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Original Research Article

The influence of gamma irradiation ^{60}Co On CoSe/Ag nanostructures material deposited via electrochemical deposition technique for photovoltaic application

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ABSTRACT

This study aimed at investigating the influence of Gamma-irradiation ^{60}Co on CoSe/Ag nanostructures material deposited on a transparent conducting substrate via electrochemical deposition technique. The cationic, anionic, and dopant precursors used were respectively 0.01 mol of cobalt (II) acetate tetrahydrate ($Co(NO_3)_2.6H_2O$), 0.01 mol of selenium (IV) oxide (SeO_2), and 0.02 mol of silver nitrate ($AgNO_3$). The structural, optical, and morphological properties of the deposited films were respectively evaluated using X-ray diffraction (XRD) analysis, UV-visible spectrophotometry, and scanning electron microscopy (SEM). The cobalt selenide/silver films exhibited cubic polycrystalline structure for both unirradiated film at 0Gy and irradiated films of CoSe/Ag material at (200Gy -500Gy) with low bandgap energies and high absorbance values. The surface morphology of the films revealed clustered nanobubbles with no evidence of pinholes. The deposited CoSe/Ag films find potential application in photovoltaic and solar cells.

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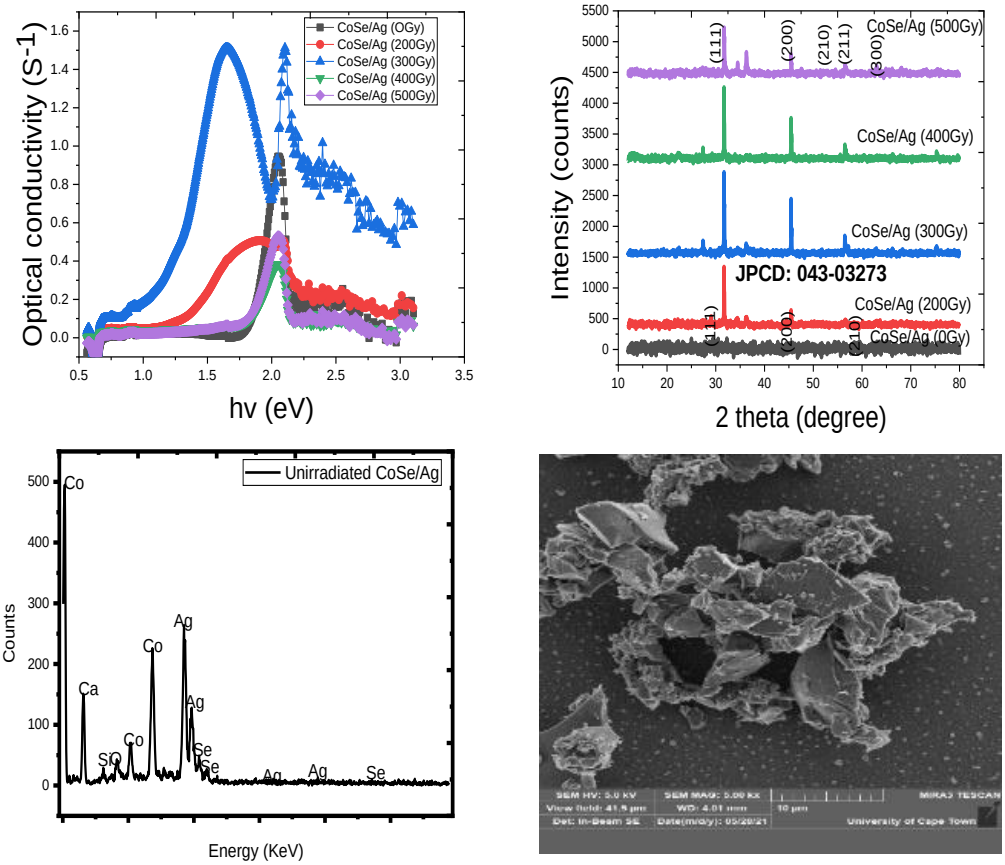
Graphical Abstract



