Structural and optical properties of TiO_2 doped ZnOmixed metal oxide nanocomposite thin films

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Abstract:

From many decades, metal oxide semiconductor materials have compensated abundant interest by means of gas sensing material by researchers. TiO_2 andZnO are more popular metal oxide materials which are formed better presentationfor the development of thin films. In this research paper, the synthesized TiO_2doped ZnO mixed metal oxide nanocomposite thin films are studied. Structural and optical properties of TiO_2 doped ZnOare incorporate.Advanced spray pyrolysis system has been used for the development of thin films.Doping of ZnO with TiO_2 might be a hopefulchoice to improve the gas sensing quality.

Keywords: *Synthesis, mixed metal oxide, nanocomposite, gas sensing.*

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1. INTRODUCTION

From many decades, the countlessinvolvement of researchers has been made ZnO films extrachoosy and to carrydown its operating temperature with reducing the response time. Either reducing the material size at nano level or by using proper dopants has been confirmedcompetently. By the addition of sure dopants one can improve the gas sensing properties of sensor effectively. The TiO_2doped ZnO (ZnO:TiO_2) is one of the utmostauspicious electrical conductivity-controlled metal oxides due to its variable electrical resistance properties [01] and it has been confirmed that ZnO films doped with TiO_2 have more electrical resistance [02]. Earlier ZnO:TiO_2 films have been shown to sense carbon monoxide [03-04] ethanol [05] at higher working temperatures. Currently, M. Zhao shown that response to low concentrations H_2S gas can be significantlyimproved by TiO_2 doping [06]. Hence, doping TiO_2 with ZnO might be aoptimistic selection to expand the gas sensors sensitivity.

In the present research, an effort has been made to synthesize ZnO:TiO_2 thin films by advanced spray pyrolysis technique. The structural and optical properties of ZnO:TiO_2 (TZO) thin films are studied as a function of TiO_2 doping concentration.

2. EXPERIMENTAL DETAILS

Advanced spray pyrolysis method has been used for the deposition of TZO films. Advanced spray pyrolysis method includes the substrate cleaning, solution preparation and deposition etc. The optimized preparative parameters were used to deposit the nano-crystalline and feasible TZO films for gas sensor application. The TZO films were characterized using various techniques in order to get information on their structuraland optical properties.

The schematic of experimental set up of advanced spray pyrolysis system to deposit the ZnO:TiO_2 thin film is shown in figure 1 [07].

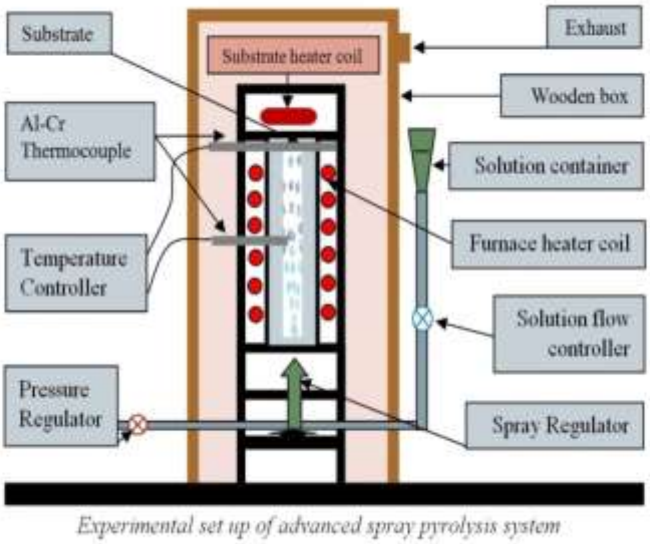


Figure 1: Advanced spray pyrolysis system

For the synthesis of TZO thin films, mainly, the spraying solution was arranged by addingproper volumes of equimolar (0.1M) non-aqueous solution was made by softening zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$]and titanium dioxide [$TiO_2 \cdot 2H_2O$] in ethanol. The consequential solution was sprayed at an enhanced substrate temperature of 723K. While deposition, the previously optimized deposition parameters such as core temperature (800K), spray rate (6ml/min), nozzle to substrate distance (40cm) and gas pressure (10LPM) were constant. During the investigation, both the substrate and core temperature were controlled using electronic temperature controllers. ZnO thin films were deposited with 1, 2, 3, and 4wt% TiO_2 doping assigned as 1TZO, 2TZO, 3TZO and 4TZO respectively.

