



CHARACTERIZATION OF CDSE THIN FILMS UNDER GREEN ILLUMINATION

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ABSTRACT

The present work demonstrates a synthesis of nanocrystalline thin films of cadmium selenide (CdSe) using monochromatic photo-assisted chemical bath deposition (CBD) techniques at room temperature. The structure of the CdSe films deposited under green coloured illumination was confirmed by X-ray diffraction and the effect of the monochromatic light on the growth rate was observed. The secondary electron microscopy (SEM) result demonstrated different morphology of the different films' surfaces, such as granular spherical, cauliflower, fiber, or wire, with a variety of porosity that was achieved by a simpler photochemical route. The results obtained from UV-visible spectra showed a decrease in the optical bandgap from 1.8 to 1.9 eV.

Keywords: CBD; Photo-assisted; CdSe; Reflux

1. INTRODUCTION

Recently, cadmium selenide (CdSe) attracted attention in many fields, such as solar cells,^[1-3] thin-film transistors, photoelectrochemical cells, lasers, gamma-ray detectors, biological applications,^[4-6] etc. due to their high absorption coefficient, radioactive recombination, photosensitivity, direct bandgap nature (1.7 eV) and quantum size effects. The CdSe nanocrystalline energy band structure can be controlled by controlling the material's chemical and physical properties.^[7,8] CdSe is an important optoelectronic material since its bandgap can be tuned to the visible spectral region by changing its particle size.^[9] Controlling geometric shape and growth, the structure of CdSe nanocrystals is critical in the actual designing of new functional devices.^[10-12] Various synthesis methods such as thermal evaporation,^[13,14] electrodeposition,^[15] spray pyrolysis,^[16,17] metalorganic chemical vapour deposition (CVD), and chemical bath deposition (CBD)^[18,19] have been recorded in the literature for the synthesis of CdSe thin films.

Chemical bath deposition (CBD) is a simple, convenient, reliable, economical, and low-temperature method for preparing CdSe thin films due to its large-scale deposition capacity and easy processability.^[20] The synthesis parameters such as complexing agents, deposition temperature, time, and pH can improve crystallites' shape, size, and quality.^[21-24] In the photochemical semiconductor deposition process, photogenerated holes and electrons are created by absorbing photons with more energy than the material's electronic bandgap energy. In that context, the nanostructure of a semiconductor can increase absorption by increasing the internal scattering of incident light and the waveguiding effects in the material. These characteristics of the nanostructures provide efficient ways to collect

photogenerated carriers to generate ionic current or chemical products.^[25] Since the intensity and wavelength of light can be easily controlled in the photochemical deposition process, the technique has better controllability than the previously mentioned methods.^[25-29] An advantage is the easy-to-control deposition rate, cost-effectiveness, and selective area deposition, which is suitable for mass fabrication.^[30]

The present study deals with CdSe film deposition on glass substrates at room temperature by photochemical deposition to investigate the effect of green colour illumination on CdSe deposited film, optical properties, structure, and morphology. The obtained demonstrate that colour illumination strongly effects on structure and morphology of CdSe film.

2. EXPERIMENTAL

2.1 Materials and Process

All the chemicals used in this experiment were the highest purity analytical grade obtained from HPLC Ltd. Mumbai, India, and Thomas baker and used as it is without further purification. Cadmium Sulphate (CdSO_4) (HPLC Ltd. Mumbai), Selenium powder (99.9% purity, HPLC), Sodium Sulphite (Na_2SO_3) (HPLC), 25% Ammonium Hydroxide (Thomas Baker), Hydrochloric Acid (Thomas Baker), LED strips, *etc.*

Cadmium selenide films were deposited on completely clean glass substrates at room temperature (27 ± 2 °C) by a selected wavelength's visible photochemical method. A 0.25 M, 0.35 M, and 0.45 M solutions of cadmium sulfate (CdSO_4) was used as the cation source (Cd^{2+}). With the aid of the reflux method, sodium selenosulphate (Na_2SeSO_3) was prepared which was used as the anionic source (Se^{2-}). In this process, 200 ml of double-distilled water was used as a solvent mixed with 3.94 g of selenium powder and 12.64 g of anhydrous sodium sulfite (Na_2SO_3). The solution was stirred continuously with heating for 5 hours at 70 °C. The obtained colourless solution was sealed and kept in a dark place to cool at room temperature, and finally, it is filtered to get a clear solution of Na_2SeSO_3 .

