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Fabrication and Characterization of High Performance Resistive Type Humidity Sensor based on ZnO/Pyrrole composite materials

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Abstract : In this study, the resistive type humidity sensor was fabricated by spin coating on ZnO/Pyrrole(Py) composite film on a silicon substrate. The thin film was characterized by XRD to study crystalline structure, UV Visible spectra and SEM provides optical and morphological information of the sample. The electrical properties of ZnO/Pyrrole composite thin films were investigated based on the component AgNO3. The resistive type ZnO/Pyrrole composite humidity sensor had the highest sensitivity, greatest linearity, rapid response time, recovery time and good long term stability. It is found that the resistance of the sensor decreases with increases relative humidity (RH) range from 10 to 90%. The result indicates that the ZnO/Pyrrole can be used in fabricating high performance humidity sensor.

Introduction

Humidity sensors are very important key for applications in environmental monitoring, industrial process control and in day today life[1,2]. The measurement of humidity is demanded in wide range of areas, including agriculture, horticulture, meteorological services, food processing, air conditioning and electronic processing. While electronic humidity sensors are commercialized, other types of humidity sensors which are thin, light-weight and cheap are still required for many applications. The constructive design of good humidity sensor is a rather complicated topic, because high performance humidity sensor claim many requirements including linear response, high sensitivity, fast response time, chemical and physical stability, wide operating range and low cost. Material have been studied for this purpose include polymer[3-10] ceramics[11-14] and composites [15,16], which have their own merits and specific conditions of application[17-19]. The humidity sensor fabricated with polymeric materials are divided into two categories of resistive-type and capacitive-type[20,21]. The resistive-type sensors are fabricated with polymer electrolytes and hydrophobic polymers, respectively. The capacitive-type sensing materials are based on the changes in dielectric constant.

Most of the resistive-type polymer humidity sensor are fabricated by synthesizing the polymer films and then coating them on a ceramic substrate [4-7,20]. Ceramic alumina has good thermal and chemical stabilities, so it is suitable to be a substrate material for humidity sensors. Recently, some papers have been reported the results of humidity sensors fabricated on Si or SiO_2/Si substrate[8,11-14]. The silicon substrates have good electrical and mechanical properties and are good material for the integrated circuits. However, their fabrication processes are completed and high cost.

The n-type semi conducting materials such as stannous oxide, zinc oxide and titanium dioxide are promising materials[23-26] for gas and humidity sensor. Out of all the material investigated, ZnO has fascinated researchers with a wide variety of morphologies and range of promising device applications [26-28]. It is a wide direct band gap (3.37 eV) semiconductor with a high chemical stability and a relatively high excitation binding energy (60 meV). ZnO is used in many applications such as surface acoustic wave (SAW) devices, laser devices, solar cells, humidity sensors and gas sensor devices and MEMS. In the past years, organic-inorganic nanocomposite materials have been considered as a new class for many new electronic, magnetic applications, since many bulk properties can be improved compared with those of base polymers[29]. Many reports have been published based on chemical polymerization and electrochemical technique to prepare conducting polymer/inorganic composites for gas[30-,36] and humidity[36] sensor applications. However, no attempts have been made to construct resistive-type humidity sensors based on TiO_2 nanoparticles (TiO_2 NPs)/PPy composite thin films.

In this work, in the first step, ZnO NPs/Py composite film was prepared on a silicon substrate as resistive type humidity sensor. The characterization of films were analyzed by scanning electron microscopy (SEM), UV absorption spectroscopy and X-Ray Diffraction. The humidity sensing and electrical properties of the ZnO/Pyrrole composite film is studied by finding resistivity, sensitivity, response time, recovery time and stability.

Experimental

Preparation of ZnO/Pyrrole composite material:

The ZnO nanoparticles are synthesized by sol-gel method at room temperature. 100 ml of 0.5M zinc nitrate solution was added drop wise into 100 ml of 1M NaOH under the constant stirring at room temperature, zinc nitrate solution added drop wise for 15min. Stirring was continued for 3 hours till a white precipitate was deposited at the bottom of the flask. Then filtrate is taken using wathman paper No.1 and washed 2-3 times with deionized water. Then the powered sample was dried at 60^0C in hot air oven.

The ZnO/Pyrrole composite materials were prepared as follows: $AgNO_3$ was added to the Py in ethanol and the mixture was sonicated until the AgNO3 was completely dissolved, and then ZnO NPs were added to the solution and sonicated to achieve a uniform dispersion of nanoparticles. The compositions are shown in Table 1.

