Enhanced Humidity Sensing Behaviour of Sol-Gel Derived ZnO-C65 Heterostructure Thin Films

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Abstract. Humidity sensing characteristics of conducting carbon C65 modified ZnO heterostructure films are reported. Pristine ZnO and it hybrid composite with C65 were processed using sol-gel technique by adding different concentration of C65 carbon. Crystalline and morphological features of the samples are examined by X-ray diffraction and scanning electron microscopy studies. Change in the morphology of the ZnO particles is observed upon addition of C65 carbon. Humidity sensing studies on ZnO-C65 heterostructure films have shown enhanced sensitivity factors than pure ZnO films. The results are attributed to the formation of heterostructures of conducting C65-semiconducting ZnO, and nanostructured morphological changes.

1 Introduction

Humidity conditions play great role not only on life forms but also in industrial, and medical processes. Humidity detection is crucial in agriculture sectors, pharmaceutical processing, incubators and many more [1-2]. This invites the attention of researchers to develop materials with high stability, large response and fast recovery for humidity sensing. Semiconducting ZnO is a multifunctional material, due to its unique physical and chemical properties. ZnO has been investigated for humidity and gas sensing applications owing to its very good surface reactivity, and adsorption of gas molecules. ZnO nanowires were studied for humidity sensors at room temperature which showed exponential sensitivity [3]. Moreover, ZnO modified with different materials were tested for the better sensing results. Graphite carbon nitride(g-C3N4) and ZnO was reported as humidity sensor for respiratory monitoring [4]. Carbon nanotubes response to humidity sensing was improved by addition of conjugate materials such as chitosan/zinc oxide [5]. Graphene with ZnO was investigated for humidity sensing [6]. These recent reports indicate the promising role ZnO based heterostructures for sensor applications.

Therefore, in the present report, humidity sensing characteristics of the ZnO-C65 heterostructures are carried out. Conducting amorphous carbon (C65) is added to the ZnO sol-gel solution to prepare the heterostructures. Samples with C65 carbon showed change in the morphology of the ZnO particles. Humidity sensing of the samples studied by monitoring the resistance of the samples in different humidity conditions in a small sample chamber.

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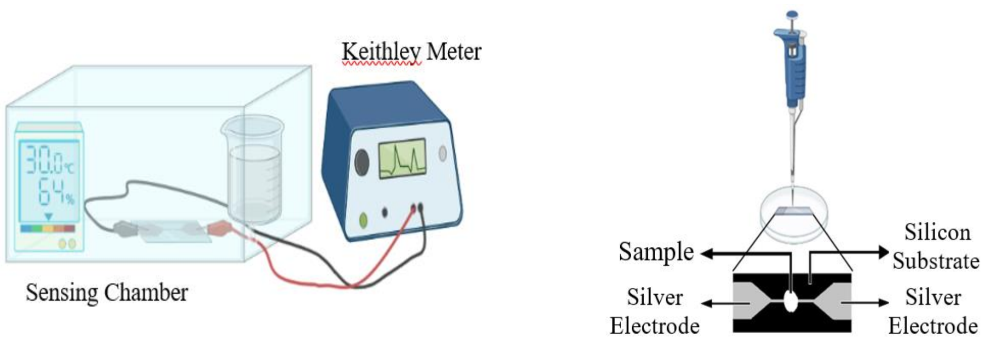
Obtained sensitivity factors from the response curves indicates the large humidity sensing at high concentrations of C65 content. The obtained results are discussed.