3. RESULTS

3.1 Structural Studies

3.1.1 X-Ray Diffraction of ZnO

Figure2, shows the XRD patterns of ZnO films deposited at different substrate temperatures. From the figure, it is evident that the structural properties of ZnO films largely depend on substrate temperature. S623 sample illustrate less crystalline nature with a weak reflection along (100) plane. S673 and S723 films display a favoredalignment along (002) direction. However, relatively weak reflections from (100), (101) and (103) plane are observed. This indicates the polycrystalline wurtzite structure of ZnO deposits [JCPDS No. 05-0664]. The intensity of the (002) peak increases with increase in substrate temperature and is mostlyfind by the number of crystallites with the c-axis alignment in the ZnO films. During deposition, the kinetic energy of atom is mainly depending on the substrate temperature [08]. As compared to S623 film, the atoms on the surfaces of S673 and S723 films can move quickly to look for the lowest energy sites and form the low energy structure i.e. the high substrate temperature enhances the mobility of the atoms on the surface and increases thermodynamic stability. The c-axis orientation and crystallinity of the film becomes better, with increase in the substrate temperature [09]. In the present investigation it is noteworthy that, though the films are deposited at substrate temperatures (623 and 673K), films exhibit good adherence and are completely free from powderiness and opacity which is not the case of previous reported work by S. M. Rozati et al [10].

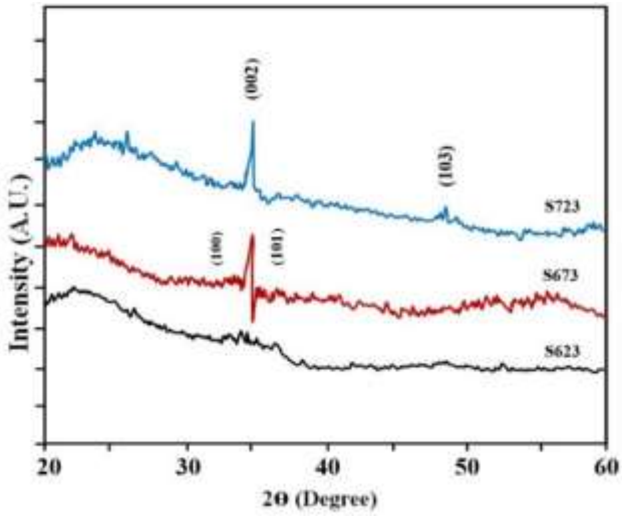


Figure2: XRD patterns for different ZnO films: (a) S623K and (b) S673K and(c) S723K.

3.1.2 X-Ray Diffraction of TiO_2

From figure 3, it shows the X-ray diffraction (XRD) patterns of TiO_2 films deposited at different substrate temperatures. It is also evident that the structural properties of TiO_2 films largely depend on substrate temperature [11]. The S673 sample shows poor crystalline nature with a weak reflection along (100) plane; while the S723 and S773 films exhibit a preferential orientation along (002) direction. However, relatively weak reflections from (100) and (101) plane are observed. This indicates the polycrystalline wurtzite structure of TiO_2 deposits [JCPDS No. 05-0664]. The intensity of the (002) peak increases with increase in substrate temperature and is mainly determined by the number of crystallites with the c-axis orientation in the TiO_2 films. During deposition, the kinetic energy of atom is mainly depending on the substrate temperature [12]. As compared to S673 film, the atoms on the surfaces of S723 and S773 films can move quickly to look for the lowest energy sites and form the low energy structure i.e. the high substrate temperature enhances the mobility of the atoms on the surface and increases thermodynamic stability[13]. In the present investigation it is noteworthy that, though the films are deposited at substrate temperatures (673 and 723K), films exhibit good adherence.

