Growth Of TiO_2 Films By RF Magnetron Sputtering Studies On The Structural And Optical Properties

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***Abstract*—Titanium Dioxide (TiO_2) thin films were deposited on glass substrates by radio-frequency (RF) magnetron sputtering under various sputtering power (75-150)W. The influence of sputtering power on the optical and structural properties of the films were studied. X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and UV-VIS-NIR spectrophotometer system were employed to characterize the deposited films. XRD results exhibited only a single prominent peak corresponding to TiO_2 (101) anatase for sputtering power 75W orientation of hexagonal close-packed (hcp) structure, while in the power (90,105,150 W) exhibited three peaks corresponding to TiO_2 (101),(004),(200) respectively. As the crystallinity of the TiO_2 films increased with sputtering power, the grain size and surface roughness of TiO_2 films increased, however, a decrease in optical transmittance were found.**

Keywords—TiO_2; thin film; XRD; sputtering; AFM.

1. Introduction

Titanium Dioxide (TiO2) has been widely used in several applications such as aerospace, motor science, chemical engineering, microelectronics, biomedical devices and functional thin layers in semiconductor devices, due to its good mechanical properties, for examples high specific strength, low resistivity and remarkable resistance to corrosion [1]. In thin film synthesis, there are a number of different techniques that can be used to grow TiO2 thin films such as electron beam evaporation ,chemical vapor deposition and magnetron sputtering .[2]

Sputtering technique is initiated due to the bombardment of energetic particles at the target. These energetic particles are generally ions. Two approaches can be followed to produce ions and sputter the target materials. The first is quite straightforward by using an ion source which is aimed toward the target Collecting the sputtered particles on a substrate enables the deposition of a thin film. However, ion beam sputtering is not widely used for industrial large scale applications. Ions guns are more often utilized in surface analytical techniques such as SIMS (secondary ion mass spectrometry) or to bombard the substrate during thin film deposition [3]. The sputtering process with the assistant of magnetron cathodes is called magnetron sputtering which is widely used in both scientific and industrial fields [4]. A magnetron uses a magnetic field to confine electrons close to the cathode, making it easier to sustain an electrical discharge at low pressure. There are various geometries but all magnets are arranged in such a way that the magnetic field lines are parallel to the cathode surface and perpendicular to the electric field lines. This causes the secondary electrons to drift in a closed path in the – E ×B direction, also known as the Hall Effect, trapping the electrons near the cathode surface. This arrangement results in enhanced ion bombardment and sputtering rates for both DC and RF discharges. Magnetron sputtering is particularly useful when high deposition rates and low substrate temperatures are required [5]. In RF magnetron sputtering, cathode and anode are changeable and for very short cycles, target functions as anode which cause the removal of insulating layer. By doing so, the process can continue [6,7].

2. EXPERIMENT

TiO_2 thin films were deposited on cleaned glass substrates by using a RF magnetron sputtering system with a 5 cm diameter x 3 mm thick TiO_2 target of 99.99% purity. Before deposition, the glass substrates were cleaned in an ultrasonic bath with ethanol for 15 mins, rinsed in distilled water, dried with nitrogen gas of 99.99% purity and clamped on the substrate holder in the chamber. The sputtering chamber was evacuated to 10^{-6} Torr by using a turbo molecular pump. During deposition, the working pressure and substrate temperature were kept constant at 5.4 x 10^{-3}Torr and (50-70 C°), respectively. Commercial argon (Ar) of 99.9% purity was used as the sputtering gas and kept constant at gas flow rate of 20 sccm that can be controlled by a mass flow controller. TiO_2 films with different sputtering power (75W, 90W, 105W and 150W) were deposited after pre-sputtering the TiO_2 target in an Ar atmosphere for 10 min in order to remove oxide layers. The structural properties of deposited TiO_2 films were characterized by using X-ray diffract meter (XRD), scanning electron microscope (SEM) and atomic force microscope (AFM). The X-ray diffraction of the films were obtained using a Shimadzu X-Ray Diffract meter 7000 with a monochromatic high intensity CuKα radiation (λ = 1.54056Å) radiation operated at 40kV and 30mA.

