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Recycling CdSe-Based Thin Film Solar Cells

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Dedication

To those candles who burn themselves to enlighten my road,

My mother and my father.

To My loving brothers.

To people who paved our way of science and knowledge,

All my teachers distinguished.

To those who shared with us the most beautiful moments,

My friends.

Sohaib M. F. Abu Alrob

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Recycling CdSe-Based Thin Film Solar Cells

أقر بأن ما اشتملت عليه هذه الرسالة هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل أو أي جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

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List of Abbreviations

Symbol	Abbreviation
E_{bg}	Energy band gap
CB	Conduction band
VB	Valance band
eV	Electron- volt
SCs	Semiconductors
PEC	Photoelectrochemical cell
PV	Photovoltaic
E_f	Fermi energy level
E_c	Conduction band energy
EV	Valance band energy
E_{redox}	Redox energy level
SCL	Space charge layer
Red	Reductant
Ox	Oxidant
ECD	Electrochemical deposition
CBD	Chemical band deposition
ECD/CBD	Combined between electrochemical and chemical bath methods
FTO	Fluorine doped tin oxide
V_{oc}	Open-circuit potential
J_{sc}	Short circuit current density
J-V	Current density potential
η	Conversion efficiency
FF	Fill factor
DC	Direct current
XRD	X-ray diffraction
SEM	Scanning electron microscope
EDX	Energy-dispersive X-ray spectroscopy

Recycling CdSe-Based Thin Film Solar Cells**By****Sohaib Mohammad Fisal Abu Alrob****Supervisor****Prof. Hikmat S.Hilal****Co-Supervisor****Dr. Ahed Zyoud****Abstract**

In order to avoid water contamination with solar cell films, and to take advantages of these films again. Cadmium selenide thin films were prepared and recycled using different techniques, electrochemical deposition (ECD), chemical bath deposition (CBD) and combined method based on electrochemical deposition followed by chemical bath deposition (ECD-CBD) techniques on fluorine doped tin oxide (FTO). The recycled CdSe thin film characteristics, in photo electrochemical (PEC) process were enhanced by different treatment methods such as changing chemical bath solution in the (CBD) method. Also, ECD-CBD CdSe was coated with carbon to enhance their PEC properties, followed by annealing at 150°C for 1hr. The annealed films are then cooled to room temperature using two different methods: fast and slow cooling. The prepared films were characterized by Scanning electron microscopy (SEM), X-ray diffraction (XRD), and electronic absorption spectra. Photo-electrochemical (PEC) characteristics of different film electrodes, such as photo *J-V* plots, dark *J-V* plots, conversion efficiency, values of short-circuit current and fill-factor (FF) were all performed. All measurements were done at room temperature, under nitrogen atmosphere using Poly sulfide NaOH/S⁻²/S_x⁻² system as a redox couple.

The PEC measurements show that the fresh and recycled CdSe films was n-type in electrical conduction. The optical absorption measurements showed that the band gap range for the fresh and recycled films is in the range 1.7 -2.15 eV. XRD results showed that the three systems involved nano-sized CdSe particles with cubic type crystals. The non-annealed recycled and fresh ECD-CBD films showed highest PEC conversion efficiency values with 11.6% and 12.8% respectively. The ECD-CBD film is superior because it combines the advantages of both ECD-CdSe film (good adherence to FTO/glass substrate) and CBD-CdSe film (suitable film thickness).

Annealing (at 150°C for 60 min) CBD-CdSe film electrodes enhanced its PEC characteristics, quenching being better than slow cooling. ECD-CdSe and ECD-CBD CdSe films showed lowering in PEC performance. So, annealing may not be desirable in this work, since heating may increase the kinetic energy of the particles and may thus increase their disorder. Covering ECD-CBD thin film electrodes with carbon enhanced their efficiency.

Chapter One

Introduction

1.1 Solar Energy

Recently, people started to look for new resources of energy instead of fossil energy sources (oil and coal). Fossil sources of energy are limited, and contaminate the environment by increasing carbon dioxide, nitrogen oxides and sulfur oxides. Such contaminants are known to cause global warming. Renewable energy sources are the best choice for clean energy [1-3].

In the 21st century, with help from materials development in technology, scientists examine many techniques to produce maximal amounts of energy from solar energy technologies [4, 5]. This energy can be used as a heat, electricity or in photosynthesis processes [6]. Moreover, solar energy reduces harmful effects of climate change and global warming. Also, most of the energy sources are basically from rays of the sun. So, the sun is considered as the source of renewable energy [7].

Solar energy is a part of life as living organisms normally depend on it [8, 9]. It also has many benefits as it does not cause pollution and does not produce toxic gases to the environment. It can be exploited in remote areas away from electricity networks. Solar energy is free and renewable [10, 11].

1.2 Energy band gap (E_{bg}) and semiconductors

A semiconductor is a material that has electrical conductivity value in between a conductor (such as copper) and an insulator (such as glass). Most pure semiconductors are electrically resistive, but by adding small amounts of some impurities (dopants) exhibit less resistance. Semiconductors are heavily used in modern technologies such as computers, telephones, (LEDs) and others.

Scientists use a concept called "energy band gap" (E_{bg}) to distinguish between conductive, semiconductor and insulating materials. E_{bg} is defined as the energy difference between the valence band (VB) and conduction band (CB) in a material [12].

Materials with high E_{bg} are mostly insulators. Those with no band gaps are conductors, while semiconductors mostly have E_{bg} between 1- 3.7 eV [13, 14]. Figure (1.1). illustrated these concepts.

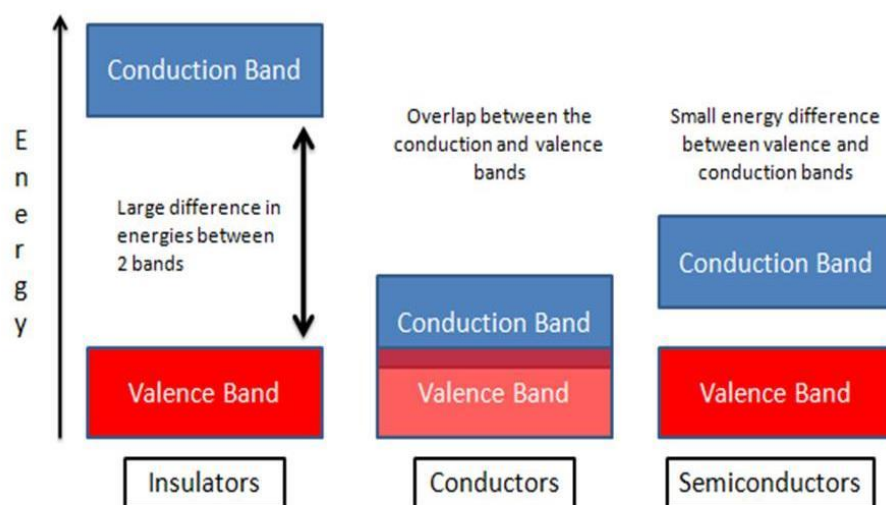


Figure (1.1): Band gap energies in conductor, semiconductor, and insulator [15].

Electrical conductivity of semiconductors is negligible at zero absolute temperature. Electrons cannot transfer from valence band to conduction band at this temperature. At higher temperatures the charge carriers could be generated. Thermally excited electrons can move from the valence band to the conduction band and conductivity may occur [12].

1.3 Types of semiconductors

Semiconductor (SC) materials are divided into two groups, intrinsic SCs and extrinsic SCs.

1.3.1 Intrinsic semiconductor

Intrinsic semiconductors don't contain any impurities (dopants). When an electron leaves the valence band to the conduction band, a hole is created in the valence band. Intrinsic SCs have limited conductivity because few electrons are excited. In intrinsic semiconductors, numbers of electrons and holes are equal, Figure (1.2) [12, 16].

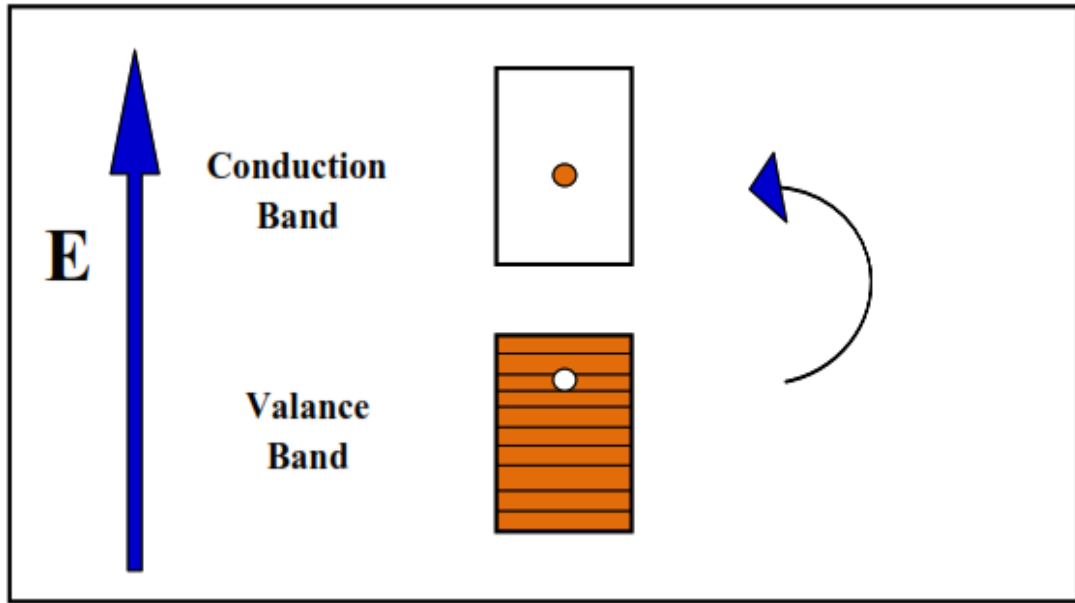


Figure (1.2): Thermal generation of charge carriers in intrinsic semiconductors [17].

1.3.2 Extrinsic semiconductor

An extrinsic SC result from presence of impurities (dopants). Extrinsic SCs are categorized into two groups:

1.3.2.1 n-type

The dopant atoms here are electron donors, with energy levels close to the conduction band. As an example, phosphorus atoms used as electron donors inside silicon crystals. The phosphorus outer shell electrons go up to conduction band. The conduction is thus called negative type (n-type) in this case [12, 16], as shown in Figure (1.3a).

1.3.2.2 p-type

In p-type SCs, the dopant atoms accept electrons with energy levels close to the valance band. Boron atoms are examples of electron acceptor for silicon crystals. Valence band electrons of silicon can thus move to valence

shells of the boron atoms. This type of conduction called positive type (p-type) [12, 16, 18, 19], as shown in Figure (1.3b).

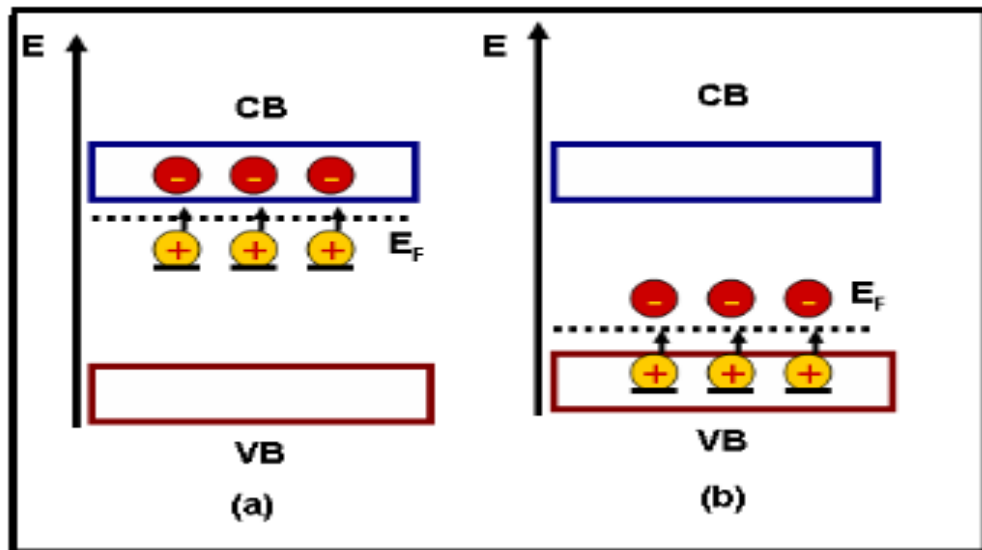


Figure (1.3) : Extrinsic types of semiconductors a) n-type SC, b) p-type SC[20].

1.4 Common semiconductor materials used in solar cells

Many semiconductor materials are used in solar cells. Example are Si and Ge as elemental semiconductors, while GaAs, GaP and InP are examples for compound semiconductors from groups III and V [21-23]. Compound of groups II and VI such as CdSe, CdTe and CdS [24, 25], oxide semiconductors as ZnO₂ and TiO₂ [26], organic semiconductors such as poly phenylene vinylene are other examples [27].

1.5 Types of solar systems

Solar energy can be converted to an electrical energy by two main methods. These main technologies are photovoltaic (PV) solar cells and photoelectrochemical (PEC) solar cells.

1.5.1 Photovoltaic (PV) solar cells.

A PV cell generates electric current from solar energy. PV cells contain two layers of semiconductors (p and n types) to form p-n junction as shown in Figure (1.4). When p-n junction made from the same material, it is called homo-junction. A hetero-junction, is made from two different materials. In PV solar cells electrons are excited from valence band to conduction band leaving holes in the valence band, when the PV cell is exposed to sun light. The electrons transfer to n-type side of the solid junction, and holes transfer towards p-type side. A photocurrent thus occurs [20].

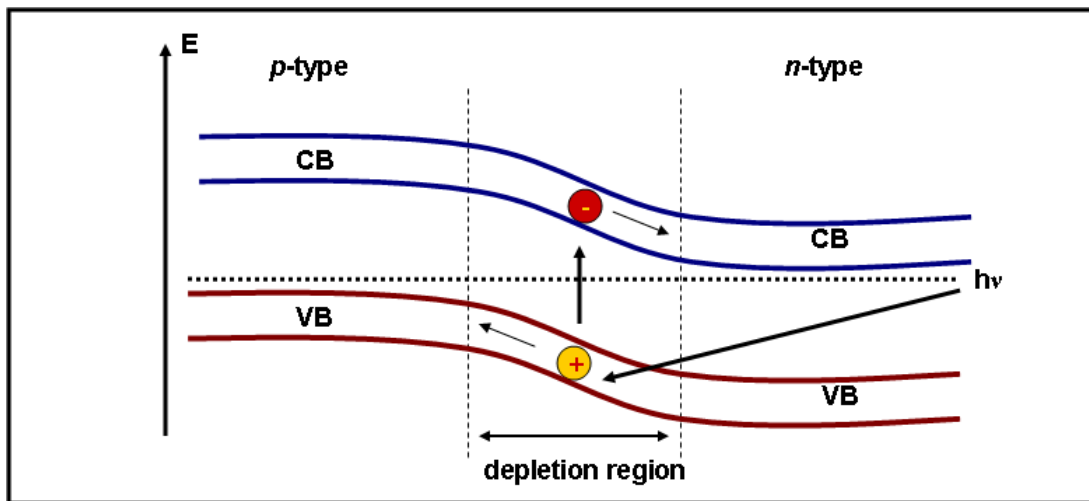


Figure (1.4): Formation of an electron-hole pair by absorption of a photon with wavelength equal or shorter than threshold wavelength [20].

