การหาค่าคงที่ทางแสงและความหนาของฟิล์มบางไททาเนียมไดออกไซด์ด้วยวิธีซอง

Determination of the Optical Constants and Thickness of Reactive Sputtered TiO_2 Thin Films by Envelope Method

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บทคัดย่อ

งานวิจัยนี้ได้เคลือบฟิล์มบางไททาเนียมไดออกไซด์ ด้วยระบบรีแอคตีฟ ดีซี อันบาลานซ์ แมกนีตรอน บนกระจกสไลด์และแผ่นซิลิกอน ฟิล์มบางที่เคลือบได้จะนำไปศึกษาโครงสร้างผลึกด้วยเทคนิคการเลี้ยวเบนรังสีเอกซ์ ความหนาฟิล์มวัดด้วยเทคนิค เอ เอฟ เอ็ม ผลการศึกษาพบว่า ฟิล์มบางไททาเนียมไดออกไซด์ที่เคลือบได้มีเฉพาะเฟสรูไทล์ (1 1 0) ($2\theta = 27.49^{\circ}$) ความหนาฟิล์มประมาณ 296 nm ค่าคงที่ทางแสงของฟิล์มบางได้แก่ ดัชนีหักเห n และค่าสัมประสิทธิ์การดับสูญ k หาด้วยวิธีซองจากค่าการส่งผ่านแสงในช่วงตามองเห็น เท่ากับ 550 nm พบว่าดัชนีหักเหมีค่าเท่ากับ 2.47 และค่าสัมประสิทธิ์การดับสูญมีค่าเท่ากับ 0.005 ตามลำดับ ค่าสัมประสิทธิ์การดูดกลืน α และความหนาฟิล์ม d คำนวณจากรูปแบบการแทรกสอดของการค่าส่งผ่านแสง พบว่าค่าแถบพลังงานและความหนาของฟิล์มมีค่าเท่ากับ 3.1 eV และ 301 nm ตามลำดับ

คำสำคัญ : ไททาเนียมไดออกไซด์ สปัตเตอริง ค่าคงที่แสง ความหนาฟิล์ม วิธีซอง

Abstract

Titanium dioxide thin films were deposited by reactive DC unbalanced magnetron sputtering system on glass slides and silicon wafers. The crystal structure was characterized by XRD (X-ray diffraction) where as film thickness was evaluated by AFM (atomic force microscopy). It was found that TiO_2 thin films showed only one peak, corresponding to the rutile (1 1 0) phase ($2\theta = 27.49^{\circ}$) with thickness about 269 nm. Optical constants namely refractive index n and extinction coefficient k, were determined from transmittance spectrum in the visible regions by using envelope methods. For 550 nm light, $n = 2.47$ and $k = 0.005$ were found. Absorption coefficient α, and the thickness of the film d were calculated from interference of transmittance spectra. The energy band gap, and the thickness of the films were evaluated as 3.1 eV and 301 nm, respectively.

Keywords : titanium oxide, sputtering, optical constants, film thickness, envelope method

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Introduction

Titanium dioxide, TiO_2, films are extensively used in optical thin film device applications owing to their appropriate optical properties, high thermal and chemical stability in hostile environments (Mardare & Hones, 1999). These films present good durability, a high transmittance in the visible spectral range and a high refractive index, so that they are suitable for many applications, such as: antireflection coatings, multilayer optical coatings (used as optical filters), optical waveguides, photovoltaic devices, photocatalysts and storage capacitors in dynamic random access memories (DRAM) (Tanemura *et al.*, 2003).

In general, TiO_2 exhibits three crystal structures, i.e., tetrahedral anatase and rutile, orthorhombic brookite. Brookite is formed in thin films only under special conditions. Each crystalline form is convenient for a different purpose. While rutile is mainly desirable for optical applications, anatase has more efficient photocatalytic properties (Fukushima *et al.*, 1999).

