International Journal of Nanoelectronics and Materials
Volume 15, No. 1, January 2022 [61-70]

Influence of Annealing Temperature on Some Properties of TiO2/Au Thin Films Prepared by RF and DC Magnetron Sputtering Methods

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Received 22 August 2021, Revised 10 November 2021, Accepted 9 December 2021

ABSTRACT

This paper uses RF and DC magnetron sputtering techniques to prepare TiO2/Au thin film on glass substrates. TiO2thin film was deposited under a power of 150 Watt for 90 min. by RF magnetron sputtering technique and achieved 132.6 nm thickness, while Au thin film was deposited under a power of 20 Watt for 15 min. by DC magnetron sputtering technique achieving 20 nm thickness. Afterward, these samples were annealed in different temperatures (150, 200, 250 and 300) °C respectively for about 1 hr that led these thin films to be more crystalline in structure after annealing. X-ray Diffraction (XRD) revealed a high grain size equal to 9.077nm, which has a sharp peak R(220) at 64.65 ° in 300 °C. Atomic force microscopy (AFM) showed the structural properties as the average roughness after annealing about 4.68 nm in 300 °C. All the obtained films are highly oriented in direction having nanocrystalline phase. The optical properties were examined by UV-VIS spectroscopy that showed increases in transmittance in the range of 35 % - 75 %, absorption coefficient from the region of high absorbing wavelength at 400nm, and reduction in energy gaps to (3.25 eV, 3.12 eV, 3.01 eV, and 2.95 eV) when annealing temperatures were increased. These results indicated the most suitable growth conditions for obtaining high-quality sputtered TiO2/Au thin films with a higher transparency performance for solar cells applications.

Keywords: RF and DC Sputtering, Thin films, Thermal Annealing, Titanium dioxide.

1. INTRODUCTION

Titanium dioxide TiO2 or titania is one of the semiconductor materials which has excellent properties like good corrosion, chemical resistance, high refractive index, and a good transmittance in the visible and near-infrared regions (1),(2),(3). These features make it suitable for applications such as solar cell, sensing, renewable energy production represented by a solar cell, smart windows, gas sensors, photoconductive, hydrogen production and biomedical applications (4),(5),(6).TiO2 occurs in three different phases as rutile, anatase that is a stable phase and brookite that is unstable and gained low interest for industrial applications (7),(8),(9). Both rutile and anatase phases are polymorphs and have some advantages one above another, where anatase has more electronic properties that make it higher photocatalytic (10) and a wide energy gap about 3.2eV as compared rutile with 3eV (11), (12) In contrast, the rutile phase has a refractive index of a higher value than the anatase phase, equal to 2.7 (13),(14).

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Several methods have been utilized to prepare thin films such as DC or RF sputtering (15),(16). sol-gel process (17),(18), chemical vapor deposition (19) and pulsed laser deposition (20),(21). RF and DC magnetron techniques provide films with high uniformity (22) as well as very good adhesions on
the substrate (23),(24). This method also can be used for depositing films on a large scale that makes it convenient for industrial applications (25),(26),(27).

Ali Ahmed Yousif (28) studied the structural, optical and gas sensing properties prepared by PLD technique of nanoparticle dopants TiO2films. These films were examined and showed that all the prepared films are polycrystalline. The average size of the crystalline grains decreased when TiO2was doped with 5% Co metal. F. U. Khan et al. (29) fabricated TiO2thin films by using sol-gel method. The structural and optical properties achieved by XRD and SEM were examined and films with a nano-scale thickness could be achieved.

Both anatase and rutile structures were studied by Yu-Jie Ma et al (30) who fabricated TiO2thin films using the ion-implantation method. The obtained results indicated that the structural properties of the prepared thin films were changed with the increase of annealing temperature. The results showed that surface porosity, optical properties and surface morphology of TiO2could be influenced by changing the annealing temperature.

The present work aims to prepare TiO2/Au thin films sputtered on a glass substrate by using RF and DC Magnetron sputtering method.The effect of annealing temperature on these films is studied. The optical and structural properties are also presented with a discussion of their behavior after the annealing process.

