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Solid State Properties of Copper- Silver- Sulphide Thin Film Deposited by Solution Growth Technique

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Abstract
Chemical bath deposited Copper Silver Sulphide (CuAgS) thin films on glass substrates were studied for its optical properties using spectrophotometer. Some of the optical properties studied include absorbance, transmittance, reflectance, refractive index, optical conductivity, absorption coefficient, dielectric constant and extinction coefficient. The direct band gap obtained is 2.3eV and the indirect band gap is 1.1eV. Some of the possible applications of the film were discussed

Keywords: chemical bath deposition; cuags thin film; optical properties; band gap energy

INTRODUCTION

Interest on the preparation and study of physical properties of ternary chalcogenide compounds for their possible applications in solar cells, light emitting diodes and non-linear optical devices (Ortega, et al. 2003) has increased in recent years.
Ternary compounds are found to be promising material for optoelectronic device applications such as green emitting devices and are also suggested to be possible material for window layer of solar cells (Woon-Jo, et al. 2003). Some of them have been investigated for specific applications for super ionic conducting materials (Sasaki, et al. 2003). These ternary compounds are increasingly being studied for efficient solar energy conversion for photo-electrochemical solar cells (Padam,et al. 1986, Estrella, et al. 2003) and have become potential materials for such applications (Pawar, et al. 1986, Jae-Hyeong, et al. 2003). Although, the deposition of ternary thin films have been reported using advanced technologies, the low cost and simple solution growth technique seems to be much better (Jae-Hyeong, et al. 2003).

This paper reports the investigation of optical and solid state properties of copper silver sulphide thin film, deposited on glass substrate using solution growth techniques. The optical properties investigated include absorbance (A), transmittance (T) and reflectance (R), which were then used to calculate other parameters such as refractive index (n), extinction coefficient (k), dielectric constant (ε) and optical conductivity (σ_o). The equations found in the literature (Pankove, 1971, Ezema, et al. 2003) were used to determine these optical properties and the band-gap energy of this thin film.

THEORY

The transmittance (T) was obtained using the equation given by (Theye, 1985). Reflectance (R) and absorbance (A) were computed using the expression given by (Pentia, et al.2004, Salem, 2002, Majumdar, et al. 2003, Quijada, et al.1998, Ramesh, et al. 2003, Shwarstein, et al. 2006, Ezema, 2004, Elliot, 1984, Chen, et al. 2003). The extinction coefficient (k) and refractive index (n) were obtained with equations in (Mitsuaki, et al. 2003, Rodrigo, et al. 2002, Ezema, et al. 2004) while the dielectric constant (ε) and the optical conductivity (σ_o) were calculated using the expression given by (Blatt,1968, Tsidikovski, 1982). The relationship between the absorption coefficient and photon energy is given by (Ndukwe, 1996, Osuji, 2003, Ezekoye, et al. 2003, Soliman, 1998, Chopra, et al. 1982, Hass, 1972, Pramanik, et al. 1987, Kittel, 1977, Rodriguez, et al. 2001, Rodriguez, et al. 1999, Numez-Rodriguez, et al. 2002, Ezema, et al. 2005,Ezema, 2004) from this, energy band gap was extrapolated.

EXPERIMENT AND MATERIALS

The chemical deposition of the thin film onto the glass substrate was carried out by using a mixture of 1M copper chloride, 0.1M Ethylenediaminetetraacetic (EDTA), 0.1M silver nitrate 7.4M Triethanolamine (TEA), 14M ammonia, 1M Thiourea, distilled water, microscopic glass slides inside a beaker. The chemical bath deposition technique was used to prepare the CuAgS thin film on glass substrate (slide) which had been previously degreased in concentrated nitric acid HNO_3 for 48hours, cleaned in cold water with detergent, rinsed with distilled water and dried in air. The degreased-cleaned surface provide nucleation centre for growth of the film, hence yielding highly adhesive and uniformly deposited films. The mixture was thoroughly stirred with a glass rod before the glass slide was vertically introduced into the beaker. The dip time of about 20 – 48 hours, at PH between 9 and 11 was observed for the deposition process, which took place at room temperature. The grown samples were removed from the reaction baths, rinsed with distilled water and allowed to dry. They were then annealed at 423 K for 1 hour to obtain adherent transparent thin films. During deposition, cations and anions in the deposition solution reacted to become neutral atoms, which either precipitated spontaneously or proceed slowly. Fast precipitation implied that thin films could not be formed on the substrate immersed in the solution. However, with the addition of TEA and EDTA, the reaction proceeded slowly for thin film of neutral atom to be formed on the substrate. The complexing agents slowed down the precipitation action for formation of CuAgS, while the NH_3 solution served to stabilize pH of the mixture. Sulphide ions were released by hydrolysis of thiourea, but Cu and Ag ions formed cuprous-ethylenediaminetetraacetic complex and silver triethanolamine complex ions by combining with EDTA and TEA, respectively. [Cu (EDTA)] and [Ag (TEA)] complexes adsorbed onto the glass substrate when heterogeneous nucleation and growth took place by ionic exchange reaction of S^{2-} ions. By the process of ion-by-ion exchange, CuAgS was deposited on the glass substrate in the form of transparent, uniform and adherent thin film.

