FABRICATION MECHANISM AND OPTICAL PROPERTIES OF PURE ZnO AND ZnS-ZnO NANOCOMPOSITE FILMS

Moe Swe[1], May Hnin Thant[2],ThanThan Win[3] ,and
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Abstract

The film of pure ZnO and ZnS – ZnO nanocomposite films have been prepared by chemical deposition method by varying the concentration ratio of pure ZnO and ZnS – ZnO nanocomposite powder. The preparation of these films grown on glass substrates were reported in this work. The optical properties of the samples were characterized by UV- Vis spectroscopy within wavelength range of 190 nm and 1100 nm. ZnS – ZnO nanocomposite (90 % - 10%) exhibited the maximum degree of optical band gap (3.295 eV) why the lowest band gap (2.749 eV) was obtained by ZnS – ZnO nanocomposite film (50% - 50 %).

Keywords : ZnO , ZnS – ZnO nanocomposite powder, 2 – methoxyethanol, Optical babd gap.

Introduction

Zinc sulfide (ZnS) is important II-VI semiconductor material for the development of various modern technologies and photovoltaic applications. II-VI semiconductors such as zinc sulfide (ZnS) have attracted growing interest owing to their possible in optoelectronics, it is important semiconductor material for the development of various modern technologies of solid-state devices such as laser diodes and solar cells. [Skwok K et al 1998] [Antony A et al 2005].

As important II-VI semiconductor, ZnO and ZnS contain only earth-abundant elements and have been intensively studied in a wide range of UV sensors, lasers, field emitters, nanogenerators, solar cells, photocatalysis, etc. [Huang X et al 2013]. Unfortunately, both ZnO and ZnS had a large band gap(Eg=3.37eV and 3.67 eV for ZnO and ZnS, respectively), and thus there is

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almost no adsorption in the visible light region, which largely limits their application in visible-light- driven water splitting. Recently, the heterostructures of ZnO and ZnS have attracted theoretical and experimental interest because the combination of these two wide band gap semiconductors can yield a novel material with the photoexcitation threshold energy lower than the individual components, leading to improved physical and chemical properties. [Huang X et al 2012] [Chen W et al 2012]. According to our knowledge, apart from ZnS/ZnO hybric nanowires, few literature was reported on ZnS/ZnO nanocomposites used as effective catalysts for visible light photocatalytic hydrogen production. [Wang M et al 2013] [Shaoo Y et al 2005]. The preparation of reported ZnS/ZnO hybrid nanowires was conducted by a high-temperature hydrothermal method involving the use of expensive and toxic, which makes it difficult to be scaled up and does serious harm to environmental protection and people's health. Therefore, new preparation strategy of ZnS/ZnO heterostructure is greatly desirable to make the best use of ZnO and ZnS for solar energy application. [Aoki T et al 2000] [Jang J et al 2008]

The ZnS/ZnO nanocomposite is easily prepared by the photo deposition of ZnS on the surface of ZnO nanoparticles in photocatalytic process, and ZnO nanoparticles can be abundantly and conveniently obtained by a facile preparation- anneal method using inexpensive and nontoxic inorganic salt and ammonium hydroxide as raw materials. The ZnS/ZnO revealed good catalytic activity and stability in visible-light-driven water splitting and natural sunlight-driven hydrogen evolution. [Nguyen et al 2004] In the present work, chemical deposition method was used because of its advantages like low cost, easy coating of large surfaces with smooth and uniform layers. The present work aims to measure the optical properties by UV-Visible spectroscopy.

Experimental Procedure

Preparation of Solution

In this procedure, ZnO (pure) powders and ZnS – ZnO composite powders were used as starting materials. Firstly, (0.3) g of ZnO(pure) powder was dissolved with 15 ml of 2-methoxyethanol and stirred by magnetic stirrer

at 800 rpm for 5 h. Then, (0.3) g of ZnS – ZnO composite powders were also dissolved with 15 ml of 2- methoxyethanol in different ratios ZnS (10%)-ZnO(90%) ZnS(20%)-ZnO(80%), ZnS(30%)-ZnO(70%), ZnS(40%)-ZnO(60%), ZnS(50%)-ZnO(50%) . It was stirred by magnetic stirrer at 800 rpm for 5 h. All samples were dissolved to reach homogenerous mixture solution in each beaker. Finally, ZnO (pure) solution and ZnS–ZnO solutions were obtained. Fig 1 (a) and Fig 1 (b) show the solution of ZnO (pure) and ZnS – ZnO nanocomposite.

