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Research Article

Investigation of Optical Properties of MnS and MnS: Cu Thin Films

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Abstract

Copper doped and undoped manganese sulfide (MnS) thin films were deposited by Spray Pyrolysis Technique at 390 ºC using copper chloride ($CuCl_2$) as an additive source using 0.1 g, 0.3 g and 0.5 g $CuCl_2$. The Mn:S ratios were adjusted to be equal and 1:1 and the spraying process was carried out completely in atmospheric environment. The optical properties of the obtained MnS thin film samples were investigated by using Shimadzu-1800 Model UV/VIS spectrophotometer. It is seen that the band gap energy range of copper-doped and undoped MnS thin films varies between 2.95 and 3.27 eV. The effects of these observed changes and the amount of copper chloride on the optical properties of MnS thin films were investigated.

Keywords: MnS, Cu doped, Spray Pyrolysis, Thin Film, Optical Properties.

MnS ve MnS: Cu İnce Filmlerinin Optik Özelliklerinin İncelenmesi

Öz

Bakır katkılı ve katkısız manganez sülfür (MnS) ince filmler, 0.1 g, 0.3 g ve 0.5 g bakır klorür (CuCl2) katkı maddesi kullanılarak 390 ºC' de Spray Pyrolise Tekniği ile biriktirilmiştir. Mn:S oranları eşit ve 1:1 olacak şekilde ayarlanmış ve püskürtme işlemi tamamen atmosferik ortamda gerçekleştirilmiştir. Elde edilen MnS ince film örneklerinin optik özellikleri, Shimadzu- 1800 Model UV/VIS spektrofotometre kullanılarak incelenmiştir. Bakır katkılı ve katkısız MnS ince filmlerin enerji bant aralığının 2.95 eV ile 3.27 eV arasında değiştiği görülmüştür. Bu gözlenen değişikliklerin ve bakır klorür miktarının MnS ince filmlerin optik özellikleri üzerindeki etkileri araştırılmıştır.

Anahtar Kelimeler: MnS, Cu katkılı, Spray Pyrolysis, İnce film, Optik özellikler.

1. Introduction

Recently, semiconductor thin film materials have opened up a new field in electronic applications. One of the important applications of semiconductor films in the technological field is photovoltaic solar cells. Single crystals such as Si, Ge, GaAs as well as polycrystalline semiconductor thin films are widely used in these devices. Polycrystalline thin films are semiconductor materials that can be grown on large surfaces such as metal, glass, ceramic, graphite, have many application areas such as solar cells, semiconductor photo-detectors due to their electrical and optical properties, and can be obtained by simple and different methods [1,2]. Manganese (II) sulfide (MnS) is a semiconductor compound of group VIIB-VIA. MnS thin films are diluted magnetic semiconductor materials, used in short wavelength optoelectronic applications such as solar cells, sensors, photoconductors, sunlight selective coatings, optical memory elements [3-5]. Today, many techniques are used to prepare MnS films [6-8]. Pure γ-MnS thin films were grown with CBD technique and their characteristics were examined [9, 10, 11]. Pathan et al. has seen that the band gap of films depends on the film thickness [12]. The properties of the thin film may vary according to the growth parameters [13]. In this study, the ionic solution prepared using the desired film materials was deposited on a preheated glass substrate. And the effect of copper chloride amount on the optical properties of the undoped and copper-doped MnS films was investigated.

