

Investigation of Annealing Effect of Electrical and Optical Properties of ZnS-CuS Thin Films Prepared by SILAR Technique.

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ABSTRACT

The thin films of ZnS and CuS have found extensive applications in various optical, electronics, and superconductor devices. This work therefore presents ZnS - CuS multilayer thin films grown by a simple and inexpensive method of Successive Ionic Layer Adsorption and Reaction (SILAR) on glass substrates at room temperature. The reaction solution is composed of copper sulphide, zinc chloride and sodium sulphide.

The deposition was carried out using 100 SILAR cycles. The thickness of the films was determined using gravimetric technique. XRD diffraction technique was used for the investigation of crystallographic structure and crystallite size of the films. The electrical and optical properties were studied using two point probe and Genway 6405 UV- spectrophotometer, respectively.

The thickness of the films was measured to be 2.4nm and the XRD study of the films showed that they exhibit polycrystalline hexagonal structure. The preferential orientation of the films is along (103) direction. The crystallite size is 28.18nm. The sheet resistance, conductivity and resistivity of the as-grown thin films are $3.38 \times 10^{11} \Omega$, $1.08 \times 10^{-12} (\Omega \text{cm})^{-1}$, and $9.198 \times 10^{11} \Omega \text{cm}$, respectively while the annealed films at 200°C showed sheet resistance, conductivity and resistivity of $1.62 \times 10^{12} \Omega$, $6.74 \times 10^{-13} (\Omega \text{cm})^{-1}$, and $1.435 \times 10^{12} \Omega \text{cm}$, respectively.

The energy band gap of the as-grown and annealed semiconducting film was found to be 2.60eV and 2.48eV and refractive index of the films are 2.33 and 2.36, respectively. By annealed the film, the energy band gap was found decreased. The annealed films were more resistive than the as-grown films while the as-

grown films were more conductive with higher conductivity values than the annealed ones.

(Keywords: SILAR deposition, CuS, ZnS, electrical and optical properties, thin films)

INTRODUCTION

During the past few years, the thin films of ZnS and CuS have received more attention due to their potential applications in various fields of science and technology. Metal-chalcogenide films have been widely studied, because of their effective applications in electronic, optical, solar cell, photoconductor and superconductor devices.

It has been studied that CuS films can be use as photo-thermal conversion application and ZnS film can also play a critical role in transmitting of solar energy due to its high optical transmission property and anti-reflective property. ZnS-CuS multilayer thin film has been extensively studied due to its potential application in optoelectronics, photoconductor, and electroluminescent devices and solar energy conversion.

As an important semiconductor with unique electronic, optical and chemical properties, CuS is a promising material with potential applications in many fields. The CuS thin films has recently received considerable attentions, due to numerous technological applications in photovoltaic solar cells, as a photo thermal conversion of solar energy and also found potential application as selective radiation filter on architectural windows minimizing the heat absorbed in the house.

The optical study shows that CuS has direct band gap of 2.36eV [M Ali Yildirim, Aytunc Ates, Aykut Astam et al 2009]. This films has been prepared by the Successive Ionic Layer Adsorption and

Reaction (SILAR). The SILAR method is an aqueous solution method based on sequential reactions at substrate-solution interface for the deposition of the thin films. It involves the alternate dipping of the substrate into aqueous solution containing ions of each component. In the SILAR technique, quality films are obtained by optimizing some parameters such as concentration, temperature and pH of the precursor solutions and the time duration for adsorption, reaction and rinsing.

Many researchers have shown interest in the development and characterization of CuS by adopting various deposition techniques such as Chemical Bath Deposition, Sol-gel, and Successive Ionic Adsorption Layer and Reaction [M Ali Yildirim, Aytunc Ates, Aykut Astam et al 2009]. In comparing with other methods, SILAR has some advantages such as easy control, simplicity, and reduced expensive. In the SILAR technique, the substrates are immersed into separated beakers containing cationic and anionic precursor solutions and rinsed with distilled water after each immersion (Nicolau 1985). There is weak interaction between CuS and bare glass substrates. The adhesion of copper thin film to the glass substrate is poor (Lindrous et al 2004). The adhesion of Zinc thin films was found to be stronger than copper film on bare glass substrate.

