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Preparation and Characterization of Chemical Bath Deposition synthesis CdS Nanocrystalline Thin Films

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Abstract

Cadmium sulfide (CdS) nanocrystalline thin films are prepared onto ITO-glass and Si(111) substrates by chemical bath deposition method. The scanning electron microscope images showed that the CdS thin film onto Si substrate is more homogenous without vacancies. The XRD patterns of the CdS nanocrystalline thin film confirm that they have polycrystalline with cubic phase. Room temperature photoluminescence (PL) spectrum of the CdS nanocrystalline thin films shows emission band located at 502nm for CdS/Si sample while the CdS/ITO-glass thin films shows a broad emission band peaked at 505nm. The Raman spectra of CdS nanocrystalline thin films prepared onto Si and ITO-glass substrates contain two main peaks which are corresponding to the first and second-order longitudinal optical (LO) phonon modes.

Keywords: Nanocrystalline materials, CdS, Photoluminescence spectra, Thin films, Chemical bath deposition.

تحضير أغشية CdS النانوية بطريقة الترسيب بالحمام الكيميائي ودراسة خصائصها

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الخلاصة

حضرت أغشية المركب CdS نانوية التركيب على قواعد ITO-glass و Si (111) بطريقة الترسيب بالحمام الكيميائي. أظهرت صور المجهر الإلكتروني الماسح أن أغشية المركب المرسبة على السليكون كانت أكثر تجانساً وقليلة الفراغات. أنماط حيود الأشعة السينية بينت أن الأغشية المحضرة كانت متعددة التبلور ويتكون مكعب. طيف الانبعاثية الضوئية (PL) لأغشية CdS/Si تتركز عند الطول الموجي 502 نانومتر بينما كان طيف الانبعاثية عريضاً لأغشية المركب CdS/ITO مع التمرکز عند الطول الموجي 505 نانومتر. أنماط رامان لكلا النموذجين المحضرين على قواعد Si وقواعد ITO أظهرت قمتان رئيسيتان تعودان للنمطين الأول والثاني من الدرجة الطولية لنمط ضوئية-صوتية.

Introduction

The fabrication of nanocrystalline materials has gained considerable interest in the field of materials research over the past decade because of their unique chemical and physical properties. Among these properties, the very high surface-to-volume ratio is the most remarkable [1]. The control on the fundamental properties of materials, such as magnetic, optical, and electrical properties, can be achieved without altering their chemical composition by controlling the size, structure type, and surface states of the nanocrystalline materials [2, 3]. Cadmium sulfide (CdS) is one of the most

important II–VI semiconductors, with a direct band gap of 2.42 eV at room temperature [4]. It is extensively used in optoelectronic devices because it tunes emission in the visible-light range; it is also widely used to fabricate solar cells with other p-type compounds, such as CdTe, Cu₂S, CuInSe₂, and Cu(In,Ga)Se₂ [5–10].

Various techniques can be used to obtain nanocrystalline CdS thin films including thermal evaporation, ultrasonic spray pyrolysis, sol–gel spin coating, pulsed-laser deposition, and solvothermal method [11–15]. Among these methods, chemical bath deposition (CBD) is a simple and convenient, inexpensive technique that produces homogeneous and high-quality thin films and don't require high temperature or vacuum system which making it preferable method compare with other techniques such as chemical/physical vapor deposition [16–19], Vary morphological, optical and electrical properties of nanocrystalline CdS thin films is very remarkable by adjusting the grain size for technological applications by using easy and low cost method. Then, NCs CdS thin films are deposited on various substrates using CBD method.

