CNTs modified ZnO and TiO₂ thin films: The effect of loading rate on band offset at metal / semiconductor interfaces

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Abstract. ZnO and TiO₂ are direct wide band gap semiconductors with intriguing properties. A wide range of applications makes it one of the most studied materials in the past decade, particularly when elaborated as nanostructures. In this work, we focus on synthesis of CNTs modified ZnO and TiO₂ thin films using sol-gel method. The morphological and optical characterizations of the based ZnO and TiO₂ films were carried out using scanning and transmission electron microscopy (SEM and TEM), XRD and UV spectroscopy. Electrical properties of the deposited ZnO/CNTs and CNTs /TiO₂ were studied using I-V measurements at room temperature in metal/semiconductor/metal configuration, by the use of an array of metallic micro-electrodes deposited on the surface of the elaborated thin films. This allows determining qualitatively the electrical conductivity of thin films and the different parameters of the Schottky junction between the composites nano-films and the substrate. This study is necessary for future applications in solar cell.

1 Introduction

Solar energy is the most inexhaustible and available renewable energy [1-5]. Therefore, the development of photovoltaic devices has attracted much interest in the scientific world.

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Many materials are suitable for the design of photovoltaic devices, but many of them do not offer an optimal efficiency/cost ratio, thus limiting their expansion. Dye photovoltaic cells are commonly developed in the last decades as the 3rd generation of solar cells [6]. It is a simple and inexpensive technology according to the literature because it uses inexpensive and available semiconductor materials; for example: titanium dioxide (TiO₂) [7-11] or zinc oxide (ZnO) [12-15]. To make these cells more competitive it is important to study their characteristics and the possibility of adding (and/or replacing some components with) other materials that can improve photon absorption and charge transport in the active layer and limiting charge recombination in order to increase the conversion efficiency of the cell. Our attention was drawn to carbon nanotubes (CNTs) because of their extraordinary physical and mechanical properties and the fact that they are good candidates for improving the performance of solar cells. In addition, they have good electrical conductivity to nanocomposite metal oxides [16-18]. It is also possible to use CNTs in the active layer with titanium dioxide (TiO₂) or zinc oxide (ZnO) as in the present study.

Titanium dioxide (TiO₂) is a semiconductor with three polymorphs: anatase (quadratic), rutile (quadratic) and brookite (orthorhombic) [19]. According to the literature, anatase is recognized as the most photo-catalytically active phase due to the mobility of electron/hole pairs within the material and the ease of their transfer to the surface [12, 20].

The exceptional electronic properties of the anatase phase of TiO₂, especially the low rates of electron-hole recombination, make this polymorph a suitable candidate for application in solar cells. Dye Sensitized Solar Cells (DSSC) systems, incorporating pure or modified anatase TiO₂ and based on the photo-catalytic principle, have been developed [21]. Due to its remarkable functional properties, the range of applications for TiO₂ is very wide. For example, for the application of self-cleaning glasses [22], filtration of wastewater into drinkable water [23-24], Dye Sensitized Solar Cells (DSSC), integrating pure or modified anatase TiO₂ and based on the photo-catalytic principle, have been developed [25].

The ZnO is a wide band gap semiconductor widely used in short wavelength optoelectronic applications. It has also been used as a photoanode material in DSSCs due to its high charge carrier (electron) mobility, transparency to visible light, the possibility of making it highly conductive by doping and its greater synthetic flexibility, as well as its advantageous morphology [26].

In this study we present a simple and economic method to elaborate thin films and we make a comparative study between ZnO and TiO₂ thin films loaded with CNTs by different mass percentage and to see the effect of CNTs in the optical and structural properties and to see the most efficient metal oxide for photovoltaic use.

2 Synthesis

2.1 Synthesis of CNT

The carbon nanotubes are of considerable interest for both fundamental and applied research. CNTs are nano-structures of the fullerene family. Their typical diameter is in the nanometre range, while their length can reach a few millimetres, or even a few centimetres [27]. Some nanotubes are semiconductors, others are good electrical conductors. CNTs have remarkable physical, mechanical and electrical properties (excellent thermal and electrical conductivity and high mechanical strength: a CNT is 100 times stronger and 6 times lighter than steel) which have opened the field to numerous and promising applications. The applications of nanotubes are numerous: new, more resistant materials, new textiles (bullet-proof vests, etc.), nanoelectronics based on nanotubes, new generation flat screens, medical applications, etc. CNTs can thus be used to elaborate high-performance composite materials, conductive polymers or technical textiles. They are already used in the fields of sports

equipment, aeronautics, automobiles, defence, medicine, etc. Nanotube powder also has multiple potential applications such as hydrogen storage, the manufacture of batteries for electric cars and photovoltaic [28]

The CNTs used in the experiments were prepared by chemical vapor deposition, and purified through the treatment of the concentrated mixed acid (nitric acid and hydrochloric acid), which was described in detail elsewhere [29-30].

