Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN

J. Mater. Environ. Sci., 2022, Volume 13, Issue 05, Page 515-525

http://www.jmaterenvironsci.com

Electrochemical Preparation and Characterization of Molybdenum Assimilated Zinc Selenide Materials for Photovoltaic and Solar Cells Application

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Received 01 Apr 2022,
Revised 05 May 2022,
Accepted 06 May 2022

Keywords
- ✓ Molybdenum,
- ✓ Photovoltaic,
- ✓ Bandgap,
- ✓ ZnSe,
- ✓ FTO.

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Abstract

In this research, zinc selenide and zinc selenide doped molybdenum were prepared and characterized via electrochemical deposition technique (ECD). The chemicals used include zinc tetraoxosulphate (VI) heptahydrate ($ZnSO_4.7H_2O$), selenium powder (Se), and molybdenum dioxide (MoO_2) subsequently as the zinc ion source, selenium ion source, and doping source. The materials for characterization ZnSe/Mo, including, the molarity, pH, deposition voltage have been improved at the commencing mount of the synthesis. The SEM, EDX, structural, optical, electrical analyses were studied. The prepared zinc selenide thin films material (ZnSe) and zinc selenide doped molybdenum (ZnSe/Mo) is polycrystalline structure with extrusive adopted orientation along (101) plane. A thick precipitate crystallite-like particles poised of different sizes were noticed for ZnSe which consist of unendingly, formed, and tightly packed together. The zinc selenide doped molybdenum image reveals crystallite-like cracks of melted scum far smaller than that of ZnSe and reduces beyond in size as the molar percentage of Molybdenum rises. The films prepared for the photovoltaic and solar cells application recorded the energy bandgap of 1.50 eV for the zinc selenide material and 1.55 - 2.55 eV for the zinc selenide doped molybdenum.

1. Introduction

The group II-VI elements have been known for their direct energy bandgap which is one of the most popular chalcogenides thin films materials because of its good optical properties. Due to the large energy bandgap and optical transmittance in the infrared and visible regions. Zinc selenide is a semiconductor compound with a 2.7 eV energy bandgap, which is used in thin-film fabrication and as n-type thin-film heterojunction solar cells [1, 2], also can be used as a window layer in photovoltaic solar cells [3]. Its use for light-emitting, laser diodes, optoelectronic, electroluminescent display, window layers in solar cells, and luminescent devices [4, 5]. Due to depletion in energy production different researcher are doing their best to find a lasting solution to the problem of energy in the world [6]. Human anthropogenic activities are the main causes of the constant emission of greenhouse gases. This is because all the technologies and industries depend solely on the consumption of fossil fuels

which is about eighty-five percent of the energy production in the world depends on non-renewable energy production. Furthermore [7-10], the alternative industries and technologies growing in the production of energy is fifteen percent which depends on renewable energy production including photovoltaic solar radiation and wind [11-15]. Particularly, the use of photovoltaic solar radiation has attracted great interest in the synthesis and fabrication of thin-film solar cells, design, and production of solar devices like solar collectors, photovoltaic systems In the applications of photovoltaic solar cells, we have a different number of cells kinds includes, including perovskites, chalcogenides, amorphous silicon, and silicon. Various methods have been used for the synthesis of ZnSe material, such as evaporation deposition, vacuum technique, chemical bath deposition, epitaxy, chemical spray pyrolysis technique, [16-17] and thermal evaporation, Among these techniques, ECD [18] is generally engaged because it is a very straightforward, low-cost technique, and, essentially used in the deposition of large-area devices that result in superbness thin films that can outright with films obtained by more refined technique. Polycrystalline zinc selenide (ZnSe) has high thermal conductivity and lower electrical conductivity than other simple crystals [19]. Many researchers have tried to achieve a comparable result to a single-crystal by doping in polycrystal zinc selenide to improve the electrical properties and lessen the thermal conductivity completely. Several techniques enhance the device's thermoelectric performance, such as large mass fluctuations, alloying, nano-structuring, bandgap engineering, and doping [20]. The properties of ZnSe thin films have been enhanced by doping with metals or transition metals such as Al, Bi, Co Sr, Mn, etc. [21-23], and these doped ZnSe have been successfully employed in various applications. Obitte et al report the effects of doping and temperature on properties of electrochemically deposited Er3+ doped ZnSe [24]. However, the effect of molar concentration on the structural, optical, and electrical properties of CoZnSe has been reported by [25]. The molar concentration Co dopant was varied within 0.1%, 0.2% and 0.3%. It was noted that the presence of Co^{2+} in ZnSe intersite contributes greatly to the properties of CoZnSe.

