Structural, Morphological, Optical and Electrical properties of 1% Cu doped TiO_2 multilayer nano structured thin films deposited by Sol-Gel spin coating technique

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Multilayer (3, 5 and 7 layers) 1% Copper (Cu) doped Titanium dioxide (TiO_2) nano structured thin films were grown by sol–gel technique having spin coating onto glass substrates. The structural, morphological, electrical and optical properties of stacked layers films were measured by X-ray diffractrometer (XRD), field emission scanning electron microscopy (FESEM), four point probe technique and UV-Vis. spectrometer, respectively. The results of XRD showed that the titanium dioxide has brookite phase. FESEM revealed that the films consisted of nano particles with increasing size as the layers increases. EDX analysis confirmed the presence of Cu and TiO_2 atoms. Four point probe results showed that the electrical average sheet resistivity for 3, 5 and 7 layers is 8×10^6, 6.5×10^6 and 1.0×10^6 ohm-cm respectively. Films have 79% transmission in the visible region of spectrum and energy band gap (E_g) for 3, 5 and 7 layers of films are 3.813, 3.822 and 3.843 eV respectively, according to UV-Vis. measurements. The present work provides an easy and low cost synthesis technique for the deposition of optoelectronic devices.

(Received November 11, 2016; accepted August 9, 2017)

Keywords: Multilayer films, $Cu:TiO_2$, Sol-gel, XRD, Optoelectronics

1. Introduction

Titanium dioxide (TiO_2) has high refractive index ranging from 2.3 to 2.7, wide band gap, and show high transmittance (above 90%) in visible region. This makes it an important semiconductor material for optoelectronic devices [1, 2]. It has three common minerals among which, the activity of anatase phase has to be found greater than that of both brookite and rutile phases. Brookite and Anatase have metastable phases and at high temperature these phases shift to stable rutile phase [3]. The band gap energies for anatase, ruttlie and brookite phases are 3.2, 3.0 and 3.2 eV. Therefore, TiO_2 absorbs UV light having wavelength smaller than 380 nm, according to the relation $\lambda = 1240/E_g$ [4-6]. However, titanium dioxide has some disadvantages: the recombination rate of photo-generated hole-electron pairs is very high and due to low absorption wavelength in the visible region, show low response in this region [3]. It is found that the optical properties and electronic structure of TiO_2 is modified under the doping of transition elements. These transition metals reduce the rate of recombination of hole-electron pairs, and improve the "interfacial charge transfer efficiency". This is reported in literature [7-10]. It was reported that the Cu has advantages over other transition metals for doping in TiO_2 [11-15]. One reason for this is that atomic radii of Cu (86 pm) and TiO_2 (74.5 pm) are nearly equal. Therefore Cu will dissolved into TiO_2 crystal lattice [16]. The second reason is that Cu doped TiO_2 ($Cu:TiO_2$) shows low electron-hole recombination rate. It may acts as "trapping centre" for the "photo electrons" [4].

Many deposition techniques for growing multilayer thin films are reported in literature. Thermal evaporation [17], sol–gel [18], chemical vapor deposition [19] and sputtering [20] are few examples of deposition multilayer thin films techniques. The sol–gel technique has many advantages over other techniques. It is low cost, simple and requires low temperature synthesis technique [21, 22].

Upto now, no work has been reported on the stacked layers of 0.01 Cu: TiO_2 nano structured thin films, grown by "sol-gel spin coating method" which is low cost and large area deposition technique. Purpose of this study is to prepare cost effective and environmental friendly $Cu:TiO_2$ multilayer thin films by using sol-gel technique. In the present study, the "structural, morphological, electrical and optical properties" of multilayer $Cu:TiO_2$ nano structured thin films have been discussed. The results thus obtained will facilitate the deposition of easy and low cost synthesis method for optoelectronics devices like LEDs and solar cells.

