ZnO/ZnS core/shell nanostructures based gas sensor for sensing Acetone gas at room temperature

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Abstract*:*In this paper ZnO/ZnS core/shell nanostructures are used to fabricate the gas sensor which can sense low concentration of acetone gas at room temperature. Due to its reducing properties, acetone gas releases electrons to the surface of the core/shell nanorods. Therefore a sharp increase in conductivity of the sensing material was observed when the sensor was exposed to the acetone gas. The fabricated sensor exhibited excellent sensitivity towards acetone gas at room temperature and is capable of detecting it to a minimum concentration of 10 ppm.

***Keywords*:**gas sensing, ZnO, ZnS, core -shell, hydrothermal.

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I. INTRODUCTION

ACETONE gas is a flammable industrial solvent which can be hazardous and lifethreatening when human are exposed to its high concentration. Gas sensors have been recognized as easy and cheap instruments for detecting and quantifying poisonous, damaging, flammable and explosive gases compared to the multiple traditional analytical technologies.Gas concentration can represent physical circumstances in the exhaled breath, thus serving as a biomarker for certain illnesses [1,2].When individuals are on a ketogenic diet, fasting, or exercising, high levels of breath acetone were recorded. In addition, there is a powerful correlation between enhanced breath acetone concentration and fat loss rate [3,4].

Gas sensors generally operate different principles andvarious gas sensing elements have been developed for the pastyears, out of which resistive metal oxide sensors compriseasignificant part.Zinc oxide (ZnO) is a wide-band semi-conducting material (Eg=3.37 eV) with excellent sensing characteristics towards different oxidizing and reducing gasses, among several gas sensing materials studied so far. It has the benefitsof low price,fabricationsimplicity and miniaturization [5,6].The fabricated ZnO/Graphene Composites film can detect 10–100 ppm acetone at 280° C [7].Recently, many reported literatures have demonstrated that the acetone-sensingperformances of ZnO could be improved by the heterostructureformation techniques. Zhou *et al*. [8]synthesized porous $ZnFeO_4$nanospheresand found good selectivity and sensitivity to Acetone gas and giving a response of 11.8 to 30 ppm acetone gas. Lemrask*et al*. [9] synthesized ZnO thin film and successfully detected Acetone gas at 200°C to 428°C.Because there are many issues in acetone detection research, acetone gas sensors are urgently required with high sensitivity, brief response time, low operating temperature, and excellent selectivity.

Acetone gas was effectively detected in all the above cases but at greater operating temperatures. In the current paper, Acetone gas detection at ppm level at room temperature has become possible using ZnO/ZnS core/shell nanostructure.

II. EXPERIMENT

A. Synthesis of ZnO seed nanoparticles

For synthesis of the ZnO nanoparticles, 2mM zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$, Merck, 99% purity] solution was prepared in 20 ml of ddH_2O with vigorous stirring at 50°C. The solution was thendiluted with another 20 ml of fresh ethanol[C_2H_5OH, Merck, 99% purity] and cooled in the ambient air. The glass slide was pre-heated at 120°C and the solution was drop and dry on the surface of the electrode for three to four times. After that the glass slide was annealing at 200°C for five hours. This process oxidizing the zinc acetate and form zinc oxide on the surface of the glass slide [10].

B. Growth of ZnO nanorods on seeded substrate

The growth of ZnOnanorods on the seeded substrate were carried out in a hot air oven at 90° C. The substrate was put inverted in a Petri dish containing zinc nitrate hexahydrate [($Zn(NO_3)_2.6H_2O$), Merck, 99% purity] and hexamine [($C_6H_{12}N_4$), Merck, 99% purity] equimolar (10mM) solution and then kept in the oven for 30 hours.

After every 5 hours the solution mixture was changed and at the completion, the substrate was washed thoroughly with deionized water [11,12].

C. Growth of ZnS shell over ZnO nanorods

After completion of the nanorods growth, the growth of ZnS shell over ZnOnanorods was done by dipping the glass substrate into 10 mM solution of thioacetamide at 90°C for 72 hours. Then washed with deionized water and annealing at 120°C for one hours.

