International Journal of Technical Research and Applications e-ISSN: 2320-8163,
www.ijtra.com Volume-2, Special Issue 6 (Nov-Dec 2014), PP. 11-13

NANOCRYSTALLINE CDS THIN FILMS GROWTH ON SILICON SUBSTRATES VIA MICROWAVE-ASSISTED CHEMICAL BATH DEPOSITION: SYNTHESIS AND CHARACTERIZATION

M. Husham[1,*], Z. Hassan[1], M.A. Mahdi[2], Abass M. Selman[1, 3]
[1]Nano-Optoelectronics Research and Technology Laboratory (N.O.R),
School of Physics, Universiti Sains Malaysia,
11800 Penang, Malaysia
[2]Basrah Nanomaterials Research Group (BNRG), Department of Physics,
College of Science, Basrah University, Basrah, Iraq
[3]Department of Pharmacology and Toxicology, College of Pharmacy,
University of Kufa, Najaf, Iraq
mhjusm@gmail.com*, zai@usm.my.com, mazinauny74@yahoo.com, alabbasiabbas@yahoo.co.uk

Abstract- Nanocrystalline cadmium sulfide thin films were successfully grown on Si(100) substrates using microwave-assisted chemical bath deposition technique. Aqueous solutions of cadmium chloride ($CdCl_2$) and thiourea [$SC(NH_2)_2$] were used as cadmium Cd^{+2} and sulfur S^{-2} ions sources, respectively to prepare nanocrystalline CdS thin films. The effect of reagents molar concentration on the quality of the prepared CdS thin films was investigated. Analysis revealed that using the chemical bath deposition technique aided by microwave irradiation good quality nanocrystalline CdS thin films can be grown on Si substrates by relatively short deposition time. Simple and cost effective way was introduced to synthesis nanocrystalline CdS thin films on Si substrates that would have potential application prospects in optoelectronic applications.

Keywords- CdS; nanocrystalline thin films; microwave; CBD technique; molar concentration.

I. Introduction

Cadmium sulfide (CdS) is one of the most important II–VI semiconductors with a direct band gap of 2.42 eV at room temperature [1]. It is a promising material for visible light detection and a wide range of optoelectronic applications including solar cells, optical sensors and light-emitting devices [2]. CdS can be prepared using various techniques [3-6]; chemical bath deposition (CBD) has been extensively utilized because of the low cost synthesis route and high production scale. It is a potential technique that produces homogeneous and high-quality CdS thin films [4]. The Properties of CBD-CdS thin films are significantly affected by preparation parameters such as molar concentration, temperature, deposition time and the pH. A substantial number of studies have been devoted to optimize growth parameters of CdS thin films prepared by CBD [7-10]. Few studies are reported on CdS growth on Si substrates using the CBD technique [11,12]. CdS thin films prepared on Si using CBD technique showed poor quality. Studies revealed that Si substrates suffered structural changes and induced defects during the deposition of CdS that would deteriorate the quality of the deposited thin films [12]. Microwave-assisted heating is considered a promising method for rapid preparation of inorganic nanostructures in the liquid solvents [13]. It is more efficient than that achieved by conventional heating methods. Microwave irradiation ensures homogenous distribution of temperature within the synthesis vessel with no thermal gradients. It provides uniform growth media that have a crucial role in improving the quality of the synthesized materials [14]. In this study, nanocrystalline CdS thin films are grown on Si substrates using the CBD technique, aided by microwave irradiation as heating source. The effect of reagents molar concentration on the quality of the prepared thin films was investigated.

II. Experimental details

Nanocrystalline CdS thin films were grown on Si(100) using microwave-assisted chemical bath deposition (MACBD) method. Aqueous solutions of cadmium chloride ($CdCl_2$) and thiourea [$SC(NH_2)_2$] were used as sources of Cd^{2+} and S^{2-} ions in the solution, respectively. Ammonium acetate (NH_4CH_3COO) was added as a buffer solution to control the release of ions during the deposition process [8]. Prior to the deposition, Si substrates were cleaned using the Radio Corporation of America (RCA) method. Different molarities (0.04, 0.06, 0.08 and 0.10 M) of $CdCl_2$ and thiourea were used to prepare CdS thin films. First, 10 ml of $CdCl_2$ were added to 100-ml beakers. Then, an appropriate amount of 0.5 M (NH_4CH_3COO) was added drop by drop under continuous stirring. After 10 min, 10 ml of thiourea were added dropwise to the solutions. Deionized (DI) water (resistivity ~18.2 MΩ cm) was added to the beakers solution to achieve a total volume of 80 ml. Ammonia solution (28% of NH_3 solution) was then added to obtain a pH of 10. The cleaned Si substrates were immersed in the beakers vertically; the beakers were then covered and heated in a microwave oven for 20 min at 75°C. After the deposition process was done, samples were washed and ultrasonicated with DI water for 1 min to remove the surface impurities, and then dried with pure nitrogen gas. structures properties of the synthesized CdS thin films were characterized using high-resolution X-ray diffraction (HR-XRD) PANalytical X'Pert Pro MRD diffractometer system, equipped with Cu K-□□radiation (□□= 1.54056 Å) at 40 kV and 30 mA. The morphological properties were studied using field-emission

scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 450) equipped with an energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments Analytical Ltd.).

III. Results and discussion

A. Structural analysis

Fig. 1 shows the XRD pattern of the grown nanocrystalline CdS thin films. The grown CdS thin films showed a predominant diffraction peak located at a diffraction angle (2θ) of ~ 26.70°. The observed diffraction peaks correspond to the (111) plane of the cubic CdS structure, as compared with the standard data (ICCD-PDF4 No. 01-080-0006). Similar observations have been reported by other authors [15,16]. As shown in the pattern, the crystallinity of the grown CdS thin films is significantly affected by varying the molar concentration of the ion sources. The diffraction peak intensity of the (111) plane increased and became sharper with increasing the molar concentration, indicating that the crystallinity of the grown CdS thin films was improved [7]. CdS thin film prepared using 0.08 M showed better crystallinity. The full width at half maximum of the (111) plane was smaller compared with other grown thin films, which indicates better crystalline structure. No other peaks attributed to impurities were detected, confirming the purity of the synthesized thin film.

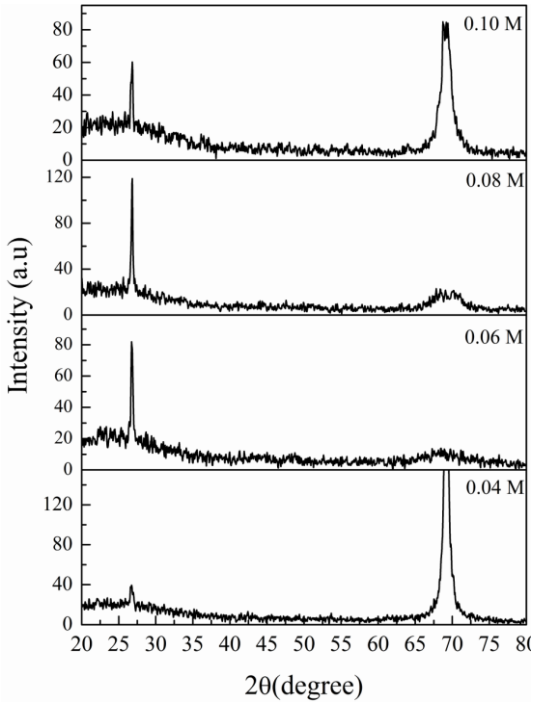

Fig.1. XRD pattern of the nanocrystalline CdS thin films grown on Si(100) substrates using different molar concentrations of reagents.

The crystallite size of the prepared CdS thin films was calculated according to the Debye–Scherrer formula [17]:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad (1)$$

Where D is the average crystallite size (nm), □□is the wavelength of the X-ray (0.15 nm), β is the full-peak width at half maximum (FWHM) of the XRD spectrum of CdS thin films (radians), and θ is the diffraction angle (radians). The calculated D for the prepared CdS thin films with 0.04, 0.06, 0.08 and 0.10 M were 18, 32, 36, and 30 nm, respectively as listed in Table 1. Values indicate that the synthesized CdS thin films are of nanocrystalline structure.

