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Physical Investigations on Ti:ZnO Thin Films by Sol-Gel Spin Coating to Detect Acetone

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ABSTRACT
The ZnO and Ti:ZnO thin films were deposited on ordinary glass, quartz glass, substrates by sol-gel spin coating. The atomic percent (at.%) of Titanium (Ti) in ZnO is varied from 1 to 6. The deposited thin films were characterized by Grazing Incidence X-ray diffraction (GIXRD) for structural determination, High - resolution Scanning Electron Microscopy (HRSEM) to determine microstructure, optical transmittance to know the type of optical transition in the films. The structure of the ZnO and Ti:ZnO films was determined by Grazing Incidence X-ray diffraction (GIXRD). The ZnO films were observed to be crystallizes in Hexagonal wurtzite structure with (002) orientation, where as Ti:ZnO films were amorphous. The intensity of (002) decrease with increasing Ti at.%. The grain size is 20 nm and is decreasing to 10 nm with increasing Ti at.%. The HRSEM images of Ti (1%):ZnO and Ti (6%):ZnO thin films reveals that the films contain nanoflakes of uniform size. These flakes contain spherical nanoparticles of uniform size. The samples were tested for their sensitivity for 300 and 600 ppm of acetone and is maximum for films contain 1 at. % of Titanium.

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Introduction

The Zinc Oxide (ZnO) is a promising compound in the oxide family that is used in various applications as bulk compound and as thin film. A few applications of ZnO films are as transparent conducting oxide (TCO) [1], gas sensing element [2], window material in solar cells [3], photoluminescence [4] etc. An improvement in the physical and chemical properties like structure, conductivity, the transmittance of these thin films is observed when doped with an element of the appropriate ionic size of Zn. Several elements like Al, In, Sn and Ti, Mo [5] were doped to ZnO and a significant improvement in the appropriate physical properties was observed. Among these Ti is observed to be the most promising material to tune the physical properties of ZnO thin films significantly [6]. Titanium is a transition element that has an ionic radius (6.8 nm), which is smaller than the Zn (7.4 nm). When Ti is doped to ZnO, some of the Zn atoms replace the Ti atoms [7]. The replacement of Zn with titanium will enhance the various physical properties like conductivity [8], chemiresistivity. Among several properties exhibited by the ZnO by Ti doping, the chemiresistivity is the most interested one, to detect reducing and oxidizing gases with high sensitivity [9–11].

In the present investigation, Ti is doped to ZnO to obtain Ti:ZnO thin films and were deposited by sol-gel spin coating technique. Sol-gel is a low cost and simple technique to synthesis bulk as well as nanostructured ZnO thin films with dopants like Au, Cd, In, Titanium etc.[13]. Nowadays the importance is growing to detect acetone which is used widely in chemical laboratories and industries. The inhale of acetone can affect the internal organs of a human body by damaging them [13]. Moreover, the sugar levels of a diabetic person can be found by detecting acetone levels from the breathing exhaust. So the acetone sensing can prevent the painful process of sugar level detection by extracting blood from a diabetic person. So, in the present investigation, ZnO and nanocrystalline Ti:ZnO thin films were prepared by sol-gel spin coating to detect acetone. The response time, reaction time, stability and selectivity are the key parameters in choosing particular material as a gas sensor [13, 14]. In this context Ti:ZnO thin films were found to be sensitive to acetone and are having a good response time to acetone vapours. The deposited films were analysed by XRD, HRSEM and UV-VIS spectroscopy and were tested their sensitivity to Acetone.

Experimental

ZnO and Ti:ZnO thin films were deposited Sol-gel spin coating technique. Zinc acetate was taken as Zn source and Titanium butoxide was taken as Ti source. The Zinc acetate was dissolved in 2-methoxy ethanol to obtain 0.2 M solution. The appropriate percent of Titanium butoxide was added to the solution to dope require at. % of Ti in ZnO. The solution is stirred continuously for 2 hours at 60 ^{o}C. The monoethanolamine was added for the formation of gel and stabilization. The obtained solution was stored for 24 hours. The stored solution was used for the formation of films using a spin coater. The 50 microlitres (µl) of gel was taken using a micro-pipette and transferred onto quartz glass (SiO_2) substrate fixed to spin coater. The spinning speed was kept at 1500 rotations per minute (rpm) and was rotated for 20 seconds. Later the films were annealed at 200 ^{o}C for 5 minutes. This process was repeated for five times. Later the coated substrate was annealed at 400 ^{o}C to get crystallinity and densification of the films. The EDAX and HRSEM were performed using FEI-Quanta FEG 200F. The XRD spectrum was recorded for the films deposited on

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quartz glass (SiO_2) substrates at a glancing angle of 0.5° to determine their structure by using a Bruker D8 Advance X-ray diffractometer. The optical transmittance spectra of the films were recorded in the 300–1100 nm wavelength range by using a UV-VIS spectrophotometer. The resolution of the instrument is 4 nm. The thickness of the films is 2000 Å which was measured by using spectroscopic ellipsometer.