Subsequently, for CdSe thin film deposition, 0.25 M CdSO_4 solution in 50 ml was poured into a 200 ml glass beaker. 25% liquor ammonia (NH_4OH) was added dropwise with continuous stirring. The solution pH was maintained at approximately 11.70 ± 0.08 . The solution appears to be cloudy and milky initially due to the formation of $\text{Cd}(\text{OH})_2$. Furthermore, with increasing ammonia, the turbidity becomes a clear and transparent solution.^[31] The solution was stirred for an additional 30 seconds. After that solution was transferred into beaker (100 ml) containing glass substrate. A similar procedure is repeated for 0.35M and 0.45M CdSO_4 was used to prepare thin films of CdSe under green color illumination condition with an equal volume ratio, for the concentration of aqueous Na_2SeSO_3 solution and different concentrations of aqueous CdSO_4 (0.35M and 0.45M).

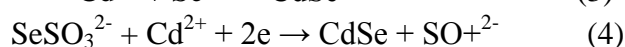
These three beakers were kept in a cylindrical box under the illumination of green light at a constant stirring speed of 100 ± 10 rpm. For uniform light intensity, the non-transparent plastic cylindrical CD boxes of the same dimension (15 cm of height and 12 cm of diameter) were used. Its internal side walls were glued with 120 commercially available light-emitting diode (LED) strips. A green-colored LED strip light, emitting at a wavelength of 515 nm and an intensity of 6360 lux, was used to produce uniform monochromatic light was used to produce uniform monochromatic light. The light intensity was measured using the Lutron LX-1102 light meter.

3. RESULT AND DISCUSSION

3.1 Film Formation under Different Colour Illumination

The wavelength was measured with the computerized Stellar Net Incorporation spectrometer with an integrating sphere. It is observed that there is no ultraviolet radiation present inside the deposition box, which was confirmed by the Lutron UV340A UV meter. The boxes were covered with opaque aluminium foil to avoid any possibility of dust contamination and the effect of external ambient light on the chemical reaction. Although the initial pH value for a solution was the same, it gradually decreased concerning the deposition time increases. It may be due to the wavelengths and intensity of the light illumination that the concentrations of negative and positive ions may get altered which leads to different growth rates in these solutions, which are elaborated in Table 1.

The bath solution's temperature maintained under monochromatic lighting conditions increased by almost an average of 8 to 10 °C than room temperature. Films deposited under green colour light illuminations with stirring at room temperature were removed after 21 hours, rinsed in double distilled water, and oven-dried at 70 °C in air. The deposited films were well adhered to the substrates and were uniform. The deposited films appeared reddish-brown, it occurs because of green colour illumination light on nanocrystalline grain growth, as shown in Fig. 1. The proposed mechanism of photochemical synthesis of CdSe nanoparticles may be as follows:



3.2 X-ray Diffraction (XRD) Analysis

The structure of the CdSe films deposited under different coloured illumination was characterized using X-ray diffraction within the range of 2θ from 20° to 80° ; the XRD analysis was performed using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) in a Bruker D-8 Advanced X-ray Diffractometer

Table 1: Change in pH in the bath solution due to photoirradiation

Time	0.25M CdSO ₄	0.35M CdSO ₄	0.45M CdSO ₄
	Green	Green	Green
Initial	11.62	11.78	11.71
15 H	11.15	11.01	10.73
18H	11.00	10.86	10.66
21H	10.65	10.68	10.63
48H	9.78	9.80	9.73



Fig. 1: The deposited films appeared reddish-brown due to green light illumination