Experimental procedure

Cadmium sulfide (CdS) nanocrystalline thin films are prepared onto ITO/glass and Si(111) substrates by chemical bath deposition (CBD) method. The ITO/glass were washed by distilled water and then cleaned ultrasonically for 2mints acetone, ethanol, and isopropanol solutions, respectively while Si substrate was first immersed in diluted HF for 20sec to remove oxide layer and then washed by ethanol. Nanocrystalline CdS thin film was deposited on the substrates by CBD method in a solution containing 0.05M of cadmium nitrate [Cd(NO₃)₂] and 0.07M of thiourea [CS(NH₂)₂] that used as a Cd²⁺ and S²⁻ ions source, respectively. Ammonium acetate [NH₄CH₃COO] with 1M is added as a buffer solution to control the reaction rate. The pH of the solution was raised to 10 by adding ammonia solution and the total volume was 100ml Ammonia. After stirred the solution for 2min, the substrates are immersed vertically in the beaker and then placed on the hot plate under temperature of 80 °C for 30min. Finally, the samples are taken out of the solution and washed by distilled water to remove any contaminants and left to dry naturally. Yellowish layer is covered the substrate indicates to synthesis CdS thin film. The morphology of the thin films was examined using a Field Emission Scanning Electron Microscope (FE-SEM) (FEI Nova NanoSEM 450). Crystalline structure is studied by X-ray diffraction (XRD; PANalytical X'Pert PRO replaced with CuKα (λ= 1.5406 Å) radiation. Photoluminescence (PL) and Raman shift are investigated using Horiba Jobin Yvon HR 800 UV equipment.

Description the chemical reaction

Reaction mechanism

Adding ammonia solution to the water lead to produce ammonium and hydroxide ions as shown below [20]:



The dissolution of CdAc₂ or CdCl₂ in water leads to provide free cadmium ions (Cd²⁺). These ions react with the hydroxide ions to create cadmium hydroxide [Cd(OH)₂], which is finally react with ammonia to produce cadmium tetramine complex [Cd(NH₃)₄]²⁺. The reactions below describe these interactions [17]:



Adding thiourea to the solution lead to the provision free sulfur S²⁻ ions, as shown in Eq. (4) and (5) below:



Finally, the CdS thin film form by the reaction the ions of [Cd(NH₃)₄]²⁺ and S²⁻. [Cd(NH₃)₄]²⁺ + S²⁻ ↔ CdS + 4 NH₃ (6)

Results and discussion

Surface Morphology

The surface morphology of the CdS nanocrystalline thin films grown on ITO and Si substrate was analyzed through FESEM images. The FESEM images of as deposited CdS are shown in Figure-1A and 1B. The surface morphology of ITO substrate clearly shows that the film is almost inhomogeneous, with thin film covered all the substrate surface. Thin film of CdS nanocrystalline prepared on Si substrate was more homogeneous with small circular shape of particles and high density were observed compare with ITO-glass substrate.

The size distribution diagrams illustrate that the size of CdS nanoparticles grown on ITO substrate is varied from 30nm to 120 nm. In the other hand, the average size of CdS nanoparticles is increasing from 15nm to 85nm for CdS thin film prepared on Si substrate. The thickness of the thin film grown on ITO and Si substrate measured from the cross-section of the FESEM image were 240nm and 201nm, respectively (see Figure- 2A and 2B).

