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Tuning Some Optical Parameters of SeA_x ($A_=$ Fe:Sn) Chalcogenides Forphotovoltaic Applications.

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Abstract ; *Polycrystalline SeFeSn thin films have been fabricated with different molar concentrations of Iron :Selenium (Fe:Se) using chemical spray pyrolysis at 400K, Spectroscopic measurements within the UV-Vis-NIR range of the thin film samples were studied at room temperature in order to understand their optical properties. The deposited films are characterized by wide bandgapenergies in the range 3.75-3.87eV , the films bandgapwere observed to be tuned from 3.75eV for Fe:Se(0.05:0.05) molar concentration to 3.87 eV for Fe:Se(0.1: 0) molar concentration in a parabolic-increase trend . These demonstrate promising optical properties of the ternary film-samples for photovoltaic technology and good miscibility of alloyed constituents in the Seleniumhost crystal lattice. The refractive index, dielectric constant and extinction coefficient were evaluated, the extinction coefficient shows a decay in value as the molar concentration of Fe increases with a simultaneous decrease in the Sn molar concentration in the multicomponent films.*
Keywords*; Polycrystalline, molar concentrations, spectroscopic measurements, miscibility, photovoltaic, refractive index , dielectric constant, extinction coefficient .*

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I. Introduction

In the last few years, considerable interest has been shown in the synthesis of semiconducting nanocrystalline films for optoelectronic applications. Nanostructured materials based on II-VI group compounds have long been known to be suitable for photovoltaic device applications because of their high optical absorption coefficients [1]. Likewise, Ternary (groupV-VI) compounds of type A_2B_3 (A = Bi and B = S, S_e or T_e) are considered important semiconductor materials due to their low cost fabrication techniques and abundance of the constituent elements [2].

However, the main advantage of binary and ternary chalcogenide semiconductors is seen in their promise of lower cost; since less energy for materials are relatively lower in cost and large scale productions are feasible [3] . Consequently, the synthesis of ternary metal chalcogenidegroups semiconductors in nanocrystalline form has been a rapidly growing area of research due to their important non-linear optical properties, luminescent properties, quantum confinement effect and other important chemical and physical properties [1].

Moreover,Semiconductors based on selenium are important class of semiconducting systems which have been widely studied too due to their fundamental electronics and optical properties. Intensive researches have been performed in the past to study the fabrication and characterization of these compounds in the form of films [4]. Examples are PbSe [5,6], SnSe [4,7], CdSe [8,9], AgSe [10], ZnSe [11] and SbSe [12]. Furthemore, Several researchers have investigated the optical and structured properties of Iron Selenide (FeSe) [4,7,13]. Literatures equally revealed some binary compounds with selenium as one of their components such as; Bismuth Selenide (Bi_2Se_3) and Silver Selenide (Ag_2Se) as narrow bandgap semiconductors with n-type conductor which are applicable in; switching devices, infra red detectors and thermoelectric generators [14].

Also, the pseudo-binary alloy $Fe_{0.03}Sn_{0.97}$ has been found to be a p-type semiconductor which could be used as a suitable material for the fabrication of thermoelectric devices [15].

In this study , we investigate the optical properties of thin-film of ternary compound formed from a combination Tin,Iron and Selenide (FeSnSe) prepared by spray pyrolysis with the hope of developing a material that could act as a substitute to the conventional silicon-based solar cell.Eventhough the combination contained earth abundant elements with high absorption coefficient and good stabilities but there have been no reports in the literature for the optical and electrical properties of the multicomponent thin film . Optical parameters such as;absorbance, transmittance, reflectance, absorption coefficient, energy band gap, optical conductivity and dielectric constants of FeSnSe would be revealed in our studies.

II. Materials and Methods

2.1 Substrate Preparation

Owing to rigidity,hardness , chemical inertness, flat and smooth surface with good transmission characteristics of the substrate needed for this investigation , borosilicate glass was used . The substrates were first washed with detergent and distilled water to remove contaminant and glass-stains, then ultrasonically cleaned for ten minutes with isopropyl alcohol. Dried and kept in desiccator for a later use .

2.2Materials Used

The materials used in the deposition of Iron-Tin- Selenide (SnFeSe) by spray pyrolysis are:

i. Tin chloride ($SnCl_2$)
ii. Iron chloride ($FeCl_2$), and
iii. Selenium dioxide (SeO_2)

The precursors used for samples fabrication were prepared following six different compositions,the variation in molar concentration of the elements at each spray is as display on ''table 2''

Table 2, The Molar ratio of Fe:Sn (Moles) in Selenium

Samples	Fe	Sn	Se
A	0.00	0.10	0.20
B	0.05	0.05	0.20
C	0.06	0.04	0.20
D	0.07	0.03	0.20
E	0.08	0.02	0.20
F	0.10	0.00	0.20

With the aid of syringe which was well washed, cleaned with distilled water and ethanol,2ml ofmethoxyethanol was added to eachprecursor to slow down the reaction sufficiently.

