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Characterization of cadmium sulfide/titania heterostructure films by utilizing microstructure and optical characteristics

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ABSTRACT

Engineering and controlling the bandgap of semiconducting metal oxide (TiO_2) to enhance photoactivity under visible light is challenging. Impact of the changing CdS thickness (50–150 nm) on the structure and optical properties of the CdS/TiO_2 heterostructure films (HSFs) which fabricated by pulsed laser deposition (PLD) was observed. XRD, FE-SEM, AFM, UV–vis and PL spectroscopy measurements were utilized to characterize structural and optical behaviors of the films. XRD measurement shows gradual increments of the lattice constants of the films with the increase of CdS thickness. The mean values of the calculated lattice constants and cell volume (V) were $a=b=0.3785$ nm, $c=0.9475$ nm and $V=13.58$ nm^3 respectively. The average of crystallite sizes estimated for TiO_2 and CdS/TiO_2 at various CdS thickness is 12.20, 13.49, 24.24 and 43.10 nm. FESEM images prove the high quality nanocrystalline nature of the films without cracks and dislocation. The root means square roughness of the films was increased with the increase of CdS thickness as showed by AFM images. UV–vis measurement reveals an improvement in the optical absorbance of HSFs in the range of 380–550 nm due to presence of CdS. Interestingly, the PL intensity was enhanced by a factor of nineteen compare to pure TiO_2 attributed to the charge carrier recombination in the band gap. The current results suggest that possibility to improve the optical and structural properties of the TiO_2 films and also it possible to fabricate high quality CdS/TiO_2 HSFs by variation of the CdS thickness.

1. Introduction

Titanium dioxide (TiO_2) or “Titania” is attractive inorganic solids because of its biologically and chemically inert, abundantly available and cheap. TiO_2 in pure form is n-type and exist in three main phases known as anatase, rutile and brookite. Among the main phases, only anatase and rutile phases are exploited for sundry technological applications [1] Normally TiO_2 is used as a powder or thin films depending on the type of application, where the powder almost uses for gas and liquid phase catalysis, whenever in the thin films form, it is usually used as a photoelectrode in photoelectrochemical system (PEC) and dye sensitized solar cell (DSSC) for photon harvesting. In addition, the thin film form of TiO_2 has the perfect energy position of the conduction and valence bands to redox the electrolyte. This helps to enhance the electron separation by the photoelectrode potential. The exotic bonding between the oxygen and titanium imparts unique properties, such as chemical inertness and high optical activity, especially under UV and insensitiveness under visible light which is detrimental for photovoltaic applications. The association of TiO_2 with other semiconducting materials of lower band gaps such as cadmium sulfide (CdS) or metals is one of the promising route for their exploitation in photo-electro-chemical cell and solar energy transformation [2–7]. TiO_2 thin films were produced by numerous techniques like chemical vapor deposition [8], sputtering, sol–gel [9,10] chemical bathe deposition [11] and pulsed laser deposition (PLD) [12–17]. Among available techniques, PLD provides a high energy process which make unique adherent film with brilliant mechanical rigidity [18] and assisted with high specific surface area [19]. Both of Ti and TiO_2 used targets to fabricate TiO_2 thin film under different conditions (i.e. substrate materials, pressures and temperature) make it difficult to compare and understand the differences in properties of the thin films in a consistent manner. Pulsed laser deposition of TiO_2 is a simple process already involves a complicated physical phenomenon.

The aim of the present work was to produce high-quality TiO_2 films by pulsed laser deposition at room temperature using the

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Nd: YAG laser and then associated with CdS to syntheses CdS/TiO_2 heterostructure film (HSF). Furthermore evaluate the structure and morphology of the deposited TiO_2 and CdS/TiO_2 HSFs via X-ray diffractometer (XRD), field emission scanning electron microscopy (FESEM) and atomic force microscope (AFM). Optical absorption and photoluminescence (PL) were also determined.

