African Journal of Basic & Applied Sciences 8 (3): 152-156, 2016
ISSN 2079-2034

DOI: 10.5829/idosi.ajbas.2016.8.3.22836

Effect of pH on Properties of CoSe Thin Films Deposited by Chemical Bath Technique

[1]*P.E. Agbo,* [1]*P.A. Nwofe,* [2]*R.A. Chikwenze and* [1]*D.A. Famuyibo*

[1]Division of Materials Science & Renewable Energy, Department of Industrial Physics, Ebonyi State University, Abakaliki, Nigeria
[2]Department of Physics, Federal University, Ndufu-Alike Ikwo, Nigeria

Abstract: CoSe thin films were successfully grown using the solution growth technique in order to determine the effect of bath pH on the properties of the films. The films were investigated using morphological, structural and optical characterization techniques. The morphological characterization was done using Scanning Electron Microscopy; structural characterization was done using X-ray diffractometry (XRD) while Optical spectroscopy was used for the optical characterization. The obtained results show the film is polycrystalline. The refractive index was in the range 1.60 - 2.38 while the bandgap is in the range of 2.80 – 3.10. Our results also indicated that the properties of the films discussed varied linearly with pH except for the films deposited at bath pH of 9.3.

Key words: Chemical bath · pH · Transmittance · Absorbance · Refractive index · Bandgap

INTRODUCTION

The search for new and advanced materials in solar energy conversion through photo- electrochemical cells and chalcogenide thin films are increasily been investigated. Similarly, there has been growing interest in developing thin films of late transition metal selenides for optoelectronics applications because of their properties which includes bandgaps that is matchable to the maximum of solar spectrum, a high optical absorption good electrical conductivity etc [1]. Worthy to note also is the fact that selenium based compounds have properties that cover the range of ionic crystal – semiconductor metal-superconductor including ferro-and ferri-magnetism [2, 3]. All these properties make the alloy useful in electrical, optical and magnetic devices such as power switches, magnetic devices, sensors etc [2]. CoSe a member of the transistion metal selenides shows promising properties such as high optical absorption coefficient of the order of 10^5 cm^{-1} bandgap of approximately 1.5eV and a good electrical conductivity. The film of CoSe had been employed recently in solar energy conversion [3, 4]. In this work, the chemical method is used to deposit thin film of CoSe. The aim is to find the effect of pH on the properties of the deposited film.

MATERIALS AND METHODS

Preparation of Reagents: The entire chemicals used were of analytical grade. They include sodium selenoslphite, colbalt II chloride, liquor ammonia (25% liq.NH_3), TEA. Sodium selenosulphite a source of selenium ions was synthesized by adding 12g of anhydrous sodium tetraosulphate VI to 5g of selenium metal into 200ml of water, stirred and heated at 90°C for 1 hour. The temperature of the resulting solution (Na_2SeO_3) was allowed to drop to room temperature, the solution was filtered to remove the undissolved selenium and the solution stored in an airtight container. The deposition was carried out on a commercially available, non-conducting micro-glass slides which served as the substrate. The slides were cleaned by washing with concentrated hydrochloric acid for one hour followed by rinsing in acetone and finally with distilled water and ultrasonically dried. Five samples of CoSe thin films were

Corresponding Author: P.E. Agbo, Division of Materials Science & Renewable Energy, Department of Industrial Physics, Ebonyi State University, Abakaliki, Nigeria.

deposited from five different reaction baths which consisted of 5ml, 1M $CoCl_2$, 10ml TEA, 5ml 1M Na_2SeO_3, 40ml of distilled water and Xml of NH_3 were X is equal to 1.0, 2.0, 4.0, 5.0 and 7.0 representing pH values of 8.4, 8.7, 9.2, 9.3 and 9.6 respectively. The deposition was allowed to take place for 10 hours at a temperature of 338 K. All the samples were subjected to post deposition annealing at a temperature of 373 K.

Characterisation: The XRD study of the deposited CoSe thin films were studied in the range of diffraction angle (2θ) 10° – 80° with CuKα(λ=1.54056Å) radiation using a Philips PW-170 diffractometer. The thickness of the film was determined using a weight difference method while the film morphology was done using Scanning Electron Microscope (SEM). The optical absorption measurements were made in the wavelength range of 200- 1200 nm by using UV 3600 Shimadzu UV-VIS-NIR double beam spectrophotometer at room temperature. An identical, uncoated glass substrate in the reference beam made a substrate absorption correction.