2. Methodology

The Cu:TiO_2 multilayer thin films were prepared by using sol-gel method and characterized for structural, morphological, electrical and optical properties. Cu is doped into TiO_2 in the ratio of 1.0% using sol-gel spin coating techniques. The coating solution is prepared using TiO_2 nano-powder (0.4 g) as the dissolved precursor material in 5 ml of ethanol and 5 ml of Diethylene glycol, 1.0% of Copper acetate as the doping material is added in this solution. The solution was stirred for 3 days (72 hours) at room temperature (25 ˚C). The solution was aged for 1 day. Once, the solution is ready, place the washed substrate on the spin coater with rotation speed of 2000 rpm for 20 seconds. Add 8 drops of the sol-gel immediately after starting the rotation then heat the sample for 10 minutes at 150 ^{o}C. Thus thin film was deposited on the substrate. Finally, samples were annealed at 400 ^{o}C for 1 hour to make the homogenous and uniform films. Similarly, the other layers were deposited.

The structure, morphology and electrical properties of multilayer films were characterized by using "X-ray Diffraction (XRD) (PANalytical X'Pert PRO), Scanning Electron Microscope" (SEM) (Quanta 250 fei) and Four point probe technique (KIETHLEY Instrument having 1nV to 120nV, 6220DC and 2nA to 105mA)" respectively. The optical absorption of these films is characterized by using "HITACHI U-2800 UV-Vis spectrometer".

3. Results and discussion

3.1. XRD Explanation

XRD patterns of the films are shown in Fig. 1.

The obtained peaks reveal that TiO_2 films are of brookite phase having orthorhombic crystal structure (PDF # 65-2448). No ruttile and anatase phases were detected.

In 3 layers of Cu:TiO_2 film, two peaks of brookite TiO_2 (111) and (212) having grain sizes of 9.4 and 10.1 nm, respectively, are obtained.

In 5 layers, three peaks (111), (212) and (123) of brookite TiO_2 phase having grain sizes of 12.9, 10.4 and 14.8 nm, respectively, are obtained.

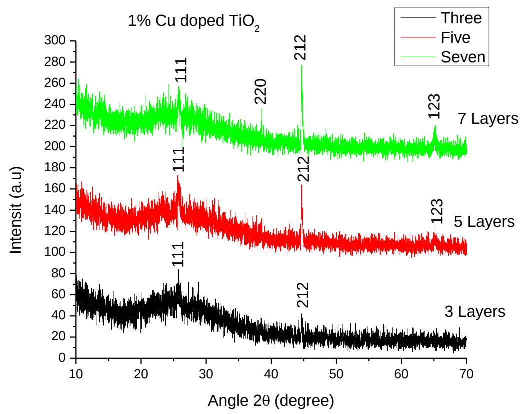

Fig. 1. XRD pattern of 3, 5 and 7 Layers of Cu doped TiO_2 thin films

Similarly, 7 layers film has four brookite (111), (220), (212) and (123) peaks with grain sizes of 14.4, 17.1, 3.82 and 14.2 nm, respectively. It is shown that when the number of layers is increased then the number of TiO_2 peaks are also increased which confirms the crystallinity of the films improve and defects decrease. This also confirms from the grain size, which is increased by increasing the number of layers. No extra peaks of Cu, CuO or cluster were detected which might be due to either very small Cu cluster size or small amount of Cu loading [23]. Peak shifts to the right according to PDF # 65-2448, which confirms the doping of Cu into TiO_2.

3.2. SEM Explanation

The surface morphology of films having 3, 5 and 7 layers is investigated by FESEM, as shown in Fig. 2 (a-c). All films consist of nano particles having average sizes of 20, 27 and 36 nm of 3, 5 and 7 layers, respectively. In layer by layer deposition, the particles of lower layer provided the base of upper layer because no extra phase has been formed which is confirmed from the XRD results. Therefore, the lattice mismatching between the particles is reduced and particle size is increased by increasing the number of layers. There is a direct relationship among the morphology and the electrical and optical properties of films which depended on the grain size and the grain boundaries. Several kinds of defects are present at grain boundaries like "dangling and impurities" [24]. As in multilayer thin films, grains boundaries are reduced by increasing the grain size therefore grain boundaries defects are also reduced. Thus the cystallinity, optical and electrical properties of the films are improved. These results are similar to literature [25].