In this present research, electrochemical preparation and characterization of molybdenum assimilated zinc selenide materials for photovoltaic and solar cells application. The materials for characterization ZnSe/Mo, including, the molarity, pH, deposition voltage have been improved at the commencing mount of the synthesis. The SEM, EDX, structural, optical, electrical studies were studied.

2. Experimental details

The chemicals were analytically graded, purchased, and used without further purification. The FTO slides were sterilized in acetone, ultrasonicated for 30 minutes, rinsed in distilled water, and oven-dried. The cationic, anionic, and dopant concentrations used were respectively 0.1 mol of Zinc tetraoxosulphate (VI) heptahydrate ($ZnSO_4.7H_2O$), 0.1 mol of selenium (IV) oxide (SeO_2), and 0.1 mol of Molybdenum dioxide (MoO_2). The electrochemical deposition technique was adopted in depositing the films. The ECD setup consists of three-electrode system; platinum mesh as the positive, a silver-silver chloride electrode (Ag/AgCl) as the reference electrode, and a working electrode/negative. The synthesis was carried out under a Potentiostat condition of −200 mV versus SCE for 10 seconds. The prepared films were therefore cleaned and dried. The voltage supply was kept at 10 V, after the syntheses, the films were annealed and heated for 30 min to eliminate centralized stresses (see table 1). Introducing the molybdenum dopant was achieved by adding 10 ml of 0.1 mol of Molybdenum dioxide (MoO_2) into the electrochemical bath. The films were prepared at room temperature, at pH values of 6.9. The zinc selenide/ Molybdenum (ZnSe/Mo) films deposited were characterized for their surface

morphological, structural, elemental, and optical properties using Scanning Electron Microscopy, Advance X-ray diffractometer with Cu Kα line (λ = 1.54056 Å) in 2 theta range from 10° - 80°, UV-1800s Visible Spectrophotometer, Four-point probe (Model T345) respectively.

Table 1: Parameter for characterization

Label	ZnSO4.7H2O (ml)	MoO2 (ml)	Se (ml)	Dopant Conc. (mol%)	Time (Sec)	Voltage (V)
ZnSe	20	00	20	00	25	10
ZnSe/Mo 0.1 mol%	20	10	20	0.1	25	10
ZnSe/Mo 0.2 mol%	20	10	20	0.2	25	10
ZnSe/Mo 0.3 mol%	20	10	20	0.3	25	10

3. Results and Discussion

3.1 Structural analysis of zinc selenide (ZnSe) and zinc selenide doped molybdenum (ZnSe/Mo) materials

The structural analysis of zinc selenide thin-film material (ZnSe) and zinc selenide doped molybdenum (ZnSe/Mo) materials were studied via X-ray diffraction (XRD) and the crystal planes (101), (111), (200) and (211) were observed in figure 1 for zinc selenide and zinc selenide doped molybdenum (ZnSe/Mo) prepared with different mol% concentrations and with JCPDS:00-033-2061 (Table 1).

