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# Energy gap of Gold-doped Titanium Dioxide Thin Films Deposited by Dip-coating on Fluorine Doped Tin Oxide Coated Glass

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## Abstract

In this study, the titanium dioxide ($TiO_2$) thin films and the gold nanoparticles-doped titanium dioxide ($Au/TiO_2$) thin films have been coated on the fluorine doped tin oxide glass (FTO) using dip-coating technique. The as-coated films were heated at 80°C and 500°C. The morphology and thickness of samples were characterised using Field Emission Scanning Electron Microscopy (FE-SEM). The band gap energy of the films have been examined from the optical reflectance spectra. The FE-SEM surface morphology results showed that the dense and uniform film deposited on fluorine doped tin oxide glass. The thickness of the prepared films was measured by taking cross sectional view of the films by FE-SEM. The average thickness of the films was approximately 820 nm. The presence of gold nanoparticles in the film is confirmed by Energy Dispersive X-ray spectroscopy (EDS). It was found that the energy gap of the prepared thin films was dependent on the heated treatment temperature. The values of energy gap for the films heated at 500°C were lower than that at 80°C. Moreover, the energy gap of gold doped titanium dioxide films was higher than the pure titanium dioxide thin film. The broadening of the energy gap can be explained by Moss-Burstein effect.

**Keywords:** $Au/TiO_2$ Thin film, Sol-gel, Band gap energy, fluorine doped tin oxide glass

## 1. Introduction

Titanium dioxide ($TiO_2$) thin films has been found to be useful for wide range of applications such as sensor [1], solar cell [2], protective and optical coating [3], antibacterial [4] and photocatalyst [5,6] due to its outstanding photocatalytic and antibacterial properties. Titanium dioxide introduces photocatalytic activity under ultraviolet (UVA: 320 – 400 nm) irradiation because of its wide band gap [7]. So far, many approaches have been endeavoured to extend optical response of titanium dioxide films from ultraviolet to the visible region (wavelength > 400 nm). In order to enhance photocatalytic activity, the doping of various metals such as silver (Ag), vanadium (V), chromium (Cr), nickel (Ni), iron (Fe), gold (Au), etc. in titanium dioxide films has been used [8-12]. Doping of a nanoparticles precious metals such as platinum (Pt), silver (Ag) and gold (Au) decreases the band gap of titanium dioxide for photo-excitation and lessens the recombination rate of electron-hole pairs [13]. Moreover, the gold nanoparticles have attracted attention because of localised surface plasma resonance which making titanium dioxide active under sunlight [14, 15]. However, the structure and optical properties of $TiO_2$ films are strongly dependent on the preparation methods. Many procedures have been used to prepare $TiO_2$ thin films such as electron beam evaporation [16,17], ion sputtering [18,19], chemical vapour deposition [20] sol-gel and dip-coating [21-23]. This paper aimed to study the effect of heated treatment temperature on the optical property of the prepared thin films. In the experiment, the titanium dioxide thin films and the

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gold nanoparticles-doped titanium dioxide thin films were prepared using dip-coating technique on FTO glass substrates.

## 2. Experimental

### 2.1 Preparation of $TiO_2$ sol and Au/$TiO_2$ sol.

All chemical reagents used in the present experiments were purchased from commercial sources and used without further purification. The reagents used for the sol preparation were listed in the Table 1 and the preparation of $TiO_2$ sol and Au/$TiO_2$ sol was shown in the Fig 1.

**Table 1.** Reagents used for sol preparation.

| Compounds | Properties |
|---|---|
| Titanium(IV)Butoxide<br>$Ti(OCH_2CH_2CH_2CH_3)_4$<br>Aldrich | M = 340.32 g/mol<br>$\rho_{20°C}$ = 1.00 g/cm$^3$<br>Reagent grade 97% |
| Ethanol<br>$C_2H_5OH$<br>Carlo Erba | M = 46.07 g/mol<br>$\rho_{20°C}$ = 0.789 g/cm$^3$<br>Reagents grade 99.9% |
| Ethylence glycol<br>$C_2H_6O_2$<br>Carlo Erba | M = 62.07 g/mol<br>$\rho_{25°C}$ = 1.113 g/cm<br>Reagents grade 99.5% |
| Diethanolamine<br>$HN(CH_2CH_2OH)_2$<br>Aldrich | M = 105.14 g/mol<br>$\rho_{25°C}$ = 1.097 g/cm$^3$<br>Reagent grade 97% |
| Gold colloidal<br>Kestrel Bio Science | Colloidal Gold -20 nm |
| Distilled water<br>$H_2O$ | M = 18.02 g/mol<br>pH = 6.9<br>$\rho_{20°C}$ = 0.998 g/cm$^3$ |

