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Synthesis of ZnO:TiO_2 Nanocomposite Thin Films by Spraypyrolysis

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ABSTRACT

In present study ZnO: TiO_2 composite thin film was successfully deposited on to glass substrate by using simple chemical spray pyrolysis technique. Effect of ZnO: TiO_2 composite on the prepared thin film has been studi-ed. The structural properties of ZnO: TiO_2 composite thin film has been investigated by X-ray Diffraction (XRD). It is seen that films are polycrystalline and having domin-ant orientation (002) and (101) for pure ZnO (hexagonal) and TiO_2 (tetragonal) thin films respectively while for coupled films it shows mixture of both phases. It depicts that required phases of respective materials has been achieved. The absorption edge of TiO_2, ZnO and ZnO: TiO_2 films are at around 391, 398 and 414 nm, respecti-vely. The optical energy gap energy is found to be, E_g = 3.11 eV, 3.27 eV, and 2.99 eV and which are deduced for ZnO, TiO_2 and ZnO: TiO_2 films respectively.

Keywords: ZnO: TiO_2 Composite; structural properties; films

INTRODUCTION

Nanocomposite films are thin films formed by mixing two or more dissimilar materials having nanodimensio-nal phase(s) in order to control and develop new and improved structures and properties. The properties of nanocomposite films depend not only upon the indivi-dual components used but also on the morphology and the interfacial characteristics. unique physical, chemical, optical, mechanical, magnetic and electrical properties

unavailable from that of the component materials and have attracted much attention for a wide range of device applications such as gas sensors. Recently, various nanocomposite films consisting of either metal-metal oxide, mixed metal oxides, polymers mixed with metals or metal oxides, or carbon nanotubes mixed with polymers, metals or metal oxides have been synthesized and investigated for their application as active materials for gas sensors. Design of the nanocomposite films for gas sensor applications needs the considerations of many factors, for example, the surface area, interfacial characteristics, electrical conductivity, nanocrystallite size, surface and inter-facial energy, stress and strain, etc., all of which depend significantly on the material selection, deposition methods and deposition process parameters.

In recent years, the photocatalytic degradation of various kinds of organic and inorganic pollutants using semiconductors as photocatalysts has been widel studied [4-7]. Among these semiconductors, TiO_2 has been extensively investigated as the most promising photocatalyst due to its high photocatalytic activity, non-toxicity, high photochemical stability, and low-cost. However, it divulged some drawbacks. For example, TiO_2 (band gap 3.2 eV corresponds to 388 nm) can only absorb the UV region (only about 4%) of the solar radiation, whereas solar spectrum has about 40% visible region (400 to 700 nm), and it shows high recombination rate of photo-induced electron–hole pairs which may affect negatively the degradation ratio and rate [8]. In order to make TiO_2 suitable for receiving solar energy efficiently in a wide range from UV to visible, many methods such as dye sensitization, metal- or nonmetal-doped TiO_2- based nanoparticles, and modification of TiO_2 by the addition of another metal oxide-based semiconductor have been used. It has been shown that coupled semiconductors seem to be simple and viable photocatalysts. Photocatalytic process is based on the generation of electron–hole pairs by means of band-gapradiation that can give rise to redox reactions with the species adsorbed on the surface of the photocatalysts. In principle, the coupling of different semiconductor oxides seems useful in order to absorb a wide range of solar radiation and to achieve a more efficient electron–hole pair separation, and consequently, a higher photocatalytic activity will be attained [9]. Various composites formed by TiO_2 and other inorganic oxides such as ZnO [10], SnO_2 [11], SiO_2 [12], In_2O_3 [13], Cu_2O [14], MgO [15], WO_3 [16], MoO_3 [17], and so on have been reported.

