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Fabrication and characterization of zinc oxide (ZnO) thin films based humidity sensor with fast response by sol-gel method

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Abstract

Present work deals with deposition of Zinc oxide (ZnO) thin films by sol-gel method. Sol was prepared using zinc acetate, 2-Methoxyethanol and monoethanolamine (MEA) as starting materials. Films were grown using spin coating method and annealed at 500° C. ZnO films morphology was investigated by Scanning Electron Microscope. SEM images reveal that films are composed with wrinkles network. Crystalline structure was studied by means of X-ray diffraction analysis. XRD patterns exhibit three strong peaks (101), (002) and (100) planes assigned to Wurtzite structure. The obtained results for electrical properties were reported. Relative humidity sensing properties has been studied and determined by variation of electrical resistance measurements at various humidity levels. Our experimental results show that the temperature and morphology have strong influence on the response and recovery times of sensing.

Keywords—ZnO; sol-gel; thin films; XRD; SEM; Humidity sensing; Response and recovery time

1. Introduction

Different sensing materials have been developed including metal oxides [1] and polymers [2] to detect different gases [3], humidity [4] and temperature [5]. These sensors are used in diverse applications such as healthcare. ZnO is n-type semiconductor; it is one of the most promising materials for sensor applications due to its sensitivity and easy doping method for improving sensing performances. ZnO has been extensively studied and proved to be an excellent gas sensitive material for detection of toxic gases, such as CH_4 [6] and CO [7]. Various studies are focused on humidity sensing [1,4]. The increasing interest to use ZnO as humidity sensor is due to its special chemical property to adsorb water molecules [8] and also to the fact that can be grown in different shape and morphologies such as nanorods [9], wrinkles network [10] and nanowires [11]. ZnO thin films having these morphologies have been successfully synthesized and applied in humidity sensing [11]. Humidity monitoring is used extensively in industrial sectors and scientific applications. Researchers have developed humidity sensing architectures using different sensing techniques including quartz crystal microbalance (QCM) [1], impedance [12] and surface acoustic wave (SAW) [13]. Electrical impedance of ZnO sensors change with humidity due to the enhancement of the adsorbed water on sensor surfaces [4]. It is well known that a powerful sensor must have narrow hysteresis [8] high sensitivity, rapid response and recovery times [14]. In present study, we prepared a humidity sensor based on ZnO thin films. The surface morphology and crystalline structure of ZnO were analyzed by SEM and XRD. Electrical properties and humidity capabilities of ZnO thin films were investigated by impedance variation technique at different temperatures and humidity levels (RH%) where the response and recovery times have been determined.

2. Experimental

2.1. Elaboration procedure

ZnO sol was prepared using zinc acetate, 2-Methoxyethanol and monoethanolamine (MEA) as the solute, solvent and stabilizer respectively. The molar ratio of MEA to zinc acetate was kept at 1.0 and

the Zn concentration was 0.5mol/L. The resulting solution was stirred by a magnetic stirrer at 70°C for one hour. The solution was aged for 24 h and then ZnO thin films were coated by spin coating method on glass substrate at 4000 rpm. After each coating, samples were dried at 280°C for 8 minutes. At the end of process, substrates were annealed at 500°C in ambient atmosphere for 2 hours. The crystalline structure was analyzed by X-ray diffraction using a XRD Bruker D8 Advance. Surface morphology of film was observed using TESCAN VEGA TS 5130 MM scanning electron microscope (SEM).

2.2. Sensing test

Sensor based on ZnO thin films was placed on a heating system (GEFRAN 1000) into an airtight chamber (fig.1). Air compressor was used to push wet air to the chamber and a vacuum pump was used to evacuate it outside. Two electrical contacts were connected through a hole fitted with a vacuum seal gasket in that chamber. System of impedance measurement was used to collect data. TESTO Worldwide hygrometer was used to measure the RH inside the chamber.

3. Results and discussions

3.1. Structural characterizations

The crystalline structure of ZnO thin films prepared was investigated by X-ray diffraction.

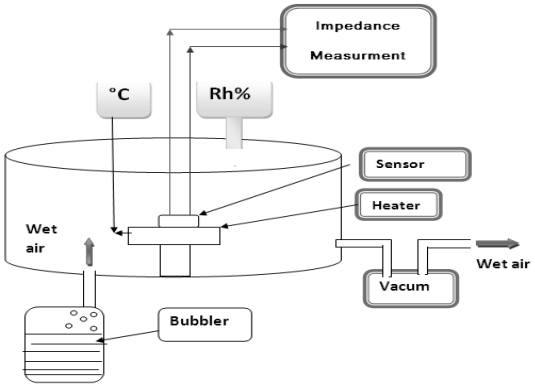

Fig. 1. Experimental setup to measure the response of sensor.