2.2 Preparation of ZnO/ carbon nanotubes composite

ZnO/CNTs nanocomposites were synthesized using a sol-gel method based on Benyounes's work with slight modifications [12]. The solution-based strategies to synthesize ZnO nanoparticles typically require a precursor solution of zinc acetate-ethanol complex [31] or a long hydrolysis method [32]. In this work, we present a way to prepare small ZnO nanoparticles by directly mixing zinc acetate and CNTs. Dehydrated zinc acetate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ was chosen as the initial material to perform the experiment. Two-methoxy ethanol was used as solvent and monoethanol amide (MEA) as stabilizer. The zinc acetate dihydrate and CNTs were initially dissolved in a mixture of solvent (MEA) and stabilizer (two-methoxyethanol) at room temperature. The zinc acetate concentration was approximately 0.35 M while the molar ratio of MEA to zinc acetate $\text{Zn}(\text{CH}_3\text{COO})_2$ was 1.0. To get a clear and homogeneous solution, this mixture was stirred at 60 °C for 2 h. After the mixture was cooled at room temperature, it was used as a coating solution. After the mixture was prepared for 24 h, the coating was performed. The solution was poured onto glass substrates, with spin cycles of 1000 rpm for only 30 s. When the spin coating was done, the films obtained were dried at a temperature of 400 °C for 20 min on a hot plate. The objective of this process was to evaporate the solvent and to remove the organic residues. This whole procedure was repeated 12 times to get a thickness of the sintered films close to 800 nm.

2.3 Preparation of carbon nanotubes/TiO₂ composite

The coating solution for titanium isopropoxide: $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ is got by dissolving 2 ml of Aldrich 98% $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ and 5 ml of isopropanol solution: $\text{C}_3\text{H}_8\text{O}$, and then different weight percentages (%) of CNTs powders ranging from 0.05 wt% to 0.9 wt% CNTs had been dispersed in the resulting mixture. This mixture was agitated at 63 °C during 11 minutes. Next, it was added 5.5 ml of acetic acid: CH_3COOH . After that, the new mixture was stirred for 18 minutes. Thereafter, after two hours, the final mixture was agitated after adding 12ml of methanol CH_3OH to make the solution of sol-gel. The latter solution was spin-coated onto plain ITO glass substrates which had been previously soaked in methanol and acetone at different spinning speeds (2800, 3000 and 5000 rpm) for 30s, followed by a drying process at 100-110°C for 10 min to evaporate the solvent. At last, the annealing temperature was subsequently raised from (100 to 500°C).

3 Characterization

After the TiO₂/ carbon nanotubes and ZnO/ carbon nanotubes thin films were prepared, the structural and morphological characterizations were characterized using AFM (atomic force microscopy) and SEM (scanning electron microscopy). UV-Visible transmission spectroscopy was used to study the optical properties. The optical transmission spectra were measured in the visible and near UV range. As a result, this method permits to determine the transmission T (%) of a material from a given wavelength λ that has been precisely selected.

The optical transmission spectra of the thin films developed were recorded using a Spectrophotometer UV-Visible: (Jasco V-530) on the range of 300-800 nm wavelength.

4 Results and discussion

4.1 Optical Properties

In this work, we focus on synthesis of CNTs modified ZnO and TiO₂ thin films using sol-gel method, and make a comparative study of the effect of CNTs on ZnO and TiO₂ thin films.

The transmittance spectrum (T) of thin films versus wavelength at room temperature in the spectral range of 300-800 nm is presented in Fig. 1. The spectrums show a highly transmittance up to 89% in the visible domain for the uncharged thin film of TiO₂ (Fig. 1(a)) and 76% for the uncharged ZnO thin film (Fig. 1(b)), which indicates that TiO₂ and ZnO are highly transparent materials, it is emphasized that the transmittance in the overall wavelength range is significantly reduced with increasing CNT filler content ranging from 0.05 to 0.9 wt.% CNT up to 64% for CNT/TiO₂ and 30% for CNT/ZnO. Decreased optical transmittance is due to the fact that CNTs are not transparent and absorb incoming light and increase light scattering.