ZnS is an effective II-VI semiconductor material with potential applications in optoelectronic devices such as blue light-emitting diodes, Mn doped electroluminescent devices, window layers of solar cells and as electro-optical modulator. ZnS is an efficient window material in solar cell. It can be a partner of different polycrystalline absorber semiconductor material such as SnO₂/ZnS/CdTe and Cd/ZnS/CuInSe₂ solar cells. It has also been studied with useful applications as phosphors and catalysts [Zhu, Bondo, Xue, et al. 2003].

The optical study shows that ZnS has a direct band gap of 3.88eV [Borah and Sarma et al. 2008]. ZnS has a low exciton Bohr radius (2.5nm) making its nanoparticle interesting as small bimolecular probes for fluorescence and laser scanning microscope. ZnS is also currently used as a shell or capping layer in core/shell nanoprobe structures such as CdSe/ZnS core/shell structures [Thakur, Fradin, Can et al. 2003].

In this study, ZnS-CuS multilayer thin films were

grown using SILAR technique. The annealing temperature effects on the electrical and optical properties of the films were investigated and it was found that the electrical resistance is higher at elevated temperature. The energy band gap decreases from 2.60eV to 2.48eV when annealed. It is very useful as electroluminescent and solar cell devices. In this paper we report on the deposition and optical, electrical and structural characterization of ZnS-CuS multilayer thin films.

MATERIALS AND METHOD

In this study, ZnS - CuS multilayer thin film were grown on glass substrates by the SILAR technique. CuS thin film was first grown on glass substrates and ZnS thin film was later deposited on the glass containing CuS thin film. For the preparation of CuS monolayer thin film the substrates were first cleaned, dried and immersed in the first reaction vessel contain aqueous cation precursor 0.1m CuCl₂ solution at pH 5.5. After the cation immersion the substrates were moved to the rinsing vessel where they are washed with purified water. The substrates were later immersed in anion precursor where the sulphide ions were adsorbed from an aqueous, 0.05m Na₂S solution with pH 12. After anion immersion the substrate is washed with purified water, thus the first SILAR growth cycle is finished. Repeating these cycles a thin film with desired thickness can be grown. For the preparation of ZnS monolayer thin film, 0.1m zinc chloride (ZnCl₂) with pH 5.5 is used as cationic precursor and 0.05m sodium sulfide (Na₂S) with pH 12 used as anionic precursor. The SILAR growth cycle is 100 times. The cation and anion immersion times were 30s and rinsing time was 50s.

After the deposition of the films, the glass substrates were cleaned for 15min in acetone. The substrates were dried and stored in desiccators.

The samples were annealed at 200°C for the investigation of annealing effect on optical and electrical properties of the films.

RESULT AND DISCUSSION

Thin film of thickness 2.4nm was grown with total number of 100 cycles. The average growth rate of ZnS-CuS films were 0.024nm/cycle. The optical

measurement was carried out at room temperature. The absorbance spectra of the films were measured as a function of incident photon wavelength. A blank substrate was placed on the reference beam for all measurement to correct the absorption of the substrate. The energy band gap of the thin film samples were calculated with the help of the $(\alpha h\nu)^2$ versus energy band gap values. The theory of the interband absorption shows that at the optical absorption edge, the absorption coefficient α varies with the photon energy $h\nu$ according to the equation below:

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

where A is a constant and E_g is the the optical band gap. Thus, a plot of $(\alpha h\nu)^2$ versus $h\nu$ is a curve line whose intercept on the energy axis gives the energy gap. The band gap energy of the film have been determined by the extrapolation of the linear regions on the energy axis $h\nu$.

The energy band gap of the as-grown ZnS-CuS films were evaluated to be approximately 2.60eV and 2.48eV for annealed sample. The optical energy gap of the pure CuS thin films deposited via this technique is 2.3eV and that of ZnS thin film is 3.64eV. The effect of putting some ZnS in CuS matrix drove the band edge to 2.60eV. There was decrease in band gap after annealing. This could be attributed to improvement in the crystal and change in grain size of the film with annealing temperature.

The absorption coefficient (α) associated with the strong absorption region of the film was calculated from absorbance (A) and the film thickness (t) using the relation:

$$\alpha = 2.303A/t \quad (2)$$

The extinction coefficient (k) is evaluated from the relation:

$$K = \alpha \lambda / 4\pi t \quad (3)$$

where λ is the wavelength of the incident radiation and t is the thickness of the film.

The substrate absorption was corrected by introducing an uncoated cleaned glass in the reference beam.

