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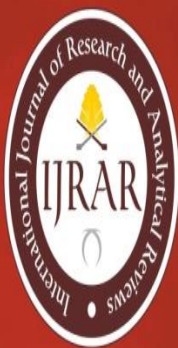


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E-ISSN 2348-1269
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International Journal of Research and Analytical Reviews

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2061-C/2/B, Nr. Adhyatma Vidya Mandir, Sanskar Mandal, Bhavnagar-364002.

Contact : 9427903033 E mail : editorsijrar@gmail.com

2019

E-ISSN 2348-1269

ISSN 2349-5138

UGC No: 43602

Periodicity - Quarterly



International Journal of Research and Analytical Reviews

International Conference on Advances in Pure and Applied Sciences - ICAPAS-2019

5th and 6th January, 2019

Organized by

Balwant College, Vita.

Dist-Sangli. (M.S.) India - 415311

Listed & Indexed in ISSN Directory, Paris
Peer Reviewed & Referred Multidisciplinary
International Journal

Special Issue

Cosmos Impact Factor 4.236

Impact Factor 5.75

Special Issue

Contents

Physics

- | | | |
|----|--|---------|
| 1 | SYNTHESIS OF Cu-Zn NANO-FERRITE BY OXALATE CO-PRECIPTATION METHOD | 01 – 07 |
| | A. D. Pawar, B.B. Patil, D. B. Bhosale, S.V. Godase, H. R. Ingawale, S. R. Bhongale & T. J. Shinde | |
| 2 | SYNTHESIS AND CHARACTERIZATION OF ZINC FERRITE BY MODIFIED CHEMICAL DEPOSITION METHOD | 08 – 11 |
| | Abhijit K. Suryavanshi | |
| 3 | X-RAY DIFFRACTION ANALYSIS OF Ni-Cu-Zn NANO-FERRITE SYNTHESIZED BY WET CHEMICAL ROUTE | 12 - 16 |
| | B. B. Patil, A D. Pawar, D. B. Bhosale, S. V. Godase, J. S. Ghodake, J. B. Thorat & T. J. Shinde | |
| 4 | SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL PERFORMANCE OF NANOSTRUCTURED V₂O₅ THIN FILM DEPOSITED BY HYDROTHERMAL METHOD | 16 – 22 |
| | C. E. Patil & C.R. Bobade | |
| 5 | H₂S GAS SENSING PERFORMANCE OF UNDOPED CADMIUM OXIDE AND MIXED CADMIUM ZINC OXIDE ADVANCED SPRAY DEPOSITED THIN FILMS: A COMPARATIVE STUDY | 23 – 28 |
| | C. R. Bobade, S.A.Mane, S.M.Ravatale, A.P.Kumbhar & M.D.Uplane | |
| 6 | Physico-electrochemical investigation of electrodeposited nanocrystalline Sb₂Te₃ thin films | 29 – 42 |
| | J. B. Thorat, S. V. Mohite, S. B. Madake, S. K. Shinde, D. S. Lee, J. Jung, K. Y. Rajpure, T. J. Shinde, V.J. Fulari & N. S. Shinde | |
| 7 | GROWTH OF CARBON NANOTUBES FOR THEIR USE IN DYE-SENSITIZED SOLAR CELL | 43 – 47 |
| | M. A. Gaikwad, M. P. Suryawanshi, C. R. Bobade & A. V. Moholkar | |
| 8 | STUDIES ON THE CONTACT ANGLE HYSTERESIS OF TRANSPARENT SILICA COATINGS PREPARED BY SOL-GEL PROCESS | 48 – 51 |
| | Mahendra S. Kavale | |
| 9 | ELECTROMAGNETIC ABSORPTION PROPERTIES OF POLYPYRROLE / POLYANILINE COMPOSITE THIN FILMS | 52 – 56 |
| | Monika L. Gavali, Ninad B. Velhal, C.R.Bobade & Vijaya R. Puri | |
| 10 | Development of Cu₃Fe₂₋₄O₃ as a gas sensor by facile combustion route | 56 – 59 |
| | P.A. Ghadage,D. S. Ghadage, L. K. Bagal, S. S. Mane & S.S. Suryavanshi | |
| 11 | A STUDY OF SILICON DIOXIDE NANOWIRE BY MOLECULAR DYNAMICS SIMULATIONS: INFLUENCE OF INTERATOMIC POTENTIALS AND BOUNDARY CONDITIONS | 60 -63 |
| | Priyanka S.Shinde, M.M.Salunkhe, N.N.Bhosale, S.S.Barate & R.S.Vhatkar | |
-

