# Optical properties of DC sputtered titanium dioxide/gold thin films

**M Sittishoktram*, E Ketsombun and T Jutarosaga**

Department of Physics, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok, Thailand

*nus_phy@hotmail.com

**Abstract**. Titanium dioxide ($TiO_2$) thin films have been generally accepted as an important material in the fields of photocatalysis, photovoltaic and photochromic. The efficiency of $TiO_2$ films as an active layer in various applications strongly depends on their optical properties. In this present study, the optical properties of sputtered $TiO_2$ thin films were modified using nanoparticles gold (Au) underlayer. $TiO_2$ thin films with 100 nm thicknesses were prepared by DC magnetron sputtering on gold coated glass substrates with the estimated thickness approximately 2, 6 and 10 nm. The deposited $TiO_2$/Au films were characterized using UV-Vis spectroscopy and photoluminescence (PL) spectroscopy. The transmittance of $TiO_2$/Au film in visible region decreased from 87% to 50% when thickness of gold underlayer increased from 0 to about 10 nm. In addition, energy gap of $TiO_2$/Au film from Tauc's plot decreased with the increase of the thickness of gold underlayer while the wavelength of peak emission spectra obtained from PL were found to be increased. The modified optical properties indicated the probability of light absorption which may lead to the increase in electron-hole pair generation in this composite film.

## 1. Introduction

Titanium dioxide ($TiO_2$) is an oxide of titanium in natural which useful as an active material in various applications such as dye-sensitized solar cell [1], fuel cell and optical coating [2]. In addition, it has also been widely used in the field of photocatalyst [3] such as anti-bacterial, water purification [4] and decomposition of various organics compound. $TiO_2$ has gained a great attention due to its non-toxic, high chemical and environmental stability, highly in the optical properties including brightness and refractive index in visible region, electrical properties and mass production from its activity [5].

The outstanding properties of $TiO_2$ thin films directly depend on the crystalline structure, morphology and especially its optical properties. Normally, $TiO_2$ film exhibits in three crystalline phases: rutile, anatase (tetragonal structure) and brookite (orthorhombic structure). Rutile phase is the most stable and mainly desirable for optical applications while anatase phase has much more attention because of its efficient photocatalytic ability and solar energy conversion. The difference in the phase and structure of $TiO_2$ film are related to its optical properties depending on deposition techniques, deposition times and deposition parameters.

$TiO_2$ thin films can be fabricated by using various techniques includes sol-gel method, pulse laser deposition, chemical vapor deposition, spray pyrolysis and sputtering technique. Among these techniques magnetron sputtering can deposit film on a large scale with highly uniform, dense and having good adherence to the substrate so it is suitable for industrial application.

Optical characteristics of $TiO_2$ thin films are important data which give the information about other physical properties like band gap energy and band structure. It was used to design the role of $TiO_2$ thin film for using in different applications. Many synthesis methods were studied and used to modify the structure and morphology of $TiO_2$ thin films for changing and improving their optical properties. Among them, sputtering of titanium in Ar-$O_2$ gas plasma on nanoparticles gold (Au) underlayer results in the change of $TiO_2$ structure. In this study, $TiO_2$ thin films were sputtered on various thickness of Au layer and the optical properties of thin film were characterized.

## 2. Experimental details

### *2.1. Thin film preparation*

Firstly, 1 cm x 1 cm glass substrates were cleaned in ultrasonic bath with deionized water, acetone and methanol at 40 $^oC$ for 10 minute then dried with nitrogen gas. Au layer was prepared on glass substrate using sputter coater (Cressington 108 auto) with approximate thickness about 2, 6 and 10 nm.

Reactive magnetron sputtering was used to deposit $TiO_2$ film on Au/glass substrate. For the deposition process, the sputtering chamber was evacuated down to the pressure about $1.8x10^{-5}$ mbar. Then argon and oxygen gas was introduced into the chamber at a constant flow rate of 10 sccm and 10 sccm, respectively. All the deposition was done with a fixed power of 200 W and a working pressure of $2x10^{-3}$ mbar. The deposition time was approximately 1 hour for 100 nm of $TiO_2$ film thickness.