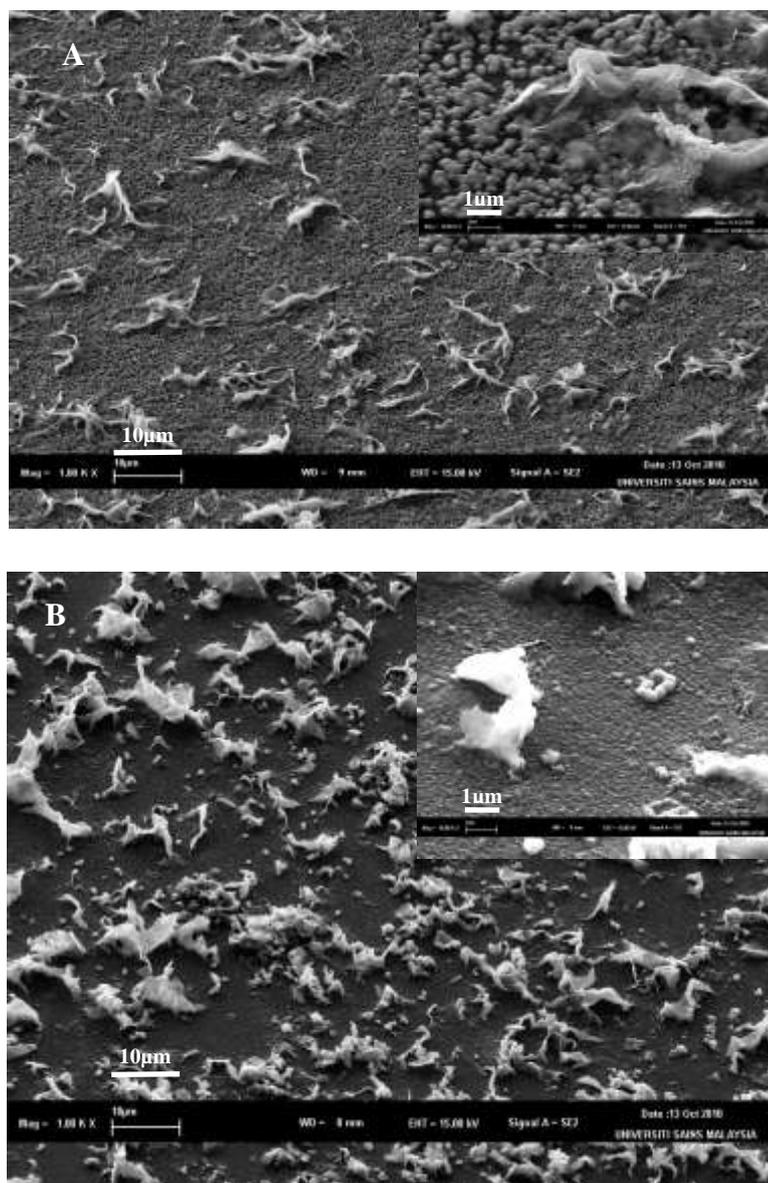


Figure 1-FESEM images for CdS nanocrystalline thin films prepared onto (A) ITO and (B) Si(111)

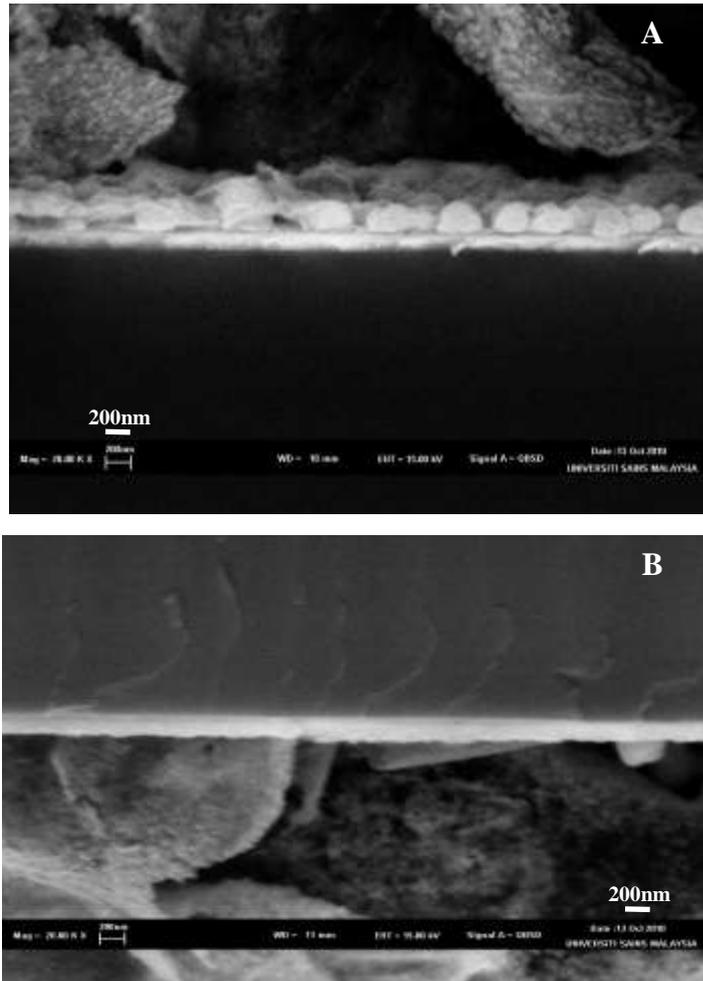


Figure 2-Cross-sectional images of CdS nanocrystalline thin films synthesized onto (A) ITO and (B) Si substrate.