D. Fabrication of the gas sensor

To fabricate the gas sensor, at first a solution was prepared from the synthesized ZnO/ZnS core/shell nanorods by scraped out the nanorods from glass substrate and put it in deionized water. To make a homogenous mixture the solution was ultrasonicated for 10 min. The interdigitated electrode which was used to fabricate the sensor were made on a Cu PCB by using a normal PCB design method. The gap between the electrodes of the interdigitated electrode is 0.32 mm as shown in the fig.1. The sensor was fabricated by dropping the ZnO/ZnS core/shell homogenous solution on the Cu interdigitated electrode at 120°C. The ZnO/ZnS core/shell nanorods as shown in fig.2 is placed on the surface of the Cu electrode. The electronic circuit used in the gas sensor set-up is shown in fig.3.

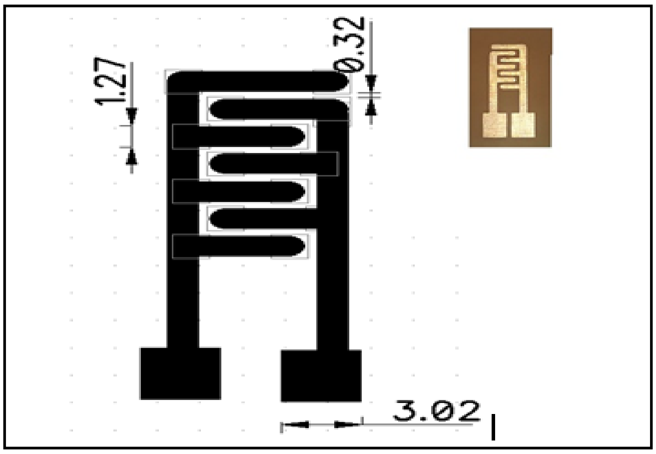

Fig. 1.Electrode design for the fabrication of gas sensor, Inset: Fabricated electrode.

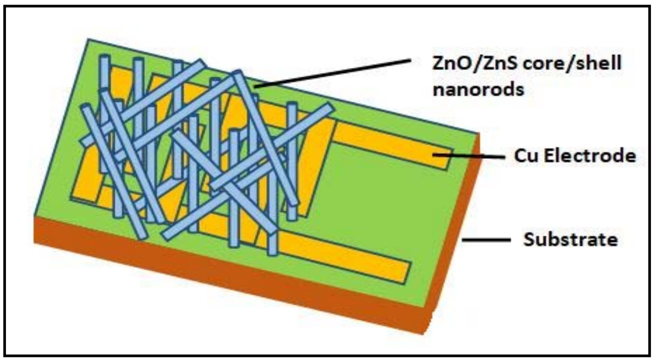

Fig. 2.ZnO/ZnS core/shell nanorods on interdigitated electrode

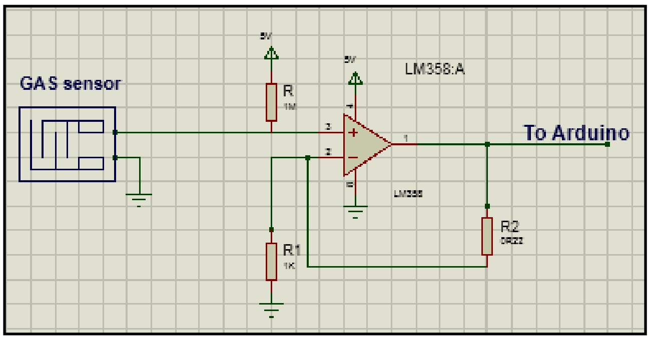

Fig.3.Sensor circuit

III. RESULTS AND DISCUSSIONS

The SEM image obtained using JEOL JSM 6390LV SEM was used to obtain the size of the ZnOnanorods and ZnO / ZnS core / shell nanorods. The SEM images is shown in fig.4. It can be seen evidently from the figures the formation of ZnS shell on the ZnOnanorods. The ZnS shell is found to be 10nm thick which is formed on a rod.