1.5.2 Photo electrochemical (PEC) solar cells

PEC cells can be used in solar energy conversion into electricity. These cells use SC/electrolyte junction instead of p-n junction. A PEC cell can be prepared by dipping an SC electrode in electrolyte solution [28]. Considering n-type SC, before equilibrium the Fermi energy level (E_f) is

above the E_{redox} as shown in Figure (1.5). So, electrons can move to redox energy level (E_{redox}) to reach equilibrium. At this point Fermi levels of SC and the electrolyte became the same [29-31].

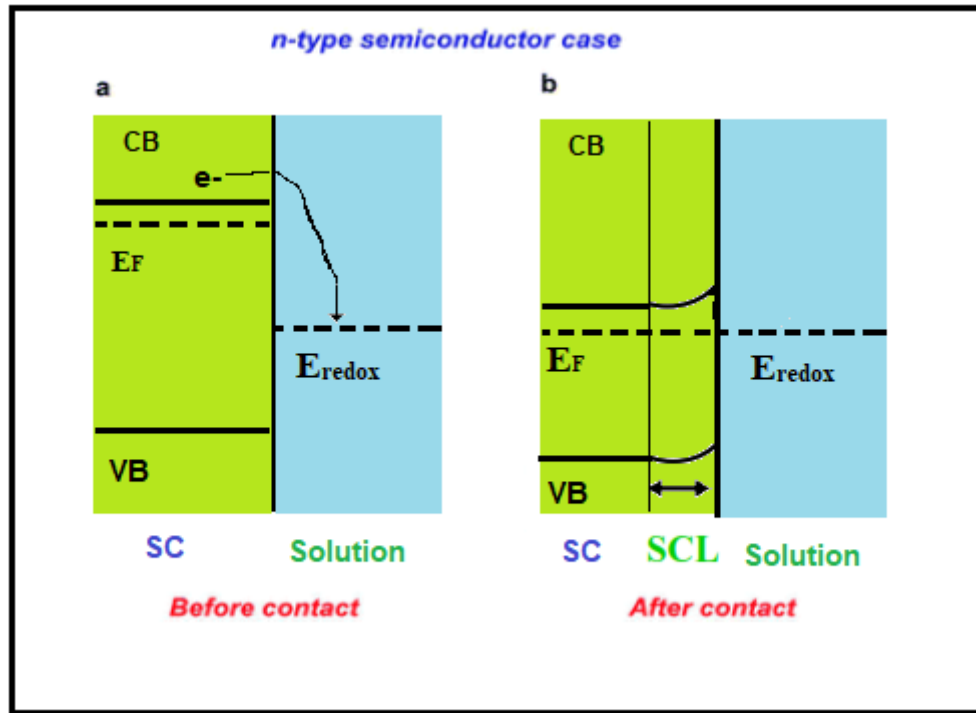


Figure (1.5): n-type semiconductor in PEC cell before and after equilibrium. With an electrolyte containing the redox couple A/A⁻. Reproduced from [32].

In the case of p-type SC the Fermi level of the p-type SC is below the Fermi level of the electrolyte, and then equilibrium occurs [31].

1.6 Dark current generation in PEC cells

When electrons move from the n-type semiconductor conduction band to the redox couple the dark current occurs. At equilibrium a potential barrier is generated by bending in conduction and valence bands. If the electrons transfer from the SC conduction band to the redox couple, dark current

occurs, Figure (1.6). this occur when electrons gain enough energy to cross this barrier by applying negative potential (ΔE_1). So, space charge layer (SCL) will not exist and flat band potential happen. Thus dark current occurs in flat band systems, Figure (1.7) [12, 33].

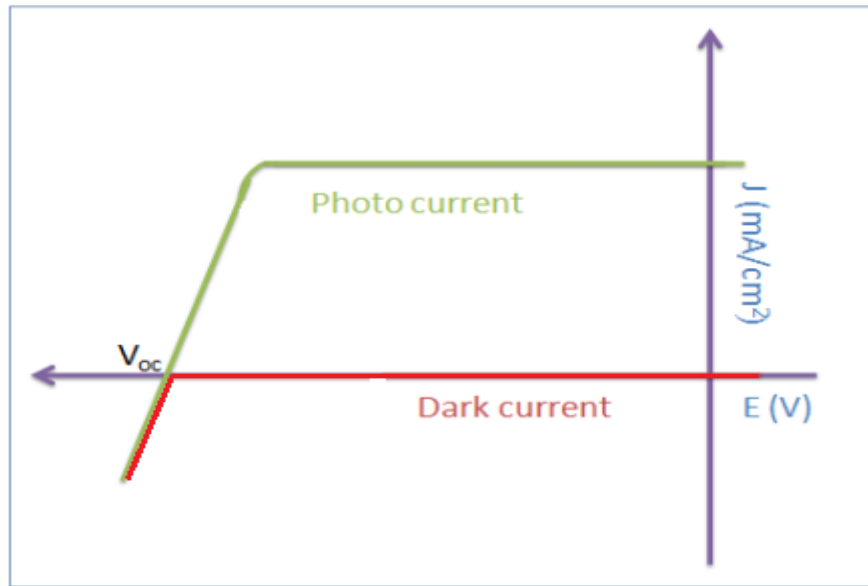


Figure (1.6): Typical dark current and photocurrent J-V plots for a n-type SC/Redox [12].

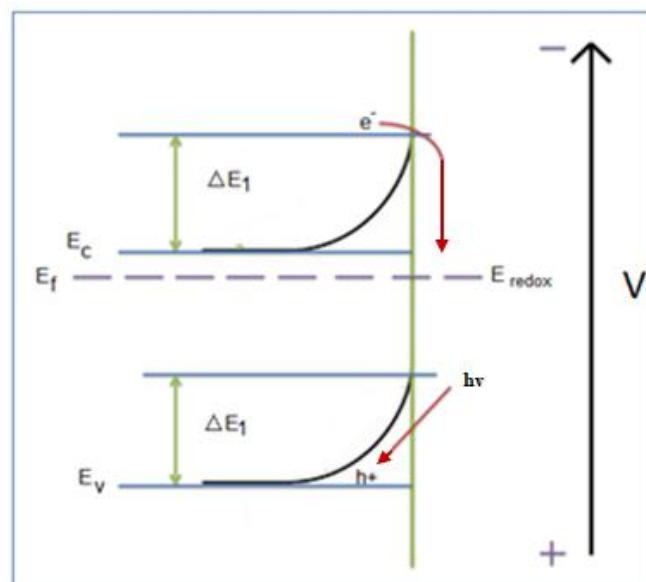


Figure (1.7): Dark current occurs with flat band in n-type SC [12].

1.7 Photo current generation in PEC systems

When light passes through PEC cell, photons with energy larger than E_{bg} are absorbed, generate excited electrons and holes. Photo current happen if the electrode forms a depletion layer (with positive potential) and the minority carriers migrate towards the electrode-electrolyte interface, Figure (1.8) [12, 33, 34].

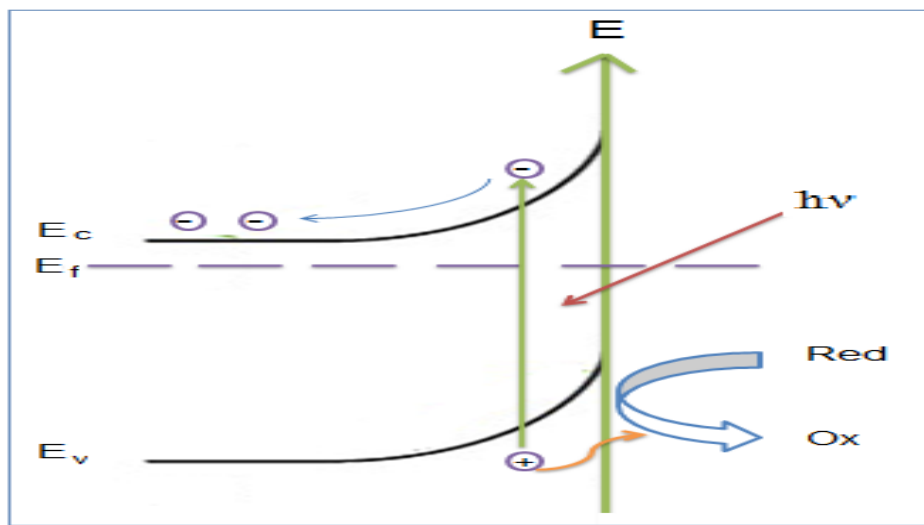


Figure (1.8): Photocurrent generation at n-type SC. Photo generated holes move to the surface and oxidize solution reduced species [12].

1.8 Thin film technology

Thin films are emerging as active materials for solar cells instead of monocrystalline semiconductor electrodes. This technology is used to deposit layers of semiconductor materials onto substrates such as fluorine doped tin oxide (FTO) [35]. Thin films are fabricated by many techniques such as chemical bath deposition (CBD) and electrochemical deposition (ECD) [36, 37]. Most of thin film solar cells have lower conversion efficiencies than mono-crystalline solar cells, but they need low cost and

less preparation materials [35, 38]. Many semiconductors can be used as a thin film electrodes in solar cells, such as CuSe, CdSe, CdTe, CuS, ZnS, CdS and others [39, 40].

1.9 Cadmium selenide

CdSe is a semiconducting material, which has electrical and optical properties suitable for photovoltaic application, such as laser diodes, electro conductive electrodes, solar control coatings and photo electrochemical solar cells [41]. Cadmium selenide is n-type semiconductor with an energy band gap value in the range 1.7 -2.3 eV [42, 43].

CdSe exists in three different crystal structures wurtzite (hexagonal), zinc blende (cubic) and rock-salt (cubic) [44]. Wurtzite structure occurs by heating CdSe, while the rock-salt appears under high pressure, Figure (1.9) [45].

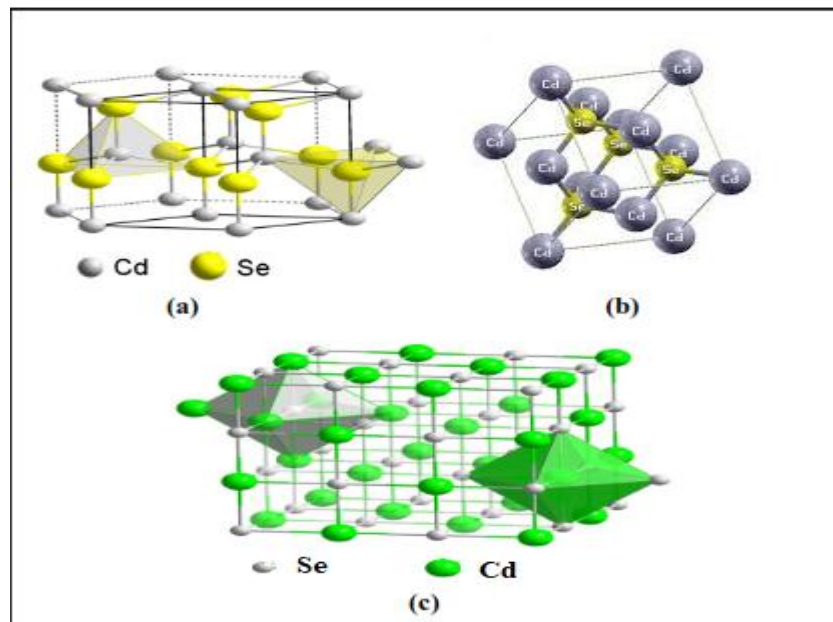


Figure (1.9): Crystal structures of CdSe with a) wurtzite (hexagonal) form, b) zinc blende (cubic), and c) rock –salt (cubic) form, [46].

Thin films of cadmium selenide are obtained by different techniques like atomic layer deposition (ALD) [47], successive ionic layer adsorption and reaction (SILAR) [48], spray pyrolysis [49], electrochemical deposition and chemical bath deposition [17, 43].

Electrochemical deposition is favored because it is simple with low cost. It is used to prepare large scale thin films where film thickness and morphology can be controlled [50].

Chemical bath deposition is also useful in preparing large area thin films of some materials on substrates inside liquid bath with suitable reagents at temperatures between 25-100°C [51, 52]. Table 1.1 summarizes some physical properties for CdSe material.

Table (1.1): Some properties of cadmium selenide (CdSe) [46].

Property	Value
Physical state	Crystalline solid
Molar mass	191.385 g.mol ⁻¹
Color	Red black
Melting point	1240 °C
Density	5.81 g.cm ⁻³

1.10 Recycling of solar cells

Cadmium and selenium have harmful effects, but are still widely used in solar cells and other applications. Both cadmium and selenium are hazardous to human and to the environment. Human bodies need trace amounts of selenium, but higher selenium uptake is hazardous. It may cause eye burning, irritation and shortness of breath. In some cases, it may cause death. Therefore, selenium content in water should always be kept to

a minimum. Any abuse of CdSe solar cells, such as disposal into environment, will be costly. Careful and wise management of CdSe based solar cells is necessary. Therefore, solar cells with hazardous species, such as CdSe films, must be recycled to avoid contamination with cadmium and selenide ions, and produce new solar cells based on them [53-55].

Solar cells are fabricated from semiconductor as active material, aluminum and iron frames. Thin film solar cells need special recycling in order to separate semiconductor materials and frames, as an example recycling process of CdTe. After separating different parts, around 90% of glass and semiconductor materials can be recovered [56].

1.11 Objectives of this work

The main objective of this work is to find out suitable techniques to recycle CdSe thin film electrode based solar cells. New CdSe thin films onto (FTO)/glass will be made for the purpose of PEC conversion of light to electricity from waste films. We look for an efficient and stable nano-film under PEC conditions. This will avoid contamination of water.

The recycled CdSe thin films will be prepared by CBD, ECD and combination of ECD and CBD techniques together. The ECD technique gives good contact between the CdSe and the FTO surface. The CBD technique gives thick layers suitable enough for light-to-electricity conversion. Therefore, the ECD-CBD technique gives a CdSe/FTO/glass film that has good contact and suitable thickness. Then the prepared thin

films will be further modified by annealing process. Comparison between these preparation methods will be made.

The technical objectives of this work are summarized as:

- 1- Recycling CdSe thin films (used in solar cells) to recover their components Cd^{2+} and Se^{2-} , instead of polluting water and environment.
- 2- Recovering Cd^{2+} and Se^{2-} from contaminated waters.
- 3- Preparing new CdSe thin film electrodes from the recycled Cd^{2+} ones. The Se^{2-} ions also will be recycled in condensed manner.
- 4- Examining the recycled film efficiency in light-to-electricity conversion. Different characteristics (such as short circuit current density J_{sc} , open-circuit photo potential V_{oc}) of the new recycled CdSe films will be examined.
- 5- Examining the stability of the prepared CdSe thin films to photo-degradation (photo corrosion) under PEC conditions.

1.12 Hypothesis

This work involves recycling of CdSe solar cells based on the following assumptions:

- 1- Recycling CdSe solar cells will be worthy, because the Cd^{2+} , Se^{2-} ions will be recovered from contaminated water.