Crystalline Structure

The XRD patterns of the CdS nanocrystalline thin films prepared using different substrates are shown in Figure- 3. A one major diffraction peak are observed in the pattern of grown CdS NCs on all substrates that which correspond to the diffraction angle (2θ) of 26.68° and 26.75° respectively. This peak position corresponds to the lattice planes of c(111) and h(002), which matches that of a cubic and a hexagonal structure, respectively. Another peak with low diffraction intensity could be observed at the diffraction angle (2θ) of (44.20° and 44.39°) for CdS c(220) or CdS h(110), respectively. The samples that prepared on ITO and Si substrate also present low diffraction peak at 50,59 and 52,1 corresponding to plane (311) of CdS cubic structure. The diffraction peak at 30.17° related to the (200) plane of the ITO appeared conspicuously in the sample prepared using ITO coated glass substrate as shown in Figure- 3. On the other hand, prepared CdS NCs on Si substrate present diffraction peak at 28.42° which belongs to the (111) plane of Si. However, R. Demir and F. Gode found that as-deposited CdS films by CBD method onto glass substrates shows a polycrystalline and a mixed phase of both cubic and hexagonal structure [21]. The grain size of the NCs CdS thin films prepared on ITO-glass and Si(111) substrates were calculated using Scherer's equation [22]:

$$P_s = \frac{0.9\lambda}{\beta \cos \theta}, \quad (7)$$

Where P_s is the grain size (nm), λ is the wavelength of the X-ray (0.15 nm), β is the full-peak width at half maximum (radians), and θ is the diffraction angle (radians). The P_s of CdS thin films prepared onto ITO-glass substrates was 28nm while the P_s for the sample that prepared onto Si(111) was 38nm.

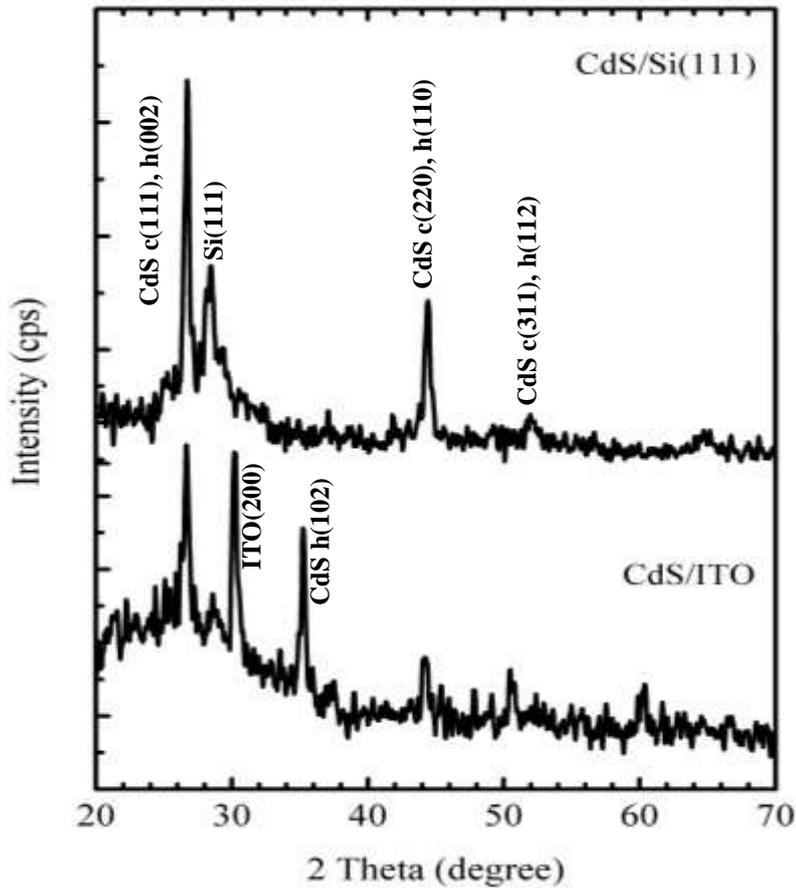


Figure 3- XRD spectra of the CdS nanocrystalline grown onto ITO-glass and Si(111) substrates.

