FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 8 No. 3, June, 2024, pp 263 - 269
DOI: https://doi.org/10.33003/fjs-2024-0803-2357

THE EFFECT OF Mg, Mn, Co DOPING ON THE OPTICAL PROPERTIES OF FeO THIN FILMS

***Okpechi, K. U. P., Joseph, U. and Nwaokorongwu, E. C.**

Physics Department, Michael Okpara University Of Agriculture Umudike, Abia State, Nigeria.

*Corresponding authors' email: okpechi.uchechi@mouau.edu.ng

ABSTRACT

Semiconductors of magnesium, cobalt, and manganese have optical properties which are very important in many applications. However, the major constraining effect in its development is the uniqueness of its optical properties at room temperature. In this work, we studied the influence of three metals of cobalt, magnesium, and manganese when doped with FeO.The thin films were successfully doped on glass substrate at room temperature using successive ionic layer adsorption reaction (SILAR) method. The films were annealed at temperatures of 120˚C, 140˚C, 160˚C respectively. The optical characteristics were carried out using UV-180 double beam spectrophotometer and a comparative study of the properties of the three systems,to understand their ability to have good optical properties at room temperature. It was observed that the three systems have their absorbance, transmittance and reflectance ability in the visible region of the spectrum along 300nm - 800nm, with manganese doped Iron oxide (Mn:FeO) having the strongest Absorbance, Transmittance, Reflection which decreased with increase in annealing temperature.

Keywords: FeO, Doping, SILAR, Optical properties, Manganese, Magnesium

INTRODUCTION

Semiconductors are special class of materials whose properties vary by external agents such as luminous intensity, temperature, pressure, electric, and magnetic fields, e.t.c. These materials are abundant with band gap energy within 0.5-4 eV. These variations makes it an interesting material for the production of electronic devices such as temperature sensors, light emitting diodes, lasers, transistors e.t.c. The study of the synthesized nano-sized semiconductor materials in recent years have been widely looked at due to the characteristic they possess such as electrical, optical, catalytic, magnetic, thermal properties in the fabrication of modern day appliances (Aliramaji,*et al.,* 2023). Presently, various techniques have been developed for the fabrication of nanostructured thin films of transition metal oxides such as spray pyrolysis, physical and chemical vapor depositions, thermionic vacuum arc methods, etc (Srinwasa *et al.,* 2023). The transition metal thin films of cobalt, manganese and magnesium are special with distinct properties in the fabrication of solar cells, light and temperature sensors, electrodes in electrolytic cells, cores of transformers, etc (Aouati*et al.*, 2021) .The Fe_3O_4 and divalent metal-doped Fe_3O_4 thin films are very good nanostructure materials with its uses in the fabrication of cores of magnetic coils, inductor transformers, tunneling devices, ferromagnetic devices, spintronic devices etc, (Srinivasa *et al.,* 2023) due to their unique and effective magnetic and electrical properties, high spin polarization effect, conducive mechanical hardness with chemical and thermal stability (Cueva *et al.,* 2023) . Various techniques such as spray pyrolysis, dip coating chemical bath techniques, Successive Ionic Layer Adsorption Reaction(SILAR)method, electro-deposition techniques, sputtering, sol-gel have been employed in the deposition of metal doped iron oxide thin films (Chyema *et al.,* 2020; Onwuemeka *et al.,* 2019). Other methods like chemical vapour deposition, electron beam evaporation, were also employed in the deposition of doped and undoped iron oxide thin films (Kumar *et al.,* 2022).The Successive Ionic Layer Adsorption Reaction (SILAR) method of deposition is one of the simplest technique used in the production of FeO thin films on glass and other substrates. It has many advantages such as homogeneity in its nucleation, low cost, thickness control, low temperature process and the possibility of vast coating over other techniques (Kumar et al, 2022).Doping allows researchers to manipulate properties of a semiconductor by utilizing the characteristics of a group of elements known as dopants. By incorporating a limited number of appropriate alternative particles, semiconductor properties may be considerably increased.Thus,doping pure FeO could reduce the optical band gap, which greatly enhances the visible light absorption and reduces the photo-charge recombination rate. This suggests that chemical doping could be an efficient route to develop newmaterials for practical application in science and technology. In this work, doped FeO is deposited by Successive Ionic Layer Adsorption Reaction (SILAR) method, and a comparative evaluation is carried out on the optical energy trends of different dopant impurities of Co, Mg and Mn impurities on FeO. Results obtained can be used to provide theoretical frame work/references on the optical properties of FeO with varying concentration of Co, Mg and Mn impurities. Mg doped FeO was seen to have the best optical property in the visible region of the spectrum.