Figure 1 shows optical absorption spectra of as-grown ZnS-CuS films at room temperature. The optical band gap was estimated as 2.60eV.

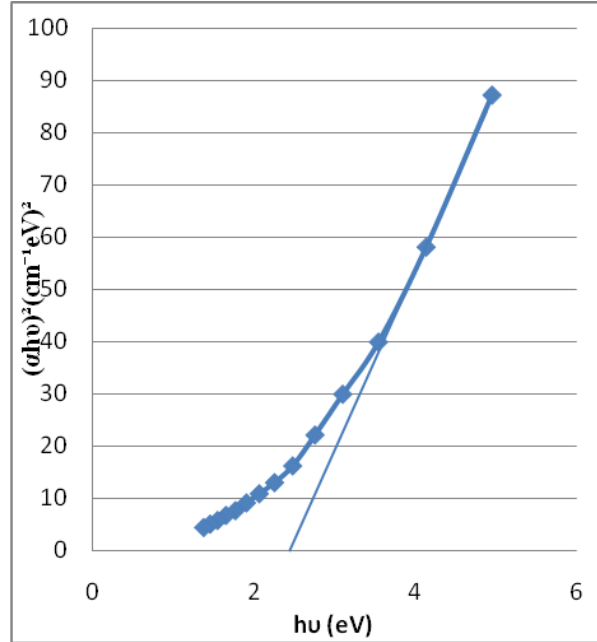


Figure 1: The Optical Absorption Spectra of As-Grown ZnS-CuS Film Grown at Room Temperature.

Figure 2 shows the optical absorption spectral of annealed ZnS-CuS film. The spectra shows optical band gap 2.48eV.

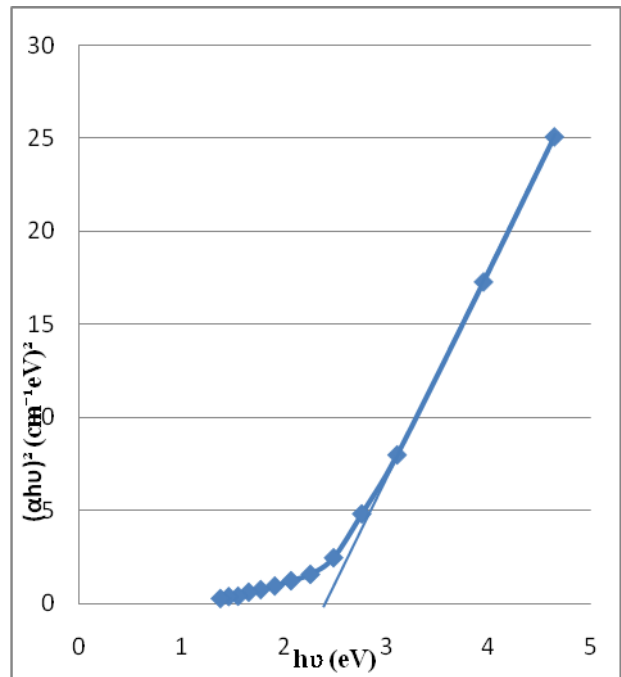


Figure 2: The Optical Absorption Spectral of Annealed ZnS-CuS Film.

Figure 3 shows the absorbance spectra of as-grown ZnS-CuS multilayer thin film. The absorbance decreases as the wavelength increases. The absorbance spectra of annealed film are shown in Figure 4.

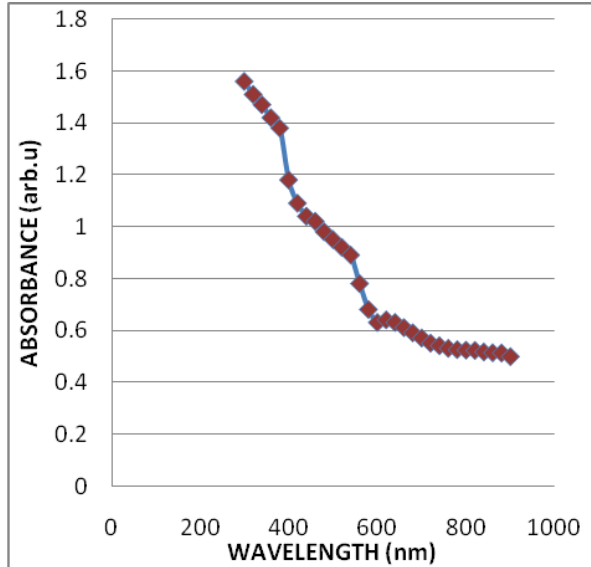


Figure 3: The Absorbance versus Wavelength of As-Grown ZnS-CuS.

