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# Research Article
# Optimization of Optical Properties of ZnS:Mn Thin Films Deposited by Co-evaporation Electron Beam

[1]Muslimin, [2]Elisa Sesa, [3]Stepanus Sahala, [1]Amiruddin Kade and [2]Badaruddin

[1]Department of Physics Education, Faculty of Teacher Training and Education, Tadulako University, Street Soekarno-Hatta KM. 9. Palu, Central Sulawesi, Palu, Indonesia
[2]Department of Physics, Faculty of Math and Science, Tadulako University, Street Soekarno-Hatta KM. 9. Palu, Central Sulawesi, Palu, Indonesia
[3]Department of Physics Education, Faculty of Teacher Training and Education, Tanjungpura University, Pontianak, West Kalimantan, Indonesia

## Abstract

**Background and Objective:** ZnS:Mn is a very potential semiconductor to be applied to various optoelectronic devices, because it has good optical properties especially transmittance and high band gap in the visible spectrum region. This study aimed to analyze the effect of percentage of deposition rate of Mn dopant on deposition rate of ZnS on each sample making that is useful for the development of science, especially in the field of optics and microelectronics. **Materials and Methods:** A thin layer of ZnS:Mn with thermal co-evaporation and electron beam method with various deposition rate of Mn dopant to deposition rate of ZnS on each sample has been made. **Results:** Analysis of transmittance pattern obtained is 67.98-85.82%, the highest transmittance obtained at deposition rate of Mn dopant 0,67%. The Reflectance pattern was obtained by 9.23-15.59%, the highest reflectance at deposition rate of Mn dopant of 0.33%. Band gap energy that was obtained 3.06 eV-3.36%, band gap changes increase along with the changing of deposition rate of Mn dopant. Absorbance was obtained from 0.69-0.77, the lowest absorbance that was obtained at the deposition rate of Mn dopant of 0.50% and refractive index ranged from 2.29-2.53, refractive index tended to increase with increasing deposition rate of Mn dopant. **Conclusion:** The best transmittance value is ZnS: Mn 0.67% equal to 85.82% with band gap value obtained between 3.06 and 3.36 eV.

Key words: Deposition rate doping, optoelectronic devices, Mn dopant, co-evaporation thin films, optical properties

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Corresponding Author: Badaruddin, Street Soekarno-Hatta KM. 9. Palu, Central Sulawesi, Indonesia Tel: (62) 8114386048



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Data Availability: All relevant data are within the paper and its supporting information files.

## INTRODUCTION

The ZnS material is an efficient material for electroluminescence belonging to the semiconductor group having two structures i.e., cubic and hexagonal[1,2]. The cubic form has a direct band gap that is smaller than the hexagonal form[3,4].

The application of wide band gap is more potential in the development of optoelectronic technology[5-7]. Thin ZnS films with Mn dopant can affect optical parameters, transmittance in visible light areas, reflectance in infrared areas so that this material is highly potential for various optoelectronic applications[8,9]. The use of ZnS:Mn as a main material because it exhibits excellent light-emitting properties and has a wide band of energy covering all visible light spectra[10,11].

Mn dopant on the ZnS lattice becomes very important because of its high solubility in the ZnS lattice. Mn dopant can substitute Zn on ZnS lattice into divalent ions so as to change band gap of ZnS[3]. Besides band gap change due to Mn dopant change, band gap will also change transmittance[6,2]. Changes in transmittance are generated in accordance with the impurities implanted in the main material. Mn impurities result in the level of illumination of light emitted by the thin film ZnS:Mn also varies. Illumination levels generated by ZnS:Mn, with various percentages of Mn as impurities, also the deposition rate is one of the factors affecting crystal size, band gap and transmittance[12].

