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Impact of temperature difference on the features of spray deposited yttrium doped cobalt selenide (YCoSe) thin films for photovoltaic application

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Abstract

In this investigation, spray deposited yttrium doped cobalt selenide (YCoSe) thin materials were synthesized in soda lime glass and the impact of substrate temperature (140 °C, 160 °C, 180 °C and 200 °C) on their elemental composition, surface morphology, structural, electrical and optical properties were investigated using scanning electron microscopy-SEM X-ray diffraction –XRD, four-point probe and UV-VIS spectrophotometer respectively. The EDX plots of the deposited undoped and Y-doped cobalt selenide revealed the major elements: cobalt, selenium and yttrium. This confirms the deposition of CoSe and Y-doped CoSe thin materials. The morphology of undoped CoSe thin materials was very rough containing randomly oriented non-uniform thin particles while addition of Y dopant (0.1 mol%) at substrate temperature of 140 °C gave a homogenous distribution of compact rectangular-like nanograins. The XRD result shows that the films are cubic polycrystalline in nature and the film grown at substrate temperature of 180 °C was seen to give the most excellent crystalline quality and a preferential orientation along (111) direction. From electrical results it was observed that increase in substrate temperature increased the film thickness with decreased resistivity and increased conductivity. The optical properties were found to vary with substrate temperature despite the fact that the variation was not totally linear, as the film deposited at substrate temperature of 160 °C deviated from the linearity in all the optical properties. The energy band gap of the deposited samples ranges from 1.25 eV–1.75 eV. The materials produced could be used in the production of photovoltaic devices.

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1. Introduction

Nanomaterials have attracted notable attention in the 21st century production industries for several purposes due to their unique features. These unique optical, mechanical, electrical and chemical features possessed by these nanomaterials as a result of their

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quantum confinement and surface effects happens during size reduction [1, 2].

Numerous researches have been carried out on the deposition, characterization and possible application of metal selenides such as CdSe, CuSe, CoSe, ZnSe, SnSe [3–19]. Generally, selenide nano materials have been instrumental in production of photovoltaic, electronics and optoelectronic devices such as laser materials, LEDs, sensors, diodes, transistors, solar cells etc [3, 5, 14–16]. The selenide material of interest in this research study is the cobalt selenide (CoSe) material which fits into group II-VI of the periodic table. The unique feature of this semiconducting nanomaterial such as optimal band gap of 1.5 eV which conforms with the optimum of the special region, a high conductivity and strong absorption coefficient 10^5 cm^{-1} makes it a suitable material for use as a photovoltaic device [14, 17].

Furthermore, Ikhioya *et al.* [15] reported that CoSe can be used as a highly performing counter electrode in dye-sensitized solar cell (DSSC), photoelectrodes, as catalysts wastewater treatment and magnetic devices. CoSe is said to be relatively abundant in nature and hence said to be renewable over time. Nevertheless, non-renewable energy sources have been the core sources of energy globally and due to its negative effect on the world climate, research is ongoing for sustainable and environmentally-friendly sources [18]. Therefore, solar energy, which is a type of renewable energy, promises a sustainable solution to the world's energy problem by utilizing photovoltaic (PV) devices that are readily capable of converting solar energy directly to electricity [15].

To enhance the performance of CoSe nano material several researchers have used the doping technique to make nano materials of Yb:CoSe [5, 15], CoSe.MoSe [13], Er:CoSe [3, 14], Zr:CoSe [16] prepared using several deposition techniques such as Spray pyrolysis, Electrodeposition, Chemical bath, SILAR [16–24]. Imosobomeh *et al.* investigated the impact of temperature on spray synthesized CoSe doped with Zr [16]. They observed that Zr:CoSe film deposited at 145 °C has no noticeable peak when compared to other film deposited at higher temperature. More so, increased thickness at increasing temperature was observed. Cobalt selenide doped with erbium (CoSe;Er) was synthesized by Imosobomeh *et al.* [3]. From the XRD result, decrease in peak intensity as the deposition temperature increases was recorded. Also, as temperature increases, the value of the bandgap increases from 1.52 eV for 140 °C to 2.35 eV for 200 °C. Xu *et al.* prepare CoSe doped with Mn. Improved conductivity and high carrier concentration caused by the incorporation of Mn was observed thereby making the films an ideal candidate for oxygen evolution reaction (OER) [25]. In this research we decided to grow CoSe doped with yttrium which is novel. Yttrium is one of the promising dopants in the family of rare earth metals due to the fact that it improves fatigue endurance, leakage current and remanent polarization. It can also act as an acceptor or donor ion. Another major effect of yttrium doping is the change in the electrical conductivity of doped material with respect to the doping site [6].

