STUDIES OF CHEMICAL BATH DEPOSITED CuNiS NANO THIN FILMS

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Abstract:

Thin films of CuNiS were grown on glass substrates by solution growth deposition (SGT) technique. Copper chloride, nickel chloride and thiourea were used as sources for copper, nickel and sulphur ions respectively. The complexing agent used was ammonia solution. The effects of volume of ammonia on the optical properties and thickness were determined. A nano film was produced when 15mls volume of ammonia was used. The compositional analysis of the grown films was done by using energy dispersive X-ray fluorescence (EDXRF) technique. The optical properties of the deposited films were investigated by measuring the optical absorbance of the films at the normal incident of light in the range 200-1000nM. This was done with the aid of a Janway 6405 UV-VIS spectrophotometer. The optical absorption data shows that the films absorb high in the ultra-violent region of 0.40-0.50μm. The film thickness was calculated using the optical method when transmittance, reflectance and absorption coefficient were known. The thickness calculated when 15mls of ammonia solution was used was of low value which correspond to nano range of 0.050μm. The plot of α^2 versus photon energy hυ showed a direct band gap range of 2.2eV.

Keywords: *nano thin films, solution growth, CuNiS, Composition, applications.*

Introduction:

Intensive research have been performed in the past and present years to study the fabrication and characterization of thin films. This is as a result of low conversion efficiency of the existing solar cells [1], more so, to find the best thin film that can be used in nano technology. Consequent upon these, scientists are growing various thin films to find which among them can boost the energy conversion efficiency as well as those that can be used in nano industries. Nano science is the study of phenomena in a nano scale. That is the science of object with typical sizes of 1-100nm.[2]. When matter is reduced into such small object, the mechanical, electrical, optical and magnetic properties also change. Interfaces rather than bulk properties dominate. Quantum effects due to the size limitation comes into play.[2].Nanoscience and nano technology are inter disciplinary, crossing boundaries between physics, chemistry, chemical, electrical and mechanical engineering. Nano science and nano technologies have huge potential to bring benefits to many areas of research and applications, and are attracting rapidly increasing investment from government and business in many parts of the world. There applications raise new challenges in the safety, regulatory or ethical domains.[3] Nanoscience has impacted into our lives with innovations such as information storage, computing, advanced applications in energy, medicine and elsewhere. For instance, in the field of medical sciences, nanoscience is used to detect the cancerous bacteria in the human body at the early stages. Again, a three dimensional structure known as nano-electro-mechanical systems.(NEMS) has been fabricated to carry out tasks too small for humans to do themselves. Also, from the principle of nanoscience, smart drugs are manufactured. A smart drug is the drug that will effectively target the areas that they need to target for effective eradication of the cause of the ailment an individual is suffering from.

Furthermore, there are many other areas in which nano technology has potential applications. Its progress will affect a wide range of industries such as cosmetics, house hold appliances, buildings, communications, security and defense, automotive and aerospace industries among others. Nano thin films can also benefit the environment as well as improving the production of cheap energy. Another applications of nanotechnologyare in the field of sports like tennis balls and golf balls. It is also applied in the manufacture of high performance tires, in the manufacture of fabrics with properties anti blemish or wrinkle,in cosmetics and drugs The new therapeutic treatments are also applications of nano structured materials. Nano materials are are also used in the design for new materials in the electronics and transport industries. There are other applications of nano materials which are too numerous to mention. The grown CuNiS nano thin films can be used for cheaper solar production and as well applied nano technology devices . This findings were not found in its equivalent II-VI semiconductor thin films (CuS). [4].

Several thin film deposition techniques have been used in fabricating thin films. Solution growth technique has been discovered to be one of the best because of its cost effective and low temperature range [5].The solution growth method produces quality films for solar cells, and solar thermal control in buildings [6]. This report the effects of variation of the volumes of ammonia on the optical properties and thickness of CuNiS films

Experimental Details:

The growth of CuNiS thin films on glass slides was carried out using chemical bath deposition technique. The glass slides were previously degreased in hydrochloric acid for 24 hours, washed with detergent, rinsed in distilled water and dried in air. The acid treatment caused the oxidation of halide ions in glass slides used as substrate thereby introducing functional groups called nucleation and epitaxial centers on which the thin films were grafted. The degreased cleaned surfaces have the advantage of providing nucleation centers for the growth of film hence yielding highly adhesive and uniformly deposited films.The reaction bath for the deposition of CuNiS contained 10mls of 1.0M of $CuCl_2$, 10mls of 1.0M of $NiCl_2$, 10mls of 1.0M of $SC(NH_2)_2$ and 10mls of 14.0M of Ammonia.50mls of distilled water was added to make up 90mls in a 100ml beaker. Ammonia solution was used for dual purposes as a complexing agent as well as provision of alkaline medium for the growth. The function of the complexing agent is to slow down the reaction in order to eliminate spontaneous precipitation.