Results and Discussion

X-ray diffraction studies

The X-ray diffraction spectra of Ti:ZnO thin films were shown in Fig.1. The XRD spectrum indicates the ZnO films crystallizes in the Hexagonal wurtzite phase with (002) orientation. Along with (002), another two predominant and low intensity orientations were observed at 2θ values of 32°, 36.64° and at 57°, 63°, 68° respectively.
The interplanar spacing is evaluated using Bragg's law,

$$n\lambda = 2d\sin\theta \qquad (1)$$

where n is the diffraction order,
λ is the wavelength of X-rays in Å,
d is the interplanar spacing, and
θ is the angle of diffraction in degrees.

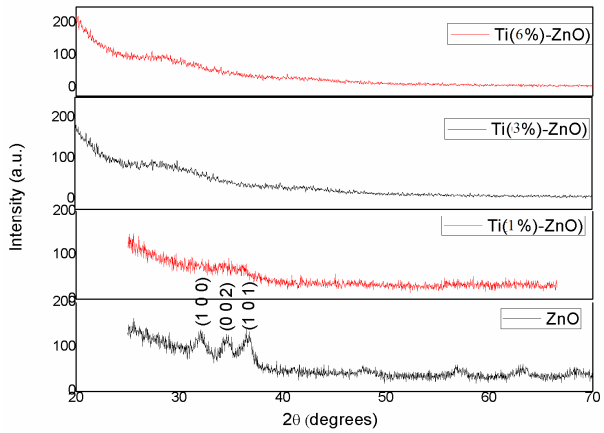

Figure 1: X-ray diffraction spectra of Ti:ZnO thin films

In the present case, the 2θ value of the (002) orientation is 34.46° and (100) and (101) were 32° and 36.64°. These three peaks lose resolution and the films were turn to amorphous with increasing Ti at. % in ZnO. The increment in Ti at.% affects the growth along (002) direction. According to Ramadan [6], Ti induces point defects and consequently affects the ZnO structure which leads to lattice mismatch between the solid solution formed by TiO_2-ZnO. Moreover, the reason for amorphous nature of the films is due to the substitution of Zn atoms with Ti and the formation of nanocrystallites [6, 7, 12, 14, 15] which are evidenced by high resolution scanning electron microscopic (HRSEM) image. Moreover, the peaks corresponding to titanium (or) titanium dioxide were not observed [12, 17], when titanium of various atomic percent is added to ZnO. The intensity of diffraction peak cannot be observed, when, either the film thickness was lower than 50 nm or sintered at lower temperature i.e. lower than 200 °C [17]. But in the present investigation ZnO and Ti: ZnO thin films thickness is more than 50 nm and were also annealed at 400 °C. So there is no possibility of the effect of thickness on the structural change from polycrystallinity to amorphous state of the films.

The inter planar spacing 'd' of ZnO films is calculated using the following formula,

$$d_{hkl} = \frac{1}{\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right]^{1/2}} \qquad (2)$$

The calculated a, c values are 2.8 A, 5.2 A. The grain size is calculated using Scherrer's law,

$$L = k\lambda/\beta\cos\theta \qquad (3)$$

L is the grain size,
k is a correction factor that is equal to 1.
β is the full width at half maximum (in radians),
θ is the angle of diffraction in degrees.

The average grain size of ZnO thin films is 185 nm. The undoped ZnO films were polycrystalline with a wurtzite structure with a predominant (002) orientation. It is observed that the titanium doping level affects the average grain size. The grain size is decreasing with increasing Ti atomic percent in ZnO. The crystallite size is decreasing with increasing Ti atomic percent due to promotion of more no. of nucleation sites of low free energy by titanium. This was evidenced by HRSEM pictures.

Microstructural studies

The microstructure of Ti (3%):ZnO and Ti (6%):ZnO thin films, recorded at low and high magnification and 500 nm and 1000 nm scales is shown in Fig.2a and 2b and Fig. 3a and 3b. The morphology reveals that the films contain nanoflakes of uniform size which contain spherical nanoparticles of uniform size [17]. The observed micro-cracks in the film were may be due to lattice mismatch between quartz glass and Ti: ZnO thin films, when annealed at 400 °C. The grain size is around 20 nm. It is observed that the films contain nanoflakes which leads to the growth of nanocrystallites of uniform size. This type of morphology prove to be more sensitive when exposed to acetone.