2.3 Methodology

Spray pyrolysis prove to be a method suitable for the deposition of large area metal oxide, spinel oxide, and different chalcogenide thin films [16,17]. This process is widely applied and very attractive for the deposition of low cost thin film photovoltaic solar cells . The set- up is shown in ''Fig 1''.

During the spray pyrolysis process, the precursor aerosol was sprayed towards the heated substrate. The component in the precursor droplets react to form film on the substrates surface and some by-productsvaporized into the open atmosphere.Since high temperature was involved, the sparying-chamberwas kept from moisture to avoid spark. The deposition time was 10 minutes and the deposition temperature was kept at 400°C.

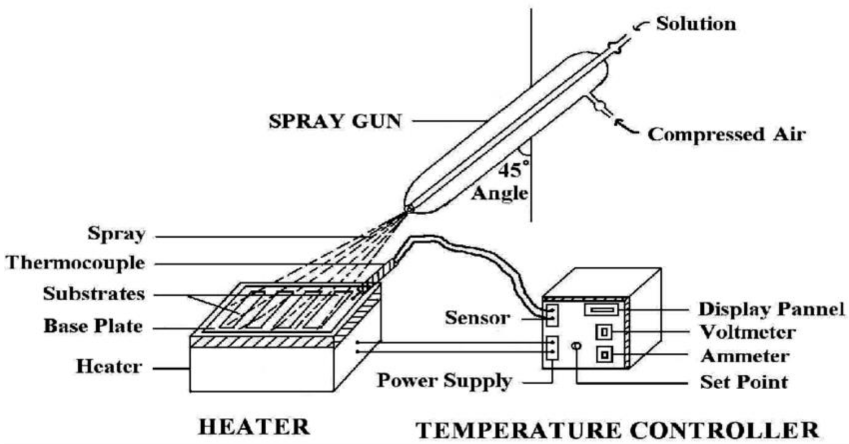


Figure 1, Spray Pyrolysis Deposition Apparatus [18]

Six samples from six different composition of precursors were use separately. After each deposition, the spraying chamber is cleaned before been re-used ,the Metal-chalcogenide thin films deposited on glass slide were cooled by air quenching and used as prepared.

The basic chemistry involved in the complex ion formation of the thin-film ofSnFeSeduring the spraying processes is as presentedbelow;

$SeO_2 + H_2O \rightarrow Se + H_2 + O_2 (g)$

$FeCl_2 + H_2O \rightarrow Fe + 2HCl + H_2O_2$

$SnCl + H_2O \rightarrow SnO + HCl$

$SnO + C_2H_5OH \rightarrow Sn + C_2H_4(OH)_2$

$Sn^{2+} + Fe^{2+} + 2Se^{2-} \rightarrow SnFeSe_2$

III. Measurements

In both crystalline and amorphous semiconductors, the absorption coefficient near the fundamental absorption edge is dependent on photon energy. In the high absorption region, the absorption coefficient takes on the following more general form as a function of photon energy ;

$\alpha hf = A(\alpha hf - E_g)^n$where; n=1/2 for direct transitions and2.1

$\alpha hf = B(\alpha hf - E_g)^n$ Where; n=2for indirect transitions 2.2

where ;*f* is the frequency of the incident photon,*h* is the Plancks constant, *A* and *B* are constants, and $E_g$is the optical energy gap . α is the absorption coefficient given by;

$\alpha = \frac{Absorbance}{optical\ density} = 2.303(A/t)$ 2.3

where;*A*isabsorbance and *t* is the film thickness.

The optical transmittance *T*is related to the absorption coefficient α and Refractive index *n* by ;

$T = (1-R)2exp(-\alpha d)/(1-R_2)exp(-2\alpha d)$2.4

The extinction coefficient *K* is related to α by ;

$K = \alpha\lambda/4\pi$ 2.5

The optical conductivityσ_o is given by ;