B. Morphological and EDX characterization

The surface morphology of the prepared nanocrystalline CdS thin films was observed through FESEM. As shown in Fig. 2, the morphology of the prepared thin films was markedly affected by the reagents molar concentration. When the molarity increased from 0.04 to 0.08 M, thin film surface became compact and consistent, without the presence of voids or pinholes. Further increasing in reagents molar concentration does not seem to enhance the quality of the deposited thin films. As the molar concentration further increased, the products of Cd^{2+} and S^{2-} ions became excessive and cluster by cluster reaction mechanism dominated [9]. CdS precipitated as clusters in the solution and consequently, fewer ions were deposited on the substrate during the reaction, resulted in poor-quality deposited thin film. As shown in Fig. 2d the resulting CdS thin film is ragged with obvious voids. EDX analysis confirmed the presence of Cd and S ions in the all prepared samples. The prepared nanocrystalline CdS thin films are Cd rich which it could be due to the due to the higher reactivity of Cd compared with S [18]. The Cd/S ratios were found to be decreased with increasing the molar concentration. Higher Cd/S ratio of 1.60 was for the CdS thin film prepared using 0.04 M. The atomic percentages of Cd and S in the prepared nanocrystalline CdS thin films are listed in Table 1. No other elements were detected, thereby confirming the purity of the grown thin films. Results are in good agreement with the XRD analyses.

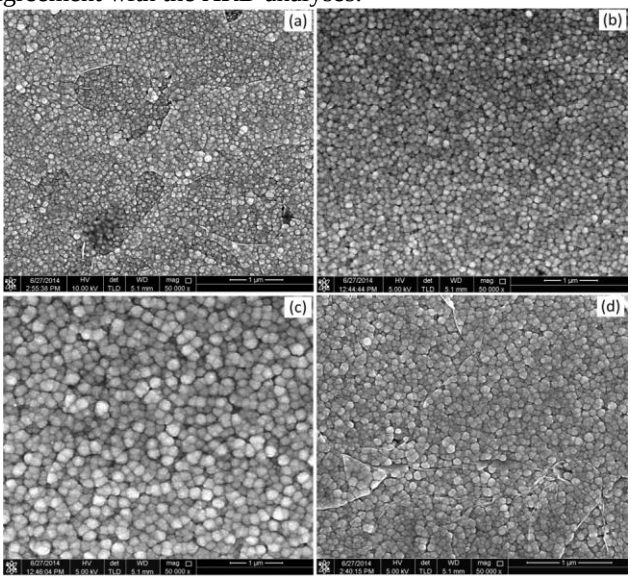

Fig. 2. FESEM images of nanocrystalline CdS thin films grown on Si(100) substrates via MACBD. (a) 0.04 M, (b) 0.06 M, (c) 0.08 M and (d) 0.10 M.

$CdCl_2$ molar concentration (M)	TU molar concentration (M)	Cd ratio (%)	S ratio (%)	Cd/S ratio	Grain size (nm)
0.04	0.04	61.59	38.41	1.60	18
0.06	0.06	58.46	41.54	1.40	32
0.08	0.08	56.59	43.41	1.30	36
0.10	0.10	60.79	39.21	1.55	30

Table.1 EDX analysis and average grain size of nanocrystalline CdS thin films prepared using different molar concentrations of reagents.

IV. Optical properties

The optical properties for the grown studied through photoluminescence (PL) measurement. Fig. 3 showed room temperature-PL spectra for the grown CdS thin films. The examined samples exhibited an efficient emission appeared at ~ 500 nm (green emission band). The observed emissions are related to the near-band edge (NBE) emission of CdS (2.42 eV), resulting from the recombination of free excitons [19]. The strong emissions are coupled with broad peaks observed around 700 nm (yellow emission band). The yellow band broad peaks are attributed to deep-level emission (DLE), which was due to crystalline surface defects and/or sulfur vacancies [20]. However, the prepared CdS thin films were S-deficient, as indicated by the EDX analysis. Therefore, the observed yellow band is possibly attributed to the emission from sulfur vacancies in radiative recombination [21]. As shown in Fig. 3, thin film prepared using 0.08 M showed the lowest-intensity defect emission. The high NBE/DLE ratio indicates a high-quality synthesized thin film with minimum defects.

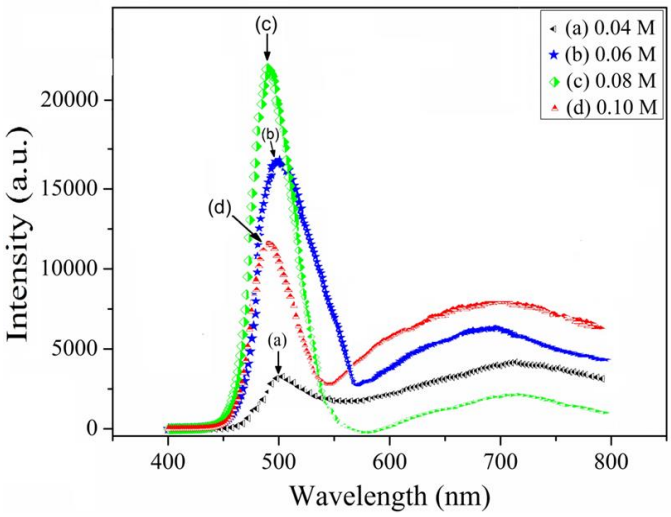

Fig. 4. PL spectra of nanocrystalline CdS thin films grown on Si(100) substrates using different molar concentration of reagents.

