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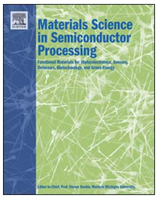

# Direct synthesis of quaternary Cd(Zn, S)Se thin films: Effects of composition

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## ABSTRACT

In the present communication, the binary CdSe and quaternary $Cd_{1-x}Zn_xSe_{1-y}S_y$ ($0 \leq x = y \leq 0.35$) thin films were synthesized using a chemical bath deposition. Thin film deposition was carried out at the optimized conditions (pH = 10 ± 0.1, deposition temperature = 70 ± 0.1 °C, deposition time = 100 min and substrate rotation speed = 65 ± 2 rpm). X-ray diffraction studies confirmed hexagonal-wurtzite crystal structure with the formation of quaternary Cd(Zn, S)Se phase along with binary CdSe, CdS, ZnS and ZnSe, phases of the as-grown $Cd_{1-x}Zn_xSe_{1-y}S_y$ thin films. Elemental analysis showed presence of $Cd^{2+}$, $Zn^{2+}$, $S^{2-}$ and $Se^{2-}$ in the deposited films. Fourier transform infrared spectroscopy shown the bands at 911.15 $cm^{-1}$ – 901.62 $cm^{-1}$ which are assigned to the stretching frequency of Cd–Se bond. Scanning electron microscopy show transformation of the microstructure from globular crystallites to a rhomboid flake like network. The electrical conductivity was typically ≈ $10^{-7}\ \Omega^{-1}\ cm^{-1}$. At low temperatures, the conduction was by variable range hopping, and this changed to thermally activated grain boundary dominated conduction for $T > 350$ K.

## 1. Introduction

Current research has evoked a considerable interest in the development of II–VI semiconductors in the era of substantial optoelectronic applications, viz. light emitting diodes and photovoltaic solar cells including the photoelectrochemical cells [1,2]. The forte of semiconductors is the tuning of the material properties through the alloy formation resulting in the ternary/quaternary, or multi phase compositions that provide a mode for band gap modulation and a facile way of tuning the electrical properties [1,2]. The particular interest on ternary semiconductors encompasses ZnSSe [3], CdZnSe [4], CdSTe [5], and CdSSe [6]. Attempts are also made on few of the quaternary compounds of the II–IV–VI type such as $Cu(In_{1-x}Ga_x)Se_2$, $Cu_2ZnSnS_4$ (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) and have been broadly studied as an alternative photo-absorber materials [7]. These higher order materials are recently drawing great attention as they are the strong contender and have a potential application by way of light absorption in thin film photovoltaics. Apart from their potential application, their synthesis is too crucial, tedious and cost intensive [8]. Very recently CdSe and $Cd_{1-x}Zn_xSe_{1-y}S_y$ are focused in the quantum dot studies [9] and for optoelectronic applications [10,11]. Because of their greater flexibility in composition control and band gap modulation, these alloy semiconductors can be proved to have wider potential application in tunable optoelectronic devices. Pan et al. [11], have shown that composition-graded ZnCdSSe alloy nanowires are useful in tunable nanolasers application. Pristine CdSe and CdS are known to have hexagonal or cubic or mixed (hexagonal-cubic) crystal structures [10,12]. Whereas, ZnSe can be synthesized as either hexagonal or cubic based on the growth conditions [13]. Also, our earlier experiences for these materials are notable and we have synthesized these materials into binary/ternary phases using a novel, scalable and least expensive chemical growth process set indigenously in our laboratory [10,13–15]. The ability to engineer and modulate the materials characteristics through composition control of these semiconductors is one of the ultimate goals of our studies. This is our first attempt to synthesize the quaternary phase of these materials in view of their promising application. This is aimed in view of high stability of ZnSe and CdS over CdSe and they can be grown suitably and efficiently to obtain a homogeneous alloy phase [12–15]. Quaternary $Cd_{1-x}Zn_xSe_{1-y}S_y$ films of various composition ($0 \leq x = y \leq 0.35$) were therefore grown in our laboratory under different growth

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conditions and then characterized to assess their suitability for use in high-tech applications.