Many deposition techniques have been used to prepare TiO_2 thin film, such as chemical vapor deposition (Battistion *et al.*, 1994), evaporation (Löbl *et al.*, 1994), reactive D.C. or R.F. diode or magnetron sputtering (Löbl *et al.*, 1994; Meng & dos Santos, 1993; Martin *et al.*, 1996), ion beam techniques (Leinen *et al.*, 1994), and sol-gel processes (Brinker & Harrington, 1981). Among lots of thin film preparation methods, sputtering methods have several advantages for optical coatings because of the high density, high adhesion, high hardness and good uniformity of the thickness in a large area.

Determination of the optical constants of thin films, e.g., refractive index, thickness, the energy band gap energy is a topic of fundamental and technological importance. Refractive index and thickness of a transparent homogeneous film on a non-absorbing flat substrate can be determined accurately from its reflectance and transmittance spectra (Borgogno *et al.*, 1982; Ylilammi & Ranta-Aho, 1993; Dobrowolski *et al.*, 1983). In general, spectral measurements made on thin films can be used to extract some of their optical properties. For instance, the wavelength dependency of the film optical constants can be examined by variable angle spectroscopic ellipsometry (Kim *et al.*, 2004). Another method is to obtain the mentioned dependences by performing optical transmission measurements and using the envelope (Swanepoel) method (Swanepoel, 1983).

In the present work, we describe the envelope method used for the determination of the TiO_2 thin film optical constants and its thickness. The accuracy is of the order of 1%, which is better than the accuracy of little elaborate computational iteration. It can be mentioned that the method does not require a dispersion model to determine the film thickness and optical parameters of the film, but it is not accurate when the film has significant dispersion and high absorption.

Materials and Methods

TiO_2 thin film was deposited onto well-cleaned glass slides and silicon wafer substrates by using home made reactive DC unbalanced magnetron sputtering system. Pure titanium (99.97%) of 54 mm diameter and 3 mm thickness has been used as sputtering target. High purity argon (99.999%) and oxygen (99.999%) were used as the sputtering and reactive gases respectively. Fig.1 shows a diagram of coating system with 2 unbalance magnetron cathodes. The cylindrical vacuum chamber of the system with 31 cm in diameter and 37 cm in height was connected to the vacuum pump system. Rotary and diffusion pump combination was used to get the desired vacuum. The base pressure of the system is less than 10^{-5} mbar. After attaining the base pressure the mixed gas of argon and oxygen in the ratio of 1:4 was let in the vacuum chamber, controlled by mass flow controller (MKS type 247D). Before deposition, the target was pre sputtered in argon atmosphere for 10 min in order to remove the surface oxide layer of the target. The depositions was carried out at a total pressure of 5.0x10^{-3} mbar. The distance between the target and substrates was kept at 80 mm and deposited for 3 hours.

X-ray diffraction (XRD) measurements have been carried out at grazing incidence diffraction (3^{O}), with a Rigaku RINT 2000 computer-controlled diffractometer with Cu Kα radiation (λ = 1.54059 Å). Atomic force microscope (AFM) (Nanoscope IV, Veeco Instrument Inc.) was used for measuring the thicknesses of the samples, in order to verify the values obtained by envelope method. The optical measurements of the TiO_2 thin films were carried out at room temperature using Shimadzu UV-VIS-NIR 3100 spectrophotometer in the wavelength range from 200 to 2500 nm. Swanepoel's envelope method was employed to evaluate the optical constants such as the refractive index n, extinction coefficient k, and absorption coefficient α from transmittance spectra (Swanepoel, 1983). The thickness of the TiO_2 thin film was determined from interference fringes of transmission data measured over the visible range.