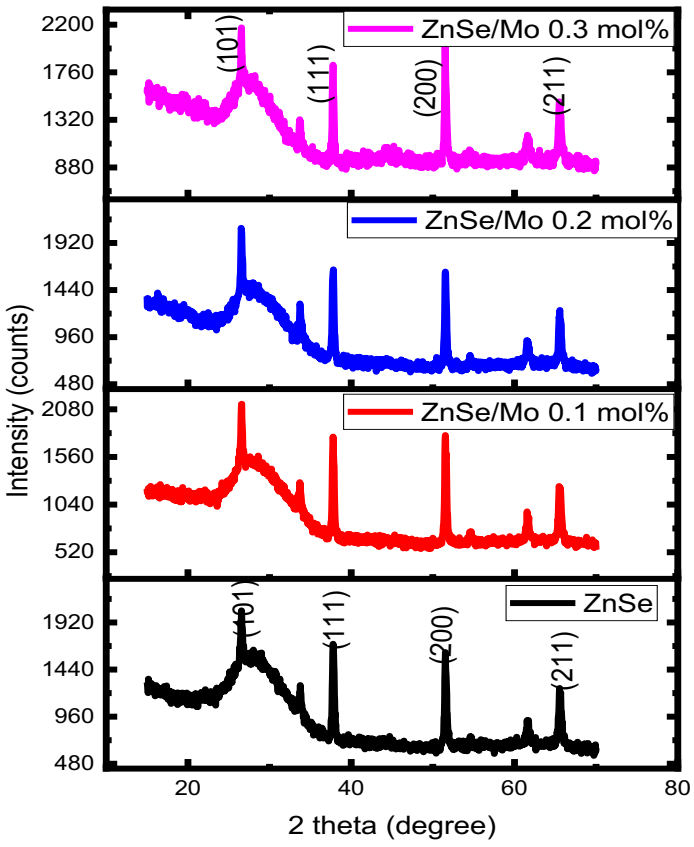


Figure 1: XRD pattern of zinc selenide and zinc selenide doped molybdenum

The prepared zinc selenide thin films material (ZnSe) and zinc selenide doped molybdenum (ZnSe/Mo) is polycrystalline and their interrelated peaks qualified to a hexagonal (ZnSe) wurtzite kind structure with extrusive adopted orientation along (101) plane. Doping zinc selenide materials with molybdenum enhanced the crystallinity as seen from the heightened peak intensity at rising dopant mol% concentrations. There are four major sharp peaks noticed from the spectrum at 26. 4°, 37.9°, 51.8°, and 65.3° with (101), (111), (200), and (211) crystal planes subsequently [22-25].

Table 2: Structural parameters for the zinc selenide (ZnSe) and zinc selenide/ molybdenum (ZnSe/Mo) films

Sample	2θ (degree)	(hkl)	d-spacing (Å)	Lattice constant (a)	FWHM (β)	Grain Size, D (nm)	Dislocation density, **σ**
ZnSe	26.422	101	3.370	5.837	0.185	0.769	5.125
ZnSe/Mo 0.1 mol%	37.982	111	2.372	4.744	0.209	0.699	6.207
ZnSe/Mo 0.2 mol%	51.840	211	1.762	3.524	0.148	1.041	2.799
ZnSe/Mo 0.3 mol%	65.321	300	1.427	3.191	0.225	0.729	5.658

3.2 Surface morphological and elemental composition of ZnSe and ZnSe/Mo

The morphological images of the prepared materials (ZnSe and ZnSe/Mo at 0.1 mol%, 0.2 mol%, 0.3 mol %) at 100 um magnifications were studied via scanning electron microscopy as seen in figure 2. A thick precipitate crystallite-like particles composed of various sizes were observed for ZnSe which consist of unendingly shaped and firmly packed together while zinc selenide doped molybdenum image reveals crystallite-like cracks of melted scum far smaller than that of ZnSe and reduces beyound in size as the molar percentage of Molybdenum rises.