### 2.2 Preparation of TiO2 and Au/$TiO_2$ Thin Film.

Fluorine doped tin oxide conducting glass (FTO glass) (Aldrich, USA) was selected as the substrate for $TiO_2$ and Au/$TiO_2$ thin film. Dip-coating technique was used to coat FTO glass substrates by $TiO_2$ and Au/$TiO_2$ film. Before coating, the FTO glass substrates were cleaned with ethanol. The films were coated on FTO glass substrates by dipping into the solution and pulling it up in 3 sec. During the dipping process, thin liquid films stuck onto the two faces of the substrate. After coating, the samples were dried in air at room temperature for 1 hour. Subsequently, the coated glass samples were heated at 80 °C and 500 °C for 1 hour in furnace.

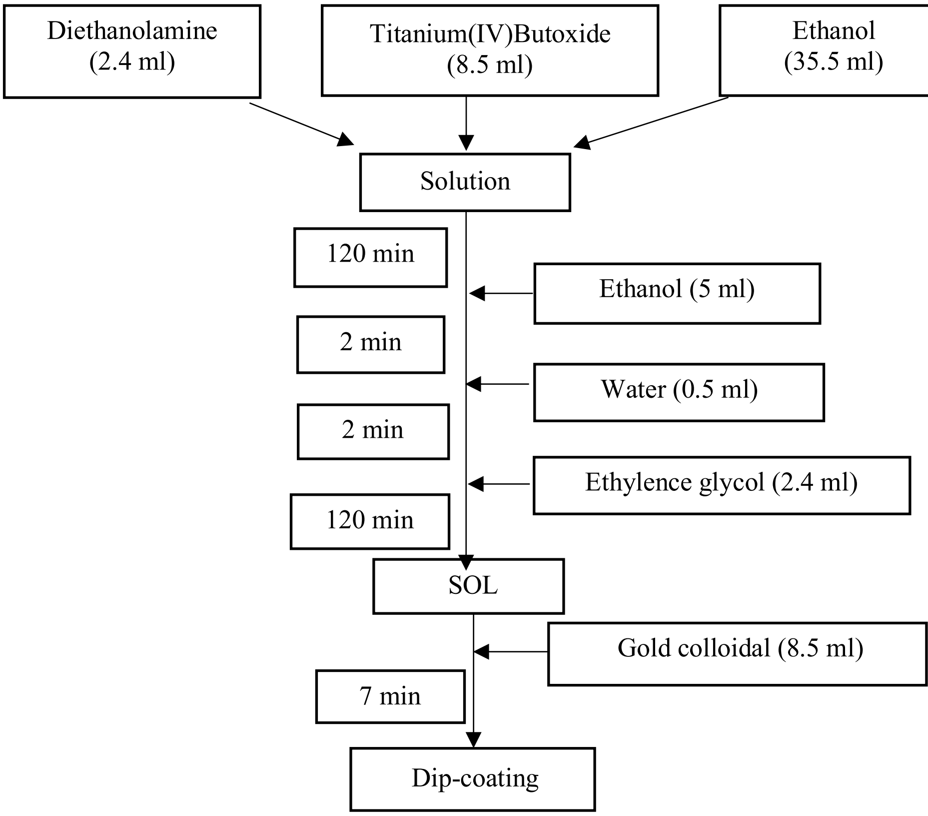



**Fig. 1.** Flow chart for the preparation of $TiO_2$ sol and Au/$TiO_2$ sol.

### 2.3 Material Characterization

The morphology and the thickness of the TiO2 and Au/TiO2 thin films were observed by means of Filed Emission Scanning Electron Microscope (FE-SEM) using JSM-7001F. The elemental composition of the samples was characterised by scanning electron microscopy-X-ray energy dispersive spectrum (SEM-EDS) with accelerating voltage of 20 kV. The optical characterisation of the TiO2 and Au/TiO2 films were recorded in the range of 200 – 1200 nm by a UV-Vis-NIR spectrophotometer (Shimadzu UV-2600).

