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SPECTRAL ANALYSIS AND APPLICATIONS OF CuNiS FILMS.

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ABSTRACT

Thin films of CuNiS were grown on glass substrates by the chemical bath deposition technique. Copper (II) chloride dehydrate, nickel (II) chloride hexahydratee and thiourea were sources of copper, nickel and sulphur ions respectively. Influence of deposition temperature on the optical and morphological properties of the films were determined. The optical characterization was done using a Shimadzu UV 1800 spectrophotometer in the wavelength range of 300-1100nm while an Olumpus microscope at X100 magnification was used to examine and produce the surface microstructure of the grown film. The optical analysis of the film revealed that the average band gap energy was 3.9 eV.

KEYWORDS: Thin film, CuNiS, chemical bath, optical properties, morphological properties.

1. Introduction:

In the past years, synthesis and physical characterization of thin film semiconductors have attracted significant interest. They have a wide variety of applications such as solar cells electroluminescent devices, photoconductors, sensor and infrared detector devices [1]. Modern day technology requires several types of thin film materials, which have been attracting an increasing interest for a variety of applications [2]. Thin films can be made of single or multi- compound (binary, ternary, or quaternary) depending on the elemental composition, alloy/compound or multilayered coatings on substrates of different types, shapes or sizes. Thin film technology is the basis of outstanding development in solid state electronics. The usefulness of the optical properties of metal films and scientific curiosity about the behaviour of two-dimensional solids has been responsible for the immense interest in the study of the science and technology of thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry, and structure of the films [3]. In ever widening sphere of industrial, scientific and technical applications of thin films, the preparation and physical properties of thin films such as optical, chemical, electrical etc. are investigated because they are very useful in many optical, electronic and optoelectronic device applications which include solar energy devices, xerography, switching devices, high resolution lithography, optic memories, photo-detectors etc. [4].

Chemical bath deposition method has been used for the deposition of thin films of sulphides and selenides. The basic principal involved in chemical bath deposition technique is the controlled precipitation of the desired compound from a solution of its constituents. This requires that the ionic product must exceed the solubility product. The use of complexing agent is very common in the preparation of thin films. Many researchers use various complexing agents such as sodium citrate, ammonia, triethanolamine and disodium ethylenediamine tetra-acetate during deposition of thin films [5].

In the present investigation, thin films of CuNiS were prepared from a solution bath containing copper (II) chloride dehydrates, nickel (II) chloride hexahydrate and thiourea as source of copper, nickel and sulphide ions respectively. Ammonium was used as complexing agent during deposition process. The optical properties of CuNiS thin films were determined. Two important factors that should be considered in producing these materials are the band gap energy matching the solar spectrum and the competitiveness of production cost. The rationale for this is that thin films modules are expected to be cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs [6]. Copper nickel sulphide is a semiconductor which is suitable for applications in solar cells, sensor and laser materials. Films of copper nickel sulphide have previously been prepared by chemical bath deposition [7].

This paper reports the spectral analysis and applications of copper nickel sulphide films which were deposited using chemical bath deposition technique. The spectral properties investigated include absorbance, transmittance, reflectance, band gap energy and refractive index.

2. Materials and Methods:

The reagents used in this work include Copper (II) chloride dehydrates, nickel (II) chloride hexahydrate, thiourea and ammonium hydroxide solutions. Copper nickel sulphide [CuNiS] was deposited by the reaction of solutions containing copper (II) chloride dehydrate [$CuCl_2.2H_2O$], nickel (II) chloride hexahydrate [$NiCl_2.6H_2O$], ammonium hydroxide [NH_4OH], thiourea $Sc(NH_2)_2$ and distilled water in a beaker where ammonium hydroxide was used as complexing agent. The addition of ammonia as a complexing agent slowed down the precipitation of metal ions of copper and nickel. Ammonia solution stabilizes or varies the pH of the mixture.