Chemical Deposition Process

ZnO (pure) and ZnS – ZnO composite films were deposited on (1x1inches) glass substrates. The substrates of simple glass were cleaned in deionized water (DIW), acetone and absolute ethanol for20 minutes in each solvent and then dried at room temperature. For the deposition of thin films, the pre-cleaned glass substrates were immersed into solution for 24 h to obtain a uniform coating. After completion of the film deposition, the samples were taken out immediately dried at room temperature for 2 days. The photographs of ZnO(pure) and ZnS-ZnO composite films were indicated in Fig 1(c).The block diagram of experimental procedure was shown in Fig 1 (d).

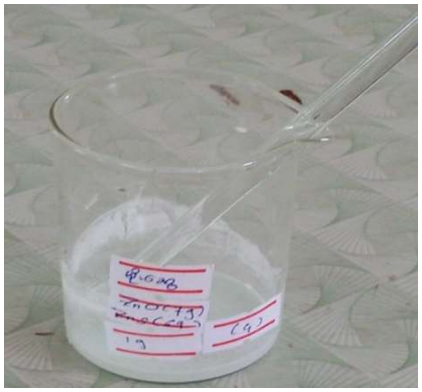
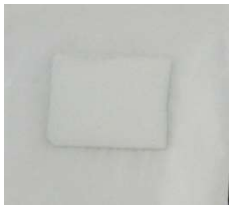
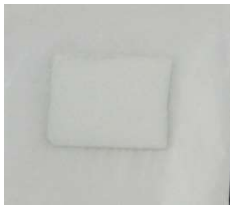