3. RESULTS AND DISCUSSION

3.1. Optical Properties

The Figure (1) shows the optical transmittance of TiO_2 films deposited with sputtering power of (a) 75W, (b) 90W, (c) 105W and (d) 150W. From these four samples, the film deposited with sputtering power of 75W exhibited high transmittance in the visible and near infrared wavelength regions, which related to its amorphous nature, As the crystallinity of the TiO_2 films increased with sputtering power from 75W to 150W, the transmittance decreased to lower than 75%. The film deposited with sputtering power of 150W showed the lowest optical transmittance, because that the decrease in the transmittance spectra was caused by the increase in the loss of light scattering as the grain size increased.

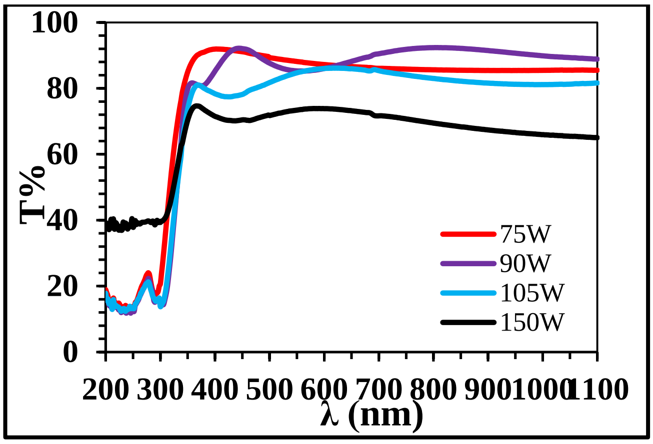


Figure (1): Optical transmittance of the TiO_2 thin films deposited at different sputtering power versus wavelength ranging from 200 nm to 1100 nm.

In figure (2) shows absorptance spectrum for pure TiO_2 films for different sputtering power. We observed when the sputtering power is increased, absorptance is also increased because the thickness of the film is increased and at high wavelength (λ) the incident photons do not have enough energy to interact with atoms.

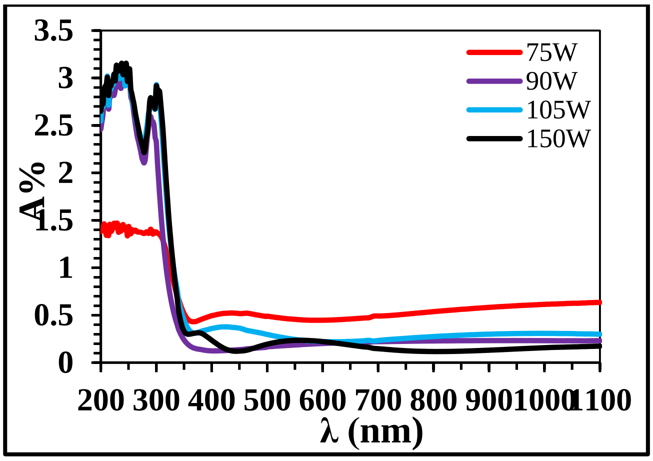
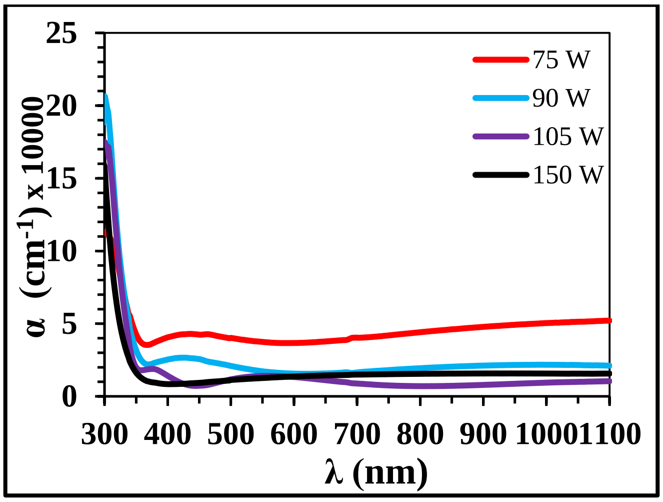


Figure (2): Absorptance spectrum of TiO_2 films for different sputtering power.

Absorption coefficient of the pure TiO_2 thin film is calculated and the figure (3) shows the variation of (α) as a function of photon energy and wavelength respectively , its value is larger than (10^4 cm^{-1}) for all films. From the same figure, we can notice an increasing in absorption coefficient with increasing of sputtering power as increasing of film thickness. This can be linked with the formation stage of anatase and with increase in grain size and density of layers and it may be attributed to the light scattering effect for its high surface roughness.



Figure(3): Absorption coefficient as function of energy photon for TiO_2 at different sputtering power.

