Int. j. adv. multidisc. res. stud. 2025; 5(3):715-720

Received: 08-04-2025
Accepted: 18-05-2025

International Journal of Advanced Multidisciplinary Research and Studies

ISSN: 2583-049X

Assessing the Optical Features of Electrodeposited Ti-Doped ZnSe Thin Films for Solar Cell Window Layer Applications

[1] **Chiedozie Emmanuel Okafor,** [2] **Azubike Josiah Ekpunobi,** [3] **Donald Nnanyere Okoli,** [4] **Jeroh Diemiruaye Mimi,** [5] **Okechukwu Emma Odikpo,** [6] **Chukwudi Benjamin Muomeliri,** [7] **Overcomer Anusiobi,** [8] **Adline Nwaodo,** [9] **Augustine Azubogu,** [10] **Lynda Adaora Ozobialu,** [11] **Evangeline Onuigbo,** [12] **Chiamaka Peace Onu,** [13] **Okoli Nonso Livinus,** [14] **Nwori Augustine Nwode**

[1, 2, 3, 4, 5, 6, 7. 10, 11, 12] Department of Physics and Industrial Physics, Faculty of Physical Science, Nnamdi Azikiwe University Awka, Anambra State, Nigeria

[8] Department of Physics/Geophysics, Faculty of Physical Science, Alex Ekwueme Federal University, Ndufu-Alike Ikwo, (AL- FUNAI), Ebonyi State, Nigeria

[9] Department of Electrical and Electronic Engineering, Faculty of Engineering, Nnamdi Azikiwe University Awka, Anambra State, Nigeria

[13] Department of Computer Education, Madonna University, Okija, Anambra State, Nigeria

[13] Nanoscience and Advanced Materials, Federal University of ABC, Santo Andre, Sao Paulo, Brazil

[14] Department of Industrial Physics, Faculty of Physical Science, Chukwuemeka Odumegwu Ojukwu University, Uli, Anambra State, Nigeria

Corresponding Author: **Nwori Augustine Nwode (E mail:** austine2010forreal@yahoo.com**)**

DOI: https://doi.org/10.62225/2583049X.2025.5.3.4333

Abstract

In this article, titanium doped zinc selenide (Ti-ZnSe) thin films have been successfully fabricated onto fluorine doped tin oxide substrate using an electrodeposition method. Zinc acetate, selenium oxide and titanium oxide were used as sources of Zn, Se and Ti ions respectively. The films were characterized for their optical properties using UV-Vis spectrometry technique. The results showed that the absorbance increase as Ti doping concentration increased while transmittance decreased at the affected wavelength ranges. Peak absorbance values in the range of 0.5-0.7 occurred at (250 nm and 350 nm), 0.3 – 0.4 at (600 – 700 nm) and 0.4 – 0.5 at (800 – 900 nm) for the films fabricated with higher concentration of Ti ion source. The films exhibited high refractive index value and increase as Ti concentrations increased with peak values of 2.25 – 3.75 occurring at 250 nm, 4.00 at 350 nm, 2.50 – 2.75 at (600 – 700 nm) and 3.00 – 3.25 (800 – 900 nm) wavelengths. The extinction coefficient of the films is generally low but increase as concentration of Ti increased. The bandgap energies of the deposited thin films are in the order of 3.0 eV, 3.10 eV, 2.70 eV and 2.70 eV for the films deposited with 4ml, 6ml, 8ml and 10ml Ti ions respectively. These bandgaps and other properties of the films are in the range suitable for many device fabrications such solar cell buffer layers and high temperature devices and the trend of the bandgaps are good mainly for photovoltaic cells fabrication for conversion of solar energy to electricity.