In this study our major focus is on the impact of different substrate temperature on the elemental composition, morphology, structural, electrical and optical properties of yttrium doped CoSe (YCoSe). As we write, there is no published article on Y doped CoSe at different substrate temperature.

2. Materials and method

2.1. Reagent used

Reagent used in this research, such as Cobalt (II) acetate tetrahydrate ($Co\ (NO_3)_2.6H_2O$), Selenium (iv) oxide (SeO_2), Yttrium and Hydrogen Chloride (HCl) were of analytical grade and used without further purification. Distilled H_2O was used as solvent throughout the deposition process.

2.2. Deposition process

Yttrium cobalt selenide (YCoSe) thin films were fabricated on glass substrates via spray pyrolysis method [25] at varied substrate temperature range of 140 – 200 °C at the interval of 20 °C. Homogeneous solution was prepared by dissolving cobalt (II) acetate tetrahydrate ($Co\ (NO_3)_2.6H_2O$) (0.01 mol.), selenium (iv) oxide (SeO_2) (0.01 mol) and yttrium (0.1 mol). Hydrogen chloride was used as a complexing agent. Glass slides were employed as substrates. Preceding the deposition these glass substrates were cleaned with water followed by immersion in acetone and methanol for 24 hours and washed in distilled water. Finally, they were ultrasonically cleaned for 30 mins, rinsed and allowed to air dry. A constant spray rate of 0.07 ml/min and substrate to spray nozzle distance of 8mm were used throughout the deposition. After the synthesis, the films were allowed to cool at room temperature. Film uniformity was achieved by moving both the substrate and nozzle (needle). Here are the chemical formulae of the synthesized material ($Y_{0.1}+Co+Se \rightarrow Y_{0.1}CoSe$)

2.3. Characterization

The deposited thin films of Y doped CoSe (at different substrate temp. 140, 160,180 and 200 °C) were analyzed for elemental composition, morphological, structural, electrical and optical properties [26]. The film thickness of the deposited thin films was obtained using a probe in the four-point probe instrument; this same instrument was used to measure the voltage drop as current flows. Through this the electrical properties were evaluated. The structural property of the films was obtained by studying the X-ray diffraction (XRD) spectrum using Cu-K_α (λ = 1.15418 Å) diffractometer. UV-Visible spectrophotometer was used to measure the optical absorbance of the thin samples in the wavelength between 300−1100 nm. The compositional and morphology analysis of the deposited YCoSe thin films was carried out using SEM/EDXs. Relevant mathematical relations were also employed to further investigate the properties of YCoSe thin film at difference temperature.

Table 1. Electrical properties of YCoSe (at different substrate temperatures).

Sample	Sample Code ($^{\circ}C$)	Thickness, t (nm)	ρ (Ω m) $\times 10^{-6}$	σ (Ω m)$^{-1}$ $\times 10^{5}$
CoSe	CO control	132.15	5.920	1.689
YCoSe (140 ^{o}C)	COY 140	152.90	6.894	1.450
YCoSe (160 ^{o}C)	COY 160	157.40	6.567	1.522
YCoSe (180 ^{o}C)	COY 180	162.20	6.456	1.548
YCoSe (200 ^{o}C)	COY 200	170.30	6.345	1.576

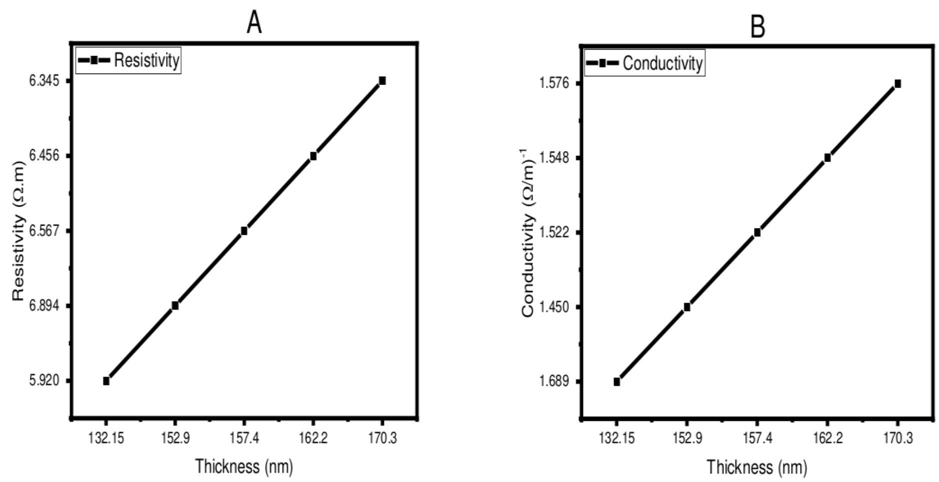

Figure 1. (a) Plot of resistivity and (b) conductivity of YCoSe (at different substrate temp) with respect to film thickness.