2- Dissolving the CdSe solar cell in a concentrated acid is possible. The Cd^{2+} ions will be recovered in minimum volume of acid, so that the resulting Cd^{2+} solution will be used in preparing new cells. The ion Se^{2-} will be recovered in the form of gaseous H_2Se that will be trapped in another basic solution trap in the form of useful Na_2Se concentrated solution for further use.

3- The newly recycled CdSe solar cells will have comparable efficiencies like freshly prepared CdSe.

4- The process will have environmental and economic value in the future.

1.13 Novelty of this work

In these laboratories, CdS based solar cells have been recycled and reused to produce efficient solar cells [57]. CdSe cells are more hazardous than CdS cells, because both the Cd^{2+} and Se^{2-} ions are highly hazardous. To our knowledge, CdSe film solar cells have not been recycled before. Therefore, this work will attempt to recycle CdSe based solar cells for the first time, from contaminated water. This highlights the novelty of this work.

Chapter Two

Experimental

2.1 Materials

2.1.1 Chemicals

$\text{Na}_2\text{S}\cdot\text{XH}_2\text{O}$, $\text{CdCl}_2\cdot 2\text{H}_2\text{O}$, solid selenium and acetone were purchased as chemically pure materials from Sigma-Aldrich. Chemically pure NH_4Cl , Na_2SO_3 , HCl were obtained from (SDFCL). FTO/glass thin films were bought from Sigma-Aldrich, and triethanolamine (TEA) from Sun pharm LTD. No further purification for the chemicals was needed.

2.1.2 Equipment

2.1.2.1 Spectrometer

The spectroscopic measurements of CdSe films were measured at on a UV-1601 Shimadzu spectrometer (wavelength range 200-800 nm) at $25\pm 1^\circ\text{C}$.

2.1.2.2 Polarograph

POL150 Polarographic Analyzer with MDE150 Polarographic Stand and Trace Master 5 software was used for the mount of Cd^{2+} .

2.1.2.3 X-ray diffractometer (XRD)

Crystallinity and crystal structure of CdSe thin films were investigated by PAN alytical X'Pert PRO X-ray diffractometer, with $\text{CuK}\alpha$ rays. X-ray

diffraction measurements were conducted in Korean Institute of Energy Research, Daejeon, South Korea.

2.1.2.4 Photo electrochemical cell (PEC)

PEC measurements were done using a computer controlled Corr Test electrochemical work station Potentiostat/Galvanostat. The working electrodes in the PEC cell were the CdSe films, and the counter electrode was a platinum sheet. The reference electrode was a calomel electrode. All electrodes were dipped inside the redox couple solution. As shown in Figure (2.1). Polysulfide S^{2-}/S_x^{2-} in NaOH solution system (prepared from 0.10 M Na_2S , 0.10 M NaOH, 0.10 M S) was used as redox couple for all PEC measurements, the conductivity of redox couple was 23 mS. N_2 gas was purged in the redox solution for ~5 min. to remove the oxygen prior to experiments, and was then placed above the solution throughout experiments to avoid electrolyte oxidations, Figure (2.1).

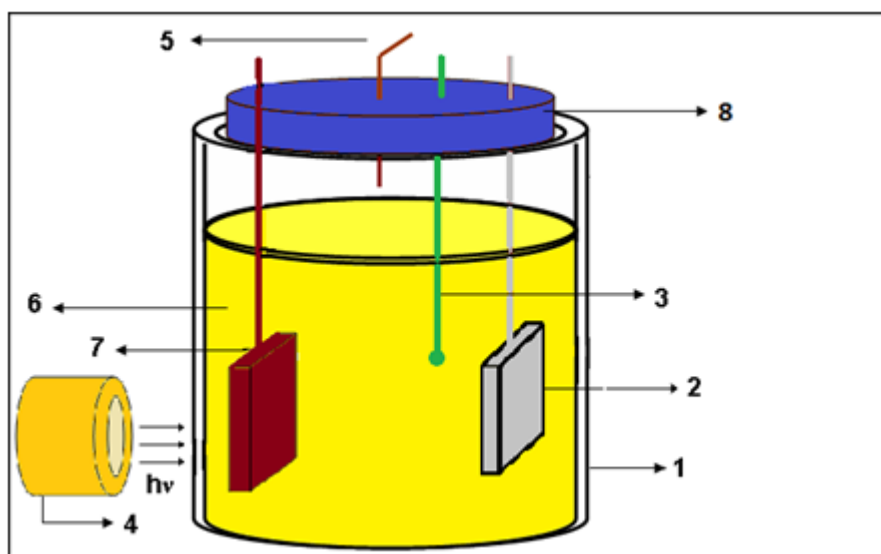


Figure (2.1): Schematic diagram for photo-electrochemical arrangement. 1) beaker, 2) platinum counter electrode, 3) internal reference electrode, 4) light source, 5) nitrogen, 6) redox couple S^{2-}/S_x^{2-} , 7) CdSe working electrode, 8) rubber seal.

Illumination was made using a high stability 50-Watt halogen spot-lamp, with mostly 450-800 nm range. The light source was fixed at constant distance from the surface of CdSe electrode so as to give illumination power of 84930 lux (0.0124 W/cm^2) on the electrode. Measurements were made using a LX-102 light meter.

2.1.2.5 Scanning electron microscope (SEM)

SEM images were recorded on an FE-SEM, JEOL JSM-6700F Field Emission SEM at Korean Institute of Energy Research, Daejeon, South Korea, the EDX measurements were conducted at the same equipment.

2.2 Cadmium and selenium ions Recovery

Pre-used CdSe films and excess powders were collected. Then they soaked in 10.00 M HCl solution for 60 min at 80°C . This is to recover Cd^{2+} aqueous ions and $\text{H}_2\text{Se}_{(\text{g})}$. The $\text{H}_2\text{Se}_{(\text{g})}$ was passed via a tube into basic solution to form Na_2Se solution. The Na_2Se solution was stored for further use. The remaining Cd^{+2} solution was neutralized with basic solution. The recovered Cd^{2+} ions concentrations of obtained from the earlier prepared CdSe thin films were analyzed by polarographic determination.

2.3 Pretreatment of FTO/glass substrate

The FTO/Glass substrates were cleaned, before deposition of CdSe films, by washing with detergent, rinsed with distilled water, and the rinsed sheets were then kept in dilute solution of 1M HCl for 1 hour inside ultrasonic cleaning bath, then the sheets were rinsed with distilled water, soaked with

acetone for any attached organic, and rinsed with distilled water before drying in air, the dried cleaned sheets were kept for deposition use.

2.4 Selenium ion precursor preparation

In the preparation of CdSe thin films selenium was used as sodium selenosulphate (Na_2SeSO_3). Solid selenium was mixed with aqueous sodium sulfite (Na_2SO_3) and with continuous magnetic stirring the mixture was refluxed in water bath for ~15 hours at 90°C. Sodium sulfite (80.0 g) was added to 400 mL of distilled water to prepare 0.25 M Na_2SeSO_3 solution, the solution was mixed with 8.0 g Se powder. The Na_2SeSO_3 solution was then filtered and kept for deposition purposes [17].

2.5 CdSe thin film preparations

Different preparation methods have been used, namely chemical bath deposition (CBD), electro-chemical deposition (ECD), and combined ECD-CBD.

2.5.1 Electrochemical deposition (ECD) technique

The electrochemical cell used in CdSe thin film deposition was consisted of a working electrode (FTO/ glass substrate), and the counter electrode (platinum sheet) which were connected to potentiostat internal reference connection. A 0.005 M Na_2SeSO_3 aqueous electrolyte mixed with 0.008 M $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (fresh Cd^{+2}) to prepare fresh films, and (0.008 M) recycled Cd^{+2} to prepare recycled films. The procedure that followed in this technique is taken from [42, 58], with making our own modification.

ECD solution was prepared by mixing CdCl_2 solution (1.60 ml, 0.50 M) or recycled Cd^{+2} solution (3.5 ml, 0.228 M) with Na_2SeSO_3 (2.00 ml, 0.25 M) in a volumetric flask (100 ml) and filled with distilled water, with continued stirring until the entire solid dissolved in distilled water. The solution was placed inside the bath cell for deposition, and then few drops of ammonium solution (2-3 drops) were added to control the pH of the solution to ~ 10 . The FTO/glass (working electrode) and counter electrode substrates were then vertically dipped inside the deposition bath.

Deposition was conducted at $25 \pm 1^\circ\text{C}$ after nitrogen purging for 5 min to remove the dissolved oxygen. The nitrogen gas was then maintained in the atmosphere above the solution to avoid O_2 leakage, with continued stirring. Deposition was performed using DC stripping at a fixed applied potential (-1.1 V), the reference electrode was Ag/AgCl for 15 min. Based on earlier reports [42, 58] this is the best potential for CdSe film production.

After completion, the Glass-FTO-CdSe thin films were taken, rinsed with distilled water, then dried under air, and preserved for characterization. The ECD experimental setup is summarized in Figure (2.2).

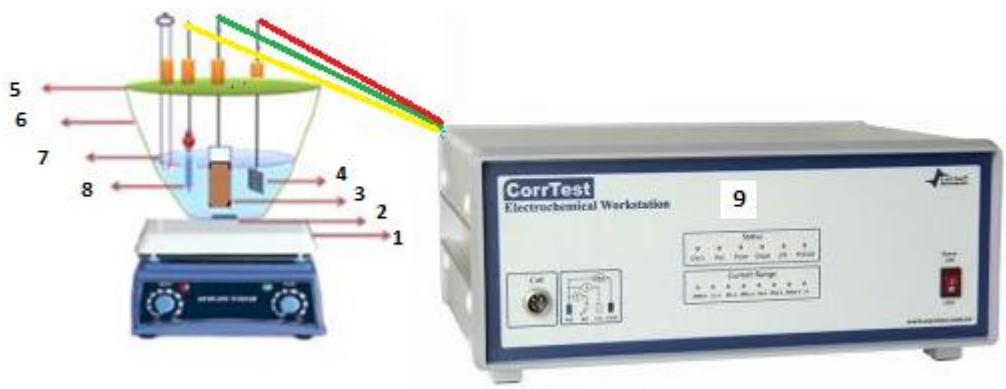


Figure (2.2): The arrangement of the electrochemical deposition of CdSe film experiment. 1) magnetic stirrer with hot-plate, 2) magnet bar, 3) CdSe glass sheet, 4) counter electrode, 5) glass cover, 6) ECD cell, 7) nitrogen, 8) internal reference electrode, 9) potentiostat.

2.5.2 Chemical bath deposition (CBD)

Additional CdSe films were deposited onto FTO/Glass thin films by chemical bath deposition. Figure (2.3) summarizes the experimental set-up for CdSe film deposition. The chemical bath involved 5.00 ml of 0.50 M CdCl_2 , 5.00 mL of 7.4 M Triethanolamine, 2.50 mL of 13.4 M NH_3 , 8.00 mL of 0.25 M Na_2SeSO_3 and 20 ml of distilled water to prepare fresh films. To prepare recycled films a chemical bath containing (11.00 ml, 0.228 M) recycled Cd^{+2} , 5.0 mL of 7.4 M Triethanolamine, 2.5 mL of 13.4 M ammonia solution, 8.00 mL of 0.25 M Na_2SeSO_3 and 14 mL of distilled water. All materials were added according to this order in the reaction container which was tightly stoppered. Solution pH value was ~ 10 . Pre-cleaned FTO/glass slice was then inserted inside the mixture vertically. The deposition temperature was maintained at 70°C for 4 hours with changing deposition solution 3 times through the deposition process, in

addition to slow stirring under nitrogen atmosphere. Deposition solution color changed from colorless through yellow then orange and finally dark red. The chemical bath deposition technique is based on earlier reports [35, 41, 44, 59, 60] with minor modification. The resulting electrodes deposited with CdSe thin films were taken, and then washed with distilled water and air dried.

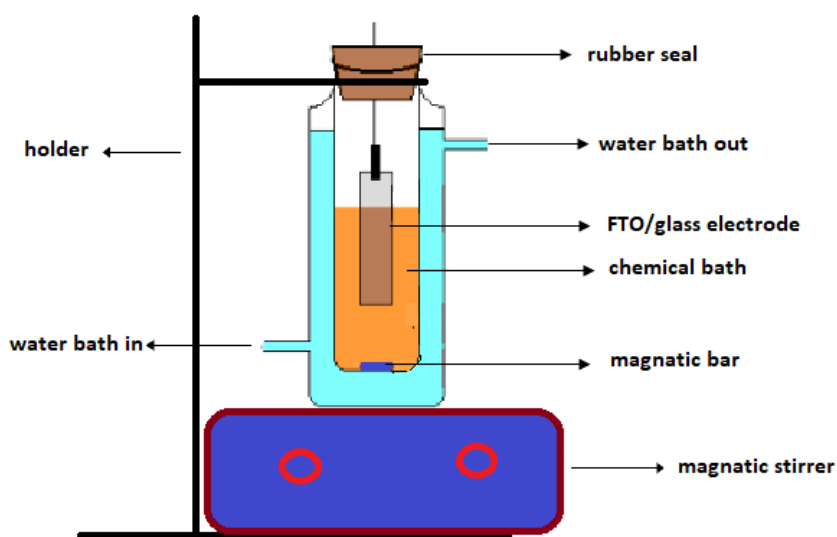


Figure (2.3): CBD set-up used to prepare CdSe thin film.

2.5.3 ECD-CBD combined technique

The CBD technique, described above was applied to the prepared ECD-CdSe films which yield two different layers within the produced CdSe films (glass/FTO/ECD/CBD). ECD gives better adherence between the FTO surface and CdSe films. CBD gives thick films that are suitable for photo-conversion. ECD-CBD should combine both advantages (good contact and suitable thickness).

2.6 CdSe thin films Modification

To modify the produced CdSe films, different methods were applied. Such methods are annealing process, cooling and cooling rate [18], and modifying the CdSe films with carbon layer.

2.6.1 Annealing process

Annealing of the prepared films was performed by using a horizontal Pyrex cylinder tube furnace with thermostated control furnace (Lindberg Hevi-Duty Control Tube Furnance). Film annealing was fixed at temperature 150°C , using N_2 gas as atmosphere for an hour. The temperature was chosen based on earlier reports [17]. The prepared CdSe thin films were inserted inside a Pyrex cylinder (30 cm long) that was then placed in the tube furnace. Figure (2.4) describes the annealing procedure.

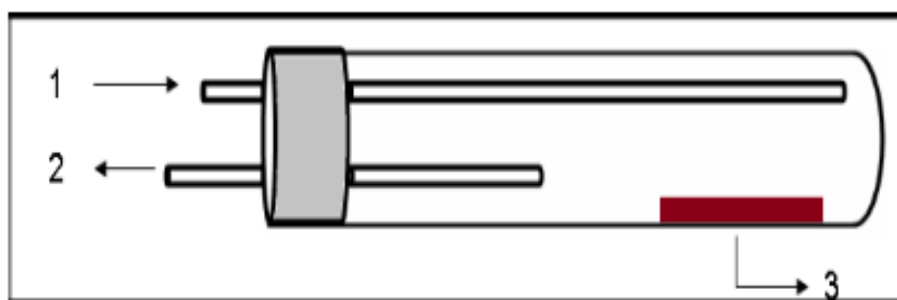


Figure (2.4): Schematic description of annealing system 1) nitrogen in, 2) nitrogen out and 3) CdSe film [20].

