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SYNTHESIS, OPTICAL AND HUMIDITY SENSING PROPERTIES OF PURE ZNO AND ZNO: SNO_2 THIN FILMS

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ABSTRACT

In the present work, we have investigated optical properties including UV-visible transmission and photoluminescence (PL) spectroscopy of titled thin films prepared by sol-gel spin coating method. In UV-visible spectroscopy result shows that the prepared thin film is transparent and transmission spectra varies between 68 to 90% in visible and infrared region with sharp cut off at 300 nm. In PL study shows several visible emission peaks ranging from 380 to 650 nm with near band edge (NBE) peak at 380 nm. The ratio 1:5 of 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 380 to 420 nm which show the violet emission. The presence of different broad peak shows the defect of the synthesis of the thin film. When the ratio are increased i.e. 1:2, 1:3, 1:4, 1:5 (ZnO:SnO_2), it shifted towards lower wavelength i.e. blue shifting takes place. The humidity sensing of pure ZnO and ZnO:SnO_2 thin films shows promising properties and the details study is included in this work. Response and recovery time of samples is very low which shows suitability of prepared samples for sensors.

KEYWORDS: Zno, Sno_2, Spin Coating, UV, PL Aand Humidity Sensing.

INTRODUCTION

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 [1–6]. ZnO is highly interesting and most widely studied transparent conducting oxide materials. Due to wide band gap semiconductor it is widely used for production of green, blue, ultraviolet and white light emitting devices. Among various synthesis methods such as thermal decomposition method, co-precipitation method, solid state reaction method, hydrothermal method and sol-gel method etc. have been applied for the preparation of metal-oxides like ZnO and SnO_2 and their composites [1, 7-11]. Different methods have been applied to obtain metal-oxide and their composites thin films, i.e. ZnO thin films are grown by different techniques such as pulsed laser deposition (PLD), magnetron sputtering, MOCVD, spray pyrolysis and spin coating etc [12-16]. In this work, sol-gel spin coating method has been used to prepare ZnO/SnO_2 thin films because sol-gel technique is most widely used and simplest approach due to its comparatively simple processing as there is no need of costly vacuum system and it has a wide-range advantage of large area deposition and uniformity of the films thickness. The sol-gel process also offers other advantages for thin film deposition including outstanding control of the stoichiometry.

The optical properties including UV-visible optical transmittance, photoluminescence (PL) and humidity sensing properties of ZnO/SnO_2 composites synthesized by sol-gel method has been invested in details. Recently many efforts have been made to investigate the sensing properties of ZnO based sensors [17]. On the other hand, given that the performance of oxide based sensors strongly depends on the fabric of the microstructures of the sensing material. Thin film of ZnO and their composites are expected to exhibit high degree of sensitivity, because the sensing mechanism involves chemisorptions followed by charge transfer at the surface lead in to change in resistance of the sensing element. In a conventional humidity sensor made of metal oxides such as ZnO, SnO_2 etc, the powder/solution of metal oxide is coated onto the surface of an inorganic insulating slide to form a humidity sensing film.

EXPERIMENTAL

Sample Preparation

The precursor for spin deposition is prepared by dissolving zinc acetate; ethanol and diethanolamine (DEA) is respectively. ZnO Solution was obtain by dissolving Zinc acetate (0.5M) under magnetic stirring at $50^{\circ}C$ in a solution of ethanol (100ml) and DEA (some drops) for 1 hour. Similarly a solution of 0.5M $SnCl_4$ in water was prepared by dissolving required amounts of $SnCl_4$ in water under magnetic stirring at 80 ^0C until colour-less and transparent solution was obtained. The solution was then heated to 120 ^0C and kept at the temperature to evaporate water and hydrochloride. Precursor solution of pure 0.5M ZnO and 0.5M SnO_2 solution was taken to obtain the ratio of the mixture of above solution in 1:2, 1:3, 1:4 and 1:5. It may be noted that when the quantity of ZnO solution is more than a precipitate is formed. Film deposited by spin coating method using spin coater at 2000 rpm for 20 sec after each layer film got annealed at 100 ^oC for proper fixing. The process of coating cycles are repeated until the desired thickness was obtained. Finally the films were subjected to rapid photo thermal processing at 450 ^oC for 2 hours in a low vacuum. When the films are deposited it is putted in oven for 30 min and then covered by butter paper in the box so that no moisture or dust particle is absorbed on the surface of film. Thus there were obtained five samples of pure ZnO and ZnO/SnO_2 composite with different ratio as 1:2, 1:3, 1:4, 1:5 films which is designated as samples a, b, c, d and e respectively.

Instrumentations

The optical properties of the samples were characterized by UV-visible absorption spectroscopy (Perkin Elmer LS-35 spectrometer) and photoluminescence (PL) spectroscopy (Perkin Elmer LS-55 fluorescence spectrometer). Humidity sensing properties have been measured using handmade device as reported in the literature [17,]. 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.