International Journal of Research and Analytical Reviews

- | | | |
|----|---|---------|
| 12 | Permeability of nanoparticle sized copper cobalt ferrites
S.S. KARANDE | 64 – 66 |
| 13 | Chemical bath deposition (CBD) of ZnO thin films in aqueous medium and its characterizations
S.V. Nikam, N.N. Bhosale, C. H. Jadhav, P. K. Pagare & A. P. Torane | 67 – 69 |
| 14 | Studies On Consequence Of Temperature On Physical Properties Of CdSe Thin Films Synthesized Using Chemical Bath Deposition Method
Vanita S. Raut, Chandrakant D. Lokhande & Vilas V. Killedar | 70 – 74 |

Electronics

- | | | |
|----|--|---------|
| 15 | Development of Breathalyzer using PIC Microcontroller
Hasabe B. R., Patil N. M., Deokate D.T. & Attar G. R. | 75 – 78 |
| 16 | LOW COST SOLAR POWERED EGG INCUBATION SYSTEM
Patil N. M., Deokate D.T., Attar G. R. & Hasabe B. R. | 79 – 82 |
| 17 | REMOTE PHYSIOLOGICAL PARAMETER MONITORING SYSTEM FOR CATTLE
Attar G.R., Patil N. M., Deokate D.T. & Hasabe B. R. | 83 – 85 |
| 18 | SCHEDULING OF CROP IRRIGATION AND FERTILIZER USING PIC
Deokate D.T., Patil N.M., Attar G. R. & Hasabe B. R. | 86 – 91 |
| 19 | CLOUD COMPUTING - DATA SECURITY CHALLENGES& SOLUTIONS
Amruta G. Dongare & Saika S. Tamboli | 92 – 94 |
| 20 | KNOWLEDGE REPRESENTATION FOR LEGAL INFORMATION NETWORK USING GRAPH DATABASE
Ms. Priyanka R. Telshinge, Ms. Saniya R. Tamboli, Ms. Priyanka D. Paul, Ms. Babyayesha I. Shaikh | 95 – 98 |
| 21 | BASICS OF ARTIFICIAL NEURAL NETWORK
Saika S. Tamboli & Amruta G. Dongare | 99 -102 |

Botany

- | | | |
|----|--|-----------|
| 22 | CYTOTOXICITY OF FUNGICIDE KREESOXIM-METHYL 44.3% ON ONION (<i>ALLIUM CEPA</i> L.) ROOT TIP CELL
Tejaswini Mane & Supriya Bargule | 103 – 105 |
| 23 | DIVERSITY OF FUNGI ASSOCIATED WITH LEAF LITTER OF MANGIFERA INDICA LINN. FROM GANGOBA SACRED GROVE, HASANE, RADHANAGARI (DIST. KOLHAPUR)
Shridevi G. Bandgar & Chandrahas R. Patil | 106 – 109 |
-

Studies On Consequence Of Temperature On Physical Properties Of CdSe Thin Films Synthesized Using Chemical Bath Deposition Method

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ABSTRACT: Chemical bath deposition (CBD) method is the most easy, low-cost and appropriate method for synthesis of compound semiconductors. Present work discusses synthesis of cadmium selenide (CdSe) thin films on stainless steel (SS) and fluorine doped tin oxide coated glass substrates by a facile chemisynthesis route. Cadmium sulfate was used as source of cations while sodiumselenosulfate was used as source of anions. Various synthesis parameters are optimized so as to obtain the best photoactive deposit. The effect of deposition temperature on structural, optical and morphological properties was studied. Thin film samples deposited at various temperatures are characterized using X-ray diffraction, field emission scanning electron microscopy (FE-SEM) and contact angle measurement techniques. Structural study reveals presence of mixed crystal structure. Wettability study reveals increase in hydrophilic nature with increase in deposition temperature.

Keywords: CdSe, chemical bath deposition, temperature, Photoelectrochemical, FE-SEM, Wettability studies.

