NANOCRYSTALLINE SnO2/TiO2 FOR SOLAR CELLS APPLICATION

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Abstract

The developments in the field of solar cells need to create a new material to improve the electrical properties, which leads to an increase in conversion efficiency. So, in this paper, nanocrystalline Tin dioxide (SnO2) as a thin film were synthesized and deposited on Titanium dioxide using chemical Spray pyrolysis technique (CSPT). The mixed aqueous solution of Tin chloride (SnCl2) was prepared at room temperature using magnetic stir and sprayed on glass slide at 300 ̊C. Our results indicated that the prepared films are smooth, homogeneous and have good adhesion to the substrate. The results of structural properties revealed that the synthesis films are polycrystalline in nature with prefer orientations (110) and (101) for SnO2 and TiO2 respectively. The optical properties results using UV-Vis spectrophotometer analysis shows that high transmittance (greater than 70 %) and wide optical energy gap 3.97, 3.93 and 3.88 eV for TiO2, SnO2 and SnO2/TiO2 respectively.

Keywords: Optical properties, pyrolysis technique, TiO2 and SnO2 thin films.

1. Introduction

Nanocrystalline Transparent Conducting Oxides (NTCO) such as SnO2, In2O3, CdO, ZnO etc., have wide range of artificial applications such as, direct energy conversion in solar collectors, transistors, optoelectronic devices, etc. [1-7]. Among the various promising NT-CO, the tin dioxide is one of the most important oxides used to manufacture solar cells and gas sensors due to excellent properties like wide optical band gap (Eg= 3.6 - 4.2 eV), n-type semiconductor material, high conductivity, lowest cost, best thermal stability, best mechanical and chemical durability[8,9]. There are several techniques used to prepare SnO2 films, including chemical vapor deposition (CVD)[10], pulsed laser deposition (PLD) [11], chemical bath deposition (CBD) [12], successive ionic layer adsorption and reaction (SILAR) [13], RF magnetron sputtering (RFMS) [14], vacuum evaporation deposition (VED) [15], spray pyrolysis deposition (SPD) [16], etc. SPD technique is a convenient and simple method, with low preparation costs and uncomplicated devices. The objective of this paper is to prepare n-type nanocrystalline SnO2 as a window layer for solar cells applications.
2. Experimental details

Commercial glass with dimensions of (25× 25× 1 mm³) was used as a substrate which cleaned ultrasonically with distilled water, methanol and acetone, finally dried with hot air. At room temperature, the high purity Tin Chloride dihydrate (SnCl₂ 2H₂O) of concentration of (0.1 M) was dissolved in distilled water and methanol with volume ratio (8:1) using magnetic stirrer (MS) for 40 minutes. In order to complete dissolving the substance, under continuous stirring, few drops of hydrochloric acid were added to the solution. The SPD technique were; The heater temperature was fixed to 300 °C, the distance between Nozzle height and substrate was 32 cm, Spray time of 5 sec and Stop time 15 sec. After ending the deposition process, the substrates were left on heater to complete the nucleation process, then after, the substrates kept in a desiccator for analysis. The same procedure was repeated to deposited SnO₂ on Crown glass coated with 200 nm titanium dioxide which provided from Sigma-Aldrich company. The set-up of SPD technique in figure (1).

3. Results and discussion

3.1. Structural properties

3.1.1. X-ray Diffraction (XRD)

X-ray diffraction (XRD) pattern of the deposited pure TiO₂, SnO₂ and SnO₂/ TiO₂ thin films are presented in figure 2. The presence peaks in this figure indicate that the films are polycrystalline. Figure 1a shows the X-ray diffraction of nanocrystalline TiO₂ thin film deposited on glass substrate using SPD technique. There are three peaks belong to TiO₂ which observed at 25.42º, 38.60º and 48.12º corresponding to (101), (112) and (200). The preferential growth orientation related to anatase phase of TiO₂. The preferential orientation of SnO₂ in figure (1 b) appears along (110) corresponding to 26.63º. Also, it can be observed three peaks along (101), (200) and (211) which are belonging to the tetragonal structure of SnO₂ which corresponding to 33.89º, 38.01º and 51.83º respectively. These results which agrees with (JCPDS card of 88-0287). Figure (1c) evidently depicts the XRD patterns for SnO₂/ TiO₂, all the peaks which appear in this figure related to a tetragonal structure of SnO₂. The increase in the intensity with decrease the full width at half maxima is attributed to increase the film thickness of composite structure of SnO₂/ TiO₂ which leads to increase of grain size of this film. The crystallite size values were calculated.
by using the Debye-Scherrer formula (equation 1) according to the FWHM of the predominant peak of each sample [17].

$$D_{hkl} = K \lambda / (\beta \cos \theta)$$  \hspace{1cm} (1)

Where: $D_{hkl}$ - Crystalline size, $\lambda$ = 1.54 Å (is the wavelength of X-ray), $K$ = 0.94 (is a constant), $\beta$ - Full width at half maximum (FWHM) intensity (rad.) and $\theta$ - Bragg’s angle. The results show that the average crystallite size values calculated from the prominent peak corresponding to the reflection planes of TiO$_2$, SnO$_2$ and SnO$_2$/TiO$_2$ were 6, 17 and 36 nm respectively.