2.6.2 Procedure of cooling

2.6.2.1 Fast cooling (quenching)

After annealing at 150°C for an hour, the Pyrex cylinder containing the CdSe slice thin film was quickly taken out and quickly cooled to room temperature (within 5 minutes) with continuous flowing of N₂ atmosphere inside the tube.

2.6.2.2 Slow cooling

After film annealing at 150° C for 1 hour, heating was switched off and the furnace, with the thin films inside left to cool slowly through (90 minutes) to room temperature with N₂ gas flowing.

2.6.3 Film coating with carbon

The ECD-CBD CdSe thin film was coated with a black layer of carbon by using kerosene flame. The coated CdSe thin film was annealed at 150°C under N₂ atmosphere for 1 hour, and then allowed to slowly cooled to room temperature under N₂ atmosphere.

2.7 J-V plots

Current density (J) vs potential (V) (J-Vplots) were constructed on a computer controlled CorrTest electrochemical workstation Potentiostat/Galvanostat. The dark current characterization was measured in dark without any light penetration. Photo current characterizations were measured using the 50-Watt halogen spot-lamp (0.0124 W/cm²) as

described in Figure (2.1). All experiments were conducted under atmosphere of N_2 at $25\pm 1^\circ C$, using S^{2-}/S_x^{-2} in NaOH redox couple solution described above. Short circuit current density (J_{sc}) values were measured by extracted values of total short circuit current (I_{sc}) divided by electrode area dipped inside solution.

2.8 CdSe thin films stability measurements

Under PEC conditions, the electrode stability was assessed by using Corr Test electrochemical workstation. The working electrode was exposed to constant illumination (0.0012 Wcm^{-2}) at 0.00 V potential (Calomel electrode). Values I_{sc} were measured with time. Experiments were performed under atmosphere of N_2 at $25\pm 1^\circ C$ and S^{2-}/S_x^{-2} with NaOH solution redox couple.

Chapter Three

Results and discussion

Chemical-bath deposition (CBD), Electro-chemical deposition (ECD) and ECD-CBD combination methods were employed to prepare fresh and recycled CdSe thin films. Different conditions were varied to enhance the produced CdSe thin films such as changing chemical bath solution in the (CBD) method, annealing temperature (150°C using N₂ gas as an atmosphere for an hour), and controlling the cooling rate (slow or fast cooling) and covering the films with carbon layer. Waste CdSe thin films were taken for recycling then to prepare new CdSe thin films.

The prepared thin film properties were studied using SEM, XRD, EDX, and spectroscopic absorption spectra. *Photo-current density* plots, stability and efficiency were studied. Comparison between ECD-CdSe, CBD-CdSe and ECD-CBD CdSe thin films is presented.

3.1 Electrochemically deposited (ECD) thin film electrodes

Properties of the prepared CdSe thin films by ECD were characterized by using spectroscopic spectra measurements, scanning electron microscopic, and Energy Dispersive X-Ray Spectroscopy and X-ray diffraction measurements. PEC studies including photo J-V characterization plots, dark J-V characterization plots, the efficiency of conversion, short-circuit current density (J_{SC}) and fill-factor (FF) are described. CdSe thin films properties were investigated by using different techniques.

3.1.1 XRD measurements for CdSe thin film electrodes

Crystal structure and size for crystalline ECD-CdSe films were determined by XRD measurements. Normally CdSe exists as either as hexagonal (wurtzite) or cubic (zinc-blende) structures or as a mixture of hexagonal and cubic phases [61]. XRD measurements were obtained for ECD-CdSe films with various parameters including annealing and cooling rate.

In earlier studies, CdSe films were prepared by ECD technique, and the effect of preparation time (15, 30 and 45 min) on its PEC properties was studied. The 15 min deposition time gave best results. Annealing temperature effect was also studied at 150, 250 and 350°C. The 150°C annealing temperature showed best characteristics [17]. This temperature was thus used here. The XRD measurements for the ECD-CdSe thin films were investigated.

3.1.1.1 Effect of annealing and rate of cooling on CdSe electrodes

XRD patterns were performed for fresh and recycled CdSe electrodes before and beyond annealing at 150 °C with slow and fast cooling. XRD data showed that both fresh and recycled films exhibited crystallinity. The particle sizes of CdSe were calculated with Debye-Scherrers' formula, $T = K\lambda/(\beta\cos\theta)$, in which T is the mean size of the crystalline domain (Å), λ is the X-ray wavelength of Cu K α radiation ($\lambda = 1.5406$ Å), and β is full-width at half-maxima in radians and θ is the Bragg angle. [62, 63] The average particle size for non- annealed fresh ECD-CdSe was~5.75 nm, the non- annealed recycled film particle size was~ 5.78 nm Figure (3.1). The

fresh and recycled annealed film particle size (which were) slowly cooled showed respectively ~ 6.37 , 6.15 nm respectively. And for fast cooled was 5.95 , 5.97 nm. Annealing at relatively low temperature (150°C) thus causes sintering in particle sizes. All films have in the cubic phase with the zinc-blende phase, as compared with earlier reports [43, 64-66].

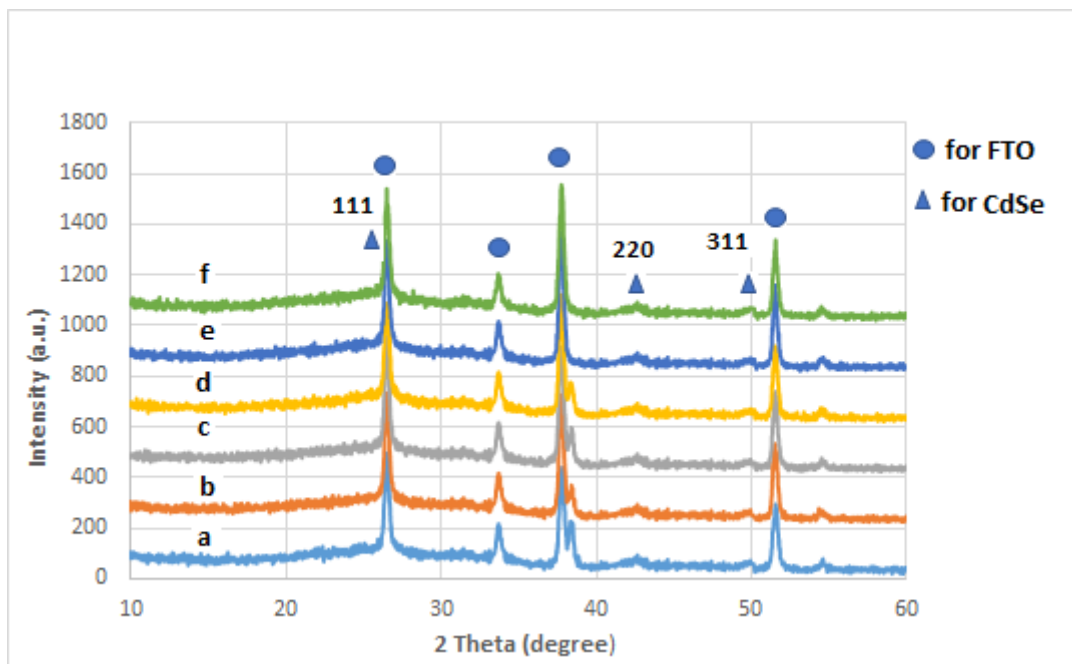


Figure (3.1): X-ray diffraction patterns performed for ECD-CdSe thin film a) fresh non-annealed, b) after annealing at 150°C and slowly cooled fresh, c) after annealing at 150°C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150°C and slowly cooled recycled, f) after annealing at 150°C and quickly cooled recycled.

Furthermore, all films had intensities with preferred orientation in the C(111) and C(220) and C(311) directions. This means that both recycled and fresh films have similar particle sizes and preferential orientations.

3.1.2 Spectroscopic absorption for CdSe electrodes

Spectroscopic absorption was measured for fresh and recycled CdSe thin films with and without annealing at 150°C with slow and fast cooling.

3.1.2.1 Effect of annealing and cooling rate on CdSe thin film electrodes

Spectroscopic absorption was measured for non-annealed fresh and recycled thin films of CdSe and for 150 °C annealed ones under nitrogen for 1 hour. Moreover, the effect of rate of cooling (slow and fast rate of cooling) on the electronic absorption spectra of the pre-annealed ECD-CdSe thin film electrodes at 150°C under nitrogen for one hour was investigated. (Figure (3.2)). The Figure showed that the fresh films gave slightly clearer absorption than the recycled ones. The non-annealed fresh film showed higher absorption than annealed films. Slowly cooled fresh films gave lower absorption comparing to quenched films. For recycled films the fast cooling film gave the highest absorption than non-annealed film and slowly cooled film.

Tauc method was used to exact determine the band gap of energy using optical absorbance data plotted with respect to energy. This is explained in the relation $(\alpha h\nu)^n = A(h\nu - E_{bg})$, where α is the absorption coefficient, h is Planck's constant, ν is the photon frequency, n represent the nature of the electronic transition, E_{bg} is the band gap and A is a proportionality constant. E_{bg} values for ECD-CdSe thin films are summarized in Table (3.1) based on Tauc plots that are attached in appendix A. The Table showed that recycled and fresh films gave comparable energy band gaps, and annealing slightly influences the energy band gaps. The recycled and fresh non-annealed films showed higher energy band gaps compared to annealed films. Slowly cooled films gave lowest energy band gap values.

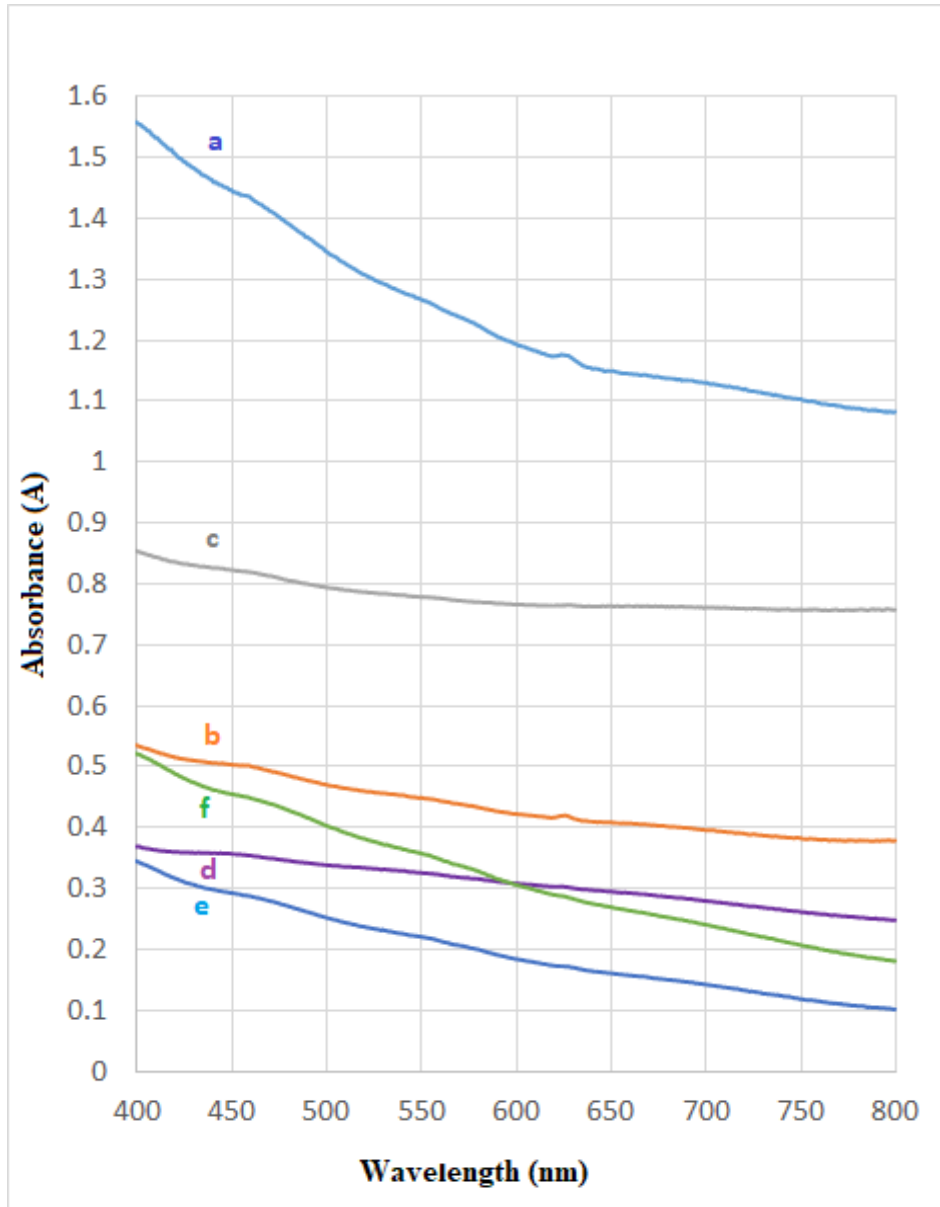


Figure (3.2): Electronic absorption spectra measured for ECD-CdSe thin film a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled.

Table (3.1): Energy band gap values of ECD-CdSe electrodes based on annealing and cooling rate.

CdSe type	sample	description	energy band gap (eV)
Fresh	a	Non-annealed	2.1
	b	Slowly cooled	1.95
	c	Fast cooled	2.05
recycled	d	Non-annealed	2.14
	e	Slowly cooled	2
	f	Fast cooled	2.03

3.1.3 PEC studies of CdSe thin film electrodes

PEC studies for ECD-CdSe thin films including dark J - V characterization plots, photo J - V characterization plots, values of short-circuit current and efficiency, were studied in aqueous S^{2-}/S_x^{2-} redox couple at $25\pm 1^\circ\text{C}$, before annealing and after annealing at 150°C with changing rate of cooling.

3.1.3.1 Dark J - V characterization plots of CdSe electrodes

Dark J - V characterization plots were measured for fresh and recycled ECD-CdSe electrodes. The measurements were conducted before and after annealing process, taking in consideration the cooling rate (fast or slow).

3.1.3.1.1 The dark current based on annealing and rate of cooling

Dark J - V characterization plots were performed for ECD-CdSe electrodes for fresh and recycled ones before and after annealing at 150°C with controlled cooling, Figures (3.3 and 3.4).