2 Experimental methods

2.1 Preparation of sensor samples

ZnO films were prepared by sol-gel process. Zinc acetate dehydrate and, Ethylene glycol were taken in an appropriate ratio as per literature reports and kept at 140°C for 30min [7]. Subsequently, small quantities of alcohol, glycerol and triethylamine were added to the cooled ZnO precursor mix to assist the hydrolysis of Zinc acetate. The resultant solution is stirred at 60°C for 1hour and used for preparing the films. To prepare ZnO-C65 heterostructures, conducting C65 carbon procured from Global Nanotech, Mumbai was dispersed (1 wt% (w/v)) in the 1-propanol medium. C65 dispersion was added to the ZnO precursor solution in different volume fractions (0, 2.5, 5, 7.5 and 10%, which are labeled as ZnO, ZC2.5, ZC5, ZC7.5, and ZC10 respectively) and well mixed with magnetic stirrer for 30minutes. Pristine ZnO and its heterostructure with C65 thin film was deposited by drop casting the sol-gel solution upon the pre-coated electrode pattern on the Si substrates for sensing studies. As deposited films were aged at 60°C for 24hr for gelation followed by drying. Further, samples were annealed in an electrical furnace at 350°C for 3 hours to obtain crystalline ZnO films. X-ray diffraction (XRD, PANalytical Multifunctional X'PERT3 Diffractometer) and scanning electron microscope (SEM, JSN-IT300 InTouchScope™) studies were carried out to determine the crystallinity and morphological nature of the ZnO and ZnO-C65 heterostructures films.



(a) (b)

Fig. 1. Schematic a) humidity sensing setup, and b) sensor electrode geometry.

2.2 Humidity sensing

Humidity sensing of the ZnO and ZnO-C65 heterostructure films were tested in a homemade sample chamber by monitoring the resistance drop by using keithley electrometer (DMM6500). Schematic setup and electrode structure used in the present studies are shown in Fig.1. Humidly in the chamber was varied by keeping the saturated aqueous salt solutions (potassium sulphate and potassium hydroxide, as humidifier and de-humidifiers, respectively) in the chamber. Change in the humidity was noted using the hygrometer placed in the chamber and resistance change in the samples was recorded as a function of humidity change.

3 Result and discussion

3.1 Structural and microstructural studies

Crystalline nature of the as received C65 carbon, pristine ZnO, and ZnO-C65 heterostructure samples are studied using XRD and corresponding patterns are shown in Fig.2. Pure C65 carbon showed broad humps, resultant of its amorphous nature, whereas ZnO samples showed crystalline peaks and all the Bragg peaks were indexed to the standard ZnO phase (hkl) planes [8]. ZnO-C65 sample (ZC10%) showed the slightly broad peaks than the pure ZnO, indicating the nanostructured ZnO particles and formation of heterostructures.

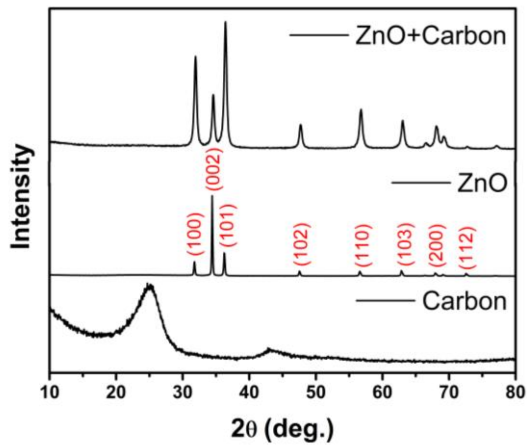


Fig. 2. XRD patterns of Carbon C65, pure ZnO and ZnO-C65 heterostructures (ZC10).

Morphological features of the pure ZnO and ZnO-C65 (ZC10) samples are shown in Fig.3 (SEM pictures). ZnO without C65 showed platelet like morphology with the size ranging <100nm to submicron, whereas change in morphology to spherical shaped clustered nanoparticles (10nm to 50nm) were observed upon the incorporation of C65 carbon to pure ZnO in the sol-gel process. It indicates that, C65 carbon in the sol-gel process modifies the nucleation and growth of ZnO, involving heterogeneous nucleation over the carbon particles, leading to formation nanostructured particles thus forming porous heterostructures.