The thin film was characterized using UNICO UV-2102 PC spectrophotometer to determine the spectral absorbance, Transmittance and reflectance of the thin film on the glass substrate with blank substrate as a reference glass slide. The experiment was carried out at Covenant University Ota Ogun State. The characterization were carried out at University of Nigeria Nsukka and Covenant University Ota

Equation of Reaction

The steps involved in the chemical deposition of CuAgS thin film are given below

$CuCl_2.2H_20 + EDTA \leftrightarrow [Cu (EDTA)]^+ + 2Cl^-$ 1

$[Cu (EDTA)] \leftrightarrow Cu^+ + EDTA^{2-}$ 2

$AgNO_3 + TEA \leftrightarrow [Ag (TEA)]^+ + NO_3^-$ 3

$[Ag (TEA)]^+ \leftrightarrow Ag^+ + TEA$ 4

$(NH_2)_2CS + 0H^- \leftrightarrow (NH_2)_2CO + HS^-$ 5

$HS^- + 0H^- \leftrightarrow H_20 + S^{2-}$ 6

$Cu^+ + Ag^+ + S^{2-} \leftrightarrow CuAgS$ 7

RESULT AND DISCUSSION

The graphs of spectral absorbance, transmittance and reflectance versus wavelengths are presented in figures 1, 2 and 3, respectively. The optical properties considered revealed high absorbance and reflectance but low transmittance in the UV; low values of absorbance and reflectance accompanied but high transmittance in the VIS. As a result of these properties, UV radiation is screened off and the infrared and visible radiation are admitted into the building by the films. The absorption coefficient ranged from $0.5x10^6$ m^{-1} to $1.28x10^6$ m^{-1}, the real part of the refractive index ranged from 1.94 to 2.28. The corresponding value of optical conductivity ranged from $0.24x10^{14}s^{-1}$ to $0.6x10^{14}s^{-1}$, the extinction coefficient ranged from 0.025 to 0.064. These properties make the films suitable for photovoltaic application, solar thermal conversion and protective coating materials.

The direct and indirect band gap energies are 2.3 eV and 1.1 eV respectively. The real and imaginary part of dielectric constant ranged from 3.8 to 5.2 and 0.100 to 0.290 respectively. The thickness ranged from 0.0103 to 0.592 μm. These results above suggest that the thin films are suitable for (i) solar fabrication, (ii) for screening off UV radiation that is harmful to human beings and animals, (iii) for opto-electronic devices and (iv) architectural design for cooling or heating buildings etc. These deductions agree with the findings of other researchers on similar ternary thin films (Ezema, et al. 2004, Ezema, 2004). Figure 4 shows the optical micrograph of deposited CuAgS thin film revealing good film uniformity over significant surface area. The films have high absorbance in UV (0.35 μm), in visible (0.39 μm) and in the near infrared (0.99 μm) of the electromagnetic spectrum and also wide energy gap. Hence they could be used to form p-n junction solar cells for photovoltaic generation of electricity and as well serve as good window layers for photocells. With this band gap, most of the incoming radiation would be absorbed by the electrons and will be excited from the valence band into the conduction band thereby narrowing the photon distribution. This is the situation with absorbing materials.