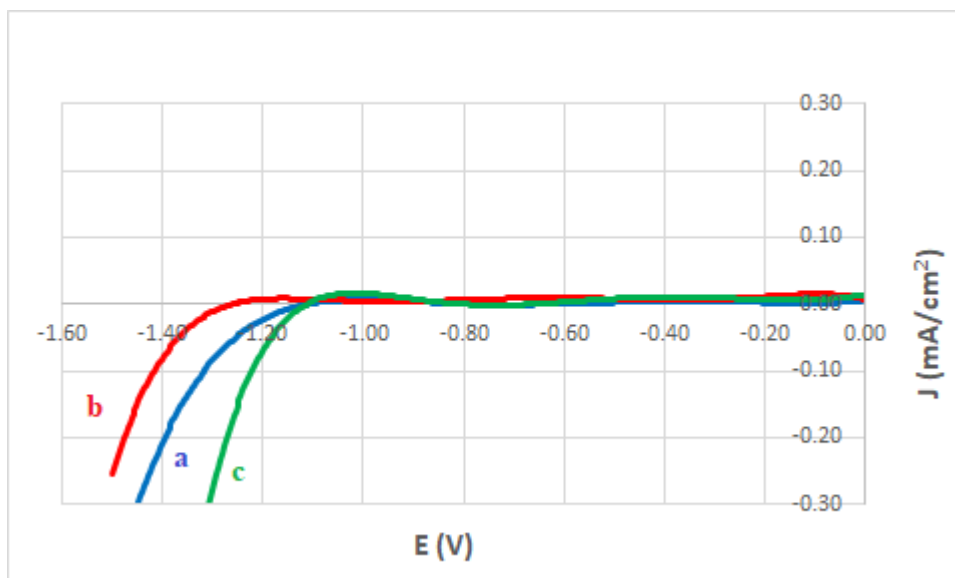


Figure (3.3): Dark J - V characterization plots for fresh ECD-CdSe electrodes *a*) no annealed, *b*) annealed at 150 °C with slow cooling, *c*) annealed at 150 °C with fast cooling. Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

The dark J - V plot of fresh non-annealed CdSe film electrode showed nearly same V_{onset} (~ -1.17 V) for the annealed (fast cooled) CdSe film, but the annealed film with slow cooling showed higher V_{onset} (~ -1.20 V) comparing with other films.

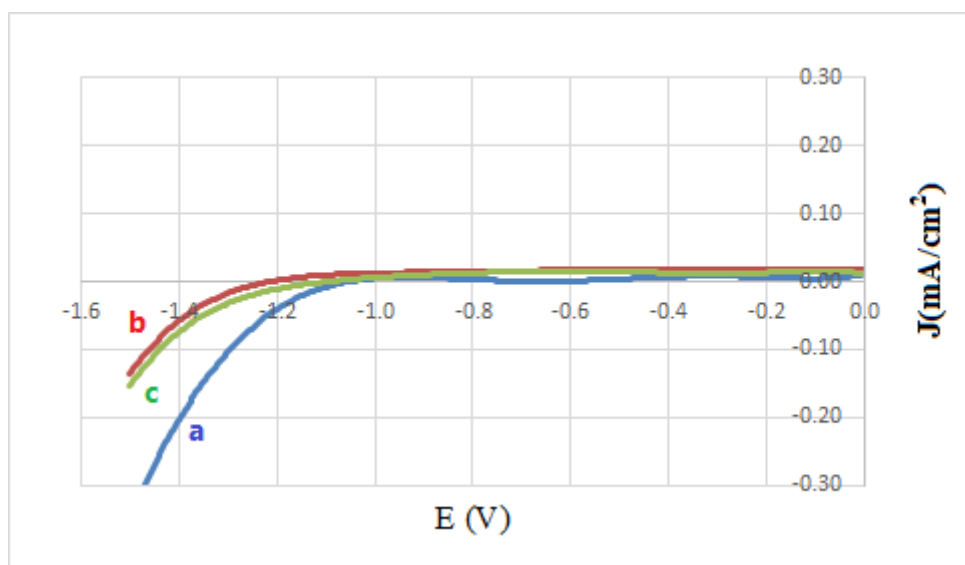


Figure (3.4): Dark J - V characterization Plots for recycled electrochemical deposition CdSe electrodes *a*) non-annealed, *b*) annealed at 150 °C with slow cooling, *c*) annealed at 150 °C with fast cooling. Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

The dark J - V plot of recycled films showed nearly the same plot of fresh films. The recycled non-annealed CdSe film electrode showed nearly same V_{onset} (~ -1.11 V) for the annealed fast cooled CdSe film, but the annealed film with slow cooling showed higher V_{onset} (~ -1.21 V) than other films.

3.1.3.2 Photo J - V characterization plots for CdSe electrodes

Photo J - V characterization plots were performed for different ECD-CdSe electrodes. The PEC measurements showed that the prepared CdSe films were n-type in electrical conduction.

3.1.3.2.1 The effect of annealing and cooling rate on photo current

Photo J - V characterization plots were performed for fresh and recycled ECD-CdSe electrodes, considering non-annealing and annealing at 150°C with control of cooling process, Figure (3.5). Table (3.2) summarizing the results of Figure (3.5).

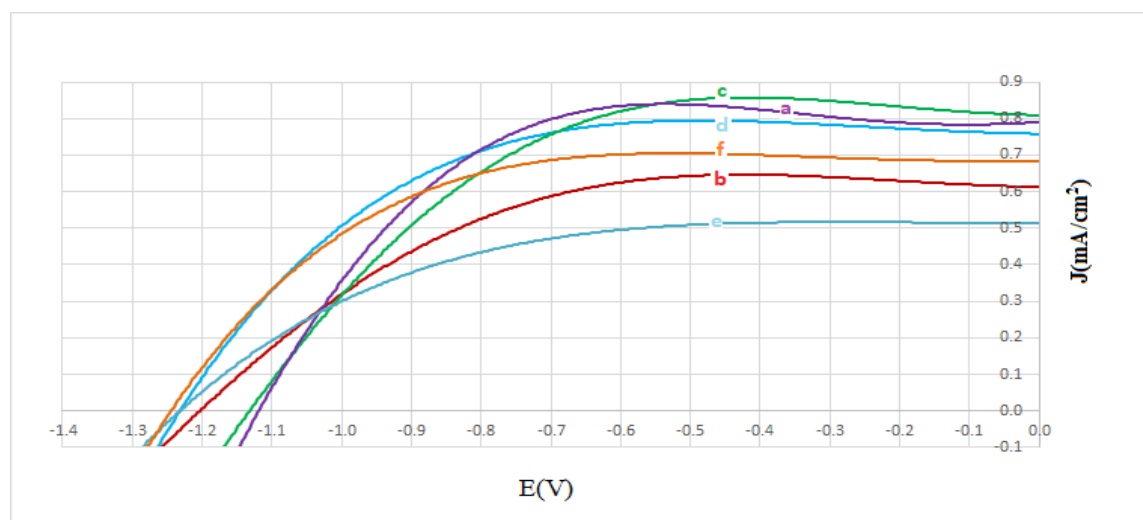


Figure (3.5): Photo J - V characterization plots for electrochemical deposition CdSe electrodes: a) non-annealed fresh, b) after annealing at 150°C and slowly cooled, c) after annealing at 150°C and quickly cooled, d) non-annealed recycled, e) after annealing at 150°C and slowly cooled, f) after annealing at 150°C and quickly cooled. Using $\text{S}^{2-}/\text{S}_x^{2-}$ redox solution at $25 \pm 1^\circ\text{C}$.

Table (3.2): Effect of annealing and cooling rate on PEC characteristics of electrochemical deposition CdSe electrodes.

CdSe type	sample	description	V_{oc} (V)	J_{sc} (mA/cm ²)	^a η %	^b FF%
fresh	a	Non-annealed	-1.12	0.79	4.6	64
	b	Slowly cooled	-1.2	0.62	3.35	55.8
	c	quickly cooled	-1.13	0.8	4.2	59.6
recycled	d	Non-annealed	-1.23	0.77	4.5	59.9
	e	Slowly cooled	-1.23	0.52	2.75	53
	f	quickly cooled	-1.24	0.68	4.15	61

$$^a\eta (\%) = [(\text{maximum observed power density}) / (\text{reach-in power density})] \times 100\%.$$

$$^bFF = [(\text{maximum observed power density}) / J_{sc} \times V_{oc}] \times 100\%.$$

The recycled films revealed higher V_{oc} comparing with fresh ones, but J_{sc} values for fresh films are still higher than recycled ones. The fresh and recycled films gave close percent conversion efficiencies, on the other hand, the fresh and recycled non-annealed films showed the highest percent conversion efficiency than the other films. And the quenched films show higher percent of conversion efficiency comparing with the slowly cooled ones.

Annealing was reported to enhance the particle properties, giving more orderly and compact surface, in addition to give more homogenous and higher crystallinity. Annealing lowers crystal defects, enhances the contact between particles, decreases surface harshness and eliminates surface states [20]. Annealing is not favorable here, because of ECD-CdSe thin films should be relatively uniform and crystalline without annealing. The kinetic

energy of the particles increases by heating, so it may increase their disorder and arrange them in a random way. [36]

As we mentioned above quenched films showed better PEC characteristics than the slowly cooled ones. Because fast cooling protects crystallites from extra exposure to heat and possibly eliminates film distortion. Annealed films with slow cooling exposes the heated crystal to more high temperature, and may thus cause more imperfection [58, 67].

3.1.4 Stability of the CdSe thin film electrodes

Stability here means ability of the solar cell to sustain its photocurrent density for long time by resisting any electrode photo-corrosion. It can be studied by measuring I_{sc} with time. Thin films which gave constant I_{sc} for a longer time showed the best stability. The stability of electrochemical deposition CdSe electrodes under PEC condition was investigated, Figure (3.6). The value of current density vs. time was measured, the applied potential with respect of Calomel electrode was 0.0 V. Effect of annealing and cooling rate on J_{sc} vs. time plots is studied. The recycled and fresh non-annealed CdSe films showed higher J_{sc} vs. time than annealed CdSe films, quenched films showed higher J_{sc} vs. time than slowly cooled films. J_{sc} vs. time plots for annealed electrodes with slow cooling went down more steeply than other films. This means relative stability for non-annealed films compared with annealed CdSe thin films under PEC conditions. Stability study showed no much difference between recycled and fresh ECD-CdSe electrodes.

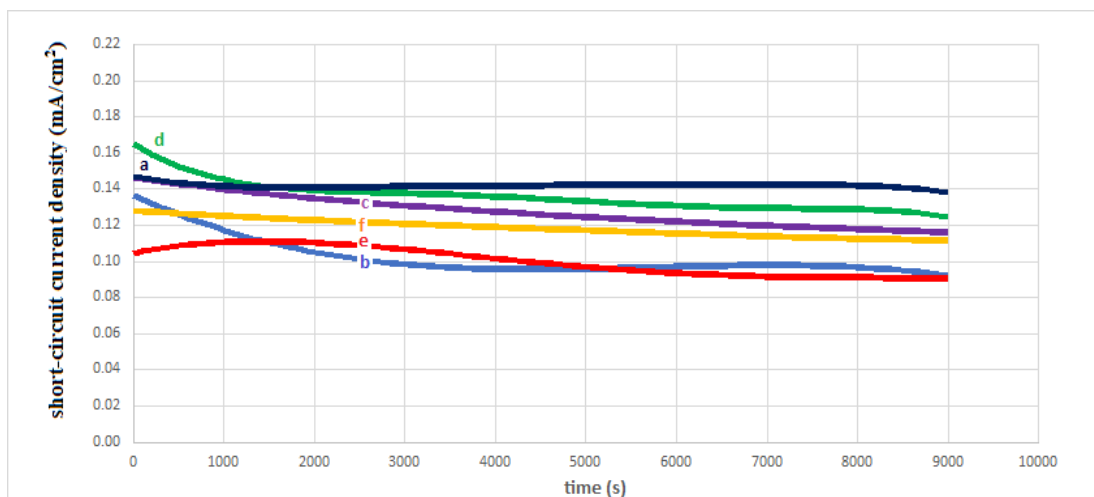
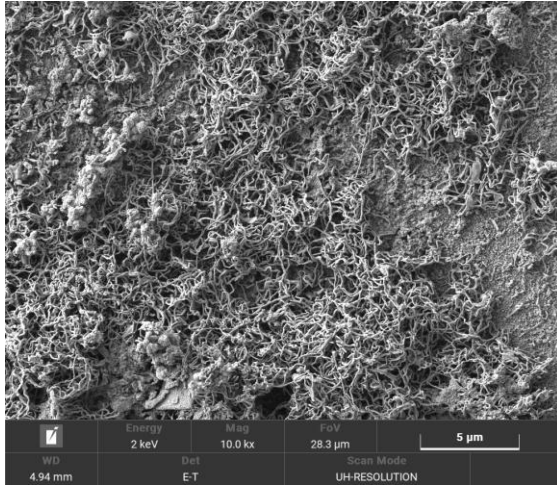


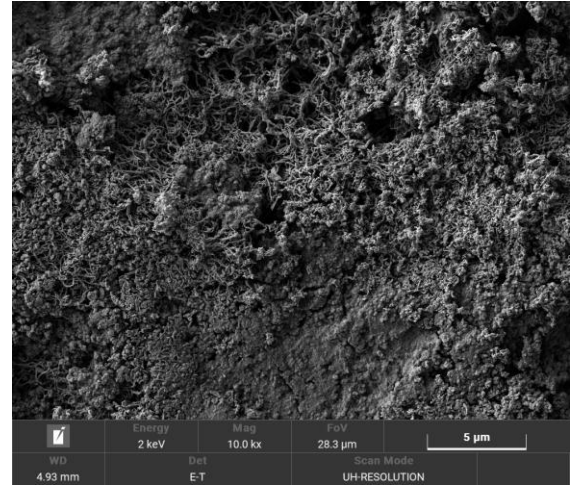
Figure (3.6): J_{sc} vs. time measurements for ECD-CdSe electrodes a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled. Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

3.1.5 SEM images for CdSe electrodes

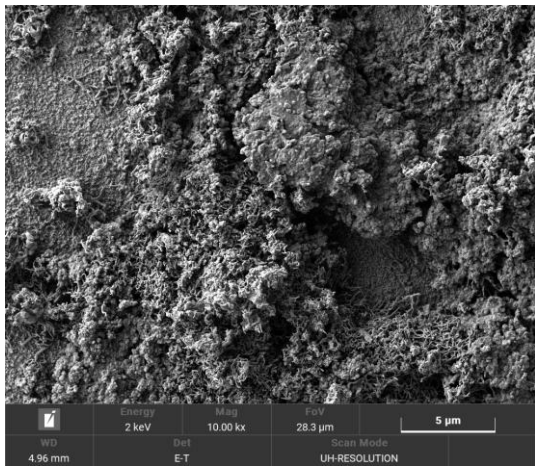
Surface quality of semiconductors has been made by SEM. As surface quality of the electrode affects its PEC processes, it is necessary to study this characteristic. SEM surface images were obtained for recycled and fresh CdSe thin films before and after annealing to see the uniformity and quality of the surfaces as shown in Figure (3.7).