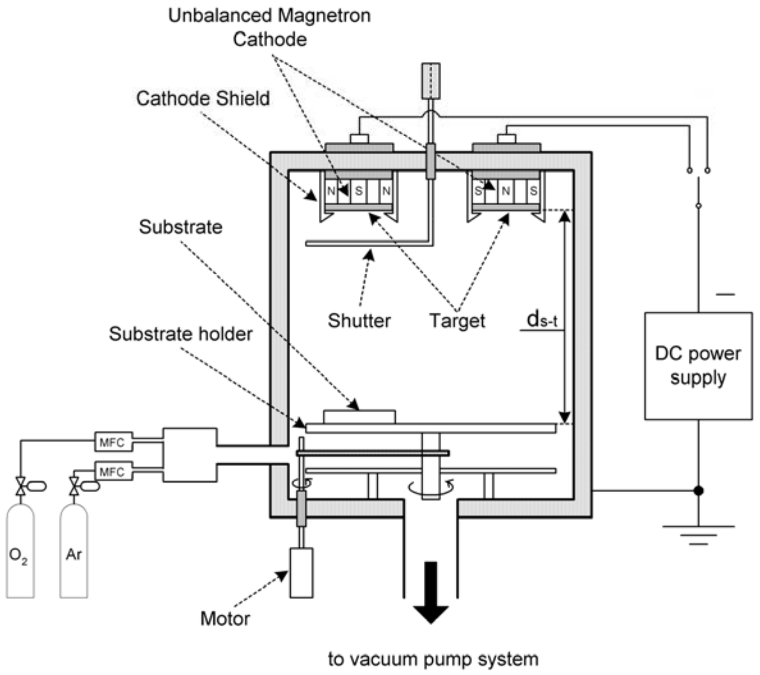

Figure 1. Schematic diagram of the DC magnetron sputtering system

Table 1 TiO_2 thin film deposited condition

Deposition method	reactive DC magnetron sputtering
Sputtering target	Titanium (99.97%)
Substrate	25x75 mm glass slide 10x10 mm silicon wafer
Substrate temperature	room temperature
Substrate to target distance	8 cm
Base pressure	3.0×10^{-5} mbar
Working pressure	5.0×10^{-3} mbar
Cathode potential	450 V
Cathode current	500 mA
Ratio of Ar:O_2	1:8
Deposition time	180 min

Results and Discussion

Structural properties of TiO_2 thin film

Fig. 2 show the X-ray diffraction patterns of TiO_2 film on silicon wafer substrate. Crystallographic phase of the film was identified as a rutile phase of TiO_2 from XRD study. Rutile peaks corresponding to (1 1 0) plane ($2\theta = 27.49^{\circ}$)

The crystallite size of TiO_2 film was determined from XRD broadening of R (1 1 0) peak using the Scherrer equation (Cullity, 2001)

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{1}$$

Where D is the crystallite size, λ the wavelength of X-ray (Cu $K\alpha$ = 1.54059 Å), β the peak full-width at half-maximum and θ the diffraction angle.

The crystallite size of as-deposited TiO_2 film was found to be in the order of 10 nm.