Figure 1 (a) ZnO (pure) Solution

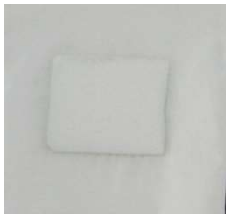
Figure 1 (b) ZnS-ZnO solution



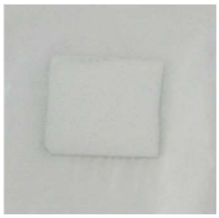
ZnO(pure) film



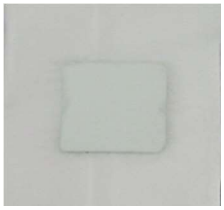
ZnS(10%)-ZnO(90%) film



ZnS(20%)-ZnO(80%) film



ZnS(30%)-ZnO(70%)film



ZnS(40%)-ZnO(60%)film

ZnS(50%)-ZnO(50%)film

Figure 1 (c) ZnO (pure) film and ZnS-ZnO nanocomposite films

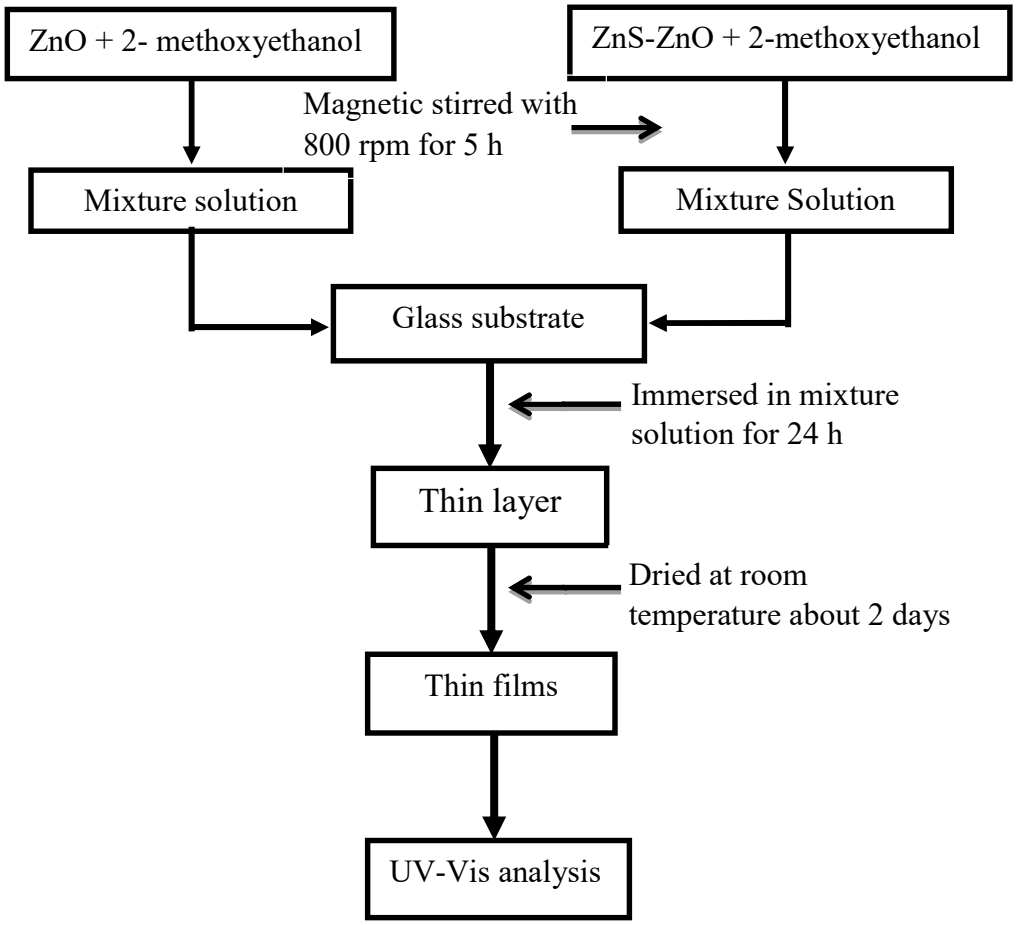


Figure 1(d) Block diagram of ZnO (pure) and ZnS–ZnO nanocomposite films

Results and Discussion

Optical Properties

The optical properties of the ZnO (pure) and ZnS-ZnO films are determined from the transmittance and absorbance measurements in the range 190nm and 1100 nm (UV-Vis IR) by spectrophotometer. Fig 2 (a-f) and Fig 3 (a-f) show the absorption spectra of ZnO (pure) and ZnS-ZnO films for different molar ratios.

Absorption coefficient α associated with the strong absorption region of the films were calculated from absorbance (A) and the thickness (t) using the relation.[Anura Kassim et al 2010][M. singh et al 2013].

$$\alpha = 2.3026A/t$$

where,

α = absorption coefficient

A =absorbance

t =thickness

The absorption coefficient of direct band gap semiconductor is given by,

$$\alpha = A(h\nu - E_g)^{1/2} / h\nu$$

where,

A = constant

hν = incident photon energy

E_g = band gap

$(\alpha h\nu)^2$ ~ hνis plotted and the intercepts of the extraplotted straight line at the$(\alpha h\nu)^2$=0 axis gives the value of the E_g of the material.

UV-Vis Analysis

UV-Visible spectroscopy was used for studying the spectral response of ZnO and ZnS. The absorption spectra of ZnO (100%) and ZnS (10%)-ZnO(90%), ZnS(20%)-ZnO (80%) , ZnS (30%)- ZnO (70%), ZnS (40%)-ZnO (60%), ZnS (50%)- ZnO (50%) films were characterized by UV- Vis spectroscopy and shown in Fig 2(a-f) and Fig 3 (a-f).The absorption spectra were observed in the wavelength between 190nm and 1100 nm which is characteristic of ZnO and ZnS. The corresponding calculated band gap values were reported in Table (1).The calculated band gap of pure ZnOwas found to be 3.808 eV. The smooth shift of the absorption edge of the ZnS- ZnO different ratios were observed and they were indicated that the band gap values of ZnS (10%)-ZnO(90%), ZnS (20%)-ZnO (80%), ZnS (30%)-ZnO

(70%), ZnS (40%)-ZnO (60%) and ZnS (50%)-ZnO (50%) films were observed 3.393 eV, 3.295eV, 3.106 eV, 2.826 eV and 2.749 eV. The variation of optical band gap with ZnS - ZnO composite was shown in Fig 4.

Table 1. The optical band gap of ZnO (pure) and ZnS-ZnO composite films with different ratios

Film	Band gap (eV)
ZnO (pure)	3.808
ZnS (10%)-ZnO (90%)	3.393
ZnS (20%)-ZnO (80%)	3.295
ZnS (30%)-ZnO (70%)	3.106
ZnS (40%)-ZnO (60%)	2.826
ZnS (50%)-ZnO (50%)	2.749

