Applied Mechanics and Materials
ISSN: 1662-7482, Vols. 773-774, pp 701-705
doi:10.4028/www.scientific.net/AMM.773-774.701

Submitted: 2014-09-12
Revised: 2014-12-24
Accepted: 2015-01-20
Online: 2015-07-15

Hydrophilic indicates Surface morphology quality of TiO_2/CdS nanocomposite film

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Keywords: Surface morphology, TiO_2/CdS NCF, Contact angle, Hydrophilic

Abstract: Engineering and decoration on the surface of metal oxide semiconductor (TiO_2) for increasing activity is challenging. Thus a novel method is introduced to determine surface morphology quality subsequently improving the photocatalytic behaviour. TiO_2 films are fabricated via laser deposition technique at various CdS thickness. Microstructural characterization and optical behaviours are characterized by felid emission scanning electron microscope (FE-SEM) and atomic force microscope (AFM). The hydrophilic property of TiO_2/CdS nanocomposite film (NCF) is examined via contact angle measurements. The grain density is found linearly increased with the contact angle. A mutual relationship is revealed between hydrophilic property and crystallization with respect to the CdS thickness. Thus, surface morphology of nanocomposite quality is quantified based on the hydrophilic measurement.

Introduction

Titanium dioxide is attractive inorganic solids because of its biologically and chemically inert, abundantly available and cost effective. It has high activity under ultraviolet but insensitive under visible light. One approach is based on an association of TiO_2 with other semiconducting materials with lower band gaps. This is a promising application in photoelectrochemical cell and solar energy transformation [1, 2]. TiO_2 thin films have been fabricated through several techniques including chemical vapour deposition [3], sputtering, sol-gel [4, 5] plasma oxidation [6] and pulsed laser deposition (PLD) [7-12]. Among available techniques, PLD of TiO_2 is a simple process to produce adherent film with brilliant mechanical rigidity[13]. On the other hand, the variation in deposition parameters such as pressure and temperature results in different chemical and structural compositions[14]. However, the critical challenge is to ensure that high quality surfaces with perfect grains distribution. Furthermore, assess surface with simple and non-destructive method. FE-SEM and AFM analysis is the best method to investigate surface morphology of the films. Nevertheless, unfortunately both of them are a destructive test and only display information to the local area. A contact angle method is used as a tool to study surface quality of the nanocomposites films, NCFs. The aim of the present work is to enhance the performance of TiO_2/CdS nanocomposite films (NCFs) surface and photocatalytic activity by controlling the thickness of CdS as doping layer. Furthermore, we are presented with a simple and efficient method to evaluate the best surface aggregation of TiO_2/CdS NCFs by contact angle method.

Experimental

A Q-switched Nd-YAG laser operating at a fundamental wavelength of 1064 nm was used as an energy source. The laser pulse duration was 10 ns with an output remain constant at energy density of 70 mJ/cm^2. TiO_2 thin films were prepared in an evacuated ablation chamber with a base pressure of 2.2 $x10^{-3}$ torr from Ti (99.9% purity) sheet in 3.5 cm diameter was used as ablation target. The target and substrates (microscope slides Corning 2947) were cleaned by a series of solutions including ethanol, acetone, and distilled water for 10 minutes in an ultrasonic bath to remove the impurity on the surface. TiO_2 film was evaporated on the glass substrates at a thickness of 400 ± 5 nm and annealed for 4 hours at 400 ˚C under the flow of oxygen. The CdS thin film at various thicknesses of 50 and 100 nm was deposited on TiO_2 film. The thicknesses of the film were measured by Edwards FTM 5 crystal thickness monitor. Finally, the samples were annealed at 400˚C for 3 hours under vacuum at a pressure of 10^{-4} torr. The surface morphology (top view), 3D surface morphology and atomic composition of the films were observed by FE-SEM model Supra 35 VP, AFM type SEIKO SPI3800N and EDS attached to FE-SEM. Contact angle (CA) measurement was used to determine the photocatalytic and the surface properties of TiO_2 film and TiO_2/CdS NCFs with a contact angle analyser at temperature 23 ˚C. A micropipette was used to measure a deionised water droplet with a volume of 6 µl. The droplets were located at five different positions on each sample for the measurement of contact angle.