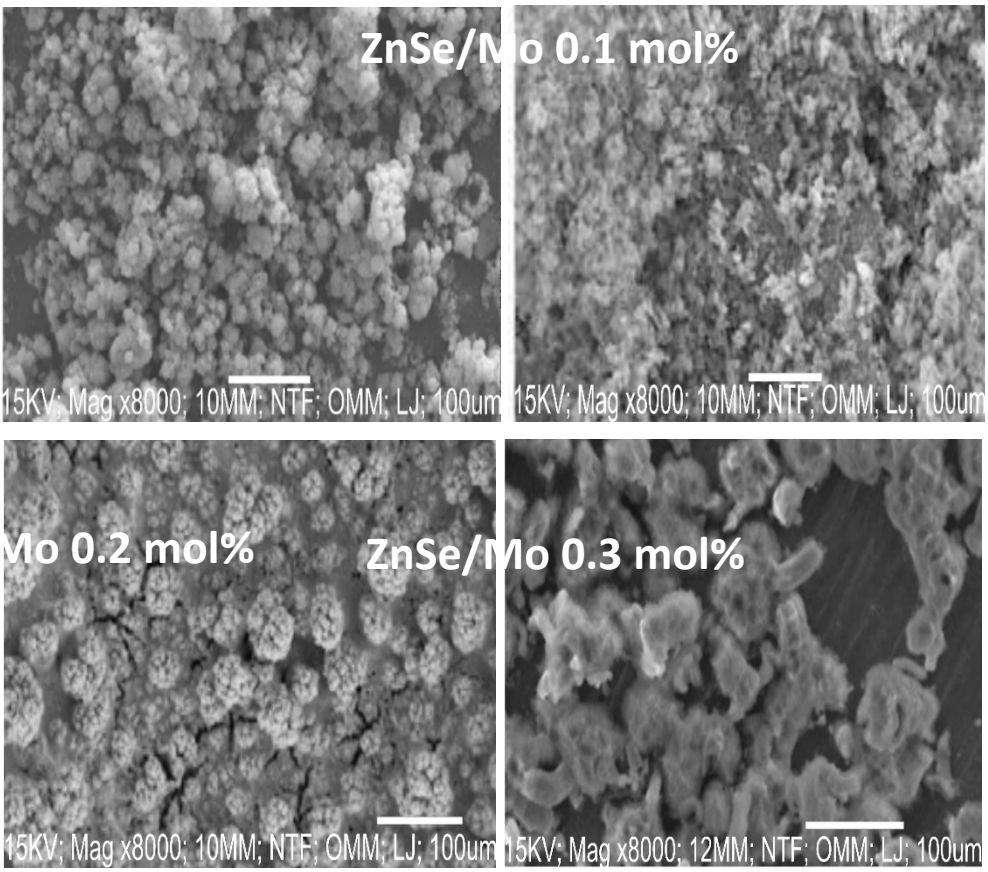
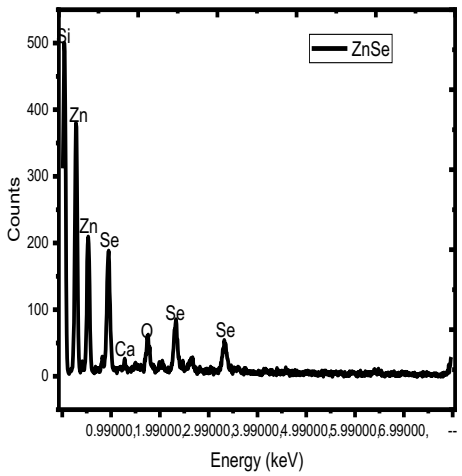
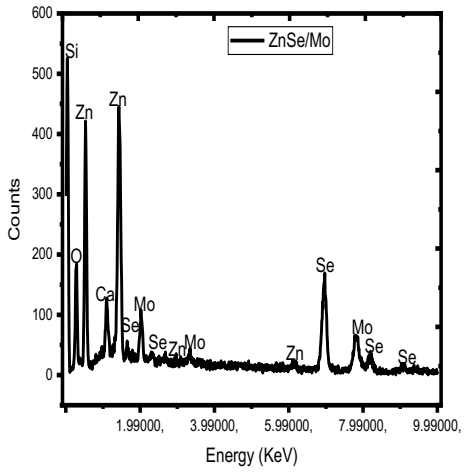


Figure 2: Scanning electron microscopy of zinc selenide and zinc selenide doped molybdenum

Agnate result trend was reported by Ikhioya et al in the growth of ZnSe doped with Zr film synthesized by electrochemical deposition technique (ECD). The elemental composition of zinc selenide and zinc selenide doped molybdenum (ZnSe/Mo) materials was carried out via the energy-dispersive X-ray diffractometer technique. The preparation of ZnSe and ZnSe/Mo was noticed in the energy-dispersive X-ray diffractometer spectra in Figure 3 with the presence of other elements from the FTO slide used in the preparation of the samples [22-25].