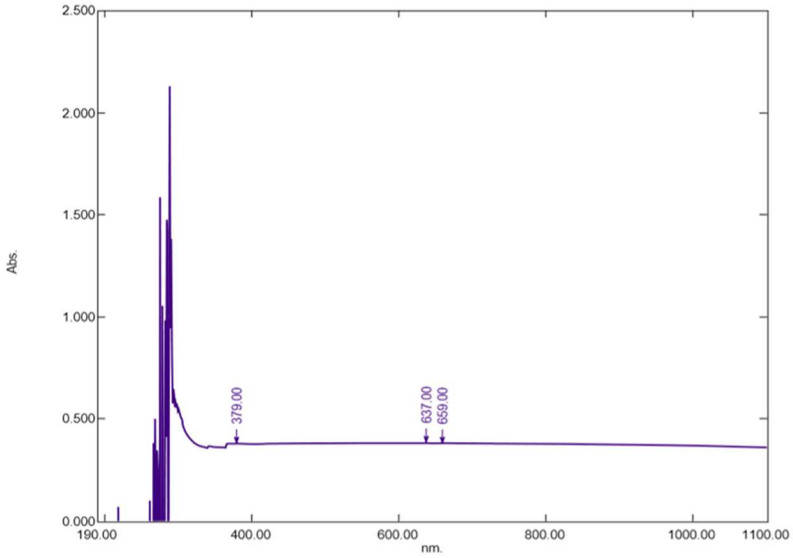


Figure 2 (a) UV-Vis absorption spectrum of ZnO (pure) film

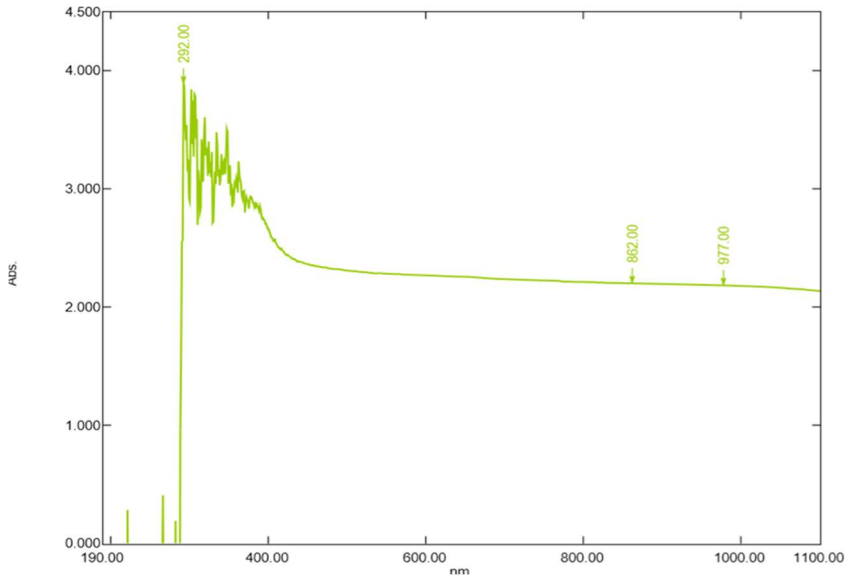


Figure2 (b) UV-Vis absorption spectrum of ZnS(10%)-ZnO(90%) film

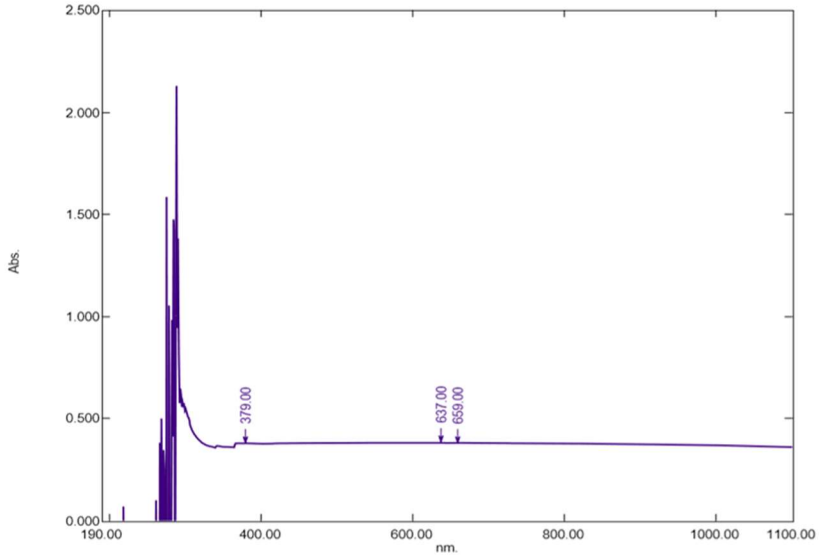


Figure2 (c) UV-Vis absorption spectrum of ZnS(20%) – ZnO(80%) film

