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The Effect of Copper Doping on Some Structural and Electrical Properties of Titanium Dioxide Nanofilms

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ABSTRACT

Thin films of titanium dioxide (TiO_2) with several copper ratios were deposited on glass substrates using pulsed laser deposition (PLD) for pure and doped samples (TiO_2 Pure, 1 % Cu, 2 % Cu, and 3 % Cu), energy (600 mJ), and frequency (6 Hz). X-ray diffraction (XRD) showed that the width of the peaks decreases with increasing the ratio of doping with copper. This leads to an increase in the crystal size and in the intensity of the copper peaks, as well as a gradual decrease in the intensity of the titanium dioxide peaks. The results of the atomic force microscope showed that increasing the inoculation percentage leads to an increase in the surface roughness and the average grain diameter, and thus an increase in the growth of the particle size. The electrical tests (Hall effect) showed that the prepared films are of (n-type) and that the concentration of carriers (n) increased with the doping ratio, while the mobility values (μ_H) decreased directly with the increase in copper. The electrical conductivity (DC) test showed an increase in the activation energy as a result of the increase in the copper inoculation percentage and thus the electrical conductivity increases.

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تأثير التطعيم بالنحاس على بعض الخصائص التركيبية والكهربائية لأغشية أوكسيد التيتانيوم النانوية

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الملخص

تم ترسيب اغشية أوكسيد التيتانيوم الرقيقة النانوية (TiO_2)على قواعد زجاجية باستعمال تقنية الترسيب بالليزر النبضي (PLD) ولنسب تطعيم (TiO_2 Pure, 1 % Cu, 2 % Cu, & 3% Cu) والطاقة (600 mJ) وتردد (6 Hz)، أظهر فحص حيود الأشعة السينية (XRD) إن عرض القمم يقل مع زيادة نسبة التطعيم بالنحاس وبالتالي يؤدي الى زيادة الحجم البلوري رافق ذلك تناقص تدريجي في شدة قمم ثنائي أوكسيد التيتانيوم عند زيادة نسبة التطعيم وتزايد في شدة القمم بالنسبة للنحاس، وبينت نتائج مجهر القوة الذرية إن زيادة نسبة التطعيم تؤدي الى زيادة خشونة السطح ومعدل قطر الحبيبات، وبالتالي زيادة في نمو الحجم الحبيبي وقد بينت الفحوصات الكهربائية (تأثير هول) إن الأغشية المحضرة من نوع (n-type) وان حاملات الشحنة (n) تزداد مع زيادة نسبة التطعيم، وان قيم التحركية (μ_H) تتناقص بشكل طردي مع زيادة نسبة التطعيم، وأظهر فحص التوصيلية الكهربائية (DC) زيادة طاقة التنشيط نتيجة الزيادة في نسبة التطعيم بالنحاس وبالتالي زيادة التوصيلية الكهربائية.

الكلمات المفتاحية: أوكسيد التيتانيوم، النحاس، الترسيب بالليزر النبضي، حيود الاشعة السينية، مجهر القوة الذرية، تأثير هول، التوصيلية الكهربائية.

Introduction

Pulsed laser deposition (PLD) depends on the deposition of a thin film as a result of the interaction between the laser and the sample material using a laser beam of high intensity. The laser system consists of three main components: laser light, deposition chamber, and vacuum system [1]. A laser beam focuses on the sample. If the laser energy is greater than the threshold energy of the sample, the material will be converted into vapor. In this way, thin films are produced [2,3]. Pulse laser deposition has achieved a great success due to its low costs compared to other technologies. It is used in many types of materials: metals, electrical insulators, semiconductors, polymers, ferroelectric and organic materials [4,5]. At this time, a recent research is heading towards the field of transparent conducting dioxides (TCOs) because of their technological importance, and their multiple uses in solar cells, infrared detectors, and transparent transistors [6,7]. Among these dioxides, titanium dioxide (TiO_2) is one of the important compounds because of its unique optical and electrical properties [8]. So, it has many uses and applications, such as microelectronic devices, electronic gates, capacitors, solar energy fields, gas sensors, paper, and plastic industry [9,10]. Titanium dioxide (TiO_2) has three phases, which are Anthase (Tetragonal), Rutile (Tetragonal), and Brookite (Rhombic). The rutile phase is the most stable phase, as it has the highest absorbance and the smallest energy gap (3.05 eV) [11,12]. Copper is a transition metal element that rarely has a natural color other than gray or silver. Copper, in its pure state, is red-orange, and when exposed to air becomes close to red [13]. Copper is characterized as a metal that has very high thermal and electrical conductivity, and it is soft, malleable, and ductile [14,15]. Copper is used in many fields, the most important of which are as a conductor of electricity and heat, and in thermocouples to measure temperature and strain gauges, and it is the main component of many metal alloys [16]. One of the chemical properties of copper is that it does not interact with water but reacts slowly with atmospheric oxygen to form a layer of black and brown copper dioxide. This layer protects the base metal from additional corrosion [17]. This study aims to improve the electrical conductivity of titanium oxide nanofilms by adding copper with different ratios.