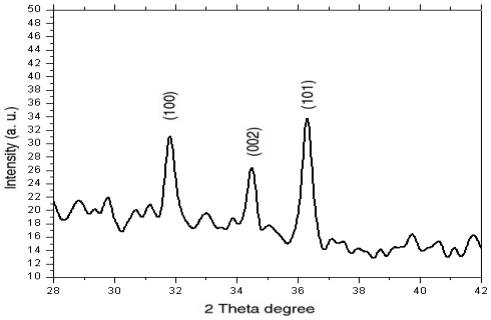

Fig. 2. XRD pattern for ZnO film prepared

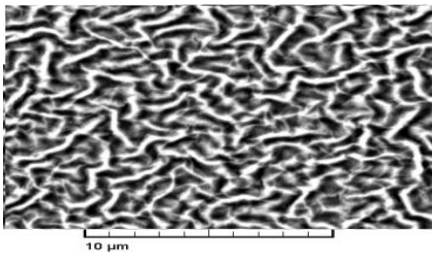

Fig. 3. SEM image of ZnO film

Figure 2 shows the recorded XRD patterns. As can be seen these patterns correspond to three diffraction peaks assigned to (100), (002) and (101) planes. The strongest one is (101), this result implies that films have a hexagonal wurtzite structure with preferred orientation along the (101) plane. Similar results have been observed by Chien-Yie Tsay et al [15] on undoped, Ga, In, and Zr doped ZnO thin films, but Sn doped ZnO thin films has randomly oriented growth behavior.

Grain size D of crystallites was found 25.62 nm; it was calculated using a well-known Scherrer's Formula [10],

$$D = \frac{0.94\lambda}{\beta cos\theta} \quad (1)$$

Where λ= 0.15406 nm is the wavelength of X ray, β is the full width at half maximum (FWHM) of the peak and θ is the Bragg's angle.

Surface morphology of thin films has been studied by a scanning electron microscope. Figure 3 shows the plan view of SEM micrograph of annealed ZnO thin films where continues surface with irregular fiber-like and wrinkle network structure were observed. The

morphology is homogenous with fibers of 500 nm and 2300 nm as width and length respectively. Similar morphologies have been observed in undoped [16] and doped ZnO thin films [17,18]. Wrinkle network structure and high roughness surface lead to much more area; it means that such area has more active sites for dissociation and condensation of water molecules which is interesting for humidity sensing.

3.2. Electrical proprieties

Electrical properties were characterized by mean of four probe resistivity and Hall effect measurement. The obtained results in ZnO film are:
$n=7.79\times10^{13}\ cm^{-3}$, $\mu = 18.33\ cm^2v^{-1}s^{-1}$ and $\sigma = 2.28\times10^{-4}\ (\Omega\ Cm)^{-1}$ for free carriers concentration, electron mobility and conductivity respectively. Zhanchang Pan et al [19] have reported that the co-doping with Al and Sn may be leading to improvement in conductivity of the ZnO thin films.

3.3. Sensing test

In order to investigate humidity sensing properties of device based on zinc oxide wrinkles network structure, we have studied resistance variation depending on relative humidity at 25°C, 50°C, 75°C and 100°C respectively. Figure 4 shows a variation of resistance according to humidity rates on adsorption process (when RH change from 15% to 95%). As we can see the corresponding resistance decreases obviously and almost linearly by enhancing humidity. The process of adsorption of water molecules due by increase of RH causes the decrement of impedance to about 0.4 MΩ in four cases. By decrement of RH level, impedance returns to initial state but not precisely in same values (not mentioned in curve). Juan Xie et al [20] reported that chemisorption occurs at relatively low RH value to form two surface hydroxyls per water molecule, when humidity rises; physisorption of water molecules takes place.

Response and recovery times corresponding to water molecules adsorption and desorption processes at RH=95% were evaluated to understand the performance of the humidity sensor and temperature effect. Figure 5 and figure 6 show relative sensitivity

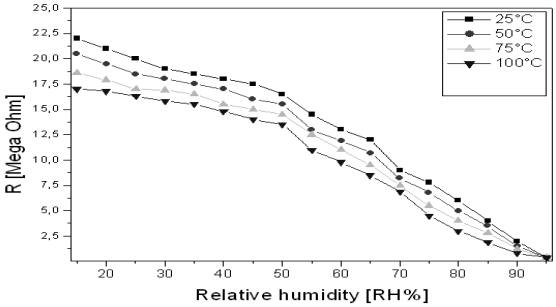

Fig. 4. Resistance variation with RH% at defferent temperatures.