The chemical equation of the reaction for the deposition is given below:

$CuCl_2 + 3NH_4 \longleftrightarrow [Cu\ (NH_3)_4]^{2+} + 2Cl^-$

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

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

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

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

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

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

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 adsorbed on the glass substrates.This process is referred to as ion by ion process and in this way, CuNiS films were deposited on glass slides as uniform and adherent thin films. Five depositions were made with five different volumes of ammonia as shown in the table below. For each deposition, the glass slide which was mounted on the beaker with the synthetic material was taken out of the beaker, rinsed with distilled water and allowed to dry in air. The thin films grown were characterized for optical absorbance using Janway 6405 UV – VIS spectrophotometer.From the values of absorbance obtained, other properties such as film transmittance, reflectance, thickness and band gap energy were determined through theoretical calculations. These optical properties were obtained in the wavelength range of 280nm – 1000nm.

Table 1: Preparation of CuNiS thin films with varied volumes of ammonia

Slide No	**Vol. $CuCl_2$ (ml)**	**Conc. (M) $CuCl_2$**	**Vol. $NiCl_2$ (ml)**	**Conc. (M) $NiCl_2$**	**Vol. $SC(NH_2)_2$ (ml)**	**Conc. (M) $Sc(NH_2)_2$**	**Vol. NH_3 (ml)**	**Vol. Distilled H_2O (ml)**	**Dip. Time (hr)**
F6	10.0	1.0	10.0	1.0	10.0	1.0	5.00	50.0	12.0
F7	10.0	1.0	10.0	1.0	10.0	1.0	7.25	50.0	12.0
F8	10.0	1.0	10.0	1.0	10.0	1.0	10.00	50.0	12.0
F9	10.0	1.0	10.0	1.0	10.0	1.0	12.50	50.0	12.0
F10	10.0	1.0	10.0	1.0	10.0	1.0	15.00	50.0	12.0

Results and discussion:

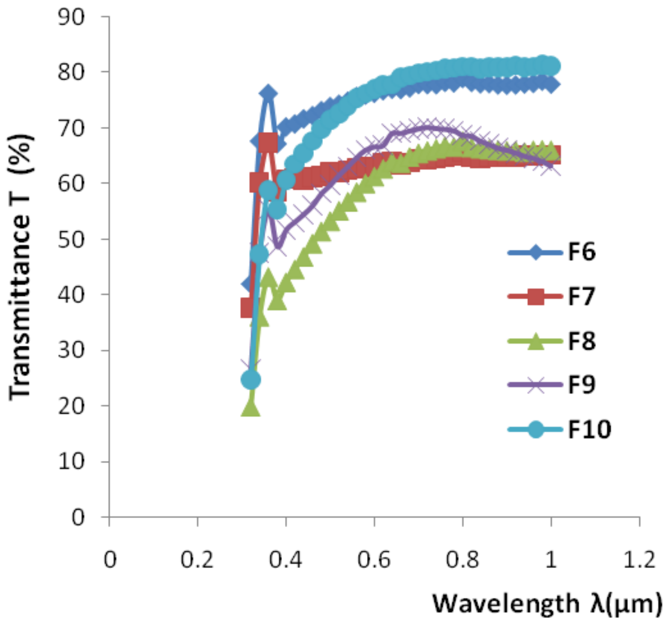

Fig. 1: Spectral transmittance of CuNiS thin film (Slide F_6-F_{10})

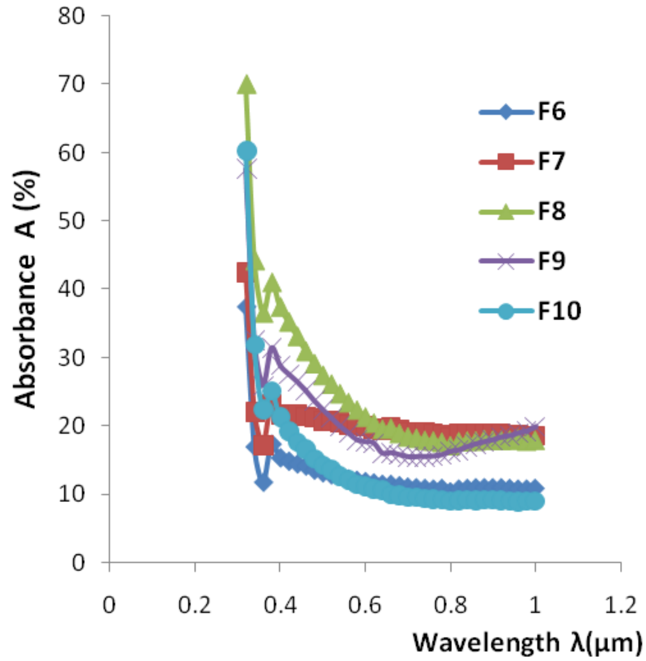

Fig. 2: Spectral absorbance of CuNiS thin film (Slide F_6-F_{10})