1- The Experimental Part

Titanium dioxide powder (TiO_2) with a high purity of (99.99 %) was compressed, and then doped with copper whose purity was (98.8 %), using different doping ratios (1, 2, & 3 %). After that, the mixed powders were compressed with a pressure of (8 ton) using a hydraulic press to prepare samples weighing (2 gm) in the form of tablets, and then deposit them on glass substrates using PLD (Nd: YAG) optical laser system, energy (600 mJ), wavelength (1064 nm), frequency (6 Hz), distance of (2 cm) between the sample and the glass substrate, the number of pulses used (1000), low pressure (10^{-3} mbar), at laboratory temperature.

2- Results and Discussion

2-1 Structural Properties

2-1-1 The Results of X-ray Diffraction

The results of X-ray diffraction (XRD) for titanium dioxide nanofilms showed four peaks (110), (101), (211), (200) for angles (27.50°, 36.04°, 54.23°, 56.78°). The crystalline structure of titanium dioxide films was (Tetragonal). The effect of doping with copper showed a gradual decrease in the intensity of the titanium dioxide peaks when the doping ratio increases and an increase in the intensity of peaks of the doping material. Copper appeared in three peaks (111, 200, 220) and angles (43.31°, 50.44°, 74.12°), the crystalline structure of copper is Cubic, as shown in Figure (1). The deposition process by pulsed laser has an effect that leads to the deposition of more layers on the outer surfaces of the thin films. This improves and increases the crystallization process and allows the largest number of granules to collect on the surface of the films. This result is consistent with the results found in [18]. It is noted that the width of the peaks decreases with the increase in the ratio of doping with copper. This leads to an increase in the crystal size, i.e. there is an inverse proportionality, according to Scherer's equation, through which the crystal size of the peaks is calculated. This result agrees with that found in [19].

$G.S = K\lambda / \beta \cos\Theta_B$............(1)

Where G.S is the grain size, k is constant= 0.9, λ is the wavelength, β is the full width at half maximum (FWHM), and Θ_B is the Bragg diffraction angle.

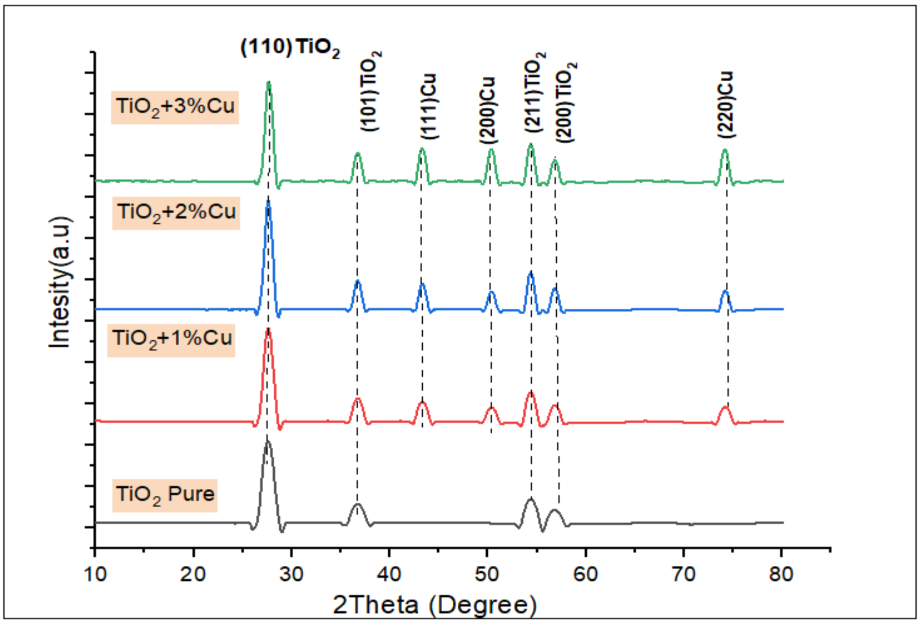

Figure (1). X-ray diffraction of titanium dioxide films doped with copper

2-1-2 Atomic Force Microscope (AFM)