ZnO is a suitable alternative to TiO_2 because its photodegradation mechanism has been proven to be similar to that of TiO_2. In fact, in comparison to TiO_2, ZnO has been reported to have higher photocatalytic efficiency [18,19]. ZnO can absorb over a larger fraction of UV radiation, and the corresponding threshold of ZnO is 425 nm [20]. Therefore, nanocomposites of ZnO/TiO_2 thin films can be used as photocatalysts to degrade/ decolorize organic dyes under solar irradiation in aqueous system.

In present investigation composite thin film of ZnO: TiO_2 have been deposited using spray pyrolysis technique. The structural and optical properties of deposited thin films were studied

METHODOLOGY

Undopped ZnO, TiO_2 and ZnO-TiO_2 composite films will be deposited by spraying zinc acetate in alcoholic solution. The films will be prepared at different parameters like solvent for deposition, substrate temperature, concentrations of dopants in the spraying solution, total quantity of spraying solution, spray rate etc. To yield good quality films in terms of transparency and conductivity. ZnO:TiO_2 were deposited at different composition, viz90ml:10ml, 80ml: 20ml, 70ml: 30ml, 50ml: 50ml. To obtain ZnO Zinc acetate $(CH_3COO)_{2Zn.2H2O}$ (0.2M) dissolve in 35 ml of distilled water, 65ml of (CH_3OH) and 5ml (CH_3COOH) is used. Substrate was heated towards the temperature on which films was deposited at 400^0C.The substrate to nozzle distance was maintained at 31cm.The time required to spray this solution is 11:45sec. To obtain TiO_2 (TAA) Titanium Acetyl Acetonate (0.1M) dissolve in methanol. Substrate was heated towards the temperature on which films were deposited about 480^0C.The time required to spray this solution is 13:21sec. The XRD study has been performed for identification of the crystal structure of ZnO: TiO_2. The Transmittance was measured by UV-Vis-NIR Spectrometer.

RESULT AND DISCUSSION

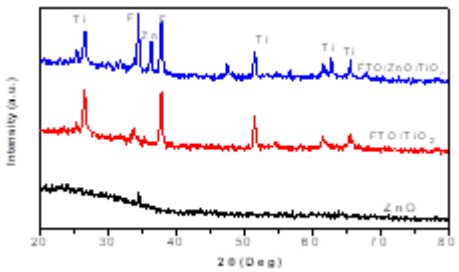


Fig.1. X-ray diffraction patterns of ZnO, TiO_2 and ZnO: TiO_2 thin films

Crystalline development of the thin films using X-ray diffraction analyzer ZnO normally forms the hexagonal (Wurtzite) structure with lattice constant (a= b=0.32 nm and c= 0.52 nm). Each Zn atom is tetrahedrally co-ordinated to four O atoms. The structural characterization of the sample was carried out by powder X-ray diffraction method performed on X-ray diffractometer Fig.1 shows the XRD patterns of ZnO and ZnO/TiO2 thin films. The entire ZnO thin films show only one diffraction peak which corresponds to the diffraction of (002) plane of ZnO with a hexagonal wurtzite structure. The diffraction peak can also be well indexed to the hexagonal phase ZnO reported in JCPDS card (No. 36-1451, a = 0.3249 nm, c = 0.5206 nm). The results indicate that the products consisted of a pure phase. This means all the ZnO thin films deposited on the glass or TiO_2 layered substrates are preferentially oriented along the c-axis perpendicular to the substrate surface. For the sample A and B their (002) peaks lie at 34.340. From the above data, it is clear that the (002) peak positions of ZnO/TiO_2 thin films are closer to the (101) peak position of ZnO powder. According to the order of sample A and B, the intensity of their (002) peaks gradually increases in sequence, but the full width at half maximum (FWHM) of the peaks gradually decreases [4,5]. It means the crystalline quality of ZnO thin films is improved after TiO_2 layers are used. The average crystallite sizes of the ZnO thin films can be calculated with Scherrer formula using parameters derived from XRD patterns. Scherrer formula is as follows:

$$D = 0.9\lambda/\beta\cos\theta$$

Where D is the crystallite size, λ is the X-ray wavelength, β is the FWHM and θ is the diffraction angle. As regards the sample B, there is not only the (002) peaks of ZnO thin films but also two peaks of TiO_2 layers in the patterns. One of them corresponds to the (200) diffraction peak (48.30°) of anatase phase, another corresponds to the (211) peak (56.05°) of rutile phase. But the main components of TiO_2 layer are anatase structured crystals**.**