The optical properties can be known from the electrons structure, how the optical properties are affected by the atomic structure, the binding energy, the impurities and the crystal defects, the heat treatment provided[9]. To produce good optical properties, adequate Mn dopant is required to substitute Zn atoms binding to the ZnS main compound. It also requires subtract temperature mix and deposition rate at the time of Co-evaporation[13,14]. Excess impurities will cause defects and degradation of crystal quality, as well as thermal voltage in this case the evaporation rate also affects the decrease of crystal quality[15]. The energy band gap shift due to impurities is formulated by Burstein-moss and the absorption coefficient as a function of photon energy[16,17].

ZnS:Mn transparent thin film is produced by chemical deposition technique (CBD) at 80°C for 4, 6 and 8 h with 1, 3 and 5% Mn dopant. The optical properties of the ZnS:Mn thin film are determined by the measurement of UV/vis spectrophotometer transmittance in the range $\lambda = 300$-1100 nm. Optical transmission of films is found from 12-92% in the visible region. The refractive index value (n) for the visible region is 1.34-5.09[18]. The thin film ZnS:Mn (0; 1; 3; 5%) is made on glass with CBD at 90°C for 4 h, at alkali (pH = 12,83), the best transmittance value is ZnS:Mn 5% visible (83% ) with a Band gap obtained between 3.43 and 3.75 eV[2]. The annealing temperature effect on the structure, morphology and optical properties of ZnS: Mn, X-ray diffraction results (XRD) results showed that the thin film of ZnS: Mn has a cubic structure with has a cubic structure with an average transmittance value of 85%[19]. The ZnS thin film was prepared using chemical spray pyrolysis technique at 400°C, the refractive index calculated in the visible region of 2.45 at 500 nm, the optical band gap of 3.1 - 3.2 eV[20].

Therefore ZnS:Mn is interesting to study in the form of thin film because of the change of its optical parameters. To produce a good layer of ZnS:Mn, then the Mn impurity must be maximized, to substitute Zn.

The purpose of this research was to analyze the effect of percentage of deposition rate of Mn dopant on deposition rate ZnS on each sample making that is useful for the development of science, especially in the field of optics and microelectronics.

## MATERIALS AND METHODS

**Research type:** This type of research is experimental research in the laboratory, Department of Physics of Universitas Indonesia, starting from April-June, 2017.

**Material:** The 99.99% ZnS evaporation from Leybold material and Mn from Merck.

**Method:** Thin films growth is conducted by variation of deposition rate percentage of Mn dopant to ZnS deposition rate. Thermal evaporation was performed at vacuum chamber pressure $<2.0\times10^{-6}$ mBarr, ZnS deposition rate between 15-40 Å/s and Mn dopant deposition rate between 0.1-0.6 Å/s. Each sample at each deposition of deposition rate of Mn dopant percentage to ZnS deposition rate is sample A 1.67%, sample B 1.00%, sample C 0.67%, sample D 0.50% and sample E 0.33% vacuum chamber temperature 50°C. The evaporated Mn material is on a ship made of Mo, while ZnS is placed on the electron beam target shot with the electron beam so as to produce the desired deposition rate at the flow meter. The co-evaporation process is stopped after the thickness measured by the quartz crystals is achieved. The results of thin films deposition will be carried out with UV-Vis transmittance measurements at the visible wavelength and then another optical property analysis is conducted by using some equation. Absorption coefficient was obtained using Eq. 2, transmittance with Eq. 3 and band gap with Eq. 4.

In general, the energy band gap shift due to impurities is formulated[16]:

$$E_g^{eff} = E_{go} + \Delta\sum_g^{BM} + \hbar\sum(k) \quad (1)$$

The energy band structure of ZnS:Mn with doping density is shown:

$$E_c^0(k) = \frac{\hbar^2 k^2}{2m_m^*} + E_{g0},\ E_v^0(k) = \frac{\hbar^2 k^2}{2m_m^*},\ E_c\ (k) = E_c^0 + \hbar\Sigma_c(k)$$

and:

$$E_v(k) = E_v^0 + +\hbar\Sigma_v(k)$$

Where:

| | | |
|---|---|---|
| $\sum(k)$ | : | Contribution of scattering impurities electron |
| $E_v^0$ | : | Valence band energy before doping |
| $E_c^0(k)$ | : | Energy in the conduction band before doping |
| $E_v$ (k) | : | Valence band energy after doping |
| $E_c$ (k) | : | Conduction band energy after doping |
| $E_{g0}$ | : | Energy bands gap before doping |
| $E_g$ | : | Energy bands gap after doping |