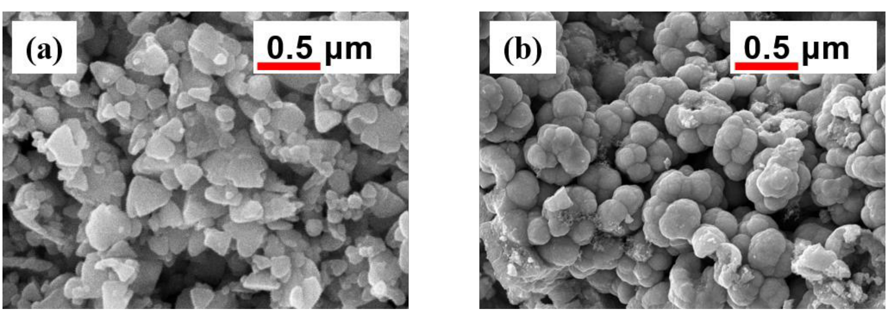


Fig. 3. SEM images of (a) pure ZnO powder, and (b) ZnO-C65 (ZC10)

3.2 Humidity sensing properties

Humidity sensing of ZnO and ZnO-C65 heterostructure thin films with different concentration of C65 were carried out in the ambient conditions using the setup explained in section 2.2. Response curves, i.e., the resistance drop of the sample as exposed to varying

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humidity are shown in Fig. 4a. It is observed that, for all the samples, resistance of the samples decreased with increasing humidity. This is due to the presence oxygen vacancy defects over the sample surface, which helps for the chemisorption and physisorption of water molecules on the surface of ZnO and ZnO-C65 samples. Adsorbed water molecules interact with the sample and dissociate into OH- and H+ ions. Proton diffusion and conduction tends to decreases the electrical resistance of the samples. Further, porous and nanostructured particles with large surface area assist in the enhanced interactions and diffusion of water molecules [9]. To compare the sensitivity of the different samples, humidity sensitivity factor is defined as [10].

$$Sensitivity\ (S\%) = \frac{R_{RH_0} - R_{RH}}{R_{RH}} \times 100 \qquad (1)$$

where R_{RH_0} is the initial value of the resistance at ambient humidity (RH_0) and R_{RH} is the change in the resistance of the sample due to the small change in the humidity RH%. The plots of humidity sensitivity factors for pure ZnO and ZnO-C65 heterostructure as projected in Fig. 4b. It can be seen that, ZnO-C65 samples have shown enhanced sensitivity factor and it increased with increasing C65 content. This is attributed to the formation of ZnO-C65 heterostructures, clustered spherical nanoparticle morphology, and increase in the surface area with the desired porosity. This helps in the better water molecules interaction, resulting in the large sensitivity.

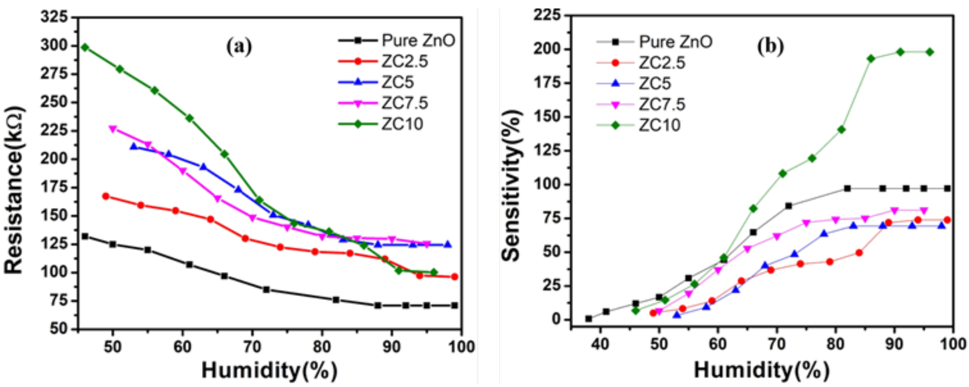

Fig. 4. a) Humidity response curves (resistance against humidity change), and b) sensitivity factors of pure ZnO and ZnO-C65 heterostructures