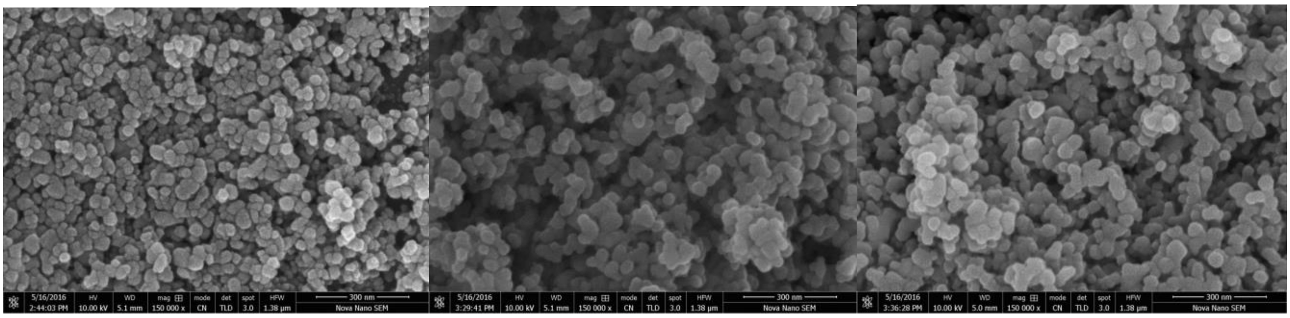

Fig. 2. FESEM micrographs of 3, 5 and 7 layers of Cu doped TiO_2 thin films

3.3. EDX

Energy dispersion X-rays (EDX) of 3, 5 and 7 layers of Cu:TiO_2 films is shown in Fig. 3. It is clear from EDX spectrum of figure 3 that the copper is successfully doped into TiO_2 because the copper peaks are shown in the spectrum. The weight percent of Copper (0.73%, 0.62% and 0.89%), Oxygen (34.14%, 37.47% and 35.51%) and Titanium (12.22%, 4.45% and 12.58%) for 3, 5 and 7 layers, respectively, are present in multilayer films. The other peaks appeared in EDX are due to elements present in substrate (glass).