The identification and assignment of the diffraction patterns were made using the JCPDS data file no. 19-191, which exhibited cubic phase structures and compared well with reported data.^[32] The CdSe phase was confirmed by Miller planes (111), (220), (311) corresponding to peaks at 2θ of 25° , 42° , and 50° . No other characteristic peaks of impurities were observed. The diffraction patterns of the three prepared samples of 0.25M, 0.35M, and 0.45 CdSO₄ solutions are shown in Figs. 2 (a-c). The indices (h k l), average grain size, bandgap, displacement density, and micro-strain of the CdSe films are shown in Table 2 for the 0.25M, 0.35M and 0.45M concentration sample explained in Table 1S and Table 2S. The average size of the crystallites is calculated using the Scherrer formula. The X-ray diffraction (XRD) pattern for all samples reflects the change in intensity and sharpness of the peaks indifferent concentration conditions under green light are probably due to the reaction rate that exists in a chemical bath, resulting in a change in the thickness and average size of the nanocrystalline particles.^[25] A small spike appeared on the shoulder of the XRD pattern of samples deposited under 0.35M and 0.45M of CdSO₄ concentration, which may be evidence of a mixed cubic and hexagonal structure with a rod or wire-like morphology of CdSe; it is also shown by X. Peng (2000) *et al.* Lattice constants, and average crystallite size of the film was calculated using standard formulations.^[33] The crystallite size is observed as a minimum, while the bandgap is maximum for 0.45M concentration, while the crystallite size is maximum, and the bandgap is minimum for 0.25M concentration. Dislocation density and micro-strain are highest for 0.25M concentration, while the lowest for 0.45M concentration indicating an improvement in crystallinity. The micro-strain (ϵ) and the displacement density (δ) of the film defects were evaluated by using the following formula,

$$\delta = \frac{1}{D^2} \quad (5)$$

From measurement, it was observed that dislocation density and micro-strain for the 0.25M concentration sample were higher while lower for the sample 0.45M concentration under green light.

3.3 Raman Spectra analysis of CdSe

The Raman spectroscopy conducted for CdSe at three different concentrations of CdSO₄ and under different illumination is shown in Figs. 3(a-c). The results exhibited from Raman spectra support the result obtained from the XRD measurements. The observed LO phonon peak is slightly below the 1LO (201 cm^{-1}) and 2LO (407 and 410 cm^{-1}) phonon frequencies (211 and 420 cm^{-1}). Multiple phonon scattering indicates resonant excitation

Raman processes in a thin film CdSe semiconductor. The peak dominates at 201 cm^{-1} and another peak is also observed around 407 cm^{-1} , confirming that CdSe is cubic. [34,35]

Table 2. Physicochemical Properties of CdSe thin films deposited under green colour for 21 hours

CdSO ₄ Concentration	Band Gap (eV)	Crystallite size (nm)	2θ ₁	Plane	Dislocation density(δ) x 10 ⁺¹⁷ lines ² /m ²	Micro strain(ε) 10 ⁻⁶	Element	
							Cd	Se
0.25M	1.8	2.2	25.85 42.82 50.59	(111) (220) (311)	2.07	16.4	47	53
0.35M	1.8	5.8	25.97 42.92 49.99	(111) (220) (311)	0.29	6.2	62	38
0.45M	1.9	6.4	24.57 41.40 49.29	(111) (220) (311)	0.24	5.6	61	39

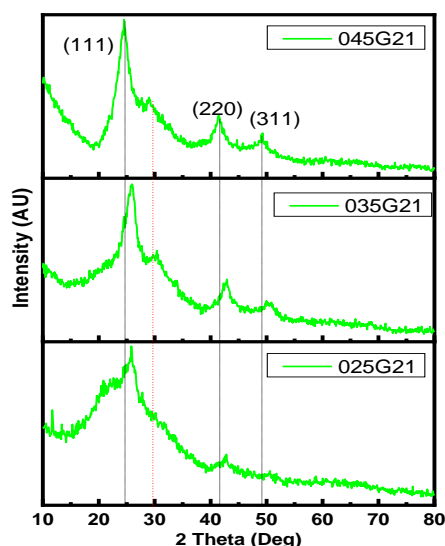


Fig. 2 XRD spectra of CdSe (a) 0.25M (b) 0.35 and (c) 0.45M CdSO₄ under green colour illuminations.