Results and discussion

Fig.1 (a and b) shows the EDS spectra and chemical composition for the TiO_2 and TiO_2/CdS-NCF at 100 nm CdS thickness. The essential constituents of TiO_2 and TiO_2/CdS NCF such as titanium, oxygen, cadmium and sulfur with their abundances are clearly evidenced. The presence of silicon is due to the glass substrate.

Fig.1(c, d and e) shows the FE-SEM micrographs of TiO_2 and TiO_2/CdS nanocomposite films on glass substrates. Fig. 1 (c) exhibits a relatively smooth and uniform surface of TiO_2 which is free of cracks and consists of little porous structure due to the limited mobility of the atoms without heating the substrate. The individual grains are very tiny and almost invisible, but it can recognize small clusters in the sample. Fig.1 (d-e) shows the surface of TiO_2 films after associated with CdS in the range 50 to 100 nm. The granular structure is better than pure TiO_2 films, and they are presented well-crystallized and uniform grains. The micrograph also showed the regular morphology of agglomerates with size ranging from 11.2 to 38.19 nm. The difference in surface morphology of TiO_2 thin films and TiO_2/CdS NCFs deposited on the PLD could be related to the grow the mechanism of thin film as a result of CdS particles aggregation [15]. It is well known that the film is deposited through nucleation, grain growth, coalescence, filling of channels, and film growth processes

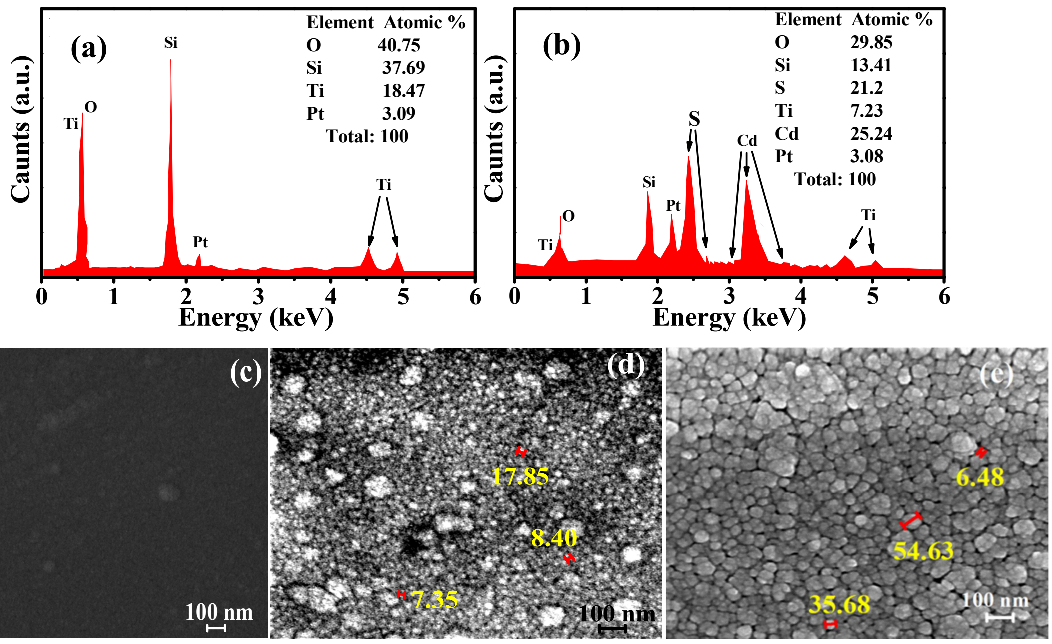

Fig.1. EDX spectra of (a) pure TiO_2 and (b) TiO_2/CdS NCF at 50 nm of CdS thickness and FE-SEM images of (c) as deposited TiO_2 and (d) TiO_2 after annealing and TiO_2/CdS nanocomposite film at different thickness of CdS of (e) 50 nm and (c) 100 nm

