

## INFLUENCE OF MOLAR CONCENTRATION OF NICKEL (Ni) ON OPTICAL PROPERTIES OF COPPER NICKEL SULFIDE (CuNiS) THIN FILMS.

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### ABSTRACT

*Thin films of copper nickel sulfide (CuNiS) were prepared by a simple inexpensive successive ionic layer adsorption and reaction (SILAR) method using ammonium hydroxide (NH<sub>4</sub>OH), hydrated copper chloride (CuCl<sub>2</sub>·2H<sub>2</sub>O) and nickel chloride (NiCl<sub>2</sub>·6H<sub>2</sub>O) and thiourea SC(NH<sub>2</sub>)<sub>2</sub>. The deposited films were optically characterized by ultraviolet-visible-near infra-red spectrophotometer. An Olympus BH2-UM microscope at 100x magnification was used to examine and produced the photomicrographs of the films. The influence of molar concentration of nickel precursor on the optical properties of the films was investigated. Optical analysis reveals a high transparent and low reflectance films, and direct band gap energy ranging from 2.9 eV to 3.9 eV. These characteristics make the film good candidates for application in photo transistors, photovoltaic, transparent electrodes and anti-reflection coatings.*

**KEYWORDS:** Thin film, copper nickel sulphide, absorbance, transmittance, band gap energy, optical thickness.

### 1. INTRODUCTION

There has been an increase in the cost of the non-renewable energy sources. This has led to the search for an alternative source of energy to maximize the depletion source of these fossils. Renewable energy sources are the only way of providing cheap energy to about two billion people who live in isolated rural area of the developing nation with minimum level of comfortable living [Cinolkosz et al., 2017]. Research is ongoing in all aspects of renewable energy sources; this research is focused on how to develop solar energy systems and technologies to provide electricity in the rural areas. The renewable sources of energy include solar energy, wind energy, mini and micro-hydro energy, geothermal energy and biomass.

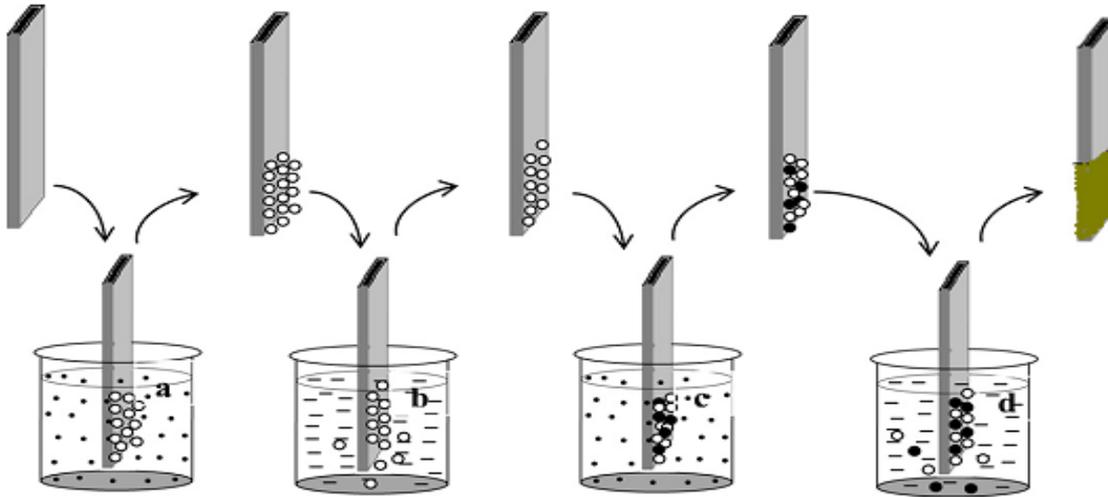
All renewable energy resources trace back to the sun. Solar energy is a source of free, natural and non-polluting, abundant energy that man can harness for useful application. Energy plays a major role in man's struggle with the sudden change of nature than merely sustaining life [Agrafiotis,2005]. The amount of energy that reaches the earth's surface in the form of solar radiation per year is  $3 \times 10^{24}$ J, which is approximately two orders of magnitudes larger than the total energy stored in all the known reserves of fossil fuels ( $24 \times 10^{22}$ J). [Agrafiotis,2005] also stated that there are many solar energy conversion methods, which includes among others, the photovoltaic (PV) methods.