From the optical absorption spectra, the band gap energy ($E_g$) of the films was estimated by the extrapolation of the linear portion of the $(\alpha h v)^n$ vs $hv$ plot using the relation [16,18,24].

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

where A is the constant, $hv$ is the photon energy, $E_g$ is the band gap energy (n = 2 for direct band gap and n = ½ for indirect band gap) and α is the absorptivity.

## 3. Results and Discussion

The FE-SEM images were taken in order to analyze the morphology and the thickness of the $TiO_2$ thin films heated at 80°C (Fig. 2(a)) and 500°C (Fig. 2(b)). According to the top

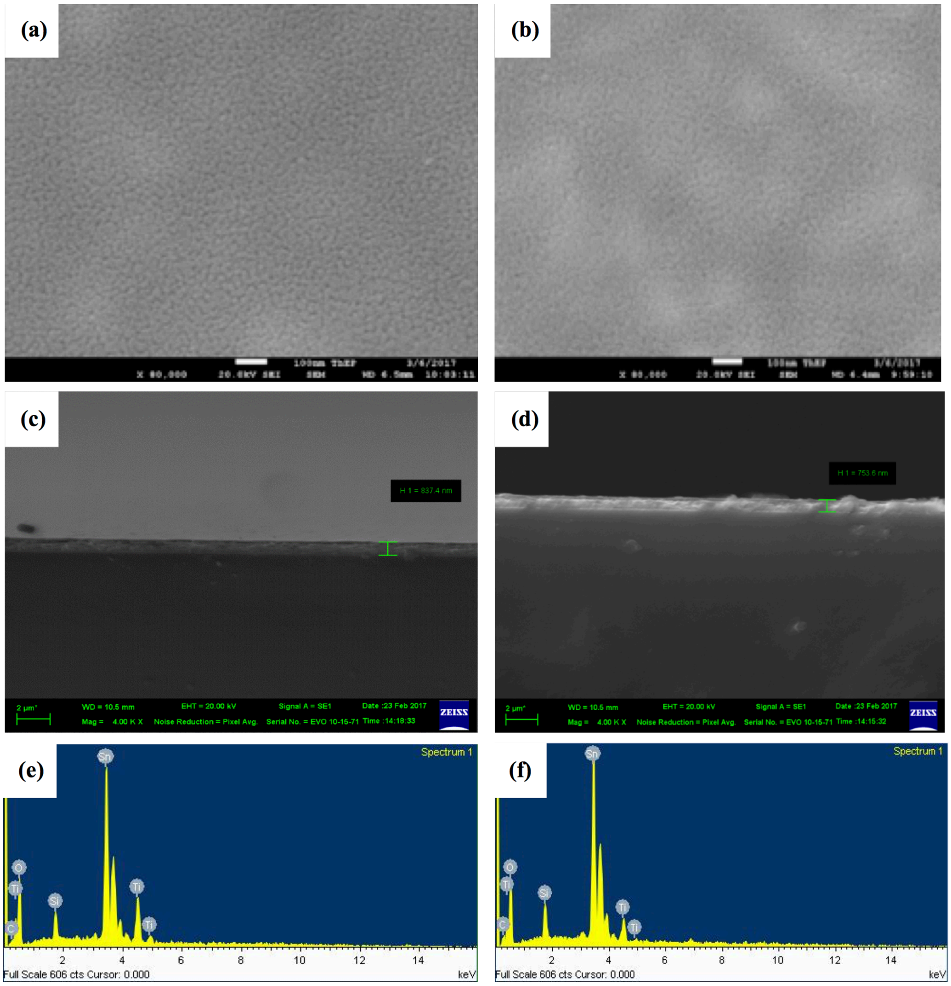



**Fig. 2.** Scanning Electron Microscopic images of top view of $TiO_2$ thin films deposited on FTO glass heated at (a) 80°C (b) 500°C and crosssectional view of $TiO_2$ thin films heated at (c) 80°C and (d) 500°C. SEM-EDS spectrum of $TiO_2$ thin films heated at (e) 80°C and (f) 500°C.