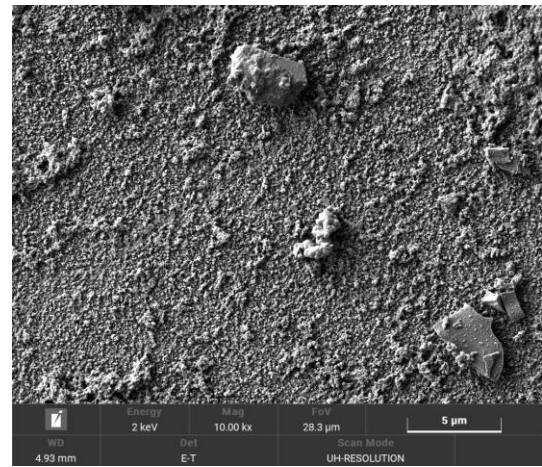
(a)



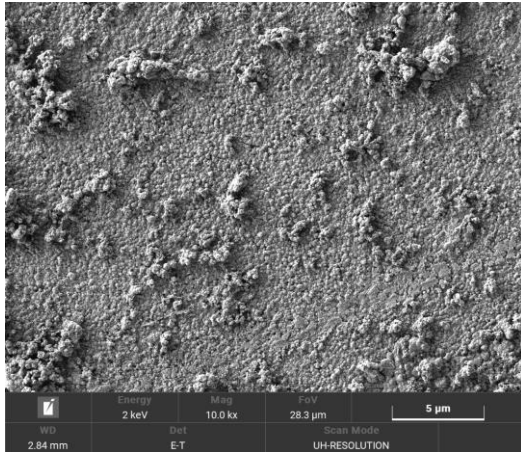
(d)



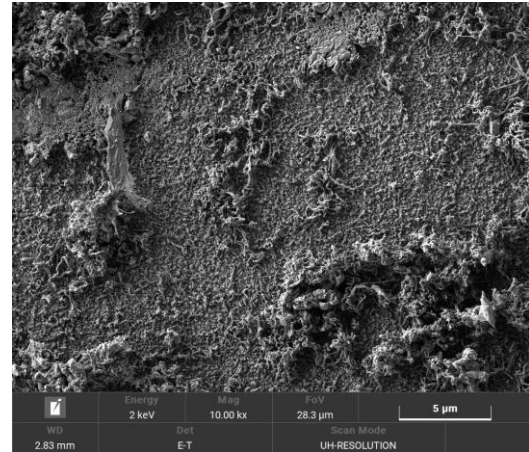
(b)



(e)



(c)



(f)

Figure (3.7): scanning electron microscope images for ECD-CdSe electrodes surface a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled.

SEM micrographs for different ECD-CdSe films are summarized in Figure (3.7). The non-annealed fresh film shows agglomerates of less than 100 nm. Long fibers of agglomerates (~70 nm in diameter) also exist at the top of the film. When annealed, the fibers disappear and yield more of spherical shape agglomerates. The slowly cooled film involves interconnected agglomerates of less than 100 nm with traces of fibers. The quickly cooled sample involves agglomerates of less than 100 nm with no fibers. All agglomerates exist inside random lumps.

The recycled non-annealed film involves agglomerates (of less than 100 nm) and fibers of less than ~100 nm in diameter. The slowly cooled film shows agglomerates of less than 100 nm with no fibers. The quickly cooled film involves agglomerates of less than 100 nm with traces of fibers. Surface morphology of both fresh and recycled films is lowered by annealing. Cross sectional SEM micrographs show that the non-annealed thin films (about 100 nm thick) become more diffuse, thicker and less uniform on annealing.

3.1.6 Energy-dispersive X-ray spectra for CdSe electrodes

Energy-dispersive X-ray spectra measurements were performed for recycled and fresh ECD-CdSe electrodes considering before and after annealing. EDX patterns are attached in appendix B. Cadmium to selenium with different atom ratios are assigned by EDX analysis results. The results are presented at Table (3.3). The Table showed that cadmium ratio was

more than selenium, due to reduction of Cd^{2+} ions to Cd atoms in the film electrode.

Table (3.3): Cadmium and selenium atom ratio for ECD-CdSe thin film electrodes based on annealing and cooling rate.

technique	type	sample	description	Cd	Se
ECD	fresh	a	non-annealed	9.5	1
		b	slowly cooled	4	1
		c	fast cooled	8.75	1
	recycled	d	non-annealed	7.5	1
		e	slowly cooled	2.98	1
		f	fast cooled	3.6	1

3.2 Chemical bath deposited (CBD) thin film electrodes

Characteristics of CdSe electrode prepared on FTO/glass by CBD method were investigated. Different techniques were used for electrode characterization such as spectroscopy, scanning electron microscopic, Energy Dispersive X-Ray Spectroscopy and X-ray diffraction measurements. PEC studies including photo J-V characterization plots, dark J-V characterization plots, the efficiency of conversion, short-circuit current density (J_{SC}) and fill-factor (FF) are described.

In earlier studies, CdSe thin films were prepared by CBD technique showed PEC characteristics. So, PEC characteristics were enhanced by changing chemical bath solution three times during deposition process in this work to enhance PEC characteristics. CdSe thin films properties were investigated by using different techniques as shown below.

3.2.1 XRD measurements for CdSe thin film electrodes

The structural phase and particle size of the CBD-CdSe electrode have been determined based on XRD measurements. CdSe was exist in either hexagonal (wurtzite type) or cubic (zinc-blende type) structure or been as a mixture of hexagonal and cubic as described above, based on literature [41]. XRD were performed for CBD-CdSe electrode with different parameters including annealing effect and cooling rate. The XRD measurements for the CdSe thin films prepared by CBD described here.

3.2.1.1 Effect of annealing and cooling rate on CdSe thin film electrodes

XRD measurements were conducted for fresh and recycled CdSe thin film electrodes considering before and after annealing at 150 °C with slow and fast cooling. XRD data showed that both annealed and non-annealed films exhibit nano crystals. Based on Scherr equation, the average particle size for non- annealed fresh CBD-CdSe was~ 6.22 nm, and for the non-annealed recycled film the particle size was~ 6.14 nm, Figure (3.8). The slowly cooled fresh and recycled annealed film particle sizes are~ 7.43, 7.4 nm, respectively. For quickly cooled samples the values were 7.48, 7.8 nm, for fresh and recycled films, respectively. Annealing at relatively low temperature (150 °C) thus causes sintering in particle sizes. All films are in the cubic phase with the zinc-blende type structure. This is based on comparison with earlier reports [43, 64-66]

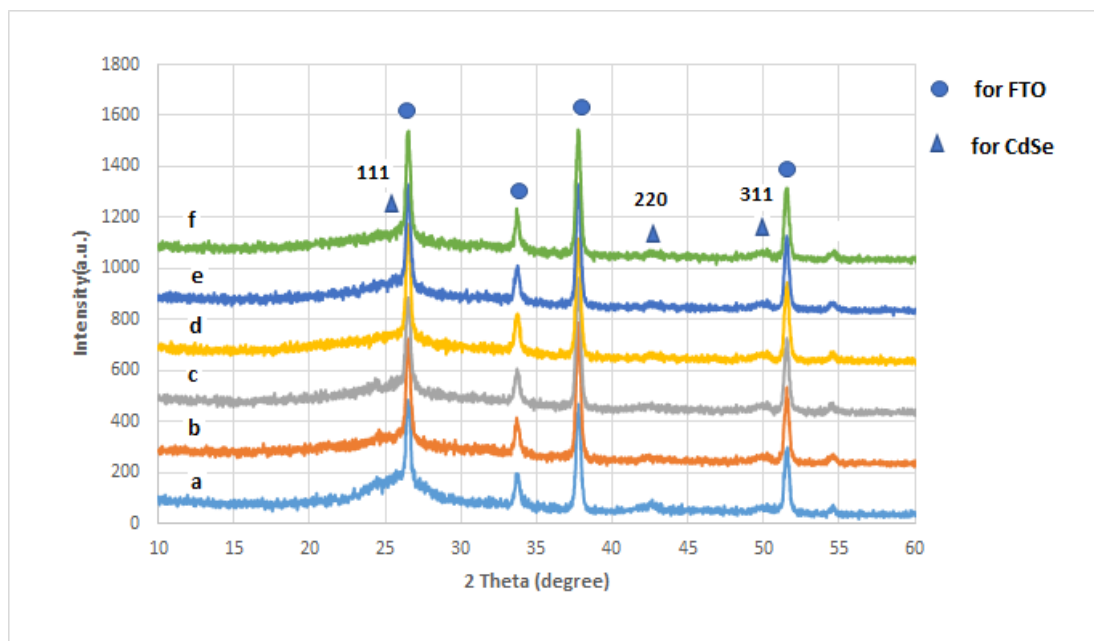


Figure (3.8): X-ray diffraction patterns performed for CBD-CdSe thin film a) fresh non-annealed, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled.

3.2.2 Spectroscopic measurements for CdSe thin film electrodes

Spectroscopic absorptions spectra were measured for fresh and recycled CdSe thin films before annealing and after annealing at 150°C with slow and fast cooling.

3.2.2.1 Effect of annealing and cooling rate on CdSe thin film electrodes

Electronic absorption spectra were measured for non-annealed fresh and recycled CdSe thin films and for annealed ones at 150 °C under nitrogen for 1 hour. Moreover, the spectroscopic absorption spectra of the pre-annealed CBD-CdSe electrodes with the effect of rate of cooling (fast and slow cooling) at 150°C under nitrogen for one hour was investigated, as shown in Figure (3.9). Table (3.4) summarized the results of Figure (3.9).

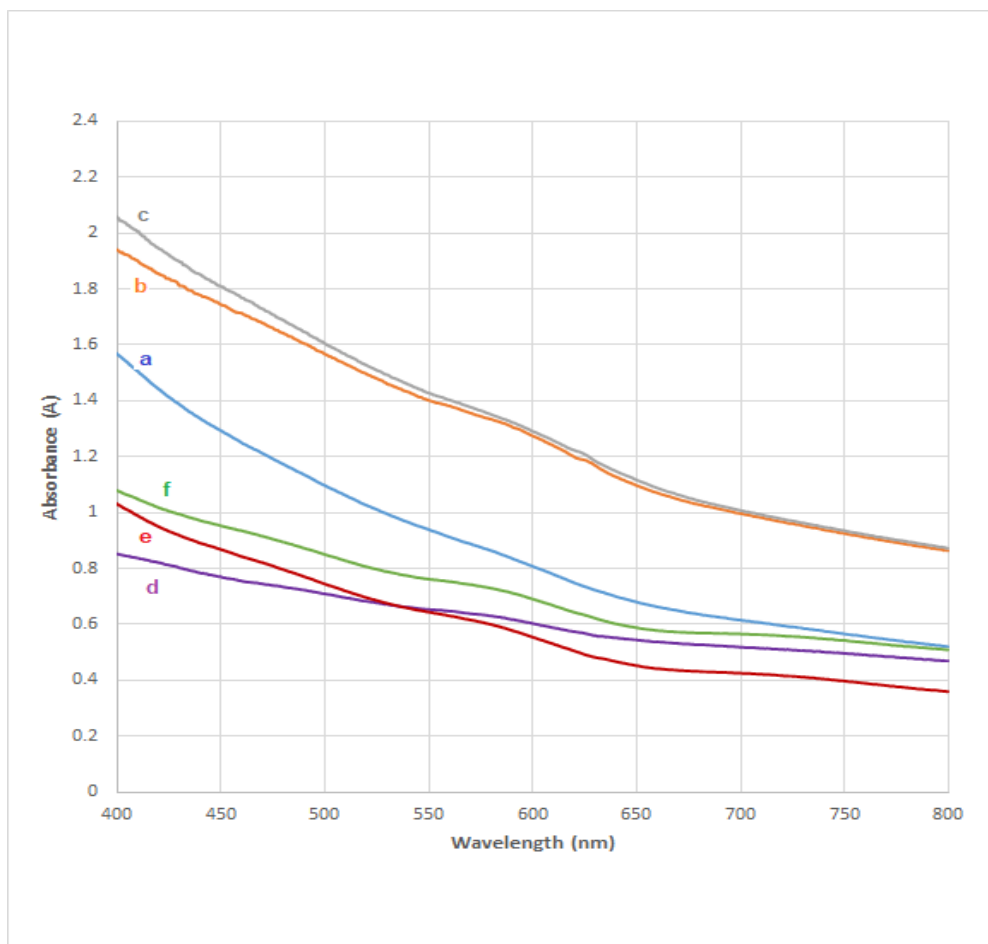


Figure (3.9): Electronic absorption spectra measured for CBD-CdSe thin film a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled.

The Figure showed that the fresh films exhibit slightly clearer absorption than the recycled ones. The fresh annealed film has higher absorption than non-annealed film. For recycled films nearly the same results were observed.

As mentioned above, the Tauc method was used to determining the energy band gap for thin films. Table (3.4) showed that recycled and fresh films gave comparable energy band gaps. Annealing process slightly influences the energy band gap values. The non-annealed recycled and fresh films showed the similar energy band gaps that are higher than annealed films. Quickly

cooled films gave smaller energy band gaps compared with slowly cooled films.

Table (3.4): The value of energy band gap of CBD-CdSe electrodes based on annealing and cooling rate.

type	sample	description	Energy band gap (eV)
fresh	a	Non-annealed	2.00
	b	Slowly cooled	1.87
	c	Fast cooled	1.85
recycled	d	Non-annealed	2.0
	e	Slowly cooled	1.93
	f	Fast cooled	1.9

3.2.3 PEC studies of CBD CdSe thin film electrodes

PEC studies for CBD-CdSe thin films including dark J-V plots, photo J-V plots and values of short-circuit current and efficiency, were all studied in S^{2-}/S_x^{2-} aqueous redox couple at $25\pm1^\circ\text{C}$, before annealing and after annealing at 150°C with different cooling rates.

3.2.3.1 Dark J-V Plots of CdSe thin film electrodes

Dark J-V Plots were measured for fresh and recycled CBD-CdSe thin film electrodes before and after annealing process with fast and slow cooling.

3.2.3.1.1 Effect of annealing and cooling rate on dark J-V plots

Dark J-V Plots were measured for CBD-CdSe thin film electrodes for fresh and recycled ones before annealing and after annealing at 150°C with control cooling. Figure (3.10, 3.11).

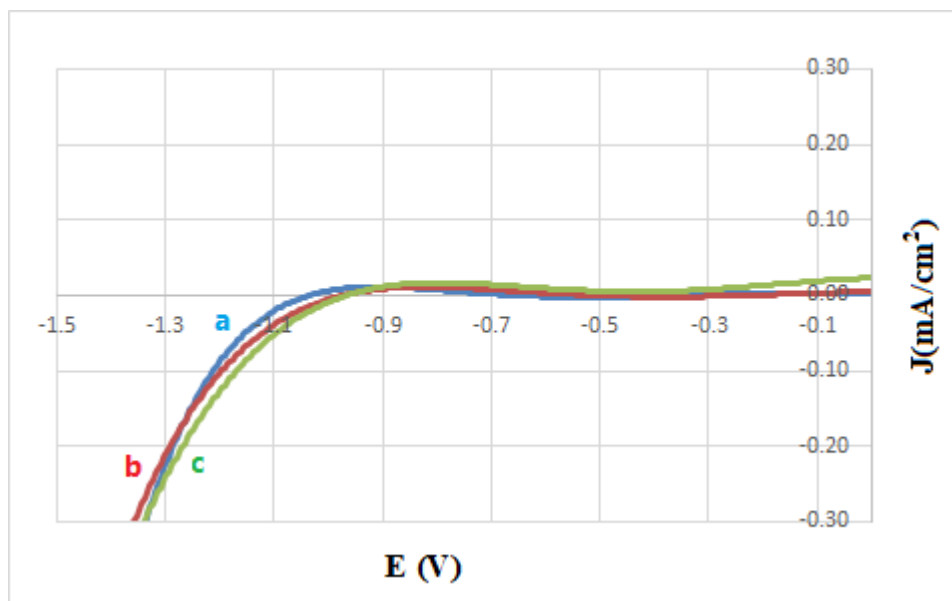


Figure (3.10): Dark J - V Plots for fresh CBD-CdSe thin film electrodes *a)* non-annealed, *b)* annealed at 150 °C with slow cooling, *c)* annealed at 150 °C with fast cooling Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

The dark J - V plot of fresh non-annealed CdSe film electrode showed highest V_{onset} (~ -1.13 V). The annealed slowly cooled CdSe film showed V_{onset} (~ -1.09 V), and the annealed film fast cooling showed lowest V_{onset} (~ -1.07 V).