When the thin films are coated on substrates and characterized, the results will show whether the films have properties that will make it suitable for solar applications. For example, if they are highly transmissible through the ultraviolet, visible and near infrared regions, they will be used for thermal control coatings, optical coatings, microelectronics, surface science engineering and technology.

This paper reports the optical and morphological analyses of CuNiS films which were deposited using SILAR method. The spectral properties investigated include absorbance, transmittance, reflectance, band gap energy.

## 2.MATERIALS AND METHOD.

Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), copper chloride dehydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), thiourea [ $\text{SC}(\text{NH}_2)_2$ ], distilled water, glass slides and beaker were used for the fabrication of CuNiS films.



**Figure 1: Schematic diagram for the deposition of CuNiS thin films by SILAR method.** ( $\circ$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ;  $\bullet$ ,  $\text{S}^{2-}$ ): (a)  $\rightarrow$  cationic precursors, (b)  $\rightarrow$  ion exchange water, (c)  $\rightarrow$  anionic precursor and (d)  $\rightarrow$  ion exchange water.

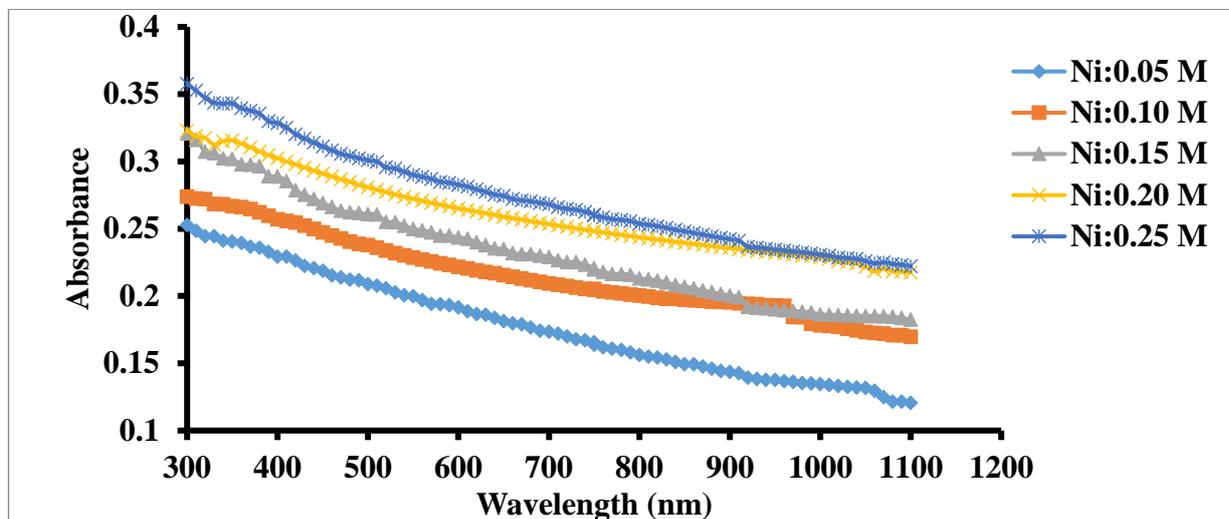
The growth of copper nickel sulfide (CuNiS) thin film was carried out by the successive ionic layer adsorption and reaction (SILAR) method at room temperature. The method comprises the successive immersion of substrate in cationic precursor solution and anionic precursor solution maintained at room temperature. Aqueous solutions of  $0.2\text{M}(\text{Cu}(\text{OH})_2$  and  $\text{Ni}(\text{OH})_2$  were used as the cationic precursor solution while  $0.1\text{ M SC}(\text{NH}_2)_2$  (thiourea) was used as anionic precursor solution. Aqueous solution containing  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  prepared by mixing concentrated  $\text{NH}_4\text{OH}$  with  $50\text{ ml}$  of  $0.2\text{ M CuCl}_2 \cdot 2\text{H}_2\text{O}$  until blue  $\text{Cu}(\text{OH})_2$  was precipitated. Further addition of  $\text{NH}_4\text{OH}$  resulted in the dissolution of the precipitates. Also, aqueous solution containing  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  was prepared by mixing  $\text{NH}_4\text{OH}$  solution with  $50\text{ ml}$  of  $0.1\text{ M NiCl}_2 \cdot 6\text{H}_2\text{O}$  until green  $\text{Ni}(\text{OH})_2$  was precipitated. Further addition of  $\text{NH}_4\text{OH}$  resulted in the dissolution of the precipitate. Both solutions of  $(\text{Cu}(\text{OH})_2$  and  $\text{Ni}(\text{OH})_2$ ) were mixed together and stirred for about  $5$  minutes resulting to a cationic precursor which becomes the sources of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , while  $50\text{ ml}$  of  $0.1\text{ M SC}(\text{NH}_2)_2$  (thiourea) was used as anionic precursor.