Introduction

Recently, interest in the chalcogenides of semiconductors, metals, and transition metals has increased tremendously due to their tunable property which makes them useful candidates in various electronics and optoelectronic devices including solar cells, sensors, laser materials, photoconductors, diodes, and transistors thin-film deposition of chalcogenides [1–4] materials has been reported by various researchers. Transition-metal selenides have received considerable attention in the past few years due to their unusual structures and electronic properties [5]. These materials, in thin-film form, have found many applications such as in solar cells, light-emitting devices, catalysts, and superionic conductors. These deposition methods include chemical bath deposition technique, evaporation [6], electro-deposition [7–9], spray pyrolysis technique [10–12]. In conparison with the other technique, electrochemical deposition technique have diverse edge including; a low cost, high rate process involving simple and low-priced equipment; a large-area, low-temperature deposition technique; deposition of films on a variety of shapes and sizes; and no use of toxic chemicals, effective material use, and minimum waste generation solution can be recycled. Many attempts have been made for the electrochemical deposition technique of late transition-metal selenide thin. However, the preparation of cobalt selenide by this effective, low-cost technique has not been reported. For this research, cobalt selenide/silver (CoSe/Ag)

thin films were syntheses by electrochemical deposition technique from an aqueous solution. The films were characterized for their elemental composition, morphology, structure, and optical properties.

Experimental

Analytical grade chemicals were purchased and used without further purification. The conducting glass substrates were sterilized in acetone, ultrasonicated for 30 minutes, rinsed in distilled water, and oven-dried. The cationic, anionic, and dopant precursors used were respectively 0.01 Mol of cobalt (II) acetate tetrahydrate ($Co(NO_3)_2.6H_2O$), 0.01 Mol of selenium (IV) oxide (SeO_2), and 0.02 Mol of silver nitrate ($AgNO_3$). The electrochemical deposition technique was adopted in depositing the films. The electrochemical setup was made up of a bath consisting of 20 mL each of the cationic precursor, anionic precursor, and distilled water in a 100 mL beaker. Direct current voltage was obtained from the power supply while the cathode and anode materials were fluorine-doped tin oxide and carbon. Introducing the silver dopant was achieved by adding 10 mL of 0.02 Mol of silver nitrate, $AgNO_3$ into the electrochemical bath. The samples were obtained at temperatures of 27 ^oC (room temperature), at pH values of 6.5. See Table 1 for other parameters that were varied during the deposition process. After the deposition, the films were further exposed with ^{60}Co radionuclide with an activity of 1109.37MBq and a half-life of 5.27 years. The irradiation dose rate of 33.626Gy/ hour was used to generate a set of irradiation doses (200Gy, 300Gy, 400Gy, and 500Gy). Then each of the films was placed in a chamber containing ^{60}Co and irradiated at room temperature at different exposure times. The cobalt selenide/silver films deposited were characterized for their surface morphological, structural, elemental, and optical features using a scanning electron microscope, Bruker D8 Advance X-ray diffractometer, energy dispersive X-ray spectroscope, UV-1800 spectrophotometer, and a four-point probe respectively.

Table 1. Varied growth parameters in the deposition process

Sample	$(AgNO_3)$ (mL)	$(Co(NO_3)_2.6H_2O)$ (mL)	(SeO_2), (mL)	^{60}Co (Gy)	Time (s)	Voltage (V)
CoSe/Ag (0Gy)	10	20	20	0	10	10
CoSe/Ag (200Gy)	10	20	20	200	10	10
CoSe/Ag (300Gy)	10	20	20	300	10	10
CoSe/Ag (400Gy)	10	20	20	400	10	10
CoSe/Ag (500Gy)	10	20	20	500	10	10

Results and Discussion

Optical studies

The absorbance of unirradiated CoSe/Ag (0Gy) and irradiated with ^{60}Co radionuclide at the different doses of (200Gy, 300Gy, 400Gy, and 500Gy) thin-film material deposited at 0.02 mol dopant concentration of silver (Ag) is shown in Figure 1**a**. All the deposited films displayed a similar trend, high absorbance value in the Uv region which declines as the wavelength shifts toward the Vis-NIR region of the spectrum. The addition of different irradiation doses to the films increases the absorbance of the CoSe/Ag thin films all through the electromagnetic region when compared to unirradiated CoSe/Ag (0Gy). Further increase of the irradiation dose

drastically reduced the absorbance value even beyond the unirradiated CoSe/Ag (0Gy) absorbance value. The high absorbance exhibited by CoSe/Ag in the Uv region makes the material suitable for p-n junction formation in solar cells and photovoltaic application in general. The transmittance of unirradiated CoSe/Ag (0Gy) and irradiated with ^{60}Co radionuclide at the different doses of (200Gy, 300Gy, 400Gy, and 500Gy) thin-film material deposited at 0.02 mol dopant concentration of silver (Ag) is shown in Figure 1**b**. All the deposited films displayed a similar trend, an increase in the percentage transmittance as the wavelength increases. Addition of different irradiation dose to the films, decrease the transmittance of CoSe/Ag thin films especially in the VIS-NIR region of the spectrum, which amounts to its use as a good material for solar energy collector and optical devices (Ikhioya *et al*., 2020a, and Ikhioya *et al*., 2020b).

