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Effect of cadmium sulfide thickness on electron beam-deposited titania/cadmium sulfide nanocomposite films

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ABSTRACT

Improving the photo-catalytic response of TiO_2 semiconductor nanocomposites to visible light is the key issue. Heterogeneous TiO_2/CdS nanocomposite films (NCFs) are successfully deposited on the p-type [110] silicon substrate using an electron beam deposition (EBD) method. We report for the first time CdS thickness dependent photocurrent response of such NCFs. Effects of varying CdS thicknesses (50–150 nm) on the structural, optical and electrical properties are examined. The lattice parameters and nanocrystallinity of these NCFs obtained from XRD measurement show gradual increment with increase of CdS thickness and preferably grow along (101), (112) and (200) directions for various CdS thicknesses. The calculated value of mean lattice parameters and volume is $a=0.371$ nm, $c=0.945$ nm and $V=13.73$ nm^3 respectively. The estimated average crystallite sizes for TiO_2 and TiO_2/CdS NCFs at various CdS thicknesses are 12.3, 24.9, 39.59 and 42.4 nm. Interestingly, the FESEM images reveal clusters-like growth pattern attributed to the mechanism of particles agglomeration towards free energy minimization. The UV–vis reflectance in the range of 350 to 700 nm decreases due to the introduction of CdS in the NCF due to increased visible absorption. The TiO_2/Si and CdS/TiO_2/Si heterojunction exhibits a rectifying behavior with considerably high photocurrent contrast and fast responses to visible light due to enhanced light absorption. The dark current increases significantly with increasing CdS thickness due to increase in grain size. Our results suggest that the structural and optoelectronic properties of TiO_2 films can significantly be improved by varying the thicknesses of CdS film useful for nanophotonics.

1. Introduction

Semiconducting titanium dioxide (TiO_2) films have attracted considerable attention due to their strong oxidizing power, non-toxicity, high photochemical corrosion resistance and cost-effectiveness [1]. Currently, they find widespread applications in environmental, chemical, medical, and energy (hydrogen production through water splitting) fields [2–6]. TiO_2 thin films are fabricated through several techniques including chemical vapor deposition [7], sputtering [8,9] sol–gel [10] pulsed laser deposition [11] and hydrothermal deposition technique [12]. Their extreme insensitiveness to visible light and strong activity to UV-light limits the application for harvesting solar energy. The association of TiO_2 with other semiconductor materials of lower band gaps like CdS is found to be promising for photovoltaic applications [13]. Conversely, the high sensitivity of CdS to visible light makes it potential candidate for photo-electrochemical cell and solar energy transformation

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[14,15]. Consequently, the deposition of different types of thin film composites for improving the optical properties of each component remains challenging. The physical properties and structural morphology of these materials are very sensitive to the preparation method and thermal treatment. Photosensitization of TiO_2 by CdS is investigated in the form of composite particles and surface-modified electrodes. Their effective charge separation and transformation of photo-excited charge carriers are reported [16,17]. Detail understanding on the mechanism of charge injection between the two semiconductors that could enhance the efficiency and possibly create a longer time for charge separation is still lacking.

We report the CdS thickness dependent properties of TiO_2/CdS NCFs fabricated using a simple and precise method called electron beam deposition (EBD). NCFs are deposited on the silicon substrate following thermal treatment. Significantly higher sensitizer and large contact area that allows enhanced light scattering and electron transport are achieved by coupling TiO_2 with CdS on Si.

