Surface morphological properties of $\text{Cd}_x\text{Zn}(1-x)\text{S}$ thin films deposited by low-cost atmospheric pressure metal organic chemical vapour deposition technique (AP-MOCVD)

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Abstract. The $\text{Cd}_x\text{Zn}(1-x)\text{S}$ films have been deposited by low cost atmospheric pressure metal organic chemical vapour deposition (AP-MOCVD) technique and the resulting morphological properties were successfully evaluated for solar cell applications. All morphological properties presented here were investigated by Field-Emission Scanning Microscopy (FESEM) and Energy Dispersive X-Ray (EDX) spectroscopy. It has been observed that the film thickness and grain size have been greatly influenced by the molar ratio of cadmium and zinc, deposition temperature and time. The average grain size of $\text{Cd}_0.5\text{Zn}_0.5\text{S}$ films (98.16 nm thick) was obtained with deposition temperature and time of 440°C and 2.5 minutes, respectively.

1. Introduction
Solar energy is one of green technologies that is rapidly evolve in the world. Second generation of solar cell known as thin film (TF) is made by depositing thin layer of photovoltaic material on a substrate such as glass or metal. The interfaces between each layer of solar cell has different application depends on the property of the layer of material. Window layer is one of the layer in solar cell which is essential to minimize recombination losses and affect the solar cell efficiency. Recombination loss might come from morphological properties of window layer such as grain size and pinholes at the layer. Deposition technique and parameters used can be optimized to minimize the problems occurred. Most of physical and chemical deposition techniques require high pressure and temperature which are costly. Therefore, in this work, ternary material cadmium zinc sulphide has been chosen as a window layer that has wide bandgap and low cost deposition technique has been implemented. Cadmium Zinc Sulphide ($\text{CdZnS}$) is a II-VI ternary compound with tunable band gap property [1]. It has been used widely in optoelectronics devices such as light emitting diodes (LED), blue lasers and optical devices [2]. $\text{CdZnS}$ thin films have been a popular choice of material with a wide bandgap window layer material in heterojunction solar cell [3] and photoconductive devices [4]. The bandgap of $\text{CdZnS}$ can be easily tuned and desirable lattice parameters can be achieved which attracts its implication in photo-conducting materials, non-linear optics, and other optoelectronic devices [5]. The band gap of $\text{CdS}$ (2.42 eV) and $\text{ZnS}$ (3.66 eV) can be tuned by varying the molar ratio of Cd and Zn via solvent engineered methods [6]. This higher energy band gap of these $\text{CdZnS}$ films...
would prevent parasitic absorption losses and results in increased short-circuit current [7]. Recently, the numerical study of CIGS based solar cells utilizing the Cd$_{x}$Zn$_{1-x}$S showed better performance than the conventional CdS buffer layer, and subsequently boosted the photovoltaic performance of the CIGS solar cell [8]. In this area, many deposition techniques have been used to fabricate film based products such as chemical bath deposition (CBD), dip-coating, spray pyrolysis, proton exchange membrane, electro-active polymer, co-evaporation, thermal evaporation, solution growth technique, plasma polymerization, reactive diffusion, sol-gel, chemical vapor deposition, magnetron sputtering, successive ionic layer adsorption and reaction, and metal organic chemical vapor deposition (MOCVD) [9]. Among them, the MOCVD involves the formation of a thin solid film on a substrate material by a chemical reaction of vapour-phase precursors. It is a specific type of chemical vapour deposition (CVD) technique which utilizes metal-organic precursors. A metal-organic (or organometallic) compound contains a direct metal–carbon bond (σ or π) (e.g. metal alkyls, metal carboxyls). However, the definition of MOCVD has broadened to include precursors containing metal–oxygen bonds (e.g. metal-alkoxides, metal-β-diketonates) or metal–nitrogen bonds (e.g. metal alkylamides), and even metal hydrides (e.g. trimethylamine alane) [10]. T.L. Chu et al. deposited Cd$_{1-x}$Zn$_x$S films on glass substrates by MOCVD with the objective of controlling the composition and resistivity of these films for optoelectronic devices. They used 2 different temperatures for deposition process which are 375°C and 425°C [11]. Most of them used CVD technique in vacuum condition. CVD processes are extremely complex and involve a series of gas-phase and surface reactions which leads to increasing cost. For these reasons an alternative method for AP-MOCVD process is anticipated.

In this work, we have developed a low cost AP-MOCVD method in atmosphere condition without using complex instrument that lead to high cost to deposit Cd$_{0.5}$Zn$_{0.5}$S thin films. Surface and cross sectional morphology as well as elemental composition analysis of Cd$_x$Zn$_{(1-x)}$S are studied with variation of deposition temperature and time. All material properties have been characterized by using Field-Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray (EDX) spectroscopy.