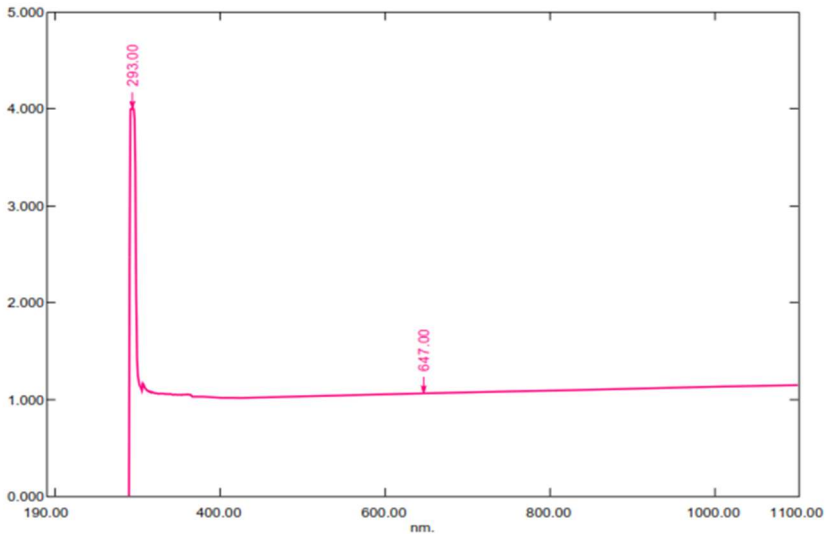


Figure2 (d) UV-Vis absorption spectrum ofZnS(30%)-ZnO(70%)film

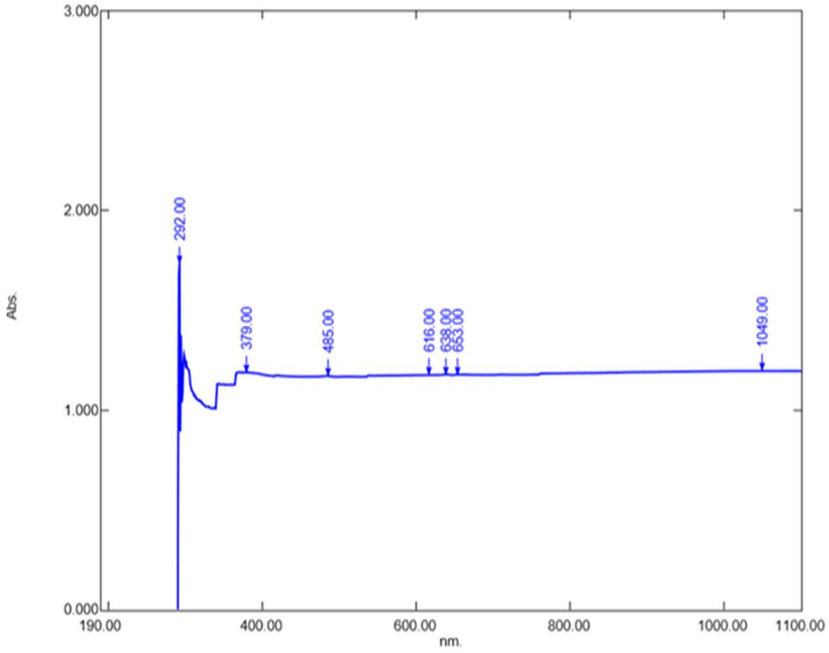


Figure 2 (e) UV-Vis absorption spectrum of ZnS(40%) - ZnO(60%)film

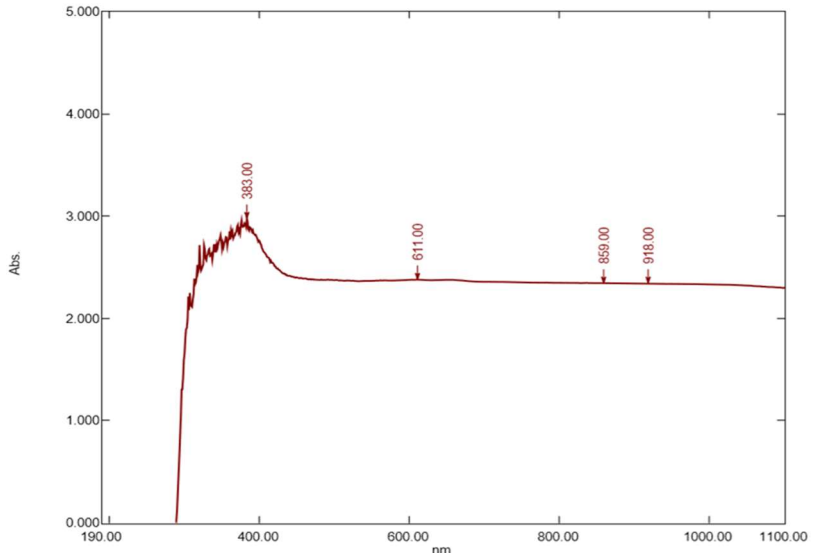


Figure2 (f) UV-Vis absorption spectrum of ZnS(50%)-ZnO(50%) film