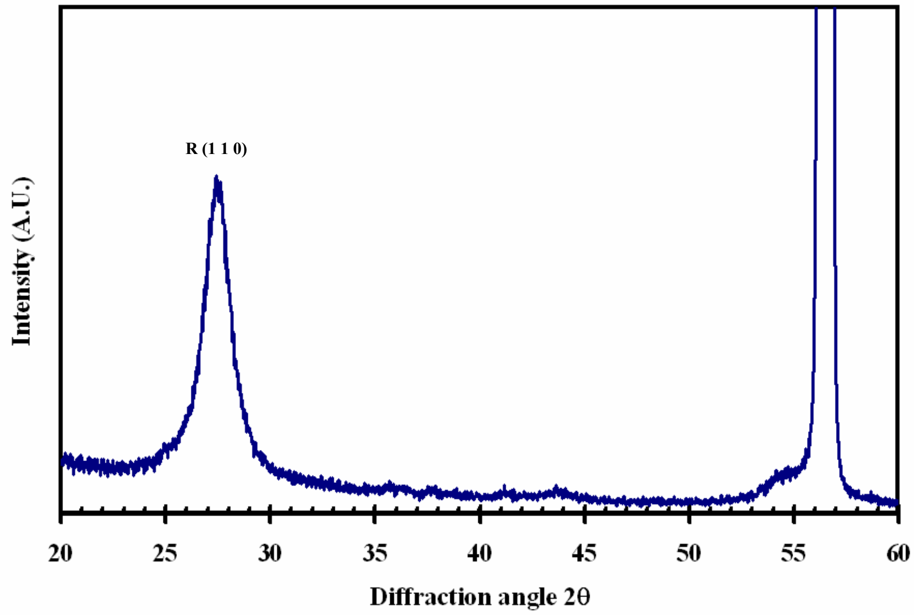

Figure 2. XRD pattern for the studied film

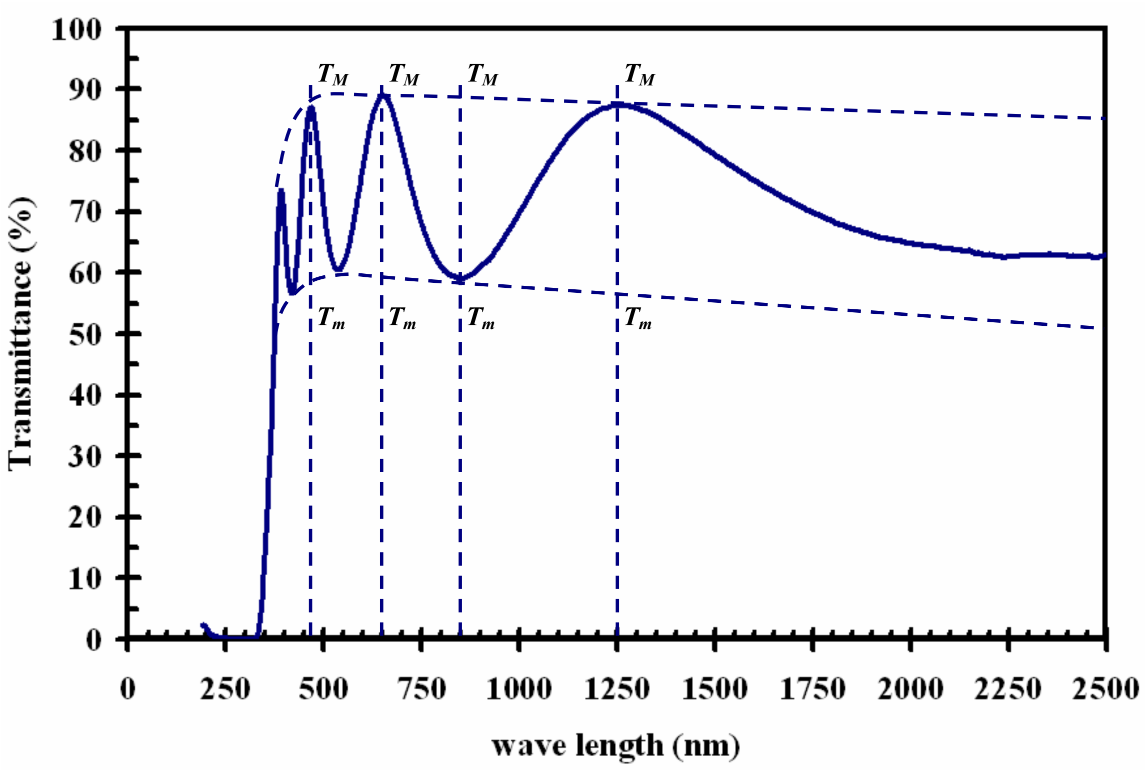

Figure 3. Transmission spectrum for the studied thin film

Optical properties of TiO_2 thin film

Study on optical properties of TiO_2 thin film is fundamentally based on transmittance (*T*) data. Fig. 3 shows the transmittance spectra of as-deposited film. As shown in Fig. 3, nature of transmittance spectra shows a series of transmittance maxima and minima of different orders. The film also show a sharp decrease of transmittance in the ultra-violet region and this is caused by the fundamental absorption of the light.