2. Experimental Modeling

Undoped and copper-doped MnS thin films were deposited at 390 ºC substrate temperature using spray pyrolysis technique. A 100 ml solution consisting of $MnCl_2$ and $[SC(NH)_2]_2$ chemicals in powder form was prepared in the spray solution prepared for the growth of thin films, with equal (1:1) ratios of Mn:S, and the spraying process was carried out completely in atmospheric environment. In addition, MnS:Cu films were obtained by adding 0.1 g, 0.3 g, and 0.5 g M copper chloride ($CuCl_2$) in powder form to the starting solution. The chemical reaction of the copper-doped and undoped films formed on the glass when this solution obtained is sprayed onto the heated glass substrate is shown below:

$$MnCl_2 + [SC(NH)_2]_2 + 2H_2O \longrightarrow MnS + 2NH_4Cl\ (steam) + CO_2\ (gas)$$

$$MnCl_2 + [SC(NH)_2]_2 + CuCl_2 + 2H_2O \longrightarrow MnS(Cu) + 2NH_4Cl_2\ (steam) + CO_2\ (gas)$$

The optical properties were examined between 300-900 nm wavelength by Shimadzu-1800 Model UV/VIS spectrophotometer as a function of wavelength at room temperature. By using the optical transmittance (%T) values were calculated the absorbance (α) with the following equation:

$$\alpha = \left(-\frac{1}{t}\right)\ln\left(\frac{T}{T_o}\right) \qquad (1)$$

A substrate of the same glass is placed against the reference beam, in order to remove the absorption of the glass substrate. The energy band gap E_g of the spray deposites films is found by the point where the high absorption region of the curve intersects with the energy axis [14]. Using the weight method, the thickness of the spray deposited thin films was calculated with the following equation [15]:

$$t = \frac{(m_2 - m_1)}{\rho A} \qquad (2)$$

In this equation, m_1 is the mass of the glass substrate, m_2 is the mass after the film is formed on the glass, ρ is the density of the film, and A is the surface area of the glass used as the substrate.

3. Results and Discussions

The energy band gap of undoped and Cu doped MnS thin films which are a direct transition semiconductor, was calculated using the equation 1. It is seen in Fig.1, a line parallel to the curve is drawn in the region where the curve becomes a straight line due to the absorbtion coeffiicient of the MnS thin films and optical band gap (E_g) are interrelated [16]. The value at the point where this line cuts the energy axis becomes the energy band gap value for that thin film. Undoped and Cu doped of the bandgap energy values of MnS thin films with (a) undoped MnS, (b) 0.1 Cu, (d) 0.3 g Cu, (c) 0.5 g Cu are given in Figure 1. It is seen from the Figure 1 that the values of the band gap energy were found between 2,95 eV and 3,27 as function of $CuCl_2$ contents. The undoped and Cu-doped MnS thin films obtained were found to have direct transition. And the results are consistent with M. Girish et al. [17] who studied the MnS thin films deposited on well-cleaned glass substratesusing nebulized spray pyrolysis technique at 350 ˚C.