1. Introduction

Since last few decades compound semiconductors of II-VI group have fascinated a great extent of attention because of their all-embracing applications [1, 2]. Among various semiconductors, Cadmium selenide (CdSe) is one of renowned II-VI group semiconductors, which has awestruck global researchers on account of appropriate properties. CdSe nanocrystals exhibit attractive properties like quantum size effect [3]. A suitable band gap energy of CdSe ($E_g = 1.7\text{eV}$) makes it more approving for various applications as laser diodes, light emitting diodes, optical sensing agents, photoelectrochemical solar cells, photodetectors, photoelectric applications etc [4-6]. Researchers employed number of deposition methods such as vacuum evaporation, successive ionic layer adsorption and reaction, spray pyrolysis, electrode position, pulse plating, chemical bath deposition to grow CdSe thin films [7-10]. Among various methods, chemical bath deposition (CBD) is one of the most suitable deposition methods with no requisite of sophisticated instrumentation. Chemical deposition is simple, economical method which is suitable for large area deposition. In CBD, deposition takes place when ionic product just goes above solubility product [11]. Various deposition parameters like precursor concentrations, deposition time, pH of solution, temperature etc strongly control growth rate of the deposition [12]. Temperature is one of the most important factors that affect growth of grains. One of the consequences of higher deposition temperature is increased crystal size in the thin film. Temperature of deposition bath plays vital role in deciding the physical properties of deposit [13]. Thus present investigation discusses the influence of bath temperature on physical properties of CdSe thin films.

2. Experimental details

2.1 Deposition of CdSe thin films

The CdSe thin films were deposited on the clean stainless steel substrates. As contaminated substrate results into nonuniform deposit thus all the substrates were cleaned by procedure reported elsewhere [9]. All the chemicals used were analytical reagent grade and used without any purification. Cadmium sulfate (CdSO_4) was used as sources of cation and sodium selenosulphate (Na_2SeSO_3) was used as anion. Further cadmium cations were complexed using 30 vol.% liquor ammonia. Preparation of Sodium selenosulphate solution was done by procedure reported elsewhere [14]. The preparative parameters were optimized with several trials and by well known photoelectrochemical method [15].

For chemical deposition of CdSe thin films, 10ml solution of 0.05 M CdSO_4 was taken into a beaker of 30ml capacity. Liquor ammonia was added drop by drop under constant stirring condition. Initially addition of ammonia to cadmium precursor solution results into formation of milky precipitate of cadmium hydroxide $\text{Cd}(\text{OH})_2$, which completely dissolves subsequent to further addition of ammonia solution. Finally,

10 ml solution of 0.05 M Na_2SeSO_3 was poured to the same. Four substrates were kept slanted by $15\text{--}20^\circ$ to wall of beaker. The pH of bath was maintained at 12. Temperature of bath was allowed to raise from room temperature to 65°C , 75°C and 85°C . At bath temperatures more than 85°C synthesis found impossible because of steaming of water. Deposition of CdSe material at room temperature was acquired after long time period from 3 to 4 days. After 8hs, deposited substrates were taken out, repeatedly dipped in doubly distilled water, air dried and stored for further study.

2.2 Characterizations

The structural properties of CdSe thin films are studied using Philips X-ray diffractometer PW-3710 with Cu K α source ($\lambda=1.54\text{\AA}$). The 2θ is varied range from 10° to 100° . Rame-Hart USA equipment equipped with a CCD camera was used in measurement of contact angle thus the study of solid-liquid interface was undertaken. The JEOLJSM 6360 unit was used for surface morphological study.

3. Results and discussion

Films deposited at 27°C and 65°C were found reddish in color, that found to be altered to brown and blackish brown, corresponding to bath temperatures, 75°C and 85°C , respectively as shown in fig. 1

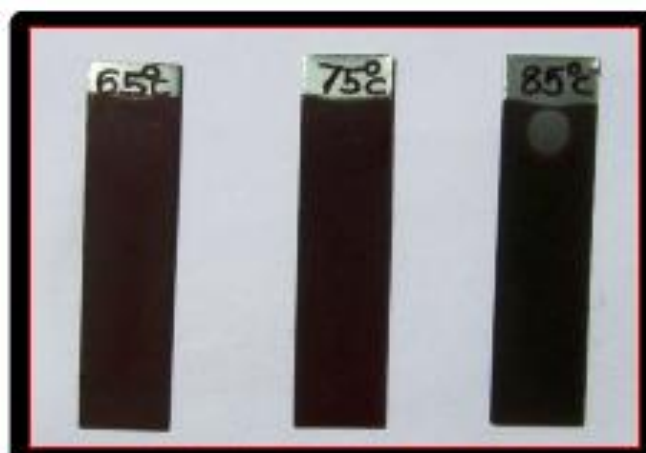


Fig. 1 Photograph of CdSe thin films deposited at different temperatures

3.1 Structural analysis

XRD patterns of chemically deposited CdSe thin films at different temperature values are shown in Fig. 2 The observed XRD patterns match well with Standard JCPDS data card no. 00-019-0191 ensuring the formation of CdSe with a metastable cubic (Sphalerite) crystal structure. The peaks designated by 'SS' corresponds to stainless steel which may be because of interference from XRD signals of the substrate. The diffraction pattern of thin film deposited at temperature 65°C (designated as (a)) shows only two diffraction peaks at $2\theta = 25.5^\circ$ and 50.6° , corresponding to (111) and (311) planes of cubic phase respectively. The diffraction pattern for thin films deposited at temperature 75°C (designated as (b)) observed to contain (220) plane, the along with (111) and (311) planes at 2θ values 42.4° , 25.6° , 50.6° , respectively.