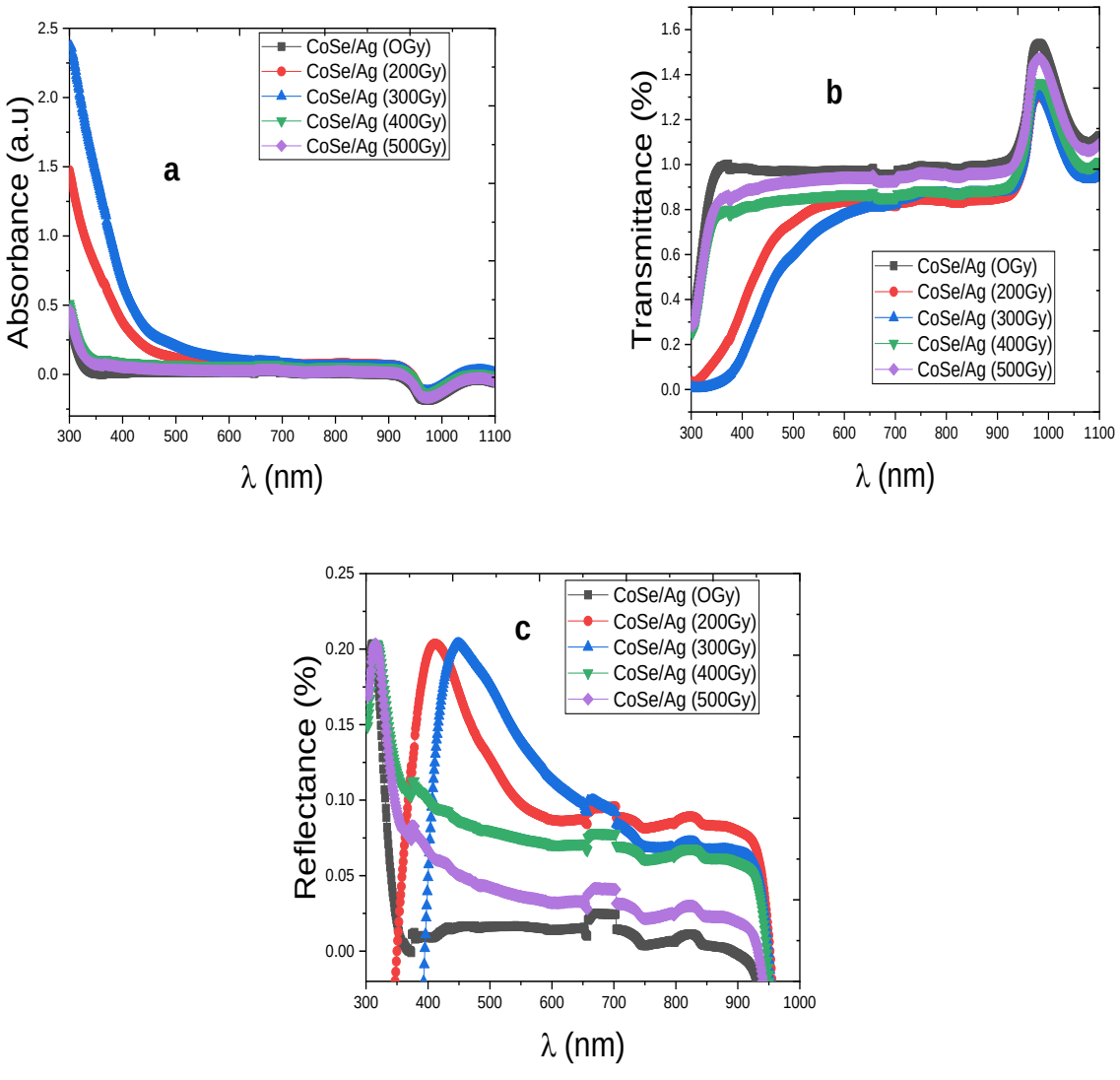


Figure 1. Absorbance a) Transmittance b) and Reflectance c) of CoSe/Ag for unirradiated @ 0Gy and irradiated @ (200-500Gy)

The reflectance of unirradiated CoSe/Ag (0Gy) and irradiated with ^{60}Co radionuclide at the different doses of (200Gy, 300Gy, 400Gy, and 500Gy) thin-film material deposited at 0.02 mol dopant concentration of silver (Ag) is shown in Figure 1**c**. All the deposited films displayed a similar trend, high reflectance in the Uv region which declines as the wavelength shifts toward the Vis-NIR region of the spectrum. The addition of different irradiation doses to the films increases the reflectance of the CoSe/Ag thin films all through the electromagnetic region when compared to unirradiated CoSe/Ag (0Gy). Further increase of the irradiation dose drastically increases the reflectance beyond the unirradiated CoSe/Ag (0Gy) reflectance. The high reflectance exhibited by CoSe/Ag in the Uv region makes the material suitable for p-n junction formation in solar cells and photovoltaic application in general.