### *2.2. Thin films characterization*

The optical transmittances of composite thin films were evaluated using UV–vis–NIR double beam spectrophotometer (Perkinelmer Instruments Lambda 35). The glass slide was used as a reference sample for baseline correction and the scan range was from 300 to 1,000 nm. To study the change in band gap when $TiO_2$ is considered as an indirect semiconductor, the optical indirect band gaps ($E_g$) of the composite thin films were determined from a Tauc plot using the relation

$$(\alpha hv)^{1/2} = A(hv - E_g)$$

where $\alpha$ is absorption coefficient, $hv$ is the photon energy and A is a constant of proportionality. The values of $E_g$ were obtained by extrapolating the linear part of the graph of $(\alpha hv)^{1/2}$ against $hv$ down to the photon energy axis.

To further investigate the optical quality of composited films, the photoluminescence (PL) spectra were recorded using fluorescence spectrophotometer (Hitachi F-2500) at room temperature. Films were excited with monochromatic light from 150W xenon lamp passing through the diffraction grating. The excitation wavelength of 285 nm, corresponding to photon energy of 4.35 eV which greater than band gap of $TiO_2$ was used to excite the electron in valence band to the conduction band.

## 3. Results and Discussion

### *3.1. Observation of thin film color*

The color in ambient light of Au nanostructure film, pristine $TiO_2$ film and composite film of $TiO_2$/Au at various Au films thicknesses was shown in Figure 1. The thickness of gold nanoparticle underlayer determined the color of Au film. A pink color changed to green and yellow when the thickness of the sputtered film changed from 2 to 6 and 10 nm due to the effect of surface plasmon resonance depending on the size of Au nanoparticle. The photograph of pristine 100-nm sputtered $TiO_2$ film on glass substrate showed light yellow while the films exhibited light green, dark green and yellow when 100-nm $TiO_2$ films were fabricated on Au layer with the thickness of 2, 6 and 10 nm, respectively. The color of $TiO_2$/Au films were related to the color of Au underlayer. However, there is a significant difference in color between 2-nm Au film and 100-nm $TiO_2$/2-nm Au film. This might occur from the reflection and destructive interference of reflected light from $TiO_2$ and that from the Au underlayer.

*3.2. UV–Vis measurement and optical band gap*

The optical properties of $TiO_2$/Au composite thin films were found to be influenced with the thickness of Au layer as shown in Figure 2. Samples showed good transparency in visible region but sharp fall in the ultraviolet region corresponding to the energy gap of film. The pristine $TiO_2$ showed strong absorption at 390 nm related to the excitonic absorption. The average percentage transmittance of $TiO_2$ film decreased from 88.4 to 69.4, 56.2 to 52.3 for pristine $TiO_2$ film and those prepared on Au layer with the thickness 2, 6 and 10 nm, respectively.

The square root of $(\alpha hv)$ versus the incident photon energy was plotted in Figure 3. The indirect band gap ($E_g$) was extracted from the x-intercept of the extension of the linear part of the graph. The $E_g$ values of each condition were presented in Figure 4. This indicated that the $E_g$ values of $TiO_2$ composite film decreased with the increase of Au layer thickness.

*3.3. Photoluminescence spectra measurement*

The Gaussian fitting of the PL spectra of pristine $TiO_2$ film and $TiO_2$/Au layer with the thickness 2, 6 and 10 nm were shown in Figure 5. PL spectra of glass substrate were observed in all samples because the film thickness is less than the penetration of excitation. The PL spectrum of pristine $TiO_2$ exhibited UV emission peak at 3.1 eV and two green emission peaks at 2.5 eV and 2.7 eV. Generally, UV emission peaks are defined as near-band-edge luminescence which is directly related to the recombination of excited electron and hole. On the other hand, green emissions directly corresponded to structural defects, such as oxygen vacancies [6].