RESULTS AND DISCUSSIONS

UV Visible Transmittance Spectroscopy

Optical transmittance spectra of the prepared ZnO/SnO_2 thin film samples have been recorded using UV-visible spectroscopy at room temperature. Figure 1 shows the UV-vis optical transmittance spectra of ZnO/SnO_2 thin films deposited by sol-gel spin coating method. UV graphs show the film is transparent and transmission spectra vary between 68% - 90% in visible and infrared region with sharp cut off at 300 nm. The measurements have been taken in the wavelength scanning mode for normal incident and at room temperature.

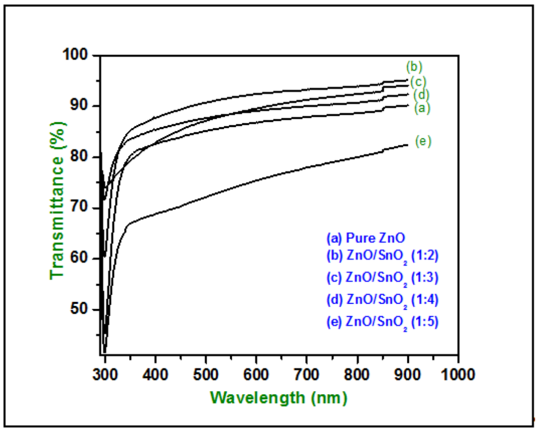

Figure 1: UV-Visible Transmittance of Pure Zno and Zno/Sno_2 Composites with Ratio 1:2, 1:3, 1:4, 1:5 as A, B, C, D and E

Photoluminescence (Pl) Spectroscopy

Photoluminescence (PL) spectra of the prepared ZnO/SnO_2 thin film samples deposited by spin coating are shown in the Figure 2. In the PL spectra several emission peaks in the visible range 380 to 650 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 380 to 420 nm which show the violet emission and the presence of different broad peaks shows the defect of the synthesis of the thin film. It is clearly evident that when the ratio are increased i.e. 1:2, 1:3, 1:4, 1:5, it shifted towards lower wavelength i.e. blue shifting takes place.

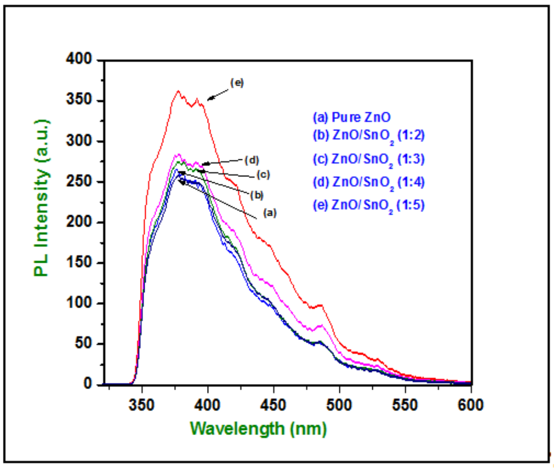

Figure 2: PL of Pure Zno and Zno/Sno_2 Composites with Ratio 1:2, 1:3, 1:4, 1:5 as A, B, C, D and E.

Humidity Sensing

Figure 3 shows that the effect of resistivity of thin film with variation of humidity. 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. 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 ration 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. 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 ration of ZnO/SnO_2 (1:4). From the graph, it indicates that the linear decrease in resistance with increasing humidity in 25-70% RH which proves the suitability of composite for humidity sensing purposes. The sensitivity was calculated with slope of curve and is found approximate at 30%RH. Further change in resistance at 90%RH with time is measured and curve which reveals the response time 10 sec. for 85 %RH of material is very low and recovery time after blowing dry air is very high i.e. 13 sec.

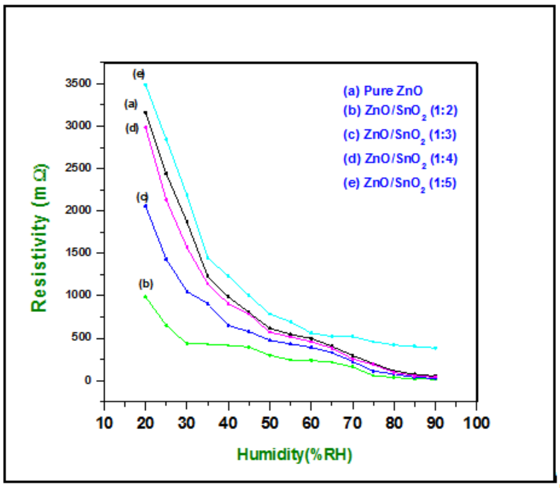

Figure 3: The Variation of Resistivity with Relative Humidity of Pure Zno and Zno/Sno_2 Thin Films with Ratio 1:2, 1:3, 1:4, 1:5 as A, B, C, D and E.

CONCLUSIONS

In conclusions, pure ZnO and ZnO/SnO_2 thin films have been synthesized via spin coating 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 sample d (ZnO/SnO_2, 1:4) shows highest response. The humidity sensing result shows a good stability and suitability for humidity sensors.

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