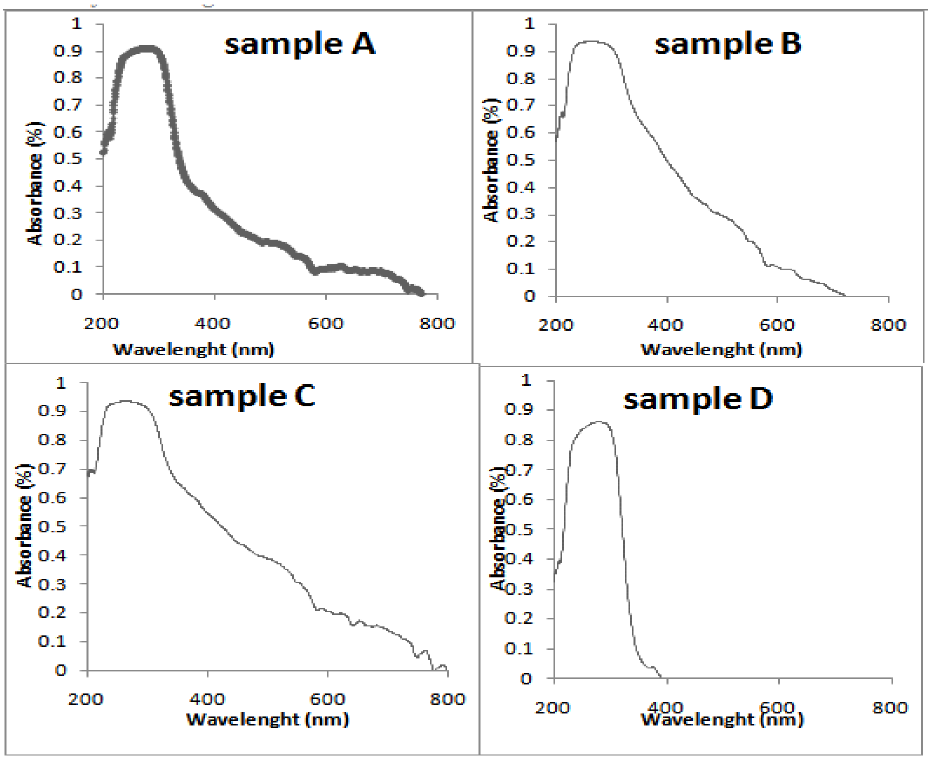
$\sigma_o = \alpha nc/4\pi$2.6 Where; *c* is the velocity of light , In metals, σ_o and k are very high as reflectance approaches unity.

The dielectric constantε is related to *K* and *n* ,it is defined as the response of the material towards the incident electromagnetic field. The dielectric constant of a compound is divided into two parts: real and imaginary, and can be written as ;

$\varepsilon^* = \varepsilon_r + i\varepsilon_i$ 2.7

IV. Result and Discussions

The thicknesses of the deposited films as determined by Profiliometer were within the range of 100nm – 105nm. The optical properties such as; absorbance, reflectance etc, of the film-samples were determined by Spectrophotometer within UV-Vis-NIR (200nm to 800nm) range , the spectrophotometer works in conjuction with a computer aided with an Avasoft software .



