Preparation Of (Cu- TiO$_2$) Thin Films, And Used as An Antibacterial

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**Abstract** Thin films of TiO$_2$ and TiO$_2$: Cu have been prepared on ITO substrates using RF magnetron sputtering technique. It is worthy to say that the thickness of the coated film was in the order of (220) nm. The films annealing in air at temperature 500°C with 2 h. Optical of structural properties were identified with various preparation conditions like Cu-doping concentration (0%, 2% and 4%). These prepared films are polycrystalline with a anatase crystal structure. The crystallinity and the size of particle of the samples of prepared were studied by (XRD), the results specified the size of particle of the samples of prepared dropped with the high of Cu doping concentrations some of the properties of structure are varied by the addition Cu levels as dopants. The films are oriented of preferentially forever the (101) direction. We have got some morphology of surface by (SEM), the results show decreasing of particle size with increasing doping concentration. The results show that the doping caused to decreased the transmittance and energy gap from (3.6 to 3.4) eV. Activity antibacterial efficiency was estimated by the un activation of E.coli. It was spotted that rising Cu levels gives better activity of antibacterial.

**Keywords:** TiO$_2$, thin films, activity of antibacterial, E.coli

1. **Introduction:**

Beings of human are often infective by bacteria, mold, microbe, and so on. To impart vainness (e.g. trays of hospital) and obviate infection (e.g. dressing of wound), the use of agents of antimicrobial is important [Wei and Chang (2011)]. Research has been carried of intensively out in materials of antibacterial containing different natural and substrates of inorganic [Bedikyan, and et al (2013)]. Present stage, antibacterial method in activity of photocatalytic of TiO$_2$ has attracted large attention reason it has minimal cost, rising activity of photocatalytic, stability of chemical and blameless side effect [Besserguenev,and et al (2003)]. It is known that TiO$_2$ has three structural phases which are rutile, anatase and brookite. In nature, rutile is the most joint phase of crystal while brookite is mingy. Rutile is the steady rising phase of temperature, whereas anatase and brookite are unstable and are convert of readily to rutile when heated up [Hartiti,and et al (2016)], the crystalline of anatase TiO$_2$ has been setup to be the most active of photocatalyst reason the slow recombination of motion rate of electron and hole compared with that of rutile and brookite. Activity of photocatalytic of TiO$_2$ highly depends...
onto its microstructure and properties of physical reason to various conditions of preparation and methods. Generally, TiO$_2$ is oftentimes used in two forms, i.e. powder or thin film. TiO$_2$ thin films can be prepared with several techniques such as sol-gel [Hartiti, and et al (2016); Moongraksathum, and et al (2018)] e-beam evaporated [Amotchkina, and et al (2014)] and vapor of chemical deposition [Besserguenev, and et al (2003); Masuda, and et al (2009)]. Which allows simply control of doping of chemical for the prepared materials. In the modern years, studies of many have been devoted to moreover get better the photocatalytic and properties of antibacterial of TiO$_2$, and the suggest of investigations that those properties can be increased by doping for metal of transition such as Ag [Sun, and et al (2008); Fakhouri, and et al (2015)], Fe$^{3+}$ [Liepina, and et al (2013)], Ni [Ganesh, and et al (2012)] and Cu [Moongraksathum, and et al (2018); Li, and et al (2015); Wojcieszak, and et al (2017)] which has also been inspected widely aiming at expanded activity of photocatalytic and antibacterial into the UV region. In this search, thin films of Cu doped TiO$_2$ deposited on glass slides were prepared by RF magnetron sputtering technique. Setup on our studies of previous, the amount of Cu in the range of 0 to 4mol% of TiO$_2$ is carry on. The influence of the Cu doping into TiO$_2$ thin films on the microstructure photocatalytic activity of antibacterial against E. coli

2. Experimental Details:

TiO$_2$ thin films were coated in clean substrates of glass by use a RF sputtering of magnetron technique with TiO$_2$ target of 99.99% pureness. Before coated, the substrates of glass were cleanout in an bath of ultrasonic with alcohol with 15 mins, wash in water of distilled, dehydrate for gas of nitrogen of 99.99% pureness and clamp on the possessor of substrate in the chamber. Chamber of sputtering was evacuated to $5.8 \times 10^{-5}$Torr by using a molecular of turbo pump. During coated, the pressure of working and temperature of substrate were constant of kept at 7x10$^{-2}$Torr and (200°C), on the other hand. Argon of commercial (Ar) of 99.9% pureness was used as the gas of sputtering and constant of kept with flow of rate of gas of 20 sccm that can be controll by a flow of mass obersever. TiO$_2$ films with sputtering power (100W).