Elements	Atomic weight (%)
Zinc	57.09
Selenium	38.12
Silicon	3.51
Oxygen	0.74
Calcium	0.08
Elements	Atomic weight (%)
Zinc	51.09
Selenium	39.07
Silicon	3.69
Oxygen	0.51
Calcium	0.62
Molybdenum	5.02

Figure 3: The energy-dispersive X-ray of zinc selenide and zinc selenide doped molybdenum

3.3 Optical analysis

The absorbance of zinc selenide material (ZnSe) and zinc selenide doped molybdenum (ZnSe/Mo at 0.1, 0.2, 0.3 mol%) thin material were obtained with a wavelength (ʎ) range of 300-1100 nm). The absorbance values of all the thin films were observed to have moderate absorption at the UV region down to the ultraviolet region and there was a downturn in the absorbance with an increase in wavelength of the electromagnetic radiation as shown in Figure 4a. From the graph, it was observed that as the dopant concentration of molybdenum increased there was a steady downturn in the absorbance of the values of the prepared film. Doping zinc selenide with molybdenum affects the films greatly, which shows that the prepared films will be suitable for application in photovoltaic and solar cell fabrication [22-25]

Figure 4b concede the transmittance graph of zinc selenide material (ZnSe) and zinc selenide doped molybdenum (ZnSe/Mo at 0.1, 0.2, and 0.3 mol%) material. The transmittance of all the films was seen to be very high in both regions and with a steady increase in wavelength up to the near-infrared region. The transmittance of ZnSe/Mo 0.2 mol/% films exhibited an average of nearly 83% with a steady increase, this rise in optical transmittance of ZnSe/Mo materials can be attributed to the enhancement in the grain boundaries which was achieved during doping [22-25]. The deposited material can be used as galvanizing materials to avert corrosion when capped in a deuce of material outside. likewise, by its high transmittance when doped with a high concentration of molybdenum, it can be used for photovoltaic and solar cell applications. The reflectance of the films had their maximum reflectance value of approximately 20% in the UV region of the spectrum which downturn with an

increase in wavelength of the electromagnetic radiation as seen in figure 4c. The downturn in the reflectance parameters of zinc selenide doped molybdenum concedes that adding molybdenum as an impurity to zinc selenide will improve the photovoltaic and solar cells application of the zinc selenide material [22-25]. The energy bandgap for ZnSe and (ZnSe/Mo 0.1-0.3 mol%) was deduced from the graph of absorption coefficient square against photon energy as in figure 5. The films prepared for the photovoltaic and solar cells application recorded the energy bandgap of 1.50 eV for the zinc selenide material and 1.55 - 2.55 eV for the zinc selenide doped molybdenum.