In other hand the energy gap of pure TiO_2 shows decrease, the energy gap values depends in general on films crystal structure, the arrangement and distribution of atoms in the crystal lattice, also it is affected by crystal regularity. E_g value is calculated by extrapolation of the straight line of the plot of $(\alpha h\nu)^2$ versus photon energy for different sputtering power of TiO_2 films. It is observed that the optical band gap of the films decreased from 3.92 to 3.61 eV with the increase of power from 75 to 150 W, that is show in fig.(4)

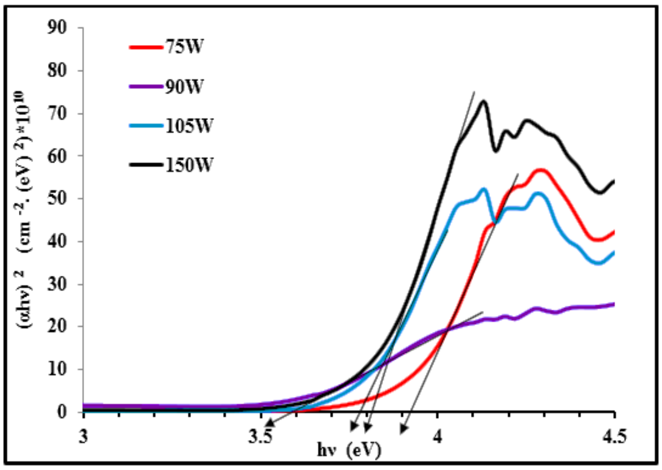


Figure (4): $(\alpha h\nu)^2$ as a function of photon energy of TiO_2 thin film at different sputtering power.

Table (1): optical band gap of TiO_2 films of

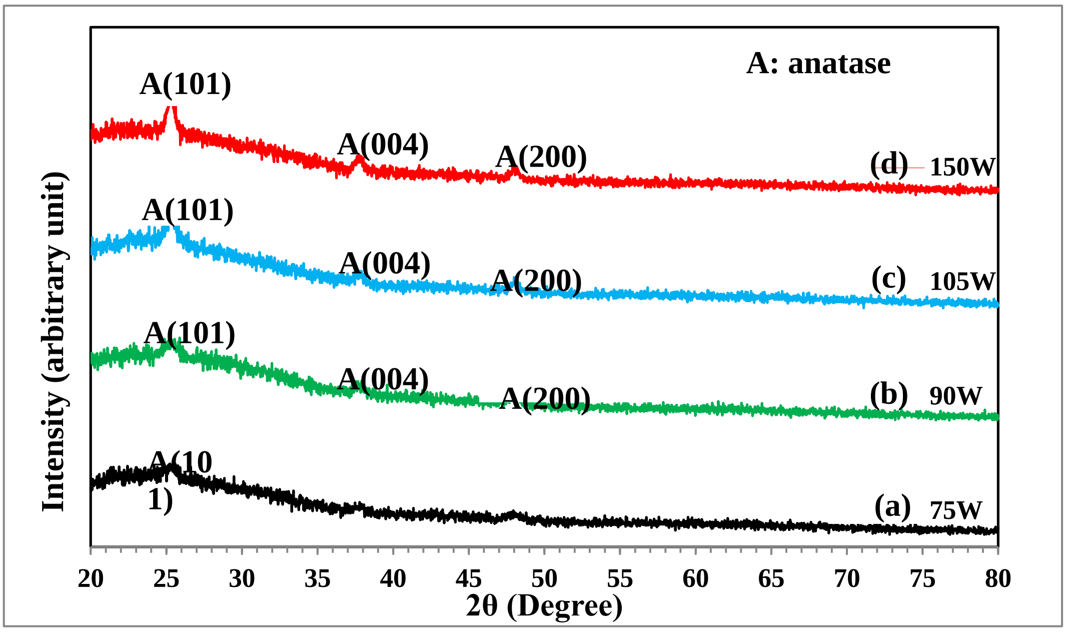
Material	Power (W)	Thickness (nm)	E_g (eV)
TiO_2	75	53.21	3.92
TiO_2	90	79.54	3.80
TiO_2	105	96.40	3.78
TiO_2	150	125.3	3.61

different sputtering power and thickness.