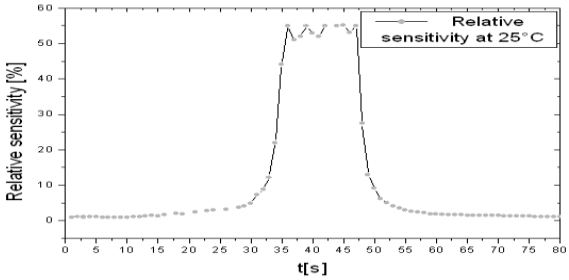

Fig. 5. Relative sensitivity of ZnO humidity sensor at 25°C.

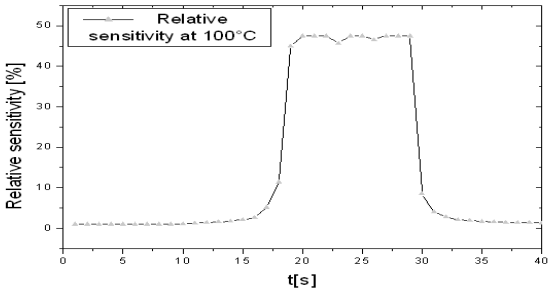

Fig. 6. Relative sensitivity of ZnO humidity sensor at 100°C

for one cycle on ZnO sensors heated at 25 and at 100°C.We defined sensitivity following this formula:

$$S = \frac{Ra}{Rh} \qquad (2)$$

Ra is the resistance at RH%=15 and Rh is the resistance measured at humidity level defined. Four different values of the response and recovery times were mentioned in fig.7 at four temperatures. It is

observed that in all cases the resistance decreases to close values. The response time (as the humidity changes from 15% to 95% RH) is about 22 s and it continues to be shorter with temperature increment until seven seconds at 100°C .the recovery time (as the humidity changes from 95% to 15%) is about 30 s and it continues to be shorter with the increasing of temperature until the 14 seconds at 100°C. The recovery time is relatively slow and it generally takes more seconds to completely recover the sensor original state once wet air evacuated and this might be induced by the chemisorption on the surface of sensing element the adsorbed water might not be entirely removed. Temperature of ZnO films surface spread toward the water layers and increase the mobility of charges carriers in it therefore hopping frequency of protons is more rapid and influence on the conductivity the consequence the response is more rapid. In order to evaluate the performance of ZnO Wrinkle network humidity sensors in practice we have studied the stability behavior the sensor were exposed in air for 60 days, followed by measuring impedances at various RH levels. As shown in fig.8 there is only an inconspicuous change in the impedances, which directly confirms the potential application of ZnO sensors for humidity monitoring.

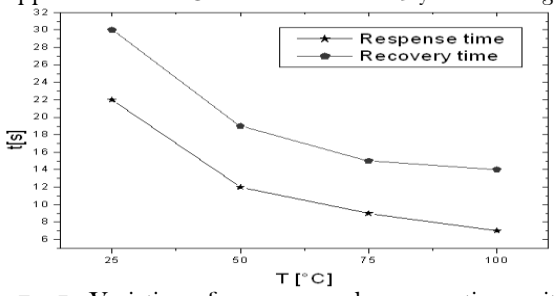

Fig. 7. Variation of response and recovery times with temperature

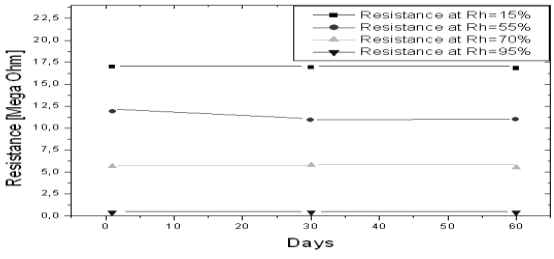

Fig. 8. Stability of the ZnO humidity sensor at various RH levels.

4. Conclusion

ZnO thin films with wrinkle network structure were elaborated by sol–gel process. Sensitivity of ZnO thin films to humidity was investigated by resistance variation, resistance of ZnO sample decrease with the increase of RH%. Shorter response time was observed when samples were heated.

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