2. MATERIAL AND METHODS

TiO2/Au thin films were prepared by using RF and DC Magnetron sputtering methods (CRC-600, USA-Torr Com.) and deposited on glass substrates. Both of these sputtering methods depend on argon pressure that was kept at less than 10-2 mbar. It has been shown that 10-2 mbar is the favorable value to create plasma in order to start the sputtering process. The work conditions are shown in Table 1 where P_1 is the base vacuum pressure and P_2 is the working argon pressure of the sputtering chamber, while T is the TiO2/Au substrates temperature of (58 °C) and (45 °C) respectively due to sputtering processes. These techniques achieved thickness of 132.6 nm for TiO2and 20 nm for Au. TiO2 with purity 99.99% has been used to prepare a thin film deposited with Au material. Then, these thin films were annealed with different annealing temperatures from 150 ºC to 300 ºC (50 ºC step) for about 1 hr by using an electric furnace which was controllable by its temperature. The samples were placed above an iron panel inside the oven to ensure the homogeneity of thermal distribution during the heating process.

Table 1 The operating conditions of TiO2/Au thin films preparing by RF&DC Magnetron sputtering techniques

POWER(W)	Base pressure P_1(Torr)	Working pressure P_2(Torr) $\times 10^{-3}$	Substrate temperature T°(C)	Sputtering time t (min)
150 RF(TiO2)	2×10^{-5}	5×10^{-3}	58	90
20 DC(Au)	4×10^{-5}	2×10^{-2}	45	15

The TiO2/Au thin films examined by XRD diffraction (Shimadzu 7000) Japanese type to study the structural properties. The crystal size of the prepared TiO2/Au thin films was measured by using Debye-Scherrer's formula as shown in Equation (1): (31),(32),(33).

$$D = \frac{K\lambda}{d\cos\theta} \tag{1}$$

where K is the mean shape factor that equals to 0.94, λ is the wavelength of X-Ray (1.5406Aº) for Cu-kα, d refers to the full width at half maximum (FWHM), and ϴ is Bragg's angle.[22] In order to study the optical properties, these films were also examined by UV-VIS spectroscopy (UV-2601 PC Shimadzu software 1700-1650). The absorbance coefficient (α) was calculated by Equation (2):(34),(35),(36).

$$\propto = 2.303 \times A/t \tag{2}$$

where A is the absorbance value(s) and t is the thickness of the film that was used in this work. The optical energy gap can be calculated by Tauc formula as in Equation (37),(38),(39):

$$(\alpha h\gamma)^{1/n} = A(h\gamma - Eg) \tag{3}$$

Where α is the absorption coefficient, h is Plank constant, υ is the frequency of radiation, A is constant and E_g is the optical energy gap.

3.RESULTS AND DISCUSSION

Figure 1 displays the XRD examination of the prepared thin films at various annealing temperatures compared with these films before annealing. The nanostructure of TiO2/Au shows the change in the film structure after annealing process with different annealing temperatures. It can be noticed that the different peaks belong to the rutile and anatase phases in the wide temperature range approach to the stable phase at 300 °C. On the other hand, the diffused nature of the peak before annealing indicates a weak crystallinity with a small grain size at an angle of 38.19 °, corresponds to (111) reflection (10),(40). This refers to the annealing process that led to an increase in the crystallinity of the films. Table 2 shows the values of the grain size, obtained by Equation (1).