3. Thin films characterization:

The properties of structural of coated TiO$_2$ films were analyses with use X-ray diffract meter (XRD), scanning electron microscope (SEM) and force of atomic microscope (AFM). The X-ray diffraction of the films were obtain use a Shimadzu X-Ray Diffract meter 7000 with a monochromatic light rise intensity CuK$\alpha$ radiation ($\lambda = 1.54056\text{Å}$) operated of radiation at 40kV and 30mA. The size of crystallite was calculated by the Scherer equation, Eq. (1), [Paul, and et al(2015)].

$$D = \frac{0.9 \lambda}{\beta \cos\theta_B} \quad \text{.........(1)}$$

where D is the average size of crystallite, $\lambda$ is the wavelength of the Cu K$\alpha$ line (0.15406), $\theta$ is the angle of Bragg and $\beta$ is the full-width at half-maximum (FWHM) in radians.
4. Structural Properties:

**XRD Analysis:**
The patterns of X-ray diffraction for copper doped TiO\(_2\) thin films in different copper-doping concentrations at 0, 2, and 4 wt.% are shown in Fig. 1. The patterns of XRD of TiO\(_2\) and TiO\(_2\)-Cu thin films are marked in peaks as correspond to anatase. It is found that thin films discover only the phase of anatase. Cu-phase of compound cannot be confirm in these peaks of XRD reason to a little amount of Cu doping. Phase of anatase fraction in TiO\(_2\)-Cu thin films seems to decrease with an rising in Cu doping. The sizes of crystallite of phases of anatase are 42.2, 28.4, and 14.2 nm for 0, 2, and 4% of Cu doping, respectively. It is clearly seen that the size of crystallite decreases with the rising of Cu dopant concentration.

![Fig.1. Pattern of XRD of TiO\(_2\) thin films at different doping level of Cu](image)

**Atomic Force Microscope Measurements (AFM):**
Fig. 2 reveals the (2-D) images of AFM of pure TiO\(_2\) thin films and doped for different concentrations of copper (0%, 2%, and 4%). The average size of grain of doped and non-doped synthesized TiO\(_2\) films is measured from AFM analysis using software and is found to be around 88 - 65 nm. AFM results show that by the addition of the Cu to TiO\(_2\) thin films they become more roughness, and size of grain became smaller. This result agree with that in literature [Wojcieszak, and et al (2017)], Table 1 shows the size of grain, roughness and root mean square of TiO\(_2\) thin films.

![Fig.2. Two dimension images of AFM of TiO\(_2\) thin films at different doping levels](image)
Table 1. Size grain and root mean square of roughness of surface obtained from AFM data

| Cu-concentration | Grain size (nm) AFM | Roughness (nm) | RMS (nm) |
|------------------|---------------------|----------------|----------|
| pure             | 88                  | 1.01           | 1.17     |
| 2%               | 74                  | 2.04           | 2.42     |
| 4%               | 65                  | 3.44           | 3.78     |

Scanning Electron Microscope (SEM):

Fig. 6 shows the Scanning Electron Microscopy (SEM) images that feature the morphology of surface of the TiO\textsubscript{2} pure and copper dopant films on substrate of glass. The SEM photograph obviously illustrates the formation spherical particle. Furthermore, it can be seen that all the films (purity and doped) have a more homogeneous morphology of surface, are intensiv with a few porosity and abide well to the substrate without any cracks. The sizes of grains obtained from SEM images are (80.22, 71.26 and 60.62 nm) at (0, 2 and 4 wt.% Cu) respectively. The distribution of particle in these films is found regular with a drop with average size of particle forever with an rising in Cu doping levels. Here it has been spotted that the non-doped film has particles of agglomerated as compared to the doped films with regular distribution of least size of particles. Forever with this decreasing in size the shape of these particles too gets varied with doping of copper in the TiO\textsubscript{2} films. This is a further substantiation of the rising in fault of stacking density, these results is in agree with the previous XRD results. These results are in agree with the results of previous [Paul, and et al (2015)]. This type of growth assists the application of these films as sensor of gas reason the film has a big open surface region to be expose for the gas. The size of particle shown by AFM, and SEM is higher than with that calculated from the XRD results. This is reason to the fact that the XRD give the average mean size of crystallite while AFM, SEM showed agglomeration of the particles. The XRD, AFM and SEM data can be reconciled by the fact that smaller particles of primary have a large surface free energy and would, thus, tend to agglomerate faster and grow into grains of bagger.