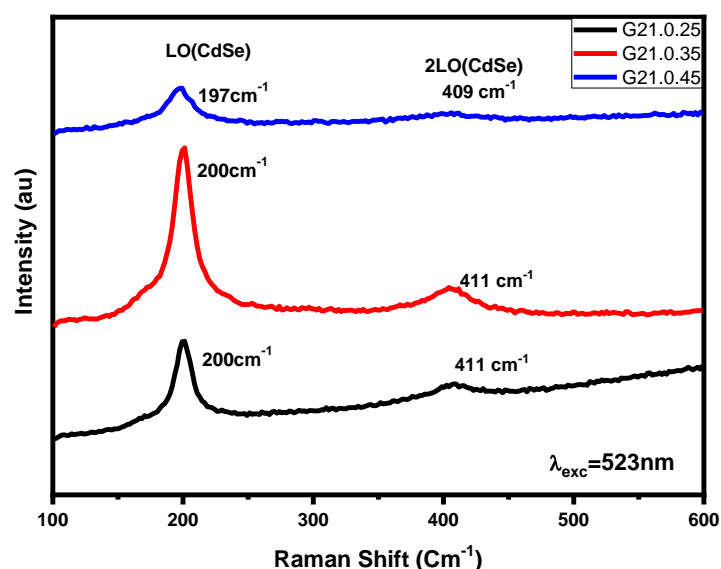
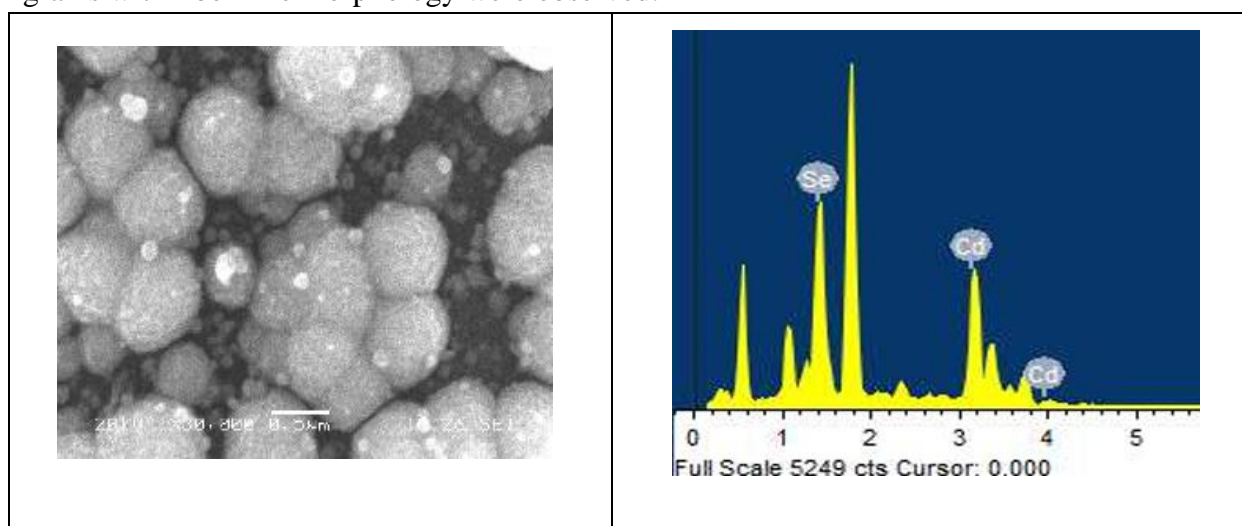


Fig. 3 Raman spectra of CdSe (a) 0.25M (b) 0.35 and (c) 0.45M CdSO₄ under green colour illuminations

3.4 Morphological study

The morphology of the prepared sample was observed using conditions (Figs. 4). It has been shown that the films scanning electron microscopy (SEM) micrographs of thin deposited on the glass surface are smooth and uniform with different surface morphologies. The films deposited with some voids, while under the impact of the green colour, aqueous solution of CdSO₄ with a concentration of 0.25 M the large size of spherical nodular fibrous grains and the films deposited with an aqueous solution of CdSO₄ with a concentration of 0.35 the long wire fiber, or rod-like surface morphology was observed. The films deposited with an aqueous solution of CdSO₄ with a concentration of 0.45M some smaller spherical grains with fiber-like morphology were observed.