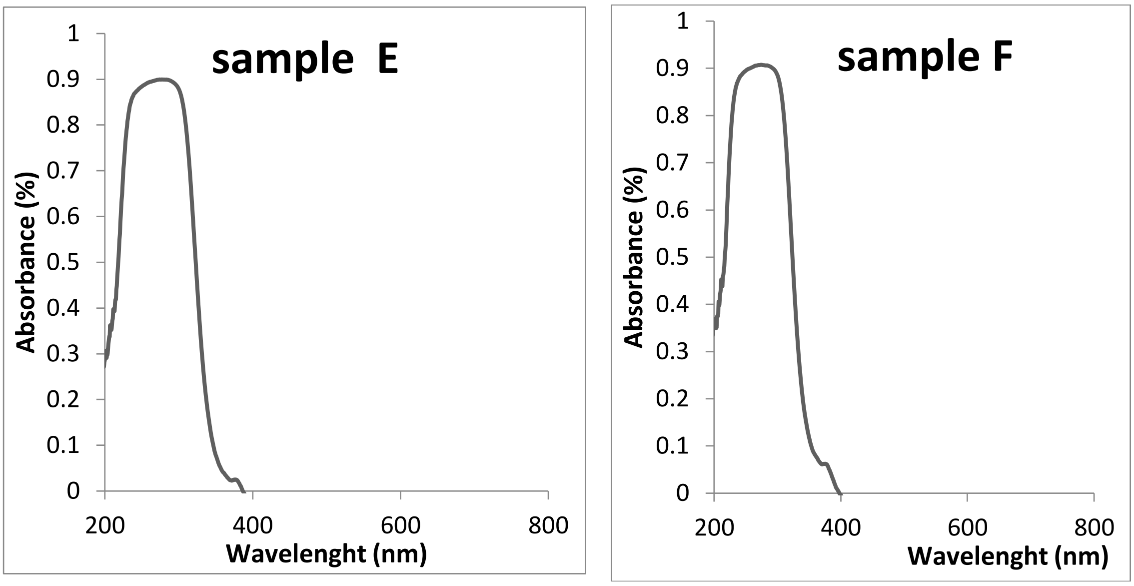
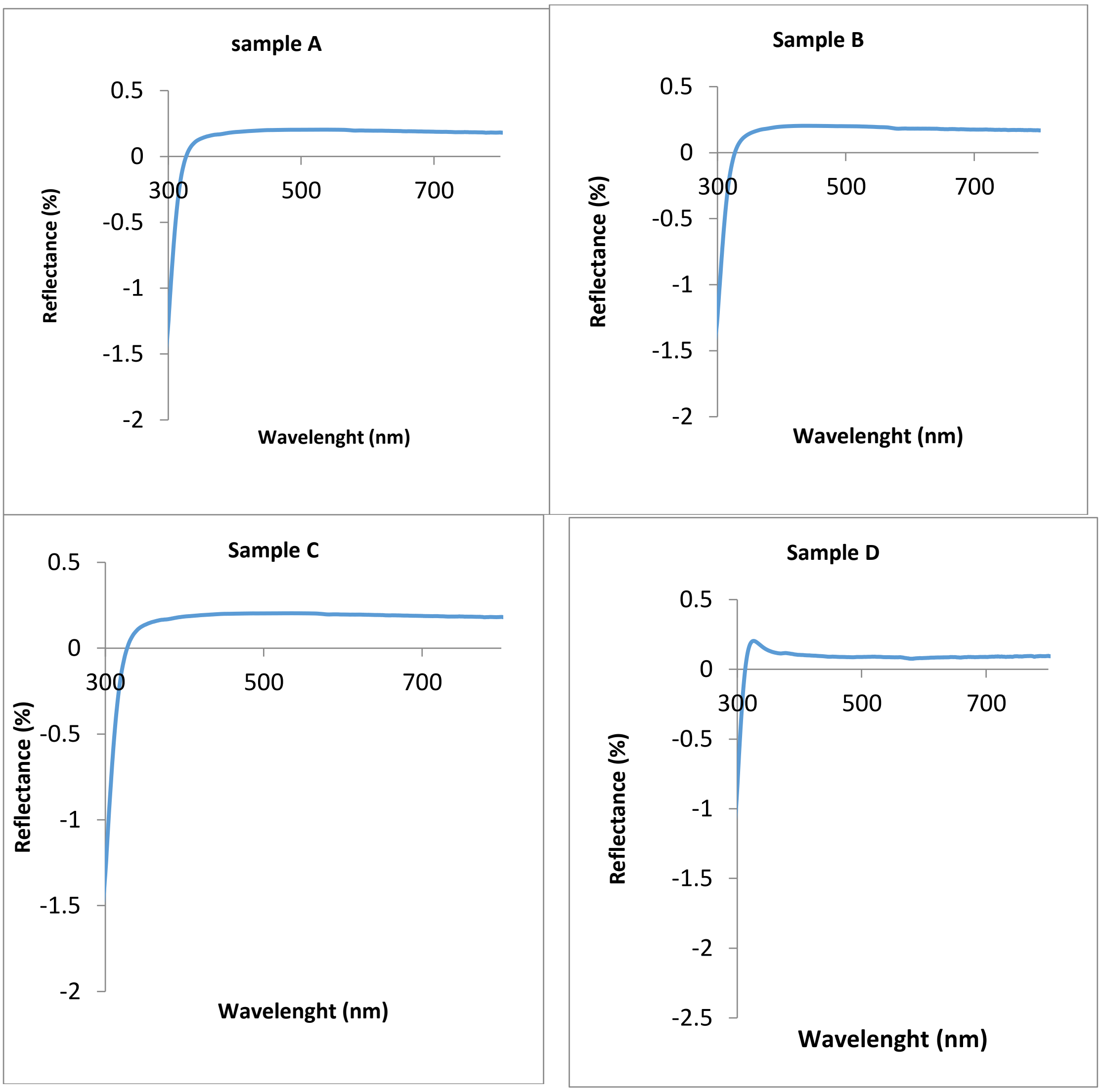


Figure 1, Absorbance Spectra of the different Samples.