4 Conclusion

ZnO and ZnO-C65 heterostructure thin films are obtained using sol-gel method which is a simple and cost effective for producing sensor materials. The prepared heterostructure samples have shown nanocrystalline and spherical clustered nanoparticle morphology. Humidity sensing behaviour of the samples are tested by monitoring the change in the resistance of the samples with increasing humidity. ZnO-C65 hetrerostructure samples have exhibited very large enhanced humidity sensitivity factors at high C65 content. This is attributed to the heterostrucutres of the conducting carbon- semiconducting ZnO, porous microstructure and nanoparticle morphology with large surface area. ZnO-C65 samples reported here are promising for humidity sensing and other gas sensing studies.

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References

1. B. A. Kuzubasoglu, Recent studies on the Humidity Sensor: A mini review. ACS Appl. Electron. Mater. **4**, 4797-4807, (2022). https://doi.org/10.1021/acsaelm.2c00721
2. H. Farahani, R. Wagiran, M.N. Hamidon, Humidity sensors principle, mechanism, and fabrication technologies: A comprehensive review. Sensors (Switzerland), **14**, 7881-7939, (2014). https://doi.org/10.3390/s140507881
3. N. M. Kiasari, S. Soltanian, B. Gholamkhass, P. Servati, Room temperature ultra-sensitive resistive humidity sensor based on single zinc oxide nanowire. Sensors and Actuators A: Physical, **182**, 101-105, (2012). https://doi.org/10.1016/j.sna.2012.05.041
4. S. Yu, C. Chen, H. Zhang, J. Zhang, J. Liu, Design of high sensitivity graphite carbon nitride/zinc oxide humidity sensor for breath detection. Sensors and Actuators B: chemical, **332**, 129536, (2021). https://doi.org/10.1016/j.snb.2021.129536
5. H. Dia, N. Feng, J. LI, J. Zhang, W. Li, Chemiresistive humidity sensor based on chitosan/zinc oxide/single-walled carbon nanotube composite film. Sensors and Actuators B: Chemical, **283**, 786-792, (2019). https://doi.org/10.1016/j.snb.2018.12.056
6. M. Saqib, S. Ali Khan, H. M. M. Ur Rehman, Y. Yang, S. Kim, M. M. Rehman, W. Young Kim, High-Performance Humidity Sensor Based on the Graphene Flower/Zinc Oxide Composite. Nanomaterials, **11**, 242, (2021). https://doi.org/10.3390/nano11010242
7. N. V. Kaneva, C. D. Dushkin, A. S. Bojinova, ZnO thin film preparation on glass substrate by two different sol-gel methods. Bulgarian Chemical Communications, **44**, 63-69, (2012).
8. J. Ashwini, T. R. Aswathy, A. R. Babu, G. M.Thara, A. S. Nair, Synthesis and characterization of zinc oxide nanoparticles using Acacia Caesia Bark extract and its photocatalytic and antimicrobial activities. Catalysts, **11**, 1507, (2021). https://doi.org/10.3390/catal11121507
9. D. Zhang, H. Chang, P. Li, R. Liu, Q. Xue, Fabrication and characterization of an ultrasensitive humidity sensor based on metal oxide/graphene hybrid nanocomposite. Sensors and Actuators B: Chemical, **225**, 233-240. (2016). https://doi.org/10.1016/j.snb.2015.11.024
10. A. Sharma, Y. Kumar, K. Mazumdar, A. K. Rana, Controlled Zn1-xNixO nanostructures for an excellent humidity sensor and plausible sensing mechanism. New Journal of Chemistry, **42**, 8445-8457, (2018). https://doi.org/10.1039/C7NJ04801G