Study The Structural Properties of Nanostructure (TiO$_2$: Cu) Thin Film Prepared By RF Magnetron Sputtering

Khalowd D Khemkheem$^1$, Najwa J Jubier$^2$ and Abdul_Hussain K Elttayef$^3$

$^{1,2}$Department of Physics, College of Science, Wasit University, Kut, Iraq
kutpc19@yahoo.com

$^3$Ministry of Science and Technology, Baghdad, Iraq

Abstract. In this research, TiO$_2$: Cu thin films deposited on a glass substrate with different thicknesses (100) and (200) nm by the radio frequency (R.F.) magnetron sputtering process using target TiO$_2$: Cu. The sputtering deposition was performed by using the power of 100 Watt. Crystalline structure, surface morphology, and electronic structure were studied using X-ray diffraction(XRD). XRD patterns demonstrate that TiO$_2$ films deposited on a glass substrate at 500 C° are observed to be brookite (orthorhombic) polycrystalline phase with preferred orientation along (111). The average surface roughness (Ra) measured with atomic force microscopy (AFM) was 0.532 nm, and the minimum grain size was 40.5 nm for TiO$_2$ doped 5%Cu.

Keywords: TiO$_2$: Cu, thin films, magnetron sputtering, grain size.

1. Introduction

Thin films are more advantageous part for gas sensing applications because of their higher surface to volume ratio and controlled surface morphology over their bulk counter [1-3]. Titanium dioxide (TiO$_2$), especially in thin film form, is widely preferred as a semiconductor material because of its unique material. In view of its versatile properties which comprise the high refractive index, wide bandgap, and resistance to chemical and physical impacts [4, 5].Titanium dioxide TiO$_2$ (titania) is a cheap, non-toxic and one of the most efficient semiconductor photocatalysts for extensive environmental applications [6].TiO$_2$ has also been preferred as a material for gas sensors due to its low resistivity to the reduced driving power of the sensor [7]. TiO$_2$ exists in three polymorphic phases: rutile, anatase, and brookite, in nature rutile is the most common crystal phase conversely, anatase thermodynamically not stable as rutile [8,9], both anatase, and rutile have tetragonal crystal structures but belong to different space groups [10]. In addition to that TiO$_2$ doped Cu are widely used in many fields including in the field of medicine and industrial applications as well as in decontamination as these particles are available in a very low cost, TiO$_2$ thin films are very good preservatives in the ultraviolet ray area due to a tape. It has been observed that copper-coated titanium membranes improve the properties as a photocatalyst in the visible region [11]. In this research, the nanostructure TiO$_2$: Cu films were synthesized using R.F. sputtering and annealed at 500 °C. The structural properties of these films were investigated.
2. Experimental Details

Thin films of TiO$_2$: Cu were deposited on glass substrates by RF plasma sputtering using TiO$_2$: Cu target (diameter 5 cm and thickness 0.3 cm) prepared from TiO$_2$ and Cu powders with a purity of 99.99% from (Merck, Germany) (Figure 1. illustrate the sputtering system). The film thickness was measured using the thickness monitor in the sputtering system and by applying, a 10-ton compression then dried at 80 OC. Before starting deposition, the glass substrates were cleaned thoroughly. The process of cleaning substrates begins by immersing in a cleaning solution to remove any oil or dust can be found on the surface and then placed under tap water for 15 minutes. The substrates are then immersed in the pure acetone solution, which reacts with the contamination such as grease and some oxides. Finally, the substrates are re-washed in an ultrasonic bath for 15 minutes, and then dried by hot air. The clean substrates and the TiO$_2$: Cu target are fixed in the chamber of sputtering system. High-purity argon was used as the sputtering and reactive gas. Then deposition of TiO$_2$: Cu films were carried out at 100 °C under a constant dc power of 100 W. The deposition time was set at 180 min. The base pressure of the deposition chamber was kept at 2-3 × 10$^{-5}$ Torr, and sputtering pressure 2.5*10$^{-3}$Torr and annealing thin films at 500°C. X-ray diffraction studies were carried out using type (SHIMADZU Japan) XRD600, wavelength 1.541 Å using CuKα radiation. AFM were studied. The morphological characteristics of the surfaces were studied using AFM (model A3000 Angstrom Advance Lns.)