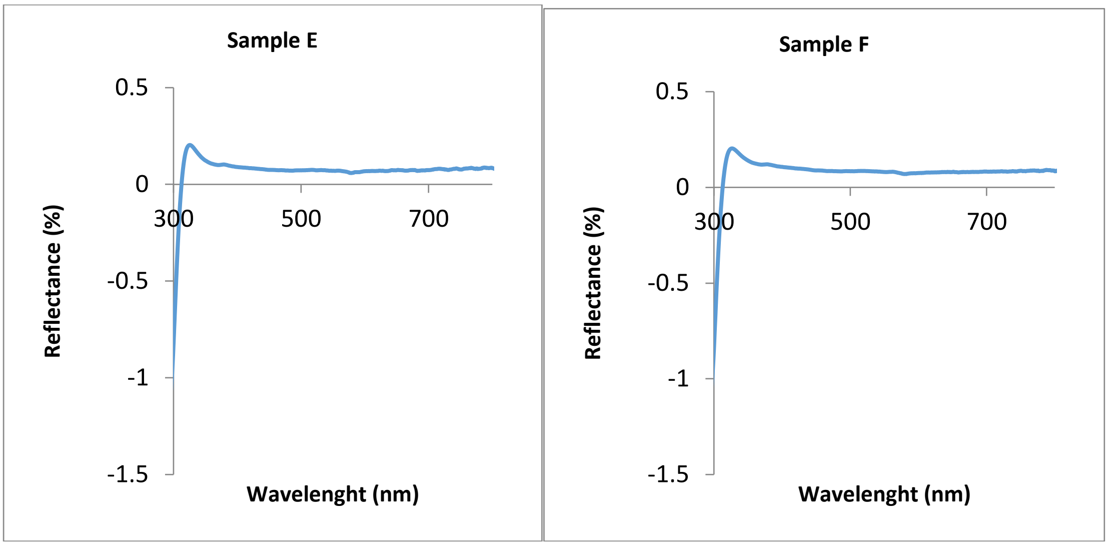
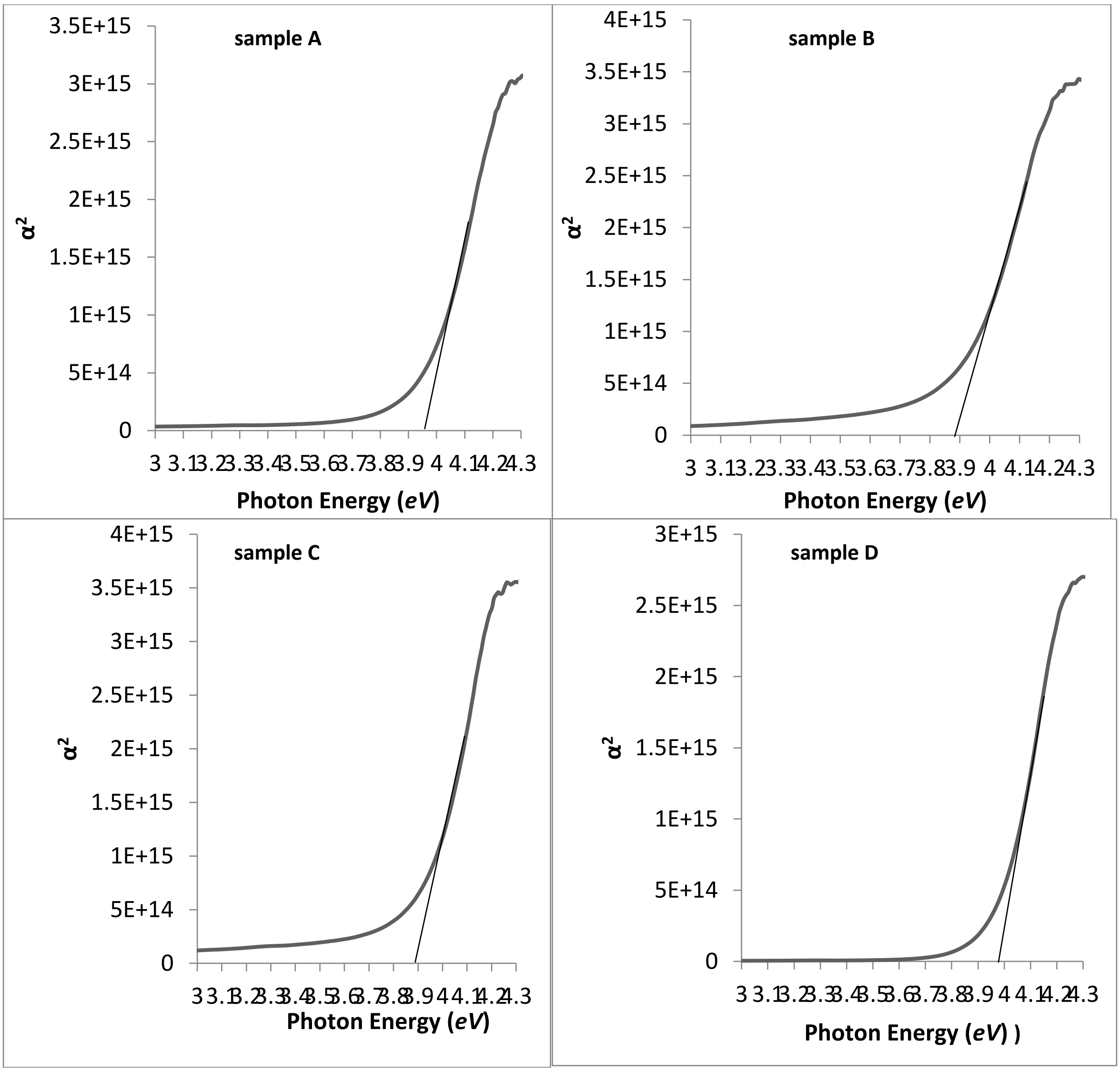


Figure 2, Reflectance Spectra of the different Samples.