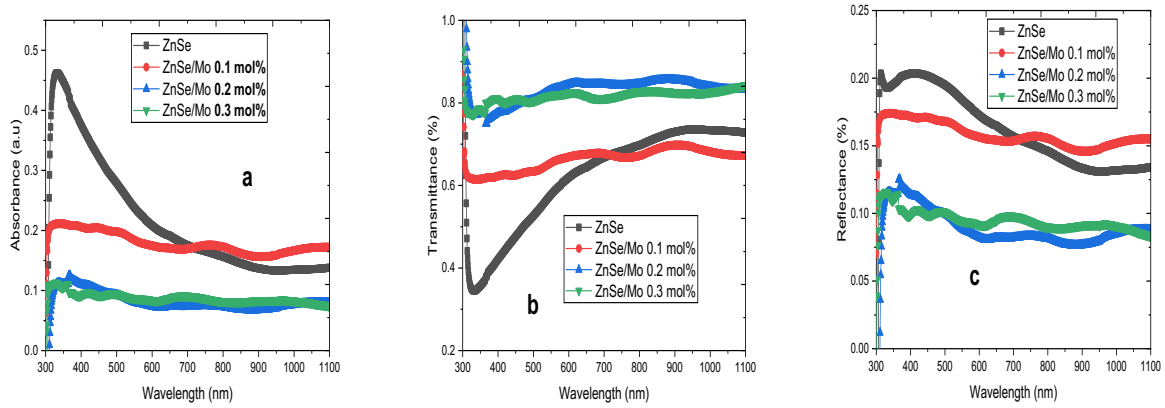


Figure 4: Plot of Absorbance (a) Transmittance (b) and Reflectance (c) with wavelength zinc selenide and zinc selenide doped molybdenum

From the result, it's seen that introduction of molybdenum into zinc selenide affects energy bandgap. The efffect of the molybdenum dopant on ZnSe which acted as a substitutional impurity in its lattice location and also due to the creation of nanosized particles and there is no recorded research report on ZnSe/Mo before this study. Due to the narrowed energy bandgap exhibited by this doped material, it will be a promising material for photovoltaic applications and solar cell fabrication in particular [22-25].

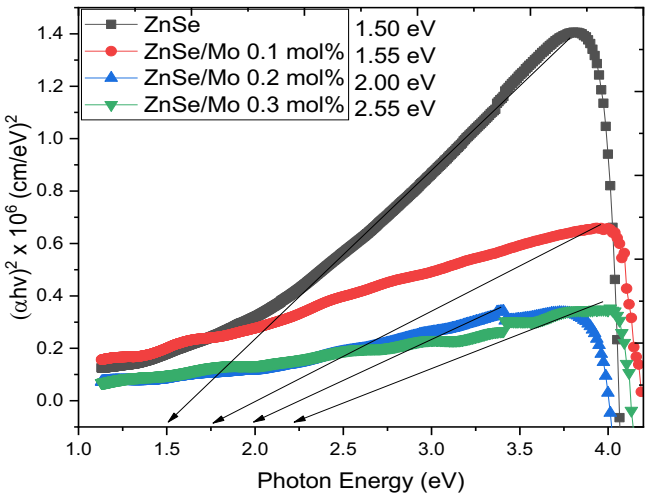


Figure 5: Energy band gap of zinc selenide and zinc selenide doped molybdenum

The optical refractive index of the prepared zinc selenide and zinc selenide doped molybdenum gain energy as the photon energy hike and is expelled, which shows the typical scattering behavior of

the films. This is so because, at the appearance of light on the material with a high refractive index, the refraction angle will be lesser than the incidence angle and light will be refracted towards the routine of the films. The graph of refractive index with photon energy in figure 6a shows that zinc selenide film absorbs more energy when expose to light and has a higher refractive index compared to the films doped with molybdenum. It was also noticed from the graph that as the dopant concentration of molybdenum increase the refractive index decreases which make the prepared films a good candidate for photovoltaic and solar cells application when fabricated. The optical extinction coefficient is the amount of energy depletion when an electromagnetic wave propagates through a material like zinc selenide and zinc selenide doped molybdenum [22-25]. The extinction coefficient graph in figure 6b reveals a downturn as the photon energy progresses, the lower the extinction value the better the material and more useful the films for photovoltaic and solar cells application.

Figure 6c reveals the graph of optical conductivity with photon energy which is the equity of a material that reveals the link between the induced current density in the films and the consequence of the inducing electric force field for a random beat. The optical conductivity has a steady rise from 1.2 eV to 4.0 eV which show the films will act as a good candidate for photovoltaic and solar cells application.