![Figure 1. a, b, & c Illustrate the sputtering system and the components used in this work.](image)
3. Results and discussion

3.1. Thin films Characterization:
The structural properties of copper-doped Titanium oxide thin films with weight percentages (3%, 5%, and 7%) were studied using x-ray diffraction and atomic force microscopy.

3.2. X-ray diffraction results
The crystalline structure of the TiO$_2$: Cu thin film can be identified by studying the phase of that substance. When a beam of X-ray incident on the surface of the thin film, the peaks appear on specific angles due to the reflection of Bragg on the surface of the parallel crystal. The diffraction of the X-ray of the pure TiO$_2$ thin film at room temperature with different thicknesses (100 and 200) nm is shown in Figure 2, and after the annealing process at 500 °C, is shown in Figure 3. It is clear from these two figures that the crystalline structures of the prepared thin films were amorphous and become crystallized of brookite (orthorhombic) polycrystalline phase after annealing especially for TiO$_2$ doped with 5% Cu and the preferred peak (111) at the angle of 31.7° as in Figure 4. Obtained results have a good agreement to the standard results according to the data file [13463-67-7]. The full –width at half maximum (FWHM) of (111) of brookite peak were also evaluated to analyze the variation of grain size in the films doped. The average crystalline size of the thin films was obtained using Scherer’s formula [12]:

\[ D = \left( \frac{k\lambda}{\beta \cos \theta} \right) \]  

Where D is the size of the crystal, k is the constant number of 0.9, \( \lambda \) is the x-ray wavelength, \( \theta \) is the angle of Bragg in degree, and \( \beta \) is the full width at half the maximum (FWHM) of the selected peak. The average crystallization size calculated after annealing at thickness (100 and 200) nm for pure TiO$_2$ thin films were 59.82 nm and 59.996 nm and for TiO$_2$: 5% Cu were found to be 58.8 and 98.17 nm as illustrate in Table 1.

![Figure 2. X-ray Diffraction of pure thin film TiO$_2$ at room temperature with thickness a: (100nm) and b: (200 nm).](image-url)
Figure 3. X-ray Diffraction of pure thin film TiO$_2$ at temperature 500ºC with thickness
a: (100nm) and b: (200 nm).

Figure 4. X-ray Diffraction of TiO$_2$:5%Cu thin film at temperature 500ºC with thickness
a: (100nm) and b: (200 nm).

Table 1. Some Synthetic Properties of TiO$_2$ Thin Films.

| Sample(at 500ºC)         | $\theta$(deg.) | hkl  | d(Å)    | FWHM (deg.) | D(nm) a | b   | c   |
|--------------------------|-----------------|------|---------|-------------|--------|-----|-----|
| (Stander)                | 31.46           | [111] | 2.766   | -           | 4.53   | 5.4 | 4.9 |
| TiO$_2$ Pure (100nm)     | 31.728          | [111] | 2.817   | 0.138       | 59.82  | 4.52| 4.78| 5   |
| TiO$_2$ Pure (200nm)     | 31.724          | [111] | 2.818   | 0.1376      | 59.996 | 3.9 | 8.05| 4.39|
| TiO$_2$:5% Cu (100nm)    | 31.7278         | [111] | 2.815   | 0.14        | 58.8   | 4.36| 5.08| 4.89|
| TiO$_2$:5% Cu (200nm)    | 31.744          | [111] | 2.816   | 0.084       | 98.17  | 4.23| 5.62| 4.72|
3.3. Results of the atomic force microscopy (AFM) Morphology

Surface morphology of all TiO\textsubscript{2}: Cu thin films with different concentration (0, 3, 5, and 7) % of Cu are measured by Atomic force microscopy (AFM), the best results were noticed at 200nm thickness as in Figure (5- a, b, c, d). It is clear that all TiO\textsubscript{2}: Cu films have a smooth surface with regular crystalline grains and a nanoscale structure. Through surface morphological study, it was noticed that the grain size of TiO\textsubscript{2}: Cu is a nanostructure. It was observed that the surface of the thin film is rougher when increasing the copper doping in TiO\textsubscript{2} films, this result agrees with [13]. Also it was noticed the particle size increases as increasing the concentration of dopant Cu in the thin film and after the annealing process. The increase in grain size reduced the grain boundaries and thus reduced the barrier between them. The results are shown in Table 2.