MATERIALS AND METHODS

Thin films of Mg:FeO, Co:FeO, Mn:FeO were each deposited on glass substrates by successive immersion of the substrates into a $Fe(NH_4)Cl_2$ solutionbath kept at 26^0C mixed with deionsed water. 3 cm^3 of 3 molar solution of ammonia used as complexing agent were measured and added into a beaker with 30 cm^3 of $Fe(NH_4)Cl_2$ containing 42.0 g of 0.6 molar solution of CoCl with 5% percent ratio of each of $MnCl_2$, $MgCl_2$, and $CoCl_2$ added as dopant to each of the Complex solutions of $Fe(NH_4)Cl_2$ separated in four different beakers respectively. 30 cm^3 NaOH containing 30.2 g of 0.5 molar solution of NaOH was also prepared into four places and pour into separate beakers for each of the magnesium, manganese and cobalt thin films. 30 cm^3 of ionized water was also poured into four separate beakers for each of the complex solution of $MnFe(NH_4)Cl_2$, $MgFe(NH_4)Cl_2$,and $CoFe(NH_4)Cl_2$. The pH of the solution was set to be 7.0 for each of the solutions. Cleaned glass substrates were immersed in the complex solutions (at temperature of 26^0C) for a time of 30secs followed by immersion into ionized water for 2secs for hydrogenation. It was then immersed into the 0.5 molar solution of NaOH for 30secs and back into ionized water. This cyclic process was repeated 20 times in order to achieve a desired result. This was done for each of the doped complex solutions .The deposited thin films were annealed at different temperatures of 120˚C, 140˚C, 160˚C. The samples were then characterized.

Mathematical relations used in the study

The optical properties of the thin films are obtained by the interaction between an electromagnetic radiation and the thin film material resulting to absorption effect, diffraction effect, polarization effect, reflection effect, and effects of refraction and scattering. In this research work, the essential optical characteristics of the thin films obtained using UV1-1800 series double beam spectrophotometer are the transmittance, reflectance and the absorbance. If any two of the properties are obtained, the other is obtained using the relation:

% absorbance+% Transmittance +% Reflectance = 100%

Reflectance (R)

The reflectance can be obtained using the equation (Akpu, 2022).

$$R = 1 - (A + T) \quad (1)$$

Where A ,T, R is the absorbance, transmittance and the reflectance of the deposited thin film respectively.

Transmittance

The values of transmittance are obtained from the absorbance using the relation:

$$\%T = \text{antilog}(2 - \text{absorbance}) \quad (2)$$

Optical energy band gap (E_g)

The absorption coefficient (α) relates theincident photon energy (hv) by a well known equation called Tauc's relations (Caceres,2023; Aouati, et al.,2021)

$$(\alpha hv) = B(hv - Eg)^n \quad (3)$$

where v is the frequency of the incident photon, h, the Planck's constant, B, a constant, E_g, the optical band gap and n, the transition type.

For direct allowed band gap, the absorption data fits well to equation (3) for n = 1/2

$$(\alpha h\nu) = B(h\nu - Eg)^{1/2} \quad (4)$$

Squaring both sides of equation 4

$$(\alpha h\nu)^2 = A(h\nu - Eg) \quad (5)$$

$(\alpha h\nu)^2$ were plotted against hν and values of optical band gap energies E_g were obtained from extrapolating the straight portion of the graphs. The wavelength(nm) is converted to electron volt by the relation

$E = (hv/\lambda) = (.626 \ x10^{-34} \ x \ 3.0 \ X \ 10^8)/$ (wave length x 1.6 $x10^{-19}$) (Lin, 2021)

Rutherford Backscattering Spectrometry (RBS)

Rutherford Backscattering Spectrometry (RBS) is a nuclear method used to analyze the near surface layer of solids. A prescribed material is bombarded with ions at an energy in the MeV with a range of 0.5–4 MeV. The energy of the backscattered projectiles is recorded with a solid state detector, an energy sensitive detector. Rutherford Backscattering Spectrometry gives the quantitative composition of a material and depth profiling of individual elements of the constituent materials (Abiodun et al, 2015). RBS has a good depth resolution of the order of several nm, it has no need for reference samples, it is nondestructive, and has a good sensitivity for heavy elements of the order of parts-per-million (ppm). It analyzes to a depth of about 2 μm for incident He-ions and about 20 μm for incident protons. RBS analysis on the films was carried out at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria. similarly the film compositions, and thickness, were also obtained by a 2.2MeV helium particle.