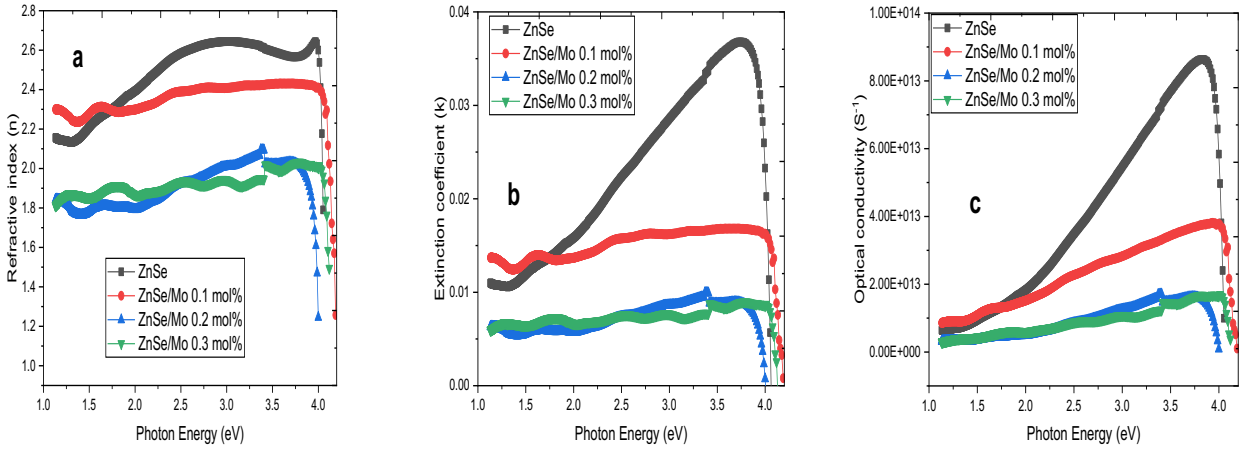


Figure 6: Plot of (a) Refractive index (b) Extinction coefficient and (c) Optical conductivity with photon energy for zinc selenide and zinc selenide doped molybdenum

3.4 Electrical properties of zinc selenide and zinc selenide doped molybdenum

Table 3 shows the electrical properties of zinc selenide and zinc selenide doped molybdenum. The materials deposited at molar percent concentration of molybdenum (0.1. 0.2 and 0.3 mol%) shows a rise in thickness from 102.86 – 122.51 nm with an increase in the resistivity of the synthesized films from $4.214x10^{5}$–$6.214x10^{5}$ Ω.cm; which results in the downturn of the conductivity of films from $2.373x10^{11}$ – $1.609x10^{11}$ S/m. The rise in resistivity makes the film suitable for photovoltaic and solar cells application whereby improving conversion efficiency as this could reduce the inevitable defects in solar cell fabrication during the production process. As a result, Molybdenum-doped ZnSe thin films are suitable for fabricating buffer layers in solar cells and photovoltaic devices [22-25]. The plots of resistivity and conductivity as a function of thickness and dopant concentration in figure 7 (a-b) concede that as the thickness of the deposited films rises there was a downturn in the resistivity whereas the conductivity of the films increases. When comparing the resistivity and conductivity of the films with the dopant concentration, it was discovered that a downturn was recorded for the resistivity and conductivity rises as the dopant concentration of molybdenum increases from 0.1- 0.3 mol%.

Table 3: Electrical parameters of the zinc selenide (ZnSe) and zinc selenide doped molybdenum ZnSe/Mo films

Label	Thickness, t (nm)	Resistivity, **ρ** (Ω.cm)	Conductivity, **σ** (S/m)
ZnSe	102.86	$4.214x10^5$	$2.373x10^{11}$
ZnSe/Mo 0.1 mol%	112.25	$5.654x10^5$	$1.768x10^{11}$
ZnSe/Mo 0.2 mol%	120.16	$5.711x10^5$	$1.751x10^{11}$
ZnSe/Mo 0.3 mol%	122.51	$6.214x10^5$	$1.609x10^{11}$