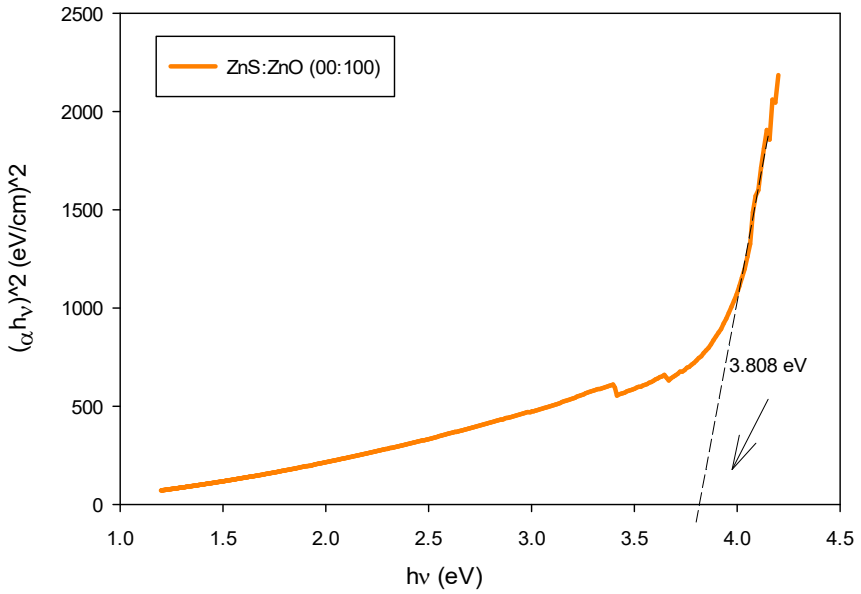


Figure 3 (a) $(\alpha h\nu)^2$Vshν plot for band gap calculation of as grown ZnO film

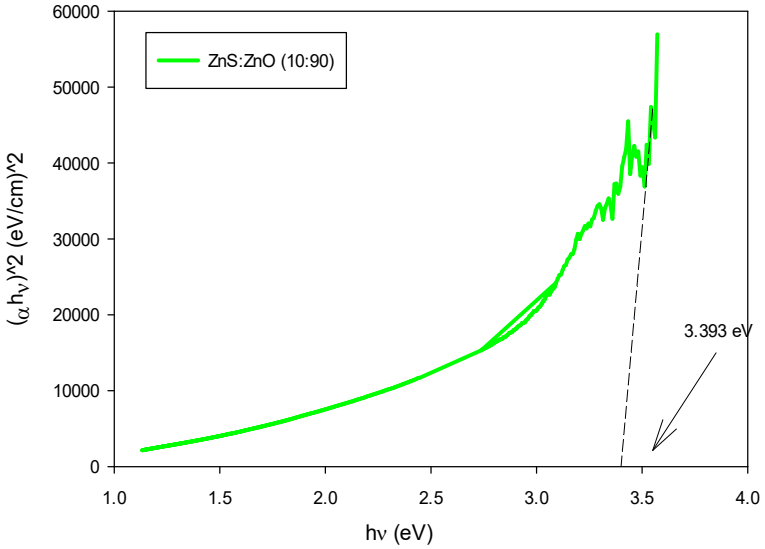


Figure 3(b) $(\alpha h\nu)^2$Vs hν plot for band gap calculation of as grown ZnS (10%)-ZnO (90%) film