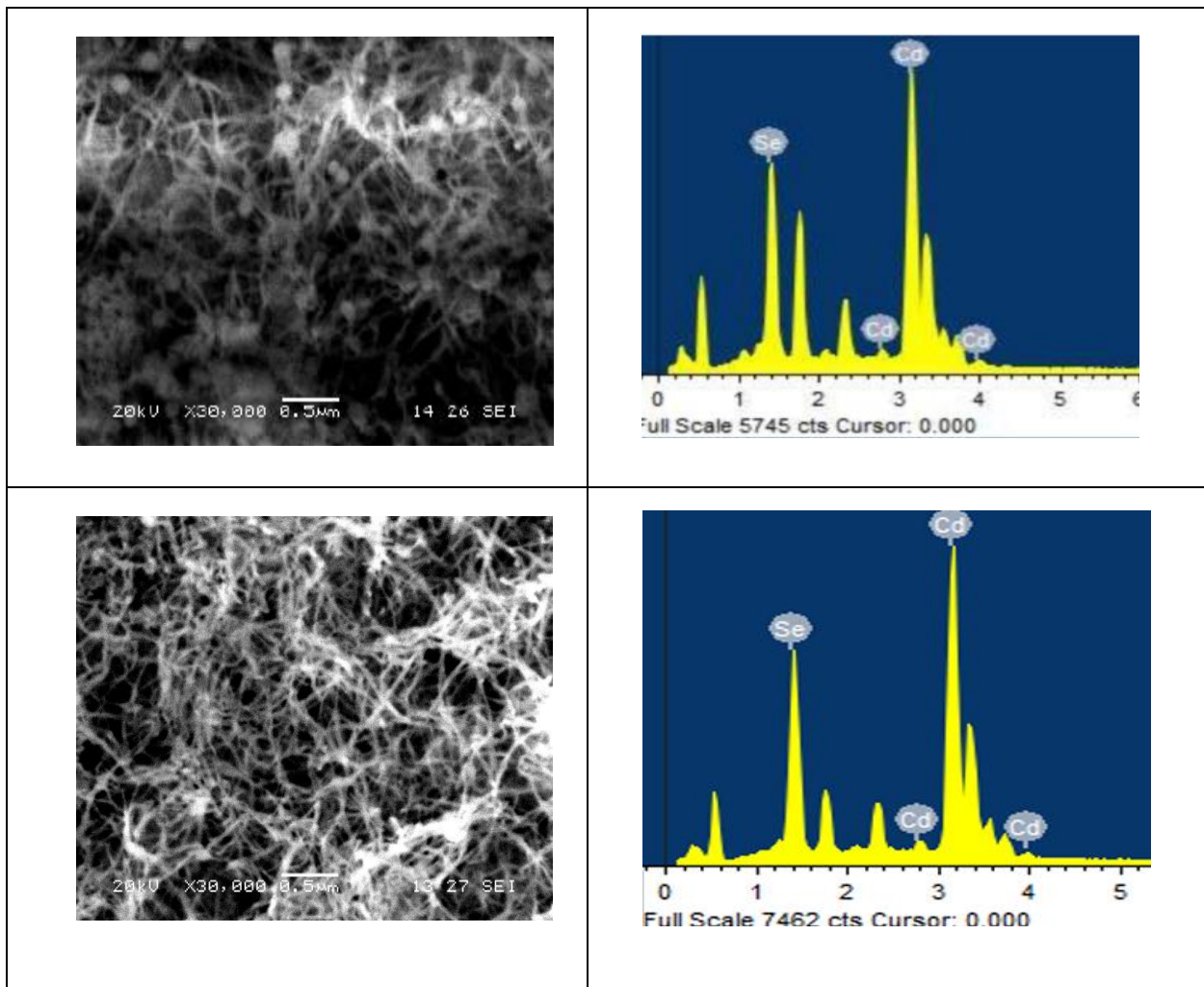


Fig. 4 CdSe thin film deposited under green colour illumination. SEM and EDAX images