![XRD spectra of nanocrystalline thin films](image)

3.1.2. Morphological analysis

Scanning Electron Microscope (SEM) was used to know the nature of the film surface. The images of nanocrystalline TiO$_2$, SnO$_2$ and SnO$_2$/TiO$_2$ thin films presented in figure (3a, b and c). The surfaces of the films were smooth, uniform and dense without cracks. Also, we observe that the clustered spherical granules of different sizes covered all the substrate. The dimensions of grains presented in three samples (a,b and c) are nearly equal.

![SEM images of nanocrystalline thin film](image)

Fig. 3: SEM images of nanocrystalline thin film: (a): TiO$_2$, (b): SnO$_2$ and (c): SnO$_2$/TiO$_2$
3.1.3. Atomic Force Microscopy (AFM) Analysis

Figure 3 shows AFM images of nanocrystalline TiO$_2$, SnO$_2$ and SnO$_2$/ TiO$_2$ thin films. It is clear that, the distribution of grains on the film surface is uniform and without cracking. The small roughness of surfaces indicated to the high homogeneity of the prepared films. This feature is important for applications in solar cells because it reduces the light reflection losses when it incident on the solar cell. The results of Root-mean-square (RMS), roughness average of surfaces (RA), Ten Point height (TPH) and average grain size (AGS) summarized in Table (1). The increase in the surface roughness and grain size of SnO$_2$/ TiO$_2$ film attributed to increase in a layer thickness.

![AFM images](image1)

Figure 4: AFM images of nanocrystalline thin film: (a)- SnO$_2$, (b)- TiO$_2$, (c)- SnO$_2$/ TiO$_2$
Table 1. The surface texture properties of the prepared samples.

| Sample     | Root mean square (nm) | Roughness average (nm) | Ten point height (nm) | Average grain size (nm) |
|------------|-----------------------|-------------------------|-----------------------|-------------------------|
| SnO\(_2\)  | 1.53                  | 1.15                    | 2.91                  | 67.08                   |
| TiO\(_2\)  | 1.75                  | 151                     | 3.02                  | 72.03                   |
| SnO\(_2\)/TiO\(_2\) | 2.39                | 2.07                    | 8.26                  | 77.36                   |

3.2. Optical properties

The optical properties of the nanocrystalline TiO\(_2\), SnO\(_2\) and SnO\(_2\)/TiO\(_2\) thin films deposited on glass substrate using the SPD technique have been investigated at room temperature using UV-VIS spectrophotometer in the range of 300-1100 nm. Figure 5 shows the transmittance as a function of wavelength of the prepared samples. The average transmittance in the visible region is greater than 70%. The transmittance spectrum depends on the chemical composition of the material, thickness, morphology and the reflectivity of the film. When the film thickness be thinner, this means that the number of atoms contained in the film is few and this leads to a smaller number of collisions between transverse atoms, which in turn leads to reduced absorption and increased transmittance.

\[
\alpha = \frac{2.3026 \, A}{t}
\]  

Figure 5: Transmittance versus wavelength of nanocrystalline thin film: (a)- SnO\(_2\), (b)- TiO\(_2\), (c)- SnO\(_2\)/TiO\(_2\)

Figure 6 shows the absorption coefficient (\(\alpha\)) versus wavelength of the nanocrystalline TiO\(_2\), SnO\(_2\) and SnO\(_2\)/TiO\(_2\) thin films were determined from absorbance measurements by using equation (2).
film was greater than $10^4$ (cm$^{-1}$) that is, the electronic transitions are direct transitions. This increase in the absorption coefficient is due to the increase in thickness, which will lead to the formation of secondary levels between the valence band and the conduction band, this means, that the electronic transitions between the valence and conduction bands occurring in addition to the normal electronic transitions.

The optical energy gap values ($E_g$) of prepared films have been determined using the following equation:

$$\alpha h\nu = A (h\nu - E_g)^n$$

Where $A$ is a constant. Figure 7 illustrate the optical energy gap ($E_g$) of TiO$_2$, SnO$_2$ and SnO$_2$/TiO$_2$ and the values of were 3.97, 3.93 and 3.88 eV respectively. These values of $E_g$ are greater than the corresponding bulk values TiO$_2$ and SnO$_2$ due to quantum confinement effect which take place due to the decrease in size from bulk to nanoparticles.
4. Conclusions

- Nancrystalline TiO₂, SnO₂ and SnO₂/TiO₂ thin films are successfully deposited on glass substrate using the SPD technique.
- TiO₂ film exhibited structure with prefer orientation (101) and SnO₂ film exhibited tetragonal structure with prefer orientation (110).
- The prepared films have low roughness and nanocrystalline grains with uniform distribution on the substrate.
- The optical transmittance in the visible region greater than (70%).
- The optical band gap values were 3.97, 3.93 and 3.88 eV corresponding to TiO₂, SnO₂ and SnO₂/TiO₂ respectively.
- Depending on the our results these films can be used as a optical window in solar cell.

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