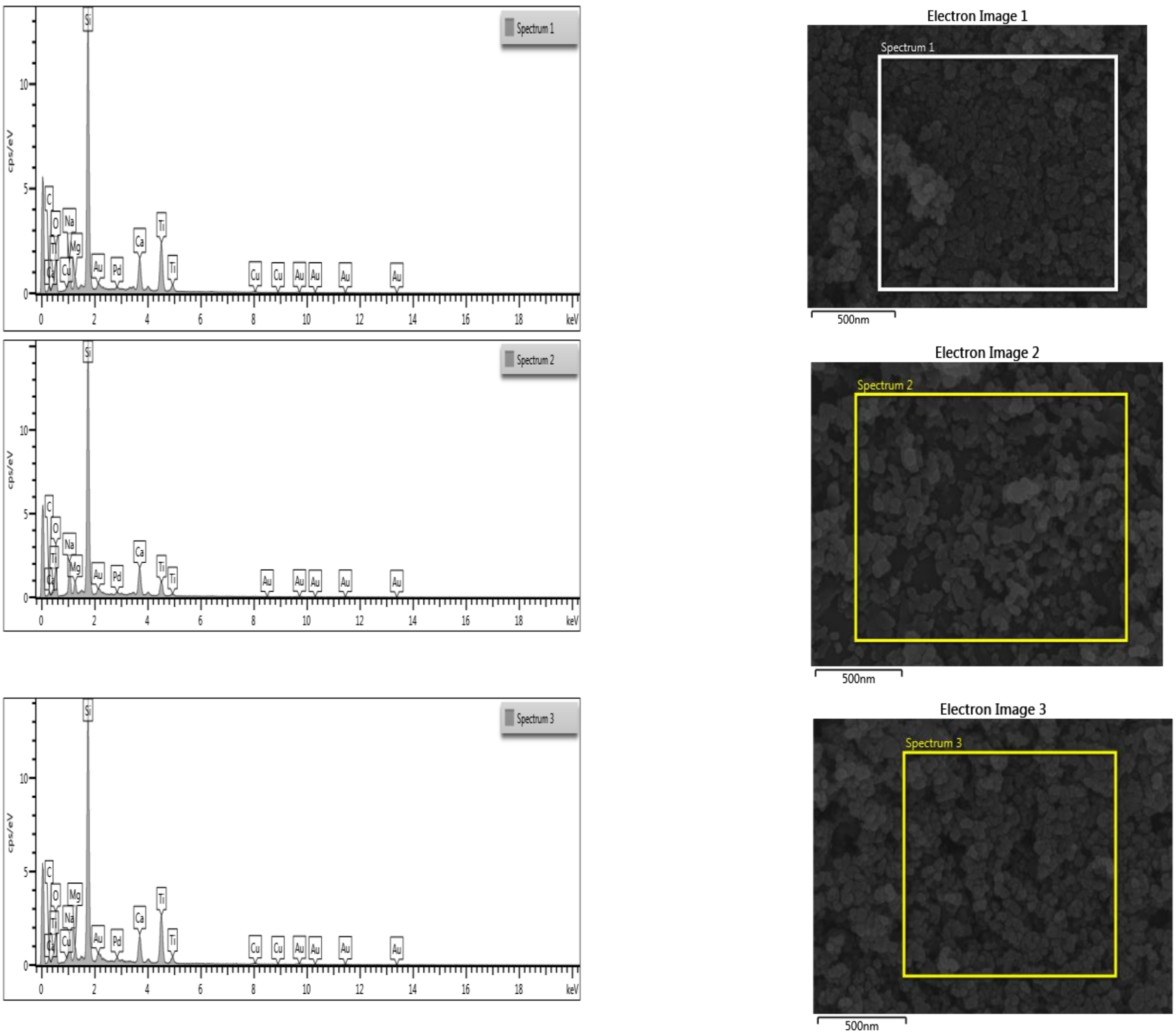

Fig. 3. EDX images of 3, 5 and 7 layers of Cu doped TiO_2 thin films

3.4. Electrical Properties

The sheet resistivity of cu doped TiO_2 (three, five and seven layers), semiconductor thin films were measured by using four point probe technique by using the following relation [26].

$$\rho = \frac{\pi}{\ln(2)} \cdot \frac{V}{I} \quad (1)$$

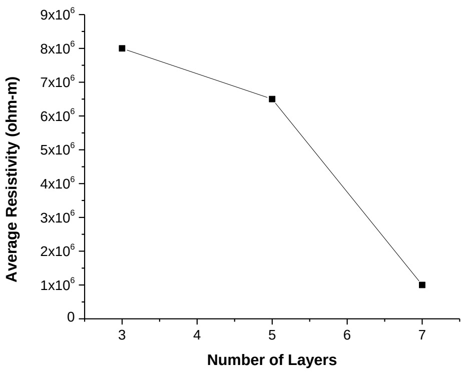

Fig. 4. Electrical resistivity vs. Number of layers (3, 5, 7) of 1% Cu doped TiO2 thin films

A graph between the average sheet resistivity and number of Cu:TiO_2 layers, plotted in figure 4. Results showed that the average resistivity of films decreased drastically by increasing the number of layers. Form graph it is observed that by the insertion of 5^{th} multilayer the resistivity gradually drops from 8×10^6 to 6.5×10^6 ohm – cm. when 7^{th} multilayer is added, there is rapid down fall in resistivity up to 1.0×10^6 ohm-cm. In multilayer films, the Fermi levels are in equilibrium because the layers are in contact with each other due to which electrons are easy to transfer from Cu to TiO_2 as like Ag/TiO_2/SiO_2 and TiO_2 [27]. Thus, the electrical properties of multilayer films are improved. Also it is observed in XRD and SEM that the grain size is increased by increasing the number of layers. Due to this, grain boundaries are reduced which increased the mobility of electrons and hence the resistivity decreased.