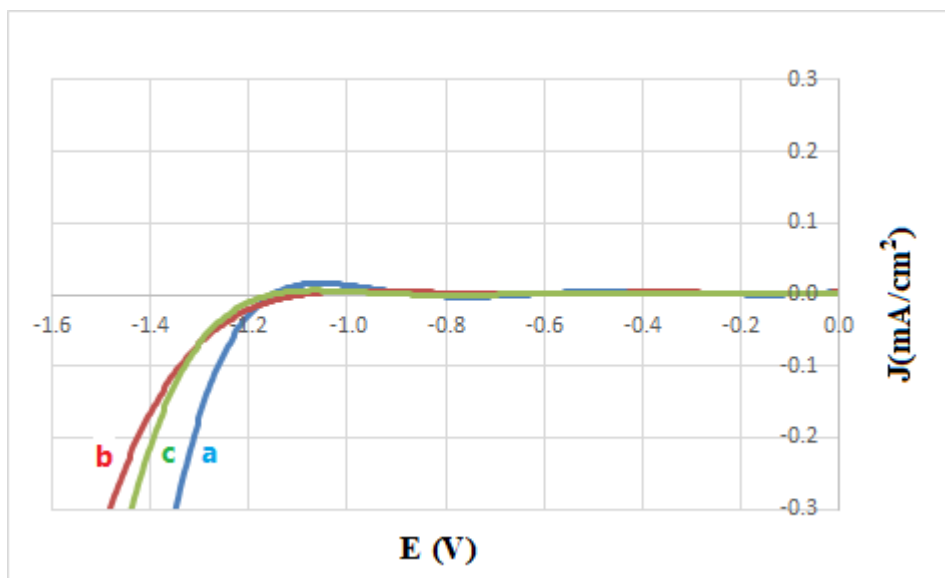


Figure (3.11): Dark J - V Plots for recycled CBD-CdSe thin film electrodes *a*) non-annealed, *b*) annealed at 150 °C with slow cooling, *c*) annealed at 150 °C with fast cooling. Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

The dark J - V plot of recycled films showed nearly the same plot of fresh films. The recycled non-annealed CdSe film electrode showed V_{onset} (~ -1.19 V), for the annealed slowly cooled CdSe film V_{onset} (~ -1.17 V), but the annealed film with fast cooling showed lowest V_{onset} (~ -1.14 V).

3.2.3.2 Photo J - V plots of CdSe thin film electrodes

Photo J - V plots were measured for CBD-CdSe thin film electrodes with different controlled parameters (annealing process and cooling rate).

3.2.3.2.1 The effect of annealing and cooling rate on photo current

Photo J - V characterization plots were performed for fresh and recycled CBD-CdSe electrodes, considering non-annealing and annealing at 150°C with control of cooling process, Figure (3.12). Table (3.5) summarizing the results of Figure (3.12).

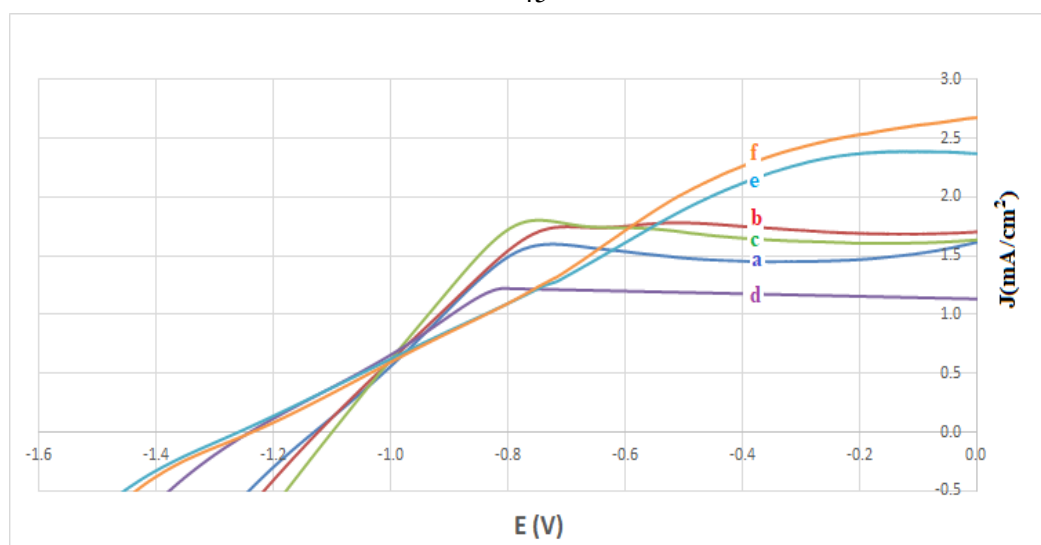


Figure (3.12): Photo J - V plots for CBD-CdSe thin film a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled. Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

Table (3.5): The PEC characteristics of CBD-CdSe electrodes based on of annealing and cooling rate.

	sample	description	V_{oc} (V)	J_{sc} (mA/cm ²)	$^a\eta$ %	bFF %
fresh	a	Non-annealed	-1.13	1.61	9.7	66
	b	Slowly cooled	-1.12	1.7	10.3	67
	c	Fast cooled	-1.10	1.63	10.8	74
recycled	d	Non-annealed	-1.24	1.15	7.7	66
	e	Slowly cooled	-1.26	2.37	7.8	32
	f	Fast cooled	-1.24	2.67	8.3	31

$$^a\eta (\%) = [(\text{maximum observed power density}) / (\text{reach-in power density})] \times 100\%.$$

$$^bFF = [(\text{maximum observed power density}) / J_{sc} \times V_{oc}] \times 100\%.$$

V_{oc} for the recycled films is higher than that for fresh ones, and J_{sc} values for annealed recycled films are higher than for other films. The fresh and recycled films exhibited similar percent conversion efficiencies. For fresh films, annealed quenched film has the highest conversion efficiency. The

recycled quenched film gave higher percent conversion efficiency than non-annealed and annealed slowly cooled films.

Annealing was reported to enhance the particle properties, giving more orderly and compact surface, in addition to give more homogenous and higher crystallinity. Annealing lowers crystal defects, enhances the contact between particles, decreases surface harshness and eliminates surface states [20]. In this study annealing CBD-CdSe thin films was found to improve PEC characteristics.

As we mentioned above quenched films have better PEC characteristics than the slowly cooled ones. Because fast cooling protects crystallites from extra exposure to heat and possibly eliminates film distortion. Annealed films with slow cooling exposes the heated crystal to more high temperature, and may thus cause more imperfection [58, 67].

3.2.4 Stability of the CdSe thin film electrodes

Stability here means ability of the solar cell to sustain its photocurrent density for long time by resisting any electrode photo-corrosion. It can be studied by measuring I_{sc} with time. Thin films which gave constant I_{sc} for a longer time showed the best stability. The stability of CBD-CdSe electrodes under PEC conditions was conducted, Figure (3.13). The current density values vs. time were measured, the applied potential was 0.0 V with respect of Calomel electrode.

Effect of annealing and cooling rate on J_{sc} vs. time plots were studied. The annealed CdSe films showed higher J_{sc} vs. time than non-annealed CdSe films, quenched films showed higher J_{sc} vs. time than slowly cooled films. This indicates relative stability of quenched annealed films compared to annealed CdSe with slowly cooled and non-annealed thin films under PEC conditions. Stability study showed no much difference between recycled and fresh CBD-CdSe electrodes.

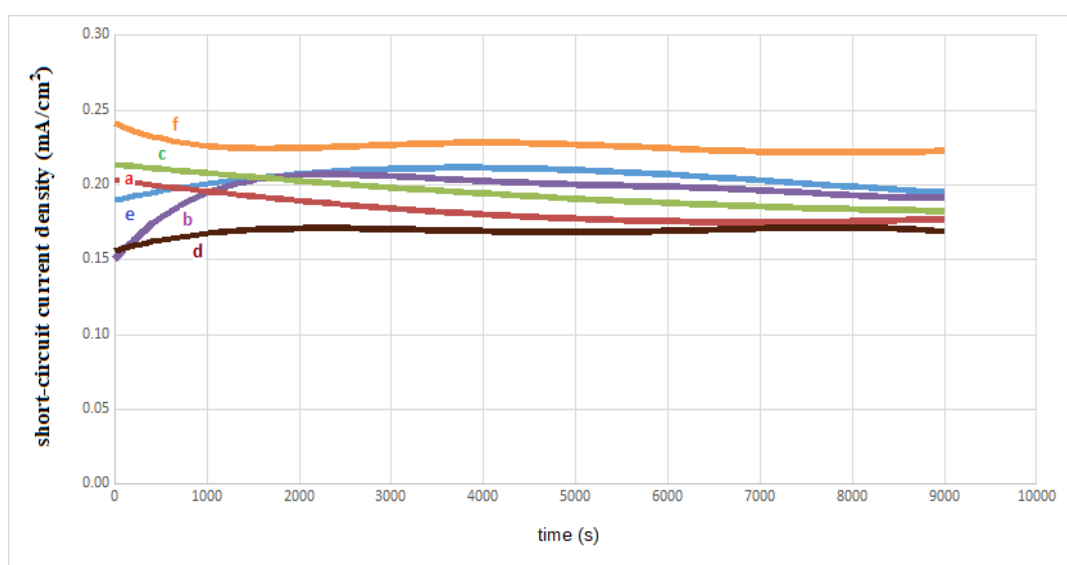


Figure (3.13): J_{sc} vs. time measurements for CBD-CdSe electrodes a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled. Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

3.2.5 SEM images for CdSe thin film electrodes

Surface quality of semiconductors has been made by SEM. SEM surface images have been obtained for recycled and fresh CdSe thin films before and after annealing to see the uniformity and quality of the surfaces, as shown in Figure (3.14).

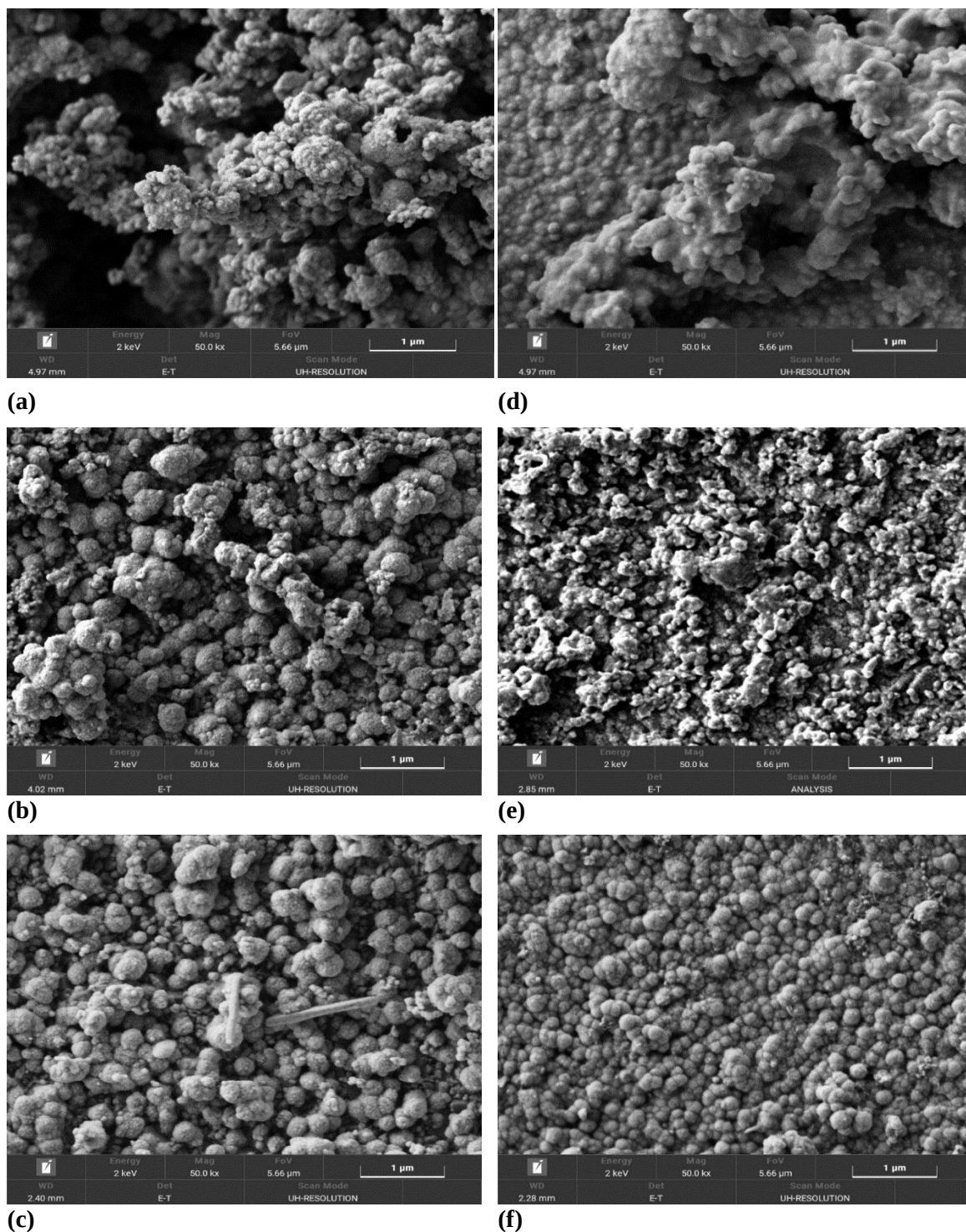


Figure (3.14): Scanning electron microscope images for CBD-CdSe electrodes surface a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled.

SEM micrographs were measured for different recycled and fresh CBD-CdSe, as summarized in Figure (3.14). All films involve agglomerates. The agglomerates exist inside lumps of various and random sizes. The non-annealed fresh and recycled films resemble each other in having ups and downs. Compared to non-annealed ECD films, the SEM micrographs show that the CBD films have more random film morphologies. This is not unexpected, as ECD films normally have more compact and higher morphological uniformity than CBD films. Upon annealing, the CBD-CdSe films show higher compactness, uniformity and interconnectivity between agglomerates. Unlike ECD films, annealing enhances film uniformity and compactness for CBD-CdSe films. Cross sectional SEM micrographs support these conclusions. The micrographs show that the CBD films become thinner, more compact and more uniform on annealing.

3.2.6 EDX spectra for CdSe thin film electrodes

Energy-dispersive X-ray spectra measurements were performed for recycled and fresh CBD-CdSe electrodes considering before and after annealing. EDX patterns are attached in appendix B. Cadmium to selenium with different atom ratios are assigned by EDX analysis results. The results are presented at Table (3.6). The Table shows that cadmium was more than selenium.

However, the Cd/Se atom ratios in CBD films are much more realistic and closer to stoichiometric ratios than in ECD films.