2. Experimental

TiO_2 thin films were prepared in an evacuated ablation chamber with a base pressure of 2.2×10^{-4} torr. Ti sheet of diameter 3.5 cm and purity 99.95% was used as the ablation target by Nd: YAG laser (1065 nm) in 10 ns duration and total energy 70 mJ/cm^2. First, the titanium target was cleaned by a series of solutions, ethanol, acetone, and distilled water for 10 min in an ultrasonic bath to remove the impurity on the surface. Second, 400 ± 5 nm of Ti films were grown on Corning glass type 2947, placed at 5 cm from the target. Ti films annealed for 4 h at 400 °C under oxygen flow for transferring to TiO_2. CdS thin film evaporated on TiO_2 film by electron beam deposition at different thicknesses (50, 100, 150 nm). Finally, the films were annealed at 400 °C, for 3 h under vacuum at a pressure of 10^{-4} torr. The structural characterization of the films was carried out by using X-ray diffraction (XRD) manufactured by Cu-Kα radiation of BRUKER's D8 ADVANCE with wavelength ($\lambda=1.5406$ Å), and 2θ (20–70°) configuration. The surface morphology (top view and crussection) of the films is observed by field emission scanning electron microscopy (FESEM) type Supra 35 VP and 3D surface morphology by Atomic Forces Microscopy (AFM) type SEIKO SPI3800N. The composition of the films was analysed by energy dispersive X-ray (EDX) attached to FESEM. Optical measurements in the Ultraviolet (UV) and visible range were performed in UV-3101 PC UV–vis–NIR spectrometer in the wavelength range of 200–800 nm was used to obtain the absorbance and reflectance spectra. Electrons transition and trapping processes are performed in Perkin Elmer LS 55 photoluminescence spectroscopy in the range of 200–800 nm in order to identify the excitation energy.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows XRD spectra of TiO_2 film and CdS/TiO_2 HSFs on glass substrate for different CdS thickness. The polycrystalline nature of TiO_2 is exhibited by the occurrence of peaks at 25.6, 36.3, 38.4, 47.8, 55.1, 62.6 and 68.9, corresponding to (101), (220), (112), (200), (211), (204) and (116) lattice planes, respectively. Furthermore, the peak for CdS at 29.42° matches with (101)H planes. XRD pattern approves the existence of two phases of TiO_2 anatase and rutile in addition hexagonal of CdS regarding to JCPDS card 21-1272, 21-1276 and 41-1049. The pre-annealed and post-annealed Ti films samples are coded as L1 and L2. Other three samples of CdS/TiO_2 HSFs for CdS thickness 50 nm, 100 nm and 150 nm are coded as L3, L4 and L5, respectively. It is worth noting that the absence of any significant shift in the principal peaks for all samples confirm the separated phases of CdS and TiO_2 lattice which is in agreement with others findings [20,21]. The presence of prominent anatase phase is ascribed to the growth dynamics associated with the activation of Ti^{+3}, O^{+2} ions evaporated to acquire minimum free energy landscape on the grown surface or due to the high kinetic energy of the ablated species impinging on the substrate at room temperature. The lattice parameters ($a=b$ and c) and cell volume (V) for the crystal plane (101) obtained by MDI JAD 6.5 software are summarized in Table1. It is found to

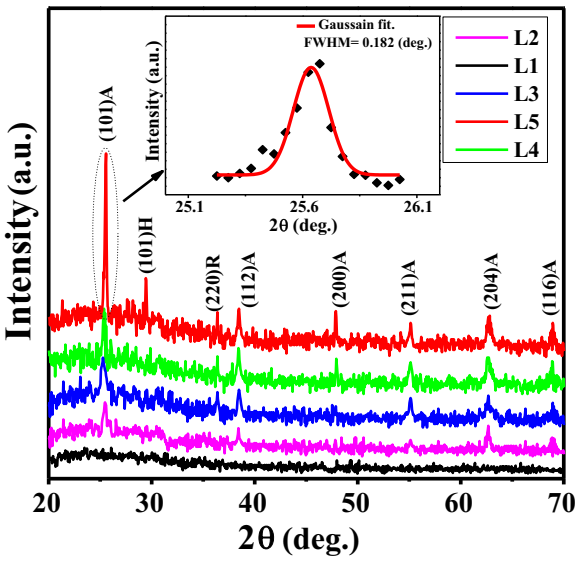

Fig. 1. XRD patterns of TiO_2 film and CdS/TiO_2 HSFs indicating the Anatase (A) and Rutile (R) phases of TiO_2 and hexagonal phase of CdS (H).

decrease regularly with the increase of CdS thickness. This decrement is resulted from the small differences in lattice constants between TiO_2 and CdS or because of the presence both of rutile and anatase within one particle [22]. The most intense peak (101) is selected to calculate the particle size (D) using Debye–Scherrer formula:

$$D = \frac{0.9\lambda}{\beta\cos(\theta)} \quad (1)$$

where λ, β, and θ are the wavelength, full width at half maximum (FWHM) the diffraction angle respectively. The achieved average particle size for samples L2, L3, L4 and L5 are 12.20, 13.48, 24.24 and 43.1 nm for CdS thickness 0, 50, 100 and 150 nm respectively. The increase in grain size with CdS thickness is attributed to the aggregate formation of CdS particle. The strong influence of the CdS thickness variation in the formation of phase and texture are clearly substantiated.

3.2. Elemental analysis

Fig. 2(a) and (b) shows the EDX spectra of TiO_2 (L2) and CdS/TiO_2 HSF (L4) respectively. The essential constituents of TiO_2 and CdS/TiO_2 HSF such as titanium, oxygen, cadmium and sulfur with their abundances are clearly detected. The presence of silicon is due to the glass substrate.

3.3. Surface morphology using FESEM

Fig. 3 shows the FESEM micrographs of Ti, TiO_2 and CdS/TiO_2 HSFs on glass substrates. Smooth and uniform surface of Ti and TiO_2 without cracks that consist of relatively little porous structure due to the rapid deposition at room temperature are manifested in (Fig. 3(a) and (b)). Inset figure of samples L1 revels very small individual grains and almost invisible. Furthermore, in the annealed sample L2 (Fig. 3(b)), the grains are clearly noticeable as relatively larger clusters. It is worth mentioning that, the growth of pre-annealed TiO_2 film deposited by PLD technique is amorphous-like. However, the post-annealed sample with oxygen flow make favorable transfer completely to TiO_2 that follows clusters by cluster growth process. Fig. 3(c–e) shows the CdS/TiO_2 surface at the thickness of 50–150 nm of CdS. The granular structure is prominent compare to pure TiO_2 films. They presented well-