3.2. Structural properties

3.2.1. XRD Analysis

The XRD diffraction patterns of the deposited TiO_2 thin films. The film deposited at sputtering power of 75W show only single prominent peak can be observed at 25.301°, TiO_2 (101) anatase as shown in Figure (5). As the sputtering power increased at 90W, 105W and 150W, the crystallinity in the films increased. The crystallinity in the films increased with increase in the sputtering power, i.e. at low sputtering power(75W), the films were only one peak and at high sputtering power, crystalline films were observed. The XRD patterns for other samples prepared at different power show only three peaks at 25.302° (101), 37.7° (004) and 48.03° (200) anatase TiO_2 for 90 W and the other show in table(2), no rutile or brookite TiO_2 is observed in all samples. These results in agreement with the standard TiO_2, XRD [X-ray diffraction data file N 1997 JCPDS card No. 96-720-6076]. However, in this work, as the sputtering power increased to 150W, the peak broadened and weakened. This might be due to a change in its phase or crystal structure as deposition parameters varied. The Grain size (D) of the TiO_2 films was calculated using the full width at half maximum (FHMW) of the peak.It is calculated by using the Scherrer Debye equation; all the results were tabulated in table (2).



Figure(5): X-ray diffraction patterns of the TiO_2 films deposited at different sputtering power, i.e. (a) 75W, (b) 90W, (c) 105W and (d) 150W.

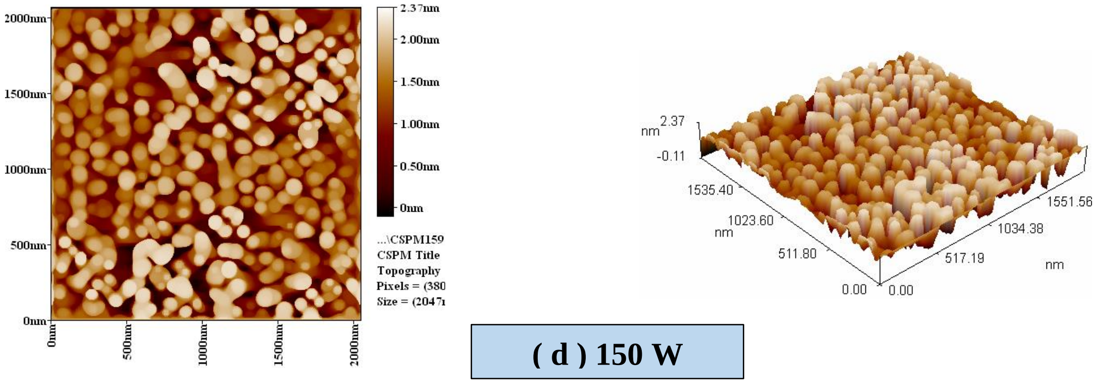
3.2.2 Atomic Force Microscope (AFM) Measurements

Figure (6) shows the two and three dimensional (2D&3D) AFM images of TiO_2 thin films deposited with different sputtering power. To study the surface topographies of the TiO_2 films from the AFM images. From this figure show that the grain size and surface roughness of TiO_2 films increased with increase in sputtering power because of increasing the thickness of the film and this is can be explain to create the localized state in the structure of the film. Particularly, the change of grain microstructure from amorphous to crystalline state can be observed as the sputtering power increased. In (Chawla *et* al. 2009), the authors also observed that the increase in sputtering power contributes in an increase of the atom mobility and the deposition rate, resulting in the growth of crystallite size and higher surface roughness of TiO_2 thin films show in table (3).

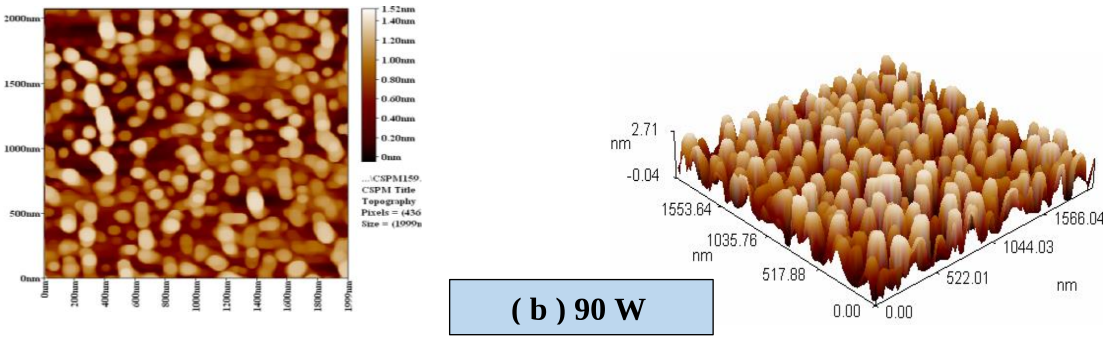
The grain size of the deposited TiO_2 films was detected to be in the range of 6.2-16.4 nm with increase in sputtering power. Higher surface roughness was resulted due to the formation of deep channels and large bulging grains on the film surface, which contributes to the smooth film surface.