The films were deposited on the glass slides which were used as substrates. The slides before used were previously degreased in hydrochloric acid for 24 hours, washed in cold water with detergent, rinsed with distilled water and dried in air. The degreased-cleaned surface provide nucleation centre for growth of the films, hence yielding highly adhesive and uniformly deposited films. The reaction bath and the cleaned slide were protected from dust particles by the use of synthetic foam cover on which the substrates were suspended. The deposition of CuNiS films were carried out at varying temperatures from 323K - 343K. 10mls of Copper chloride dehydrate and nickel chloride hexahydrate were measured and transferred into the beaker. The mixture was stirred after which 5mls of thiourea was added and stirred to have a homogeneous mixture. Addition of thiourea formed a sky blue jelly – like solution, followed by ammonium solution. The solution was stirred for 5 minutes followed by addition of 40*mls* of distilled water. The first final solution was stirred to have a homogeneous mixture which was put in the water bath and allowed to boil for 1hr. Three depositions were made with deposition temperature 323 K, 333 K and 343 K respectively. The substrates were removed at the end of each deposition temperature, rinsed in distilled water, and dried in air. The chemical equation of the reaction for the deposition is given below:

$$CuCl_2 + 3NH_4 \leftrightarrow [Cu(NH_3)4]^{2+} + 2Cl$$

$$[Cu(NH_3)_4]^{2+} \leftrightarrow Cu^{2+} + 3NH_4$$

$$NiCl_2 + 3NH_4 \leftrightarrow [Ni(NH_3)_4]^{2+} + 2Cl$$

$$[Ni(NH_3)_4]^{2+} \leftrightarrow Ni^{2+} + 3NH_4$$

$$SC(NH_2)_2 + OH^- \leftrightarrow CH_2N_2 + H_2O + HS$$

$$HS^- + OH^- \leftrightarrow H_2O + S^{2-}$$

$$Cu^{2+} + Ni^{2+} + S^{2-} \leftrightarrow CuNiS$$

The sulphide ions are released by the hydrolysis of thiourea but Cu^{2+} and Ni^{2+} ions are from complexes which the solution of $CuCl_2$ and $NiCl_2$ formed with NH_3. The Cu^{2+}, Ni^{2+} and S^{2-} present in the solution combined to form CuNiS molecules which were absorbed on the glass substrate. The heterogeneous nucleation and growth took place by ionic exchange of reactive S^{2-} ions. This process is referred to as ion by ion process and in this way, CuNiS films were deposited on the substrates as uniform and adherent thin films.

3. Results and Discussions.

Optical spectra of CuNiS thin films were recorded in the wavelength range of 300nm – 900nm at varying deposition time. The relation between the absorbance and wavelength of the film at different temperatures is shown in figure 1.

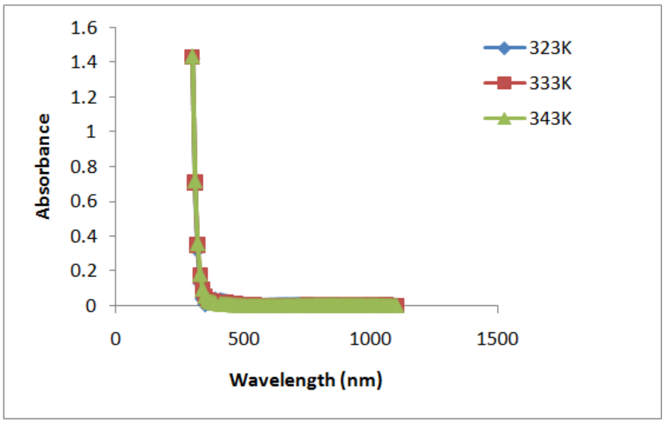

Fig. 1 Absorbance spectra of CuNiS thin films.

The spectra clearly indicate that lower wavelengths correspond to maximum absorbance compared to higher wavelengths. The high absorbance shown by the grown films in the UV region will transmit only negligible amount of UV thereby saving the cell more from overheating resulting from lattice vibrations. The absorbance of the films produced in the visible region indicates the possibility of these materials to be used in the photo electrochemical cells.

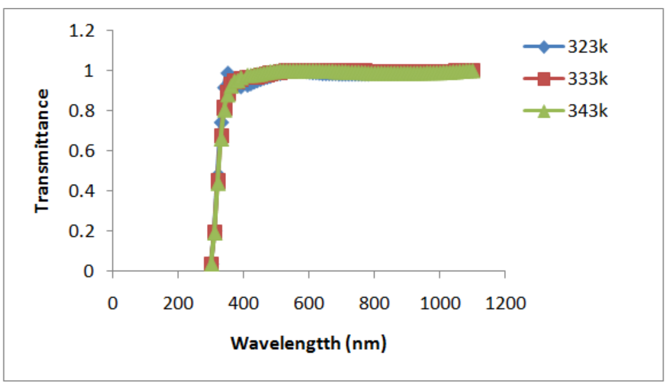

Fig. 2 Transmittance spectra of CuNiS thin films.