2. Methodology

2.1 Material preparation

Soda lime glass substrates were cleaned in methanol-acetone-methanol-DI water using ultrasonic bath for 15 to 30 minutes in each solution followed by compressed nitrogen gas drying. After drying, the cleaned glass substrates were placed under the mask for screen printing process to prepare the source for AP-MOCVD. The precursor of Cd$_{0.5}$Zn$_{0.5}$S was prepared using Cadmium Chloride (CdCl$_2$), Zinc Chloride (ZnCl$_2$) and Sulphur source in organic compound, which was dried overnight. Table 1 shows the molar ratio of each source used for the precursor preparation.

| Material                        | Source                  | Ratio |
|---------------------------------|-------------------------|-------|
| Sulphur source in organic compound | Sulphur source         | 1     |
| Cadmium Chloride (CdCl$_2$)      | Cadmium source          | 0.5   |
| Zinc Chloride (ZnCl$_2$)         | Zinc source             | 0.5   |

The dried precursor was mixed with three to four drops of 2-propanol for screen printing process. Then the AP-MOCVD source is dried in a convection oven at 100 °C for 10 minutes and then the samples are left in the oven for 1 day for natural cooling.
2.2 Experimental work
Deposition of Cd$_{0.5}$Zn$_{0.5}$S thin film is carried out by low cost AP-MOCVD technique by using two hot plates in atmospheric pressure. One hot plate is used to heat up the glass substrate while another hot plate is used for film deposition and post annealing process. For temperature variation, the temperature is varied up to 440 °C for certain time. After the deposition, air annealing was carried out. For deposition time variation, the time is varied with a constant post deposition annealing time. The temperature of deposition was kept constant at 440 °C.

3. Result and discussion
3.1 SEM images for temperature variation
Surface morphology of Cd$_{0.5}$Zn$_{0.5}$S films deposited by AP-MOCVD is studied by FESEM. Different temperature yielded variation in surface morphology of Cd$_{0.5}$Zn$_{0.5}$S. Figure 2(a) shows the FESEM surface morphology of Cd$_{0.5}$Zn$_{0.5}$S film which has been deposited at 400°C. It shows that the grain sizes are small possibly due to insufficient thermal energy needed for film growth. The film also possesses pinholes which can lead to leakage current in a semiconductor device particularly in solar cell. Figure 2(b) shows the image of Cd$_{0.5}$Zn$_{0.5}$S deposited at 420°C. The grain sizes are very uniform and the substrate is completely covered by Cd$_{0.5}$Zn$_{0.5}$S film which could also act as a compact layer to prevent leakage current. Larger grain sizes have been observed in figure 2(c) and figure 2(d). The grain sizes are less uniform in terms of grain size as compared to the films deposited at 420°C but are more compact.

![Figure 1. Surface FESEM image of CdZnS film on glass substrate at different temperature.](image-url)
The grain sizes were also measured in respect to temperature variation as shown in table 2. Average grain sizes increased with deposition temperature. The deposited films were almost uniform with AP-MOCVD techniques and found that the largest grain size can be formed at 440°C temperature deposition. In figure 3, the line of the graph indicates that increase in average grain size with increasing deposition temperature.

| Sample | Temperature (°C) | Average grain size (nm) |
|--------|------------------|-------------------------|
| 1      | 400              | 34.55                   |
| 2      | 420              | 57.37                   |
| 3      | 430              | 69.12                   |
| 4      | 440              | 98.16                   |

Figure 2. Graph of average grain size versus temperature of deposition.

3.2 SEM images for variation of time
Surface morphology properties of Cd$_{0.5}$Zn$_{0.5}$S films deposited by AP-MOCVD is also studied by varying the deposition time and fixing the deposition temperature at 440°C. Figures 3(a) to 3(c), show that deposition of Cd$_{0.5}$Zn$_{0.5}$S by this method produces films were compact, uniform and with good coverage. There are no significant changes of grain sizes with increased deposition time. The grain size varies from 28 nm to 72 nm for deposition time from 2.0 minutes to 3.0 minutes.

Figure 3. FESEM image of CdZnS (a) 2.0 min (b) 2.5 min and (c) 3.0 min deposition time.
The composition of deposited Cd$_{0.5}$Zn$_{0.5}$S thin films was determined by Energy Dispersive X-ray (EDX) analysis and the results are provided in table 3. Figure 4 shows that the EDX spectrum of Cd$_{0.5}$Zn$_{0.5}$S film with stoichiometric composition. The peak at 0.5 keV and 1.8 keV shows the presence of oxygen and silicon which most probably originate from the underlying glass substrates.

![Figure 4. Composition of Cd$_x$Zn$_{1-x}$S from EDX result](image)

| Element   | Atomic % |
|-----------|----------|
| Silica (Si) | 37.31    |
| Sulphur (S) | 14.03    |
| Zinc (Zn)  | 7.53     |
| Cadmium (Cd) | 4.57     |

| Table 3. Composition of the elements on the substrate. |

4. Conclusion
Deposition of Cd$_x$Zn$_{1-x}$S by low cost AP-MOCVD has been investigated in this study. The Cd$_{0.5}$Zn$_{0.5}$S thin films were deposited by this method under atmospheric pressure condition with various deposition time and temperature. From FESEM, it was found that by varying the temperature of deposition, the surface morphology and crystallinity of deposited film can be altered. By varying the deposition time, no significant difference in grain size and morphology was observed. These morphological results highlights the suitability of Cd$_x$Zn$_{1-x}$S in semiconductor devices particularly as buffer layer in thin film photovoltaic devices.

5. References
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Acknowledgement
The authors would also acknowledge the contribution by the research grant of Universiti Kebangsaan Malaysia (UKM) as coded DIP-2015-027 and Fundamental Research Grant Scheme (FRGS) with code FRGS/1/2014/TK06/UKM/02/3 of the Ministry Of Higher Education, Malaysia (MOHE).