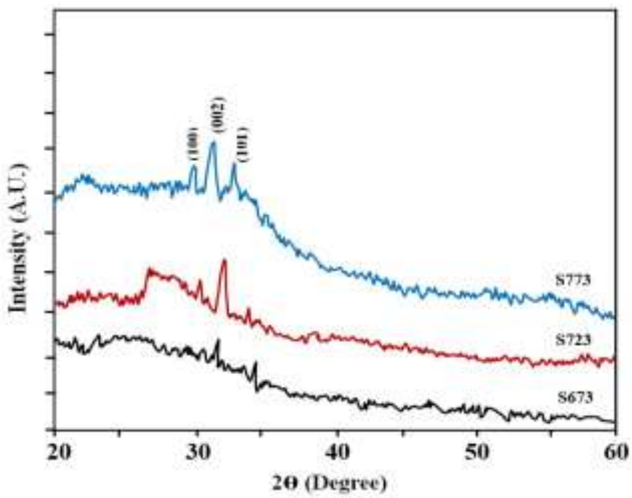


Figure3: XRD patterns for different TiO_2 films: (a) S673K (b) S723K and (c) S773K.

3.1.3 X-Ray Diffractionof ZnO:TiO_2 thin films

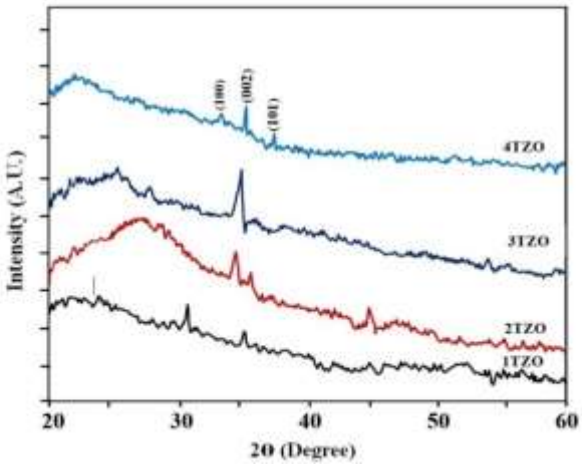


Figure4: XRD patterns of ZnO:TiO_2 thin films deposited at 723 K with concentrations of TiO_2 doping.

Figure4, shows the XRD patterns of TZO films fabricated at different TiO_2 doping concentrations. In figure, the peaks at 34.1, 34.4 and 36.8 are identified as (100), (002) and (101) reflections of wurtzite structure of ZnO, confirming that all the polycrystalline films retain the ZnO structure and are randomly oriented at low TiO_2 concentrations. At 1wt %, the (002) peak is very pathetic as compared to the (100) and (101) peaks. However, with increase in TiO_2 doping concentrations peak intensity corresponding to (002) plane is improved. 3wt % of TiO_2 doping film shows the most intense single topmostequivalent to (002). For further increase in doping concentration (at4wt%) the (002) peak intensity decreases. The improvement in peak intensity/c-orientation of ZnO films as an effect of TiO_2 doping up to 3wt% of TiO_2 was detected by others and results can be explain on the bases of Lee et al [14-15]. According to Lee et al the increase in the extent of c-orientation may be due to the fact that a moderate quantity of TiO_2 atoms exist as interstitials sharing the oxygen with Zn atoms and hence improve the (002) orientation [09].

3.2 Optical Absorption Studies

Figure5, shows the optical transmittance and absorbance spectra of ZnO:TiO_2 thin films with different TiO_2 doping concentrations in the wavelength range of 350 to 850 nm. Figure (b) shows the corresponding optical absorption of ZnO:TiO_2 films. The transmittance of all titanium dioxide doped ZnO films stays over 80 % at 550 nm. The optical transmittance is observed to increasing with TiO_2 doping concentration up to 3wt%; however, it again decreases slightly for 4wt % sample. The observed change in transmittance may be the effect of change in film thickness and consequent surface scattering of incident photons with variation [16] in TiO_2 doping concentration in ZnO.

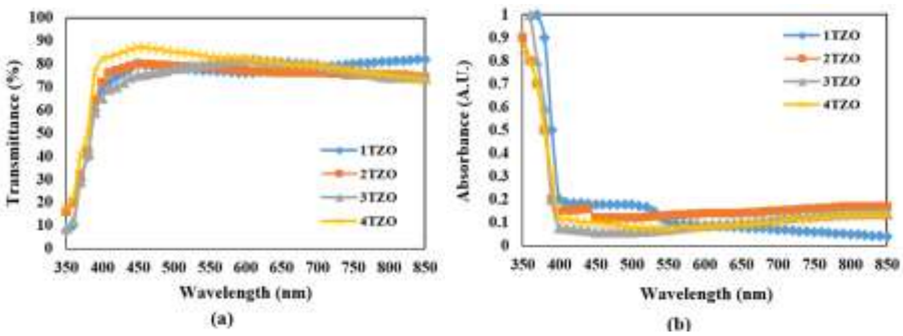


Figure5: Optical transmission spectra of ZnO:TiO_2films at TiO_2 doping concentrations.