3. Result and discussion

3.1. Electrical results of CoSe and YCoSe at different substrate temperature

The electrical analyses of CoSe and yttrium doped CoSe thin materials at difference substrate temperature (140, 160,180 and 200 ^{o}C) are shown in Table 1. The film thickness was observed to increase with increase in substrate temperature. More so, the substrate temperature and the film thickness vary inversely with resistivity and directly with conductivity which is one of the features of a typical semiconductor [19]. The difference in film thickness and other electrical parameters were observed due to the spray process. Figure 1(a-b) displayed the relationship between resistivity and conductivity with film thickness of the thin film materials.

3.2. X-ray diffraction (XRD) result of YCoSe at different substrate temperatures (140, 160, 180 and 200 ^{o}C)

The result of the X-ray diffraction (XRD) of CoSe and yttrium-doped CoSe at different substrate temperature is displayed in Figure 2. The clearly defined peaks in the XRD pattern corresponding to (111), (200), (210), (211) and (300) crystal plane suggests that the films are cubic polycrystalline in nature. Effect of substrate temperature was evident. Increased in substrate temperature from 140 ^{o}C to 180 ^{o}C was observed to improve the crystallinity of the films, further increase to 200 ^{o}C was observed to decreases the crystalline. In summary YCoSe grown at substrate temperature of 180 ^{o}C was observed to give the most excellent crystalline quality with preferential orientation along (111) direction. Table 2 displays some of the structural parameters such as the full width at half maximum (FWHM) (β), crystallite size (D), inter-planar spacing (d), and dislocation density (δ) estimated via mathematical relations [27]:

$$D = \frac{k\lambda}{\beta\cos\theta}, \tag{1}$$

$$d = \frac{\lambda}{2\sin\theta}, \tag{2}$$

and

$$\delta = \frac{1}{D^2}. \tag{3}$$

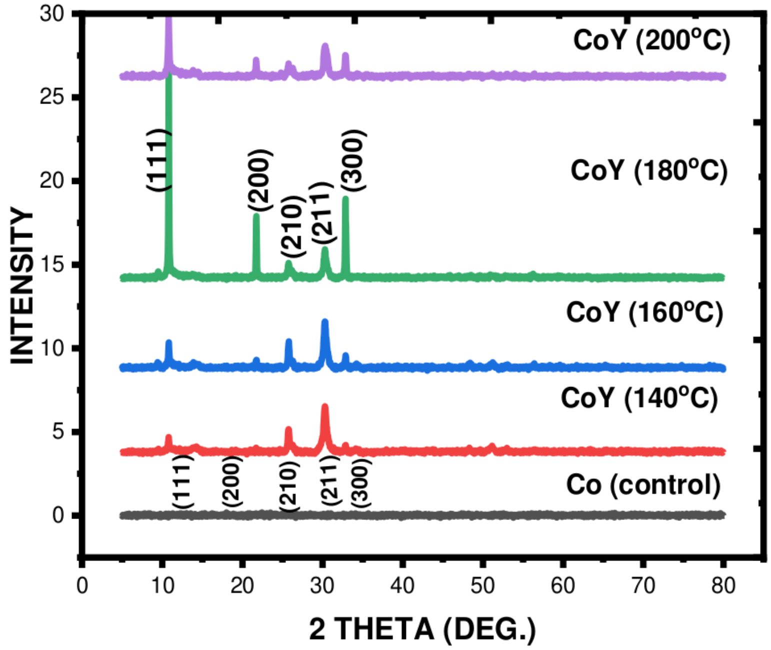

Figure 2. XRD spectrum of YCoSe thin film at different substrate temp (140, 160, 180 and 200 °C).

Table 2. Structural features of YCoSe thin film at varied substrate temp (140, 160, 180 and 200 °C).