## 2. Thin film deposition and characterization

Deposition of the $Cd_{1-x}Zn_xSe_{1-y}S_y$ ($0 \le x = y \le 0.35$) thin films was carried on the spectroscopic grade glass slides using AR grade precursors. Cadmium acetate, zinc acetate, thiourea, selenium metal powder, sodium sulfite, liquor ammonia and triethanolamine (TEA) were used for the purpose. Se-precursor ($Na_2SeSO_3$) was obtained by refluxing selenium metal powder in the presence of sodium sulfite at 80 °C for 9 h. [10]. First, 10 ml (1 M) cadmium acetate was taken in a 250 ml beaker and complexed with 2 ml TEA. The yellowish translucent thick $Cd^{2+}$-TEA complex was formed which was then dissolved with the addition of 15 ml ammonia. To this, 33 ml of 0.33 M $Na_2SeSO_3$ was gradually added under the dynamic mechanical stirring. The reaction bulk was then diluted to 200 ml by adding double distilled water. The pH of the reaction bath was found to be 10.1 ± 0.1. The reaction bath thus prepared was transferred to a PID controlled temperature oil bath maintained at 70 ± 0.1 °C. Carefully pre-cleaned glass slides were attached to a specially designed bakelite substrate holder which was attached to a constant speed AC/DC motor. The film deposition was carried out for 100 min at the substrate rotation speed of 65 ± 2 rpm. For different compositions of $Cd_{1-x}Zn_xSe_{1-y}S_y$ samples, calculated quantities of 1 M zinc acetate and thiourea were added so as to define the values of $x$ and $y$ between 0.01 and 0.35. After the successful deposition, substrates were detached from the system and rinsed with double distilled water to remove any loosely adhered particles from the surface, dried and preserved carefully.

SEM JEOL 6360-JED2300 equipped with energy dispersive spectroscopy (EDS) tool was used to view the microstructure and determine the composition, respectively. The atomic percentages of the constituent elements were also determined by an X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, Thermo-Scientific, UK). Structural studies were carried out on the samples using a Rigaku X-ray diffractometer with Cu Kα (λ = 1.5406 Å) radiation in the 2θ range from 20° to 80°. FTIR spectra were recorded at room temperature in the wavelength range from 4000 $cm^{-1}$ – 600 $cm^{-1}$ using a Thermo Scientific Nicolet iS10 FTIR spectrometer. The temperature dependence of an electrical conductivity was carried out in the temperature range from 300 K to 550 K. A two-probe technique was used for the purpose and contacts were drawn using silver paint.

## 3. Results and discussion

### 3.1. Chemical analysis

The elemental compositional analysis of the as-deposited CdSe and $Cd_{1-x}Zn_xSe_{1-y}S_y$ ($0.01 \le x = y \le 0.35$) thin films was carried out by an energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy. Accounting the simultaneous integration of $Zn^{2+}$ and $S^{2-}$ in CdSe, actual atomic percentages of Cd, Se, S, and Zn were determined and are cited in Table 1. The close observation of Table 1 confirmed near stoichiometric CdSe deposits (Cd/Se = 0.985). It appeared that, when $Zn^{2+}$ and $S^{2-}$ were added simultaneously in the lattice of CdSe, the percentage of $Cd^{2+}$ went on increasing for $0.01 \le x = y \le 0.075$ composition range. The percentage content of $Zn^{2+}$ is also found to be continuously increased throughout the composition range. However, the percentage of $S^{2-}$ is initially high for very small doping values and it decreased a little when doping concentration was raised to 0.075. At higher concentrations of $Zn^{2+}$ and $S^{2-}$ ($0.1 \le x = y \le 0.35$), the $Se^{2-}$ concentration enhanced significantly (≈ 11% average) with decrease in $Cd^{2+}$-content (≈ 15% average) and almost no change in $S^{2-}$ content. We can attribute this observations to the tendency of ZnSe and CdS formation at higher doping concentrations. This is very clear from the XRD observations. From the SEM micrographs, it is observed that ZnSe forms spherical crystallites and CdS forms a kind of layer forming rhomboid/flakes, petal type crystallites grown over deeply embedded into spherical crystallites. The atomic percentages of the constituent elements were also determined by an XPS analysis. From the Table 1, it is seen that the as-deposited pure CdSe films are stoichiometric. These results closely match with the EDS results (Table 1). With the increase in $Zn^{2+}$ and $S^{2-}$ contents in the bath, both $Zn^{2+}$ and $S^{2-}$ contents ($x, y$) in the film increased and the deposits are $Cd^{2+}$-rich throughout the composition range ($0 \le x = y \le 0.35$). From Table 1 it can also be observed that both $Zn^{2+}$ and $S^{2-}$ replace $Se^{2-}$ significantly from the lattice of CdSe. Therefore, the content of $Se^{2-}$ in the films decreased drastically (50.53–15.5%), especially for the lower range of x values ($0 \le x = y \le 0.075$). In this range of composition, $Cd^{2+}$-content in the film went on increasing although it was expected to be around 50%. The probable reason is that $Zn^{2+}$ and $S^{2-}$ are simultaneously entering into the lattice of CdSe replacing $Se^{2-}$. As $S^{2-}$ is more reactive, its concentration in the lattice is more than $Zn^{2+}$. As a result, the crystal may become more electronegative and in order to meet the charge balance, $Cd^{2+}$ content must increase. In the higher range of x values ($0.1 \le x = y \le 0.35$), $Zn^{2+}$-content has been increased continuously and so also the $S^{2-}$-content increased but comparatively at a lower rate. This makes crystal electropositive and in turn $Se^{2-}$ concentration goes on increasing for charge balance of the crystal [16,17].

