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Novel synthesis method for quaternary Cd(Cu, Zn)Se thin films and its characterizations



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ABSTRACT

Keywords: Cd(Cu, Zn)Se thin films XPS Raman AFM EFM Nowadays, the search for novel compounds by chemical synthesis is in trend. Herein, we report the deposition of $Cd_{1-x-y}Zn_xCu_ySe$ ($0.025 \le x = y \le 0.15$) films by facile, industry-oriented chemical synthesis. The $Cd_{1-x-y}Zn_xCu_ySe$ thin films were deposited at the optimized growth conditions (temperature = 70 ± 0.1 °C, pH = 10.3 ± 0.1 , substrate rotation speed = 70 ± 2 rpm and time = 100 min). As-synthesized thin films were characterized for physical, chemical, topographical and electrical attributes. The study of vibrational modes in $Cd_{1-x-y}Zn_xCu_ySe$ thin films was done with the help of Raman spectroscopy. Improvement in surface topography with the integration of Cu^{2+} and Zn^{2+} into the CdSe lattice has been noticed by the atomic force microscopy (AFM). The electrochemical impedance spectroscopy revealed lower values of R_s and R_{ct} for x = y = 0.05 composition. Chemical deposition of $Cd_{1-x-y}Zn_xCu_ySe$ thin films may offer an excellent way to fabricate quaternary chalcogenide-based absorber materials for solar cells.

1. Introduction

The design and development of multi-functional earth-abundant compounds for solar cell technology, batteries, and fuel cells play a vital role in sustainable energy solutions [1–3]. Such an arduous task of developing clean, cheap and efficient renewable energy sources have called an up-gradation in the existing photovoltaic (PV) raw materials [1,2]. Recently, II-VI, I-III-V, and IV-VI group chalcogenides are in the limelight for their high-end applications in microelectronics, optoelectronic devices, solar cells, selective coatings, window layers, photo-luminescent devices, TFT, lasers, LED's, photodetectors, gamma-ray detectors, and catalysis, etc. [4–7].

The CuIn_xGa_{1-x}Se₂ (CIGS) and CdTe chalcogenide thin-film based solar cells are gaining scientific and industrial attention owing to the high efficiency and commercialization viewpoint. Nevertheless, both compounds are suffering from drawbacks of low abundance (e.g. Te, In

and Ga) which hampers their large-scale utilization [8,9]. In contrast, chalcogenides such as CuSe, CuS, Cu₂Se, Cu₂S, ZnSe, ZnS, Cu₂MSnX₄ (M = Zn, Co, Ni, Fe, and X = Se, S), Cu₂Sn(S_xSe_{1-x})₃ (CTSSe) and Cu₂ZnSn(S_xSe_{1-x})₄ (CZTSSe) have been showing a ray of light as a promising substitutes to highly efficient Cu(In, Ga)(S, Se)₂ absorbers in thin-film solar cells due to earth-abundant elements, and excellent optoelectronic properties [8–11]. The improvement in the synthesis methods of mixed metal sulfides/selenides with precise shape, size and composition modulation is presently a hot topic of active research [12]. Since the physical deposition technique requires expensive high-vacuum environment, the potential of chalcogenide semiconductors can be efficiently exploited when coupled with facile, inexpensive chemical methods [13]. The chemical deposition offers benefits for employment in economical industrial production, as it involves simple and economic synthesis route and non-hazardous precursors [2,5,7,14].

From the perspective of photovoltaic applications, here, we propose

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Fig. 1. Schematic diagram of the indigenously developed chemical arrested precipitation set up.



Fig. 2. (a) Variation in the film color as a function of the composition *x* and *y*, **(b)** Variation in the film thickness. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

a synthesis of quaternary $Cd_{1-x-y}Zn_xCu_ySe$ thin films via industry preferred chemical synthesis. The foundation of our selection of Cd(Cu, Zn) Se system is based on the following facts.