Table 1. Composition of the composite films used to prepare humidity sensor.

Sample	Pyrrole (g)	$AgNO_3$ (g)	ZnO (g)
1	0.125	0.0314	0.0012
2	0.125	0.0314	0.0480

Humidity sensor preparation:

Thin films for humidity sensitivity sensors were prepared by ZnO NPs/Py composite materials. The composite material was first dispersed in ethanol and the solution is then coated on silicon with a pair of electrode using spin coating method. Ohmic contacts were made by silver paste. Schematic diagram of the sensor is given in fig. 2 and experimental setup in fig.3.

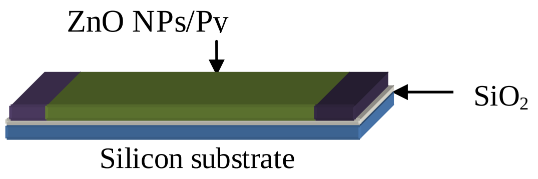

Fig. 2. Schematic sketches of sensor device.

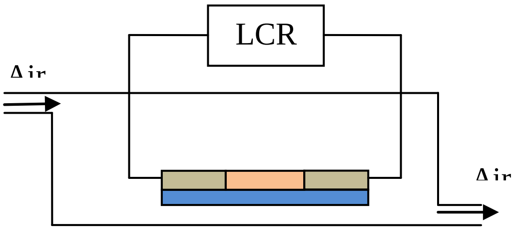

Fig. 3. Experimental setup to study humidity response.

Instruments and analysis:

The humidity sensitive properties of the sensors were studied by recording their electrical response at different humidities at room temperature. The sensor was placed in a chamber where humidity was controlled by adjusting the mixed ratios of dry and wet gases. Resistance of the sensor was measured with an LCR meter in a test chamber under the conditions of a measurement frequency of $1kH_z$, an applied voltage of 1V, an ambient temperature of 25^0C, and different humidity levels in the range of 30-90% RH.

Result and Discussion

Material structural characterization.

The UV- visible spectroscopy (Systronic-119) was carried out to study the optical property of the nanoparticles. The UV-Vis spectroscopy was performed by ZnO nanoparticles dispersed in Dimethylsulphoxide in room temperature, is shown in Fig. 4a. and dispersing ZnO/Py composite NPs in ethanol shown in Fig. 4b respectively. A UV absorption peak and peak shift (from 376.27nm to 460nm) is seen due to the size difference. Generally shift from 376.27nm to 460nm indicates that the size of ZnO becomes larger with the addition of Pyrrole.

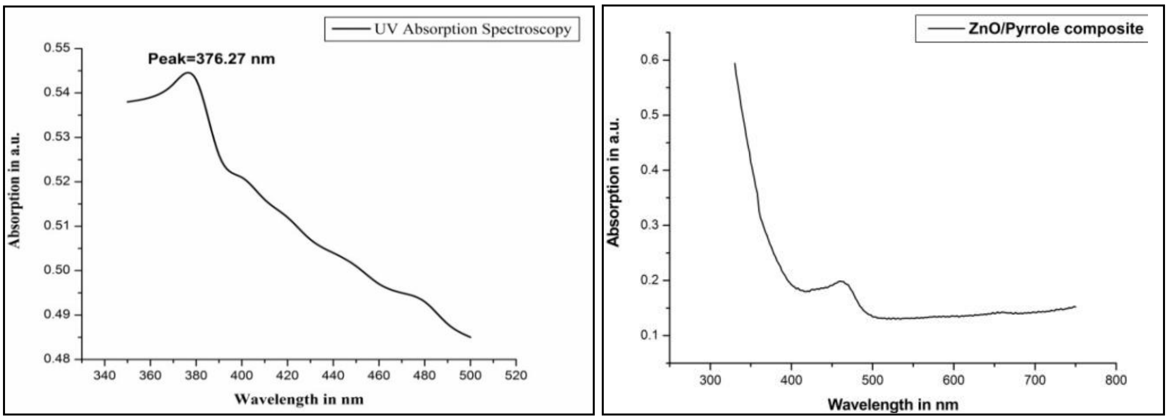

Fig. 4. UV Vis absorption spectrum of ZnO and ZnO/Py composite nanoparticles.