The absorption coefficient α(hυ)[14]:

$$\alpha = \frac{4\pi k}{\lambda} \quad (2)$$

where, α is the absorption coefficient, k is refractive index of attenuation and λ is wavelength. Generally, the absorption of α radiation is a function of the T transmittance, the R reflectance and the thickness of the film are denoted[13]:

$$T = (1\text{-}R)^2\ e^{-\alpha d} \quad (3)$$

where, T is transmittance, R reflectance. The absorption coefficient as a function of the photon energy can be determined from the transmittance data of electrons undergoing a direct transition:

$$\alpha h\upsilon \approx (h\upsilon\text{-}E_g)^n \quad (4)$$

where, $E_g$ is a band gap of transition energy, hυ is photon energy and n = 1/2 for direct transition.

**Data analysis:** The analysis of optical properties by looking at the spectrum value on each parameter, comparing each sample with the use of variation percentage of deposition rate of Mn dopant to ZnS deposition rate.

## RESULTS AND DISCUSSION

The transmittance and reflectance patterns, bandgap optical parameters, absorbance and refractive index are shown Table 1. Transmittance and optical reflectance patterns obtained wavelengths between 350-800 nm, with a thin film ZnS:Mn made as co-evaporated at substrate with different Mn dopant rates deposition. Transmittance increases with respect to coat rate[13,15]. The highest transmittance of 85.82% is obtained at the deposition rate of Mn dopant of 0.67%. While, the deposition rate of Mn dopant of 1.67% has the lowest transmittance.

The change of transmittance and reflectance has something to do with the Znsaat atomic vacuum at the main lattice and density Mn dopant as fewer donors to replace the disengaged Zn position. As a result, the vacancy serves as an impurity contribution, in accordance with the equation formulated by Burstein-moss that is due to the contribution of vacancy and density Mn dopant as the scattering of impurities[16]. At a deposition rate of Mn dopant of 1.67% transmittance decreases due to excessive density doping resulted in increasing impurities so that the crystallinity rate decreases.

Transmittance and reflectance changes along with the deposition rate of Mn dopant change. The generally obtained layer shows that transmittance tends to decrease with the increasing rate of deposition doping, whereas reflectance tends to increase at deposition rate of dopant increase. The transmittance level shift corresponds to the energy band gap due to the crystallinity level[12].

The transmittance results appear to have a fairly high limit value of 67.98-85.82%, the change of transmittance is not too far when compared to the maximum results of the research Ozge Erken *et al.*[18] with the value of transmittance 12-92%. This is influenced by the change in percentage deposition rate of Mn dopant to the rate ZnS deposition is quite small (0.33-1.67%). This result also showed that the best transmittance of 85.82% is not much different from the results of Talantikite *et al.*[2] research on the best transamination of 83% and Wang and Hu[19] best transmuting experiments 85% of the literature.

Bandgap calculation is conducted plot $(\alpha h\upsilon)^2$ versus hυ (Fig. 1), where α is optical absorption coefficient and hυ is energy of photon. The band gap energy is estimated by extrapolating the straight-line portion of the spectrum to the absolute value of zero. The change in thin layer band gap

Table 1: Variation of deposition rate of Mn dopant terhadap deposition rate of ZnS

| Samples | Persentase deposition rate of ZnS:Mn (Å/s) | Wavelength (nm) | $Trans_{max}$ (%) | Reflect (%) | Bandgap (eV) | Absorb | Refractive index |
|---|---|---|---|---|---|---|---|
| A | 1.67 | 710 | 67.98 | 13.04 | 3.06 | 0.72 | 2.29 |
| B | 1.00 | 680 | 83.33 | 11.85 | 3.15 | 0.77 | 2.53 |
| C | 0.67 | 560 | 85.82 | 9.23 | 3.20 | 0.70 | 2.47 |
| D | 0.50 | 670 | 85.33 | 10.73 | 3,28 | 0.69 | 2.40 |
| E | 0.33 | 690 | 78.55 | 15.59 | 3.36 | 0.74 | 2.41 |