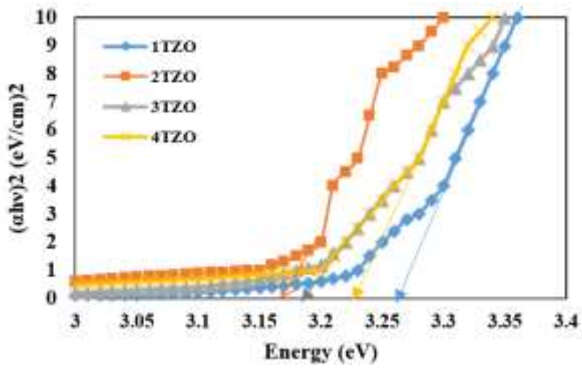
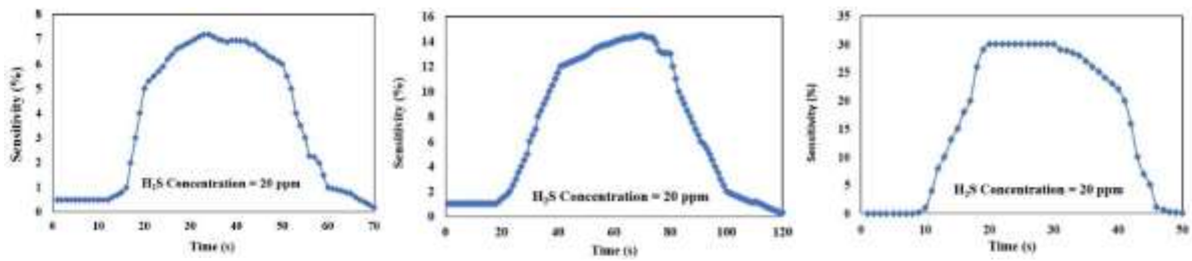


Figure6: Plot of $(\alpha h\nu)^2$ vs (hv) for $ZnO:TiO_2$ films at different TiO_2 doping concentrations.

The variations of the absorption coefficient of $ZnO:TiO_2$ films with respect to the incoming photon energies are given in figure6. It is seen that the dependence of the $(\alpha h\nu)^2$ on (hv) is linear about the fundamental absorption region which can be taken as an indication of the direct transition. The optical band gap values are determined from these plots by means of the extrapolation of the linear portion of $(\alpha h\nu)^2$ vs. (hv) curves (figure6). It is seen in the plot, the optical band gap of 1, 2, 3 and 4wt% TiO_2 doped ZnO films varies from 3.26 to 3.17 eV. Similar effect of TiO_2 incorporation in ZnO on band gap was observed[10]. The observed behavior of band gap variation with the TiO_2 doping concentration is likely to be attributed to a variation of crystallite size and a modification of the grain boundary configuration during growth.

Figure7(a, b, c) shows the transient response to 20 ppm of H_2S of Pd-sensitized 4TZO film at 673 K, 723 K and 773 K respectively. Figure shows that, the Pd-sensitized 4TZO sample exhibits enhanced sensitivity as compared to that of the un-sensitized sample. Though not much improvement was observed in the response time, the sensitization effect was found to enhance the rate of recovery slightly faster. Here, in electronic type of palladium sensitization, the Pd in its oxidized state acts as a strong acceptor for electrons of the 4TZO film. This induces an electron-depleted space-charge layer near the interface.



(a) 673 K **(b) 723 K** **(c) 773 K**

Figure7: The transient response to 20 ppm of H_2S of Pd-sensitized 4TZO film.

By reacting with reducing analyte such as H_2S, the palladium additive is reduced releasing the electrons back to the TZO film[17].

CONCLUSIONS:

The structural and optical properties of ZnO, TiO_2 and $ZnO:TiO_2$ films are studied. It is seen that, 4TZO sample exhibits enhanced sensitivity.

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