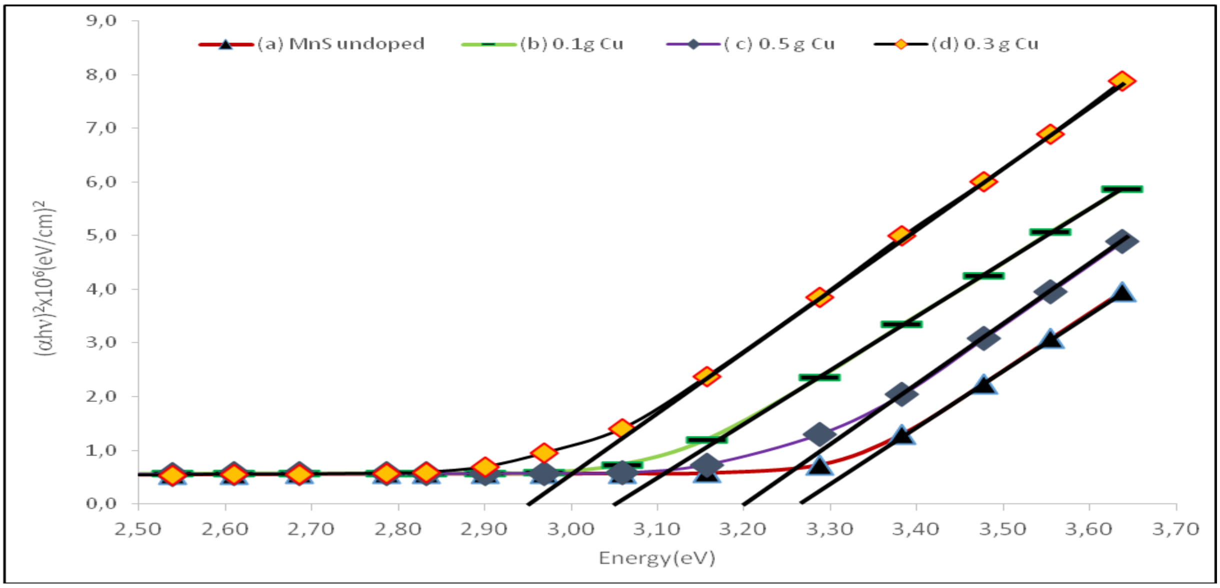

Figure 1. $(\alpha h\nu)^2$ Versus hν plots of (a) MnS, (b) MnS:Cu(0.1g), (c) MnS:Cu(0.5g), (d) MnS:Cu(0.3g) thin films deposited at 390 ºC

As seen in Fig.1, naturally the graphs are parabolic and and the in exion number gives the number of transitions. And the $(\alpha h\nu)^2$ versus hν (energy) is plotted by using the expression [18,19].

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (3)$$

In Eq.(3), A is a constant, hν shows the energy of the photon and Eg shows the bandgap energy for direct transitions. It is seen from Figure 1 that the band gap energy value of undoped and Cu doped MnS thin films was determined between approximately 2.95 eV and 3.27 eV. With the increase of the $CuCl_2$ additive added to the thin films up to 0.3 grams, the decrease in the optical band gap can be associated with the increase of the grain size. Another reason may be the increased crystallinity with decreasing band gap energy and increasing grain size of the film. This may be due to the propagation of the impurity phase, electronic states of precipitates and clusters into the band gap of MnS and MnS: Cu thin films. This situation tells us that the $CuCl_2$ added to MnS thin films is affected by the change of the band gap energy of the thin films. The same situation has been observed in ZnO: Cu films grown by spray pyrolysis method [17].