Fig. 5. shows the X-Ray diffraction pattern recorded using an X-Ray diffractometer (-Hitachi) was Cu Kα as target at 30Kv and 15mA, and radiation of wavelength λ=0.15418nm in the scan range 6^0-60^0. Using the Scherer's relation, $d=K\lambda/\beta\cos\theta$, the average primary particles size is estimated corresponding to the highest peak and it is found to 21.6nm.

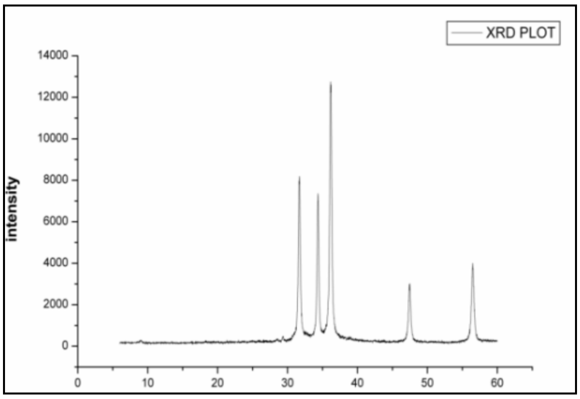

Fig. 5. XRD pattern of the ZnO nanoparticles

Scanning Electron Microscope (VEGA3 TESCAN) image of pure ZnO nanoparticles and ZnO/Pyrrole composite is shown in Fig. 6a and Fig 6b respectively.

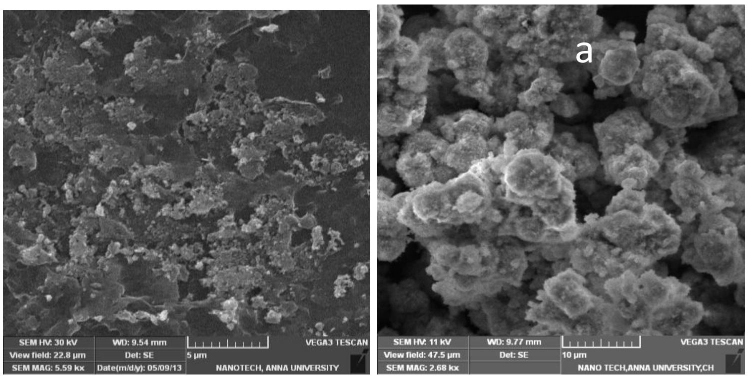

Fig. 6. SEM Images of ZnO NPs and ZnO/Py NPs.

Humidity sensing properties of ZnO/Py composite thin films.

Fig. 7. shows the resistance varies with the relative humidity (RH) in the range of 10-90% at 25^0C. Plots A-C represents the resistance versus RH for the devices of ZnO NPs/Py composite materials. It can be seen in the device that the resistance drops rapidly as the humidity increases. The plot of resistance versus RH from 10% to 90%, illustrates good reproducibility and excellent humidity sensitivity.

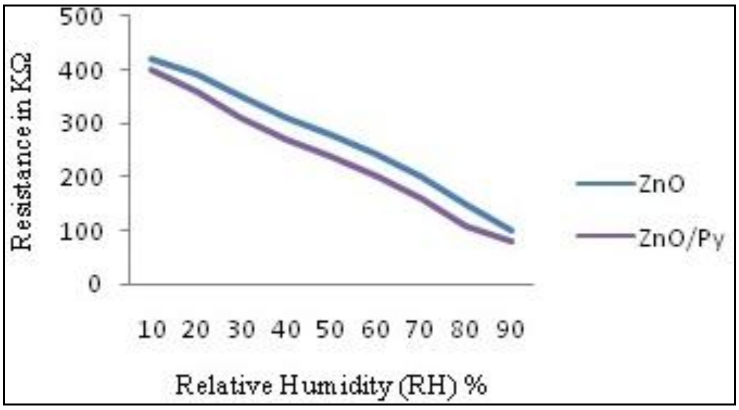

Fig. 7. The plot of resistance v/s relative humidity for ZnO and ZNO/Py based sensors.

Fig. 8. depicts the resistance-temperature behavior of the both ZnO and ZnO/Py composite based sensor, in air (RH is ~50%) the variation of resistances of sample strongly dependent on the temperature. Resistive values decrease as the temperature increases. And these decreases are compatible with the change arising from the RH, so temperature compensation should be made when film is used at different temperatures. This negative temperature effect indicates that the concentration of carrier in the samples increases when temperature increases then consequently leads to the increase of the conductivity of the samples, which results in decrease of the resistance of the film.