Fig. 3 shows transmittance curves for the crystalline TiO_2 thin film, where the film due to interference phenomena between the wave fronts generated at the two interfaces (air and substrate) defines the sinusoidal behaviors of the curve's transmittance vs. wavelength of light. TiO_2 thin film showed interference fringe pattern in transmission spectrum. This revealed the smooth reflecting surfaces of the film and there was not much scattering loss at the surface. In transparent metal oxides, metal to oxygen ratio decides the percentage of transmittance. A metal rich film usually exhibits less transparency.

The excellent surface qualities of the film were confirmed from the appearance of interference fringes in the transmission spectra. This occurs when the film surface is reflecting without much scattering or absorption in the bulk of the film. The films exhibited good transparency in the visible and infrared region (~90%).

The spectral refractive index n as well as the absorption coefficient α can be found by a transmittance spectrum of the film deposited on transparent substrate. When the film is deposited on thick absorbing substrate, only spectral reflectance measurement is possible. Manifacier *et al.* (1976) have developed a rather straight forward procedure for extracting n, α and k from transmission spectra provided $k^2 << n^2$. This method was further developed by Swanepoel (1983) and also found in the commercial thin film software. The method is applicable to any transmission spectrum showing appreciable interference fringes. From the transmission spectrum, envelopes around the transmittance maxima and transmittance minima are constructed.

The envelopes should ideally be constructed from the tangent point touching the transmission curves, not from the interference extremes: it is easy to see that, especially in a region where the transmission is changing fast, connecting the extremes will yield $T_M(\lambda)$ and $T_m(\lambda)$ curves that are actually too close to each other. The accuracy of the method decreases with decreasing film thickness, since at lower film thickness, the interference extremes are spaced further apart and interpolation between these extremes becomes more difficult.

The envelopes method to be used most successfully, the films should be sufficiently thick so that the interference fringes are closely spaced, thus defining $T_M(\lambda)$ and $T_m(\lambda)$ more precisely. The method fails if the absorption in the film is so high that interference fringes are not visible and $T_M(\lambda)$ and $T_m(\lambda)$ curves coincide. When carefully implemented, the envelopes method is applicable as a routine analysis technique. Recently, the effect of substrate absorption has been incorporated in the method (Sisonyuk, 1996; González-Leal *et al.*, 2002).

The transmission coefficient for the film-substrate system, taking into account interference due to multiple reflections at the system interfaces is given by (Swanepoel, 1983).

$$T = \frac{Ax}{B - Cx\ \cos\varphi\ + Dx^2} \tag{2}$$

where

$$A = 16n^2 n_s \qquad D = (n-1)^3(n - n_s^2)$$

$$B = (n-1)^3(n + n_s^2) \qquad \varphi = \frac{4\pi nd}{\lambda} \tag{3}$$

$$C = 2(n^2 - 1)(n^2 - n_s^2) \qquad x = \exp(-\alpha\ d)$$

The refractive index, n and the absorption coefficient, α of the film depend on the wavelength, λ. The refractive index of the substrate in our case n_s =1.52 (glass).

The interference fringes are obtained when $\cos\boldsymbol{\varphi} = \pm1$ or:

$$2nd = m\lambda \tag{4}$$

where m is an integer for maxima and half integer for minima. Under this circumstance the envelopes for minima and maxima are given by (Swanepoel, 1983).

$$T_{m,M} = \frac{Ax}{B \pm Cx\ + Dx^2} \tag{5}$$

From equation (5) we obtain an equation that is independent of x:

$$\frac{1}{T_m} - \frac{1}{T_M} = \frac{2C}{A} \tag{6}$$

Substituting the constants A and C from (3) into equation (6) and solving for n yields

$$n = \sqrt{N + \sqrt{N^2 - n_s^2}} \tag{7}$$

where

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \tag{8}$$

The method to determine the optical constants is based on the parabolic fitting procedure of adjacent maximum T_M and minimum T_m, which can be easily made on a computer.