Fig. 1. Plot of transmittance (T) versus wavelength of doped thin films, a) TiO₂/CNT, b) ZnO/CNT

The value of the optical gap energy (E_g) of the film, the refractive index of the films, the optical constants and their thickness is determined from the spectrophotometer, which can record the optical transmission of the films according to the wavelength. This technique is based on the double relation light-matter. When the films under study absorb ultraviolet or visible light, the absorbed energy leads to the excitation of electrons that move to a higher energy level. For this purpose, we will use the following formulas given by the method of Manifacier and Swanepoel [33-34]. The thickness of the nanostructures is determined from the following equation:

$$d = \left(\frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \right) \quad (1)$$

With n_1 and n_2 present, respectively, the refractive indices of the films for the wavelengths λ_1 and λ_2 adjacent. The refractive indices in the spectral region of the transparent, low and medium absorption zones can be calculated as follows:

$$n_1 = \left[N_1 + (N_1^2 - S^2)^{1/2} \right]^{1/2} \quad \text{and} \quad n_2 = \left[N_2 + (N_2^2 - S^2)^{1/2} \right]^{1/2} \tag{2}$$

In addition, the Swanepoel coefficient (N) in the transparent spectral region can be calculated by the following expression:

$$N_1 = 2S \left(\frac{T_{\max 1} - T_{\min}}{T_{\max 1} \times T_{\min}} \right) + \left(\frac{S^2 + 1}{2} \right) \quad \text{and} \quad N_2 = 2S \left(\frac{T_{\max 2} - T_{\min}}{T_{\max 1} \times T_{\min}} \right) + \left(\frac{S^2 + 1}{2} \right) \tag{3}$$

Where S is the refractive index of the glass, $T_{\max}(\lambda)$ and $T_{\min}(\lambda)$ represents the maximum and minimum values for the transmission curve.

Using the equation 2 and 3 to determine equation 1 and determine the thickness d to determine the absorption α of the of the Epoxy/Silicone N-CNT nanocomposite films of which it is made using the Bouguer-Lambert-Beer relation [34]:

$$T = \exp(-\alpha d) \tag{4}$$

If transmittance T is expressed in (%), the absorption coefficient is shown by:

$$\alpha = \frac{1}{d} \ln \left(\frac{100}{T} \right) \tag{5}$$

We can from the transmittance spectra (T) calculate the optical Gap value of semiconductors from the Tauc formula (E_g (eV)) defined by the following equation using [35-36]:

$$(\alpha h\nu) = B (h\nu - E_g)^n \tag{6}$$

The relation can be rewritten in a logarithmic form such as:

$$\ln(\alpha h\nu) = \ln B + n \ln(h\nu - E_g) \tag{7}$$

Where α is the absorption coefficient, ν is the absorption frequency, B is constant, h is Planck's constant and n is dependent on the type of optical transition, The constant n depends on the nature of the optical Gap, it is $1/2$ for a direct optical Gap and 2 for an indirect optical Gap. To determine whether the electronic transition that occurred in the studied samples is direct or indirect, “ $\ln(\alpha h\nu - E_g)$ ” is plotted as a function of “ $\ln(h\nu)$ ” that has been fitted by equation 7 in the linear region in the plot, employing the means squares method, where B, n, and E_g are the fitting parameters, with this method being able to indicate the type of the optical transition of the TiO_2/CNT and ZnO/CNT thin films are direct.

The band gap energy has been obtained using the extrapolation of the linear part of the absorption edge $(\alpha h\nu)^2$

Table 1. Eg values versus loading rates of TiO_2/CNT @ wt % and ZnO/CNT @ wt %

TiO2/CNT wt %.	0	0.05	0.07	0.9
Eg(eV)	3.98	3.48	3.46	3.2
ZnO/CNT wt %.	0	0.05	0.07	0.9
Eg(eV)	3.45	2.76	2.71	2.31