The interactive 3D AFM surface topography (analyses by Image J software) is illustrated in Fig.2. These images clearly show the nanostructured nature of the films and how the granular structure changes with increasing CdS thickness. Fig.2 (a) presents the pure TiO_2 thin film shows smaller individual grains with 23% grain density (ratio of grains area to the whole sample area). Fig.2 (b-c) displays surface morphology of the samples at 50 and 100nm CdS thicknesses. The grain size of the films doped with CdS to syntheses TiO_2/CdS NCFs has a tendency to become bigger at higher CdS thickness. Moreover the vertical height takes a larger than pure TiO_2, and it is synchronised with increasing the grains distribution from 42% to 93% at 50 and 100nm of CdS thickness respectively. These increases in grains distribution are referring to larger roughness by reducing the separation between the grains at CdS equal 100nm. However, grains size and films topography of the NCF is related to the thermal process during CdS deposition that caused diffusion of CdS into the TiO_2 film as reported [1].

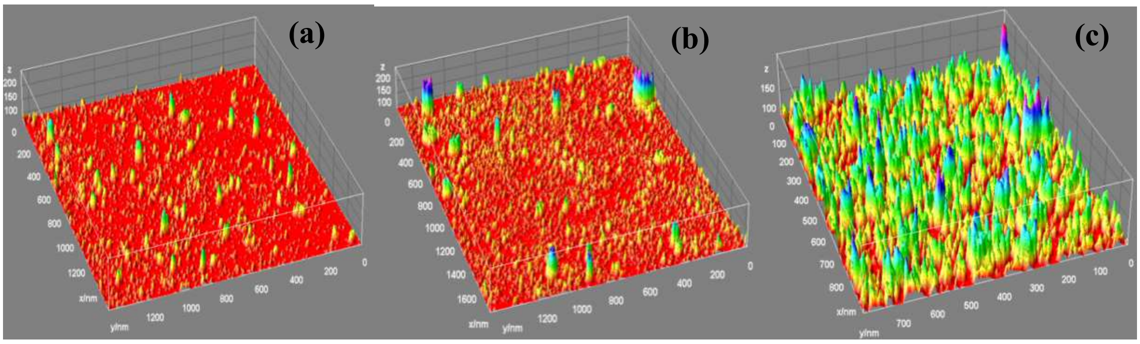

Fig.2 AFM surface morphology of the (a) pure TiO_2 and TiO_2/CdS nanocomposite film at different thickness of CdS of (b) 50 nm and (c) 100 nm

It is very clear the surface topography of the films present regularly-shaped grains, which suggests the growth of the nanocrystalline of composite grains for all the CdS thicknesses. Undoubtedly, the un-doped films appeared to be smooth, defect-free and homogeneous as displayed by FE-SEM results. Conversely, the TiO_2/CdS NCF exhibits higher porosity due to heterogeneous redistribution of the nanoparticles on the surface. The best surface quality and with good grains density of TiO_2/CdS-NCF is obtained for CdS thickness of 100 nm. We assert that the surface can be improved with high density distribution of CdS nanoparticles by the pulsed laser technique. Earlier findings suggest that for distinct catalytic and synthetic properties, the TiO_2 film must exist in the crystal structure with minimal defects and high charge carrier mobility [2]. However based on the finding in this experiment result the possibility to achieve better crystallinity and higher photo-catalytic activity in TiO_2/CdS-NCF is highly depending on CdS thickness.

Contact angle

Fig.3 shows the results for contact angle measurements for pure TiO_2 and TiO_2/CdS NCFs at different CdS thickness. It can be seen from Fig.3 that the contact angles are found~ 59^o, ~ 65^o and ~$74^o \pm 0.2^o$ for the TiO_2 and TiO_2/CdS at 50, and 100 nm of CdS thickness respectively. This behaviour is attributed to surface strain energy, which is generally lower at higher CdS thickness. Based on the results of Fig.3 the contact angles are less than 90^o this means, the material is classified as hydrophilicity[16]. The contact angle of water drops gradually increases with CdS thickness as well as synchronization with the increased of grain density (G_D). This indicates that the hydrophilic nature of the surface also depends on the grain density[17].