RESULTS AND DISCUSSIONS

The results of the growth and characterized samples of annealed thin films of Co, Mg, Mn doped FeO are shown in Table 1. The films were deposited by Successive Ionic Layer Adsorption and Reaction (SILAR)method. The spectral properties of the films that is the Absorbance (A), Transmittance (T) and Reflectance(R) were determined in the spectral range of 300nm to 800nm in the (UV-VIS-NIR) regions of the electromagnetic spectrum using appropriate mathematical relations . The results of the deposited thin films were compared to understand the effects of each dopant on the optical properties of FeO thin film.

Table 1: Samples and sample codes

Samples	Mg doped FeO	Mn doped FeO	Co doped FeO
unannealed	G1	E1	A1
120˚C	G2	E2	A2
140˚C	G3	E3	A3
160˚C	G4	E4	A4

Figs 1, 2, 3 and 3b shows the spectral properties of Mg doped FeO thin film. It shows that the films had strong absorbance in the visible region of the spectrum in the range of 400nm–700nm.The un-annealed samples of the deposited films had the highest absorbance of 0.8 but it decreases randomly with increase in annealing temperature.Similar work observed by (Cheyma et al, 2020)shows that increase in annealing temperature of MgO reduces the absorbance of the thin film making it a poor absorber. Moreso, the optical band gap had a red shift from 1.57eV for the un-annealed to 1.52eV for the annealed but remained slightly stable throughout the annealing.Fig 4 and Fig 5 shows the RBS (Rutherford backscattering) analysis used to ascertain the elemental composition and film thickness of the deposited samples while Fig 6 is the EDS analysis used to backup the elemental composition of the film samples deposited. It shows that the deposited film thickness increased with increase in annealing temperature. An impressive percentage of the Fe, Mg ,Co deposited were found present in the deposited films . For the unanneald Mg:Fe thin film in Fig 4, the percentage composition was 2.14% for Mg and 24.96%, Fig 5 reveals the %composition of Mg:Fe with the unannealed at 9.15% for Mg and 12.96 for Fe annealed at 140℃ to be 24.96%.The film thickness in nanometers were found to increase with increased annealing time. The distinct nature of the peaks revealed in the spectra inferred that the formed material is a polycrystalline material with various crystallite sizes which are relatively uniform with proper adhesion on the substrate. The results shows that there were proper thermal decomposition of the precursors which produced stable

Mg:FeO thin film which has little trace of impurities of calcium and sodium which were part of the constituent of the of the chemicals used and could affect film the composition of the samples. In all the spectra, it is also observed that the peaks corresponding to each element are well separated.