The calculated values of refractive index n of TiO_2 film at different wavelength from the transmission spectra in the range of 400 nm - 800 nm is shown in Fig. 4. Refractive index values almost constant with the increasing of the wavelength.

The thickness of the films was calculated using the equation:

$$d = \frac{\lambda_1 \lambda_2}{2\ (\lambda_1 n_2 - \lambda_2 n_1)} \tag{9}$$

where n_1 and n_2 are the refractive indices corresponding to wavelengths λ_1 and λ_2, respectively (Swanepoel, 1983). The thickness of the film was about 301 nm which is very close to that obtained from AFM technique (296 nm).

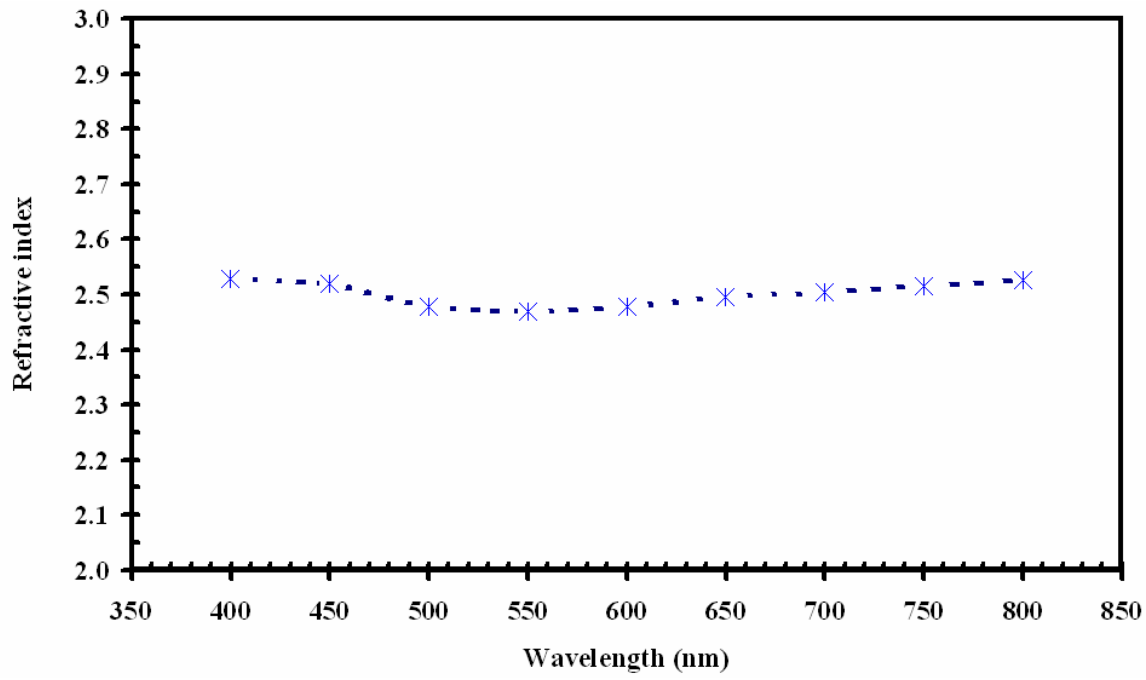

Figure 4. The refractive index n vs. λ for the studied thin film

For determining the absorption coefficient, Swanepoel (1983) has recommended, in the case of uniform films, to use the transmission curves, *T(λ)*, over the whole range of the spectrum. Knowing the values of refractive index, n, and the film thickness, d, all constants in relations (3) are known and the x value can be calculated. Addition of the reciprocals of equation (5) gives

$$\frac{2T_M T_m}{T_M + T_m} = \frac{Ax}{B + Dx^2} \tag{10}$$

Solving for x this gives

$$x = \frac{F - \sqrt{F^2 - (n^2-1)^3 (n^2 - n_s^4)}}{(n-1)^3 (n - n_s^2)} \tag{11}$$