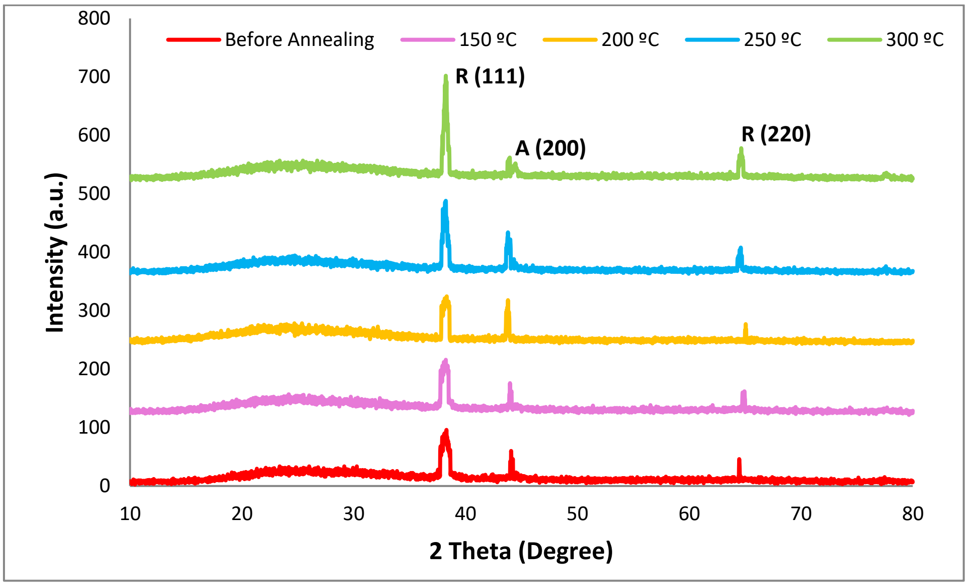

Figure 1. XRD pattern of TiO2/Au thin films before annealing and after different annealing temperatures

It can be observed from Table 2 that the increase in annealing temperature has led to an increase in grain size that resulted in more crystalline films. The grain size values were found from 1.819 nm to 9.077 nm. It can be noticed that the diffraction peaks are sharp and more intense due to reduction in FWHM. The crystalline size increased as according to Equation (1), which shows an agreement with the results by F. U. Khan et al. (29). It can also be indicated that the phases have become more irregular when transformed from the rutile phase to the anatase and returned to the same phase, which showed more stability when the annealing temperature reached to 300° C (41),(42),(43). i.e. the annealing temperature at 300 °C resulted a high crystallinity.

Table 2 Characteristics of the prepared thin films as anatase (A) and rutile (R) phases before annealing, and after different annealing temperatures estimated from XRD data

Annealing temperature(°C)	2Θ (deg)	FWHM (deg)	d(A°)	hkl	D (nm)
Before annealing	38.1902	0.82	2.35	R111	1.819
	44.0881	0.52	2.03	A200	2.787
	64.0011	0.42	3.76	R220	4.133
150	38.2052	0.82	2.35	R111	1.821
	44.3776	0.52	3.45	A200	2.873
	64.4128	0.40	3.69	R220	5.144
200	38.3231	0.52	2.06	R111	2.921
	44.4523	0.38	3.75	A200	3.917
	64.4012	0.36	4.05	R220	5.682
250	38.5827	0.43	2.35	R111	3.724
	44.4810	0.29	2.06	A200	5.151
	64.5431	0.27	2.03	R220	8.186
300	38.2235	0.31	2.35	R111	4.834
	44.4961	0.30	2.03	A200	4.848
	64.6528	0.26	1.44	R220	9.077

Figure 2 displays the optical transmittance spectra of TiO2/Au thin films in the wavelength domain of 300-1100 nm prepared at different annealing temperatures and compared with thin films before the annealing process. The magnitude of transmittance does not change and it shows flat, or more accurately slightly changed before annealing as compared with all annealed samples that show clear effect after annealing in the range from 35 % - 75 % depending on spectra. This means that transmittance decreased when the crystal arrangement becomes more regular because of the action of a high degree of annealing temperature that agrees with (37). On the other hand, it can be observed that the value of transmittance decreased at 400 nm due to absorbing occurred at the visible wavelength region (44),(45).