RESULTS AND DISCUSSION

Growth Mechanism: The rate of deposition of CoSe thin films is a function of super saturation, pH and temperature of the bath and the composition of the reactive constituents [3]. A series of experiments were performed to optimize the parameter of interest to get a good quality and reproducible films. The deposition process is based on the slow release of $Co^{2+}$and Se^{2-} ions. This is followed by ion-by- ion combination process. Generally, for the deposition to take place the ionic product of Co^{2+} and Se^{2-} must exceed the solubility product. The reaction mechanism is as follows:

$$\begin{aligned}
&CoCl_2 + TEA \leftrightarrow [Co(TEA)]^{2+} + 2Cl \\
&[Co(TEA)]^{2+} \leftrightarrow Co^{2+} + TEA \\
&Na_2SeSO_3 + OH \leftrightarrow Na_2SO_4 + HSe^- + HSe^- \\
&HSe^- + OH^- \leftrightarrow H_2O + Se^{2-} \\
&Co^{2+} + Se^{2-} \leftrightarrow CoSe
\end{aligned} \tag{1}$$

The average thickness of the films as measured using the weight density technique was found to be 420 nm. The film thickness was observed to be lowest at pH of 9.3 while the highest thickness was observed at pH of 9.5.

Film Morphology and Structure: Fig. 1 shows the scanning electron microscopy of the representative sample of the deposited films. The figure shows that the films have well defined boundaries, uninterrupted long chains of particle and well defined grains indicating structural homogeneity. The XRD pattern of the representative sample of the CoSe film deposited in this work is displayed in Fig. 2. The well-defined and narrow peaks in the XRD indicate that the film is polycrystalline in nature. The X-ray diffraction patterns show diffraction peaks at 2θ angles of 28.71, 30.19, 39.49, 40.90 and 41.17 degree corresponding to crystallographic orientations (121), (112), (-222), (212) and (032) respectively according to card number 25-0125 indicating that the film is cubic Co_2Se_3. This is in agreement with result obtained by Pramanik *et al*. [1]. The mean grain size as calculated using the Scherer's formula is 30.61 nm. The average inter planar distance is 2.213 nm.

Optical Properties: The optical properties of the CoSe thin films deposited on glass substrate were recorded on a double beam spectrophotometer at wavelength range of 200 to 1200 nm at room temperature. Reflectance and refraction losses were neglected. The plot of absorbance against wavelength is shown in Fig. 3, while the plot of transmittance against wavelength is depicted in Fig. 4. The absorbance plot indicates that all the film irrespective of the deposition pH absorb very well in the UV region of the spectrum. Highest absorbance was recorded by the film deposited at lowest pH. The trend also show that the films absorbance decreases with increase in the pH of the deposition solution with slight deviation at pH of 9.3. The film deposited at pH of 9.5 has the lowest value of absorbance in NIR and FIR regions while the film deposited at pH of 9.3 has the highest value of absorbance in the NIR and FIR regions.

In Fig. 4 it is observed that the films showed low values of transmittance in the UV region. In the NIR and FIR region all the films transmitted very well. The film deposited at pH of 9.5 recorded the highest value transmittance of about 76%, while the film deposited at pH of 9.3 recorded the lowest value of transmittance of about 47%. This behavior suggests that the films can be used as shields for UV rays.

The observed difference in the absorbance and transmittance behavior could be attributed to the differences in the film thickness at different pH value of