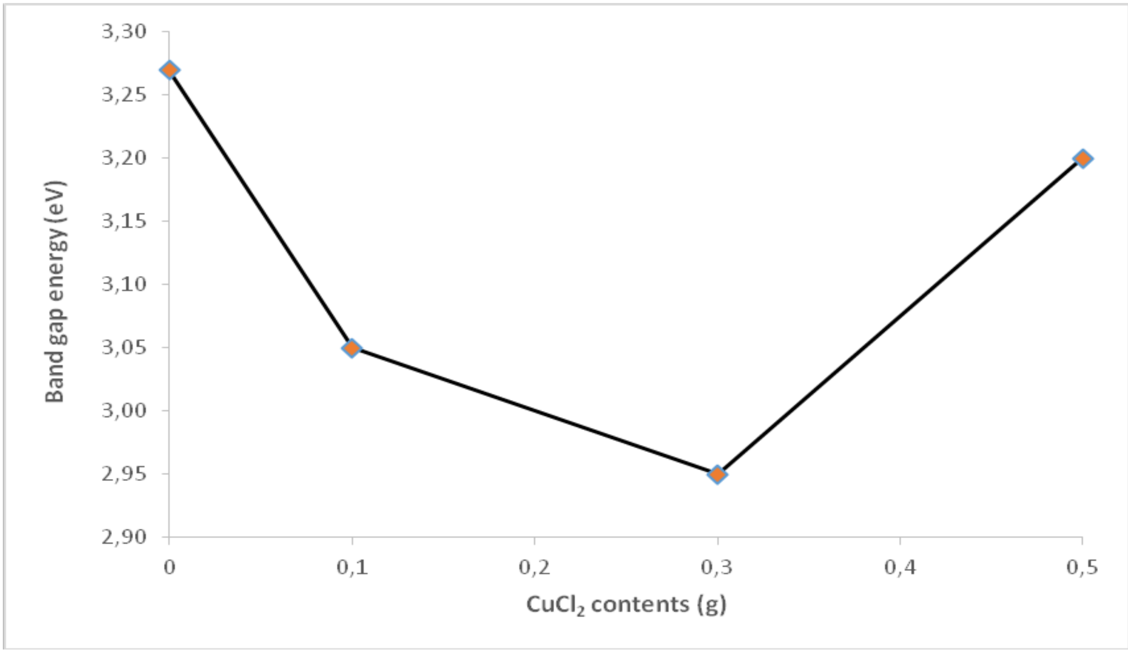

Figure 2. Plots of band gap energy vs. $CuCl_2$ contents of MnS:Cu thin films deposited at 390 °C.

Figure 2 shows the effect of $CuCl_2$ contents on the E_g value of films. It is seen in Fig.2 that the band gap first decreases as the $CuCl_2$ contents increases up to 0,3g. However, the high value of $CuCl_2$ content for 0,5 g increase the E_g values at deposited 390 °C substrate temperature. This behavior can be attributed to the state of incorporation of copper atoms added to films into MnS and MnS:Cu thin films. The amount of $CuCl_2$ added to the thin films up to 0,3 g increases the Cu ratio in the substituent regions of the semiconductor, which probably leads to an increase in the carrier concentration and consequently, the narrowed band gap may be due to the Moss-Burstein effect [20]. According to the Moss-Burstein theory, donor electrons formed in heavily doped manganese sulphide thin films form a donor level below the conduction band. The Pauli principle is due to the fact that the optical transitions are vertical, preventing the states from being occupied twice, the valence electrons need an extra energy to move to higher energy levels of the conduction band. At the same time, it seems that the bandgap energy of the thin films increases when the amount of Cu is increased to $CuCl_2$ content value of 0,5 g, and this situation leads to a weakening of the crystallinity of thin films or the formation of a new compound due to Cu and Mn. Therefore, it said that the band gap of 0.5 g Cu doped manganese sulfate thin films is wider than the band gap of other thin films. As a result, from thermal mismatch between the MnS thin film and substrate, which causes a tension attributed to the smaller grain size due to the accumulation of defects at grain boundaries may be another reason for results. This situation shows that a large number of grain boundaries are formed in thin films, and the defects in the film increase. This situation shows that the change of the energy band gap of all the thin films grown in our study may be due to the quantum size effect observed in semiconductors.

4. Conclusion

This study has shown that the all spray deposited thin films are strongly dependent on $CuCl_2$ contents. It can be said that the band gap energy Eg of undoped and Cu doped MnS films decreases with increase of the $CuCl_2$ contents up to 0.3g, due to the improved crystallization of the films. For this reason, we can say that the grain size of the thin films increases. This can be attributed to the effect depending on the size of the grain size in semiconductor crystals. Thus, it can be said that the contents of 0.3 g $CuCl_2$ incorporations are the most suitable to improve the crystallinity of MnS: Cu films.

References

[1] Characteristics of annealed ZnO:Cu nanoparticles prepared by spray pyrolysis, Öztas M, Journal of Materials Science: Materials in Electronics,, 17, 937-941, (2006).

[2] Thickness dependence of structural, electrical and optical properties of sprayed ZnO:Cu films, Öztas M, Bedir M., Thin Solid Films, 516, 1703-1709, (2008).

[3] Preparation and characterization of amarphous manganese sulfide thin films by SILAR method, Pathan, H. M., Kale, S. S., Lokhande, C. D., Han, S. H., Joo, O. S., Materials Research Bulletin,, (2006).