Pre-cleaned substrate was immersed in the reaction in a beaker containing cationic precursor solutions of  $0.2\text{ M}(\text{Cu}(\text{OH})_2$  and  $\text{Ni}(\text{OH})_2$  for  $30$  seconds so that copper and nickel ions [ $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ] adsorbed on the substrate followed by  $10$  seconds rinsing in distilled water to remove loosely bound species of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . Next, the substrate was immersed in anionic precursor solution of  $0.1\text{ M}$  thiourea [ $\text{SC}(\text{NH}_2)_2$ ] for  $30$  seconds. The sulfide ( $\text{S}^{2-}$ ) ions reacted with absorbed  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  on the active center of the substrate to form CuNiS films. The substrate was finally rinsed in distilled water for  $10$  seconds to remove loosely bound ions of copper, nickel and sulfide present on the substrate. In this way one SILAR cycle of CuNiS deposition was completed and  $40$  such deposition cycles were repeated to get a uniform film with the desired thickness.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Optical Properties of the Deposited Copper Nickel Sulfide (CuNiS) films.

Optical studies were carried out in the wavelength range of 300-1100 nm to investigate the optical absorption properties of CuNiS thin films. Figure 2 shows the variation of absorbance for CuNiS film as a function of wavelength ( $\lambda$ ). The change in the optical absorbance is observed as molar concentration of nickel is increased. These changes are attributed to structural and crystallinity changes taking place when nickel is incorporated in the CuS lattice. The result shows that the deposited CuNiS thin films have moderate absorbance in ultraviolet (UV) region which decreases towards the visible (VIS) and near infrared (NIR) regions. A peak absorbance value of 0.36 at 300 nm (UV region) was obtained for the film deposited with 0.25 M concentration of nickel while minimum absorbance value of 0.25 was obtained for film deposited with 0.05 M in the same region. The result obtained is in line with the result of [Okereke and Ezenwa, 2015].



**Figure 2: Variation of absorbance of Copper Nickel Sulfide thin film with wavelength.**

Figure 3. shows the variation of transmittance with wavelength. The result shows that CuNiS thin films have low transmittance in UV which increases towards VIS and NIR regions. A maximum transmittance value of 75.74 % at 1100 nm (NIR region) was obtained for the film deposited with 0.05 M concentration of nickel while minimum transmittance value of 59.96 % was obtained for the film deposited with 0.25 M in NIR region. This result is comparable with the value of greater than 60 % transmittance obtained by Otthi et al, [2011]. The obtained results show that transmittance of deposited films decreases as molar concentration of nickel ion increases. It also revealed that absorbance has opposite behavior as compared to the transmittance.