Sample Code	2θ (degree)	d(Å)	Latt. constant (Å)	FWHM, β	Hkl	D(nm)	δ (m^2)
CO	13.0287	6.7887	11.7585	0.18517	111	0.75366	5.3380
COY-140 °C	21.6407	4.1027	8.2054	0.20958	200	0.673559	6.6945
COY-160 °C	25.861	3.4419	6.8839	0.1480	210	0.961232	3.2875
COY-180 °C	30.5272	2.9256	6.5419	0.22584	211	0.636403	7.4297
COY- 200 °C	32.9974	2.7120	6.6431	0.22499	300	0.642738	7.3123

3.3. SEM And EDX result CoSe and YCoSe at different substrate temperature

The SEM imaging as seen in Figure 3(a-b) were carried out to investigate the morphologies and microstructural details of CoSe and YCoSe. SEM image, as shown in Figure 3a revealed that the undoped CoSe thin material was very rough containing randomly oriented non-uniform thin particles. Addition of 0.1 mol% of Y dopant on CoSe thin material deposited at substrate temperature of 140 °C as seen in Figure 3b shows a homogenous distribution of compact rectangular-like nanograins. The densely packed grains could be due addition of dopant which was seen to significantly alter the morphology of the undoped sample. The EDX plots of the deposited CoSe and YCoSe thin films are shown in Figure 3(a-b). The major elements: selenium, cobalt and yttrium were seen as constituents of the synthesized thin materials. This confirms the deposition of CoSe and Y-doped CoSe as seen in Figure 3a and Figure 3b, respectively.

3.4. Optical analysis of CoSe and YCoSe at different substrate temperature

The Optical features of Yttrium doped cobalt selenide (YCoSe) thin materials were investigated as a function of substrate temperature at 140, 160, 180 and 200 °C with a constant yttrium concentration of 0.1mol% using spray pyrolysis deposition method.

The absorbance of Yttrium doped cobalt selenide (YCoSe) thin materials at varied substrate temp. as a function of wavelength were displayed in Figure 5(a). The absorbance spectral of all the samples varies with wavelength in the same way, decreasing slowly with increase in wavelength and substrate temperature. The figure indicates that all the samples absorb very well irrespective of the substrate temperature. The maximum absorbance value for all the samples occurred in the UV-region with sample synthesized at the lowest substrate temperature of 140 °C having the maximum absorbance value of 1.05 amidst the other samples synthesized at 160 °C, 180 °C and 200 °C with 0.80, 0.60 and 0.70 as their maximum respectively at 300 nm. Synthesized films' absorption capacity is enhanced by substrate temperature, with higher temperatures leading to better absorbance. The plot shows that lower substrate temperatures result in higher absorbance, while higher substrate temperatures produce lower absorbance, making them more suitable for photovoltaic applications. A similar result was reported by Okoli and Okoli [28] for Chemical bath deposited CoSe and Agbo *et*

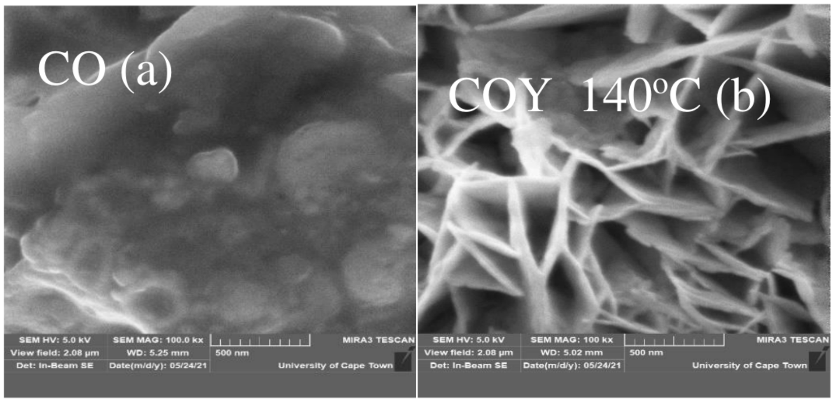

Figure 3. Pictorial view of the SEM images of (a) CoSe and (b) YCoSe at substrate temp. of 140 °C.