Keywords: Window-layer, Bandgap, Solar-cell, Zinc-selenide

Introduction

Meeting the theoretical solar cell efficiency of any solar cell device through experimental procedure has remained one of the major puzzles to overcome for high performance and swift conversion of solar energy to electricity. The theoretical solar cell efficiency limits have been proposed based on various models, [1]. Reaching these theoretical limits through experiments has become a great issue because it has been found that achieving high percentage efficiency for high performance centers on number of factors. These factors among other things include; temperature, amount of sun light received, the material the cell is made and the nature of inverter used, [2-4]. Each of these factors has been noted to play a very crucial role in effort to improve the overall cell efficiency of solar system. The amount of electromagnetic radiation or sun light that the active layer of solar cell received is subject to the material that constitute the interfacing layer; also known as window layer of the solar cell. The window layer of a solar cell system is most often transparent to broad wavelength of light and conductive in nature. Hence, window layer is known to facilitate the entering of electromagnetic radiation of suitable wavelength range to the active layer of solar cell and at the same time aid the flow of electron as a conductive material. This scenario has been identified as one of the core factors/phenomena that can led to solar cell efficiency improvement if the materials that have the requisite properties are properly harnessed and fabricated. Materials such as cadmium sulfide (CdS), zinc oxide (ZnO), zinc sulfide (ZnO), zinc selenide (ZnSe) etc., have been identified to possessed the characteristic features to be applied as window layer for solar cell device fabrications. These materials have the requisite properties such as high transmittance in the visible region and wide bandgap energy values for this purpose, [5, 6]. The most commonly used window layer material is CdS. However, reported has shown that these CdS is highly toxic and thus not environment friendly, [7].

Researching on the alternative materials that are eco-friendlier and have the requisite properties to be used as window layer have been of great interest for high power conversion efficiency (PCE) [8, 9]. Zinc selenide (ZnSe) is one of the stable and eco-friendly materials that has been identified to possess suitable properties for solar cell window layer applications. It is one of the II-VI chalcogenide semiconductors that has demonstrated many promises for vast applications regarding its identified properties such as; low electrical resistivity, small lattice mismatch, high percentage transmittance and wide bandgap energy values, [10-12]. These attributes have been known to be the pre-determine factors required of solar cell devices for high efficiency attainment. This is because wide bandgap window layer materials permit transmission of maximum incident light (photons) to the active layer for high performance growth. ZnSe has also find good applications in other optoelectronic devices such as laser diodes, photodetectors and light emitting diodes (LEDs) etc., [13, 14].

The alteration of the properties of ZnSe has been of significant in the effort to utilize the material to improving the efficiency of solar cells as window layer and other identified applications. The alterations of the basic properties have been known to be achieved through different processes such as doping or alloying with different materials/elements, deposition temperature, method of material fabrications and other conditions, [15]. Doing/alloying strategy has been applied to doped quite several structures of ZnSe in order to optimize their properties for the different potential applications using different elements/materials of suitable form/structures [16].

In this respect, the properties of electro synthesized thin films of cobalt doped ZnSe fabricated under different deposition period has been reported by [17]. The authors inferred that the obtained bandgap energy and improvement in the electrical conductivity position the films suitable for absorber layer of solar cells. The effect of pH variation on the optical and electrical properties of cobalt doped ZnSe has also be reported by [18]. It was observed that both the bandgap energy and electrical conductivity of the deposited films were influenced as result of pH variation. The authors concluded that based on the obtained results, the Co-doped ZnSe demonstrate great potential for photovoltaic cell applications. Optical Properties of Co-doped ZnSe Thin Films Synthesized by Pulsed Laser Deposition has equally been reported by [19]. The various optical properties such as bandgap, transmittance and refractive of the films were found to be altered and the results were attributed Co incorporation and quantum confinement effect do exhibit by ZnSe material. The Ab-initio density functional theory calculations utilizing local spin density approximation (LSDA) and generalized gradient approximation plus Hubbard parameter (GGA+U) as exchange-correlation potential has been employed to study the mechanical and magneto-electronic behavior of half-metallic ferromagnetism in Ti-doped ZnSe alloyed as reported by [20]. Their calculation reveals based on the electronic band structure and DOS that the materials have half-metallic behavious which is a great technological attribute for spintronic applications. On the other hand, the structural and optical properties of polyvinyl pyrrolidone-doped with zinc selenide obtained through casting approach has been reported by [21]. The authors discovered that there were decrease in the energy bandgap from 4 to 3.1 eV for indirect allowed transition and decrease from 3.94 to 2.9 eV for indirect forbidden transition. They inferred that based on the obtained results, the PVP-ZnSe nanocomposite exhibited exceptional optical properties suitable for photodetector applications, mainly as UV detectors.

In this research, electrodeposition will be adopted to fabricate thin films of Ti-doped ZnSe and study their optical properties for solar cell window and other optoelectronic applications.