Figure 2 shows a graph of $(\alpha h\nu)^2$ as a function hν for unirradiated CoSe/Ag and irradiated CoSe/Ag with ^{60}Co radionuclide at the different dose of (200Gy, 300Gy, 400Gy, and 500Gy) thin-film material deposited at 0.02 mol dopant concentration of silver (Ag). The energy bandgap of the materials was evaluated by extrapolating the linear portion of the graph down to the hv axis at $(\alpha h\nu)^2 = 0$. The unirradiated CoSe/Ag had an energy band gap value of 1.80 eV while the and irradiated CoSe/Ag with ^{60}Co radionuclide at the different doses of (200Gy, 300Gy, 400Gy, and 500Gy) recorded 1.30 eV, 1.25 eV, 1.62 eV, and 1.70 eV respectively.

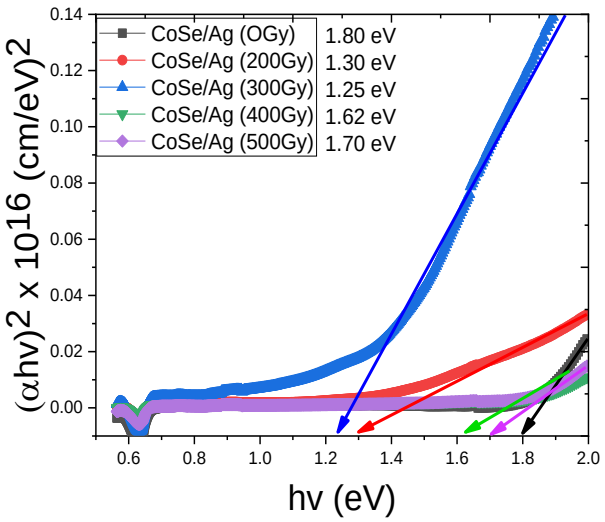


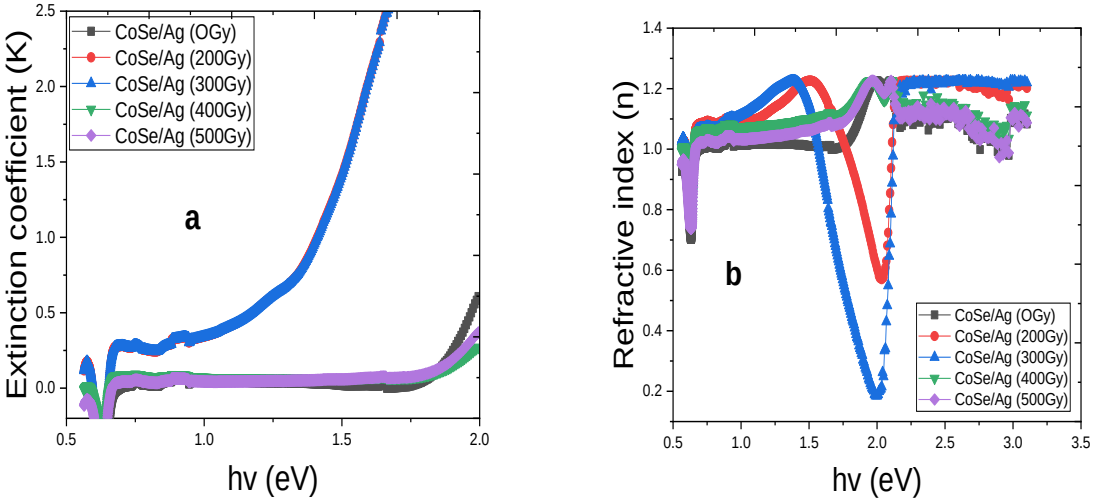
Figure 2. Energy band gap of CoSe/Ag for unirradiated @ 0Gy and irradiated @ (200-500Gy)