The optical transmittance spectra in figure 2 indicate a narrow range of variation with increase in deposition temperatures. The film deposited with higher deposition temperatures shows lower transmittance compared to others. The plots show an average transmission of above 90% in the visible range. All the films at 323K – 353K show gradually increasing transmittance throughout the visible region which makes it possible to use as a buffer layer for solar cell application. The films exhibited higher transmittance at longer wavelengths. The films having high transmittance in NIR region can be used as window coating for the inhabitants in the cold region. Such films are used in the construction of poultry houses because the films allow much infrared heat to penetrate and warm the house.

The optical band gap of the films has been determined from the relation (αhυ) = A (hυ-Eg)n [8, 9 and 10] where A is a constant, hυ is the incident photon energy, α is the absorption coefficient and n is an exponent that determines the optical absorption process. For allowed direct transition $n = \frac{1}{2}$ indirect allowed transition $n = 2$, for direct forbidden $n = \frac{3}{2}$ and finally for indirect forbidden transition n =3. The optical absorption data is used to plot a graph of $(\alpha h\upsilon)^2$ versus hυ (Tauc's plot) where α is the optical absorption coefficient and hυ is the photon energy. The plot is linear indicating the presence of direct transition. Extrapolation of the (fig.3) plot to the x-axis gives the band gap energy of CuNiS films deposited at 323 K, 343 K and 353 K. The band gap value is found to be 3.9 eV. The result compares favourably with the findings of [7] that got the energy band gap of 3.6 eV. This implies that CuNiS has high band gap energy and can be used as an absorber layer of a solar cell. Fig 3 shows that the deposition temperature has no significant effect on the band gap of the films.

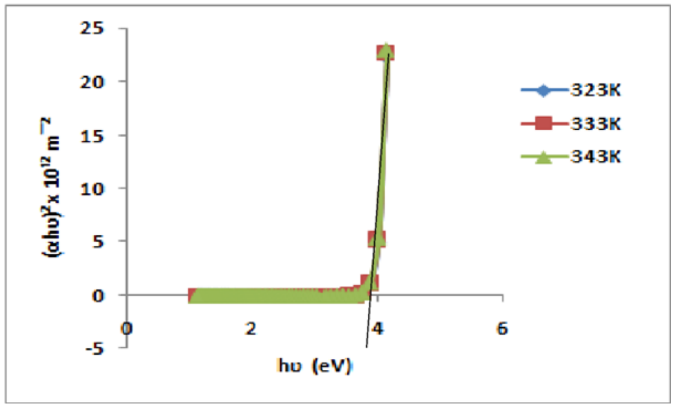

Fig.3 Variation of $(\alpha h\upsilon)^2$ versus hυ for CuNiS thin film at various deposition temperature.

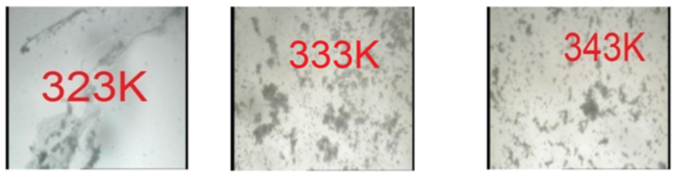

Fig.4 Micrographs for CuNiS deposited at (a) 323 K, (b) 333 K and (c) 343K

The micrograph of CuNiS films prepared at different deposition temperatures are shown in figure 4. Critical observations of the morphologies of the films reveal a clear dependence on the deposition temperature. The film prepared at lower deposition temperature (323K) revealed incomplete coverage of the substrate surface and the grains are not distributed uniformly over the substrate. However, the grains coalescence take place in the films obtained at higher deposition temperature (333K). It has a homogenous and uniform surface. The micrograph of the film deposited at 343 K shows that the substrate is covered completely indicating that more nucleation sites have formed and the number of grains has increased. On the other hand, the grain size increases as the deposition temperature increases from 323 K to 343 K according to micrographs.

4. Conclusion.

The spectral analysis and applications of CuNiS thin films have successfully been investigated. There was no significant influence on the spectral absorbance, transmittance and band gap energy of the films at varying deposition temperature. Substantial influence was obtained on micro structural properties of CuNiS films as the deposition temperature are increased resulting to the formation of more nucleation sites and increase in the number of grains.

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