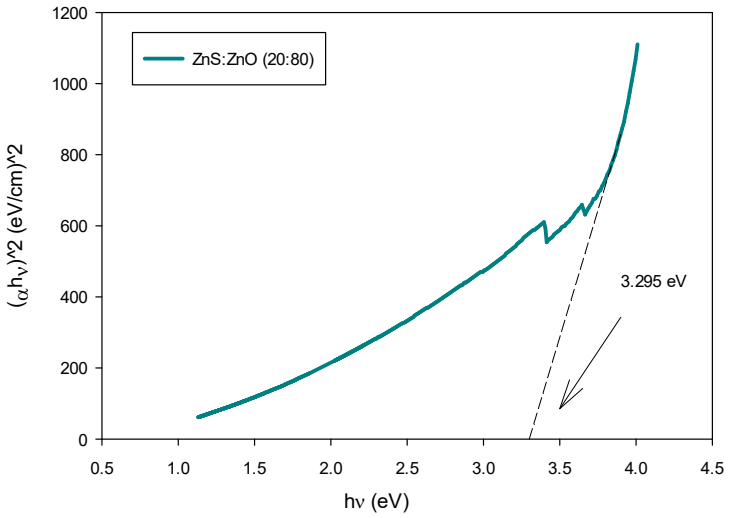


Figure 3 (c) $(\alpha h\nu)^2$Vshν plot for band gap calculation of as grown ZnS (20%)-ZnO (80%)

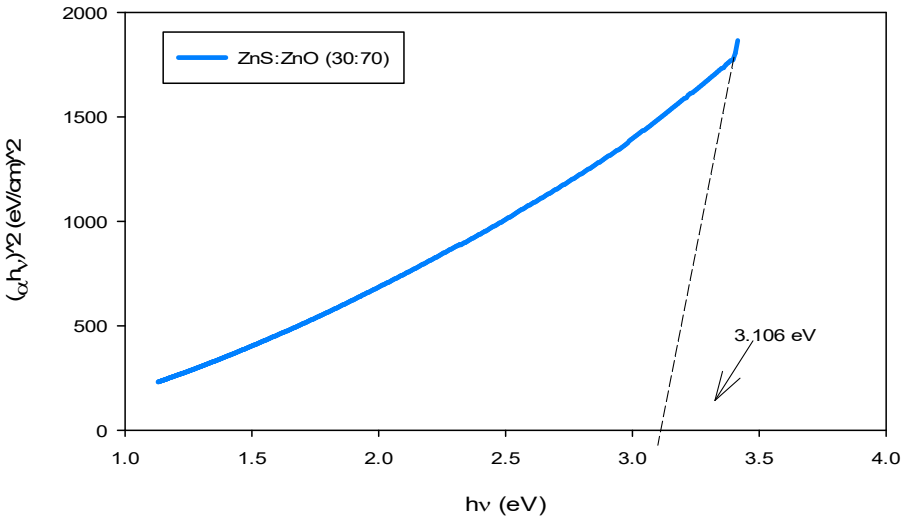


Figure 3 (d) $(\alpha h\nu)^2$Vs$h\nu$ plot for band gap calculation of as grown ZnS(30%)-ZnO(70%) film

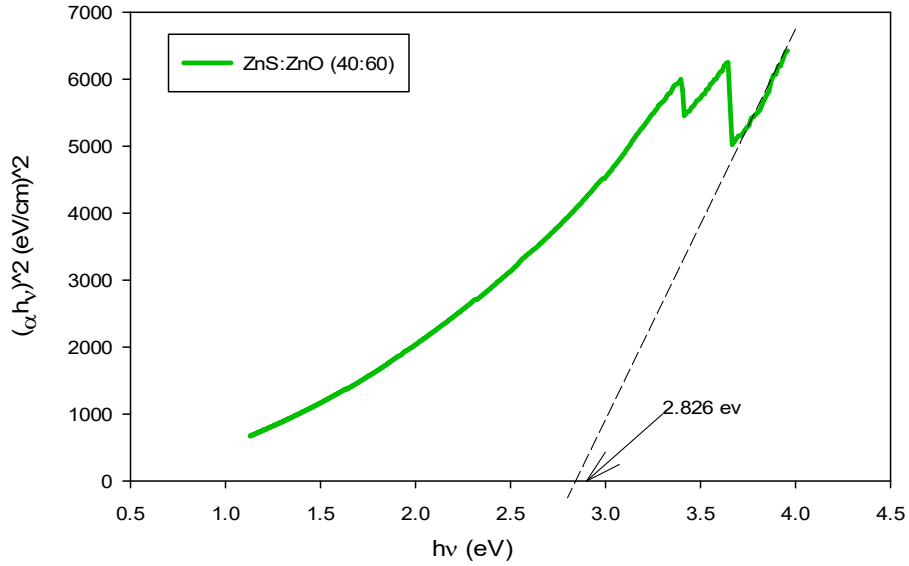


Figure 3 (e) $(\alpha h\nu)^2$Vs$h\nu$ plot for band gap calculation of as grown ZnS (40%)-ZnO (60%) film