Figure 3**a** displays the plot of extinction coefficient as a function of photon energy for unirradiated CoSe/Ag and irradiated CoSe/Ag with ^{60}Co radionuclide at the different doses of (200Gy, 300Gy, 400Gy, and 500Gy) thin-film material deposited at 0.02 mol dopant concentration of silver (Ag). The unirradiated CoSe/Ag and irradiated CoSe/Ag were observed to increase with a rise in photon energy at both regions of the spectrum. This infers that the deposited films recorded a minimum extinction coefficient in the UV region and maximum in the IR region which is a captivating property for photonic devices (Ikhioya 2020). Figure 3**b** displays the plot of refractive as a function of photon energy for unirradiated CoSe/Ag and

irradiated CoSe/Ag with ^{60}Co radionuclide at the different doses of (200Gy, 300Gy, 400Gy, and 500Gy) thin-film material deposited at 0.02 mol dopant concentration of silver (Ag). It was observed that CoSe/Ag unirradiated increases with an increase in photon energy and the irradiated films of CoSe/Ag decrease with an increase in photon energy with the maximum value of 1. 2 at 3.4 eV. Figure 3**c** shows the plot of optical conductivity for unirradiated CoSe/Ag and irradiated CoSe/Ag with ^{60}Co radionuclide at the different doses of (200Gy, 300Gy, 400Gy, and 500Gy) thin-film material deposited at 0.02 mol dopant concentration of silver (Ag). All the samples exhibited a similar trend of a slight increase in optical conductivity with an increase in photon energy. The irradiated CoSe/Ag recorded the highest optical conductivity. It was also observed that dosimetry of Gamma ^{60}Co exposure has little or no effect on the optical conductivity of CoSe/Ag.

Structural study

The XRD pattern of CoSe/Ag thin films materials deposited at 0.02 mol% concentration of silver (Ag). The pattern reveals cubic polycrystalline structure for both unirradiated film at 0Gy and irradiated films of CoSe/Ag material at (200Gy -500Gy). It has shown well-defined peaks corresponding to (111), (200), (210), (211), and (300) that were obtained in the XRD analysis. Subjecting the films to high gamma irradiation of Co-60 source enhanced the crystallinity of CoSe/Ag as seen from the increased peak intensity (Figure 4). Ikhioya et al., (2020) also reported improved crystallinity of CoSe when doped with ytterbium. The information obtained during the XRD analysis was used to calculate some structural parameters (Ikhioya *et al*., 2020) like crystalline size (D), dislocation density, etc as outlined in Table 2.



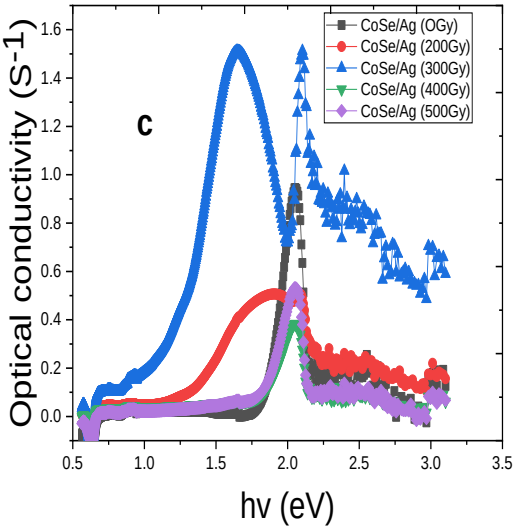


Figure 3. Extinction coefficient a) Refractive index b) and optical conductivity c) of CoSe/Ag for unirradiated @ 0Gy and irradiated @ (200-500Gy)

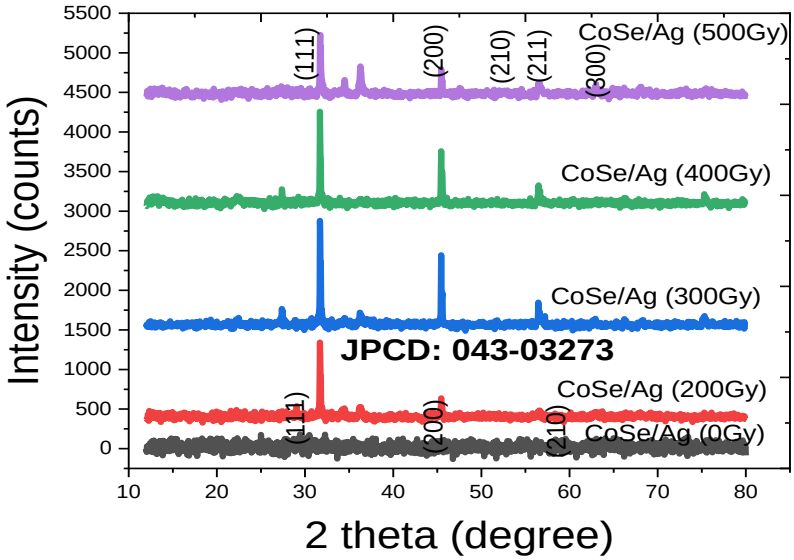


Figure 4. XRD pattern of CoSe/Ag for unirradiated @ 0Gy and irradiated @ (200-500Gy)