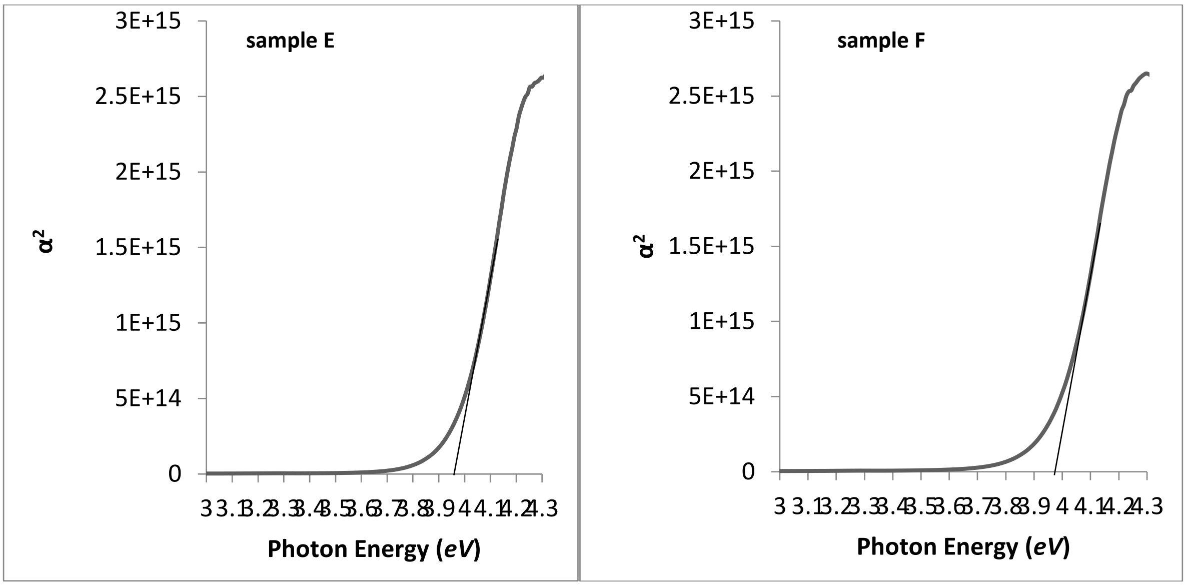


Figure 3, α^{2}versus Photon Energy (*eV*) for the different Samples.

The absorption Spectra for the different Se:Fe concentrations in the samples are shown in ‘’fig 1’’. From the graph , it is clear that there is an improvement in optical absorption spectra of samples A,B and C within the visible region while samples D , E and F recorded Zero value of absorption in same region. However , all samples examined had improved absorption in the Ultra-violent region . In general, the intensity of absorption peak was recorded in the UV-Vis region followed bya sudden decay inVis-NIR region, It is evidence that samples D,E and F which recorded virtually Zero absorbance in the Vis – NIR region could be used as transparent conducting material.

‘’Fig 2’’ shows how the reflection response changes in the different film-samples examined.Within theUv-Vis-NIR range nearly all thesamples recorded low reflectance except for a very little improvement for samples A ,B and C, this reflects the information that nearly all the samples could be used as anti-reflector materials.

The plots of α^2versus Photon Energy *(E=h√)* for the different Samples are depicted in ‘‘fig 3’’. The forbidden gap / Energy gap (E_g) is obtained by the extrapolation of the linear portion of the curve to α^2 =0 (where$E=h\surd = E_g$). However, the summary of results obtained from the plots is display on a bar chart in ‘’fig4’’. It is evident that the E_g recorded for the film-samples falls within the range 3.75 – 3.85eV , the peak value of 3.87eV was recorded in sample F while sample B had the lowest $E_g$of 3.75eV, also samples A and E are of equal value of $E_{g.}$ .These revealed the fact that all the film samples are wide band-gap material that could be useful in photovoltaic technology.

Other parameters recorded in the course of furthering investigation onthe optical properties of the thin-samples are shown in ‘’fig 5-8’’. The refractive indices obtained are within the range 2.77 -3.60 with sample A having the highest and B with the least . The extinction coefficient takes the value 1.54 - 4.43 , sample C had the highest and E the least. For the optical conductivity (σ_o)of the samples, the highest value of 56.5 was obtained for sample A and the lowest 4.21 for sample F , generally there is a decrease in σ_o as the Molar concentration of Snincreses/Fe decreases . In addition , the dielectric constants recorded were in the range 15.34 -29.92 with sample A having the least and B having the highest.

In summary,the high value of the refractive index equally attestedto the usefulness of SeFeSn –ternary films in photovoltaic applications, alsothe highest value in dielectric permittivity recorded by sample B (where Fe:Sn is 0.5:0.5M) can be attributed to the equal contributions of the multicomponent polarizability, which are deformational and relaxation. Deformational polarizability is the mutual displacement of the oppositely charged partciles under the action of applied field. On the other hand, the relaxation plorizability originated from limited mobility of the permenantdipoles usually at lower frequencies. The unequalmulticomponent polarizabilitycontributions brought about the low values of ε recorded in the other samples.