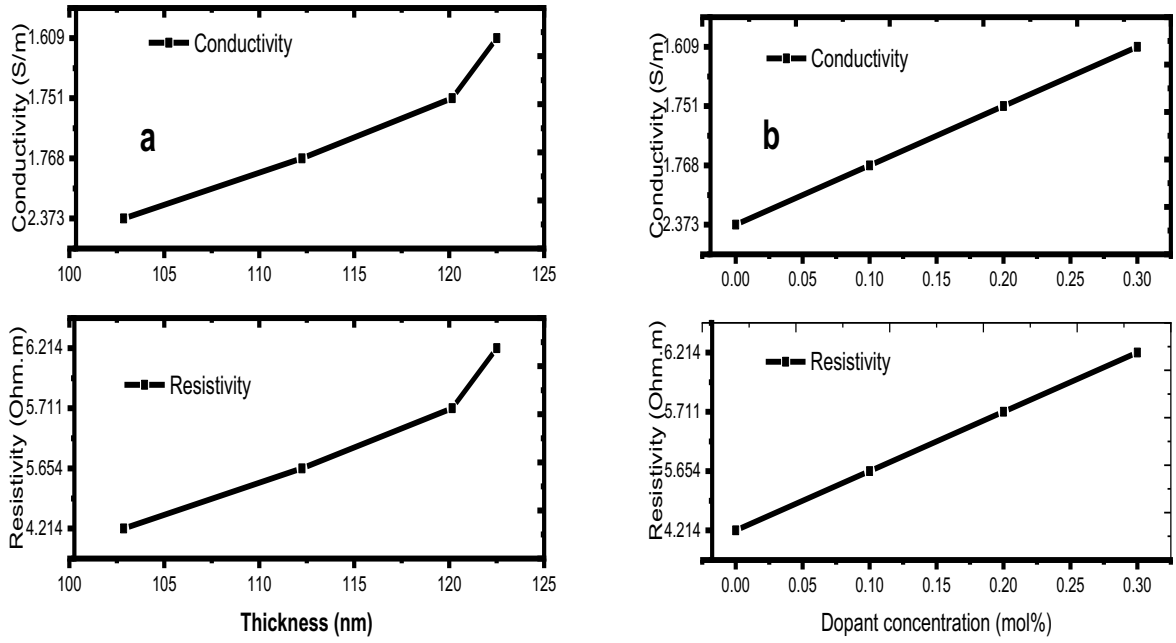


Figure 7: Plot of Resistivity and Conductivity as a function of Thickness (a) and Dopant concentration of molybdenum (b)

Conclusions

Zinc selenide and zinc selenide doped molybdenum have been successfully prepared on a fluorine-doped tin oxide slide (FTO) via electrochemical deposition technique where Zinc tetraoxosulphate (VI) heptahydrate ($ZnSO_4.7H_2O$), selenium powder (Se), and molybdenum dioxide (MoO_2) subsequently as the zinc ion source, selenium ion source, and doping source. The materials for characterization ZnSe/Mo, including, the molarity, pH, deposition voltage have been improved at the commencing mount of the synthesis. The scanning electron microscopy, energy dispersive X-ray, structural, optical, electrical analysis were studied. The prepared zinc selenide thin films material (ZnSe) and zinc selenide doped molybdenum (ZnSe/Mo) is polycrystalline structure with extrusive adopted orientation along (101) plane. A thick precipitate crystallite-like particles poised of different sizes were noticed for ZnSe which consist of unendingly, formed, and tightly packed together. The zinc selenide doped molybdenum image reveals crystallite-like cracks of melted scum far smaller than that of ZnSe and reduces beyound in size as the molar percentage of Molybdenum rises. The films prepared for the photovoltaic and solar cells application recorded the energy bandgap of 1.50 eV for the zinc selenide material and 1.55 - 2.55 eV for the zinc selenide doped molybdenum. The absorbance measurements of all the thin films were observed to have good absorption at the UV region down to the ultraviolet

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Declarations
Funding: The authors received no funding for this research.
Conflicts of Interest: None to declare
Ethical Statement: The *paper* reflects the authors' *research* and analysis truthfully and completely.
Data Availability Statement: The data that support the findings of this study are available on request from the corresponding author

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