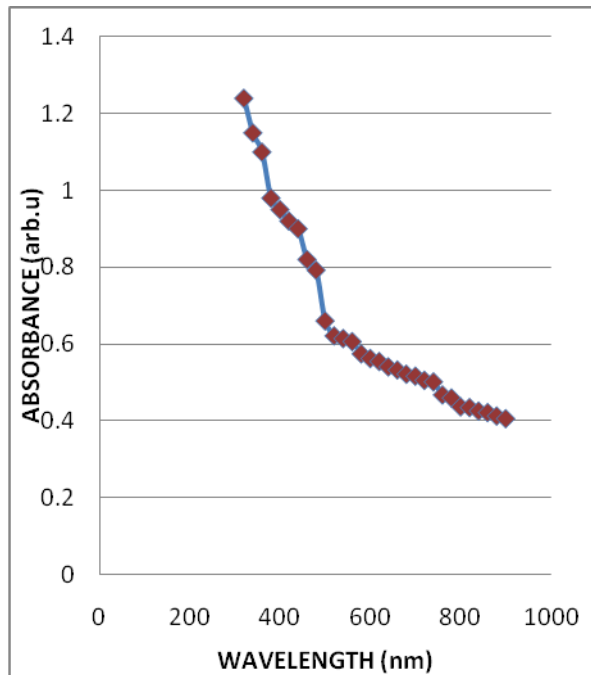


Figure 4: The Absorbance versus Wavelength of Annealed ZnS-CuS Film.

Figure 5 shows the percentage transmittance spectra of as-grown ZnS - CuS multilayer thin film. The transmittance increases as the photon wavelength increases.

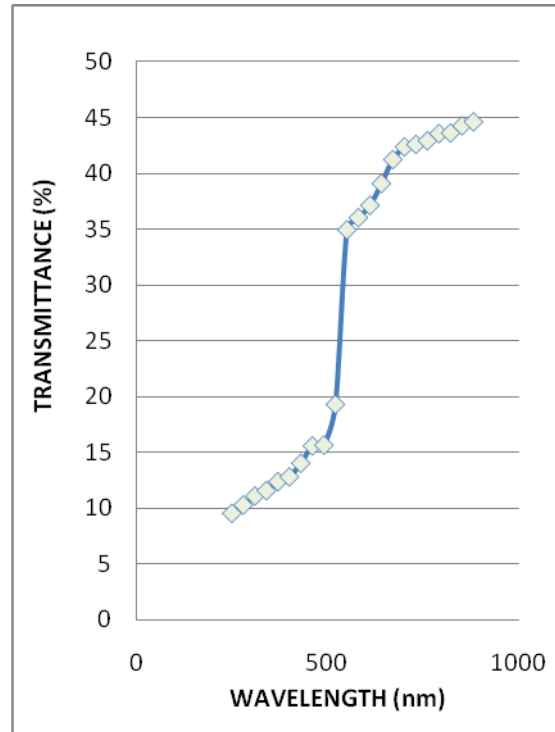


Figure 5: Transmittance Spectra of As-Grown ZnS-CuS Film.

The transmittance spectral of annealed film is shown in Figure 6. The annealed films showed a better transmittance than as-grown film. The optical study of annealed ZnS - CuS films show very high absorbance near the middle of the visible region but falls off in the near infra red region.

The as-grown film showed a maximum transmission of about 42% in visible region and peak transmission of about 45% in NIR region but minimum transmission in the UV region. The annealed film showed a maximum transmission of about 65% in the VIS region which is higher than 42% recorded for as-grown film. It showed peak transmission of about 70% in NIR region. The annealed film showed a higher transmission than as-grown film.

The high transmission of the films in the NIR regions could be exploited in glazing applications for space heating. The films showed low transmission in UV regions. The films could

therefore act as effective UV filter and can be use in architectural windows for UV filter. The films provide ultimate protection from ultraviolet radiation. The UV control is important for the protection of both people and goods, since UV radiation is one of the prime causes of fading and dermatological damage. The high optical transmission and antireflective of the annealed makes it suitable for solar cell transmission in photovoltaic solar cell devices.