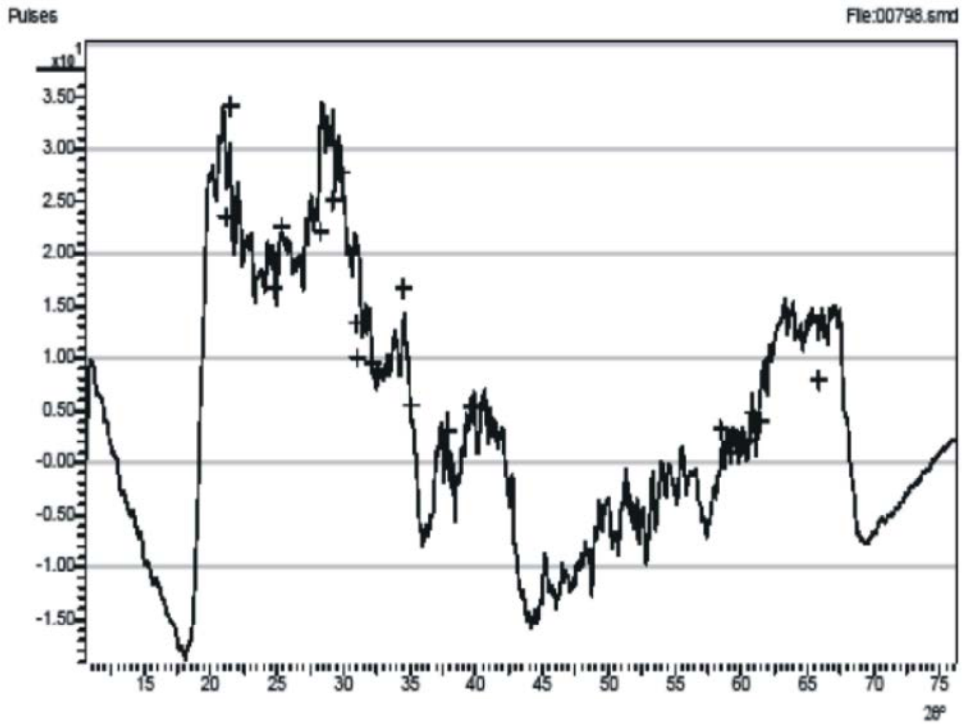

Fig. 1: XRD pattern of representative sample of CoSe

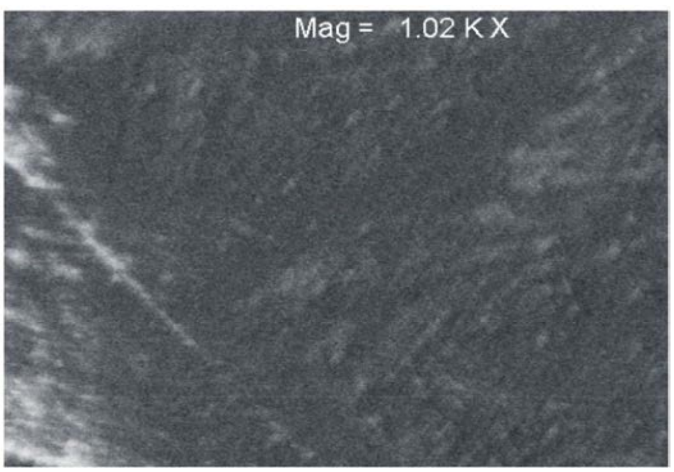

Fig. 2: SEM of representative sample of CoSe thin film

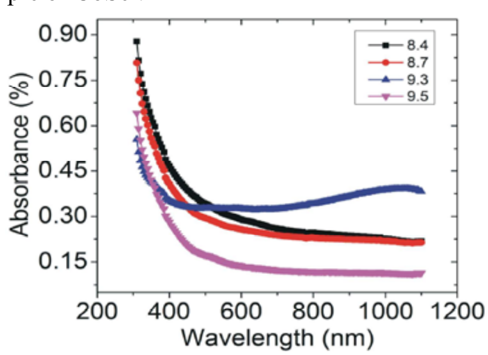

Fig. 3: Absorbance vs wavelengthfor CoSe thin films

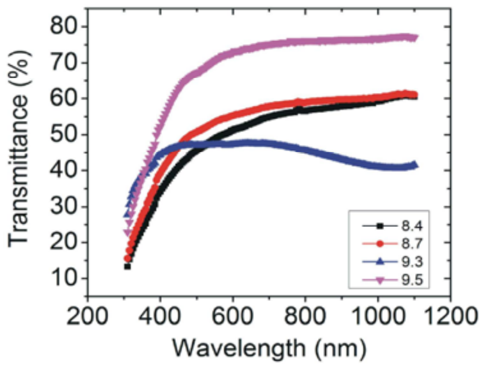

Fig. 4: Transmittance against wavelength for CoSe thin films

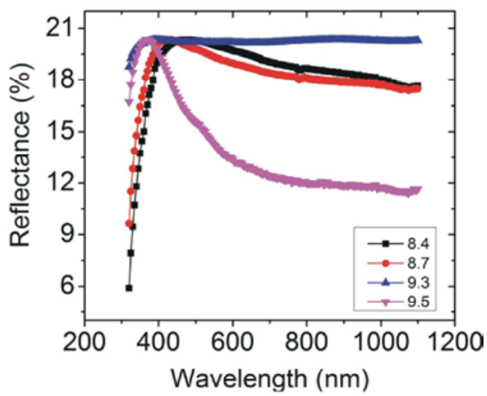

Fig. 5: Reflectance against wavelength for CoSe thin films

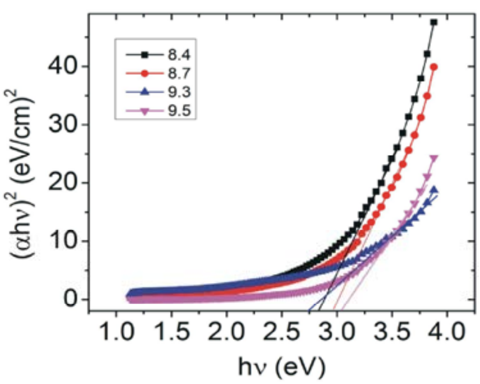

Fig. 6: $(\alpha h\nu)^2$ against hν for CoSe thin films

the solution [5]. The plot of reflectance against wavelength is shown in Fig. 5. The plot indicates that the film deposited at pH of 9.3 and 9.5 recorded the highest value of reflectance in the UV region. The plot equally show that the reflectance were almost constant at the higher wavelength irrespective of the value of pH. Ideally, solar control coatings must enable controlled optical transmittance and low reflectance in the visible region (400-700 nm) [6]. Such characteristics have been shown to provide an adequate natural illumination of the interior of buildings, while rejecting as much of the incident radiation which may lead to an undesirable increase in indoor temperature and thereby increase the cost of indoor cooling in warm areas. In view of these characteristics, we believe that some of the CoSe films can be used efficiently for solar controls.

The variation of absorption coefficient function i.e $\alpha = f(hv)$ with wavelength is shown in Figure 6. The bandgap of the material obeys the relation near the absorption edge as given by:

$$\alpha hv = k(hv - E_g)^n \tag{2}$$

where, K is a constant, λ is the wavelength of the light used, E_g is the bandgap of the material, n is a factor that depends on the type of transition that occurs [1]. When n=1/2, it implies direct transition. Rearranging equation 1 to linear equation of the form y= mx+c, we obtain that y-αhν and x = hν. Thus the linear portion can be extrapolated to the x-axis (i.e. the hν axis) to obtain the value of the bandgap. Therefore Fig. 6 shows the plot of absorption coefficient $(\alpha h\nu)^2$ against photon energy for the films deposited at different pH. The extrapolation of the portion of the graphs gives direct bandgap energies (E_g) of 2.80eV, 2.96eV, 2.69eV and 3.10eV for films deposited at pH values of 8.4, 8.7, 9.3 and 9.6 respectively. The trend clearly indicates that as the pH increases, the bandgap increases except for the deviation at pH of 9.3. The bandgaps obtained are higher than the reported values [1, 8]. The higher bandgaps could be attributed to quantum effects caused by the orderly arrangement of the CoSe structure.

The high transparency in the visible region and the wide direct bandgap exhibited by these films make them good as window layers in heterojunction solar cells [9, 10, 11]. The primary function of a window layer is to form a junction with the absorber layer while admitting maximum amount of light. It is our believe that CoSe stand high as alternative for possible incorporation in CIGS solar cells.