view FE-SEM images shown in Fig. 2(a) and 2(b), homogeneous and dense films were observed. The FE-SEM cross-section images showed that the thickness of $TiO_2$ thin films heated at 80°C (Fig. 2(c)) and 500°C (Fig. 2(d)) were 853.4 nm and 753.6 nm, respectively. Fig. 2(e) and (f) shown the EDS spectra of $TiO_2$ thin films heated at 80°C and 500°C. Tin (Sn), silicon (Si) and titanium (Ti) were detected. The quantification of $TiO_2$ thin films heated at 80°C led to 13.33 at% Sn, 2.97 at% Si and 2.65 at% Ti. For $TiO_2$ thin films heated at 500°C demonstrated to 13.10 at% Sn, 2.66 at% Si and 2.65 at% Ti. The $TiO_2$ thin films shown a high content of tin and silicon which originated from the FTO glass substrate.

The FE-SEM images of the Au/$TiO_2$ thin films which deposited on FTO glass heated at 80°C and 500°C in Fig. 3(a) and (b) shown dense and homogeneity film. Moreover, the Au/$TiO_2$ films were transparent with good adhesion on the FTO glass. The cross-section views

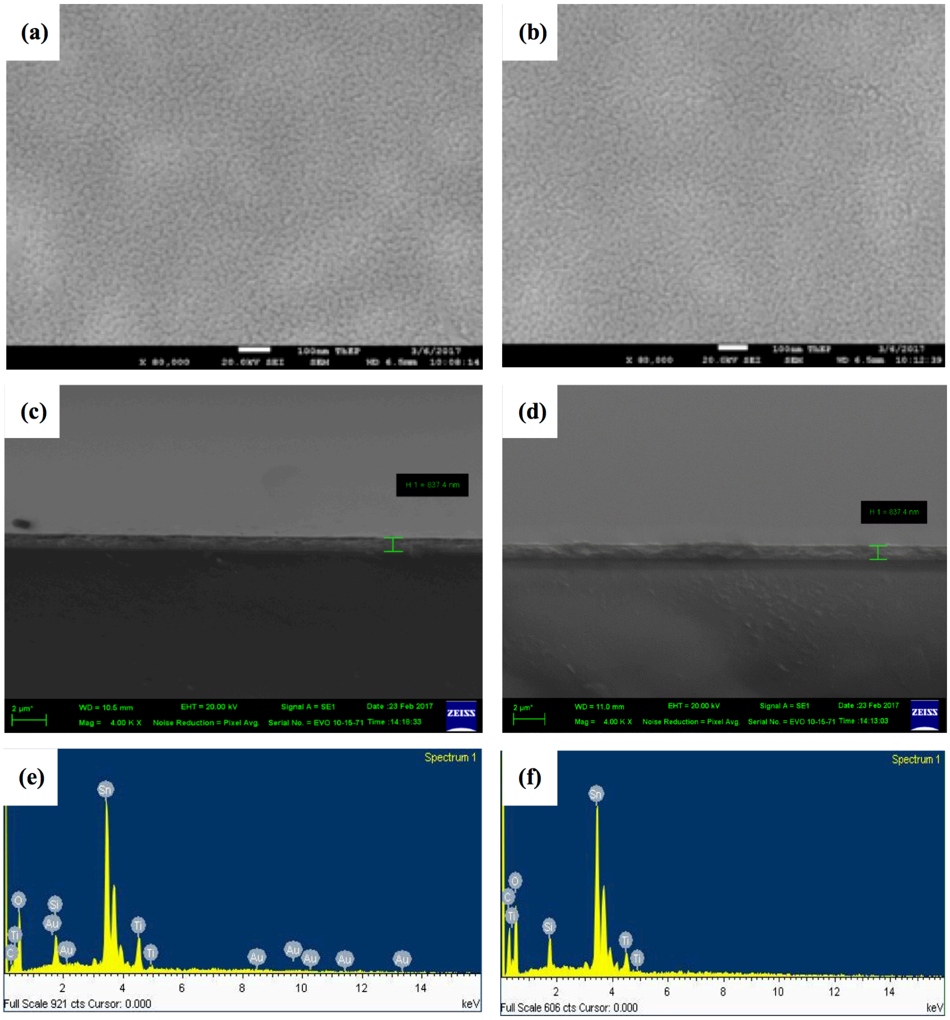



**Fig. 3.** Scanning Electron Microscopic images of top view of $Au/TiO_2$ thin films deposited on FTO glass heated at (a) 80°C (b) 500°C and crosssectional view of $Au/TiO_2$ thin film heated at (c) 80°C and (d) 500°C. SEM-EDS spectrum of $Au/TiO_2$ thin film heated at (e) 80°C and (f) 500°C.