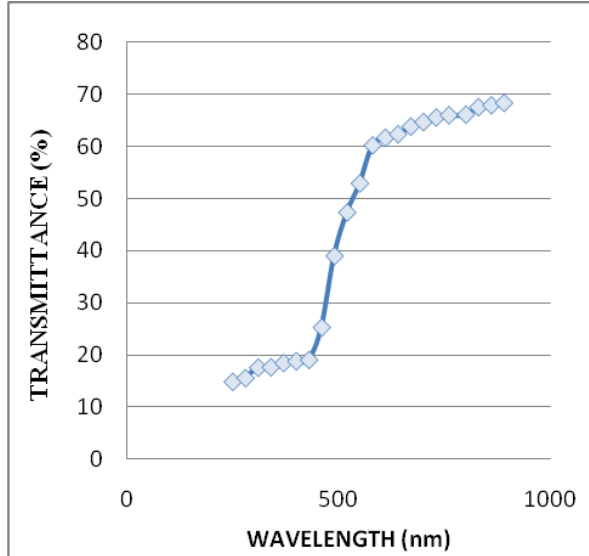


Figure 6: Percentage Transmittance Spectra of Annealed ZnS-CuS Film.

The optical studies of the films showed a very high absorbance in the UV regions and low absorbance in the NIR region. In the VIS region, it absorbs only slightly. This causes the material to act effectively in windscreens coating and driving mirrors to prevent the effect of the dazzling light into driver eye. The high refractive index of 2.36 makes the film to be very applicable in solar cell and anti-dazzling coating. The refractive index was determined using Moss rule:

$$n^4 E_g = 77 \quad (4)$$

n =refractive index and E_g is the energy band gap.

The refractive index of as-grown and annealed samples are 2.33 and 2.36.

The I-V characteristic was recorded using two point probe. A variety of measurements are made to determine the electrical characteristics of the films. Characterizing the film often involves

measuring the current as a function of an applied voltage. The measurements are usually done under light. Important device parameters can be extracted from the current-voltage (I-V) measurements, such as sheet resistance, electrical conductivity and electrical resistivity of the material. Current-voltage (I-V) characteristics were examined and sheet resistance, resistivity and conductivity of the sample were calculated using the following relations:

$$R_s = \pi / \ln 2 (V/I) = k (V/I) \quad (5)$$

K is a geometric factor which is 4.53 in the case of thin sheet material.

R_s = sheet resistance

$$\rho = \pi t / \ln 2 \times (V/I) = R_s \times t \quad (6)$$

t = thickness of the film

$$\sigma = 1/\rho \quad (7)$$

The I-V behavior of as-grown and annealed films at 200°C temperature was investigated. As the applied voltage increases, the current increases. The sheet resistance, conductivity and resistivity of the as-grown thin films are $3.38 \times 10^{11} \Omega$, $1.08 \times 10^{-12} (\Omega \text{cm})^{-1}$, and $9.198 \times 10^{11} \Omega \text{cm}$, respectively, while the annealed films showed sheet resistance, conductivity, and resistivity of $1.62 \times 10^{12} \Omega$, $6.74 \times 10^{-13} (\Omega \text{cm})^{-1}$, and $1.435 \times 10^{12} \Omega \text{cm}$, respectively. Thus the annealed thin film was found to be more resistance than as-grown film. The current values are about 10^{-10} A.

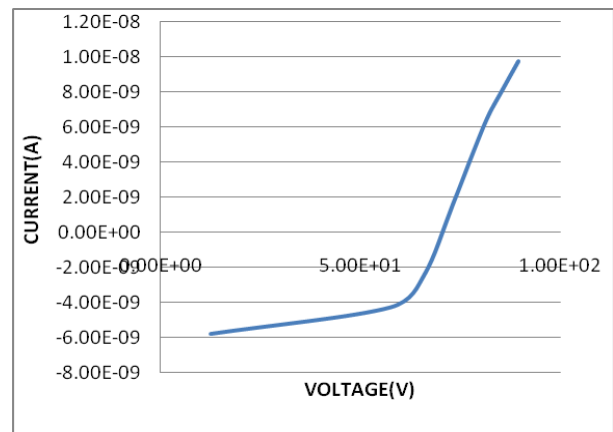


Figure 7: The I-V Behavior of Annealed ZnS - CuS Sample.