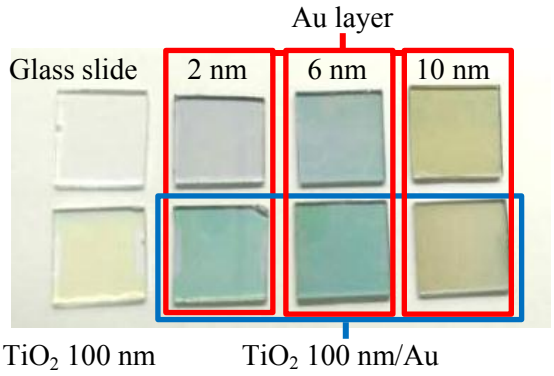


**Figure 1.** Coloring of Au film with the thickness 2, 6 and 10 nm, $TiO_2$ 100 nm and composite film $TiO_2$/Au.

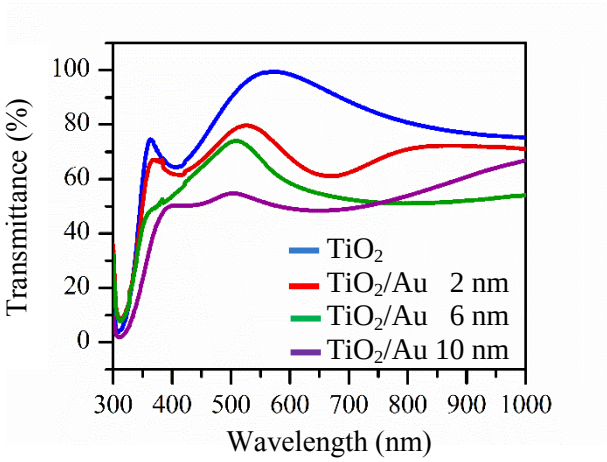


**Figure 2.** Transmission spectra of $TiO_2$ film and composite film $TiO_2$/Au.

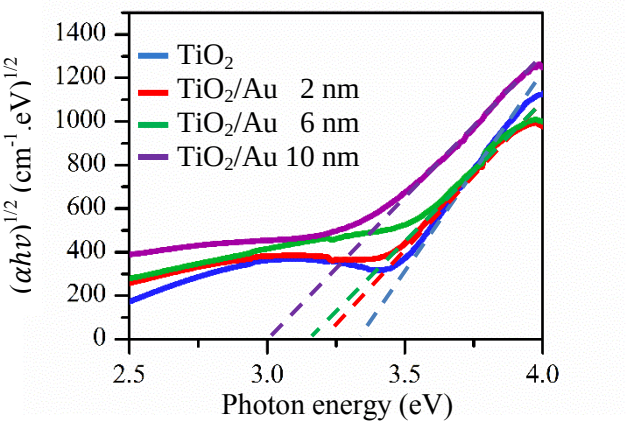


**Figure 3.** Plot of $(\alpha hv)^{1/2}$ versus photon energy $(hv)$ of $TiO_2$ and $TiO_2$/Au composite films.

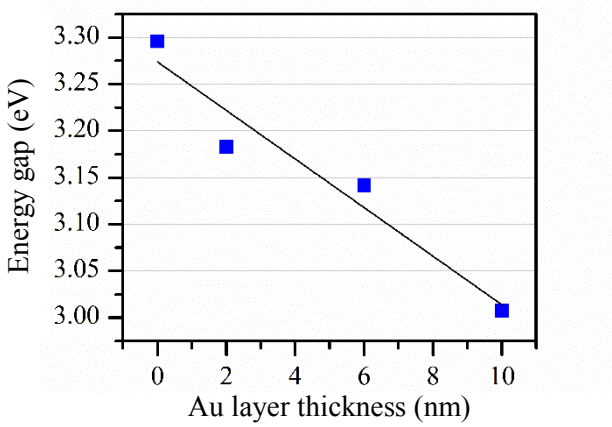


**Figure 4.** Variation of optical band gap energy of $TiO_2$ film on various Au layer thickness.

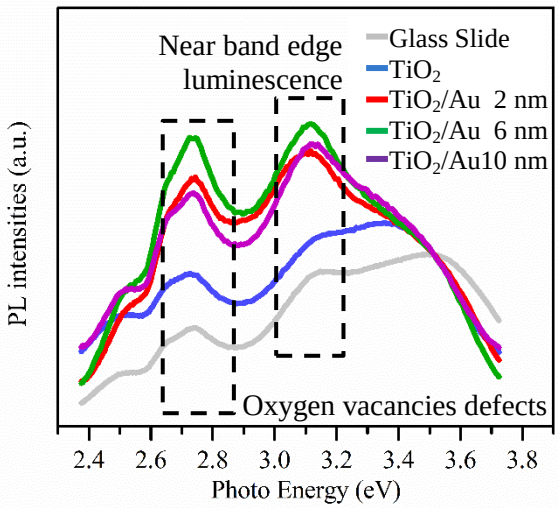


**Figure 5.** Room-temperature PL spectra of $TiO_2$ film on various Au layer thickness.

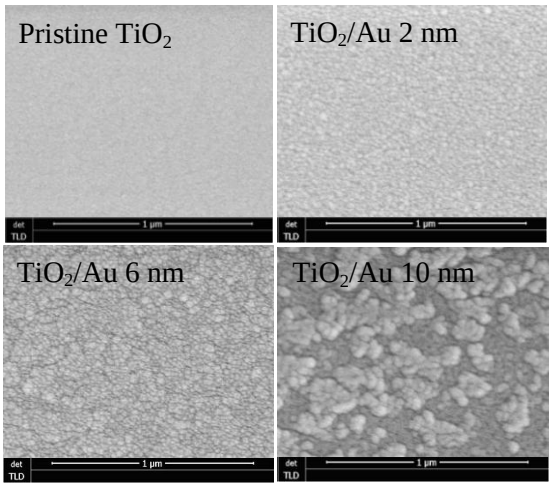


**Figure 6.** SEM images of 100 nm $TiO_2$ thin films on different Au layer thickness.

As shown in Figure 5, the intensities of PL peaks at 3.1 eV and 2.5-2.7 eV significantly increased when $TiO_2$ films were deposited on Au underlayer. The change of PL intensities might be due to the growth of $TiO_2$ nanostructures caused from the Au underlayer. During the growth process of $TiO_2$, there might be stress developed at the interface between the molecules of deposited $TiO_2$ and Au layer [7]. The driving force from stress-assisted growth process leads to the change in $TiO_2$ structure. This result could be confirmed by the $TiO_2$ film morphology from FESEM images. In Figure 6, agglomeration of $TiO_2$ nanoparticles were observed as the Au thickness increased. This agglomeration might one of the reasons that facilitated the radiative recombination of the electron-hole between conduction and valence band resulting in the enhancement of near band-edge emissions intensity. The other reason might be that Au nanoparticles embedded in the $TiO_2$ films contributed their excited electrons to the conduction band of $TiO_2$. The recombination of these contributed electrons increased the intensity of the near band edge of $TiO_2$. Moreover, the less uniform distribution of $TiO_2$ and their agglomerates caused the rough and high surface area of the film leading to the formation of oxygen vacancies. Therefore, the oxygen vacancies are responsible for the higher in green emissions peaks.

## 4. Conclusion

The optical properties of $TiO_2$ film prepared by dc magnetron sputtering on various thickness of Au layer coated on glass substrate were investigated in detail. The change of composite films' color depended on the color of Au layer. The UV-Vis spectroscopy revealed the decrease of film transmittance with the increase of Au underlayer thickness. The indirect band gap energy for composite of $TiO_2$ on Au underlayer with the thickness of 0, 2, 6 and 10 nm were 3.29, 3.18, 3.14 and 3.00 eV, respectively. Furthermore, PL spectra investigation showed the effect of Au underlayer on the morphology and structure which affect the optical changing of $TiO_2$ film.

## References


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