3.5. Optical Properties

The transmittance spectra of films are obtained by UV-Vis. spectrophotometer in the wavelength range between 250 to 750 nm (Fig. 5).

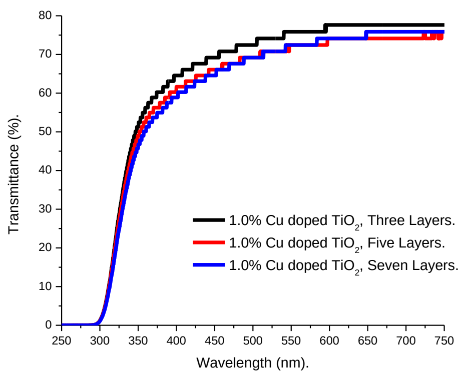

Fig. 5. Transmittance Spectra of 3, 5 and 7 layers of Cu doped TiO_2 thin films

It is clear that when the number of layers increases then transmittance slightly decreases. All films show high transmittance in the visible region with transmittance values between 62 to 79%. Since the calculated energy band gaps of multilayer films are approximately 3.8 eV. Therefore, these films absorbs photons with wavelength less than 326 nm, according to the relation λ_g (nm) = 1240/Eg (eV) (*6*). All these films show high absorption in the wavelength below than 300nm. When the wavelength of light increased from 300nm, then its transmittance increases. Upto 350 nm, the maximum obtained transmittance is 42%. Therefore, these films can be used for the protection of optoelectronic devices from UV radiations.

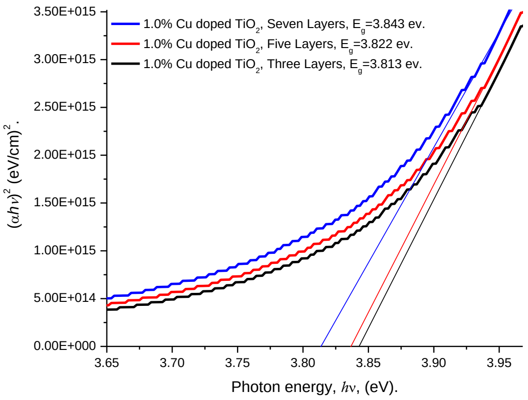

Fig. 6. Band Gap of 3, 5 and 7 layers of Cu doped TiO_2 thin films

The optical energy band gap of doped TiO_2 multilayer thin films are calculated by the following Tauc's relation [28].

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^n \quad (2)$$

Where, $h\upsilon$ is photon energy, E_g is band gap energy and n is transition. n = 2 and 1/2 for indirect and direct transitions, respectively [29,30]. "Optical band gap energy" is determined by plotted a graph between $h\nu$ and $\alpha h\nu$ is explained in Fig. 6. The calculated band gap energy for 3, 5 and 7 layers of Cu doped TiO_2 films are 3.813, 3.822 and 3.843 eV, respectively. This increase band gap is due to the increase in thickness of the films which is according to the literature [29]. Also, the reported value of optical band gap of TiO_2 is less than these calculated values, it might be due to the thermal stress effects produced in thin films [31].

4. Conclusion

Cu doped TiO_2 (Cu:TiO_2) multilayer thin films have been successfully grown on "glass substrate" by using "sol-gel spin coating technique". We have investigated the effect of multilayer on the *"structural, morphological,* *optical and electrical properties"* of the films. XRD confirmed the brookite phase of TiO_2. FESEM showed the nano particles on the films which have increasing trend with the number of layers. Electrical resistivity decreased by increasing the number of layers because the connection of multilayer with each other, align the Fermi levels in equilibrium by the transfer of electron from Cu to TiO_2. E_g is increased by increasing the layers which is due to increasing the thickness of the films.

Acknowledgement

This research project was partially supported by a grant from the "Research Center of the Female Scientific and Medical Colleges, Deanship of Scientific Research", King Saud University.

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