The plot of refractive index against photon energy is displayed in Fig. 7. The plots indicate that between photon energy of 1.0 to 3.5eV, the refractive index were almost constant for the films deposited at different pH. A plateau was observed at approximately 3.5eV before the refractive index began to decrease with increase in photon energy. However the film deposited at pH of 9.3 has the

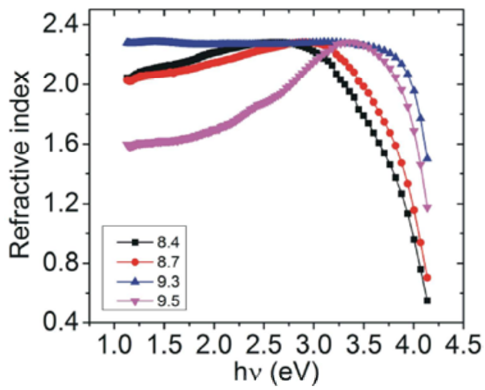

Fig. 7: Refractive index against hν for CoSe thin films

highest value of index of refraction of about 2.38 while the film deposited at pH of 9.5 has the lowest value of refractive index of about 1.6 in the lower wavelength region. The films deposited at pH of 8.4 and 8.7 displayed almost the same trend both in the lower and higher wavelength regions.

CONCLUSIONS

The chemical bath method has been used to fabricate thin film of CoSe. The chemically deposited film was found to be polycrystalline in structure and the grains were orderly arranged. The films optical properties were found to vary with the bath pH. However the variation was not totally linear as the film deposited at bath pH of 9.3 deviated from the linearity in all the properties of the film discussed. And the behavior of the film deposited at pH of 9.3 is suggestive that it may be optimum pH for deposition of CoSe thin films. The films were all transparent in the visible region and the band gap of the films ranges from 2.80 eV to 3.10 eV. The high transparency in the visible region and the wide direct bandgap exhibited by these films make them good as window layers in heterojunction solar cells.

REFERENCES

1. Pramanik, P., S. Battacharya and P.R. Banu, 1987. A solution growth technique for the deposition of cobalt selenide thin film. Thin Solid Films, 149: L81-L84.
2. Agbo, P.E. and M.N. Nnabuch, 2012. Effect of Annealing on the thickness and Bandgap of novel crystalline thin Film. J. Ovonic. Res., 8: 127-133.
3. Nwofe, P.A., K.T. Reddy, R.W. Miles and R.W. Mile, 2013. Influence of Deposition Time on the Properties of Highly-oriented SnS. Thin Films Prepared Using the Thermal Evaporation Method. Adv. Mater. Res., 602: 1409-1412.
4. Agbo, P.E. and P.A. Nwofe, 2015. Structural and Optical Properties of Sulphurised Ag_2S Thin Films. International. J. Thin Film. Sc. Tech., 4(1): 9-12.
5. Nwofe, P.A. and P.E. Agbo, Effect of Deposition Time on the Optical Properties of Cadmium Sulphide Thin Films. Intern. J. Thin. Film. Sc. Tech., 4(2): 63-67.
6. Agbo, P.E., F.U. Nweke, P.A. Nwofe and C.N. Ukwu, 2014. Effects of Concentration on the Properties of Zn-doped Cadmium Sulphide Thin Films, Intern. J. Sc. & Res., 3(11): 1832-183.
7. Agbo, P.E. and M.N. Nnabuchi, 2012. Effect of Annealing on the thickness and Bandgap of novel crystalline thin Film. J. Ovonic Res., 8: 127-133.
8. Hankare, P.P., B.V. Jadhav, K.M. Garadkar, P.A. Chate, I.S. Mulla and S.D. Delekar, 2010. Synthesis and characterization of Nickel Selenide thin films deposited by chemical bath method. J. Alloys & Compds., 490: 228-231.
9. Moloto, N., M.J. Moloto, N.J. Coville and S.S. Ray, 2009. Optical and structural characterization of nickel selenide nanoparticles synthesized by simple methods. J.Crys. Growth, 311: 3924-3932.
10. Petkov, K., R. Todorov, D. Kozhuharova, I. Tcky, E. Cernoskova and P.J.S. Ewen, 2006. Changes in the physiochemical and optical properties of chalcogenides thin films from the system of As-S to As- *S*-Ti, J. Mat. Sci., 39: 961.
11. Agbo, P.E., 2011. Effect of Thermal Annealing on Optical and Band gap of Chemically Deposited /Fe_2O_3 Core/shell Oxide Thin Films. Adv in Appl, Sc. Res., 2(6): 393-399.