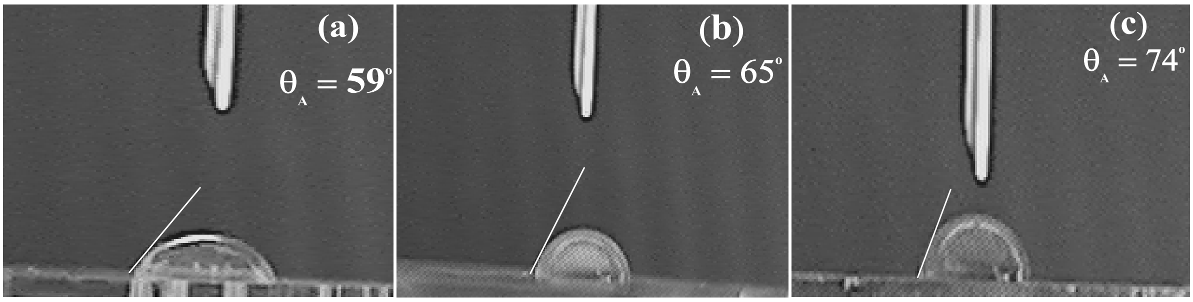

Fig.3. The results of contact angle measurement which produced at different CdS thickness. (a) 0 nm. (b) 50 nm, (c) 100 nm

Fig. 4 (a) presents a linear relationship between contact angle and grain density. Hence expressing by the following empirical equation:

$$G_D = m\,\theta_A \qquad (1)$$

where G_D, θ_A and m represent the grain density, contact angle and constant respectively. These two factors (thickness and crystallization) are mutually related to the hydrophilicity property of the nanocomposite film. Since crystallization dependent directly to hydrophilicity hence a contact angle can be a simple way to determine a surface quality. Fig. 4 (b) illustrates the proportionality between contact angle, grain density ratio and CdS thickness. It is obviously shown that the three parameters have a mutual relationship. CdS thickness is responsible to increase both the crystallization as well as the hydrophilic property of the nanocomposite film. This shows the important role of CdS thickness in synthesizing the TiO_2/CdS NCFs. The thicker layer of CdS film means the better performance of photocatalytic material as well as the photochemical properties [15].

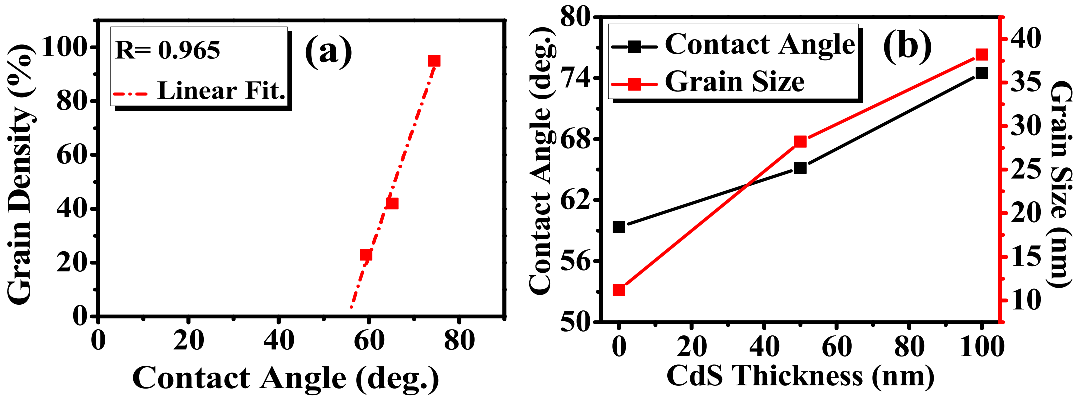

Fig.4 (a) indicates the relationship between contact angle and grain density ratio of TiO_2 and TiO_2/CdS NCFs and (b) the variation of contact angle and grain size with CdS thickness

Summary

A useful tool to evaluate the relation between hydrophilic properties and crystallization of material is presented. A linear relationship is observed between the contact angle and the grain density. Such linearity is entirely dependent on the thickness of the CdS which deposited on TiO_2 to improve the photocatalytic material TiO_2/CdS nanocomposite property. The contact angle is explanatory to the morphology changes. The enhancement surface quality of the nanocomposite thin film is based on the increasing of CdS thickness.

Acknowledgements

The authors are grateful to MOHE through UTM grant Flagship 00G79 for the financial support in this project. We are thankful to Wasit University, Iraq for providing the experimental facilities.

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