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Optical And Humidity Sensing Properties Of Pure Zno And Zno/Sno$_2$ Thin Films Deposited By Spray Paralysis Method

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The present study, we have synthesized ZnO/SnO$_2$ thin films prepared by spray paralysis method and characterized by UV-visible transmission and photoluminescence (PL) spectroscopy and humidity sensing. In UV-visible spectroscopy thin film found to be transparent and its transmission is 20% - 85%. In visible and infrared region with sharp cut off at 310 nm. In PL study shows UV emission which shift to lower wavelength as SnO$_2$ is introduced. The ratio of 1:5 in ZnO:SnO$_2$, shows maximum PL intensity. The PL intensity is found to decrease with increase the ratio of SnO$_2$ in ZnO. The highest intensity peak centered at 375 to 415 nm which show the violet emission. The presence of different broad peak shows the presence of defect states during synthesis and fabrication of the thin films. The humidity sensing of ZnO:SnO$_2$ thin films shows very low values of response and recovery time indicating potential candidature. Response and recovery time of samples is very low which shows suitability of prepared samples for humidity sensors.

KEYWORDS: ZnO, SnO$_2$, Spray paralysis, UV, PL and Humidity Sensing.

INTRODUCTION

Wide variety of metal oxide semiconductors such as iron oxide, copper oxide, tungsten oxide, molybdenum oxide, zirconium-titanium mixed oxides, indium oxide, tin-oxide and zinc-oxide etc. having their potential relevance's such as gas, bio, chemical sensors, optical sensors, pressure sensors, lithium ion batteries, electrochemical performance for energy storage, dye-sensitized solar cells and humidity sensors etc. [1-3]. Currently, various metal-oxides have been investigated due to their remarkable properties and applications in sensing, catalysis [9-10]. Zinc-oxide (ZnO), being a wide band-gap (~3.37 eV, at 300 k) and having large exciton binding energy of ~60 meV at room temperature, is one of the most potential and attractive semiconducting materials for applications in various photonic and optoelectronic devices [4–9]. Similarly, tin oxide (SnO$_2$) is one of the most intriguing materials to be investigated today; this is because tin dioxide is a well-known n-type semiconductor with a wide band gap of 3.6-3.8 eV [2, 3]. Especially, ZnO thin film, which is widely used as gas sensing element which can be made porous with the addition of small amount of SnO$_2$

and results in the availability of larger effective area for interaction with the sensing gas molecules [10, 11]. Some composites also have the unique properties that are not observed in each of the constituent components.

A number of synthesis methods such as thermal decomposition method, co-precipitation method, solid state reaction method, hydrothermal method and sol-gel method etc, have been used for the synthesis of metal-oxides such as ZnO and SnO_2 and their composites [4, 12-16]. Several methods have been used to deposit the metal-oxide and their composites thin films such as pulsed laser deposition (PLD), magnetron sputtering, MOCVD, spray pyrolysis and spin coating etc. [17-20]. In the present work, spray pyrolysis method has been used to deposit ZnO/SnO_2 thin films because it is most widely used and easiest technique.

In the present work, optical properties such as UV-visible transmittance, photoluminescence (PL) and humidity sensing properties of ZnO/SnO_2 films synthesized by spray pyrolysis method are studied. Currently, many efforts have been made to investigate the sensing properties of ZnO based sensors [10-11].

2. EXPERIMENTAL

2.1 Preparation of precursor solution

Stannic Oxide

A solution of 0.5 M $SnCl_4$ in water was prepared by dissolving appropriate amounts of $SnCl_4$ in water under magnetic stirring at 80^0C until colorless and transparent solution was obtained.

$$SnCl_4.5H_2O + H_2O \rightarrow SnO_2 + HCl$$

Zinc Oxide

The precursor solution for spray deposition is prepared by dissolving zinc acetate, ethanol and diethanolamine (DEA). Appropriate amount of zinc acetate is dissolved in ethanol maintain 0.5M molarity of solution. The solution is magnetically stirred at 50^0C for 1minute.

$$Zn(CH_3COO)_2 + C_2H_5OH + DEA \rightarrow ZnO + \text{other product}$$

Firstly, make pure precursor solution of 0.5M ZnO and 0.5M SnO_2 solution. Then the solution has been mixed in the proportion in pure ZnO, ZnO/SnO_2 as 1:2, 1:3, 1:4, 1:5 and pure SnO_2 which is designated as a, b, c, d, e and f respectively.

2.2 Instrumentations

UV-visible absorption spectroscopy was done using Perkin Elmer spectrometer and photoluminescence (PL) spectroscopy was done using Perkin Elmer LS-55 fluorescence spectrometer. Humidity sensing properties have been measured using already reported method [10-11]. The observation is obtained by Keithley resistivity meter. To test the stability, the sensor was exposed in air for 2-3 days, followed by measuring resistance at various %RH. The variations of resistance for all the deposited thin films were studied as a function of relative humidity (RH). Further for resistance measurements, we have deposited electrodes with silver paste on both sides of thin films. The humidity sensing properties of ZnO/SnO_2 have also been investigated in details.

3. RESULTS AND DISCUSSIONS

3.1 UV-visible transmittance spectroscopy

Optical transmittance spectra of the pure and ZnO/SnO_2 thin film samples have been recorded using UV-visible spectroscopy at room temperature. UV-vis optical transmittance spectra of ZnO/SnO_2 thin films deposited by spray pyrolysis method are shown in Figure 1. UV-vis graphs show the film is transparent and transmission spectra vary between 20% -80% in visible and infrared region with sharp cut off at 310 nm. Pure ZnO sample shows sharp edge at 360nm. The measurements have been taken in the wavelength scanning mode for normal incident and at room temperature.