2. Experimental

Samples of TiO_2 and TiO_2/CdS composite are prepared on p-type [110] silicon substrates by an electron beam deposition (EBD) method which operates at energy of 3 keV and 2×10^{-5} Torr pressure with the evaporation rate of 0.5 nm/min. TiO_2 film is evaporated on cleaned substrates of thickness 400 nm and annealed for 4 h at 400 °C under the flow of oxygen. The CdS thin film with varying thicknesses (50, 100 and 150 nm) is then deposited on TiO_2 film. The thicknesses of the film are measured by crystal thickness monitor type Edwards FTM 5. Finally, the samples are annealed at 400 °C, for 3 h under vacuum at a pressure of 10^{-4} Torr. The structures of the films are investigated by an X-ray diffractometer model Bruker D8 Advance using Cu Kα line ($\lambda=1.5406$ A) with 2θ varying in the range of 20–70°. The surface morphology is analyzed using a field emission scanning electron microscope (FE-SEM) model Supra 35 VP. Average particles diameter (D) is estimated by considering the mean of 50 particles (different sizes) from the FE-SEM micrograph using an Image J 1.48 software (developed at the National Institutes of Health—USA). The UV–vis measurements in the wavelength range of 200–1000 nm are performed via a UV-3101 PC UV–vis–NIR spectrometer. I–V characteristics are examined using Source Meter-Keithley 2400. A 50 W halogen lamp model MR16 GU10 from Philips is used as the excitation source for recording the photo-response.

3. Results and discussion

3.1. Structural, morphological and compositional studies

Fig. 1(a) shows the XRD patterns of the TiO_2 (S1) and TiO_2/CdS NCFs for different CdS thicknesses of 50, 100 and 150 nm corresponding to samples labelled as S2, S3 and S4 respectively. All the samples (except tetragonal TiO_2) are in the anatase and hexagonal CdS (except S1) crystalline phases according to JCPDS Card no. 21-1272 and 41-1049 respectively. The predominant anatase phase consists

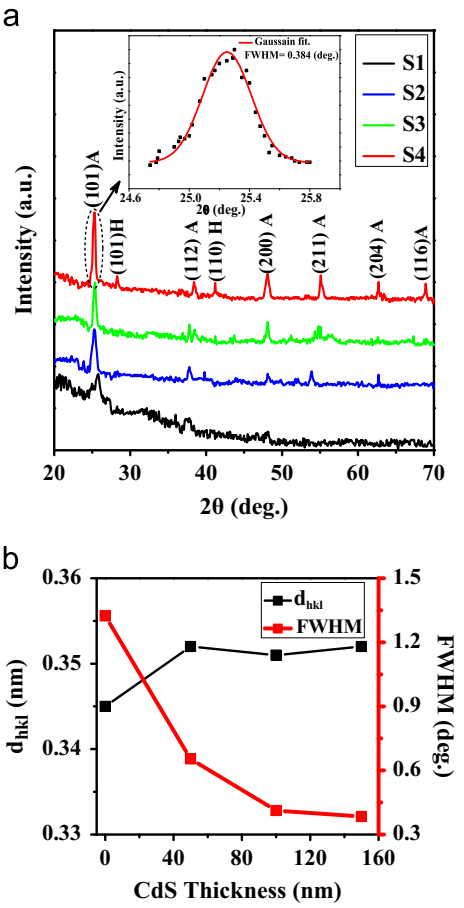

Fig. 1. (a) XRD patterns of TiO_2 film and TiO_2/CdS NCFs for the samples S1, S2, S3 and S4. The anatase (A) phases of TiO_2 and the hexagonal phase of CdS (H) are indicated. (b) The variation of d_{hkl} and FWHM with CdS thickness.

of $(TiO_6)^{2-}$ octahedral which shares edges and corners differently. The anatase possess four edges shared per octahedral without corner sharing forming a zigzag chains of octahedral linked to each other through shared edges. Our observation is supported by the experimental results of Ti–O phase diagram which displays the higher stability of the anatase phase compare to the rutile one under natural conditions [18]. The growth reaction leads to anatase phase because the zigzag configuration is statistically favorable [19]. Despite the rutile phase is more stable than other phases of TiO_2, anatase structure is highly suitable for solar cells application.

Fig. 1(a) clearly displays that the preferential growth direction of all the samples are along (1 0 1), (1 1 2) and (2 0 0) directions appearing at 25°, 37°, and 47.8° respectively for S1. This is in agreement with other work deposition of CdS which causes two new peaks at 53.9° and 62.7° for the samples S2 and S3 corresponding to the crystal planes (2 1 1) and (2 0 4), respectively. In addition, S4 displays new peaks at 28.3° and 41.2° related to the direction of (1 0 1) and (1 1 0) for the hexagonal CdS and at 68.9° related to (1 1 6) planes of TiO_2, which are in good agreement with previous report [20]. Meanwhile, the