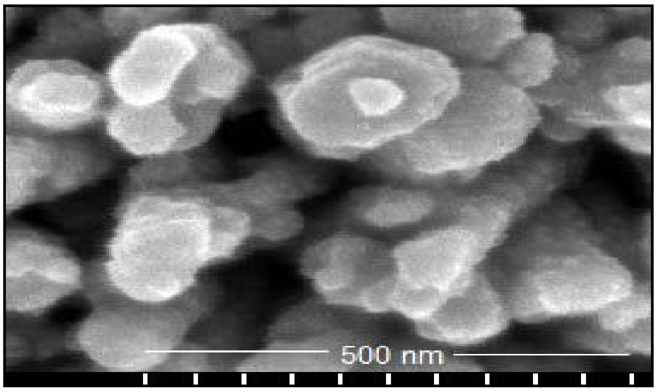

Fig.4.SEM image of ZnO/ZnS core/shell nanorods.

The ZnO/ZnS core/shell nanorodsformationmechanism can be described as follows.WhenZnOnanorods are immersed in a 10 mMthioacetamide solution, S^{2-} released from thioacetamide decomposition reacts with Zn^{2+}which is gently dissolved from the ZnOnanorods surface to generate ZnS nanoparticles around the ZnOnanorods.A non-uniform shell consisting of ZnSnanoparticles is gradually developed around the ZnO nucleus at the beginning.As time increases, more and more ZnS nanoparticles are developed to form a uniform and thick ZnS shell, resulting in ZnO / ZnS core / shell nanorods being formed [13].

The ZnO / ZnS core / shell structure has the advantage of being able to absorb visible light even though ZnO and ZnScan not absorb visible light when used individually.The band gap of the material was calculated using UV-Visible spectroscopy. The UV–Vis absorption spectra at room temperature of ZnO/ZnS core/shell nanorods are shown in Fig.5 (a). Fig.5 (b) shows the band gap of 2.9eV was obtained from the Tauc plot.

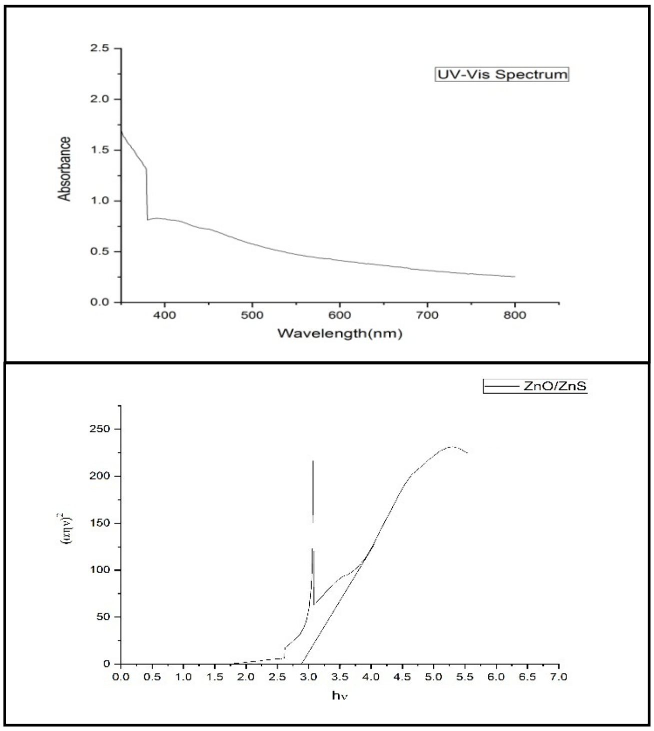

Fig.5. (a) UV-Vis absorption spectrum of ZnO/ZnS core/shell structure, 5.(b) Tauc plot of ZnO/ZnS core/shell structure

Since the ZnO / ZnS core / shell structure absorbs visible light, electron hole pairs will be photogenerated, which can be written as in equation (1):

$$h\nu \rightarrow h^{+} + e^{-} \qquad (1)$$

where, $h\nu$is the photon energy of visible light, h_{+} is a photogenerated hole in the valence band and e_{-} is a photogenerated electron in the conduction band.