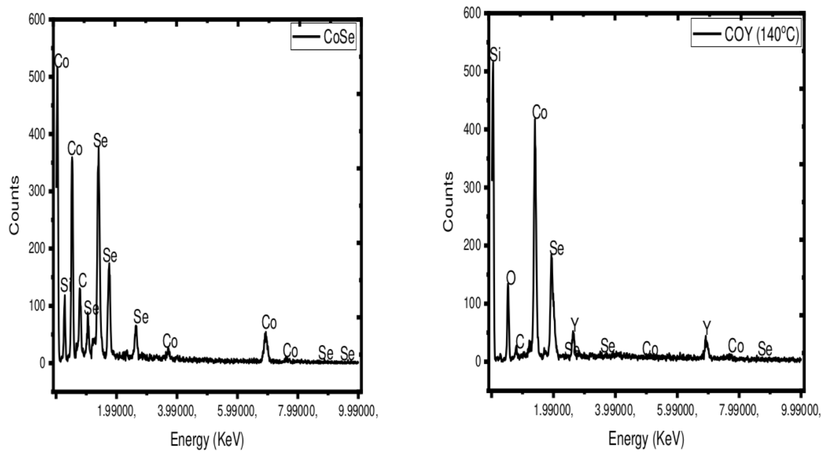

Figure 4. EDX result of (a) CoSe and (b) YCoSe at substrate temperature of 140 °C.

al. [21] for CoSe thin films synthesized using Chemical bath technique. The high absorbance exhibited by YCoSe in the UV region makes the material suitable for p-n junction formation in solar cells and photovoltaic application in general [29]. It can also be used as UV filter [28]. Figure 5(b) reflects the graph of transmittance against wavelength for YCoSe thin materials deposited at different substrate temperatures. Figure 5(b) reveals that the thin films transmittance values increase with increase in wavelength and substrate temperature. The transmittance plot indicates that the deposited films generally showed low transmittance. YCoSe deposited at substrate temperature of 200 °C had the highest transmittance value of approximately 27 % while the YCoSe synthesized at substrate temperature of 140 °C had the lowest value of approximately 7 %. The variation of reflectance with wavelength is shown in Figure 5(c) for YCoSe thin materials deposited at different substrate temperatures. The plot depicts that the reflectance of the deposited films increases gradually with increase in wavelength and substrate temperature. Generally, all the deposited samples showed extremely low reflectance, thereby making it a good material for anti-reflectance device production [28]. Figure 5(d) gives the plot of absorption coefficient vs photon energy for YCoSe thin film materials deposited at different substrate temperatures. This shows that absorption coefficient of the deposited films increased gradually from 4.86×10^6 to 101×10^6 within the photon energy range of 0.55 eV to 2.00 eV. The high absorption coefficient values exhibited by YCoSe agrees with Liu *et al*. [20] report in electrodeposited CoSe and this shows that this material can be very useful for solar energy conversion (photovoltaic). It further shows that the absorption coefficient of the deposited films decreased with increase in substrate temperature. Plot of $(\alpha\hbar v)^2$ against photon energy for YCoSe thin materials synthesized at different substrate temperatures is presented in Figure 5(e). The energy band gap was estimated from the plot of $(\alpha\hbar v)^2$ against photon energy by extrapolating the straight part of the graph down to the hv axis. The energy band gap of the deposited samples ranges from 1.25 eV – 1.75 eV and it was observed to increase upon increase in substrate temperature as shown in Figure 5(e) except for sample deposited at subtract temperature of 160 °C. The range of energy band gap values obtained in this study agree with those reported by Liu *et al*. [20] for electrodeposited CoSe thin films.