The results of the atomic force microscope measurement showed a change in the surface shape and roughness of the titanium dioxide films depending on the increase in the doping ratios. This means that the increase in the ratio of copper leads to an increase in the regularity and arrangement of the atoms and their growth in size and an increase in the value of the root mean square of the films. This in turn leads to an increase in the roughness of films and the growth rate of the size of the particles [20]. At the same time, increasing the doping ratio leads to an increase in the surface roughness and particle diameter. So, the increase in the surface roughness leads to an increase in the particle size growth [21], as clarified in Table (1) and Figure (2).

Table (1): The results of the atomic force microscope

Content %	Average Roughness (nm)	r.m.s (nm)	Average diameter(nm)
TiO_2 Pure	4.751	5.123	70.543
1% Cu	6.432	7.432	73.765
2% Cu	7.789	8.564	82.467
3% Cu	8.543	8.979	91.758

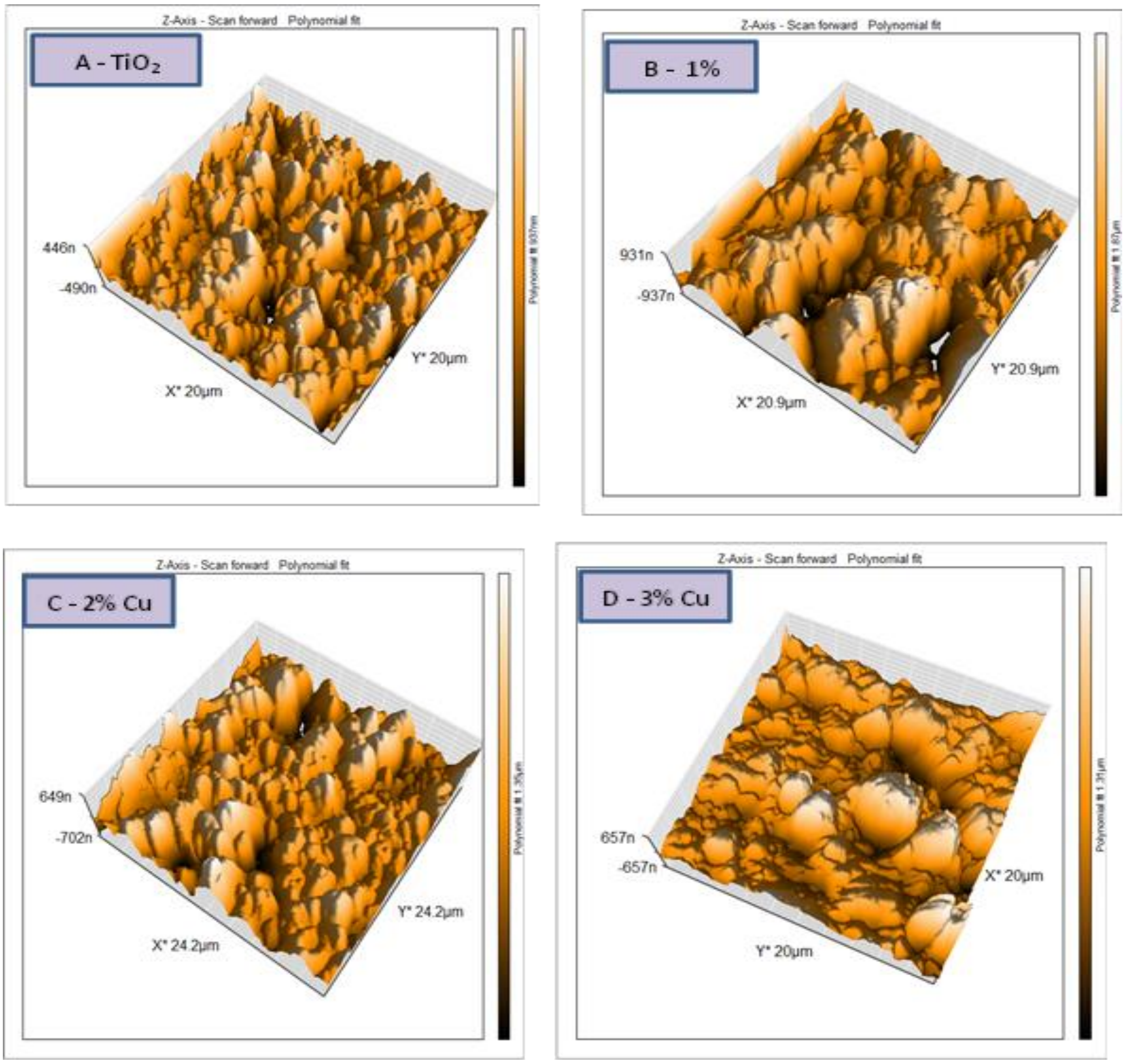

Figure (2): A: Pure titanium dioxide, B: Titanium dioxide doped 1 %, C: Titanium dioxide doped 2 %, D: Titanium dioxide doped 3 %