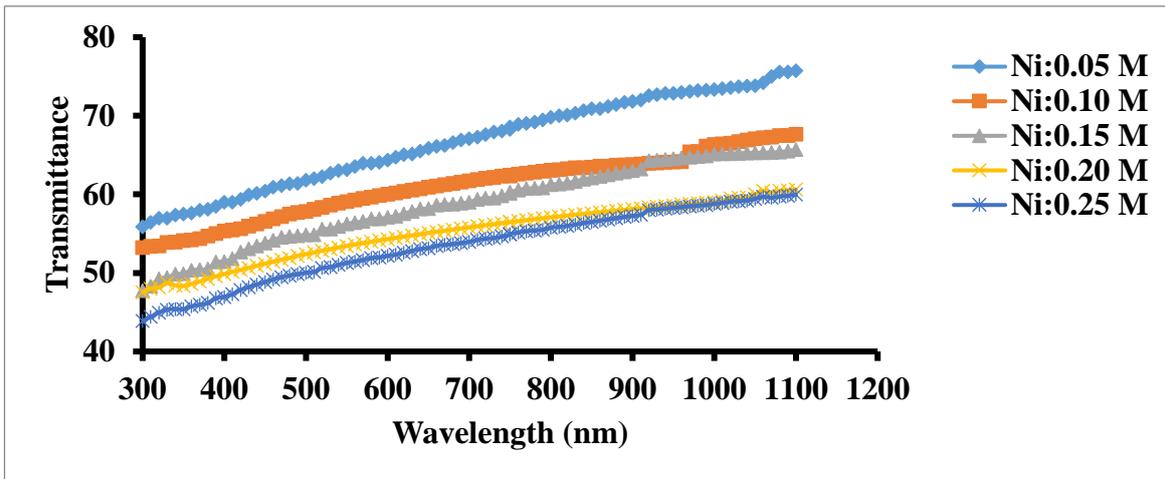


Figure 3.: Variation of transmittance of Copper Nickel Sulfide thin film with wavelength.

Figure 4 shows the graph of reflectance of Copper Nickel Sulfide thin film against wavelength. The reflectance increases slightly as wavelength increases in all the regions of the electromagnetic spectrum under study. The result shows that the deposited films of CuNiS are of low reflectance value and this shows the possibility of using these deposited films in antireflective coating industry. Film deposited with 0.05 M concentration of Ni<sup>2+</sup> has minimum reflectance value of 18.84 % in UV region while a maximum reflectance value of 20.35 % was obtained for the film deposited with 0.25 M concentration of Ni<sup>2+</sup> in the same region. This indicates that reflectance of the films increases as the concentration of nickel precursor increases.

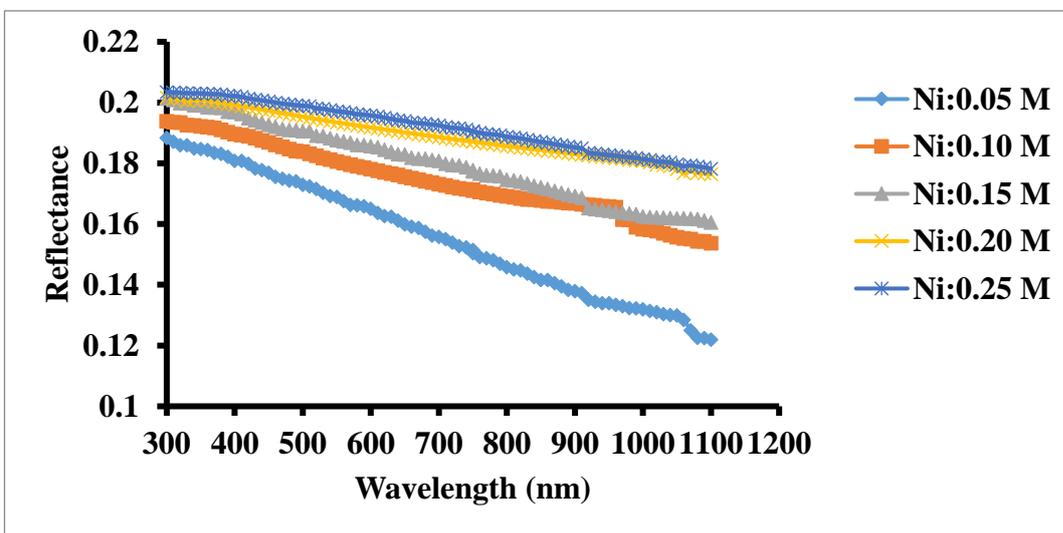
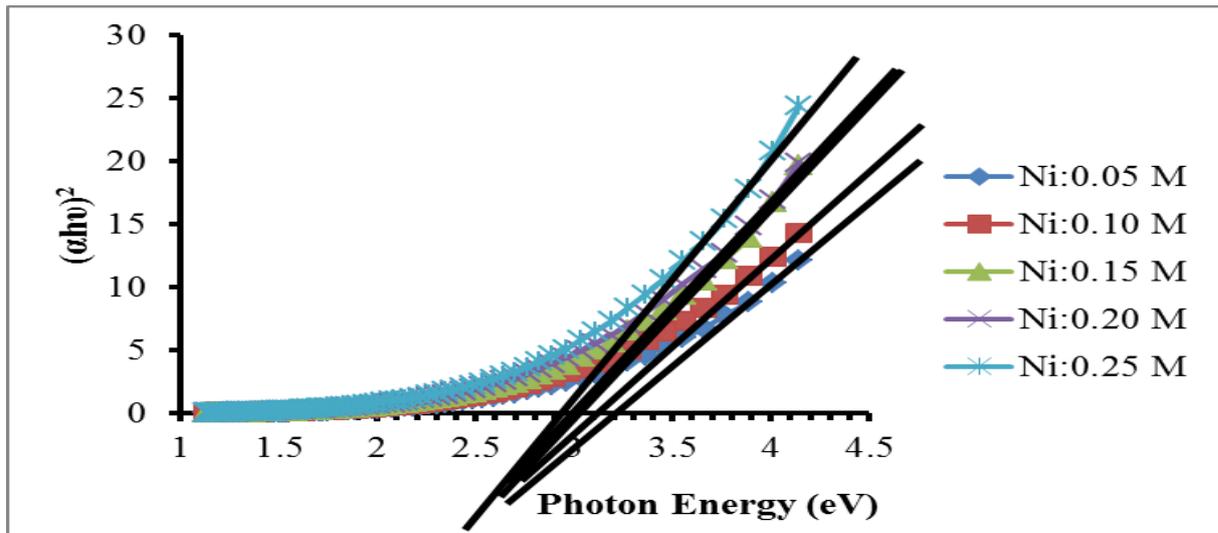