Table (2): characteristics of TiO_2 thin film estimated from XRD data.

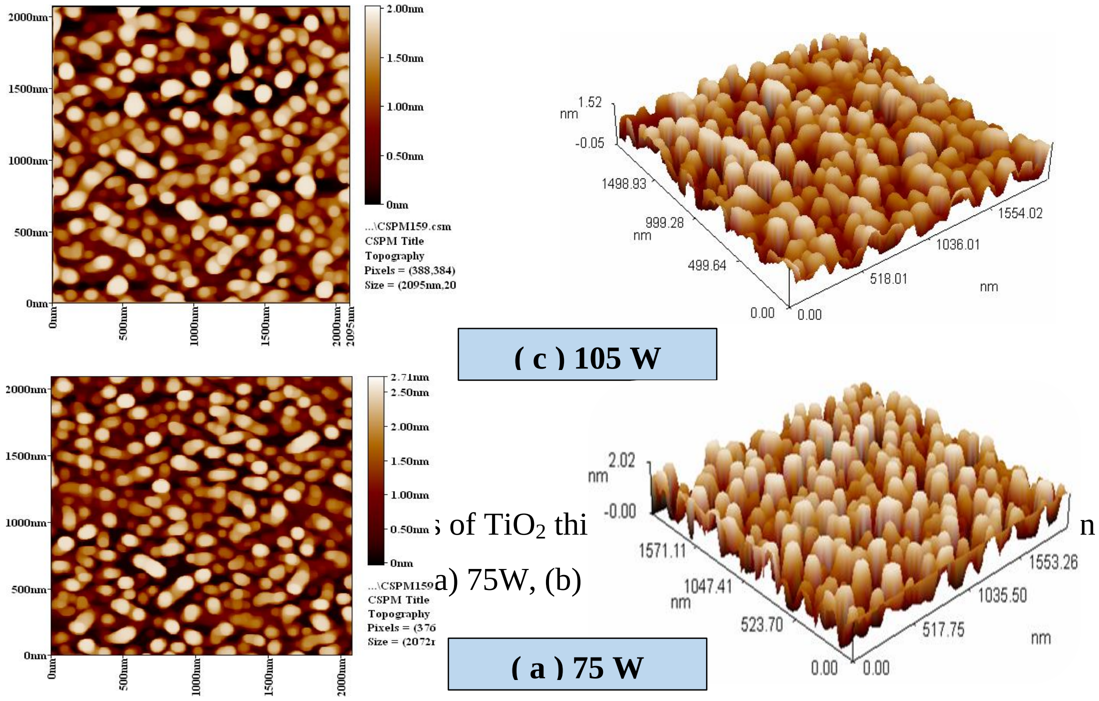
Energy	**2θ (Deg.)**	**FWHM (Deg.)**	**d_{hkl} Exp.(Å)**	**G.S (nm)**	**hkl**	**Phase**	**d_{hkl} Std.(Å)**	**Card No.**
75W	25.3012	1.3200	3.5173	6.2	(101)	Anatase	3.5172	96-720-6076
90W	25.3024	1.2390	3.5171	6.6	(101)	Anatase	3.5172	96-720-6076
	37.7662	0.7438	2.3801	11.3	(004)	Anatase	2.3799	96-720-6076
	48.0333	0.7344	1.8926	11.8	(200)	Anatase	1.8925	96-720-6076
105W	25.3036	1.0090	3.5169	8.1	(101)	Anatase	3.5172	96-720-6076
	37.7674	0.6322	2.3801	13.3	(004)	Anatase	2.3799	96-720-6076
	48.0345	0.6242	1.8926	13.9	(200)	Anatase	1.8925	96-720-6076
150W	25.3048	0.7910	3.5168	10.3	(101)	Anatase	3.5172	96-720-6076
	37.7686	0.5374	2.3800	15.6	(004)	Anatase	2.3799	96-720-6076
	48.0357	0.5306	1.8925	16.4	(200)	Anatase	1.8925	96-720-6076



