Optical properties of Mn-doped CdS thin films grown by the SILAR method

N Phasook1*, S Kamoldirok1 and W Yindeesuk1

1 Department of Physics, Faculty of Science, King Mongkut’s Institute of Technology Ladkrabang, Bangkok 10520, Thailand

59605113@kmitl.ac.th

Abstract. In this research, the manganese doped cadmium sulfide (Mn-doped CdS) thin films were synthesized on glass substrates using successive ionic layer adsorption and reaction (SILAR) method. The thin films were prepared by different mixing percentage of manganese with cadmium sulfide precursors in the range of 1 - 20 mole%. The optical properties were investigated by ultraviolet-visible spectrophotometer. The morphology and elemental analysis were measured by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS), respectively.

1. Introduction
Cadmium sulfide (CdS) is semiconductor with good optical absorption properties in the range of visible light, and the direct band gap of 2.42 eV at room temperature. For this reason, cadmium sulfide has been applied to many photonic devices such as photovoltaics, photodetectors, laser and light emitting diode [1-3]. Consequently, Cadmium sulfide is adapted to suit the application.

In recent year, the study of CdS thin films has many ways to study and develop to improve the efficiency of the thin film. Doping is an interesting technique to increase the efficiency of cadmium sulfide thin films. Recently, Santra and Kamat published the manganese doped cadmium sulfide (Mn-doped CdS) thin films for use in solar cells and they succeeded in the improved power conversion efficiency at 5.42% [4]. After that, there was more research on Mn-doped CdS thin films [5-7].

In this research, we studied the optical properties and morphology of manganese doped cadmium sulfide Mn-doped CdS thin films. We use cadmium sulfide as a precursor that doped by manganese on glass substrates using successive ionic layer adsorption and reaction (SILAR) method. The preparation of the Mn-doped CdS sensitized thin films were optimized mixing percentage of manganese with cadmium sulfide precursors. The effect of dopant on the Mn-doped CdS thin films were analyzed.

2. Experimental
In this experiment, ethanol, methanol, DI water, manganese (II) acetate tetrahydrate [(CH₃COO)₂Mn·4H₂O, 99%], cadmium nitrate tetrahydrate (Cd(NO3)₂·4H₂O, 99%) and sodium sulfide nonahydrate (Na₂S·9H₂O, 98%) were used for preparing films. Glass slides were used as substrates of films.
The preparation of the Mn-doped CdS sensitized thin films were prepared by the successive ionic layer adsorption and reaction (SILAR). The mixing of cadmium nitrate tetrahydrate with manganese (II) acetate tetrahydrate 0.1 M in 1:1 ethanol and deionized water was used as the cation source. This experiment has six differences mixing percentage of cadmium nitrate tetrahydrate with manganese (II) acetate tetrahydrate including 0 mole% (pure CdS films), 1 mole%, 5 mole%, 10 mole%, 15 mole% and 20 mole%, respectively. The 0.1 M of sodium sulfide nonahydrate in 1:1 methanol and deionized water as the anion source. First, the glass substrate was dipped into the cationic solution for 30 seconds then rising in ethanol for 30 seconds. Next, the glass substrate was dipped into the anionic solution for 30 seconds then rising in methanol for 30 seconds. One SILAR cycle has been completed as shown in figure 1. In this experiment, the thin films were synthesized by SILAR for 30 SILAR cycles at room temperature. The morphology and elemental analysis were measured by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS). The optical absorbance measurements were measured by ultraviolet-visible (UV-visible) spectrophotometer (Model HITACHI U-2900 Spectrophotometer).

3. Results and Discussion

The morphology and elemental analysis of thin films were investigated by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS).