- 1. CdSe is one of the most studied compounds owing to its high absorption coefficient and direct bandgap in the visible range.
- 2. Out of different transition metals, Cu exhibits a great tendency to form an alloy with various chalcogens and offers a tuning of physiochemical and optoelectrical properties [15,16].
- 3. Next to Cu, Zn is present in the periodic table which has a comparable ionic size (Cu⁺² = 0.72 Å and Zn⁺² = 0.74 Å) and hence when used as a dopant can be expected to act as low density non-radiative recombination center which sequentially can reduce the losses of photocurrent and photovoltage in PV devices [17–19].
- The Cu based compound semiconductors, such as Cu–Zn–Cd–Se/ Cu₂ZnCd(S, Se)₃ are known to have a flexible energy gap ranges from 2.4 eV to 3.7 eV [20].

2. Methods and measurements

2.1. Chemical deposition

The synthesis of $Cd_{1.x.y}Zn_xCu_ySe$ films was done on the micro-glass slides and conducting FTO substrates via an arrested precipitation technique. The substrates before deposition were cleaned in an ultrasonic bath for 5 min by rinsing in successively in ethanol, acetone and double-distilled water. AR grade precursors, namely, cadmium acetate $Cd(CH_3COO)_2$, cupric acetate $Cu(CH_3COO)_2$, zinc acetate $Zn(CH_3CO_2)_2$, selenium metal powder (Se), sodium sulfite (Na₂SO₃), ammonia (NH₃) and triethanolamine (C₆H₁₅NO₃) were used for the synthesis. Selenium precursor (Na₂SeSO₃) was acquired using a reflux action of selenium metal powder with sodium sulfite at 80 °C temperature for 9 h [2,6,21].

In actual synthesis; initially, 2 ml of triethanolamine (TEA) was mixed into 10 ml of 1 M cadmium acetate and 15 ml of 25% NH₃ was added gradually under constant mechanical agitation. To this, 33 ml of 0.33 M sodium selenosulfate was added. A calculated amount of 1 M zinc acetate and cupric acetate were mixed into the reaction mixture to define the *x* and *y* values. The reaction container was shifted to a constant temperature paraffin oil bath having $70 \text{ }^\circ\text{C} \pm 0.1 \text{ }^\circ\text{C}$



Fig. 3. The Survey spectra for Cd_{1-x-y}Zn_xCu_ySe thin films.

temperature. The thoroughly cleaned substrates were then attached to a special substrate holder which was then set into rotation of 70 \pm 2 rpm by using AC/DC motor. After 100 min of the deposition time, the substrates were removed from the holder, cleaned and preserved carefully in the dark desiccator.

2.2. Characterization of thin films

An AMBIOS Make XP-1stylus profilometer was used to determine the terminal layer thickness of the as-grown films. The X-ray photoelectron spectroscopy (XPS) was performed by Thermo Scientific equipment (ESCALAB250) with a base pressure of 10^{-9} T using an Al anode with a monochromatic K_{α} line from quartz filters. The equipment was calibrated with the C 1s core position in 284.55 eV. Raman spectra were measured in the backscattering configuration in a Jobin Yvon HR 800UV equipment operating with a 514.5 nm laser line. Atomic force microscope (AFM) from Innova Instruments-Bruker was employed to observe the surface roughness and topography in a tapping mode (tip curvature < 10 nm, frequency = 290 kHz and k = 40 N/m). The electrostatic force microscopy (EFM) measurements were done by Innova Bruker Instrument. The topographic and phase imaging map (phase shift during the first pass) were obtained at 40 nm lift mode. The Pt-Ir tip coated cantilever having 1 N/m spring constant, 60 kHz resonance frequency and 2 V applied bias voltage was used for the purpose. The electrochemical impedance spectroscopy (EIS) was done using 0.5 MH₂SO₄ electrolyte via (AUTOLABPGSTAT100 FRA 32) potentiostat.

3. Results and discussion

3.1. Growth and reaction mechanisms

The film quality in a chemical deposition is strongly governed by the concentration of reacting agents as the film formation occurs only when



Fig. 4. Core level XPS spectra of (a) Cd3d, (b) Zn2p, (c) Cu2p and (d) Se3d for $Cd_{1.x.y}Zn_xCu_ySe$ (x = y = 0.05) thin film.

Table 1 Binding energy values of Cd, Zn, Cu, and Se acquired from core-level spectra of $Cd_{1.x.y}Zn_xCu_ySe$ thin films.

