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Optical Properties of Zinc Sulphide Thin Films Fabricated using Chemical Bath Deposition Technique

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Abstract

Thin films of Zinc Sulphide were deposited on glass substrate using Chemical Bath Deposition Technique. The optical properties of the deposited films were determined using M501 Single Beam Scanning UV/VIS Spectrophotometer at normal incidence of light in the wavelength range of 380nm-700nm. The results show that films exhibited poor absorbance value of 0.001-0.027 and reflectance value of 0.001-0.033 within this region of electromagnetic spectrum. In this same region, the transmittance of the incident radiation was found to be very high with value range of 0.939-0.998. Other calculated properties such as absorption coefficient and optical conductivity were found to be high with respective values of 0.154 x $10^4 m^{-1} - 7.105 \times 10^4 m^{-1}$ and $0.0395 \times 10^{12} S^{-1} - 2.45 \times 10^{12} S^{-1}$. The refractive index of the films was observed to have a value range of 1.10-1.45 with extinction coefficient recording a value range of 0.0000796 – 0.00016. The computed values of real part dielectric function were found to be within the range 1.155-2.092 with imaginary part dielectric function having a value range of 0.000171 -0.00621. The films were found to exhibit band gap energy of 3.18eV -3.20eV. All these desirable properties made thin films of Zinc Sulphide to be a good candidate for fabrication of opto-electronics and photovoltaic devices.

Keywords: Thin films, Spectrophotometer, Absorbance, Reflectance, Transmittance, Refractive index, Optical conductivity, Dielectric function and Band gap energy.

Introduction

Zinc Sulphide is an inorganic compound with the chemical formula of ZnS. It is a group II-VI compound semiconducting material with a wide band gap of 3.65eV in bulk form. It exists in two main crystalline forms and this dualism is a typical example of polymorphism. In each form, the coordination geometry at Zn and S is tetrahedral. The more stable cubic form is known as Zinc blende or sphalerite and the hexagonal form is known as the mineral wurtzite though this form can be synthesized synthetically¹. Owing to the wide band gap nature of ZnS, it can be used for optoelectronics application such as blue light emitting diodes², cathode-ray tubes³, electroluminescence devices⁴, and buffer layers in photovoltaic cells³. Zinc sulphide thin films can be prepared using different deposition techniques such as molecular beam epitaxy⁶, thermal evaporation⁷, metal-organic vapour epitaxy⁸, chemical vapour deposition⁹, spray pyrolysis¹⁰, and chemical bath deposition¹¹.

Among all these techniques, chemical bath deposition has become widely accepted means of deposition because it is simple, cost effective, and reproducible, and with it large area of substrate can be coated with thin film of semiconducting material. In this research work, chemical bath deposition technique was used in deposition of thin films of Zinc Sulphide on a glass substrate.

Materials and Methods

The glass substrates used for the deposition were first immersed in a dilute acid solution of HNO₃ for 24hours after which they were removed and wash in distilled water; the essence is to clean the substrates thereby creating a nucleation center necessary for the formation of the films. The 50ml beakers which served as the bath were equally cleaned. For this experiment, 5ml of 0.1M ZnCl₂ was put in the bath and this was followed with addition of 5ml of triethanolamine (TEA) and the resulting mixture was stirred for 2minutes. After which 5ml of ammonia solution was added and this was followed with addition of 5ml of 0.1M thiourea. The mixture was also stirred before distilled water was added to make up the solution to 50ml mark on the bath. The pre-cleaned substrate was finally clamped in the bath and allowed to stand for 12hours after which the substrate was removed, rinsed with distilled water and allowed to dry in open air. Two other set-ups were prepared in this way and allowed to stand for 24hours and 36hours respectively with the same treatment employed.

After deposition of the films on the substrates, M501 Single Beam Scanning UV/VIS spectrophotometer was used to obtain the absorbance measurement of the films and other optical properties of the films were computed using this absorbance data.

Results and Discussion

The other optical properties and solid state property studied in this work include; transmittance, reflectance, refractive index, absorbance, optical conductivity, extinction coefficient, real and imaginary parts of dielectric function, absorption coefficient and band gap energy.

Figure-1 shows the plot of absorbance against wavelength for the deposited films. From Figure-1 it could be seen that the film deposited at 12hours time interval has the lowest absorbance property than the other two films deposited at 24hrs and 36hrs respectively. This poor absorbance of incident radiation is indicative that the films possess high transmittance property making the Zinc Sulphide semiconductor a good candidate for photovoltaic devices application

The plot of transmittance against wavelength is illustrated in Figure-2.



Figure-1 Absorbance spectra for the three samples



Figure-2 Plot of transmittance against wavelength for the three films

Research Journal of Recent Sciences Vol. 5(4), 12-18, April (2016)

From the Figure-2, it was observed that the film deposited at 12hours period has the highest transmittance property with value range of 0.973-0.995.

The variation of reflectance with wavelength is depicted in Figure-3. The spectra show that the films exhibited poor reflectance characteristics of incident radiation in this region of electromagnetic spectrum with the film deposited at 12hrs period having the lowest value. This poor reflectance property makes the semiconductor a desirable material for anti-reflection coating of devices for photovoltaic application as used in solar cells fabrication.