Fig. 3. The SEM image (top view) of TiO\textsubscript{2} thin films (a) pure (b) 2% Cu (c) 4 wt.% Cu.
5. The Optical Studies:

Fig. 4 shows the spectrum of optical transmittance of TiO$_2$ films doped with copper at different doping concentrations. The transmittance of the coated films was measured in the ultraviolet, visible regions of the spectrum of electromagnetic. The transmittance of the films drop from range 88.88% , 81.85 and 77.9% when the doping levels a rise from 0, 2 and 4 wt., the optical transmittance values are decrease with increase copper concentration this behavior by reason the increase in set free electron with the increase in copper concentration. This result agree with previous works [Li, and et al (2015); Wojcieszak, and et al (2017)]. The coefficient of absorption $\alpha$ has been studied from equation[Bedikyan, and et al (2013)].

$$\alpha = 2.303 \frac{A}{t} \ldots \ldots \ldots \ldots (2)$$

Where $\alpha$ is the coefficient of absorption, $A$ is the absorbance, $t$ is the thickness of film. Fig. 5 show the change of the coefficient of absorption of pureness and doped films with wavelength.

Fig. 4. Variation of transmittance with wavelength of TiO$_2$ thin films for different doping levels of Cu ((a) pureness , (b) 2% , and (c) 4%.

Fig. 5. Variation of absorption coefficient $\alpha$ with wavelength of TiO$_2$ thin films for different doping levels of Cu ((a) pureness , (b) 2% , (c) and 4%.
The band gaps of films are determined from the equation [Sun, and et al (2008)].

\[ \alpha h\nu = A(h\nu - E_g)^r \]  

where \( h \) is the constant of Planck’s, \( \nu \) is the frequency of light of fallen, \( E_g \) is the energy of optical gap of the material, \( r \) is the factor controlling the direct, indirect translation of the electrons from the valence band to the conduction band. Where \( A \) constant, \( h \nu \) is the energy of photon and \( E_g \) is the optical band gap. Fig. 6 shows the relationship between \( (\alpha h\nu)^2 \) and energy of photon \( h\nu \). Results show an rising in the Cu content between 0 to 6 wt.% resulting in a drop in the band gap from 3.6 eV to 3.4 eV. This drop in gap of energy is due to the impurities of prohibited that led to the forming of levels of donor within the gap of energy near the conduction band, this results is an agree with [Li, and et al (2015); Grass, and et al (2012)].

**Fig. 6.** \((\alpha h\nu)^2\) versus. Energy photon plot of (a) pure \( TiO_2 \) thin films (b) 2% Cu, (c) 4% Cu
6. **Study of Antibacterial Activity depicts:**

the results of the antibacterial property on the . The 0% Cu sample almost formed no zone of antibacterial, and this probably impute to the failure of the doped Cu. With the rising of the Cu doped in the TiO$_2$ films, 2% Cu and 4% Cu sample the zone of antibacterial formed and became larger as shown in fig.7. It also indicates that the TiO$_2$ doped with 4 % Cu thin films display higher activity of antibacterial compared to TiO$_2$ and TiO$_2$ doped with 2% Cu thin films, respectively. The E. coli kill rate percentages of TiO$_2$ and TiO$_2$-Cu thin ions of Copper—which are charged of positively, are easy to join with charged of negatively bacterial protein-further add with groups of sulfhydryl (-SH) of protein due to inactivation of the active of enzyme, which leads to death of bacterium [Grass,and et al (2012)]. The above of results prove that the Cu doped TiO$_2$ thin film properties of antibacterial, which was correlated of positively with the lilts of doped Cu; muncy doped Cu give to good properties of antibacterial. Thence, 4% Cu possessed the better antibacterial function in this search.

![Fig. 7. Antibacterial experiment of E. coli on the (1) 0% Cu, (2) 2% Cu, (3) 4% Cu, surfaces after 24 h of incubation.](image)
7. Conclusion:

In this research, TiO$_2$ and TiO$_2$ doped with Cu thin films were fabricated by technique RF Magnetron Sputtering. TiO$_2$ and TiO$_2$-Cu thin films discover only the phase of anatase. Phase of anatase fraction in the TiO$_2$-Cu thin films tends to decrease with rising Cu dopant. The sizes of crystallite of phases of anatase decreases with an rising in Cu dopant. All TiO$_2$ and TiO$_2$-Cu samples have the thickness 220 nm. Their surfaces are intense and very smooth. The activity of antibacterial of TiO$_2$-Cu thin films rising with Cu doping concentration. It can be noted that TiO$_2$ doped with 4 % Cu thin films exhibits higher activity of antibacterial under UV irradiation.

8. References:

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