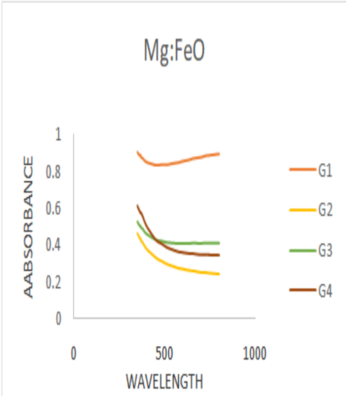

Figure 1: Plot of absorbance versus wavelength of Mg doped FeO thin film

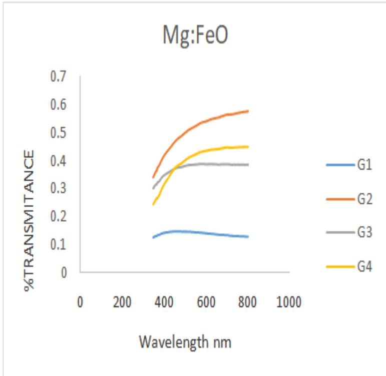

Figure 2: Plot of %transmittance versus wavelength of Mg doped FeO thin film

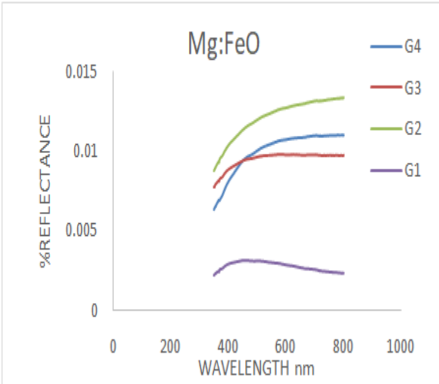

Figure 3: Plot of %Reflectance versus wavelength of Mg doped FeO thin film

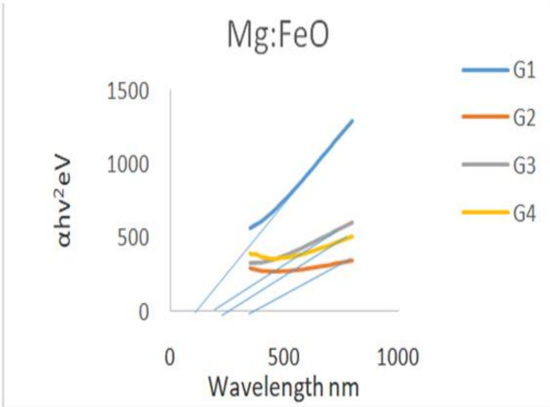

Figure 3b: Plot of optical band gap versus wavelength of Mg doped FeO thin film

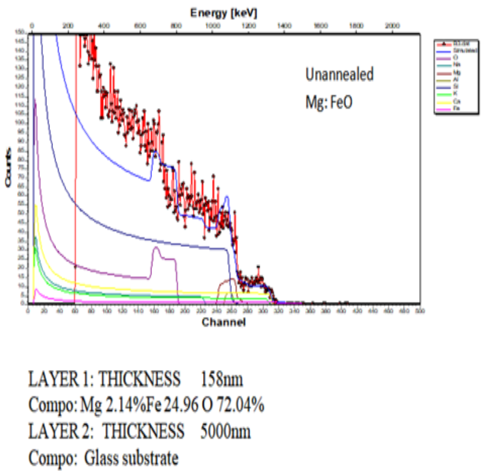

Figure 4: Plot of RBS for unannealed Mg doped FeO thin film

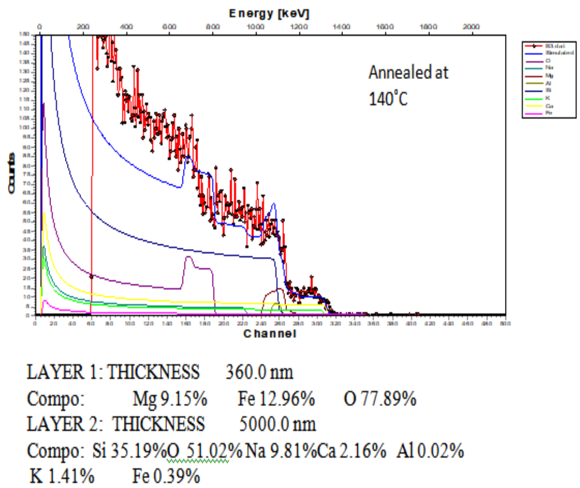

Figure 5: Plot of Mg doped FeO thin film annealed at 140°C

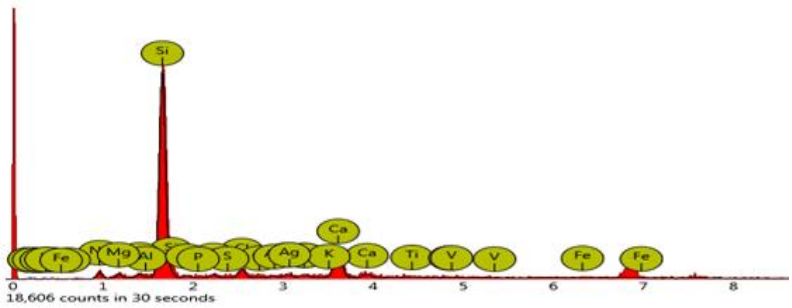

Figure 6: EDS analysis for Mg doped FeO thin film annealed 1t 140°C

Fig 7, 8, 9 and 9b shows the spectral properties of Mn doped FeO thin film. It shows that the films had low absorbance in the visible region of the spectrum in the range of 300nm–800nm.The un-annealed film sample has the lowest absorbance of 0.1 but increased uniformly with increase in annealing temperature. The sample of the film annealed at 120˚**C** has absorbance of 0.4, while at 140˚C the absorbance was 0.5. For film annealed at 160˚C, was found at 0.6. It was observed that increase in annealing temperature increases the absorbance value of the films. Although the films absorbance were generally low, making them poor absorbers. This is in line with (Pathan *et al.*, 2004) who observed that increase in annealing temperature increases the absorbance value of FeMnO thin films. Moreso, the optical band gap had a red shift from 2.12eV for the un-annealed to 3.52eV for the film annealed at 120˚C and 3.6eV for film annealed at 160˚C but remained slightly stable throughout the annealing process. Fig 10 and fig 11 gives the RBS (Rutherford backscattering) analysis result which shows the elemental compositions of the films were represented satisfactorily in the percentage of 5.42% in the un-annealed and 6.32%, at 140˚C while the thickness of the film for un-annealed was 120nm which was observed to reduced with increased annealing temperature to 75nm. Viewing through all the spectra, it was observed that the peaks corresponding to each element are well separated. Fig 12 shows the EDS of the thin film of Mn doped FeO which was used to backup the RBS.