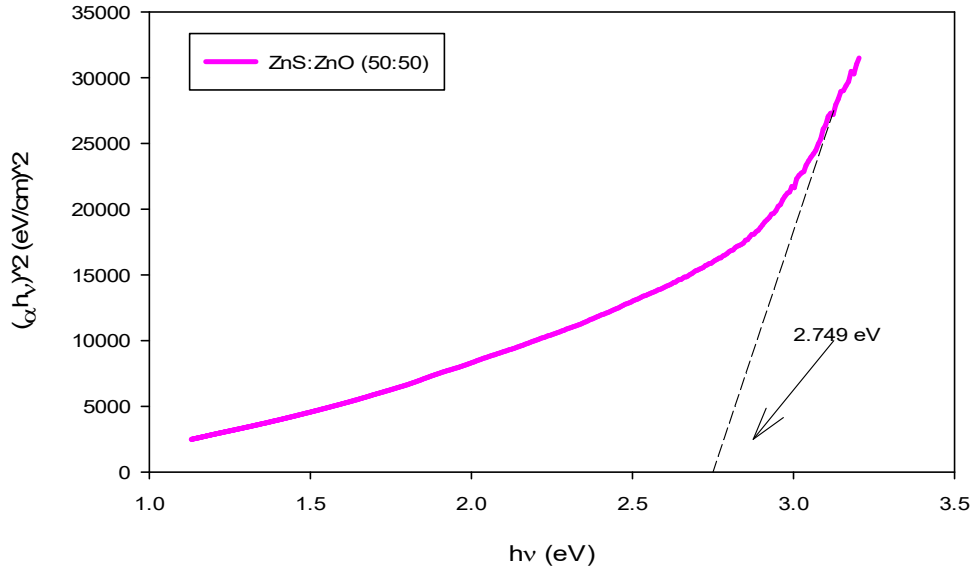


Figure 3 (f) $(\alpha h\nu)^2$Vs$h\nu$ plot for band gap calculation of as grown ZnS(50%)-ZnO(50%)film

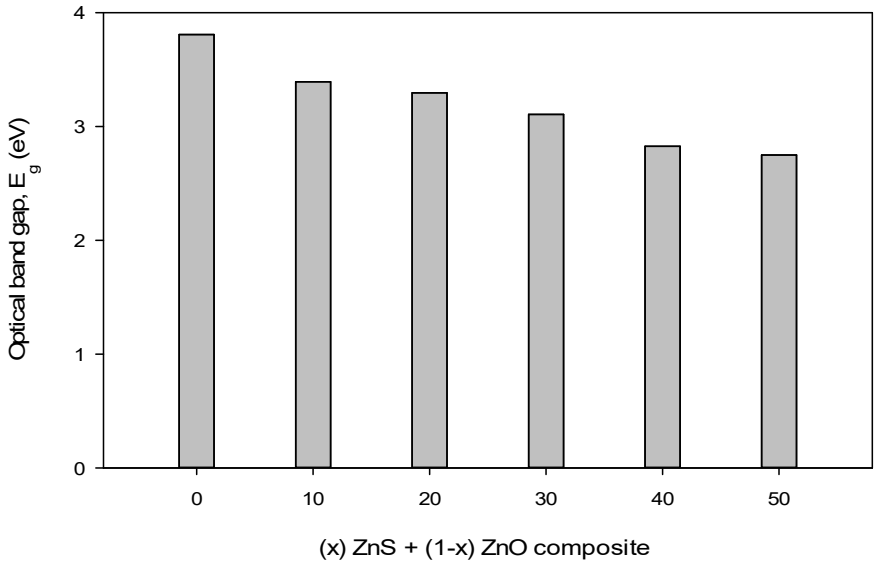


Figure 4. The variation of optical band gap with ZnS – ZnO nanocomposite

Conclusion

Preparation and characterization of ZnS – ZnO composite films have been studied. From the absorbance spectra, the optical band gap values were calculated and the band gap of pure ZnO was found to be 3.808 eV with direct transition. The values of ZnS-ZnO composite films were calculated to be 3.393 eV, 3.295 eV, 3.106 eV, 2.826 eV and 2.749 eV at the different ratios. From the UV-Vis results, it is sure that ZnO and ZnS-ZnO composite films can absorb the light in visible range. When the ZnS composition increased, the energy band gap of composites decreased due to the ability to control the properties of the material decoration through the changes on the synthesis parameters.

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