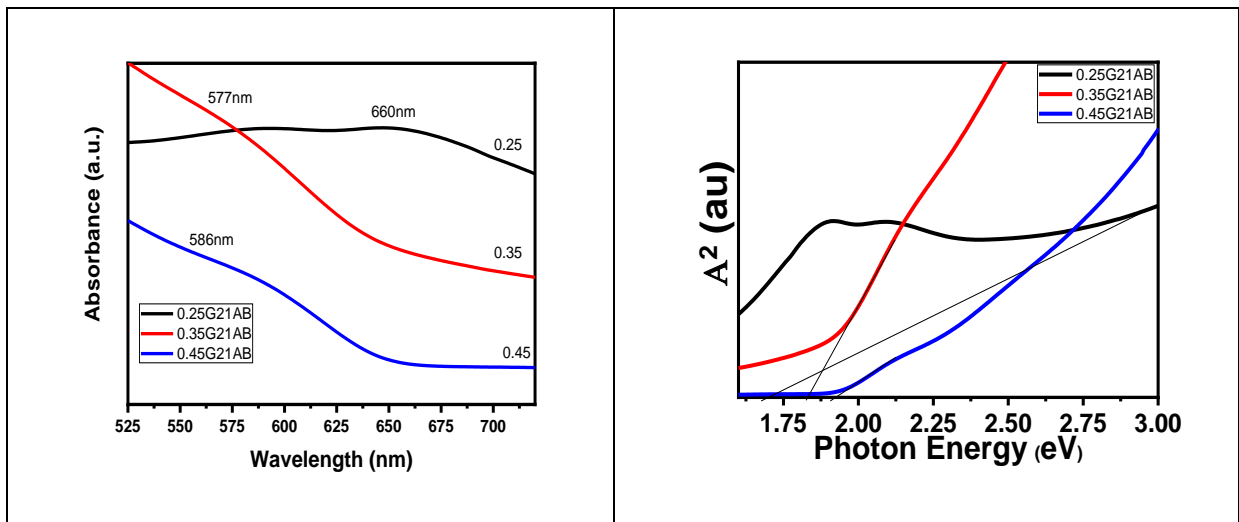


Fig. 5 CdSe thin film deposited under green colour illumination (i) Optical Absorption Spectra (ii) Bandgap Energy.

Control of nanocrystal shape can be achieved by manipulating growth kinetics. When the overall growth rate is rapid, growth is generally faster along the longitudinal axis.

If the overall growth rate is slow, an almost spherical shape is favoured that minimizes the surface area. If the growth rate increases significantly, the result is a faceted rod or wire-like shape.^[36]

Energy Dispersive Spectroscopy (EDS) was used for the quantitative analysis of CdSe thin films (Figs. 4). In a 0.25 M CdSO₄ solution, the film is almost stoichiometric, but in a 0.35 M and 0.45 M CdSO₄ solution, a film rich in Cd was obtained. The stoichiometry of the film deposited under different colours was different; this could be the effect of monochromatic radiation elaborated in Table 2. At such large intensity of 6360 lux intensity and at a wavelength of 515 nm minimises the defect mechanism of CdSe thin films which leads to morphology change and became the cause of the increase of optical absorption. With the interaction of the green color photon aqueous solution reaction, decomposition of Na₂SeSO₃ occurred, which may alter the concentration of Se²⁻ and Cd²⁺ ions, and hence the stoichiometry of the film changes.^[37]

3.5 Optical Absorption Spectra of CdSe Thin Film

The CdSe thin films' absorption to a bare glass substrate was carried out in a JASCO (UV-Vis-NIR) spectrophotometer (350-850 nm). The absorption peaks of samples deposited under green colour light condition with various concentration of aqueous CdSO₄ concentrations at 0.35M is maximum while at 0.45M is minimum, as shown in Fig. 5a. The observed increase in grain size and the colour change of the deposited films from orange to reddish-brown with different concentrations of CdSO₄ may be due to different reaction rates under the effect of monochromatic green light radiated in the reaction bath, which results in different morphology with reduced grain density and trapping centers. Fig. 5b shows a decrease in the bandgap energy from 1.9 to 1.8 eV of the sample material, indicating the improvement in the films' crystallinity.^[33, 37-40]

From obtained results, it is observed that prepared material can be used for quantum dot solar cell applications and is expected to achieve superior performance.

4. CONCLUSIONS

Nanocrystalline thin films of CdSe have been successfully synthesized using photo-assisted CBD techniques with stirring and without stirring at room temperature. The effect of monochromatic light on the growth rate was observed. The thickness and color appearance of nanocrystalline thin films were different in different CdSO₄ concentration under green color light illumination. From the results, it was clear that for different concentrations of CdSO₄ under green illumination generates the elemental ratio of selenium to cadmium for thin films was different. The films have a cubic phase with crystallite sizes obtained from about 2.2 nm to 6.4 nm. Also, the morphology obtained was different for other lighting conditions. With different concentrations of CdSO₄ under a green light color variety of morphologies such as granular spherical, cauliflower, fiber, or wire, having porous structures was achieved by using a simpler photochemical route.