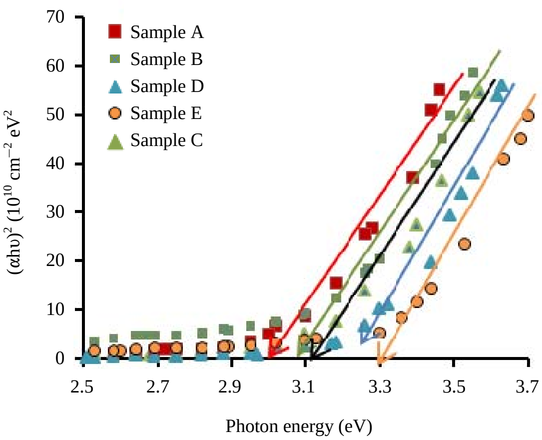


Fig. 1: Analysis of band gap energy

energy due to change in deposition rate of Mn dopant is obtained between 3.06-3.36 eV. The largest band gap of 3.36 eV is obtained from the smallest deposition rate of Mn dopant of 0.33%. The changes in band gap deposition rate of due to Mn dopant concentration which may affect composition, surface morphology, crystallinity, grain size[3]. The energy band gap will shift due to the contribution of scattering electron impurities and high doping density. In general, bandgap changes due to changes in Mn doping density can change the crystallinity of thin film.

A thin layer of Mn which is doped ZnS (0.33-1.67%) with a fixed temperature in a 50°C vacuum, obtained a bandgap of 3.06-3.36 eV. Bandgap change is not too far from the research done by Choi *et al.*[12] with optic band gap of 3,29-3,36 eV, this research mention the increasing of band gap value influenced the increase of temperature. Similarly, band gap results by Saeed[20] with optical band gap of 3.1-3.2 eV and the results obtained by Talantikite-Touati *et al.*[2] with percentage Mn to ZnS (0, 1, 3, 5%) at temperature vacuum 90°C. The results are obtained not far from the literature value, where ZnS is an important II-VI binary compound with large energy gap of 3.66 eV. It is appropriate that producing good optical properties is not only required sufficient Mn dopant to substitute bonded Zn atoms on the parent compound of ZnS but also it is influenced or required the combination of subtract temperature and deposition rate at the time of co-evaporation[13,14].

The highest absorption and refractive index is obtained at a 1.0% deposition rate of Mn dopant against ZnS deposition rate. The changes in optical properties along with doping changes density[21]. Refractive index obtained from 2.29-2.53, this result is suitable for anti-reflection[17]. Refractive index thin film has increased slightly along with increasing percentage deposition rate of doping at wavelength 560-710 nm. While absorbance was obtained from 0.69-0.77, the highest absorbance was obtained at the deposition rate of Mn dopant of 1.00% to the ZnS deposition rate. The change is related to the level of impurity and irregularity of the thin film surface due to doping.

## CONCLUSION

The results of the optical properties of transmittance changes, absorption coefficient and refractive index tend to increase along with an increase in Mn deposition rate doping to the ZnS deposition rate, while reflectance, the band gap decreases as the Mn deposition rate doping increases with ZnS deposition rate.

## SIGNIFICANCE STATEMENT

The research found that the effect of administering various percentage rates of deposition of Mn dopant to ZnS deposition rate can be used in various optical and microelectronic applications. This research will help researchers to utilize the percentage of Mn depreciation rate usage as well as being affordable in terms of price and easy to obtain. Thus, the new theory of ZnS:Mn shows a high value of transmittance of 85.82% in percentage deposition rate ZnS: Mn 0.67 (Å/s), has a high anti reflection, band width 3.36 eV at percentage deposition rate ZnS: Mn 0.33 (Å/s).

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