Optical Transmittance

The optical transmittance spectra of the films were studied to know the optical quality and type of optical transition of the films. The optical transmittance of the ZnO and Ti:ZnO films are shown in Fig. 4. The transmittance of the films is 98% and decreases with increasing Ti at. %. The absorption edge is shifting to higher energies with increasing Ti atomic percent due to the Moss-Burstein shift [18]. The energy gap of the films was estimated by the formula, [19].

$$(\alpha h\nu) = B\,(h\nu - Eg)^{1/n} \qquad (4)$$

where exponent 'n' takes the values 2 and ½ based on the type of electronic transition.
In the present investigation, the films showed a better fit for n=2 which indicates that the electron transition is direct. The energy gap is found by extrapolating the graph of $(\alpha h\nu)^2$ versus hν. The estimated energy gap of the ZnO films is 3 eV and increase to 3.4 eV with increasing Ti at. % [17, 20] to 6. The titanium substitution in the Zn place increases the Fermi level which in turn increases the energy gap of Ti:ZnO films [10]. The observed increase in the energy gap of the films is due to the change in an electronic structure near the conduction band edge. [21].

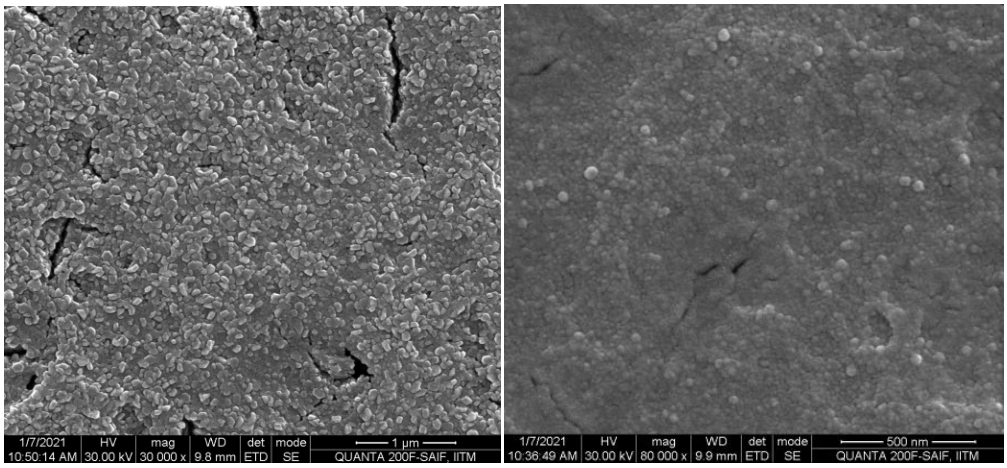

Figure 2: (a) HRSEM image of Ti(3%):ZnO thin films (1000 nm), (b) HRSEM image of Ti(3%):ZnO thin films (500 nm)

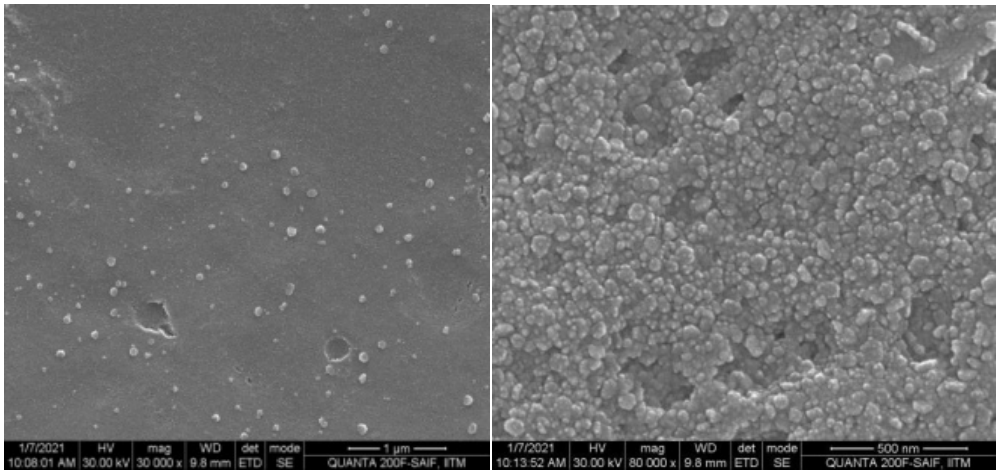

Figure 3: (a) HRSEM image of Ti(6%):ZnO thin films (1000 nm), (b) HRSEM image of Ti(6%):ZnO thin films (500 nm)