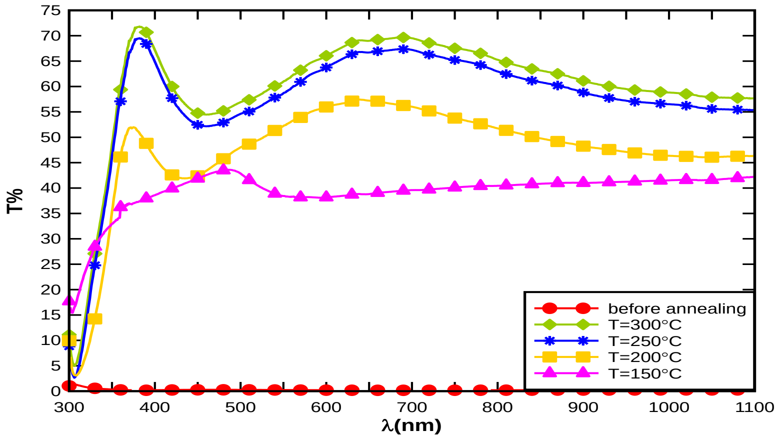

Figure 2 Transmittance versus of wavelength for TiO2/Au thin films before annealing, and after different annealing temperatures

The absorption coefficient versus the wavelength for TiO2/Au thin films prepared at various annealing temperatures from 150 to 300 °C (50 °C step) shown in Figure 3 and compared with thin films before the annealing process. It is considered an important optical property that determined the light-absorbing character for each material (46),(47). In general, increasing in annealing temperature led to increase the absorption coefficient from the region of high absorbing wavelength at 400nm. These refer to the increase of the grain size and the light scattering effect (48),(49),(50).

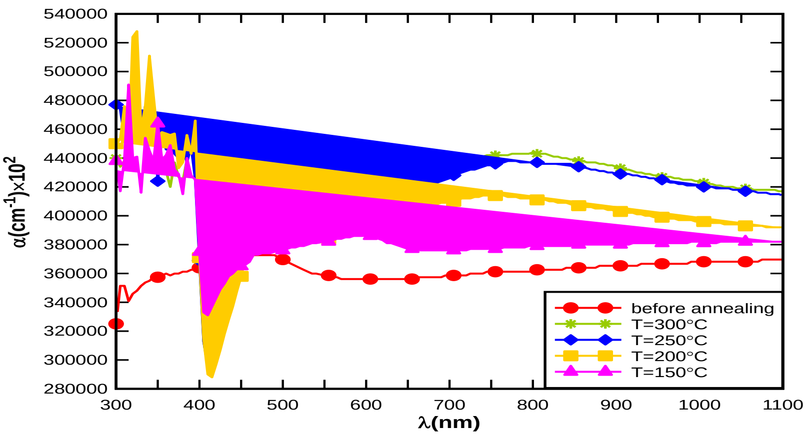

Figure 3 Absorption coefficients versus of wavelength for TiO2/Au thin films before annealing, and after different annealing temperatures

From Equation (3), the allowed direct energy gaps were estimated before annealing, which were equal to 3.45eV as well as (3.25 eV , 3.12 eV , 3.01 eV, and 2.95eV) with respect to different annealing temperatures of (150 °C, 200 °C, 250 °C, and 300 °C) respectively as shown in Figure (4). Higher annealing temperatures reduced energy gaps that related with increasing crystalline size found by XRD. Since these values of annealing temperatures produced large grain size particles, light scattering was reduced. Thus, increasing grain size plays a great role in bandgap value with the effect of mixture of different TiO2thin films.(37),(51).

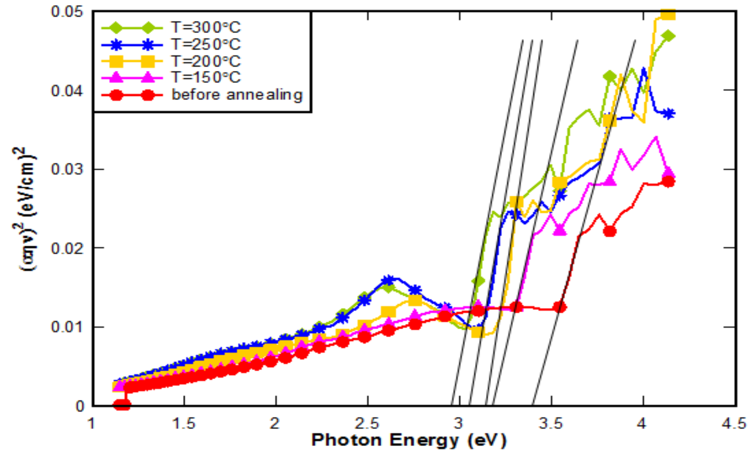

Figure 4 The relation between (αhυ)2 and (hυ) of TiO2/Au thin films before annealing and at after different annealing temperatures