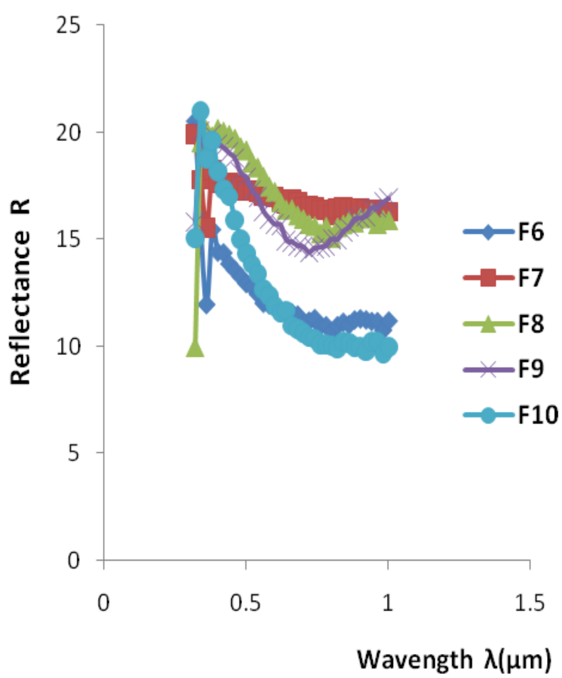

Fig. 3: Spectral reflectance of CuNiS thin film (Slide F_6-F_{10})

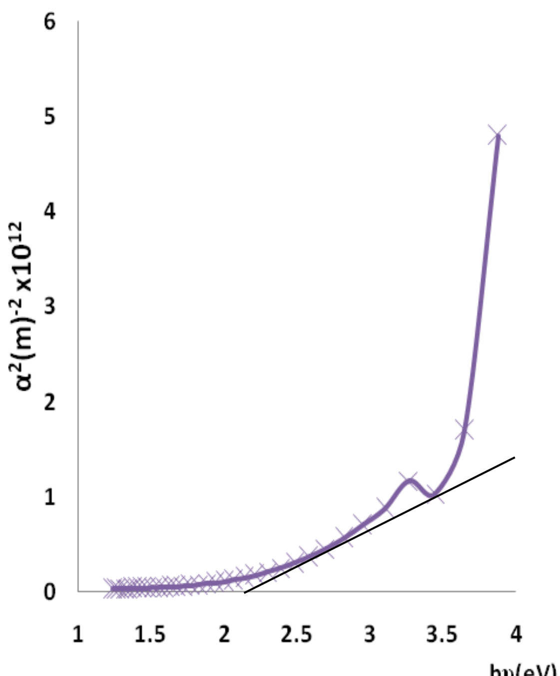

Fig. 4 A plot of absorption coefficient squared versus photon energy for F_6 - F_{10}

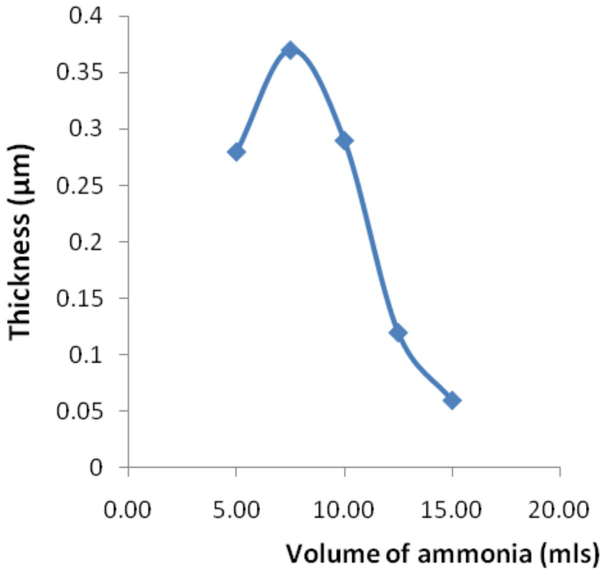

Fig. 5: Variation of thickness with volume of ammonia for CuNiS thin film (slide F_6-F_{10})