3- Electrical Properties

3-1 Hall Effect

Deposition conditions and crystal structure affect the electrical properties of thin films. The electrical properties were studied by employing Hall effect. Titanium dioxide nanofilms were of (n-type) conductivity, and thus the charge carriers were electrons, resulting from interfacial threads of titanium nano-ions or donor oxygen vacancies [22]. Table (2) and Figure (3) illustrate the main values of Hall effect. The increase in the concentration of carriers (n) decreases with the Hall potential. It is noted that probability (μ_H) decreases directly with the increase in the doping ratio, while the decrease in potential is due to the inverse relationship between probability (μ_H) and concentration of carriers (n) [23].

$\mu_H = \sigma / n_e.q$ …………(2)

Where μ_H refers to probability, σ is conductivity, n_e is the concentration of carriers, and q is the electron charge = 1.602×10^{-19} C.

Table (2): The Hall Effect Values for Titanium Dioxide

Samples	$n_H \times 10^{14}$ (cm^{-3})	$\mu_H \times 10^3$ $(\frac{cm^2}{eV.s})$	$\sigma \times 10^{-2}$ $(\Omega^{-1}.cm^{-1})$	$R_H \times 10^4$ (cm^3/C)	Type
TiO_2 Pure	4.109	2.33	1.54	-1.365	N
1% Cu	4.624	2.177	2.646	-1.784	N
2% Cu	5.147	0.323	2.865	-2.312	N
3% Cu	5.769	0.136	3.145	-2.857	N

