhang X, et al. 2D Sn-doped ZnO ultrathin nanosheet networks for enhanced acetone gas sensing application. Ceramics International. 2017;43(2):2418-23.
23. Sadeghian Lemraski M, Nadimi E. Acetone gas sensing mechanism on zinc oxide surfaces: A first principles calculation. Surface Science. 2017;657:96-103.
24. Zhang J, Liu X, Neri G, Pinna N. Nanostructured Materials for Room-Temperature Gas Sensors. Advanced Materials. 2015;28(5):795-831.
25. Bhoi BB, Banerjee R, Mohanty S, Kamilla SK, Pattanaik P, Tripathy HP, et al. Volatile Organic Compounds Sensing Characteristics of Nanocrystalline Co Doped ZnO Pallet. Advanced Science Letters. 2016;22(2):374-7.
26. Efafi B, Sasani Ghamsari M, Aberoumand MA, Majles Ara MH, Hojati Rad H. Highly concentrated ZnO sol with ultra-strong green emission. Materials Letters. 2013;111:78-80.
27. Vafaee M, Sasani Ghamsari M, Radiman S. Highly concentrated zinc oxide nanocrystals sol with strong blueemission. Journal of Luminescence. 2011;131(1):155-8.
28. Sasani Ghamsari M, Alamdari S, Han W, Park H-H. Impact of nanostructured thin ZnO film in ultraviolet protection. International Journal of Nanomedicine. 2016;Volume 12:207-16.
29. Alamdari S, Ghamsari MS, Ara MHM, Efafi B. Highly concentrated IZO colloidal nanocrystals with blue/orange/red three-colors emission. Materials Letters. 2015;158:202-4.
30. Alamdari S, Tafreshi MJ, Ghamsari MS. The effects of indium precursors on the structural, optical and electrical properties of nanostructured thin ZnO films. Materials Letters. 2017;197:94-7.
31. Yang Z, Huang Y, Chen G, Guo Z, Cheng S, Huang S. Ethanol gas sensor based on Al-doped ZnO nanomaterial with many gas diffusing channels. Sensors and Actuators B: Chemical. 2009;140(2):549-56.
32. Wang C, Yin L, Zhang L, Xiang D, Gao R. Metal Oxide Gas Sensors: Sensitivity and Influencing Factors. Sensors. 2010;10(3):2088-106.
33. Hsueh T-J, Hsu C-L. Fabrication of gas sensing devices with ZnO nanostructure by the low-temperature oxidation of zinc particles. Sensors and Actuators B: Chemical. 2008;131(2):572-6.
34. Tan Q, Fang J, Liu W, Xiong J, Zhang W. Acetone Sensing Properties of a Gas Sensor Composed of Carbon Nanotubes Doped With Iron Oxide Nanopowder. Sensors. 2015;15(11):28502-12.
35. Liu L, Chi X, Wang G-G, Liu C-B, Shan H, Zhang X-B, et al. Synthesis and Improved Acetone Sensing Properties of Porous α-Fe2O3Nanowires. Chinese Physics Letters. 2013;30(2):020701.
36. Shokry Hassan H, Kashyout AB, Morsi I, Nasser AAA, Ali I. Synthesis, characterization and fabrication of gas sensor devices using ZnO and ZnO:In nanomaterials. Beni-Suef University Journal of Basic and Applied Sciences. 2014;3(3):216-21.
37. Saydi J, Karimi M, Mazhdi M, Seidi J, Mazhdi F. Synthesis, Characterization, and Gas Sensing Properties of Pure and Mn-doped ZnO Nanocrystalline Particles. Journal of Materials Engineering and Performance. 2014;23(10):3489-96.