V. Conclusions

Nanocrystalline CdS thin films were successfully grown on Si substrates using MACBD. Analysis revealed that the quality of the synthesized thin films was significantly affected by the reagents molar concentration. Better CdS thin film characteristics were obtained using 0.08 M. The structural and morphological properties of the prepared thin film were markedly improved. PL measurement demonstrates the good optical properties of the prepared thin film using 0.08 M. The high band-edge to defect emission indicates that the synthesized thin film possesses a high-quality structure with minimal defects. A cost effective and simple method was introduced to synthesis high-quality nanocrystalline CdS thin films on Si substrates that would have potential applications in the field of optoelectronics.

VI. Acknowledgment

The authors gratefully acknowledge the support from FRGS grant (203/PFIZIK/6711353) and University Sains Malaysia.

REFERENCES

[1] M. Cao, L. Li, B.L. Zhang, J. Huang, K. Tang, H. Cao, Y. Sun, Y. Shen, J. Alloys Comp. 530 (2012) 81–84.
[2] R.B. Kale, C.D. Lokhande, Appl. Surf. Sci. 252 (2005) 929 – 938.
[3] K. Ravichandran and P. Philominathan, Sol. Energy 82 (2008) 1062–1066.
[4] Z. Yu, Y. Zhiqiang, L. Jun, W. Aixiang, Mater. Sci. Semicond. Process. 16 (2013) 1592–1598.
[5] X-P. Shen, A-H. Yuan, F. Wang, J-M. Hong, Z. Xu, Solid State Commun. 133 (2005) 19–22.
[6] Z-W. Peng and B-S. Zou, Chin. J. Chem. Phys. 25 (2012) 226–230.
[7] M. Husham, Z. Hassan , M.A. Mahdi , Abbas M. Selman, Naser M. Ahmed, Superlattices Microstruct. 67 (2014) 8–16.
[8] M.A. Mahdi, Z. Hassan , S.S. Ng , J.J. Hassan , S.K. Mohd Bakhori, Thin Solid Films 520 (2012) 3477–3484.
[9] I.O. Oladeji and L. Chow, J. Electrochem. Soc. 144(1997) 2342–2345.
[10] M. Husham, Z.Hassan, M. A. Mahdi, Adv. Mat. Res. 925 (2014) 263–267.
[11] J-H. Lee, Thin Solid Films 515 (2007) 6089–6093.
[12] A.I. Oliva, R. Rodr´ıguez, O. Ceh, P. Pe´rez , F. Briones , V. Sosa, App. Sur. Sci. 148 (1999) 42–49.
[13] V.P. Singh, R.S. Singh, G.W. Thompson, V. Jayaraman, S. Sanagapalli, V.K. Rangari, Sol. Energy Mater. Sol. Cells, 81 (2004) 293–303.
[14] K. Ngoen, T. Thongtem, S. Thongtem, A. Phuruangrat, Mater. Lett. 101(2013) 9–12.
[15] A. Kariper, E. Guneri, F. Gode, C. Gumus, T. Ozpozan, Mater. Chem. Phys. 129 (2011) 183–188.
[16] Z.H. Xiang, W.X. Ai, Z. Yu, L. Jun, J. Mater Sci.: Mater Electron. 24 (2013) 457–462.
[17] C. Ni, H. Ding, X.J. Jin, J. Alloys Comp. 546 (2013) 1–6.
[18] G.S. Shahane, B.M. More, C.B. Rotti, L.P. Deshmukh, Mater. Chem. Phys. 47 (1997) 263–267.
[19] S. Manna, S. Das, S.P. Mondal, R. Singha, S.K. Ray, J. Phys. Chem. 116 (2012) 7126−7133.
[20] M. Thambidurai, N. Murugan, N. Muthukumarasamy, S. Agilan, S. Vasantha, R. Balasundaraprabhu, J. Mater. Sci. Technol. 26 (2010) 193–199.
[21] L.M. Qi, H. Colfen, M. Antonietti, Nano lett. 1 (2001) 61–65.