revealed the film thickness and found to be constant throughout the film thickness. The thickness of the $Au/TiO_2$ thin films (Fig. 3(c) and (d)) was around 837.4 nm. In Fig. 3(e) and (f), the EDS spectrum of the $Au/TiO_2$ thin films can be seen. The results revealed the elemental composition of the films. The $Au/TiO_2$ thin film heated at 80°C was found to have 13.91 at% Sn, 3.64 at% Si, 2.73 at% Ti and 0.12 at% gold (Au). For the $Au/TiO_2$ thin films heated at 500°C were found to have 9.11 at% Sn, 2.07 at% Si and 1.97 at% Ti. The results showed that the gold nanoparticles were secreted from the film during annealing. This is in agreement with the similar study [25].

Figure 4 shown UV-vis transmittance spectra of the prepared thin films on the FTO glass substrates over the 200 – 1200 nm ranges for the samples heated at 80°C and 500°C. It is clear

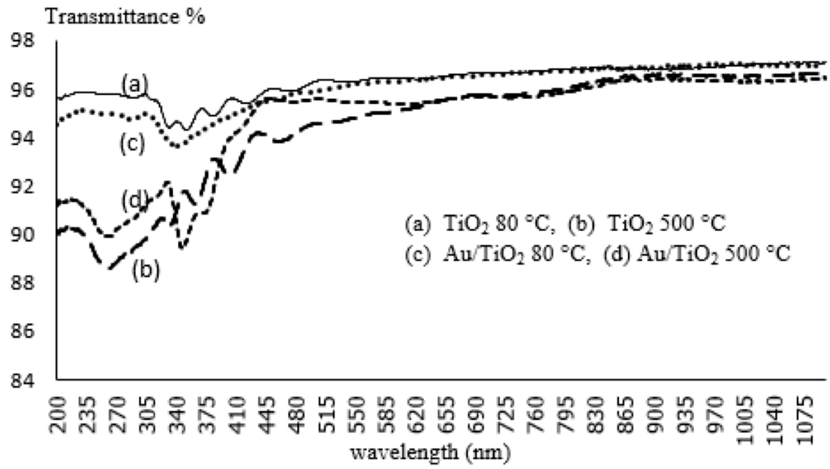



**Fig. 4.** The transmittance spectra of (a) $TiO_2$ heated at 80 °C (b) $TiO_2$ heated at 500 °C (c) $Au/TiO_2$ heated at 80 °C and (d) $Au/TiO_2$ heated at 500 °C under the same coated conditions.

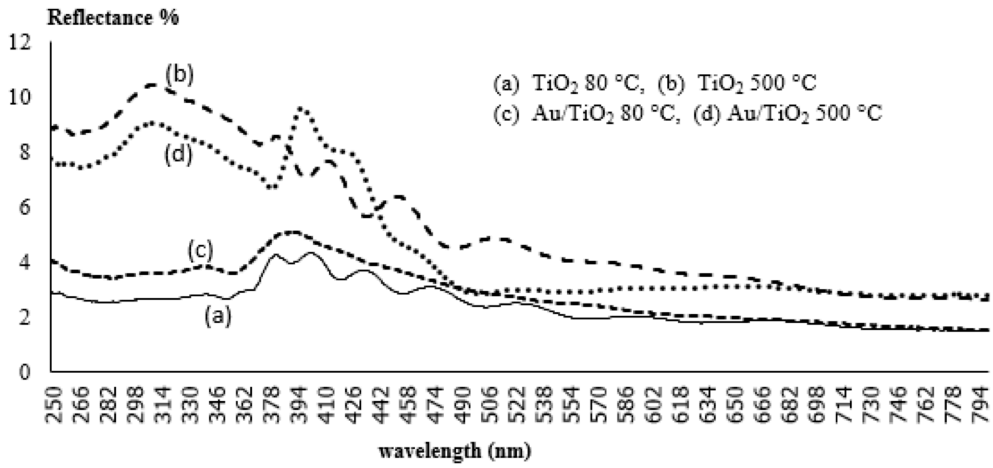
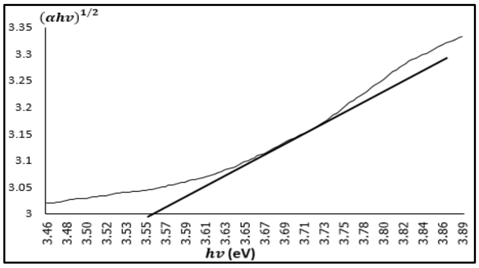