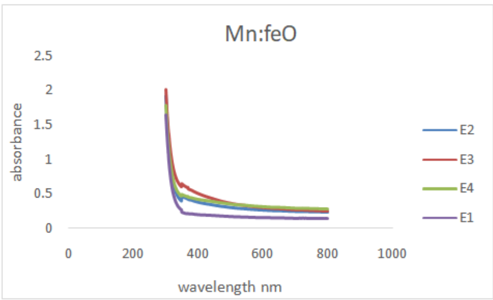

Figure 7: Plot of absorbance versus wavelength of Mn doped FeO thin film

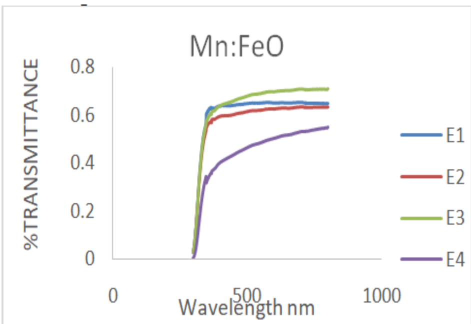

Figure 8: Plot of %transmittance versus wavelength for Mn doped thin film

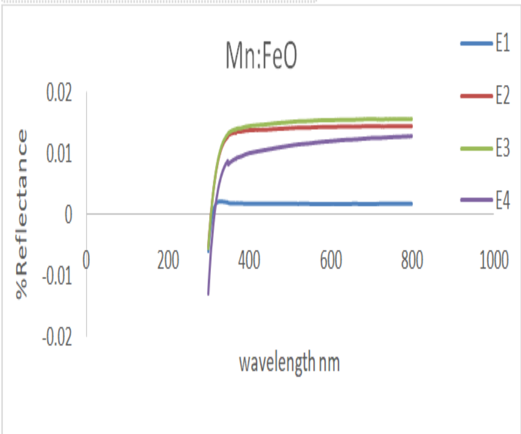

Figure 9: Plot of reflectance versus wavelength for Mn doped FeO thin fim

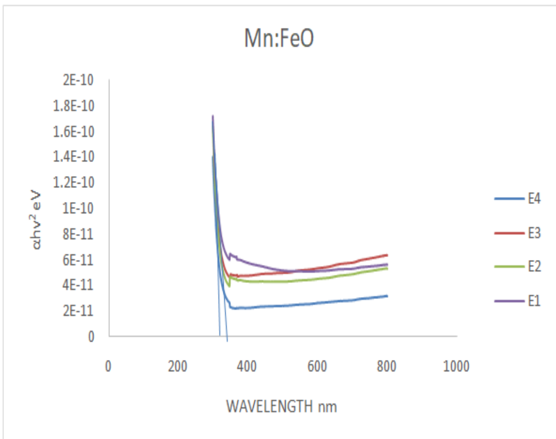

Figure 9b: Plot of ahv^2 versus wavelength for Mn doped FeO thin film

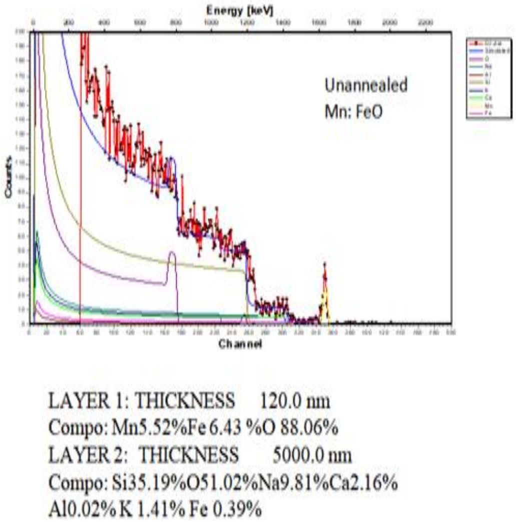

Figure 10: Plot or RBS for unannealed Mn doped FeO thin Film

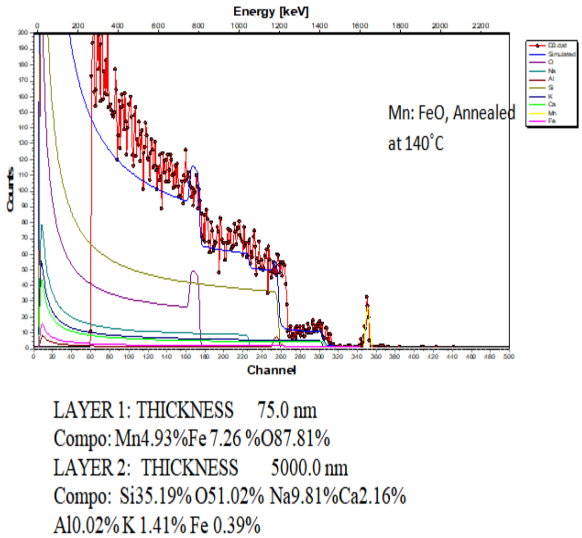

Figure 11: RBS analysis of Mn doped FeO annealed at 140°C

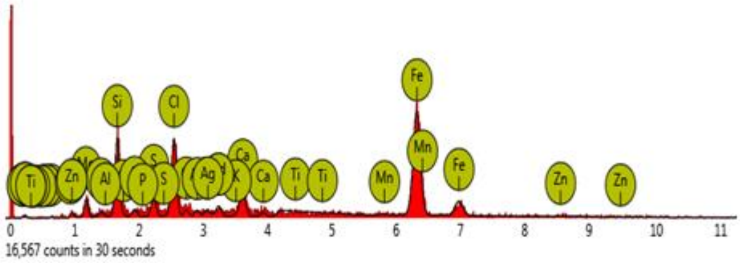

Figure 12: EDS analysis for Mn doped FeO thin film annealed at 140°C

Fig. 13 shows the absorbance property of Co doped FeO thin films in the visible region of the spectrum having low absorbance which decreases with increase in annealing temperature. The un-annealed Co:FeO thin film has an absorbance value of 0.5 but decreased to 0.3 when annealed at 120˚C, 0.2 when annealed at 140˚C and 0.1 when annealed at 160˚C, all in the visible region of the spectrum., in the range of 300nm to 800nm. Fig. 19 shows the optical band gap calculated to be 3.03 eV for the un-annealed film but with a blue shift of 3.8eV observed at annealing temperature of 120˚C and 4.0 eV at a temperature of 160˚C. Fig. 14 shows high transmittance values of the films which decreases randomly with increase in annealing temperature. The transmittance value dropped from 0.9% for the un-annealed to 0.5% for film annealed at 120˚C, 0.55% for films annealed at 140˚C and 0.65% for films annealed at 160˚C, in the range of 300nm -700nm. Fig 15 shows the % reflectance of the film at 0.25% for the un-annealed thin film. This value decreases randomly with increase in annealing temperature thereby having low reflectivity property. In fig. 16, the RBS (Rutherford backscattering) analysis, the elemental compositions of the films were represented satisfactorily in the percentage of 2.42% and 24.96%, in the un-annealed for Co and Fe respectively. The thickness of the film for un-annealed was 158nm. Fig 17 shows the RBS for film annealed at 140˚C with percentages of Co, 2.5% and Fe, 25, 22%, the thickness was observed to increase with increase in annealing to about 160nm. The peaks corresponding to each element were well separated in all the spectra. Fig 18 shows the EDS of the thin film of Co doped FeO, which was used to backup the RBS.