Optical properties:

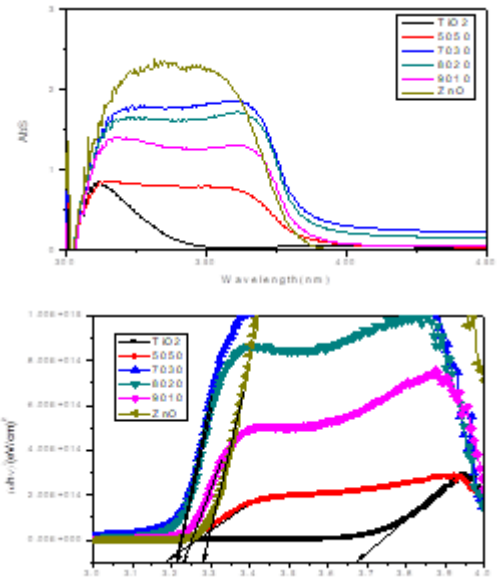
The absorption coefficient (α) has been determined as a function of wavelength from measured reflectance, R and transmittance, T, using following equation,

$$\alpha = 1/d \ln [(1-R)^2 / T]$$

Where d is the thickness of thin film, R and T the reflection and transmission, respectively. In high absorption region close to the beginning of band-to-band optical transmission, the absorption is characterized by the following relation,

$$\alpha = A (h\nu - E_{opt})^r$$

Where A is a constant, E_{opt} the optical band gap and r is the integer number which characterizes the transmission process.



The usual method for determining the values of E_{opt} involves plotting a graph of $(\alpha h\nu)^r$ vs hν. The optical energy gap, E_g = 3.11 eV, 3.27 eV, and 2.99 eV are deduced for ZnO, TiO_2 and ZnO: TiO_2 films respectively. The absorption edge of TiO_2, ZnO and ZnO: TiO_2 films are at around 391, 398 and 414 nm, respectively and similar results are reported by Zhang et al. The significant red-shift with lower band energy of ZnO: TiO_2 film comparing with the ZnO film and TiO_2 film may be owing to the differences in the surface state. The ZnO: TiO_2 film need lower energy to

be excited than the ZnO film and TiO_2 film. The reflectance of the films is shown in Fig. and inset shows transmittance. Transmittance is decreases from ZnO, TiO_2 to ZnO: TiO_2. The TiO_2, ZnO and ZnO: TiO2 film shows about 30 %, 8 % and2 % reflection respectively in visible region.

CONCLUSION

Composite of ZnO: TiO_2 thin film was deposited by a spray pyrolysis technique. The films were deposited onto glass as well as on FTO substrate at the selected temperature 450^0 C, 480^0 C respectively. The films has good optical quality properties and are well-suited for Solar Cell application. The optical energy gap, E_g = 3.26 eV, and 3.66 eV are deduced for ZnO, TiO_2 films respectively. The significant red-shift with lower band energy of ZnO: TiO_2 film comparing with the ZnO film and TiO_2 film may be owing to the differences in the surface state. The ZnO: TiO_2 film need lower energy to be excited than the ZnO film and TiO_2 film. It is seen that films are polycrystalline and having dominant orientation (002) and (101) for pure ZnO (hexagonal) and TiO_2 (tetragonal) thin films respectively while for coupled films it shows mixture of both phases. XRD depicts that required phases of respective materials has been achieved.

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