From the transmission spectra, we deduced the optical gap of ZnO/CNT and TiO_2/CNT films using the relation (6). based on the plot of $(\alpha h\nu)^2$ versus incident photon energy (h ν) shown in Table 1, we can estimate the optical band gap by extrapolating the linear region in the x-axis $(\alpha h\nu)^2$. The obtained optical gap is high for the uncharged thin films of TiO_2 and ZnO (3.98 eV for TiO_2 and 3.45 for ZnO), because it is optically transparent and it means that no absorption is possible in the visible, they cannot be excited without being charged with another element to decrease the E_g , so we charge with CNT and we see in Table 1, that there is a decrease of E_g from 3.98 to 3.2 eV for CNT/TiO_2 and from 3.45 to 2.31eV for ZnO/CNT , this decrease in optical gap with the increase in charge rate is mainly caused by the addition of CNTs which influences the overall carrier concentration and the increase in free electron concentration which decreases the band gap (approximation between the

valence band and the conduction band). The band gap reduction effect has been clearly observed in ZnO films doped with CNTs than TiO₂. Therefore, the system becomes progressively more conductive with the addition of CNTs, which seems to slightly change the electronic band structure of the ZnO and TiO₂ film. Furthermore, the optical gap shift with increasing concentration of charged CNTs can also be correlated with the surface roughness and density of the film which explains the small Eg decrease of the CNT/TiO₂ thin film from 3.98 to 3.2 eV due to the film roughness. Absorption shift of ZnO/CNT and TiO₂/CNT nanocrystal line films can be explained by the Burstein-Moss effect [37-38]. In fact, the reduction of the band gap is beneficial for the photovoltaic efficiency of broadband semiconductors such as ZnO, as it is more efficient to use visible light.

4.2 Microstructural insight

4.2.1 Transmission electron microscopy (TEM) of CNT

Fig. 2. TEM images of CNTs

The CNTs were synthesized by CVD by using ethylene as the carbon source (CNT). Transmission electron microscopy (TEM) images of the CNT sample indicate the existence of uniform multi-walled CNTs, see Fig. 2.

4.2.2 Atomic force microscopy (AFM)

The surface condition of the films was observed by AFM microscopy. Fig. 3 shows the morphology, in three dimensions, associated with the TiO₂ and ZnO films.

Fig. 3. Atomic force microscopy (AFM) image. (a) 3D morphology of TiO₂ and (b) 3D morphology of ZnO

Indeed, the roughness depends on the chosen method of fabrication. This leads to different thicknesses of the films, which suggests different grain sizes of the ZnO and TiO₂ layer. Similarly, the observation of AFM images clearly shows a layer thickness of 650 nm for the TiO₂ sample and a value of 500 nm for ZnO

4.2.3 SEM micrographs of TiO₂/CNT and ZnO/CNT

Morphological study was performed on the surface of TiO₂/CNT and ZnO/CNT thins to understand the surface quality and size distribution of representative TiO₂ and ZnO thins films on top of ITO and show the homogeneous surface of the substrates, the characterization of each of the TiO₂ and ZnO nanoparticles samples was carried out with SEM (Scanning Electron Microscopy) microscope respectively.

Fig. 4. (a) SEM micrograph of ZnO and (b) SEM micrograph of TiO₂

Fig 4 (a) and (b) show SEM images of the fabricated ZnO/CNT and TiO₂/CNT thin films respectively. The images show a clear granular surface morphology that reveals the formation of crystallized TiO₂ and ZnO.

The hardened composites showed a very dense and with good relative smoothness on the surface. The SEM images showed that the CNTs particles were uniformly dispersed in the ZnO and TiO₂ films. As a result, it is clear that there is a good miscibility of the particles between the phases, and that CNTs are well inserted in the porous layer of TiO₂ and ZnO, that CNT surfaces are covered by the TiO₂ and ZnO particles, which mean that TiO₂ and ZnO is well grafted on CNTs. The SEM allows us to clearly see the connection between the CNT particles and the TiO₂ and ZnO films will increase the efficiency of the charge transport in the device since they have very good electrical conductivity.

5 Charge carrier effect on Schottky contact barrier

The Schottky junction is the simplest way to construct the photovoltaic cell. It is a single layer of semiconductor deposited between two electrodes. One electrode provides ohmic contact with the thin film, while the second should provide current rectifying properties. It is the electric field generated at the blocking surface which allows the dissociation of the excitons by forming a potential barrier. The mobilities of the carriers are generally low in such materials, which tends to increase the value of the series resistance.

The both studied oxides (ZnO and TiO₂) based nanocomposites thin films were investigated on optical point of view. Thin films showed high transmission property (up to 80%) in the visible wavelength region. The optical band gap narrowing is more likely caused by light absorption.

The obtained nanocomposites thin films are likely to be investigated for the feasibility of Schottky junction. To the best of our knowledge, this is the first time that such kind of composites is proposed for a photovoltaic application. In order to verify the origin of the photovoltaic effect, The energy band diagram metal-semiconductor is drawn. The depicted junction (Fig.5) is of a typical metal- ZnO/CNTs and metal-TiO₂/CNTs.