Table 2. Structural parameters of CoSe/Ag for unirradiated @ 0Gy and irradiated @ (200-500Gy)

Sample	2θ (degree)	(hkl)	d-spacing Å	a (Å)	FWHM (β)	Crystallite Size, D (nm)
CoSe/Ag (0Gy)	29.2196	111	3.0535	5.2888	0.1851	0.7738
CoSe/Ag (200Gy)	31.8266	200	2.8090	5.6181	0.2095	0.6879
CoSe/Ag (300Gy)	45.3758	210	1.9968	3.9936	0.1481	1.0154
CoSe/Ag (400Gy)	56.5583	211	1.6257	3.6351	0.2258	0.6971
CoSe/Ag (500Gy)	62.9728	300	1.4746	3.6121	0.2249	0.7227

Elemental composition and surface morphological of CoSe/Ag for unirradiated @ 0Gy and irradiated @ (200-500Gy)

The elemental composition of unirradiated CoSe/Ag and irradiated CoSe/Ag materials was carried out using the energy dispersive X-ray diffractometer (EDX) technique (see Figure 5**a**,**b**). The deposition of CoSe/Ag was noticed in the EDX spectra in Figure 5 with the presence of other elements as a result of the elemental composition of the FTO substrate used to deposit the materials.

Figure 6 displays the surface morphological images of the deposited materials CoSe/Ag. It was observed that for the unirradiated CoSe/Ag @ 0Gy flat crake stones with no evidence of pinholes in between the crake stones and the irradiated CoSe/Ag @ 200-400Gy thick precipitate like crystallite particles all pack together composed of various sizes were observed which consist of unevenly shaped and firmLy packed particles, the crystallite size is like cracks of melted metals. The irradiated CoSe/Ag @ 500Gy showed a nanowire shape all packed together with no evidence of pinhole. The deposited CoSe/Ag films find potential application in photovoltaic and solar cells.