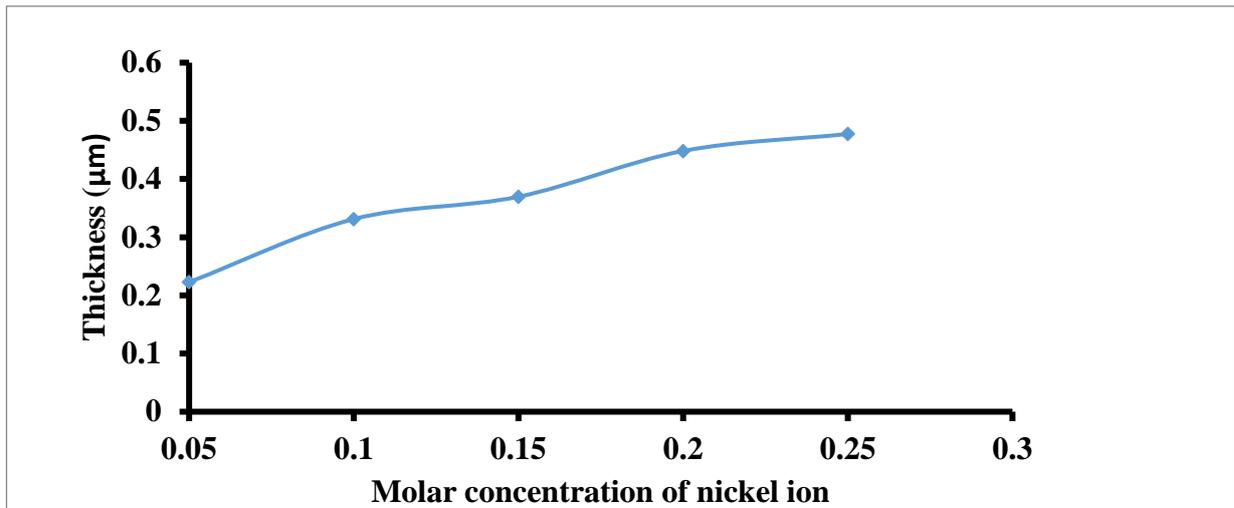
Figure 4: Plot of reflectance of Copper Nickel Sulfide thin film against wavelength



**Figure 5: Plot of  $(\alpha hv)^2$  of Copper Nickel Sulfide thin film against photon energy.**

Figure 5 shows the graphs of  $(\alpha hv)^2$  against photon energy ( $hv$ ) for films of 0.05 M, 0.10 M, 0.15 M, 0.20 M and 0.25 M concentration of  $Ni^{2+}$  precursor. The plot is linear indicating the presence of direct transition. The direct band gap energy was extrapolated at the axis of the photon energy ( $hv$ ) where  $(\alpha hv)^2 = 0$ . The band gap values are found to be 3.2 eV , 3.1 eV , 3.0 eV , 3.0 eV and 2.9 eV indicating decrease in band gap as the molar concentration of nickel ion increases. In semiconductors, several effects contribute to change of the energy gap value with respect to the change in bath parameters. In the present case, varying parameter is molar concentration of nickel precursor. The decrease in the band gap energy for CuNiS thin films grown at varying molar concentration of nickel ion could be viewed as increasing the energy of electrons in the materials. Lower energy is therefore needed to break the bond. Reduction in the bond energy of a material also reduces its band gap. These results compare favorably with the values of energy band gap obtained by Okereke and Ezenwa, [2015] who obtained the band gap energy of 3.90 eV, Ottih et al, [2011] whose value of band gap energy is 3.60 eV and Feng, [1994] whose range of band gap energy is between 3.34 eV to 3.74 eV. The above results show that the deposited CuNiS film has wide band gap energy and can be used as an absorber layer of solar cell.