Optical properties

Photoluminescence spectra

Figure -4 shows the room temperature photoluminescence (PL) spectrum of the CdS nanocrystalline thin films prepared onto ITO-glass and Si wafer substrates. The CdS/Si(111) sample shows emission band located at 502nm while the CdS nanocrystalline thin films that prepared onto ITO-glass shows a broad emission band peaked at 505nm. The optical band gap (E_g) of bulk CdS is 2.42eV (512nm) thus, the blue shift of PL emission peak means the E_g of both prepared CdS nanocrystalline thin films is expanded. However, when the value of E_g is higher than the bulk phase that is happen because of the quantum confinement that caused by the small particle size.

No other emission peaks were observed; thus, consequences arising from the defect are not shown. W. D. Park found that the CdS thin films prepared via CBD with thickness of 250nm emitted two bands, a broad red band at 1.7eV and high-energy band centered at 2.7eV[23].

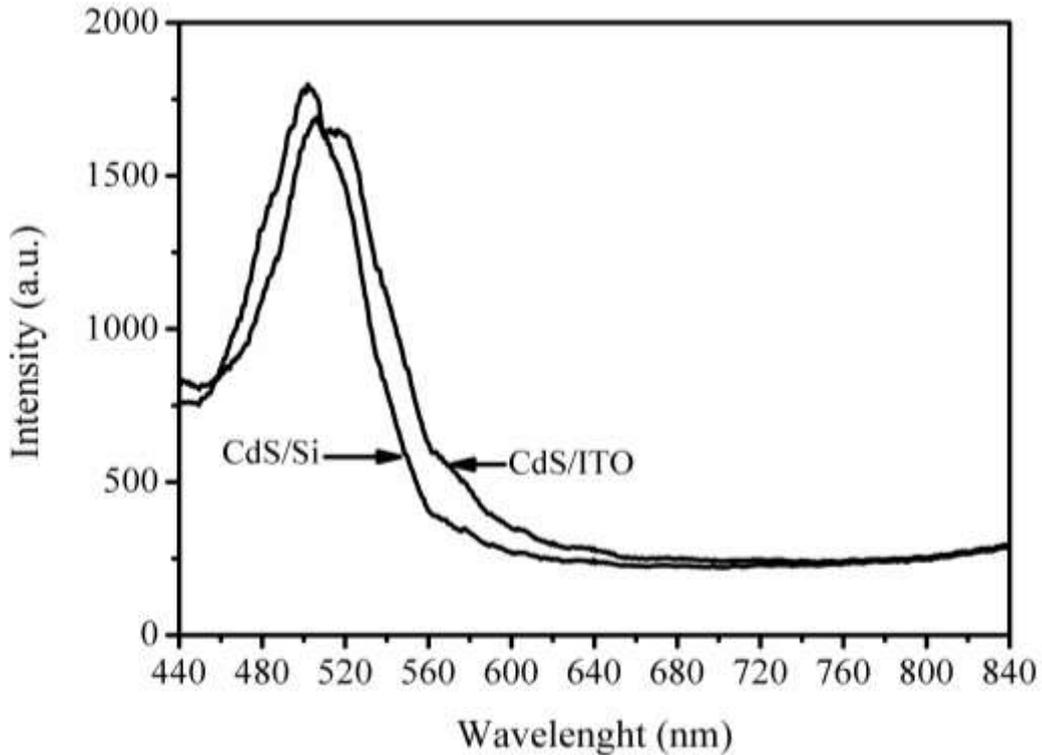


Figure 4- The PL spectra of the CdS nanocrystalline grown onto ITO-glass and Si(111) substrates.