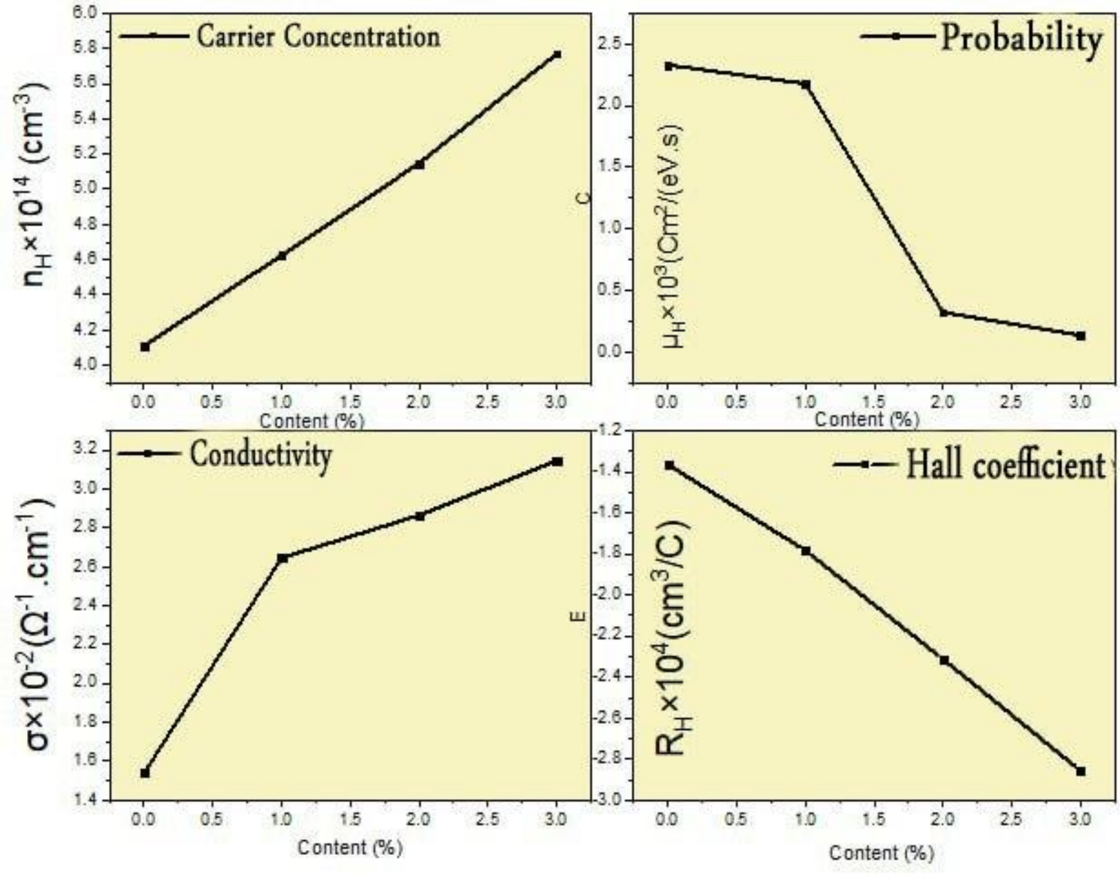

Figure (3). Diagrams of Hall values

3-2 Electrical conductivity (DC)

A study of the electrical conductivity of the prepared samples showed that the electrical properties had a significant effect on their crystal structure and deposition conditions. When the temperature increases, there is an increase in conductivity with a decrease in resistance. This is a prevalent characteristic in semiconductors. Then, the activation energy is calculated, i.e. the first activation energy is within the range (239 – 373)K, while the second activation energy is within the range (373 – 453)K, which is greater than the energy of the first activation [24]. While increasing the concentration of carriers leads to an increase in the electric current with an increase in electrical conductivity. Table (3) and Figure (4) illustrate the electrical conductivity values.

Table (3): the electrical conductivity values

Samples	$E_{a1} \times 10^{-2}$ eV	Rang(K)	$E_{a2} \times 10^{-2}$ eV	Rang(K)
TiO_2 Pure	0.732	293 – 373	4.13	373 – 453
1% Cu	1.84	293 – 373	5.41	373 – 453
2% Cu	2.31	293 – 373	5.97	373 – 453
3% Cu	2.93	293 – 373	6.32	373 – 453

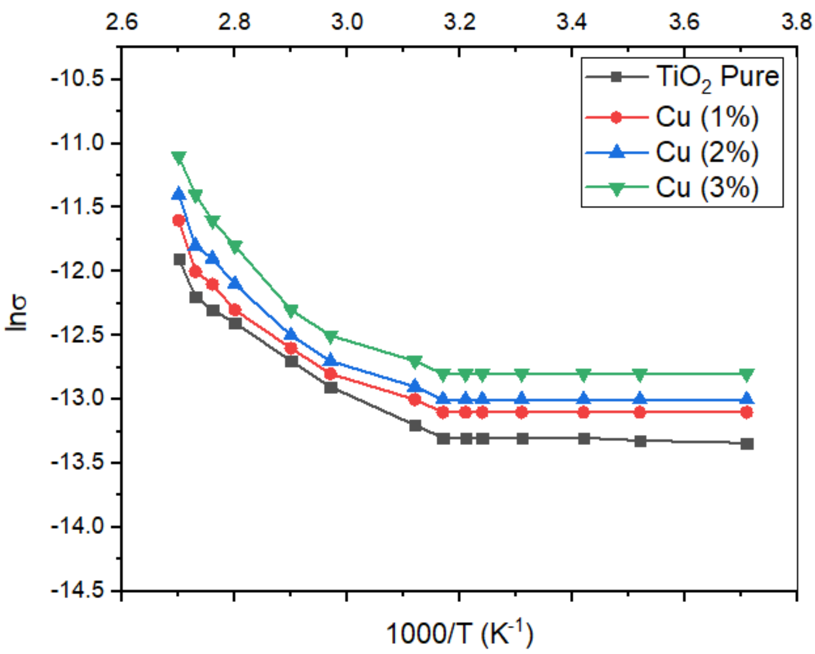

Figure (4). the electrical conductivity graph

Conclusions

In this study, the pulsed laser deposition (PLD) technique was used to prepare titanium dioxide nanofilms and study the effect of copper on some of its structural and electrical properties. The X-ray diffraction results showed an increase in crystalline size with an increase in doping ratio. The results of the atomic force microscope showed an increase in the regularity and arrangement of the atoms, along with the root mean square value of the films leading to an increase in the roughness. The electrical tests using Hall effect showed that the films prepared are of (n-type) and the increase in doping leads to an increase in conductivity and a decrease in the probability value (μ_H). The electrical conductivity test shows an increase in conductivity and a decrease in resistance when the temperature rises. Also, the increase in the doping ratio leads to an increase in the electric current. These films could be used in thermoelectric applications and gas-sensing devices.

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