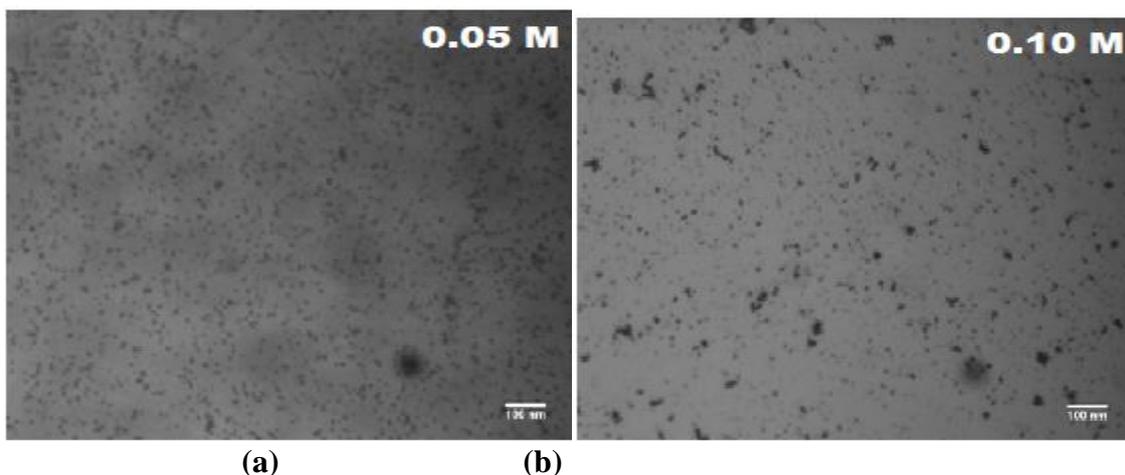
Figure 6 gives the average optical thickness as a function of molar concentration of nickel precursor. Optical thicknesses of CuNiS films were found to be 0.22  $\mu m$ , 0.33  $\mu m$ , 0.39  $\mu m$ , 0.45  $\mu m$  and 0.48  $\mu m$  respectively. Peak value of thickness was found to be 0.48 $\mu m$ , while the least value of optical thickness was 0.22  $\mu m$ . Optical thickness of the films increases as molar concentration of nickel ion increases.



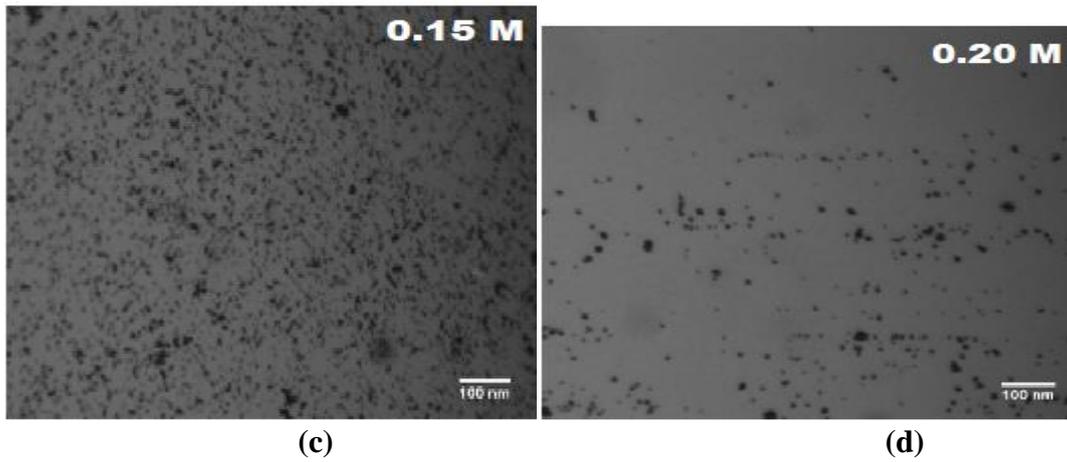
**Figure 6: Plot of optical thickness against molar concentration of nickel precursor.**