REFERENCES

- [1] Robel, V. Subramanian, M. Kuno, P. Kamat, *Journal of the American Chemical Society*, 2006, **128**, 2385-2393.
- [2] S. K. Kokate, A. T. Supekar, P. K. Baviskar, B. M. Palve, S. R. Jadkar, K. C. Mohite, H. M. Pathan, *Materials Science in Semiconductor Processing*, 2018, **80**, 179-183.
- [3] R. Prasad M B, H. M. Pathan, *Nanotechnology*, 2016, **27**, 145402.
- [4] X. Pang, J. Pan, L. Wang, W. Ren, P. Gao, Q. Wei, B. Du, *Biosensors and Bioelectronics*, 2015, **71**, 88-97.
- [5] S. Ananthakumar, J. Ramkumar, S. Moorthy Babu, *Materials Science in Semiconductor Processing*, 2014, **22**, 44-49.
- [6] S.-K. Min, O.-S. Joo, R. S. Mane, K.-D. Jung, C. D. Lokhande, S.-H. Han, *Journal of Photochemistry and Photobiology A: Chemistry*, 2007, **187**, 133-137
- [7] V. Biju, Y. Makita, A. Sonoda, H. Yokoyama, Y. Baba, M. Ishikawa, *The Journal of Physical Chemistry B*, 2005, **109**, 13899-13905
- [8] M. S. Kang, A. Sahu, D. J. Norris, C. D. Frisbie, *Nano Letters*, 2010, **10**, 3727-3732,
- [9] Y.-L. Yan, Y. Li, X.-F. Qian, J. Yin, Z.-K. Zhu, *Materials Science and Engineering: B*, 2003, **103**, 202-206,
- [10] Z.A. Peng, X. Peng, *Journal of the American Chemical Society*, 2002, **124**, 3343-3353, doi: 10.1021/ja0173167. [11] S. Liu, W.-H. Zhang, C. Li, *Journal of Crystal Growth*, 2011, **336**, 94-100
- [11] N. T. N. Truong, W. K. Kim, U. Farva, X. D. Luo, C. Park, *Solar Energy Materials and Solar Cells*, 2011, **95**, 3009-3014
- [12] Z. Aneva, D. Nesheva, C. Main, S. Reynolds, A. G. Fitzgerald, E. Vateva, *Semiconductor Science and Technology*, 2008, **23**, 095002,
- [13] M. Dey, N. K. Das, M. Dey, S. F. U. Farhad, M. A. Matin, N. Amin, *International Journal of Renewable Energy Research IJREER*, 2021, **11**, 495-503.
- [14] D. Pan, G. Yang, H. M. Abo-Dief, J. Dong, F. Su, C. Liu, Y. Li, B. Xu, V. Murugadoss, N. Naik, S. M. El-Bahy, Z. M. El-Bahy, M. Huang, Z. Guo, *Nano-Micro Letters*, 2022, **14**, 118
- [15] Y. Zhao, Z. Yan, J. Liu, A. Wei, *Materials Science in Semiconductor Processing*, 2013, **16**, 1592-1598
- [16] K. Diwate, A. Pawbake, S. Rondiya, R. Kulkarni, R. Waykar, A. Jadhavar, A. Rokade, A. Funde, K. Mohite, M. Shinde, H. Pathan, R. Devan, S. Jadkar, *Journal of Semiconductors*, 2017, **38**, 023001
- [17] Y. Choi, M. Seol, W. Kim, K. Yong, *The Journal of Physical Chemistry C*, 2014, **118**, 5664-5670, doi: 10.1021/jp411221q.
- [18] R. S. Kapadnis, S. B. Bansode, A. T. Supekar, P. K. Bhujbal, S. S. Kale, S. R. Jadkar, H. M. Pathan, *ES Energy & Environment*, 2020, **10**, 3-12, doi: 10.30919/ese8c706.
- [19] N. Gopakumar, P. S. Anjana, P. K. Vidyadharan Pillai, *Journal of Materials Science*, 2010, **45**, 6653-6656, doi: 10.1007/s10853-010-4756-1.
- [20] O. Yamamoto, T. Sasamoto, M. Inagaki, *Journal of Materials Research*, 1998, **13**, 3394-3398, doi: 10.1557/jmr.1998.0462.