Bath composition $(x = y)$	Cd 3d _{3/2} eV	Cd 3d _{5/2} eV	Spin-Orbital splitting eV	$Zn \ 2p_{1/2} eV$	Zn 2p _{3/2} eV	Spin-Orbital splitting eV	Cu $2p_{1/2} eV$	Cu 2p _{3/2 eV}	Spin-Orbital splitting eV	Se3d eV
0.05 0.075 0.15	411.92 412 411.89	405.17 405.18 405.06	6.75 6.82 6.83	1045.06 1045.27 1045.34	1022.21 1022.15 1022.12	22.85 23.13 23.22	952.65 952.28 952.35	932.49 932.41 932.48	20.16 19.87 19.87	53.99 54.08 53.96
Standard	411.56	404.8	6.76	1044.5	1021.45	23.1	952.75	933	19.75	55.3



Fig. 5. Raman spectrum of Cd_{1-x-y}Zn_xCu_ySe thin film samples.

the ionic product (K_p) exceeds the solubility product (K_{sp}) of metal ions. The control over free metal ion discharge and formation of the highquality output product can be accomplished using the optimization of various growth parameters, such as TEA, a quantity of NH₃, deposition temperature, substrate rotation and deposition time, etc. [21]. Fig. 1 shows a schematic drawing of a facile arrested precipitation technique set up indigenously developed in our laboratory. The reaction mechanism for Cd_{1-x-y}Zn_xCu_ySe film formation is summarized as follows;

Firstly, triethanolamine makes a complex with $Cd^{2+}/Zn^{2+}/Cu^{2+}$ and reduces the release rate of the free cation concentration in the reaction mixture and governs the growth rate [7,21].

$$Cd^{2+} + n(TEA) + NH_3 + 2\overline{O}H \rightarrow Cd(TEA)_n^{2+} + NH_4OH$$
(1)

 $Zn^{2+} + n(TEA) + NH_3 + 2\overline{O}H \rightarrow Zn(TEA)_n^{2+} + NH_4OH$ (2)

$$Cu^{2+} + n(TEA) + NH_3 + 2\overline{O}H \rightarrow Cu(TEA)_n^{2+} + NH_4OH$$
(3)

The release of Se^{2-} ions from sodium selenosulfate is given by following reaction mechanism [7,21];

$$Na_2SeSO_3 + \overline{O}H \leftrightarrow NH_2SO_4 + HSe^-$$
 (4)

$$HSe^{-} + \overline{O}H \leftrightarrow Se^{2-} + H_2O \tag{5}$$

The overall reaction mechanism between $Cd^{2+}/Zn^{2+}/Cu^{2+}$ cation complex and free Se^{2-} anions can be given as;

$$(1 - x - y)Cd(TEA)_n^{2+} + (x)Zn(TEA)_n^{2+} + (y)Cu(TEA)_n^{2+} + HSe^{2-}$$

+ $OH \rightarrow$
 $Cd_{1-x}Zn_xCu_ySe + n(TEA) + HO_2$
(Thin Solid Film) (6)

3.2. Physical observations and thickness measurement

The as-deposited $Cd_{1-x-y}Zn_xCu_ySe$ films are physically adherent to the substrates and uniform in nature. The color of the binary CdSe is dark orange-red [7,21] which changes from cherry-red to reddish-black suggesting the incorporation of Zn^{2+} and Cu^{2+} in CdSe host as revealed in Fig. 2 (a). The film thickness was found to be decreased after x = y = 0.05 as shown in Fig. 2 (b). In our case, Zn^{2+} and Cu^{2+} ions act as the foreign in-homogeneities/nuclei that impact the growth process. At higher doping concentrations (> 0.05), Zn and Cu ions can occupy the interstitial sites of CdSe lattice resulting in a substantial impurity scattering and causing the decrease in film thickness [7].