Metal is characterized by fermi level below which there is a pool of electrons. It could be due to two overlapping bands generally. The work function of metal is greater than the work function of the semiconductor. Within this study we made the ohmic contact using gold (Au).

Fig.5. Band diagram of Schottky junction at metal/semiconductor interface

According to Anderson Energy band law (also known as the electron affinity model), the characteristics of the band alignment are determined. The conduction band offset and valence band offset are expressed [39]:

$$\Delta E_c = \chi_2 - \chi_1 \tag{8}$$

$$\Delta E_v = (\chi_2 + E_{g2}) - (\chi_1 + E_{g1}) \tag{9}$$

Where χ is the electron affinity, E_g is bandgap, and subscripts 1 and 2 correspond to metal and ZnO or TiO₂, respectively. In our case, the work function is about 4.5 eV for ZnO [40], 1.39 eV for anatase TiO₂ [41] and 5 eV for Au. The studied interfaces produce Schottky

barrier, this barrier is not allowing the charge carrier transfer from semiconductor to the metal as indicated in Fig. 5 (a). The solution to this problem is the incorporation of more charge carriers and forward bias application (Fig. 5 (b)) so as to make higher level E_C offset leading to the occurring of fluent charge transfer, this is in a good consistence with the band gap narrowing, which is considered as an important key factor of the good conversion yield in solar cells. This effect was highlighted by some researchers who have used n-ZnO thin films to make potentially high-efficiency and low-cost solar cells [42-44]. Also in some other work, a nickel (Ni)-doped ZnO film was prepared by spray pyrolysis, and the optical band gap was reduced from 3.47 eV for un-doped ZnO film to 2.87 eV for 15% Ni-doped film [45].

Sundaram et al. evidenced that when ZnO is highly doped, the fermi level almost overlaps with the conduction band edge giving a rise to band alignment. Hence, the work function of ZnO is considered the same as electron affinity. Thus, in our case, these values result in ΔE_C and ΔE_V of ~ 0.5 eV and 1.81 eV, respectively.

6 Current-voltage characteristics

Two distinct junctions, Au-TiO₂/CNTs and Au-TiO₂/CNTs, were made to verify the cause of the photovoltaic effect.

Fig.6. (a) Current–voltage profile of Au-TiO₂/CNTs, (b) Current—voltage profile of Au-ZnO/CNTs

After obtaining the highly filled thin films, we evaluated the current–voltage characteristics of Au-ZnO/CNTs and Au-TiO₂/CNTs two junctions, Fig. 6; this clearly indicates two ohmic connections.

7 Conclusion

In this study, we succeeded to elaborate TiO₂/CNT and ZnO/CNT thin films by sol-gel method and deposited on ITO glass substrates. TiO₂ and ZnO are known for their applications in the fields of photovoltaic and photoactivity, the choice of the substrates is based on these applications. Indeed, the indium oxide coated glass substrate (ITO) is used in solar cells. Structural and morphological characterizations were determined by radiation diffraction, scanning electron microscopy (SEM) and atomic force microscopy (AFM), UV-vis transmission spectroscopy was used to study the optical properties, the results obtained suggest that the films are of fairly high optical quality.

We were able to see the effect of increasing the dopant concentration of our CNT material as absorption elements, the average transmittances in the visible region are decreased due to the induction of CNT which went from 89% in the visible region for the uncharged TiO₂ thin film to 64% for CNT/TiO₂ 0.9 wt.% CNT and 76% in the visible region for the uncharged ZnO thin film to 30% for ZnO/CNT 0.9 wt.% CNT, the increase in the amount of carriers leads to an increase in the visible absorption.

The results indicate that the film exhibits a direct optical transition with an E_g of 3.98 (uncharged TiO₂) to 3.2 eV for CNT/TiO₂ and 3.45 (uncharged ZnO) to 2.31 eV for ZnO/CNT as a function of loading rate which is in good agreement with the similar gap of the semiconductors. These results are very encouraging, they show an improved opto-electronic property compared to undoped materials and deserve to be further explored for the development of advanced devices especially for loaded ZnO that has very favorable optical character and their E_g decreases more than TiO₂ when loaded with CNT. These results also show that it was possible to modify the charged ZnO and TiO₂ films by inserting a charge and suggest that these thin films are good candidates for optoelectronics and solar cells applications especially for ZnO based thin films since the highly loaded samples exhibited band alignment at Au/ZnO-CNTs Schottky interface.

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