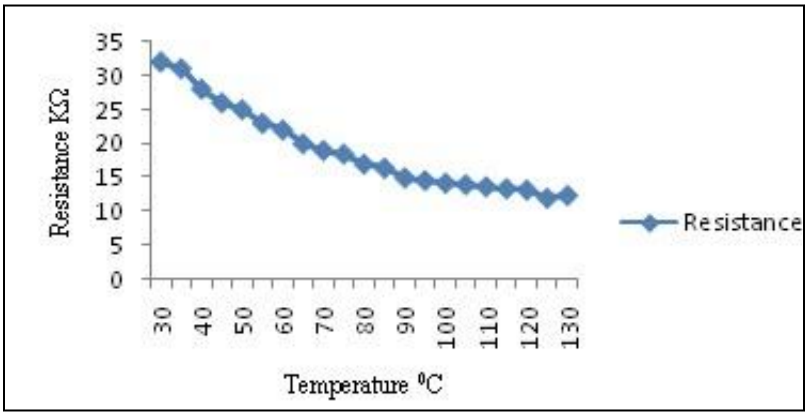

Fig. 8. resistance v/s temperature variation for ZnO/Py based sensor.

In order to evaluate the reliability of the sensor, tests for long term stability were also carried out. The results are shown in Fig. 9. The measurements of resistance-RH characteristics were repeated every 5 days for one month. Only slight variation in resistance at each humidity region is observed over time after aging, proving good stability and durability of the ZnO/Py based sensor.

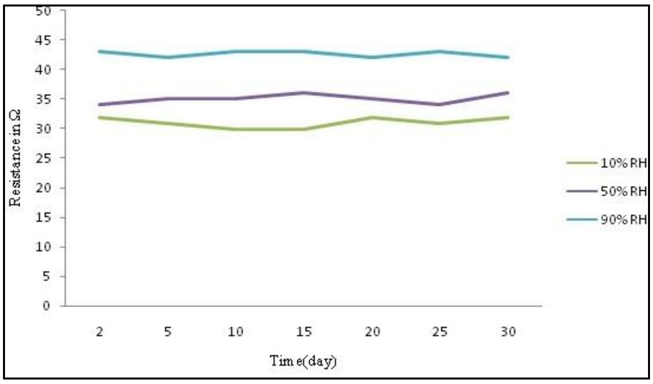

Fig. 9. The long term stability of ZnO/Py based sensor at room temperature.

Meanwhile, the response and recovery behavior of ZnO/Py composite sensor was also tested by applying a humidity pulse between laboratory atmosphere and 90% to the sensor. Fig.10. illustrate the time dependent response and recovery curve of the sensor. In this experiment, the sensor was exposed to laboratory atmosphere first and its stable output in the initial stage was recorded as a baseline. Next, the sensor was put into chamber with 90% RH for the uptake of water molecule until equilibrium is attained. Finally, the sensor was exposed to laboratory atmosphere again for release of water molecule. The measured response time and recovery time (defined as the time reached 90% of the final steady voltage value) were 15s and 10s, respectively. It indicated that the sensor shows a clear and fast response-recovery behavior for humidity sensing.

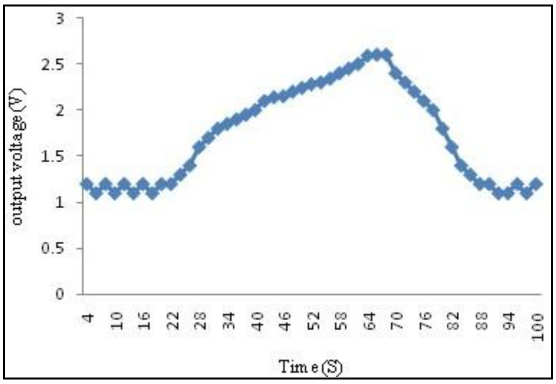

Fig. 10. Time dependent response and recovery curve of the ZnO/Py based sensor.

Conclusion

In summary, ZnO and ZnO/Py composite material were synthesized by the sol-gel technique and investigated for their humidity sensing characteristics. The sensor made up of ZnO/Py composite film, with 0.048g ZnO showed the highest sensitivity and best linearity. The surface topography and morphological information are studied by UV and SEM. The crystalline structure was characterized by XRD. The electrical properties of ZnO/Pyrrole composite thin films were also investigated based on the $AgNO_3$. The sensor based on composite thin film showed higher sensitivity, faster response (15s) and recovery time (10s) and better long term stability than the sensor without ZnO NPs.

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