Figure 2. (a) SEM images of (1:10) Mn-CdS thin film and (b) EDS Spectrum of (1:10) Mn-CdS thin film.
Figure 2(a) is the SEM image of the (1:10) Mn-CdS thin film shown that the uniform distribution of the cadmium (Cd), sulfur (S) and manganese (Mn) elements in the (1:10) Mn-CdS film. The EDS spectra of the (1:10) Mn-CdS thin film as shown in figure 2(b). The EDS spectra show that cadmium (Cd), sulfur (S) and manganese (Mn) elements are in the thin films. The plot of mixing percentage of Mn-CdS precursor with the concentration of manganese in thin films from EDS analysis is shown in figure 3. It is shown that mixing percentage precursor at 5 mole% and 10 mole% is similar because the Mn can replace Cd at around 5 mole% of mixing percentage precursor, then the doping ratio of Mn-doped CdS thin films depends on mixing percentage of manganese with cadmium sulfide precursors.

Figure 3. The plot of mixing percentage of Mn-CdS precursor with the concentration of manganese in thin films.

Figure 4. (a) Absorbance spectra of CdS thin film, (1:100) Mn-CdS thin film, (1:10) Mn-CdS thin film and (1:5) Mn-CdS thin film and (b) Tauc plot of (1:10) Mn-CdS thin film.

The absorbance spectra of Mn-doped CdS thin films were measured at room temperature by ultraviolet-visible spectrophotometry (UV-Vis) as shown in figure 4(a). The absorbance depends on different mixing percentage of Mn-CdS precursor in the range of 1 - 10 mole%. The absorbance decreases when the mixing percentage increases. The (1:10) Mn-CdS thin films were the highest absorption. The energy band gap of Mn-doped CdS thin films were calculated using the Tauc relation as in equation (1):

\[
\alpha h\nu = A(h\nu - E_g)^n
\]

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the photon energy, \(E_g\) is the band gap, \(n = 0.5\) for direct band gap transition and \(A\) is constant which is different for different transitions. The energy bandgap values
as shown in table 1. The energy band gap of (1:10) Mn-CdS thin films is 2.43 eV using Tauc’s plot technique as shown in figure 4(b). The change of band gap energy is affected by the changing structure of Mn-CdS thin films due to the Mn-doped concentrations.

### Table 1. A slightly more complex table with a narrow caption.

| Sample                     | Band gap (eV) @room temperature |
|----------------------------|----------------------------------|
| Pure CdS thin film         | 2.36                             |
| (1:100) Mn-CdS thin film   | 2.34                             |
| (1:20) Mn-CdS thin film    | 2.31                             |
| (1:10) Mn-CdS thin film    | 2.43                             |
| (1:6.67) Mn-CdS thin film  | 2.28                             |
| (1:5) Mn-CdS thin film     | 2.31                             |

### 4. Conclusion

The manganese doped cadmium sulfide (Mn-doped CdS) thin films were synthesized on glass substrates using successive ionic layer adsorption and reaction (SILAR) method. The thin films were prepared by different mixing percentage of manganese with cadmium sulfide precursors in the range of 1 - 20 mole%. The optical properties were investigated by ultraviolet-visible spectrophotometer shown that the 10% Mn-doped CdS thin films were the highest absorption with band gap is 2.43 eV using Tauc’s plot technique. The morphology and elemental analysis were measured by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS). The doping ratio of Mn-doped CdS thin films depends on mixing percentage of manganese with cadmium sulfide precursors.

### References

[1] Jun H K, Careem M A and Arof A K 2013 Renew. Sust. Energ. Rev. 22 148–67
[2] Jun H K, Careem M A and Arof A K 2014 Int. J. Photoenergy 2014 939423
[3] Doosthosseini F, Behjat A, Hashemizadeh S and Torabi N 2015 J. Nanophotonics 9 093092
[4] Pralay K S and Prashant V K 2012 J. Am. Chem. Soc. 134 2508–11
[5] Tianxing L, Xiaoping Z and Hongquan Z 2014 Int. J. Photoenergy 2014 569763
[6] Sainita J, Suganthi D and Suthagar J 2015 J. Mater. Sci-Mater. Electron 26 5668–76
[7] Chandramohan S, Kanjilal A, Tripathi J K, Sarangi S N, Sathyamoorthy R and Som T 2009 Jpn. J. Appl. Phys 105 123507