### 3.2 Micro structural Analysis

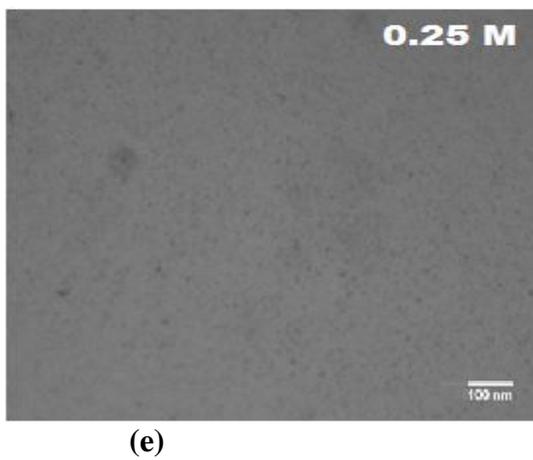
Optical microscopy is a promising technique for the morphology study of samples, as it provides valuable information regarding the growth mechanism and shape of the particles and grains. The optical microscopic images of the deposited CuNiS films in figure 7 (a-e) for films deposited with 0.05 M, 0.10 M, 0.15 M, 0.20 M and 0.25 M of nickel ion precursor reveal the uniform distribution of spherical grains over total coverage of the substrate with a compact and fine grained morphology. The microscopic images depict the presence of particles of varying sizes which suggest that the deposited films are polycrystalline in nature. Image-J for Microscopy Image Analysis [Abramoff et al., 2004] software was used to determine the average particle size of the films from the micrograph images. The average particle size was found to be between 26.18 nm and 11.70 nm as shown in table 3.1. The particle count shown in the table, reveals the number of possible particles contained in the sample.



**Figure 7(a-b): Optical micrograph of CuNiS film deposited with 0.05 M & 0.10 M nickel.**



**Figure 7(c-d): Optical micrograph of CuNiS film deposited with 0.15 M & 0.20 M nickel.**



**Figure 7e: Optical micrograph of CuNiS film deposited with 0.25 M nickel.**

**Table 1: Image-J Analysis of Microscopic Image of Deposited CuNiS Films**

Samples (a-e)	Count	Average Size (nm)
0.05 M	9022	11.70
0.10 M	8130	26.18
0.15 M	3300	18.30
0.20 M	2348	14.56
0.25 M	2452	15.15

#### 4 SUMMARY AND CONCLUSION

We have successfully deposited CuNiS thin films onto non-conducting microscopic glass substrates using Successive Ionic Layer Adsorption and Reaction (SILAR) method at room temperature. To achieve the said deposition of CuNiS, some reagents such as Copper chloride dehydrate; nickel chloride hexahydrate, thiourea, ammonium hydroxide and distilled water were used. Copper chloride was the source of  $\text{Cu}^{2+}$  while Nickel chloride hexahydrate served as precursor for  $\text{Ni}^{2+}$ , thiourea served as precursor for  $\text{S}^{2-}$ , ammonium hydroxide was used as a pH adjuster and EDTA served as complexing agent for slow precipitation of the cations ( $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ) from the solution. The deposited films of CuNiS were subjected to optical and microstructural characterizations. The optical characterization was achieved with the use of Stellar Net UV – VIS – NIR spectrophotometer (Blue-Wave Miniature; Model: UVNb). The micrographs of the films were obtained using Digital Microscope of magnification of 100X at Centre for Energy and Research Development (CERD), Obafemi Awolowo University, Ile-Ife, Osun State. The absorbance result obtained showed that CuNiS thin films are moderately absorbing films with absorbance values ranging from 0.36 to 0.12. The absorbance of the films increases as molar concentration of nickel precursor increases but decrease with increase in wavelength. Transmittance results revealed a high transmittance mostly in visible light and near infrared region. The transmittance decreases as molar concentration of nickel ion increases. Reflectance of the films is generally low as a result; it could be regarded as a non-reflective thin film material. The band gap energy of the deposited films ranged from 3.20 eV to 2.90 eV.

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