- [21] C. A. VanderHyde, S. D. Sartale, J. M. Patil, K. P. Ghoderao, J. P. Sawant, R. B. Kale, *Solid State Sciences*, 2015, **48**, 186-192, doi: 10.1016/j.solidstatesciences.2015.08.007.
- [22] M. P. Deshpande, N. Garg, S. V. Bhatt, P. Sakariya, S. H. Chaki, *Materials Science in Semiconductor Processing*, 2013, **16**, 915-922, doi: 10.1016/j.mssp.2013.01.019.
- [23] M. P. Deshpande, N. Garg, S. V. Bhatt, P. Sakariya, S. H. Chaki, *Advanced Materials Letters*, 2013, **4**, 869-874, doi: 10.5185/amlett.2013.4467.
- [24] C. Tan, C. Qin, B. Sadtler, *Journal of Materials Chemistry C*, 2017, **5**, 5628-5642, doi: 10.1039/C7TC00379J.
- [25] S. Erat, H. Metin, M. Ari, *Materials Chemistry and Physics*, 2008, **111**, 114-120, doi: 10.1016/j.matchemphys.2008.03.021.
- [26] M. Froment, D. Lincot, *Electrochimica Acta*, 1995, **40**, 1293-1303, doi: 10.1016/0013-4686(95)00065-m. [28] G. Hodes, *Physical Chemistry Chemical Physics*, 2007, **9**, 2181, doi: 10.1039/b616684a.
- [27] O. Madelung, M. Schulz, H. Weiss, *Landolt–Bornstein Tables, Springer, Berlin*, 17a, and b (1982).
- [28] M. Ichimura, N. Sato, A. Nakamura, K. Takeuchi, E. Arai, *Physica Status Solidi (a)*, 2002, **193**, 132-138, doi: 10.1002/1521396x(200209)193:1132::aid-pssa132>3.0.co;2-4.
- [29] S. A. Pawar, R. S. Devan, D. S. Patil, A. V. Moholkar, M. G. Gang, Y.-R. Ma, J. H. Kim, P. S. Patil, *Electrochimica Acta*, 2013, **98**, 244-254, doi: 10.1016/j.electacta.2013.03.016.
- [30] E. Gholami Hatam, N. Ghobadi, *Materials Science in Semiconductor Processing*, 2016, **43**, 177-181, doi: 10.1016/j.mssp.2015.12.013.
- [31] A. L. Stroyuk, V. V. Shvalagin, A. E. Raevskaya, A. I. Kryukov, S. Y. Kuchmii, *Theoretical and Experimental Chemistry*, 2008, **44**, 205-231, doi: 10.1007/s11237-008-9037-6.
- [32] R. B. Kale, S. D. Sartale, B. K. Chougule, C. D. Lokhande, *Semiconductor Science and Technology*, 2004, **19**, 980-986, doi: 10.1088/0268-1242/19/8/006.
- [33] A. V. Baranov, Y. P. Rakovich, J. F. Donegan, T. S. Perova, R. A. Moore, D. V. Talapin, A. L. Rogach, Y. Masumoto, I. Nabiev, *Physical Review B*, 2003, **68**, 165306, doi:10.1103/physrevb.68.165306.
- [34] X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature*, 2000, **404**, 59-61, doi: 10.1038/35003535.
- [35] W.-B. Zhao, J.-J. Zhu, H.-Y. Chen, *Scripta Materialia*, 2004, **50**, 1169-1173, doi: 10.1016/j.scriptamat.2004.01.017. [38] Y.-L. Yan, Y. Li, X.-F. Qian, J. Yin, Z.-K. Zhu, *Materials Science and Engineering: B*, 2003, **103**, 202-206, doi: 10.1016/s0921-5107(03)00155-7.
- [36] W. Zhao, J. Zhu, H. Chen, *Scripta Materialia*, 2004, **50**, 1169-1173, doi: 10.1016/j.scriptamat.2004.01.017
- [37] J. Zhu, X. Liao, X. Zhao, J. Wang, *Materials Letters*, 2001, **47**, 339-343, doi: 10.1016/s0167-577x(00)00263-9.