According to (Okujagu, et al. 1997) the visible transmitting film (VTF) has energy band gap ranging from 1.5 eV to 3.0 eV and since CuAgS thin film has band gap of 2.3 eV. It then means that it is a VTF which behaves more like transparent and ionic insulator. A detailed structural / compositional analysis of this film have not been carried out, however, the source composition of a $Cu_2S - Ag_2S$ ratio is 1: 1 There could be variations in the properties of the film reported here due to crystal nature and deposition conditions for the films. The film was tested for conductivity with multimetre and found to be photo-conducting with values ranging from 0.1 mV to 0.6 mV inside the room and 0.6 mV to 15 mV outside the room around 9.30 a.m

CONCLUSION

New ternary thin films of copper silver sulphide using solution growth technique (SGT) have been grown on glass substrate and characterized using a spectrophotometer. From these results, it can be deduced that the thin films have the property of screening off UV portion of the electromagnetic radiation by absorbing, reflecting and admittance of visible and infrared radiation by transmission. These properties confirm the films good materials for coating poultry buildings, eye glasses coating, solar thermal conversion, anti-reflection coating and solar cells fabrication which are in agreement with (Ezema, et al. 2003, Ezema, et al. 2004, Ezema, 2004). The films were found to be photo-conducting with voltage ranging from 0.1 mV to 0.6 mV inside the room and 0.6 mV to 15 mV outside the room around 9.30 a.m Nigeria time

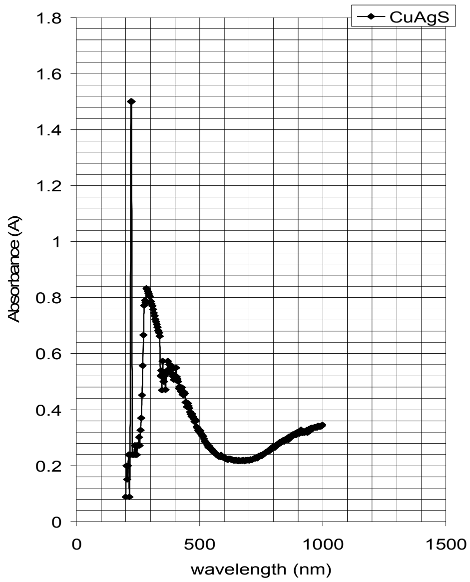

Figure 1 : Absorbance (A) as function of wavelength (λ) for CuAgS Thin Film

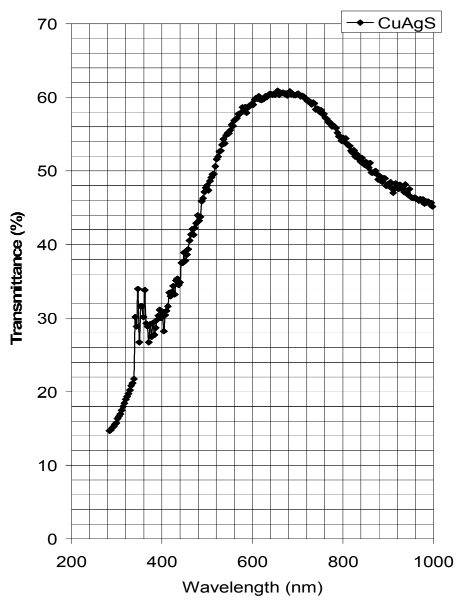

Figure 2 : Transmittance (T) as function of wavelength (λ) for CuAgS Thin Film

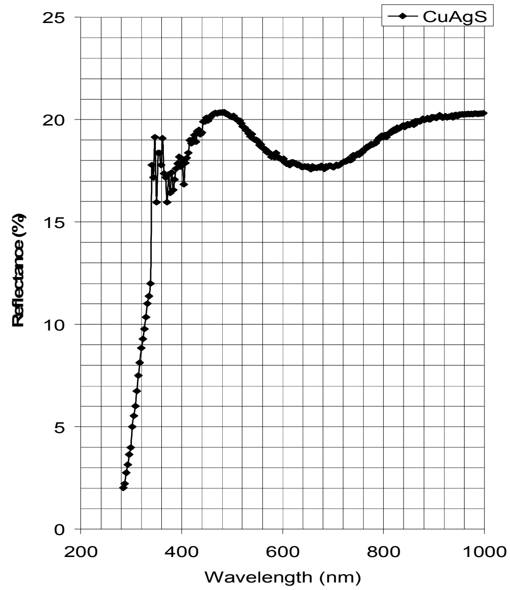

Figure 3 : Reflectance (T) as function of wavelength for CuAgS Thin Film

Figure 4: Photomicrograph of CuAgS thin film

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