**Table 1**
Atomic percentages of the Cd, Zn, S and Se as-observed from the EDS and XPS core level spectra of the $Cd_{1-x}Zn_xSe_{1-y}S_y$ ($0 \le x = y \le 0.35$) thin films.

| **Bath composition ($x = y$)** | **Atomic % by EDS** | | | | **Atomic % by XPS** | | | |
|---|---|---|---|---|---|---|---|---|
| | **Cd** | **Zn** | **S** | **Se** | **Cd** | **Zn** | **S** | **Se** |
| 0 | 49.57 | – | – | 50.43 | 49.47 | – | – | 50.53 |
| 0.01 | 51.21 | 0.09 | 16.7 | 32 | 52.32 | 1.33 | 6.52 | 39.83 |
| 0.025 | 61.11 | 0.29 | 16.35 | 22.25 | 64 | 1.47 | 9.33 | 25.2 |
| 0.05 | 69.66 | 1.35 | 13.45 | 15.54 | 67.95 | 1.82 | 12.08 | 18.15 |
| 0.075 | 75.20 | 1.14 | 11.34 | 12.32 | 69.39 | 1.97 | 13.14 | 15.5 |
| 0.1 | 63.56 | 1.34 | 12.79 | 22.21 | 62.77 | 2.94 | 13.6 | 20.69 |
| 0.15 | 52.41 | 2.70 | 13.46 | 31.43 | 57.29 | 3.3 | 14.52 | 24.89 |
| 0.2 | 54.26 | 2.30 | 14.26 | 29.18 | 55.06 | 3.85 | 14.76 | 26.33 |
| 0.25 | 58.42 | 3.97 | 14.72 | 22.89 | 57.8 | 3.94 | 15.02 | 23.24 |
| 0.3 | 58.33 | 4.28 | 15.02 | 22.37 | 56.52 | 6.15 | 15.23 | 22.1 |
| 0.35 | 58.20 | 6.37 | 15.77 | 19.66 | 55.24 | 7.55 | 16.19 | 21.02 |

The atomic % observed by an XPS also indicated the films to be stoichiometric. This is a function of $Zn^{2+}$ and $S^{2-}$ dopant concentrations. Fig. 1 reveals the XPS survey spectra of the CdSe and Cd(Zn, S)Se

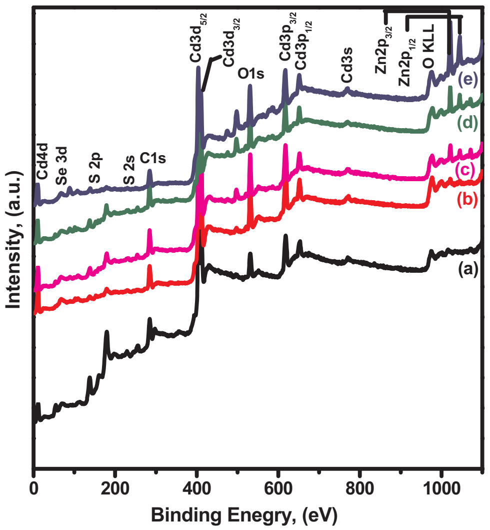

Fig. 1. XPS survey spectra for the CdSe and $Cd_{1-x}Zn_xSe_{1-y}S_y$ thin films for different values of [$x = y$ = (a) 0, (b) 0.01, (c) 0.1, (d) 0.15 and (e) 0.25].