where

$$F = \frac{4n^2 - n_s (T_M + T_m)}{T_M T_m} \tag{12}$$

The absorption coefficient $\alpha(\lambda)$ can be calculated from x and d using the following relation

$$\alpha(\lambda) = -\frac{1}{d} \ln x \tag{13}$$

The values of the extinction coefficient k for TiO_2 film was calculated from the relation

$$k = \frac{\alpha\lambda}{4\pi} \tag{14}$$

The calculated values of extinction coefficient k were plotted as function of wavelength in the range of 400 nm - 800 nm are shown in Fig. 5. The extinction coefficient k values decrease with the increasing of the wavelength.

The band gap energy of TiO_2 thin film

Determination of the band gap energy (E_g) is often necessary to develop the electronic band structure of a thin film material. In the high absorption region (>10^4 cm^{-1}), absorption coefficient α is related to the energy $h\nu$ of incident photons by the relation (Zhao & Fendler, 1991; Lucy *et al.*, 1996):

$$\alpha = \frac{B(h\nu - E_g)^p}{h\nu} \tag{15}$$

where *B* is a constant and *p* is an index that characterizes the optical absorption process and is theoretically equal to 1/2, 2, 3/2 or 3 for direct allowed, indirect allowed,

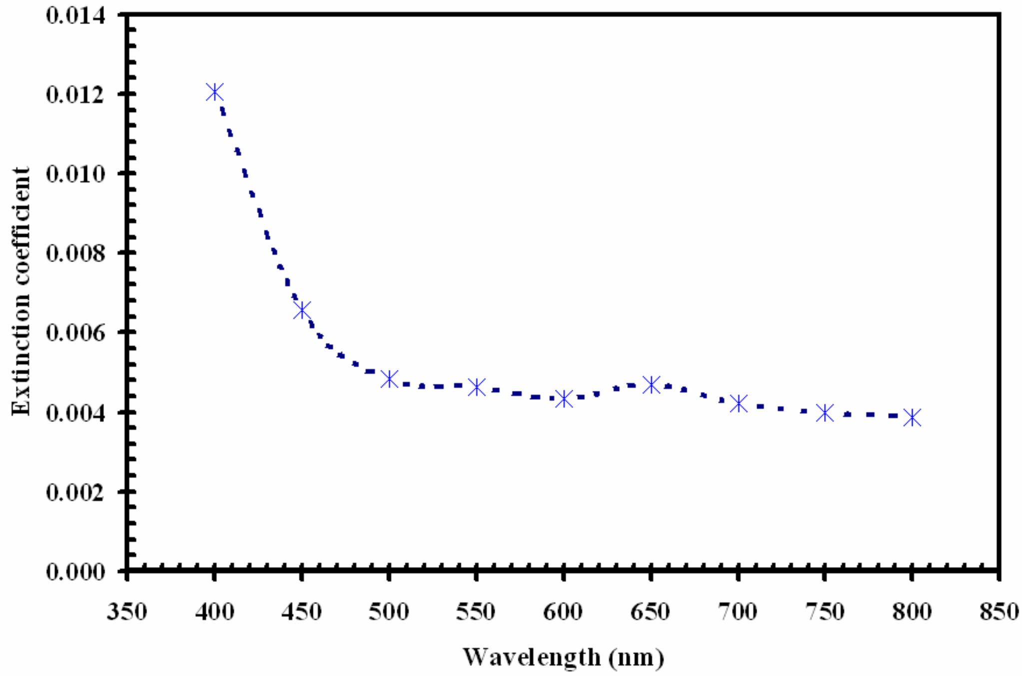

Figure 5. The extinction coefficient k vs. λ for the studied thin film

direct forbidden and indirect forbidden transitions, respectively. Best fit in optical absorption data obtained from many oxide films is achieved when $p = 2$ (Lucy *et al*., 1996). In the present study, the value of p of Eq. (15) is taken as 2.