Materials and Method

The thin films of Ti-doped ZnSe were fabricated onto Fluorine-doped tin oxide (FTO) conductive glass substrate by employing an electrodeposition method. The conductive glass substrates were ultrasonically cleaned using acetone for about 20 minutes and rinsed with distilled water for another 20 minutes and kept to dry at room temperature. The materials used for the fabrication of the Ti-ZnSe thin films were zinc acetate, selenium dioxide (SeO_2), rutile (titanium dioxide) and hydrofluoric acid (HF). The basic apparatus used were; magnetic stirrer and DC supply unit supply (model Long Wei: PS-305D). Zinc acetate dihydrate served as zinc source, selenium dioxide as selenium source, fluorine-doped tin oxide (FTO) conductive glass substrate: -used as working electrode while silver/silver chloride (Ag/AgCl) was used as reference electrode, platinum rod used as the counter electrode, 50 ml glass beaker served as reaction bath, distilled water served the purpose of reaction medium for the precursors, DC supply unit is the electrodeposition device while magnetic stirrer was used for the sole purpose of proper dissolution of the solute in the solution.

In fabricating the thin films of Ti-doped ZnSe onto the FTO glass substrate, aqueous solutions of different volumes of 1.0 M zinc acetate and equal volume (15 ml) of 0.5 M selenium oxide were measured in a bath container. 2 grams of titanium oxide were dissolved in 40 ml of HF upon vigorous stirring using magnetic stirrer for one hour and obtained solution was used as dopant by varying its volume from 4ml to 10ml. Three-electrodes configuration system was adopted and the three electrodes were immersed into the bath containing the electrolytic solution and a voltage of 5 volts was maintained from the DC supply unit for deposition time of 30 seconds for each bath. The details of the experimental procedure are summarized in Table 1. The deposited films on the FTO substrate were removed from the bath solution and allowed to dry at room temperature for characterizations.

Table 1: Optimization of Bath Parameter for Ti-ZnSe Thin Films

D.C Supply		Zinc acetate Vol (ml)	SeO_2 Vol (ml)	TiO_2 Vol (ml)	Time (s)	pH
V (v)	I (A)					
5.0	0.18	15	15	10	30	1.80
5.0	0.15	17	15	8	30	2.20
5.0	0.09	19	15	6	30	2.60
5.0	0.07	21	15	4	30	4.11

Characterizations and Calculations

The optical properties of the deposited thin films of Ti-ZnSe were investigated using UV-Vis spectrometer machine to measure the absorbance of the films in the wavelength of 200 nm to 800 nm at scan rate of 20 nm. The absorbance data were recorded and analyzed while other properties were calculated based on the absorbance values using the relations as shown below:

Transmittance: This was calculated using the equation as provided by [22-24]

$$T = 10^{-A} \quad (1)$$

Reflectance: This other property was evaluated using the formula given by [25, 26]

$$R = 1 - \sqrt{\frac{\exp(A)}{10^{A}}} \quad (2)$$

Refractive index (η): This was calculated using the relation as given by [27, 28]

$$\eta = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (3)$$

Extinction coefficient (k): This property was also obtained for the films using the equation given by [29, 30]

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

Bandgap energy of the films: This property for the deposited thin films of Ti-ZnSe was obtained via the relation provided by [31-33]

$$(\alpha h v)^r = A(hv - E_g) \quad (5)$$

Where hv is the photon energy, α represents the absorption coefficient, A is a factor known as the autonomous constant, E_g is the bandgap energy of the films and r is the transition factor which has the values of 2 for allowed direct transition and ½ for indirect allowed transition.