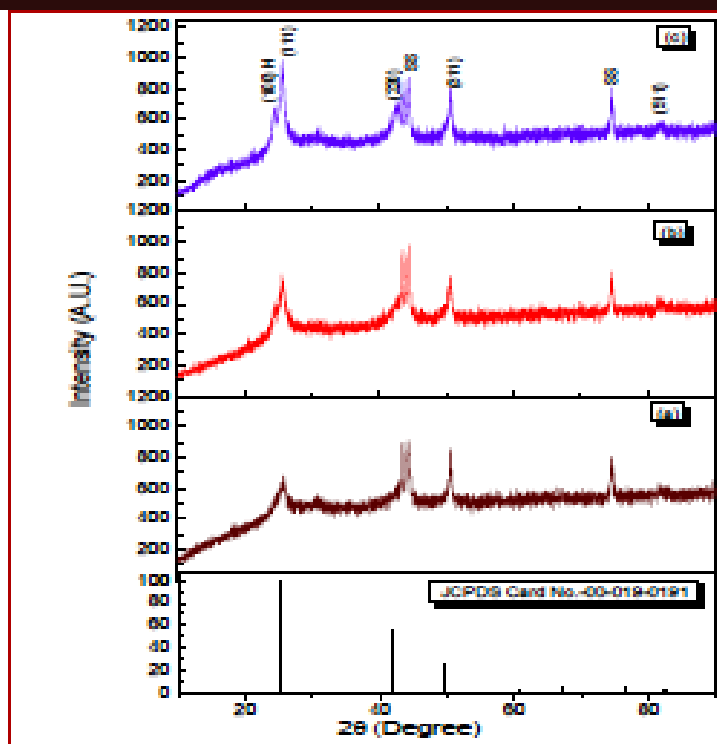


Figure 2: X-ray diffraction spectra of chemically deposited CdSe thin films at deposition temperature (a) 65 (b) 75 and (c) 85°C.

The XRD pattern corresponding to deposition temperature 85°C (designated as (c)) reveals that the diffraction peaks become sharper with drop off in full width at half maximum showing enhancement in crystallinity and particle size in company with phase transformation. The diffraction pattern contains five diffraction peaks at 2θ values 24.3°, 25.5°, 42.7°, 50.5° and 81.0°. The diffraction peaks observed at 25.5°, 42.7°, 50.5° and 81.0° are indexed as (111), (220), (311) and (511) planes confirming formation of cubic phase which are in good agreement with earlier reports [16]. While the diffraction peak observed at 24.3° is indexed as (100) plane of wurtzite hexagonal phase [JCPDS data card no.00-002-0330] confirming phase change. Good enhancement in crystallinity is observed with increase in temperature. The observed values of interplaner spacing 'd' are found to be matches well with standard values of interplaner spacing 'd' signifying the formation of CdSe in thin film form. In all XRD patterns obtained at different temperature, a peak corresponding to the plane (111) is found to be prominent as compared to the other planes. Intensity of this plane increases with increase in temperature.

This can be explained as, since the rate of reaction mainly depends upon temperature. At lower deposition temperature, rate of reaction is slow, which increases with increase in temperature. Increase in bath temperature, increases thermal dissociation of cadmium cations from complex in conjunction with fast liberation of selenium anions from hydrolysis of Na_2SeSO_3 . It guarantees high concentration of free cadmium cations and selenium anions in the deposition bath, which increases rate of reaction in combination with deposition rate. Consequently the crystallite size of CdSe thin film increase by way of deposition temperature. It shows that the temperature deposition bath has an effect on the crystal structure and crystallinity of the deposited thin film.

3.2 Wettability studies

Wettability study discusses the interaction between electrode with electrolyte which is described by value of contact angle.