3.3. XPS analysis

An XPS measurement was done to detect the presence and chemical states of Cd, Zn, Cu, and Se elements. Fig. 3 displays the complete survey spectra of three representative Cd_{1-x-v}Zn_xCu_vSe samples. The C1s peak at ~284.55 eV is taken as a specimen charging by standard reference [7]. The survey spectra display the presence of O 1s peak at \sim 532.12 eV, because of the adsorbed oxygen on the film surface due to exposure to air [7]. Fig. 4(a-d) shows core level spectra of Cd(3d), Cu (2p), Zn(2p) and Se(3d) at x = y = 0.05 sample. In the as-deposited $Cd_{1-x-y}Zn_xCu_ySe$ films Cd peak splits into a doublet $3d_{5/2}$ and $3d_{3/2}$ with binding energy (B.E.) of 405.17 eV and 411.92 eV. The spin orbitsplitting value for Cd element is 6.75 eV which is very close to the reported values, which suggests that Cd prefers +2-oxidation state [7,22]. Table 1 recites the binding energy and core level splitting values of Cd(3d), Cu(2p), Zn(2p) and Se(3d) for three representative Cd_{1-x}- $_{\rm v}$ Zn_xCu_vSe samples. The trivial shift in the binding energy values of the Cd peak may be accredited to the influence of strain-induced distortion owing to the simultaneous integration of Cu^{2+} and Zn^{2+} [7].

The Zn 2p peak splits into $2p_{1/2}$ and $2p_{3/2}$ located at B.E. of 1045.06 eV and 1022.21 eV, respectively. At x = y = 0.075 composition, spin-orbit splitting value is in close consonance with the reported 23.1 eV [5,7]. The small shift in core-level splitting value at the higher composition can be ascribed to the different chemical environment interaction with the surface atoms [23]. Thus, these results confirm the oxidation state of Zn is + 2 [5,7,23]. The Cu2p peak (Fig. 4 c) splits into Cu $2p_{3/2}$ and Cu $2p_{1/2}$ at 932.49 eV and 952.65 eV respectively. The presence of a strong shake-up satellite designates the oxidation state of Cu as + 2 [24,25]. Fig. 4 (d) shows the Se 3d peak at B.E. \sim 54 eV which is the best match with reported value [7]. The small core level B.E. energy shift in the Se 3d peak may be attributed to fluctuations of Fermi level location in the energy gap owing to the incorporation of x and y [7].

3.4. Raman spectroscopy analysis

Fig. 5 display the Raman spectra of $Cd_{1-x-y}Zn_xCu_ySe$ thin films consisting of a fundamental LO phonon peak at ~204.47 cm⁻¹ with a 2LO peak at ~410.96 cm⁻¹ of host CdSe material [7]. The detected 1LO phonon peak of CdSe (~205 cm⁻¹) is a little bit lower than bulk 1LO phonon frequency (210 cm⁻¹ – 213 cm⁻¹). The shift in (1LO) phonon peak is caused by the crystallinity and strain development in films



Fig. 6. The AFM results of $Cd_{1-x-y}Zn_xCu_ySe$ (0.025 $\leq x = y \leq 0.15$) thin films. (a) 2D-AFM. and 3D-AFM topographs, (b) height histograms, Sobel transforms and angular spectra.

during the synthesis process. The small peak at $\sim 262.61 \text{ cm}^{-1}$ related to the second phase of CuSe [26]. The peaks at 123 cm^{-1} and 140.30 cm^{-1} belong to a prominent A1 and B1 modes in the I–III-VI chalcopyrite structure [27]. The peak at $\sim 179 \text{ cm}^{-1}$, related with A1 vibrational mode in the chalcopyrite structure and the peaks detected at $\sim 230.87 \text{ cm}^{-1}$ confirms the contribution of B2 mode [28].

3.5. AFM observations

The 2D AFM-topography for $Cd_{1-x-y}Zn_xCu_ySe$ samples shows the presence of agglomerated globular grains (Fig. 6 a). At x = y = 0.15, 2D-topography revealed small threaded/needle-like elongated crystallites. The hillocks and valleys are observed from 3D-topographic images presented in Fig. 6 (a). The surface topography tends to become rough (Table 2) with increased grain size, increased hillocks and valleys. The

Table 2

Some parameters obtained from AFM and EIS measurements.

Bath composition (x = y)	AFM Parameters								
	Particle height nm	Average roughness S _a nm	RMS roughness S _q nm	Total roughness S _t nm	Skewness S _{sk}	Kurtosis moment S _{ku}	Surface area ratio, S _{dr} (%)	R _s (kΩ)	R_{ct} (k Ω)
0.025	210	439.6	486.	1629.6	1.210	1.64	65.7	4.24	2.66
0.05	500	584.6	623	1734.1	1.2246	1.74	111.60	4.16	1.20
0.075	510	498.65	540.62	1875.7	1.3646	2.45	78.71	4.29	8.19
0.1	530	559.73	599.56	1890.6	1.2341	1.75	64.09	4.01	3.71
0.15	1170	1028.2	1103.8	2206.6	1.1788	1.49	105.67	4.43	5.18



Fig. 7. Representative EFM topographs for the $Cd_{1-x-y}Zn_xCu_ySe$ thin films.