The plot of absorption coefficient against photon energy is shown in Figure-4. From Figure-4, it could be seen that as the photon energy increases the absorption coefficient increases. The film deposited at 12hrs has the lowest absorption coefficient value than the other two films deposited at 24hours and 36hours respectively. The absorption coefficient was obtained from the relation; $\alpha = 4\pi k/\lambda$ (

Where λ is the wavelength of incident radiation, k is the extinction coefficient and π is a constant with value equals 3.142.



Figure-3 The plot of reflectance against wavelength for the three deposited films



Figure-4 Variation of absorption coefficient with photon energy for the films

The plot of refractive index against photon energy is illustrated in Figure-5. From Figure-5, it was observed that the films exhibited moderate refractive index value range of 1.10-1.45 in this region of electromagnetic spectrum (380-700nm). This value makes ZnS semiconductor material a good candidate for application in photonic devices. The refractive index was computed using the relation;

$$\mathbf{n} = (1 + \mathbf{R}^{0.5}) / 1 - \mathbf{R}^{0.5} \tag{2}$$

Where R is the reflectance of the films to incident radiation within this region of electromagnetic spectrum.

The optical conductivity of the films to incident radiation was also determined using the relation;

$$\sigma_{\rm op} = \alpha nc/4\pi \tag{3}$$

where: α is the absorption coefficient, n is the refractive index and c is the velocity of light.

The plot of optical conductivity against photon energy is depicted in Figure-6.



Figure-5 Plot of refractive index against photon energy



Figure-6 Plot of optical conductivity against photon energy

Figure-8 Variation of real part dielectric function with photon energy for the films

Vol. **5(4)**, 12-18, April (**2016**) The films were found to exhibit high optical of

Research Journal of Recent Sciences

The films were found to exhibit high optical conductivity with peak at $2.45 \times 10^{12} \text{S}^{-1}$ for film deposited at 36hours. This peak value was observed beyond 3eV. High optical conductivity is indicative that the material can be used for fabrication of electroluminescent devices.

The extinction coefficient k is an optical property of the semiconductor material and is related to the refractive index n which merely determines how much light is absorbed by the material. If k>0, it means there is absorption of radiation and if k=0, it means the light travels straight through the material. The plot of extinction coefficient as a function of photon energy is shown in figure 7 below. It was calculated from the relation;

$$K = \alpha \lambda / 12.568 \tag{4}$$

Where: α is the absorption coefficient and λ is the wavelength of incident radiation.

From Figure-7, it was observed that the extinction coefficient was generally low and the film deposited at 12hours has the lowest value range of 0.000159-0.000955. This low value of extinction coefficient confirms Zinc Sulphide thin films to be a good semiconductor material for application in fabrication of photovoltaic devices.

The real part dielectric function spectra of the deposited films are shown in Figure-8.

2.5 Real part dielectric function (£1) 2 1.5 er (12hrs) 1 εr(24hrs) 0.5 er (36hrs) 0 0 1 2 3 4 Photon Energy (eV)

Plot of extinction coefficient against photon energy





The real part dielectric function was obtained using the relation;

$$\varepsilon_r = n^2 - k^2 \tag{5}$$

Where: n is the refractive index and k is the extinction coefficient.

The plot of imaginary part of dielectric function against the photon energy is illustrated in Figure-9 below.

The film deposited at 12 hours was found to have lowest value of imaginary part dielectric function when compared with the other two films deposited at 24hours and 36hours respectively. The imaginary part dielectric function represents the absorption associated with radiation by the free electron carriers and was calculated using the relation; ϵ_i = 2nk (6) Where: n is the refractive index and k is the extinction coefficient.

The band gap energy of the films was determined from where the straight part of the plot of absorption coefficient squared against the photon energy intercepts the photon energy axis. It is the energy value involved when an electron undergoes transitions from the upper part of the valence band to the lower part of the conduction band and it causes dispersion near the fundamental absorption edge. This could happen without phonon participation and without change in the material especially when the semiconductor is of direct transition type. Figure 10 shows the plot of absorption coefficient squared against the photon energy.



Figure-9

Plot of Imaginary part dielectric function against photon energy for the three samples



Figure-10 Plot of absorption coefficient squared against photon energy for the three samples



Figure-11 The plot of absorption coefficient against photon energy for film at 36hours

From Figure-10, it was observed that the film exhibited band gap energy of 3.20eV. The plot of absorption coefficient squared against photon energy for film deposited at 36hours is shown in Figure-11 above.

From figure 11 the band gap energy of the deposited film was found to be 3.18eV. These band gap energy values of 3.20eV and 3.18eV were close to the value of 3.39eV- 3.59eV reported by kurbatov D. *et al*¹².

Conclusion

Thin films of Zinc Sulphide were successfully deposited on glass substrate using chemical deposition technique from the aqueous solution of Zinc Chloride, ammonia solution, thiourea and in which triethanolamine (TEA) was used as a complexing agent. The films were optically characterized using M501 Single Beam scanning UV/VIS spectrophotometer. The results show that the film exhibited poor absorbance and reflectance of incident radiation with high transmittance property. The films were also found to possess high optical conductivity, absorption coefficient, and moderate refractive index. The extinction coefficient was observed to be generally low with wide band gap energy. All these desirable properties made Zinc Sulphide semiconductor material to be a good candidate for application in opto-electronics and photovoltaic devices.

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