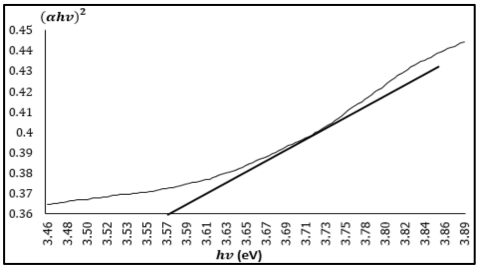

**Fig. 5.** The reflectance spectra of (a) $TiO_2$ heated at 80°C (b) $TiO_2$ heated at 500°C (c) $Au/TiO_2$ heated at 80°C and (d) $Au/TiO_2$ heated at 500°C under the same coated conditions.

from this figure that the prepared thin films were fully transparent in the visible-light region of spectrum with high visible transmittance. The average optical transmittance of the prepared thin films was 95%. A high transmittance of the thin film was an indication of low surface roughness and homogeneity [26]. The fringes effect from the multiple interface of the light reflected from the interfaces: air-thin film and thin film-substrate [27]. As a result, the transmittance of the prepared film and optical band gap decreased while the the refractive index increased with the heat treatment which explained on the basis of phase transformation from amorphous to anatase phase. This is in agreement with the result reported by the literatures [28-29].

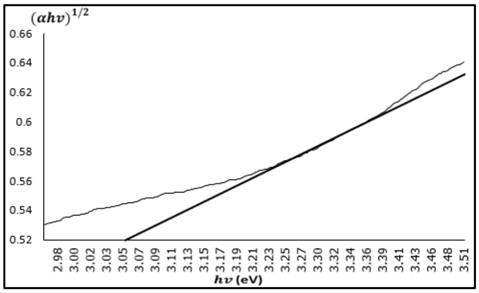
(a) $TiO_2$ thin film on FTO glass substrate heated 80 °C