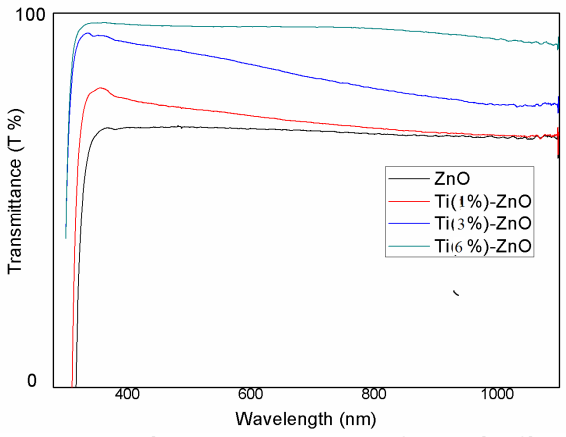

Figure 4: Optical transmittance spectrum of Ti:ZnO thin films

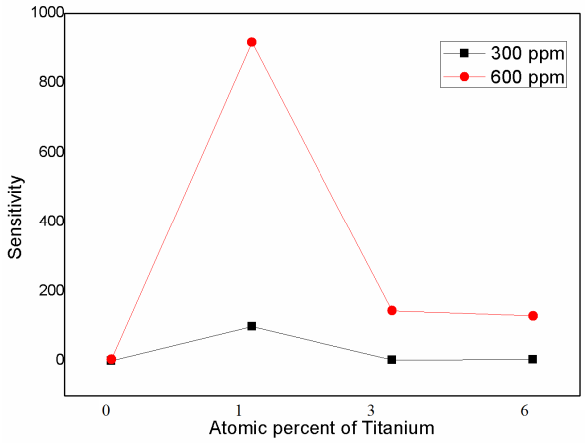

Figure 5: Sensitivity of Ti:ZnO thin films to acetone

Gas sensing studies

Ti:ZnO thin films were deposited on quartz substrates (10 mm x 5 mm) to study their gas sensing properties. Silver was evaporated to obtain the contacts to test the samples for gas sensitivity. The contacts were found to be ohmic for a wide range of voltages. The testing of samples for acetone was performed by placing them on a sample holder inside the stainless steel chamber. Specific arrangements for made to evaporate acetone and to transfer the acetone vapour on to film surface. The sensor is operated at room temperature to prevent the kinetics of gas molecules which affects the sensing responses. [11,22]. At a particular thickness, ZnO posses oxidizing nature for acetone vapours [23]. The samples were exposed to acetone and showed good sensitivity (see Fig. 5).

The sensitivity calculated by using

$$S = \frac{R_a - R_g}{R_a[gas]} \quad (5)$$

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where R_a is the resistance of the film in air,
R_g is the resistance of the test gas and
[gas] is the concentration of the test gas.
A Keithly multimeter was used to measure the resistance of the sample.
It was found that the sensitivity of the films to Acetone is increasing with increasing Ti at. % in the Ti:ZnO composite. The sensitivity of the films is maximum for Ti at. % of 1. The doped sensing materials have high sensitivity when compared to undoped ones [22]. The decrement in the resistance of the sensor is due to the reaction of oxygen ions (O_2^-, O^- and O^{2-}) with molecules of acetone on the surface of the ZnO thin film. This in turn produces CO_2 and H_2O. The Ti atoms on the Ti: ZnO thin film surfaces attract more oxygen molecules to chemisorb on its surface. This enhances the production of more O_2^-, O^- and O^{2-} species which reacts with adsorbed acetone vapours on Ti: ZnO surface. With further increase of Ti at. % reduces the conductivity due to films turns to amorphous which further decreases the formation of O_2^-, $O^-$and O^{2-} species which results in decrement of electrical conductivity. The process of reaction between acetone and oxygen adsorbents on Ti: ZnO thin film layer is given below.

$$CH_3\text{-}CO\text{-}CH_3 + 8O\ (ads) \rightarrow 3CO_2 + 3H_2O + 8\ e^-$$

The electrons released in this process are released back to the conduction band of Ti: ZnO which in turn reduces the resistance [24]. The sensitivity of Ti:ZnO thin films for different concentrations of acetone is shown in Fig. 5. The sensitivity is decreasing with a further increase of Ti at. % to 6. This may be due to films turn to amorphous with Ti addition.

Conclusions

The ZnO and Ti: ZnO thin films were deposited by sol-gel spin coating onto quartz substrates. The polycrystalline structure was observed in ZnO thin films where as Ti:ZnO films were amorphous. The optical transmittance of the films is increasing with increasing Ti at.%. The energy gap of ZnO films is 3 eV and is increasing to 3.4 eV with increasing Ti at. % to 6. The ZnO thin films showed better sensitivity to lower doping levels of Ti and the sensitivity is maximum at 1 at. % of Ti in ZnO. This indicates ZnO thin films doped with 1 at. % Ti is more effective in the detection of Acetone at lower ppm levels. The results revealed that the Ti-doped ZnO thin films are effective acetone sensors.

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Compliance with ethical standards

Conflict of interest: The authors have no conflict of interest.

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