The response of ZnO/ZnS core/shell nanorods to different concentration of Acetone gas is influenced by the adsorption and desorption of oxygen on its surface. Oxygen molecules from the ambient air are adsorbed onto the ZnS shell surface as well as ZnO core exposed by capturing free electrons from them, as shown in equation (2) [13].

$$O_2 + e^{-} \rightarrow O_2^{\ -} \qquad (2)$$

where, O_2 is an oxygen molecule, $e^{-}$is a free electron, and $O_2^{-}$is an adsorbed oxygen on the surface of the core/shell nanorods.

In presence of Acetone gas(CH_3COCH_3), which is a reducing gas, electrons will be released on the surface of the ZnO/ZnS core/shell nanorods. Therefore the conductivity of the surface will be increased.This can be shown by equation (3).

$$CH_3COCH_3(gas) + O^{-} \rightarrow CH_3CO\overset{+}{C}H_2 + OH^{-} \qquad (3)$$

The result obtain from the sensor are shows in fig.7.In this figure it is seen when the concentration of the acetone gas is increase, resistance of the sensor decreases. With the available gas sensor setup the sensor can sense minimum concentration of 10 ppm.At first the acetone gas at different ppm level was generated inside the gas chamber and after that it was send to the sensor setup, and after 20 sec gas was thrown out from the sensor setup with an exhaust fan. An equation is derived by applying mathematical curve fitting to the plot which is shown in the fig.8 and the microcontroller is trained as per the equation.

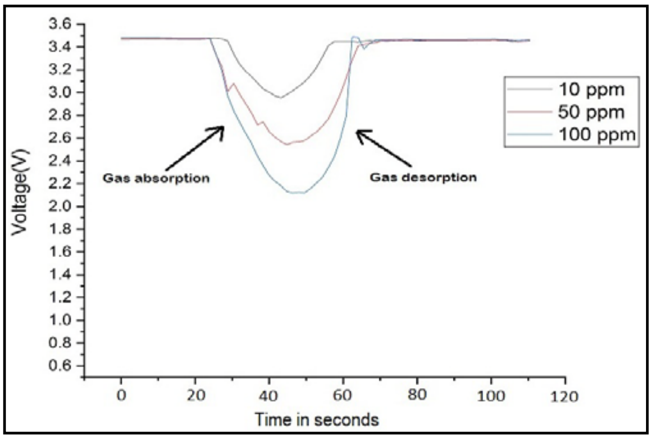

Fig.7. Sensor response at different concentration of acetone gas

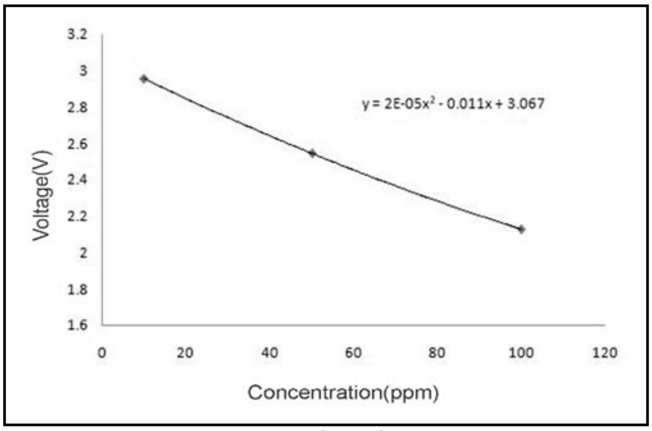

Fig.8. Concentration Vs minimum voltage plot

IV. Conclusion

Using theZnO / ZnS core / shell nanostructure, which was synthesized using a two-stage hydrothermal process, gas sensing at room temperature has become possible. Reducing gas like Acetonehas been detected successfully using ZnO/ZnS core/shell nanostructures as the sensing material. Because of the lower band-gap of the heterostructures which can absorb visible light and enough electron hole pairs are photo-generated without any external thermal energy, this gas sensing at room temperature is possible.

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