Results and Discussion

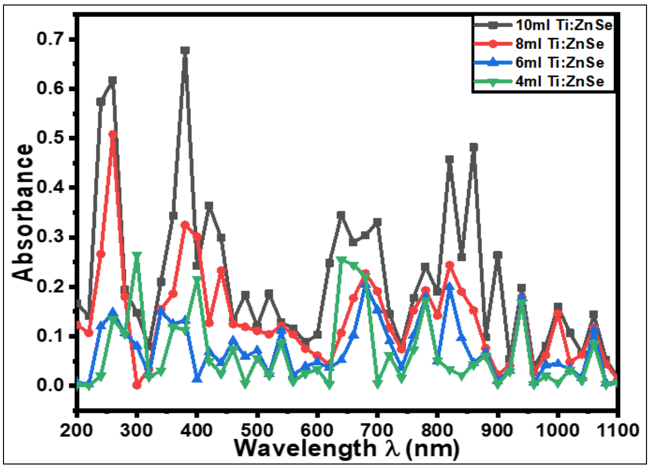

Fig 1: Plot of Absorbance against wavelength for the synthesized Ti:ZnSe thin films

Fig 1 represents the graph of measured absorbance of the deposited thin films of Ti-doped ZnSe as a function of wavelength to determine the absorption behaviour of the films at different electromagnetic spectrum for device applications. From the graph, it can be observed that the deposited thin films have low absorbance values which tend to improve by increasing the volume concentration of the Ti dopant. In the UV-region, the films have peak absorbance values at 250 nm and 350 nm with the film 10ml Ti:ZnSe having the highest values. In the VIS and NIR regions, the peak values occurred at wavelength ranges of 600 – 700 nm and 800 – 900 nm respectively. The increase in the absorbance of the films as a result of Ti-doping is significant for many applications of the material such as buffer layers for solar cells etc.

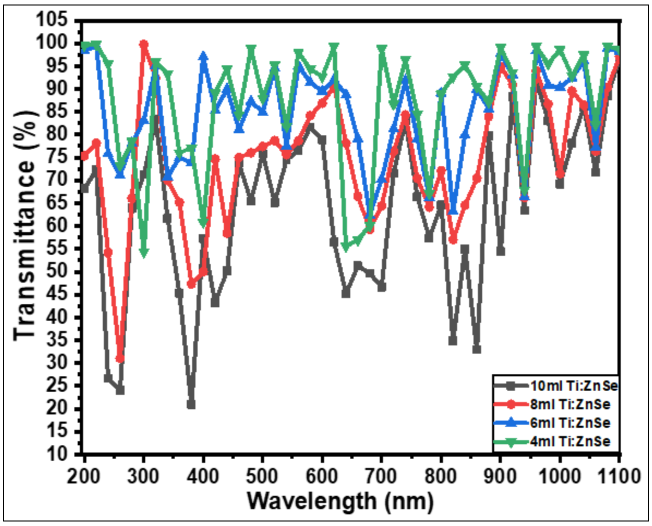

Fig 2: Plot of % Transmittance against wavelength for the synthesized Ti:ZnSe thin films

The plot of percentage transmittance of the deposited thin films of Ti:ZnSe against wavelength is presented in Fig 2. The figure showed that the films as a consequent of low absorbance demonstrated high values of transmittance but decreased as volume concentration of Ti dopant increased.

The high transmittance of the films formed with lower volume concentration of Ti dopant within the UV, VIS/NIR regions of electromagnetic spectrum position them for photo-thermal device applications.

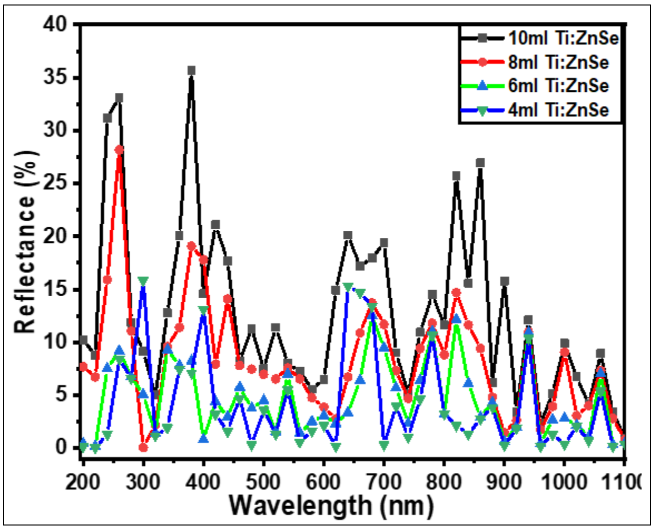

Fig 3: Plot of % Reflectance against wavelength for the synthesized Ti:ZnSe thin films

The plot of percentage reflectance of the films of Ti:ZnSe is presented in Fig 3 as a function of wavelength to determine the degree of reflection of the films at various wavelength for device applications. From the graph, it can be observed that the reflectance of the films is quite low within the wavelength of interest. However, the percentage reflectance of the films increased with an increase in the volume concentration of Ti ion source with the peak values occurring at about 250 -350 nm in the UV region. In the VIS-NIR regions, the peak values occurred at the wavelength range of 600 – 700 nm and 800 – 900 nm which correspond to the range of low transmittance for the films.