The morphology modification of TiO2/Au thin films surface was examined by AFM as shown in Figure (5) displaying 2D and 3D images and data. Increasing of annealing temperature led to increase in the grain size of TiO2/Au thin films, therefore increasing the roughness of the surface due to grain growth to bigger size which it is considered an important reason to enhance the crystallinity of these films (40),(52),(53),(45). The AFM results have a good agreement with the XRD results, showing the changes in structural properties.

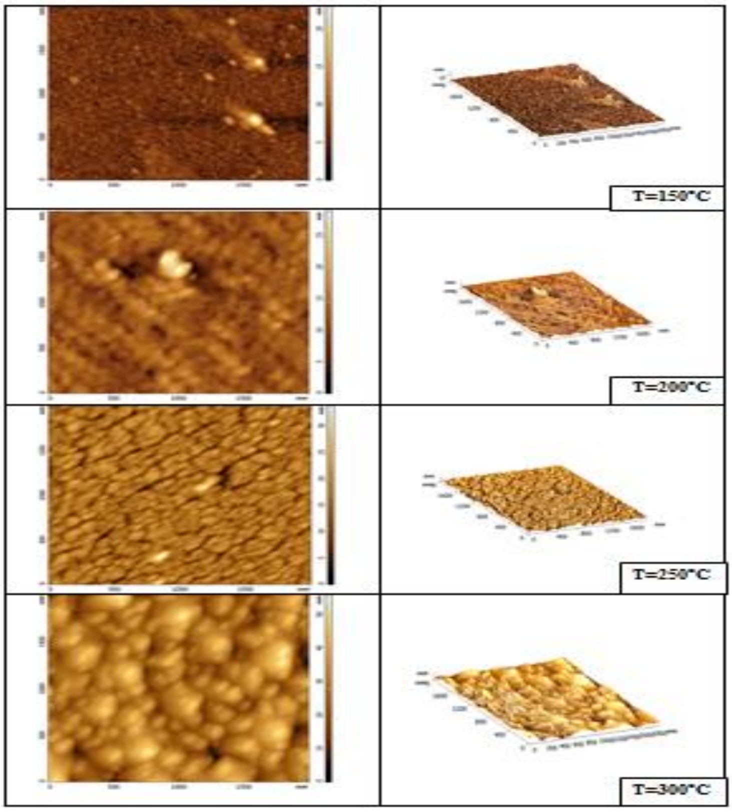

Figure 5. 2D and 3D images of TiO2/Au thin films at varies annealing temperatures

Both of the average grain size and the average roughness values are listed in Table 3, which displays all these values as AFM parameters (55).

Table 3. AFM parameters of TiO2/Au thin films at varies annealing temperatures

Annealing temperatures T(°C)	Average grain size(nm)	Average Roughness(nm)
150	15.5	3.92
200	22.4	4.18
250	32.6	4.54
300	41.2	4.68

2. CONCLUSION

In this work, all structural and optical properties of TiO2/Au thin films were investigated. RF and DC Magnetron sputtering techniques were used to efficiently grow TiO2/Au thin films and deposited on glass slides. The optical transitions of TiO2/Au were direct, and the amount of absorbance coefficient increased with the increase of the annealing temperatures that is related to the increase in the absorbed wavelength region. The peaks became sharper and narrower. Moreover, the grain size became larger with increasing annealing temperature that is related to the increasing in crystalline dimensions and surface alterations after annealing. This shows a good agreement with the resulted values of TiO2/Au thin films that can be utilized as photovoltaic applications such as solar cells, sensors, smart windows and biomedical applications.

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