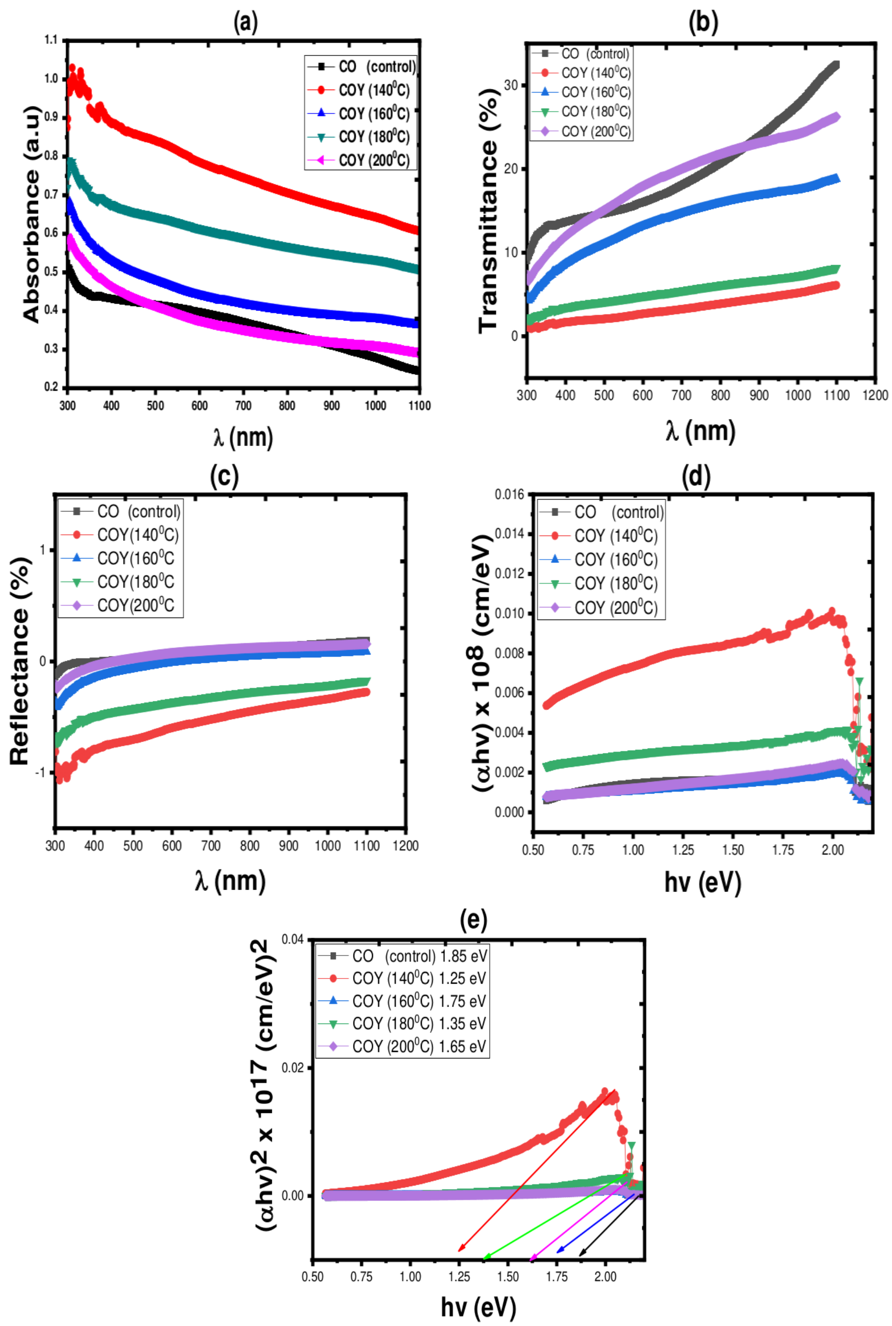

Figure 5. (a) Absorbance, (b) Transmittance, (c) Reflectance, (d) Absorption coefficient, and (e) Bandgap energy.

4. Conclusion

Spray pyrolysis deposited CoSe and Y doped Cobalt selenide (YCoSe) at different substrate temperature (140 °C–200 °C) have been successfully done. The impact of different substrate temperatures on the elemental composition, morphological, structural, electrical and optical properties of yttrium doped CoSe (YCoSe) is reported in this study. For variation in substrate temperature, the film thickness was seen to increase with increase in substrate temp. More so, the substrate temperature and the film thickness vary inversely with resistivity and directly with conductivity which is one of the properties of a real semiconductor. The morphology of undoped CoSe thin materials was very rough containing randomly oriented non-uniform thin particles while addition of Y dopant (0.1 mol%) at substrate temperature of 140 °C gave a homogenous distribution of compact rectangular-like nanograins. The densely packed grains could be due addition of dopant plus increase in temperature which was seen to significantly alter the morphology of the undoped sample. The EDX plots of the deposited undoped and Y-doped cobalt selenide revealed the major elements: cobalt, selenium and yttrium. This confirms the deposition of CoSe and YCoSe thin materials. The XRD result reveals that the thin materials are cubic polycrystalline in nature. Effect of substrate temperature was evident and YCoSe grown at substrate temperature of 180 ^{o}C was seen to give the most excellent crystalline quality and a preferential orientation along (111) direction. The optical properties were found to vary with substrate temperature despite the fact that the variation was not totally linear as the film deposited at substrate temperature of 160 ^{o}C deviated from the linearity in all the optical properties. The energy band gap of the deposited samples ranges from 1.25 eV−1.75 eV. The materials produced could be used in the production of photovoltaic devices such as solar cell.

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