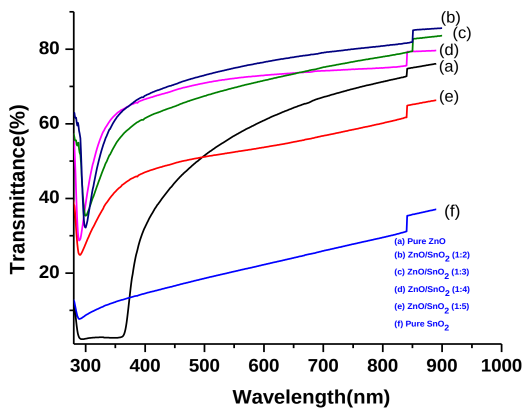

Figure 1: UV-visible transmittance of pure ZnO and ZnO/SnO_2 composites with ratio 1:2, 1:3, 1:4, 1:5 and pure SnO_2 as a, b, c, d, e and f.

3.2 Photoluminescence (PL) spectroscopy

Figure 2 show the photoluminescence (PL) spectra of the ZnO/SnO_2 thin film samples deposited by spray pyrolysis method. From the Figure it is clearly seen that several emission peaks in the range 350 to 600 nm is observed. Thin film of 1:5 i.e. sample "e" is found to be maximum PL intensity. The pure ZnO shows minimum PL intensity where as the SnO_2 concentration added in the pure ZnO sample, it is found the improvement in the PL intensity. The highest peak centered at 375 to 415 nm which show the violet emission and the presence of different broad peaks shows the defect in the synthesis of thin film. It is clearly evident that when the ratio are increased i.e. 1:2, 1:3, 1:4, 1:5 and pure SnO_2, it shifted towards lower wavelength i.e. blue shifting takes place.

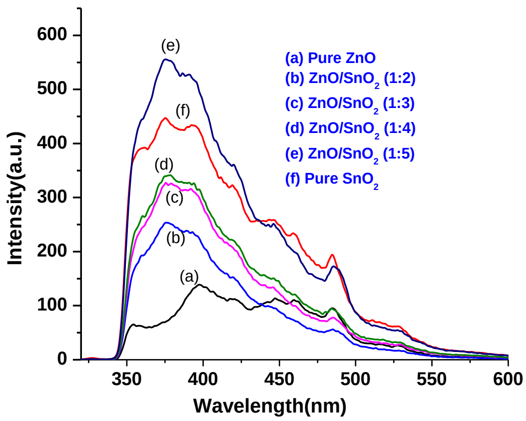

Figure 2: PL of pure ZnO and ZnO/SnO_2 composites with ratio 1:2, 1:3, 1:4, 1:5 and pure SnO_2 as a, b, c, d, e and f.

3.3 Humidity sensing

Figure 3 shows that the effect of resistivity of thin film with variation of relative humidity. The observation is measured by Keithley electrometer. To test the stability, the sensor was exposed in air for 2-3 days, followed by measuring resistance at various %RH. There are almost no changes in the resistance, which also indicates the good stability of the sensor. From the criteria as discussed above, the sensor has prominent stability and is quite promising for a practical humidity sensor. The thin films sample of ZnO/SnO_2 with ratio 1:4 i.e. sample "d". It is means that the ratio of 1 ml of zinc-oxide and 4 ml of stannic oxide can be used as a good sensor because it shows very high resistivity at low humidity with giving maximum slope at 65 %RH. Every sample has a different slope and different response and recovery time. Those sample which have a maximum slope and minimum response and recovery time which used as a suitable sensor i.e. 1:4. When one temperature is increased by air blower outside one chamber the humidity suddenly falls and as a result the resistivity increases. Again as compared to ZnO, ZnO/SnO_2 thin films gives lower slopes and its response and recovery times are more than sample "d" having ratio of ZnO/SnO_2 (1:4). From the graph, it indicates that the linear decrease in resistance with increasing humidity in 20-65% RH which proves the suitability of composite for humidity sensing purposes. The sensitivity was calculated with slope of the curve. The response time 10 sec. and recovery time 13 sec. is achieved.

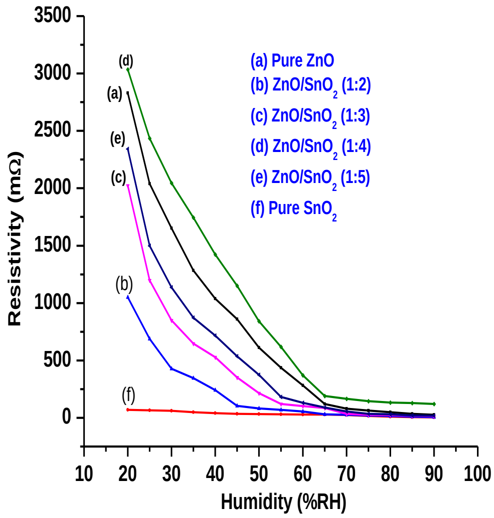

Figure 3: The variation of resistivity with relative humidity of pure ZnO and ZnO/SnO_2 composites with ratio 1:2, 1:3, 1:4, 1:5 and pure SnO_2 as a, b, c, d, e and f.

4. CONCLUSION

Pure ZnO, ZnO/SnO_2 and SnO_2 thin films have been synthesized by spray pyrolysis method at room temperature. The optical properties have been studied using UV-vis and PL spectra. The PL analysis shows a violet emission and blue shift with increasing SnO_2 content in pure ZnO. In humidity sensing properties, response and recovery time is found to be low. The highest response shows by sample d i.e. (ZnO/SnO_2 ratio as 1:4). The humidity sensing result shows a better stability for humidity sensors.

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