**Figure (5-a).** AFM image for Pure TiO\textsubscript{2} thin film.

**Figure (5-b).** AFM image for TiO\textsubscript{2}:3%Cu thin film.
Figure (5-c). AFM image for TiO2:5%Cu thin film.

Figure (5-d). AFM image for TiO2:7%Cu thin film.
Table 2. The values of surface roughness root mean square and grain sizes for TiO$_2$: Cu thin films.

| Thin Film  | Surface Roughness (nm) | RMS (nm) | Average diameter (nm) |
|------------|------------------------|----------|-----------------------|
| Pure TiO$_2$ | 0.416                  | 0.073    | 102.3                 |
| TiO$_2$+3%Cu | 0.532                  | 0.226    | 40.5                  |
| TiO$_2$+5%Cu | 0.793                  | 0.353    | 62.2                  |
| TiO$_2$+7%Cu | 0.895                  | 0.421    | 86.8                  |

4. Conclusion

1. The radio frequency (R.F.) magnetron sputtering technique was used in this work to prepare thin films of TiO$_2$: Cu with various Cu contents (0, 3, 5 and 7) %.

2. XRD analysis showed a crystalline structure to be a brookite polycrystalline phase of pure TiO$_2$ when annealed at 500 °C with preferred orientation along (111). The same structure also observed for TiO$_2$ doped with 5%Cu.

3. AFM analysis showed a smooth surface with regular crystalline grains with nanoscale structure films. It was noticed that the average surface roughness (Ra) measured was 0.532 nm, and the minimum grain size was 40.5 nm for TiO$_2$ doped 5%Cu.

5. Reference

[1] Dainius P and Ludwig J, 2005 *Journal of Electroceramics*, 14,111–103.

[2] Chowdhuri A, Gupta V, Sreenivas K, 2003 *Sensor Actuators B*, 93, 579–572.

[3] Haridas D, Sreenivas K, and Gupta V, 2008 *Sensor Actuators B*, 133, 270-275.

[4] Chopra K, 1969 *Thin Films Phenomena* (New York: McGraw – Hill Book Company).

[5] Lever k D, 1971 *Thin Films* (London: Wykeham Pub p.32).

[6] Peter C S, 2004 CdO thin films deposited by spray pyrolysis, *Electronics, Vol.15*, pp. 22-24.

[7] Gurumuru K, Mangalaraj D, Narayandass S K, NakanishiY and Hatanaka Y, 1997 *Applied surface science, Vol.113*, pp.422-425.

[8] Adawiya J H, Raad M S AL-Haddad, and khaled Z Yahya, 2011, *IJAPVOL.7*,NO.2 pp. .27-31.

[9] Kingon A I, Maris J and Stiffer S, 2000 Materials Fundamentals of Gate Dielectrics *Nature* 406, p 1032.

[10] Fries M and Simko R, 2012 Nano-Titaniuim dioxide (part1) Basics, Production, Applications *Nano trust dossiers*, 33.

[11] Tribble A, 2002 *Electrical Engineering Material and Devices*, University of Iowa.

[12] Cullit B D, 1978 *Elements of X-Ray Diffraction* (Adison: Wesley).

[13] Sreedhar M, Reddy I N, Bera P, Amachandran K D, Saravanan G, Ms Rabel A, Anandan C, Kuppusami P and Brijitta J, 2015 *Applied Physics A, Materials Science & Processing*, Springer-Verlag Berlin Heidelberg.