The band gap energies (E_g) for indirect allowed transitions of TiO_2 film evaluated from $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) plots, Fig. 6 is a best fit of $(\alpha h\nu)^{1/2}$ vs. energy ($h\nu$) of the studied film. The values of the optical band gap E_g were taken as the intercept of $(\alpha h\nu)^{1/2}$ vs. ($h\nu$) at $(\alpha h\nu)^{1/2} = 0$, Fig. 6, which equal to 3.1 eV.

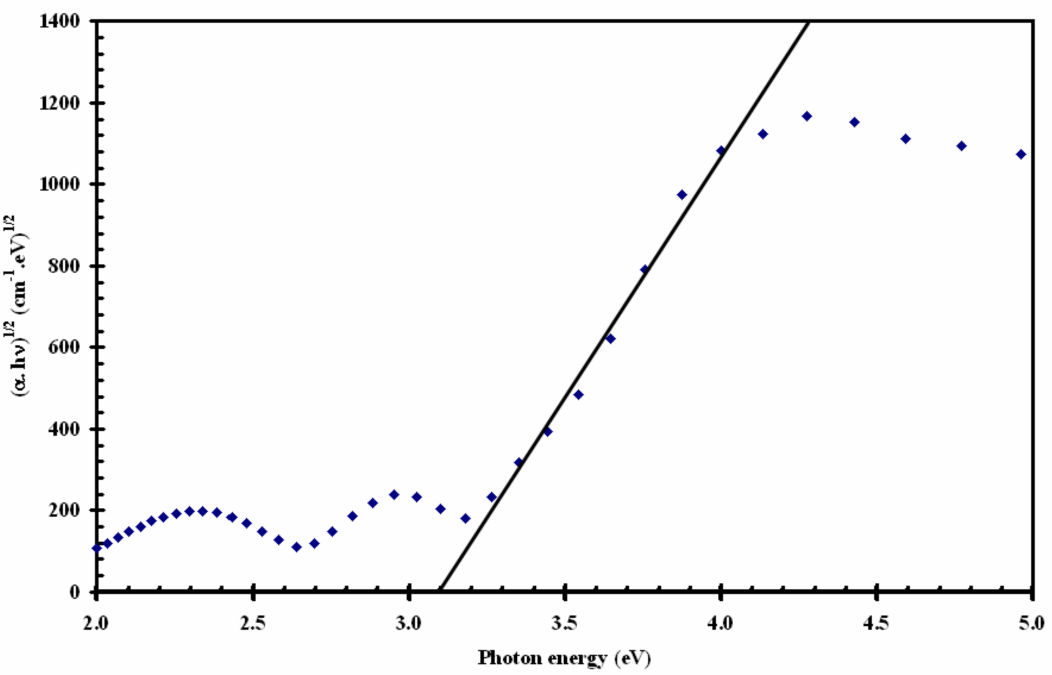

Figure 6. The dependence of $(\alpha h\nu)^{1/2}$ vs. ($h\nu$) of the studied thin film

Conclusions

TiO_2 thin film has been deposited onto well cleaning Si-wafers and glass slides substrates by a reactive DC unbalanced magnetron sputtering technique at room temperature. The films are mainly rutile, as seen from XRD patterns. Optical constants such as refractive index n and extinction coefficient k were determined from transmittance spectrum in the visible regions using envelope method. The thickness of the film d was calculated from interference of transmittance spectra and energy band gap E_g value was calculated. In conclusion, it may be considered that the deposited TiO_2 thin film was suitable for many optical devices, such as solar cells, gas sensors, etc., because of well-crystallized, high transmittance (~90%) and wide-band gap value (3.1 eV). By using the envelope method proposed by Swanepoel we have calculated the optical constants as a function of wavelength and the thickness of the film. The values of refractive index n and extinction coefficient k at 550 nm were 2.47 and 0.005 respectively. The thickness of TiO_2 film was found to be about 301 nm which very close to the value obtained by the AFM technique (296 nm).

Acknowledgment

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