(d) 150 W



(b) 90 W



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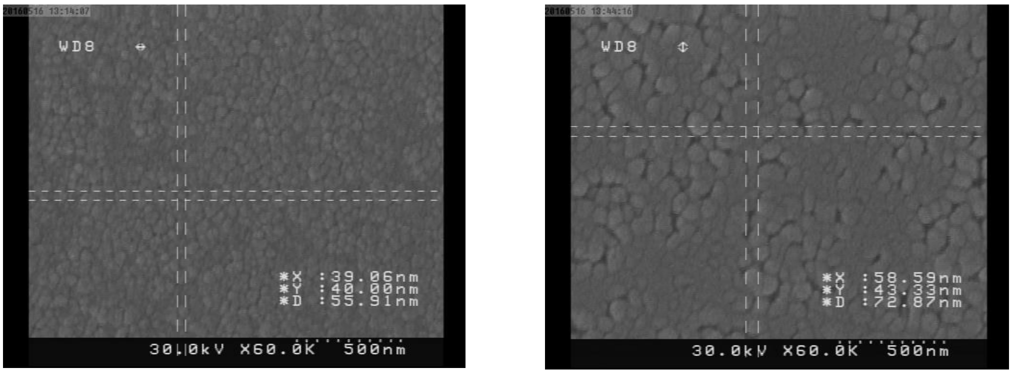
a) 75W, (b)

3.2.3 Scanning Electron Microscope (SEM):

Scanning electron microscopy is used to examine the structure of the film surface and study of surface morphology. From the figures below, the film is homogeneous, it can covers the entire surface area of the substrate, it has dense morphology and compact structure. The SEM photographs of pure thin films with various sputtering power are shown in Fig.(4-14)(a,b,c&d). These images were taken at different acceleration voltages, hence giving different signal, in order to obtain good resolution of the grains.

Fig. 4.14(a) for TiO$_2$ with sputtering power of 75W, showing the amorphous nature of the film with grain size (D=20nm). Fig.4-14 (b) and (c) show good crystallite resolution at 500nm magnification. The crystallite dimension increased with sputtering power from 90W to 105W as also observed in AFM measurements. Grain growth can also be seen from Fig.4-14 (d) which refers to TiO2 film deposited with sputtering power of 150W. According to (Lu et al. 2001), at high sputtering power, the TiO2 atoms are more energetic to reach the substrates resulting in the formation of nuclei. Hence, more nuclei present on the substrate, suggests more sites for grain growth. The average grain size in the deposited TiO2 films was estimated to be 23.5 nm, 33.0 nm, 38.6 nm, 44.3 nm with increase in sputtering power 75W, 90W, 105W, 150W, respectively.[8]



Power=105W **Power=150W**

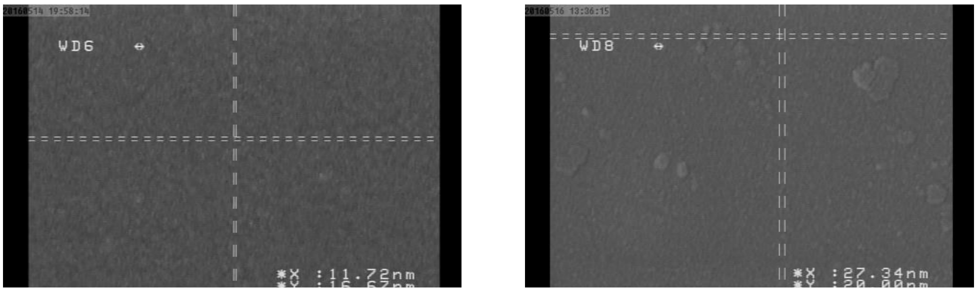


Figure (7) The SEM images of (TiO_2) thin films deposited on glass substrate at different sputtering power.

Power=75W **Power=90W**

4.concolosion

In this paper, we have done several studies on the structural and optical properties of TiO_2 thin films prepared by using RF magnetron sputtering under sputtering power of 75W to 150W at relatively low temperature (20-75 C°). XRD results showed only single prominent peak corresponding to TiO_2 (101) orientation of hexagonal close-packed (hcp) structure at sputtering power of 75W. As the sputtering power increased, the grain size and the surface roughness of TiO_2 films was found to be increased. Moreover, as the crystallinity of the TiO_2 films increased with sputtering power from 75W to 150W, the optical transmittance decreased. The significant changes in structural properties with increasing sputtering power lead to the growth of atomic mobility, therefore, the electrical resistivity of the TiO_2 films decreased.

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