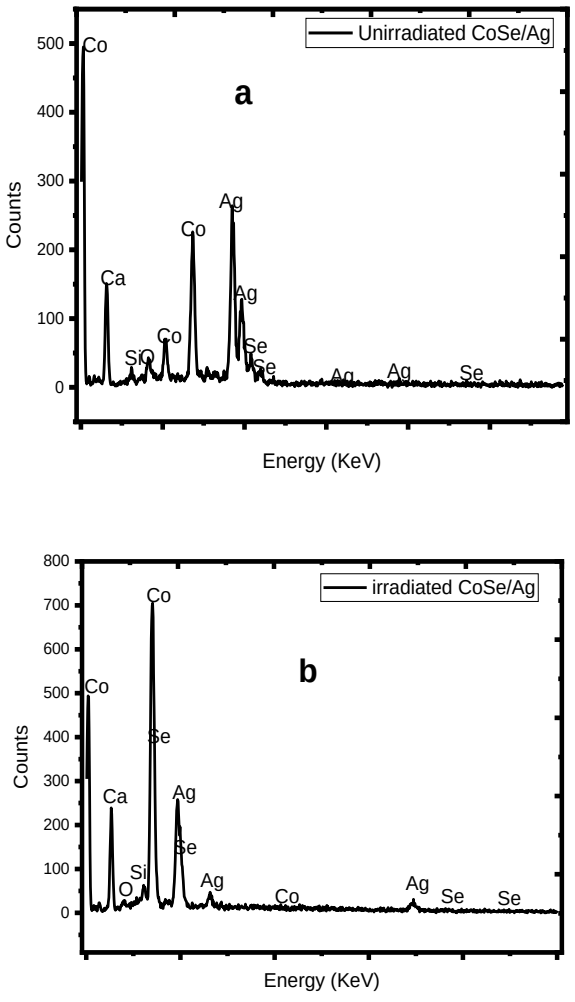


Figure 5. EDX spectra of CoSe/Ag for unirradiated and irradiated

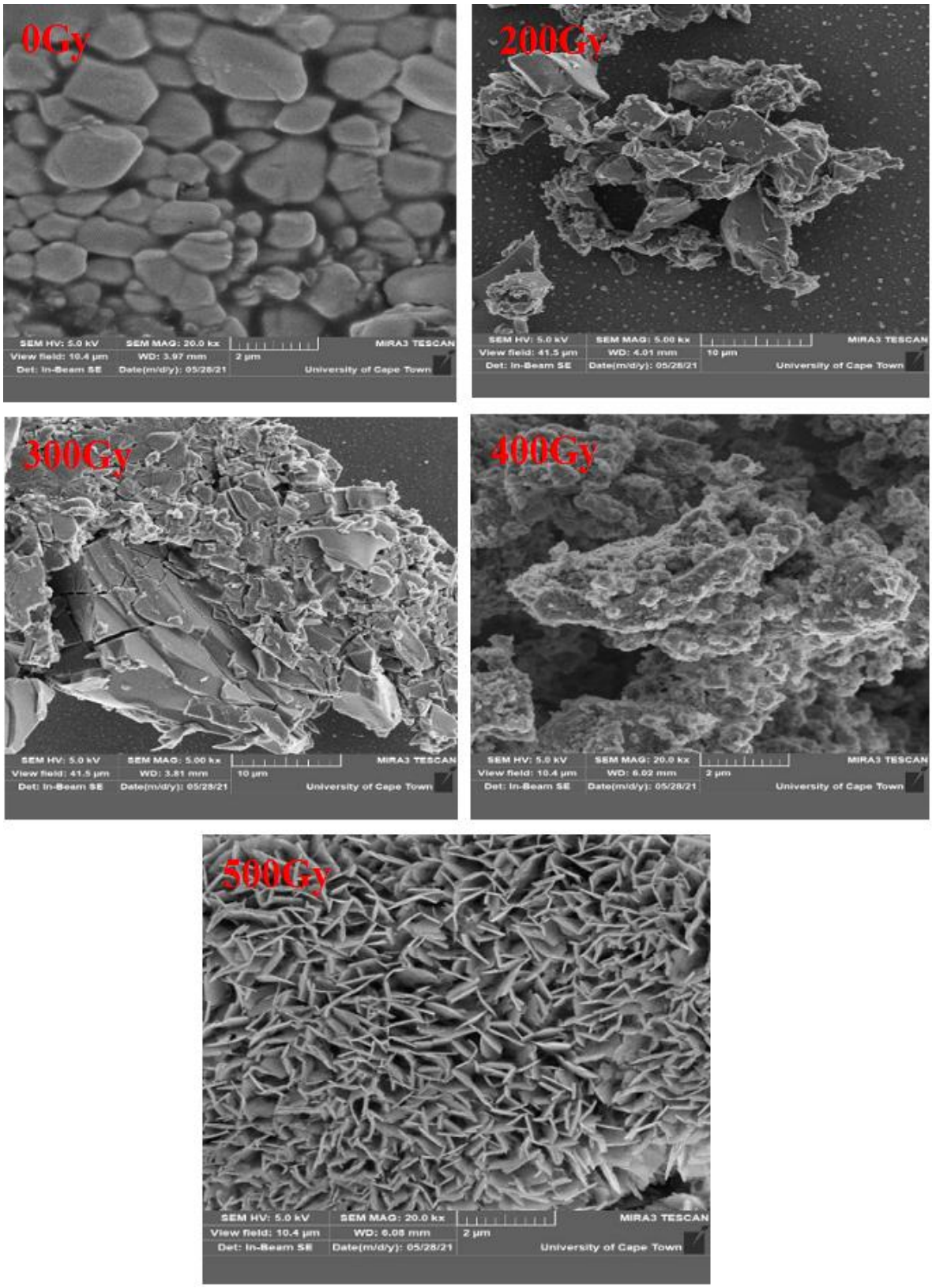


Figure 6. SEM of CoSe/Ag for unirradiated @ 0Gy and irradiated @ (200-500Gy)

Electrical studies

Electrical parameters of CoSe/Ag for unirradiated @ 0Gy and irradiated @ (200-500Gy) films prepared using the ECD technique are presented in Table 3. The unirradiated sample recorded the thickness of 124.54 nm while the irradiated samples with a thickness of 120.05 – 103.09 nm with the increase in the resistivity of the deposited material from $4.893x10^6$ – $8.204x10^6$ Ω.cm; thereby resulting in decreased conductivity of the deposited material from $2.043x10^9$ – $1.218x10^9$ S/m. As the dose rate increases, the vibrations of the deposited materials increase; thereby increasing the resistivity and reducing the conductivity of the films. The high resistivity value makes this thin film useful in solar cells application to improve conversion efficiency as this could reduce the inevitable defects in solar cell fabrication during the production process. Figure 6 revealed the plots of conductivity a), resistivity b) against thickness and conductivity c), resistivity d) against dose rate.