The transmittance spectra of copper nickel sulphide thin films grown in this work at a room temperature are shown in figure 1.0. A close observation of the plot reveals that the transmittance of CuNiS is high across the UV, VIS and NIR regions. Thin films of high transmittance values are used for photosynthetic coatings. This is because such films exhibit selective transmittance of photosynthetic active radiation which is useful in the process of photosynthesis. Again, thin films of high transmittance in visible and near infrared regions are be used for coating in windows for those living in the cold parts of the world and in poultry houses where they provide warmth to the chicks [7]

Figure 2 shows the absorbance spectra of CuNiS prepared in this work. The plot reveals that the films have low absorbance values in visible and near ir regions. This is in agreement with what [8] who reported on the optical properties of Ni doped CuS. The low absorbance value of the deposited films indicates that the films are of high transmittance in the visible and near infred regions. From the figure it is observed that only the thin film grown with 10mls of ammonia solution has the highest absorbance value in the UV region. This particular thin film can also be used to coat windows for solar control in the hotter parts of the world. This is because the harmful UV rays will be absorbed leaving inside cool.

The reflectance spectral of CuNiS thin films are displayed in figure 3. The plot reveals that the reflectance of the films are low across the regions of the UV, VIS and NIR regions of electromagnetic spectrum. This is in agreement with what [9] reported on CuS thin films. This implies that the introduction of transition metal Ni exhibits same reflectance property. Films of low reflectance are used as anti-reflection thin films which are used to coat the flat plates of solar cell collectors in solar energy production. This film is very important because it prevents the loss of incident solar radiation by the process of reflection in solar collector plates.

The optical band gap of CuNiS thin films is shown in figure 4. The band gap value is determined through the plots of absorption coefficient squared α^2 versus the photon energy hυ. An average band gap value of 2.2eV was obtained from the graph. This is done by extrapolating the straight portion of the graphs to a value of $\alpha^2 = 0$. The value of the photon energy becomes the energy gap. It is noted that the band gap of CuNiS thin film obtained above is 2.2eVand is less than the band gap of CuS (2.6 eV and 2.9eV) as reported by [10]. This in agreement with what [11] reported on the effect of transition metal doping on II-VI semiconductors. The band gap of the film is high and can be used to coat the absorber layer of a solar cell.

Figure 5 is a plot of thickness versus volume of ammonia. The thickness values were calculated using the optical method. A close observation of the plot reveals that the thickness value first increases as the volume of ammonia increases until it reaches a terminal value of 0.37μm when 7.5mls of ammonia was used. The least value of 0.05μm was obtained when 15mls of ammonia was used. This implies that a nano thin 0f CuNiS can be produced when 15mls of ammonia is used in the preparation. These films(nano films) have various applications to mankind.Only few are discussed in the introduction.

Compositional Characterization

The determination of the composition of thin films is very necessary particularly for films deposited by CDD growth technique and electro chemical deposition methods. In this research, the compositional analysis was done with Energy dispersive x-ray fluorescence (EDXRF) technique. This was done for a period of 3000 seconds after which the spectrum was saved for quantitative analysis. In this work, samples F_5, F_8 and F_{10} were selected for this analysis. Cd^{109} source was used to analyze the quantity of Cu while ^{55}Fe was used for the determination of the quantity of sulphide. The contents of Cu^{2+}, Ni^{2+} and S^{2-} for various films are shown in table 2 below.

Table 2 Compositional analysis of Cu_{1-x} Ni_x S thin films

Slide No	Composition (x)	Cu content Wt%	Ni content Wt%	S content Wt%	ImpurityCl_2 Wt%
F_6	0.100	52.17	1.81	45.00	1.00
F_8	0.150	51.19	3.98	44.83	-
F_{10}	0.300	50.77	4.14	44.09	1.00

From the composition studies, the grown films are slightly rich in Cu^{2+} whereas S^{2-} is almost constant. The above table shows that the content of Cu^{2+} decreases with increasing nickel content. This also show that as the volume of ammonia increases, the Cu^{2+} content decreases while the Ni^{2-}.

Conclusion

CuNiS thin films have been successfully deposited on glass slides using chemical bath deposition techniques. The optical studies showed that the films have low reflectance values in the UV, VIS – NIR regions. This makes the film suitable for coating in solar collector plates as anti reflection films. With these thin films,the loss of incident radiation due to reflection on the solar collector plates is reduced. Also, CuNiS films were found to have high absorbance in the UV region when 10mls of ammonia used. This property makes the film a good material for solar control coatings. The thickness of the film was calculated using the optical method. Its values are of the range 0.05μm – 8.50μm.A thin film of 0.05μm is of the range of nanoscale The importance of these films are found in different aspects of life as seen in the introductory aspect of this research.The film band gap energy was determined to be 2.2eV. From this large band gap value, the films are used to coat the absorber layer of solar cell. The high transmittance value of the visible and near infrared regions makes the films good materials for coating in poultry houses.

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