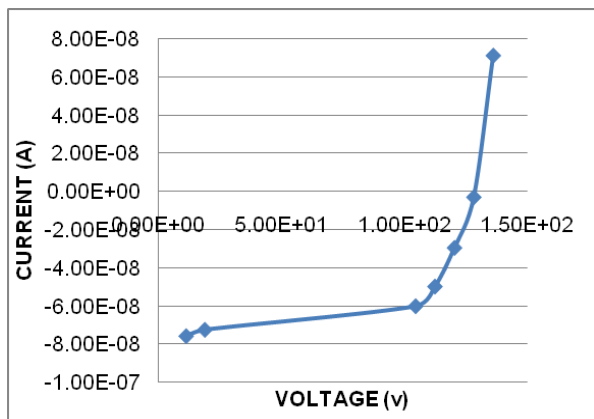


Figure 8: The I-V Behavior of As-Grown ZnS - CuS Film at Room Temperature.

Figure 9 shows XRD spectra of ZnS-CuS film. The crystallographic structure, the crystallite size and inter atomic distance of the film was analyzed using X-ray diffractometer method.

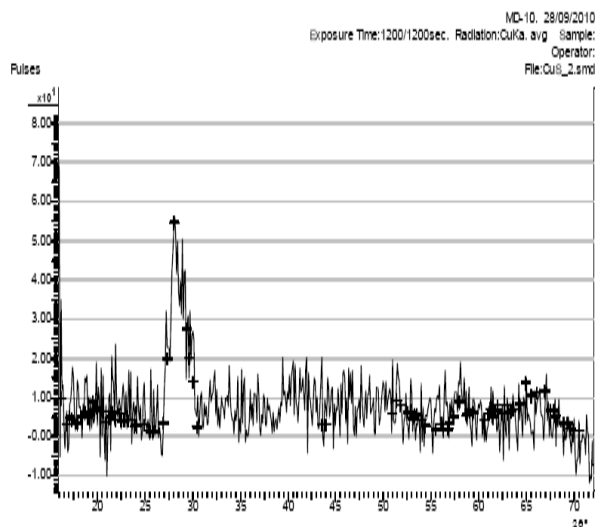


Figure 9: X-ray Diffraction Patterns of ZnS-CuS Thin Films with 100 Cycles.

The structural analysis was done using Radicon MD-10 mini diffractometer. The XRD spectral of ZnS-CuS thin films grown on amorphous glass substrate was obtained.

ZnS-CuS thin films had a polycrystalline hexagonal structure and oriented towards different directions. Many diffraction peaks of different intensity were obtained from the XRD

spectra. In the XRD obtained from the aqueous solvent, the highest intensity peak was noted at diffraction angle 28.03° corresponds to (103) preferred orientation. The (103) peak is stronger than other peaks. In general, the preferential orientation of the films is along the (103) direction. The broad hump in the range $2\theta = 27^\circ - 30.5^\circ$ is due to the amorphous glass substrate. However, the XRD spectrum of the ZnS-CuS layer deposited by SILAR technique from aqueous only exhibit the (103) direction.

The grain size of the film was calculated from XRD pattern by using Debye Scherer's formulae:

$$D = 0.9\lambda / \beta \cos\Theta \quad (8)$$

where D is the grain size, λ is the X-ray wavelength, β is the full wave at half maximum and Θ is the Bragg's angle. The crystallite size is 28.18nm and the inter-planar spacing is 3.182nm.

CONCLUSION

ZnS-CuS thin film was grown by the SILAR method on glass substrate at room temperature. Optical absorption measurement indicates a material with optical band gap of 2.60eV and 2.48eV for as-grown and annealed samples which fall between 2.36eV for CuS and 3.64eV for ZnS previously prepared by this technique.

The energy band gap of the films decreased to 2.48eV when annealed. The absorbance is high near the middle of VIS region. The annealed sample exhibit high transmittance than as-grown sample.

The I-V behavior of the as-grown films was investigated. However, the current increases as the applied voltage increases. The current value is about 10^{-10} A. The thickness of the film was determined as 2.4nm.

From the XRD patterns, ZnS-CuS thin film is compose of hexagonal phases. The crystallite size was found to be 28.18nm. The film is a polycrystalline material. The annealed film was found to be more resistive than as-grown film while the as-grown was more conductive than annealed film.

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