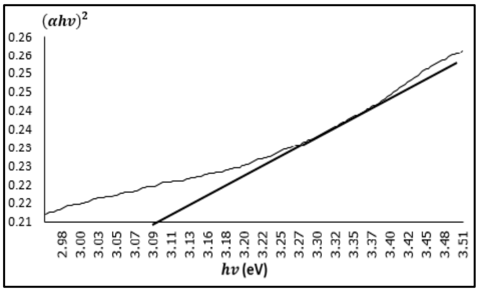

(b) $TiO_2$ thin film on FTO glass substrate heated 80 °C



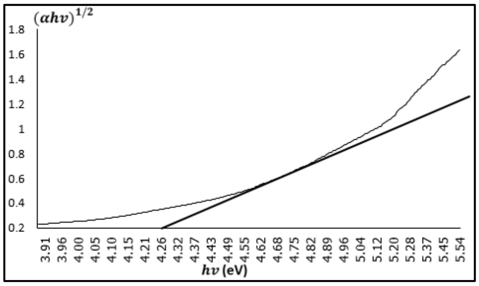

(c) $TiO_2$ thin film on FTO glass substrate heated 500 °C



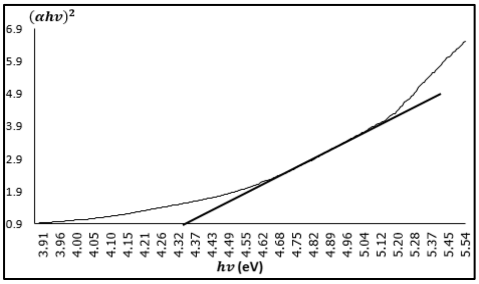

(d) $TiO_2$ thin film on FTO glass substrate heated 500 °C



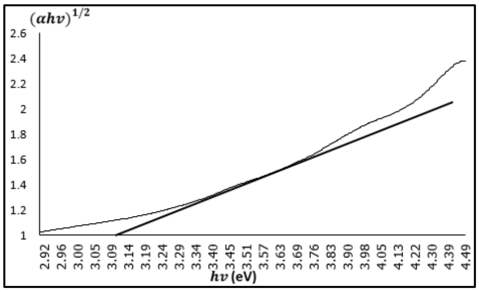

(e) Au/$TiO_2$ thin film on FTO glass substrate heated 80 °C




(f) Au/$TiO_2$ thin film on FTO glass substrate heated 80 °C




(g) Au/$TiO_2$ thin film on FTO glass substrate heated 500 °C




(h) Au/$TiO_2$ thin film on FTO glass substrate heated d 500 °C

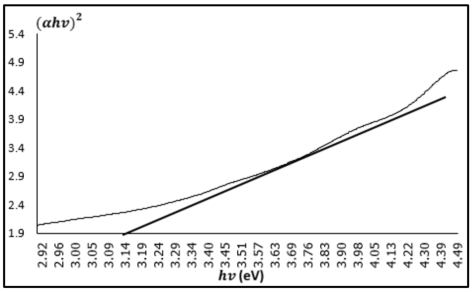



**Fig. 6.** A plotted of$(\alpha hv)^n$ vs $hv$ for determination of band gap.

Figure 5 shown UV-Vis reflectance spectra of the prepared thin films on the FTO glass substrates over the 200 – 1200 nm ranges for the samples heated at 80°C and 500°C. As can be seen, the prepared thin films have a low reflectance. The reflectance spectra for the prepared thin films can be noted that opposed to the transmittance.

The band gap of the samples was calculated from the plotted between $(\alpha h\nu)^n$ vs $h\nu$ (n = 2 for direct band gap and n = ½ for indirect band gap) as shown in figure 6. The estimated of band gap energies for the prepared thin films coated on FTO glass substrates are listed in table 2. The results shown that all cases of Au/$TiO_2$ thin films have higher band gap compared to $TiO_2$ thin films. The broadening of the band gap of the Au/$TiO_2$ thin films can be described by Burstein-Moss effect which the lowest states in the conduction band were blocked and transitions can take place when energies higher than Fermi energy [30,32]. Additionally, the gold nanoparticles constrained the grain growth leads to widen band gap [33]. The band gap of $TiO_2$ and Au/$TiO_2$ thin films decreased with increasing of the heated temperature from 80°C to 500°C. The decreased of the band gap with increasing temperature was owing to the lowering of the interatomic spacing (amorphous to crystalline). For the heated treatment at 500°C, amorphous thin films converted to crystalline anatase structure which decreased energy gap of all cases of the films. This phenomenon has been reported by the literatures [34-36]. The energy gap of the Au/$TiO_2$ thin films heated at 500°C decreased significantly to the value of 3.09 eV and 3.14 eV for an indirect-transition and direct-transition, respectively. This decrease in energy gap was due to the absence of the gold nanoparticles in the film.

**Table 2.** Variation of band gap with different heated treatment of the $TiO_2$ and Au/$TiO_2$ thin film on FTO glass substrates.

| Samples | Heated at 80 °C Eg (eV) | | Heated at 500 °C Eg (eV) | |
|---|---|---|---|---|
| | Indirect-transition | Direct -transition | Indirect-transition | Direct-transition |
| $TiO_2$ thin film on FTO | 3.55 | 3.57 | 3.05 | 3.09 |
| Au/$TiO_2$ thin film on FTO | 4.26 | 4.32 | 3.09 | 3.14 |

## 4. Conclusion

The The titanium dioxide thin films and the gold doped titanium dioxide thin films has been coated successfully onto FTO glass using dip-coating technique. It has been found that the heat treatment temperature affected the elemental composition and energy gap of the prepared thin films. FE-SEM images revealed that the prepared films were dense and homogenous. EDS analysis shown that the titanium dioxide thin films heated at 80°C and 500°C contain tin, silicon and titanium elements. In the case of the gold doped titanium dioxide thin film heated at 500°C, the gold nanoparticle emitted from the film. The prepared thin films demonstrate high transparency in the visible-light region of 400-800 nm. Calculation band gap of the prepared thin films were studied through UV-Vis spectroscopy. Band gap of all gold doped titanium dioxide thin films increased in comparison to titanium dioxide thin films. Moreover, thin films heated at 500°C shown lower band gap.

## Acknowledgements

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