Raman spectra

Raman spectroscopy is a powerful tool for investigating the doping concentration, lattice defect identification, and crystal orientation of materials [20]. In order to further investigate the structural properties of CdS nanocrystalline thin films grown on different substrates, Raman scattering measurements were carried out, as shown in Figure-5. For bulk CdS, the fundamental (1LO) and overtone (2LO) modes were located at 305cm^{-1} and 605cm^{-1} , respectively [24]. The Raman spectra of the nanocrystalline CdS thin films prepared onto Si(111) substrate contains two main peaks are located at 301.47cm^{-1} and 596.53cm^{-1} , which correspond to the first- and second-order longitudinal optical (LO) phonon modes polarized in the x-z face with strong coupling to excitons along the c-axis [25]. However, the CdS thin film that synthesis onto ITO-glass substrate shows two Raman bands are peaked at 299.25cm^{-1} and 596cm^{-1} related to fundamental (1LO) and overtone (2LO) modes of CdS material. Moreover, Raman peak that appeared at 520.3cm^{-1} is corresponding to crystalline silicon substrate [26]. The positions of the 1LO and 2LO modes in all prepared samples were red-shifted toward low frequencies is because of the phonon confinement effect [27].

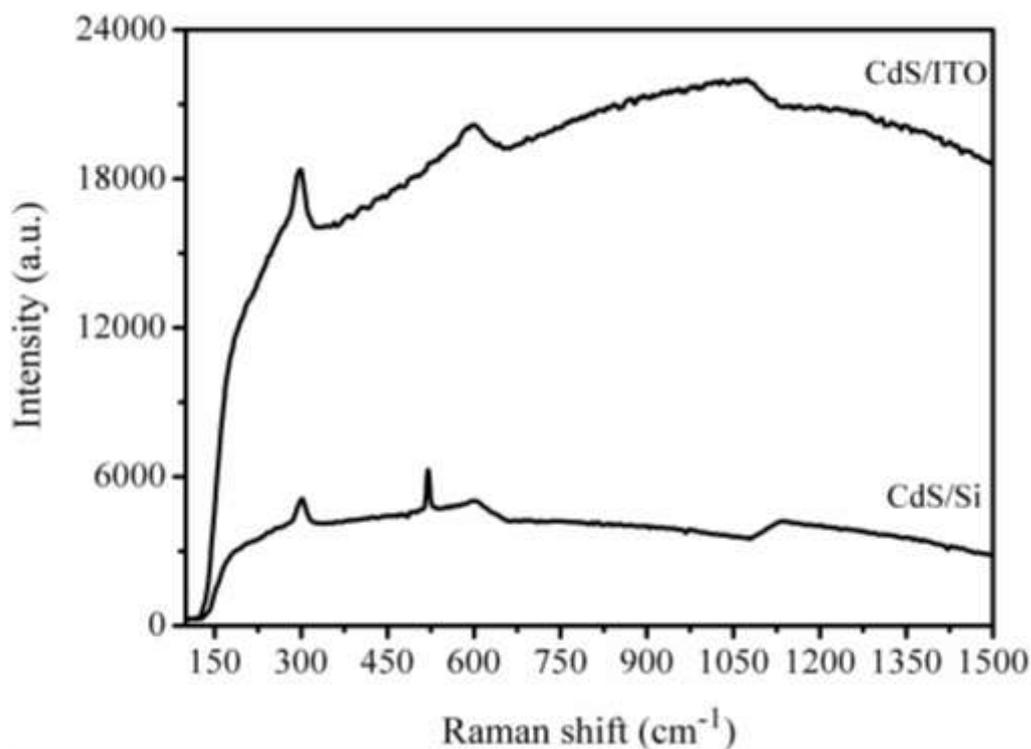


Figure 5- Raman spectra of the CdS nanocrystalline grown onto ITO-glass and Si(111) substrates.

Conclusions

Nanocrystalline CdS thin films are prepared onto ITO-glass and Si(111) substrates via CBD method. FESEM images showed that the CdS thin film prepared onto Si(111) substrate was more homogeneous with small circular shape of particles and high density were observed. The crystalline structure of CdS thin films that synthesized onto ITO-glass and Si(111) substrates was polycrystalline and the Ps of CdS thin films prepared onto ITO-glass substrates was 28nm while the Ps for the sample that prepared onto Si(111) was 38nm. The CdS/Si(111) sample shows emission band located at 502nm while the CdS nanocrystalline thin films that prepared onto ITO-glass shows a broad emission band peaked at 505nm. Raman spectra shows that the positions of the 1LO and 2LO modes in all prepared samples were red-shifted toward low frequencies that is could be because of the phonon confinement effect which appear in low dimensions of nanomaterials.

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