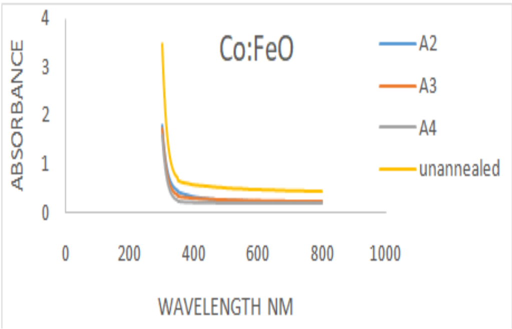

Figure 13: Plot of absorbance versus wavelength of Co doped FeO thin film

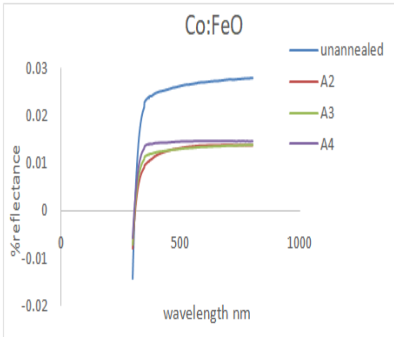

Figure 14: Plot of %Reflectance versus wavelength of Co doped FeO thin film

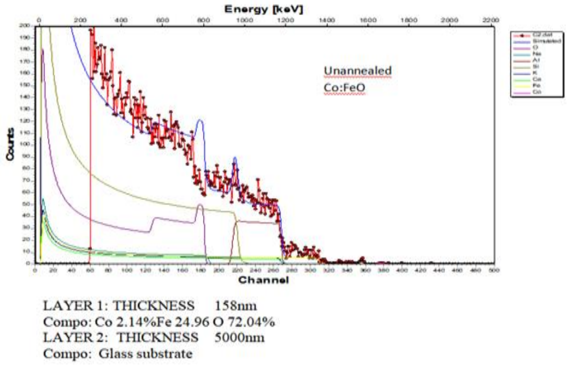

Figure 15: Plot of RBS for unannealed Co doped FeO thin film

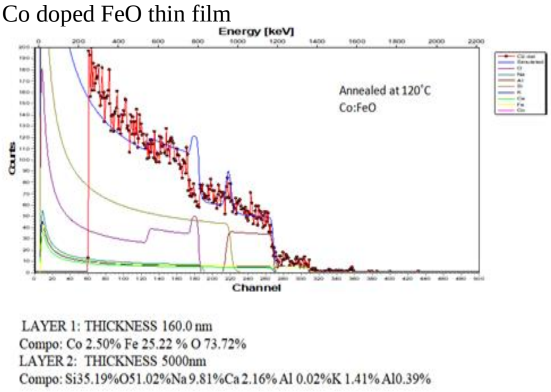

Figure 16: Plot of RBS for Co doped FeO thin film annealed at 140°C

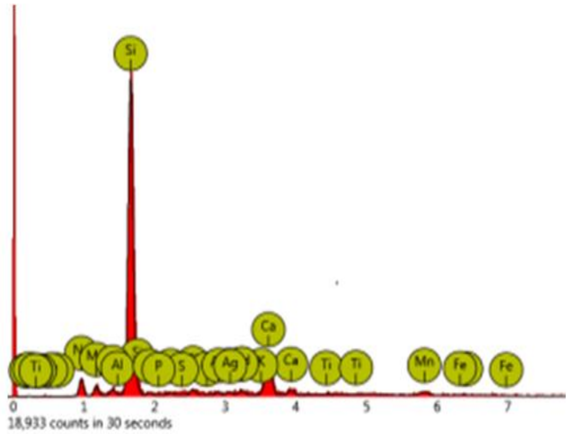

Figure 17: EDS analysis for Co doped FeO thin film annealed at 140°C

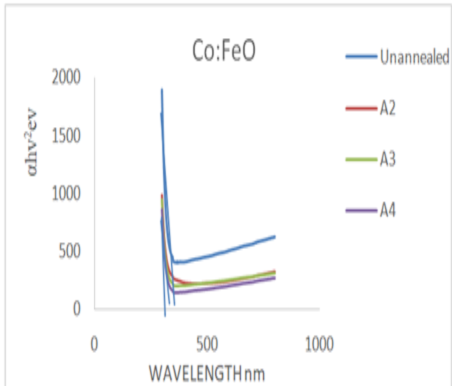

Figure 18: Plot of ahv2 versus wavelength for Co doped FeO thin film

REFERENCES

Abiodun, E. A., Emmanuel, A., Bidene, A. T. and Fasasi, A. Y. (2015). Rutherford Backscattery Spectrometry Analysis and Structural Properties of Thin Films Deposited by Chemical Spray Pyrolysis. *Journal of Materials*, (20); 210-215. https://doi.org/10.1155/2015/215210

Aouati, R., Djaaboube, H., Bouabelloul.A., Taabouche, A., Bouachiba. Y., Daranfad, .O., Oudina, A., Kharfi, F. (2021). Structural and Optical Properties of MgO Thin Films Prepared by Dip-Coating Process: Effect of Thickness. *Semiconductors*. 55.(10).1134/S1063782621070058DOI:10.1134/S1063782621070058

Akpu, N.I., Asiegbu, A.D., Nnanna, L.A. (2022). Synthesis and characterization of novel yttrium-incorporated copper selenide (CuSe:Y) thin materials for solar energy applications. *J Material Science: Material Electron*33, 1154–1161 https://doi.org/10.1007/s10854-021-07397-x

Aliramaji, Shamsa, Philipp Keuter, Deborah Neuß, Marcus Hans, Daniel Primetzhofer, Diederik Depla, and Jochen M. Schneider. 2023. "Effect of Growth Temperature and Atmosphere Exposure Time on Impurity Incorporation in Sputtered Mg, Al, and Ca Thin Films"*Materials* 16, no. 1: 414. https://doi.org/10.3390/ma16010414