Table 3. Electrical parameters of CoSe/Ag for unirradiated @ 0Gy and irradiated @ (200-500Gy)

Samples	Thickness, t (nm)	Resistivity, ρ (Ω.cm)	Conductivity, σ (S/m)
CoSe/Ag (0Gy)	124.54	$4.893x10^6$	$2.043x10^9$
CoSe/Ag (200Gy)	120.05	$7.343x10^6$	$1.361x10^9$
CoSe/Ag (300Gy)	118.34	$7.774x10^6$	$1.286x10^9$
CoSe/Ag (400Gy)	111.45	7.954x106	$1.257x10^9$
CoSe/Ag (500Gy)	103.09	$8.204x10^6$	$1.218x10^9$

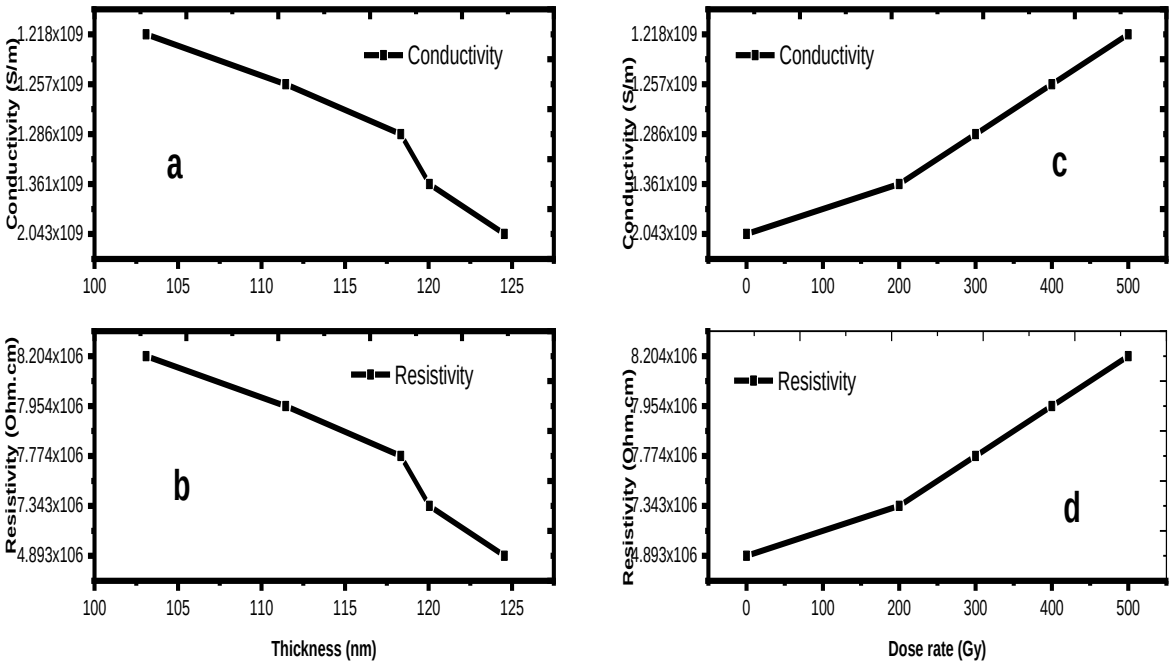


Figure 6. Plot of conductivity a), Resistivity b) against thickness and conductivity c), Resistivity d) against dose rate

Conclusions

The cobalt selenide/silver (CoSe/Ag) was successfully deposited, irradiated, and characterized using the ECD technique, irradiation dose rate of 33.626Gy/ hour was used to generate a set of irradiation doses (200Gy, 300Gy, 400Gy, and 500Gy), X-ray diffractometry was used to obtain the structural of the films, UV-visible spectrophotometry was used to obtain the optical features, scanning electron microscopy was used to obtain the surface morphology. All the deposited films displayed a similar trend, high absorbance value in the Uv region which declines as the wavelength shifts toward the Vis-NIR region of the spectrum. The addition of different irradiation doses to the films increases the absorbance of the CoSe/Ag thin films all through the electromagnetic region when compared to unirradiated CoSe/Ag (0Gy). Further increase of the irradiation dose drastically reduced the absorbance value even beyond the unirradiated CoSe/Ag (0Gy) absorbance value. The high absorbance exhibited by CoSe/Ag in the Uv region makes the material suitable for p-n junction formation in solar cells and photovoltaic application in general. The unirradiated CoSe/Ag had an energy band gap value of 1.80 eV while the and irradiated CoSe/Ag with ^{60}Co radionuclide at the different doses of (200Gy, 300Gy, 400Gy, and 500Gy) recorded 1.30 eV, 1.25 eV, 1.62 eV, and 1.70 eV respectively.

Disclosure Statement

No potential conflict of interest was reported by the authors.

Orcid

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