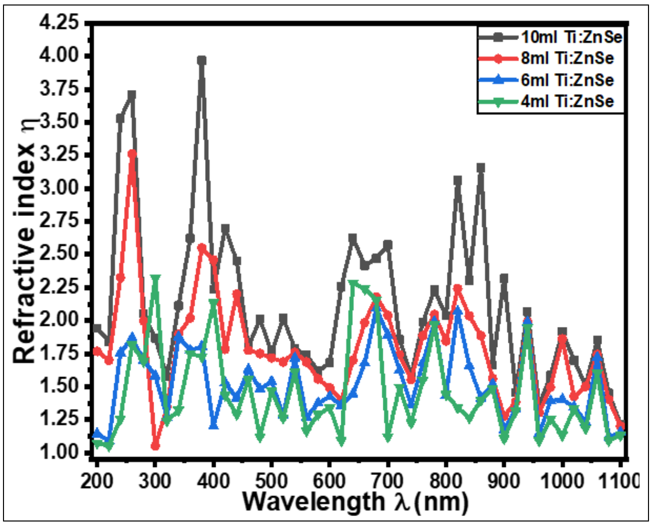

Fig 4: Plot of Refractive index against wavelength for the synthesized Ti:ZnSe thin films

The graph of refractive index of the deposited thin films against wavelength is shown in Fig 4. The figure revealed that the films exhibited a quite high values of refractive index throughout the wavelength of measurement but however increased as doping concentration increased. The film deposited with 10 ml of Ti dopant concentration depicted the highest values with peak values of 3.75, 4.00 at wavelengths of 250 nm and 350 nm within the UV region. Peak refractive index values were also observed at wavelength order of 650 nm, 800 nm and 850 nm in the VIS- NIR regions. These increase in the refractive index values for the films as a result of Ti doping is crucial for many device applications such as optical fiber and waveguide devices.

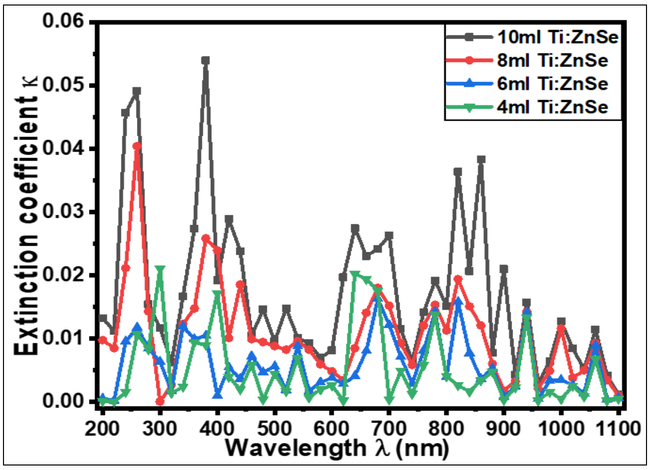

Fig 5: Plot of Extinction coefficient against wavelength for the synthesized Ti:ZnSe thin films

The graph of extinction coefficient of the deposited thin films Ti:ZnSe against wavelength is presented in Fig 5 to investigate the rate photon of light energy got lost in the material for any application. The figure indicated that the extinction coefficient of the synthesized thin films of Ti:ZnSe generally have low values of extinction coefficient. However, increase in the volume concentration of titanium ion dopant tend to increase the extinction coefficient of the films throughout the UV, VIS and NIR regions of electromagnetic spectrum. The film doped with 10 ml Ti doping has the highest value of extinction coefficient with peak values of 0.05, 0.055, 0.03 and 0.04 that occurred at wavelengths of 250 nm, 350 nm, 600 – 700 nm and 800 – 900 nm respectively. The low values of extinction coefficient exhibited by the films are significant for photo-detector device application.