[4] Influence of S/Mn molar ratio on the morphology and optical property of γ-MnS thin films prepared by microwave hydrothermal, Yu, X., Li-yun, C., Jian-feng, H., Jia, F., Chun-yan, Y., Journal of Alloys and Compounds, (2012).

[5] Preparation and hydrothermal annealing of pure metastable β-MnS thin films by chemical bath deposition (CBD), Shi, Y., Xue, F., Li, c., Zhao, Q., Qu, Z., Materials Research Bulletin, (2010).

[6] ɤ-MnS thin films prepared by chemical bath deposition: Effect of bath temperature on their physical properties, C. Ulutas, et all, Materials Chemistry and Physics, 138, 817-822, (2013).

[7] Influence of S/Mn molar ratio on the morphology and optical property of γ-MnS thin films prepared by microwave hydrothermal, Yu, X., Li-yun, C., Jian-feng, H., Jia, F., Chun-yan, Y., Journal of Alloys and Compounds, (2012).

[8] Effect of Boric Acid Content on the Structural and Optical Properties of MnS Films Prepared by Spray Pyrolysis Technique, Bedir M., et all, Acta Physica Polonica A, 126 (3), 840-845, (2014).

[9] Preparation of crystalline MnS thin films by chemical bath deposition, Fan, D., Wang, H., Zhang, Y., Cheng, j., Wang, B., Yan, H., Materials Chemistry and Physics, (2002).

[10] Preparation and characterization of crystalline MnS thin films by chemical bath deposition, Gümüş, C., Ulutaş, C., Esen, R., Özkendir, O. M., Ufuktepe, Y., Thin Solid Films, Adana, (2005).

[11] Process and characterization of chemical bath deposited manganese sulphide (MnS) thin films, Lokhande, C. D., Ennaoui, A., Patil, P. S., Giersig, M., Muller, M., Diesner, K., Tributsch., Thin Solid Films, (1998).

[12] Deposation of metal chalconide thin films by succesive ionic layer adsorption and reaction (SILAR) method, Pathan, H. M., Lokhande, C. D., Bull. Mater. Sci., 27(2), 85-111, (2004).

[13] Bedir M., et all, Influence of Preparation Conditions on the Dispersion Parameters on Sprayed In_2S_3 films, Arab. J. Sci. Eng., 39, 503-509, (2014).

[14] D. Sreekantha Reddy, D. Raja Reddy, N. Koteeswara Reddy, K.R. Gunasekhar, R.P. Vijayalakshmi, B.K. Reddy, P. Sreedhara Reddy, Solid State Commun. 142, 466, (2007).

[15] Püskürtme Yöntemi Elde Edilen CdSe İnce Filmlerin Optiksel ve Elektriksel Özelliklerinin İncelenmesi, Bedir M., Öztas M, SD Üniversitesi FB Enstitüsü Dergisi, 8 (2), 252-254, (2004).

[16] G. Kim, J. Bang, Y. Kim, S.K. Rout, S.I. Woo, Appl.Phys. A 97, 821, (2009).

[17] Mustafa Öztas, Metin Bedir Thickness dependence of structural, electrical and optical properties of sprayed ZnO:Cu films Thin Solid Films 516, 1703-1709, (2008).

[18] L. Zhengang, B. Yujun, C. Deliang, W. Qilong, Solid State Sci. 5, 1037, (2005)

[19] E.S. Shim, H.S. Kang, S.S. Pang, J.S.Kang, I. Yun,S.Y. Lee, Mater. Sci. Eng. B102, 366, (2003).

[20] Zachary M Gibbs, Aaron Lalonda and G. Jeffrey Snyder, Optical Band Gap and The Burstein-Moss Effect in Ionide Doped PbTe Using Diffuse Reflectance İnfrared Fourier Transform Spectroscopy, New Journal of Physics, 15, 075020, (2013).