Fig. 8. EIS spectrums of $Cd_{1-x-y}Zn_xCu_ySe$ (0.025 $\leq x = y \leq 0.15$) thin films.

surface properties such as average roughness (S_a), skewness (S_{sk}), RMS roughness, kurtosis (S_{ku}) and (S_q) total roughness (S_t), etc. were evaluated via standard relations [7]. For x = y = 0.15 composition the higher values of average roughness ($S_a = 1028.2$) and RMS roughness ($S_q = 1103.8$) were observed and it is due to a considerable increase in Cu content at this composition. The surface topography comprises of more hillocks (peaks) than valleys as it was suggested by the positive skewness (1.1–1.3) in the composition range studied. The kurtosis moment (S_{ku}) was found to be < 3, and the surface shows spiky nature (platykurtic) for all the films. For the better readability of fine structures, the Sobel transformation (Fig. 6 b) was done [7]. The Sobel transforms revealed the complete substrate coverage by unevenly sized nano ball/globular grains. The observed nano ball-like features were few nm in diameter and particularly remarkable due to some level of

the ordering. The angular spectrum graph (Fig. 6 b) confirms the dominating orientation of the nano ball-like features within a single object. The height distribution (Fig. 6 b) is sharp and symmetric up to x = y = 0.1 which testifies the uniform distribution of grains/crystallites in as-deposited Cd(Zn, Cu)Se thin films. The maximum surface to area ratio (S_{dr} = 111.60%) for x = y = 0.05 and it is beneficial for superior device performance.

3.6. EFM observations

Electrostatic force microscopy (EFM) revealed several hill-like agglomerated grains existing in the sample surfaces (Fig. 7), which verifies the presence of electrical charges on the surface [29]. With increased Zn and Cu concentrations, the EFM images become well defined with protruding grains up to composition x = y = 0.05. Such protruding of grains and surface coverage is favorable for boosting of energy conversion efficiency. Generally, the increased crystallite size enhances the surface coverage and finally decreases the resistance within the grains. The color variations of EFM images can be ascribed to the presence of several arbitrarily oriented electric domains and the color contrast specifies the accumulation of charges on the surface of $Cd_{1-x-y}Zn_xCu_ySe$ films [30].

3.7. Electrochemical impedance spectroscopy

Fig. 8 displays the impedance spectra which consists of a semicircle in the higher frequency range and an almost straight line in the lower frequency range. The intercept on the real axis of the plot in higher frequency region signifies the series resistance (R_s) [31]. The Faradaic charge transfer resistance (R_{ct}) is calculated from the diameter of the semicircle in the higher frequency region. Table 2 shows EIS parameters and sample x = y = 0.05 shows smaller semicircle in higher frequency range with R_s = 416 k Ω and R_{ct} = 1.20 k Ω . The smaller semicircle indicates the lower values of R_{ct} among all the samples suggesting a lower value of resistance, easy diffusion of the electrolyte in the electrode material thus forming an efficient transport pathway for electrons and ions [32].

4. Conclusions

Here, we have successfully synthesized quaternary Cd_{1-x-y}Zn_xCu_ySe thin films via facile chemical synthesis. Physical observations strongly support the integration of Zn and Cu into the CdSe host. The XPS outcomes confirmed oxidation states of the requisite elements as Cd²⁺, Cu²⁺ Zn²⁺, and Se²⁻, which indicates the formation of Cd_{1-x-y}Zn_xCu_ySe thin films. The AFM topography showed the maximum surface to area ratio (S_{dr} = 111.60%) with sharp and symmetric height distribution for x = y = 0.05. The EIS measurement showed that a lower value of R_s and R_{ct} resistance at x = y = 0.05 composition. Thus, the quaternary Cd(Zn, Cu)Se thin films deposited via an economic arrested precipitation process assure low-cost replacements to conventional photovoltaic materials.

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