Fig 6 are plots of $(\alpha h\nu)^2$ as a function of photon energy in order to determine the direct bandgap energy of the films for suitable areas of application. From the figure, the bandgap energies of the films can be estimated to be about 3.0 eV, 3.10 eV, 2.70 eV and 2.70 eV for the films 4ml Ti:ZnSe, 6ml Ti:ZnSe, 8ml Ti:ZnSe and 10ml Ti:ZnSe respectively. These bandgap energies were estimated by extrapolating the band edge portion of Tauc relation on the photon energy axes where $(\alpha h\nu)^2$ equal to zero as depicted in the plots. The obtained band-gap energy values for the films are in the range suitable for many device fabrications such solar cell buffer layers and high temperature devices. The trend of the band-gap energy of the films showed that Ti doping decrease the band-gap energy of ZnSe material. This trend is suitable for device applications such as photovoltaic cells for conversion solar energy to electricity.

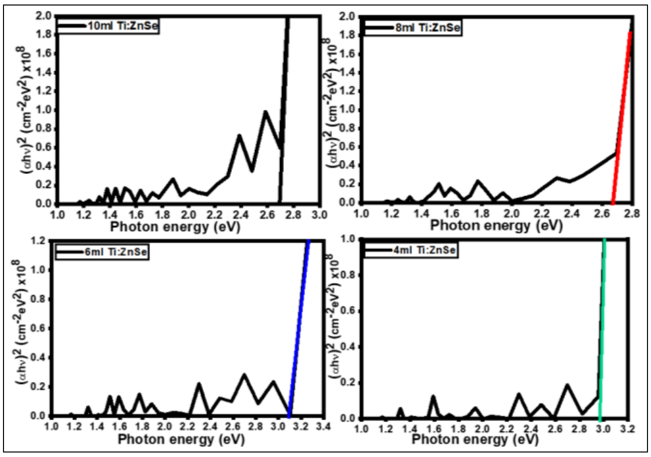

Fig 6: Plots of Squares of (αhν) against photon energy for the synthesized Ti:ZnSe thin films

Conclusion

Thin films of Ti-doped ZnSe deposited onto FTO conductive glass substrates have been analyzed for their optical properties to determine their suitability for device applications. The results of the analysis showed that the films deposited with higher concentration of Ti ions have higher absorbance values with peak values which occurred at wavelength ranges of 250-350 nm, 600 – 700 nm and 800 – 900 nm in the UV, VIS and NIR regions respectively. The increase in the absorbance of the films as a result of Ti doping can be of significant for many applications such as buffer layers for solar cells. The films subsequently exhibited high transmittance for those formed with lower volume concentration of Ti dopant within the UV, VIS/NIR regions and thus position them for photo-thermal device applications. The bandgap energies of the films were extrapolated to be 3.0 eV, 3.10 eV, 2.70 eV and 2.70 eV for the films deposited with 4ml, 6ml, 8ml and 10ml respectively. The obtained band-gap energy values are found to be in the range suitable for many device fabrications such solar cell buffer layers and high temperature devices. Moreover, the trend of the band-gap energy indicated that Ti doping decrease the band-gap energy of ZnSe films and this trend is suitable for device applications mainly photovoltaic cells for conversion solar energy to electricity.

Acknowledgements

The authors are pleased to acknowledge and express their profound gratitude to our sponsor; the Federal Government of Nigeria through the TETFUND-NRF 2021, NO 6 Zambezi Crescent off Aguiyi Ironsi, Maitama, Abuja, Nigeria, for the release of research grant that helped to take this work this far. We are indeed very grateful for the research grant. The authors also appreciate the team of scientists and technologists in the Department of Chemistry Nnamdi Azikiwe University Awka, Nigeria Nsukka, for allowing us make us of their optical Equipment for characterization of the samples of the work.

Funding Agency

This research was carried through the fund released by the Tertiary Education Tax Fund (TETFUND-NRF grant number (TETFUND-NRF) 2021. The Federal Republic of Nigeria Education Tax Agency-NO 6 Zambezi Crescent off Aguiyi Ironsi, Maitama, Abuja, Nigeria, (www.tetfund.gov.ng).

Conflict of Interest

No conflict of interest during the period of this work.

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