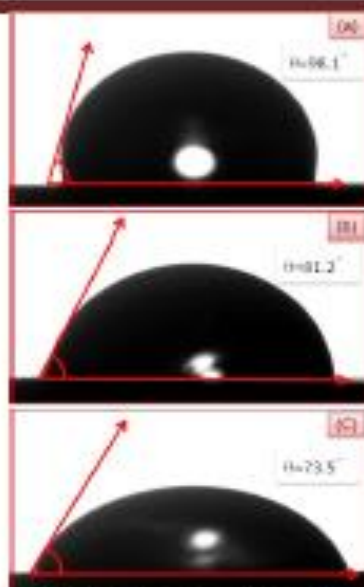


Figure 3. Contact angle measurement images of CdSe thin films deposited at different temperature values ((a), (b) , (c) corresponds deposition temperature 65, 75 and 85°C)

Water contact angle measurement images for CdSe thin films deposited at different temperatures are shown in Fig.2. This decrease in water contact angle is attributed to increase in surface roughness. Smaller the contact angle more is the hydrophilic nature of electrode surface which results into intimate contact between photoanode and redox electrolyte in solar cell.

The water contact angle values found to be decreased from 98.1° to 73.5° with increase in temperature. Smaller be the contact angle more will be the hydrophilic nature of electrode surface [17].

3.3 Morphological studies

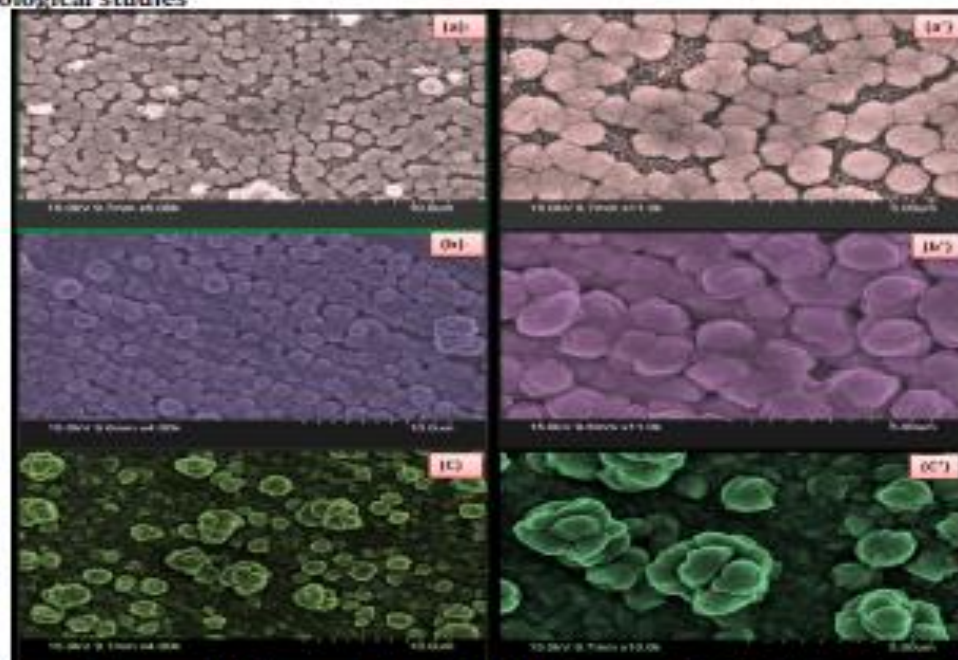


Figure 4: Lower and higher magnification FESEM images of CdSe thin films deposited at different bath temperatures [(a),(a')-65°C, (b),(b') -75°C and (c),(c')- 85°C].

The surface morphology of CdSe thin films deposited at different temperature values was inspected using field emission scanning electron microscopy (FESEM). Figure 4 shows lower and higher magnification FESEM images of CdSe thin films. Fig. 4(a), (a') show lower and higher magnification FESEM images of CdSe thin films deposited at deposition temperature 65°C. It shows pebble like morphology covered by fiber like structure on it. Pawar et al [2] reported analogous morphology of chemically synthesized CdSe thin films on glass substrates. Films deposited at lower temperature are detachable. FESEM image (b), (b') of thin films deposited at temperature 75°C shows more compact morphology. It shows fused pebbles like morphology. Compact structure with agglomerated grain like structure found to be deposited corresponding to temperature 85°C. Well adherent and good quality films with cauliflower like morphology are found to be obtained corresponding to deposition temperature equal to 85°C. Surface morphology found to be significantly altered with the deposition temperature.

4. Conclusions

CdSe thin films are successfully synthesized by the chemical bath deposition method at different deposition temperatures. Structural studies reveal enhancement in crystallinity and particle size in company with phase transformation with increase in temperature from 65 to 85°C. Wettability study shows, film deposited at temperature 85°C has more hydrophilic nature with contact angle of 73.5°. Surface morphology of CdSe thin films found to be significantly modulated via the parameter, bath temperature.

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