Cáceres D., Vergara. I., & González .R J.(2023), Microstructural Characterization of MgO thin films grown by radio-frequency sputtering. Target and substrate-temperature effect. *Applied. Physics*.93, 4300.DOI:10.1063/1.1558964

Cheyma. A., Susana F., Habib E.,(2020).Studies of optical properties of ZnO:MgO thin films fabricated by sputtering from home-made stable oversize targets,Optik,Volume 216,164934,ISSN 0030-4026,https://doi.org/10.1016/j.ijleo.2020.164934.

Cueva,. A., and Enrique .C.,(2023). "Comparison of the Optical Properties of Different Dielectric Materials (SnO_2, ZnO, AZO, or $SiAlN_x$) Used in Silver-Based Low-Emissivity Coatings"*Coatings* 13, no. 10: 1709. https://doi.org/10.3390/coatings13101709

Lin. Y., Shaofei L., Zhengguang S., Kun X., Jingtao .H., Hualong T. Zhi Z.,(2021) Influence of Mn and Co doping on optical and magnetic properties in 3C–SiC,*Journal of Physics and Chemistry of Solids*,Volume 153 ,110002,ISSN 0022-3697, https://doi.org/10.1016/j.jpcs.2021.110002.

Kumar. K., Saeed S.H., Pandey N.K, Verma V., Singh P., Yadav B.C., (2022) ,Influence of tin doping on the liquefied petroleum gas and humidity sensing properties of NiO nanoparticles,. *Journal of Material Resources* 37 (1) 369–379https://doi.org/10.1557/s43578-021-00418-9.

Onwuemeka, J. J., Nwofor, O. K., Nwulu, N. C., Nwosu, E.I., Ezike, F. M., and Obizo, C. G., (2019). The Optical Study of ZnO Thin Films at Different Times of Annealing and Varying Temperatures. *Journal of Applied Physics (IOSR-JAP)*, 6(1), 47-51.

Pathan, H. M. and Lokhande, C. D. (2004). Chemical deposition and characterization of copper indium disulphide thin films. *Applied of Surface Science*, 239(1); 11-18.https://doi.org/10.1016/j.apsusc.2004.04.003

Srinivasa N.V, Haunsbhavi .K, Srinatha .N., (2023) Preparation and characterization of Sn doped NiO thin films by sol–gel spin coating technique, *Materials Today: Proceedings* 5.597 https://doi.org/10.1016/j.matpr