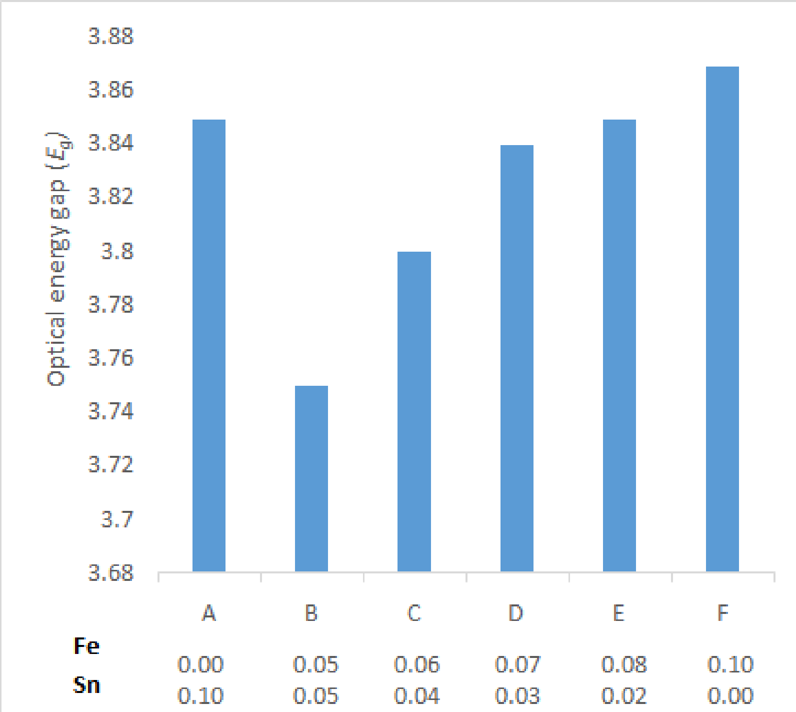


Figure 4, Optical energy gap (E_g)versus sample compositions

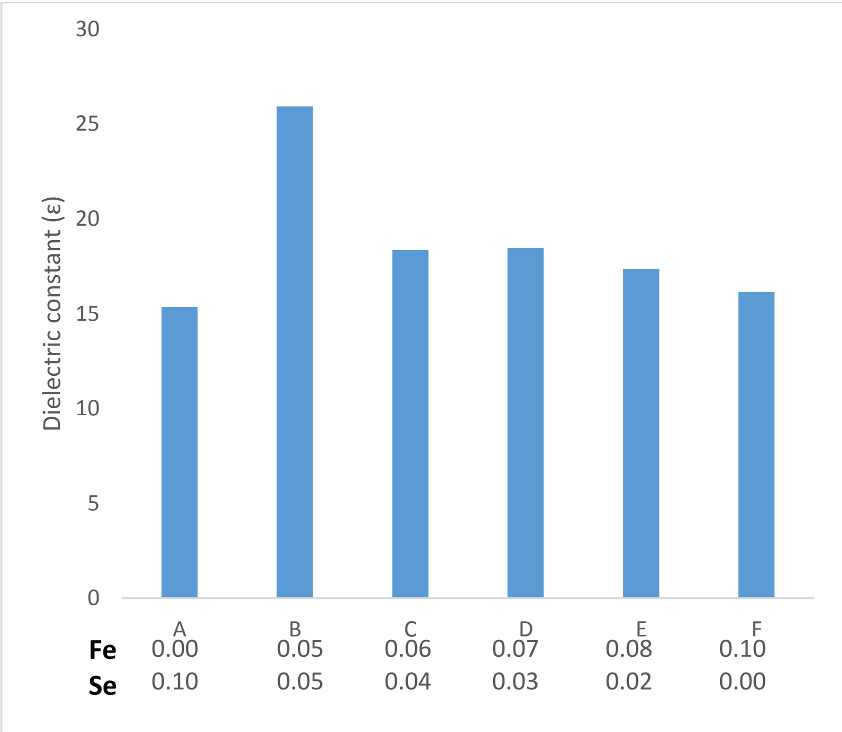


Figure 5, Dielectric constant (ε) versus sample compositions

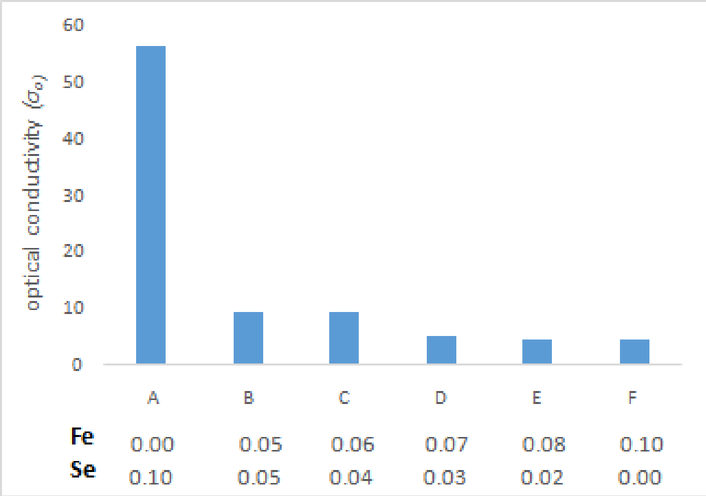


Figure 6, Optical Conductivity (σ_o) versus sample compositions

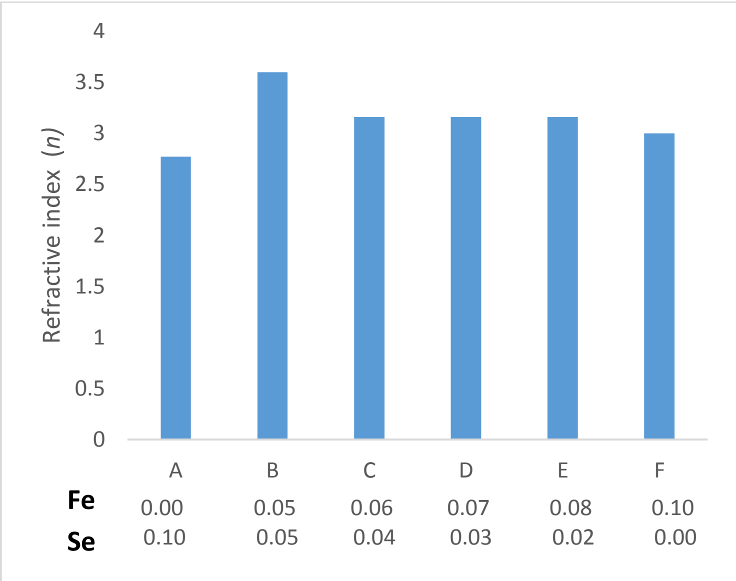


Figure 7, Refractive index (*n*) versus sample compositions

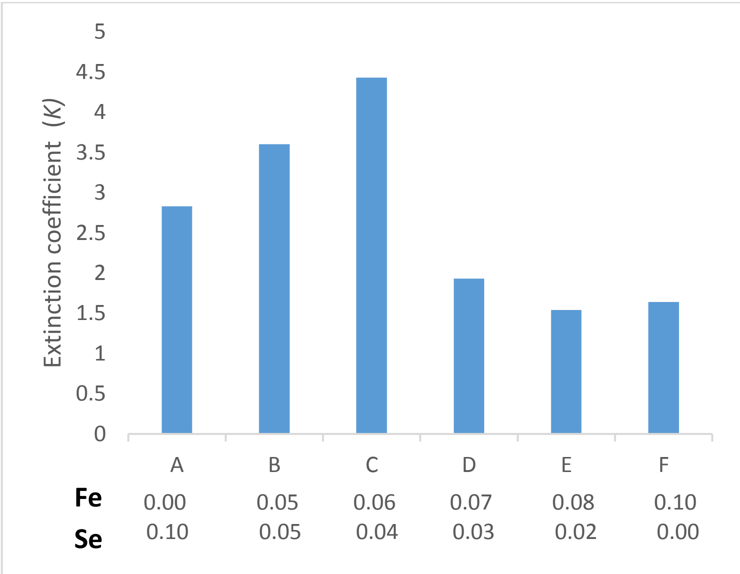


Figure 8, Extinction coefficient (*K*) versus sample compositions

V. Conclusion

Generally, the optical properties of thin-film ; transmission *T*, reflection *R* and absorption A are determined by its refractive index n, extinction coefficient *K*, bandgap*Eg* and geometry . Geometry include ; film thickness , thickness uniformity and film surface roughness.*T*, *R* and *A* are intrinsic - depending on the chemical composition and solid structure of the material, whereas the geometry is extrinsic[19].

In this work for the first time,the optical behaviour of Sn doped with varying molar concentrations of Fe:Semulticomposition thin films were studied. The Ternarythin films were deposited on soda lime glass by spray pyrolysis at a temperature of 400K . Spectroscopic measurements of thethin- films were carried out in the UV-Vis-NIR range at ambient temperature. The energy bandgaps exhibited by the film investigated fall within the energy range required for a semiconductor to effectively function as either buffer or window layers for photovoltaic applications. The small values of absorbance and reflectance in the visible region depicts that the theSnFeSe semiconducting materials could be useful as light emitting diodes (LED) and visible laser diodes (VLD).

Moreover, much is still needed to be done by researchers on the structural and electrical properties of this multicomposition thin films to compliment this research findings for industrial applications.

Acknowledgement

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