Table (3.6): Effect of annealing and cooling rate on cadmium and selenium atom ratio for CBD-CdSe thin film electrodes.

technique	type	sample	description	Cd	Se
CBD	fresh	a	non-annealed	1.7	1
		b	slowly cooled	1.8	1
		c	fast cooled	2.17	1
	recycled	d	non-annealed	1.4	1
		e	slowly cooled	1.84	1
		f	fast cooled	1.5	1

3.3 Combined electrochemical/chemical bath deposited (ECD-CBD) thin film electrodes

Fresh and recycled (ECD-CBD) CdSe thin films prepared by combined chemical bath deposition and electrochemical deposition methods, and the CdSe thin films modified by coating with carbon were studied under different conditions utilizing different techniques such as spectroscopy, EDX, XRD and SEM. PEC studies including photo J-V characterization plots, dark J-V characterization plots, the efficiency of conversion, short-circuit current density (J_{SC}) and fill-factor (FF) are described.

In earlier studies, a new type of CdSe film prepared by ECD-CBD technique was reported. The effect of deposition time (15 min ECD + 120 min CBD), (15 min ECD + 240 min CBD) on film PEC characteristics was studied. The (15 min ECD + 240 min CBD) deposition time gave best results [17]. These times are therefor used here for fresh and recycled film

electrodes. Annealing at 150 °C was chosen based on earlier reports for CdSe [17].

Characteristics of combined ECD-CBD CdSe films were investigated by using different techniques as shown below.

3.3.1 XRD measurements for CdSe thin film electrodes

The structural phase and particle size of the ECD-CBD CdSe electrode have been determined based on XRD measurements. CdSe was exist in either hexagonal (wurtzite type) or cubic (zinc-blende type) structure or been as a mixture of hexagonal and cubic as described above, based on literature [41]. XRD were performed for ECD-CBD CdSe electrode with different parameters including annealing effect and cooling rate. The XRD measurements for the CdSe thin films prepared by ECD-CBD described here.

3.3.1.1 Effect of annealing on CdSe thin film electrodes

XRD measurements were conducted for fresh and recycled CdSe thin film electrodes considering before and after annealing at 150 °C with slow and fast cooling. XRD data showed that both annealed and non-annealed films involve monocrystal. Based on Scherr equation the average particle size for non- annealed fresh ECD-CBD CdSe was~ 6.85 nm, the non- annealed recycled film particle size was~ 6.8 nm Figure (3.15). The slowly cooled fresh and recycled annealed film particle sizes were ~ 7.13, 7.42 nm, respectively. Quickly cooled films showed particle sizes of 7, 6.9 nm,

respectively. All films were in the cubic phase with the zinc-blende type of structure. This was based on comparison with earlier reports [43, 64-66]. The results showed that fresh and recycled have comparable particle sizes.

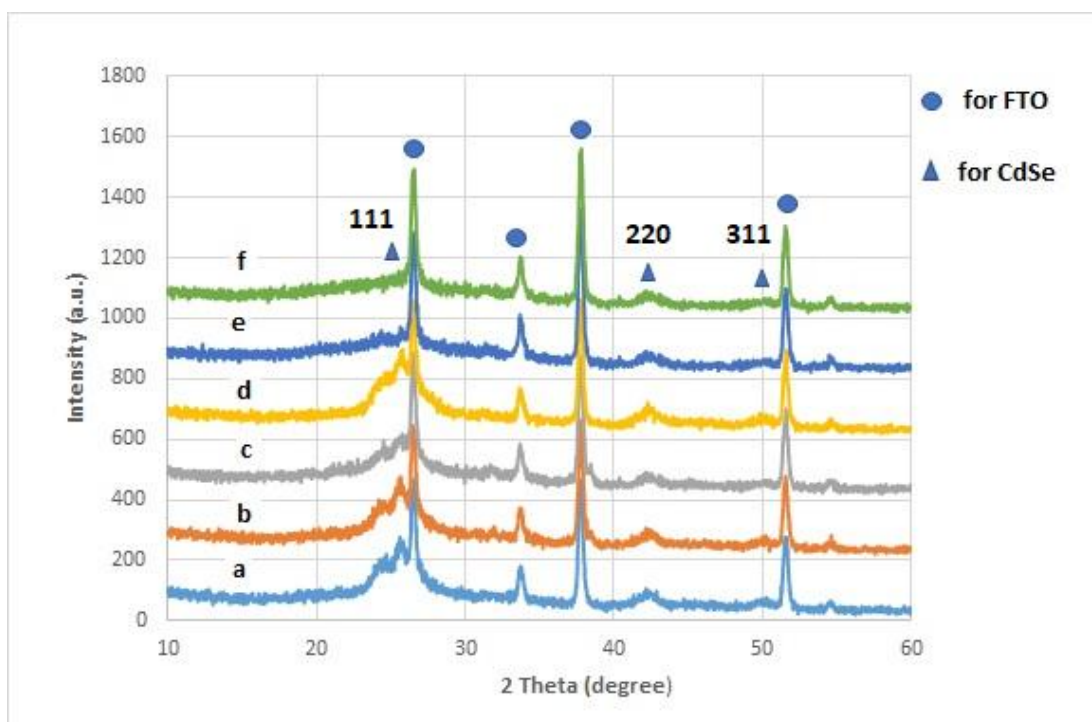


Figure (3.15): X-ray diffraction patterns performed for ECD-CBD CdSe thin film a) fresh non-annealed, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled.

3.3.1.2 Effect of coating CdSe thin film electrodes with carbon.

XRD measurements were acquired for non-annealed CdSe thin film electrodes with carbon and without carbon coating, Figure (3.16). The Figure showed that both films have the same position of CdSe peaks, but film coated with carbon has higher intensity than the other film. Based on Scherrer equation, the average particle size for naked ECD-CBD CdSe was ~6.8 nm, while the coated film has particle size ~7.2 nm.

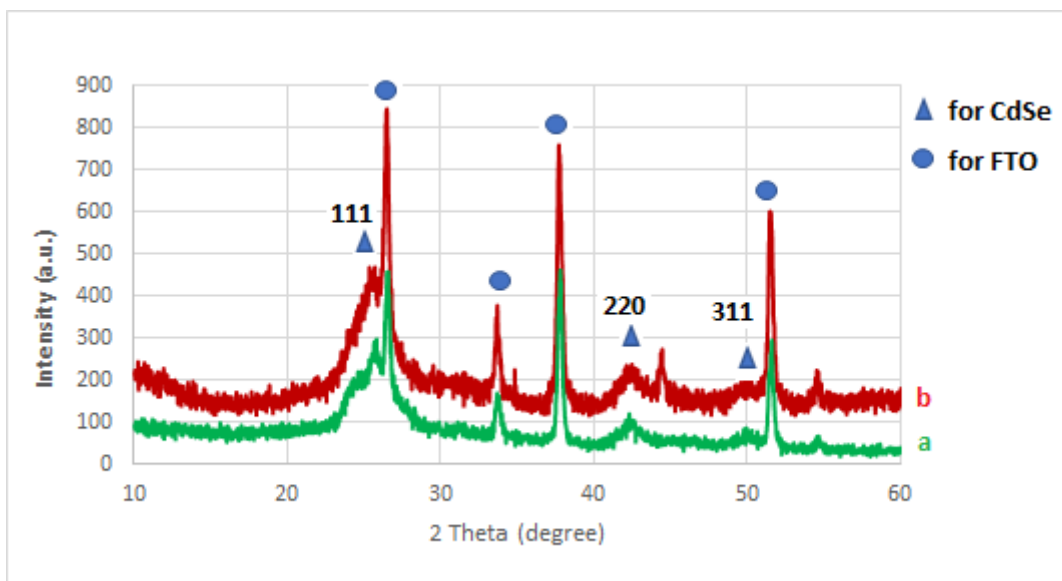


Figure (3.16): XRD patterns measured for non-annealed CdSe thin films, a) without carbon, b) with carbon.

3.3.2 Electronic absorption spectra for CdSe thin film electrodes

Electronic absorption spectra were measured for fresh and recycled CdSe thin films before annealing and after annealing at 150°C with slow and fast cooling.

3.3.2.1 Effect of annealing and cooling rate on CdSe thin film electrodes

Electronic absorption spectra were measured for non-annealed fresh and recycled CdSe thin films, and for annealed ones at 150 °C under nitrogen for 1 hour. Moreover, the effects of addition carbon and cooling rate (fast and slow cooling) on the electronic absorption spectra of the pre-annealed ECD-CBD CdSe thin film electrodes under nitrogen at 150°C for one hour were investigated, Figure (3.17).

The results showed that the recycled non-annealed film gave slightly clearer absorption than other films. Fresh films showed slightly clearer absorption than the annealed recycled ones. As mentioned above, the Tauc method was used to determine the energy band gap for thin films. Table (3.7) showed that recycled and fresh films had comparable energy band gaps, and annealing slightly influences the energy band gaps. The non-annealed films gave highest energy band gaps compared with annealed films. Fresh and recycled slowly cooled films showed lower energy band gaps compared to rapidly cooled films.

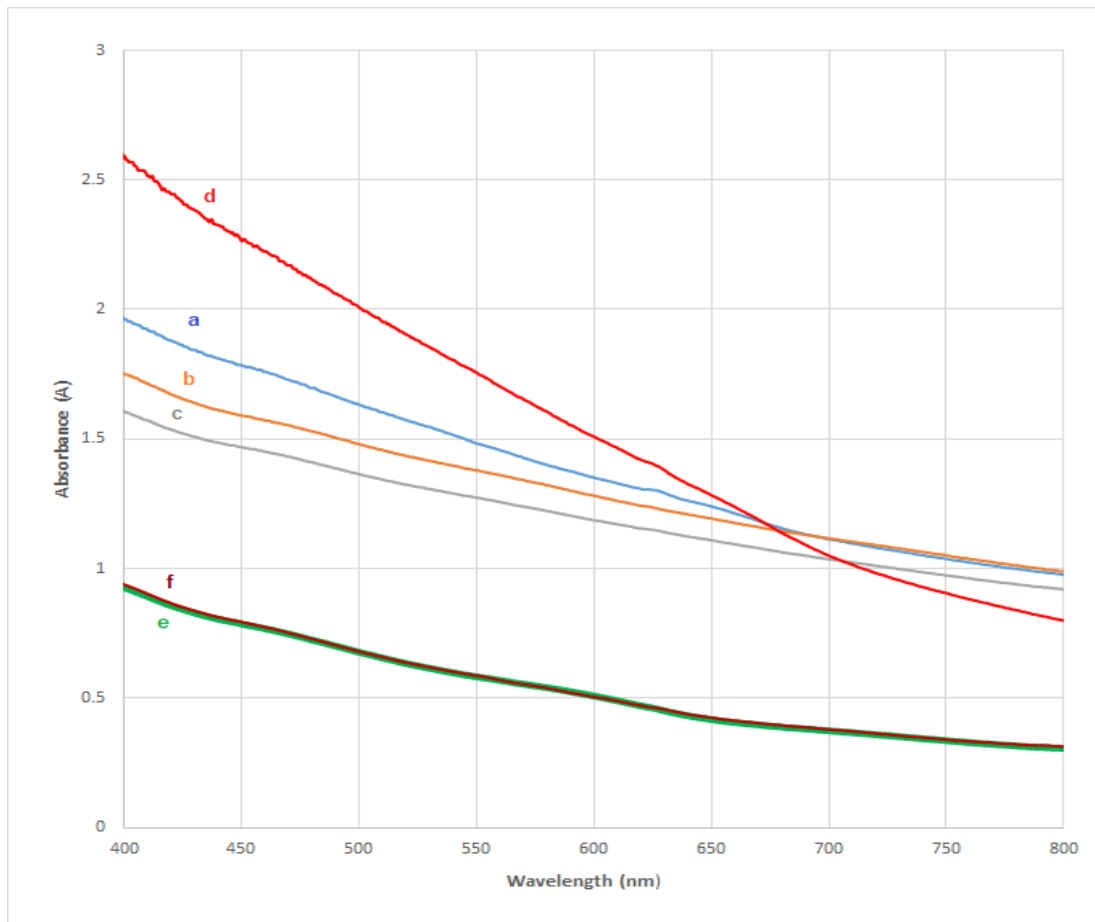


Figure (3.17): Electronic absorption spectra measured for ECD-CBD CdSe thin film a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled.

Table (3.7): Energy band gap values of ECD-CBD CdSe electrodes based on annealing and cooling rate.

	sample	description	Energy band gap (eV)
fresh	a	Non-annealed	1.83
	b	Slowly cooled	1.77
	c	Fast cooled	1.79
recycled	d	Non-annealed	1.85
	e	Slowly cooled	1.81
	f	Fast cooled	1.82

3.3.3 PEC studies of CdSe thin film electrodes

PEC studies for ECD-CBD CdSe thin films including dark J-V plots, photo J-V plots, short-circuit current values and efficiency, were studied in aqueous S^{2-}/S_x^{2-} redox couple at $25 \pm 1^\circ\text{C}$, considering before annealing and after annealing at 150°C with changing cooling rate.

3.3.3.1 Dark J-V Plots of CdSe thin film electrodes

Dark J-V Plots were measured for fresh and recycled ECD-CBD CdSe thin film electrodes before and after annealing process with fast and slow cooling.

3.3.3.1.1 Effect of annealing and cooling rate on dark J-V plots

Dark J-V Plots were measured for fresh and recycled ECD-CBD CdSe thin film electrodes before and after annealing at 150°C with control cooling. Figure (3.18, 3.19).

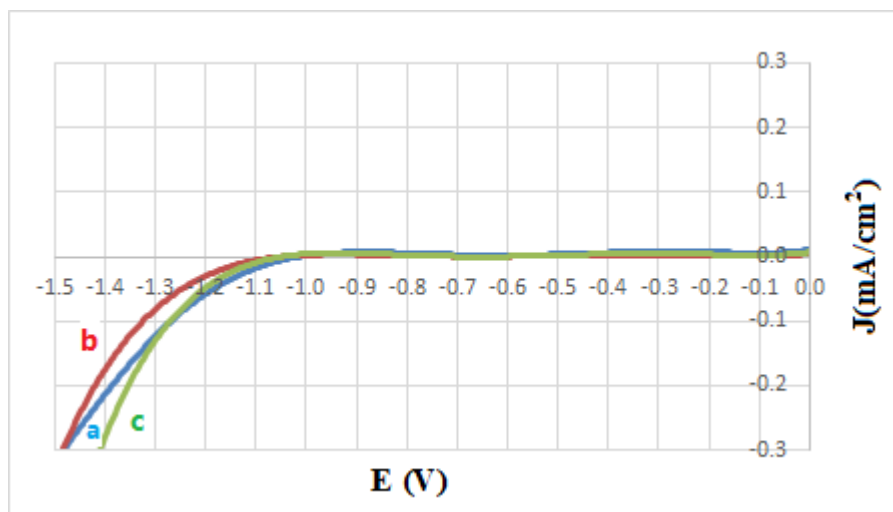


Figure (3.18): Dark J - V Plots for fresh ECD-CBD CdSe thin film electrodes *a*) non-annealed, *b*) annealed at 150 °C with slow cooling, *c*) annealed at 150 °C with fast cooling. Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

The dark J - V plots for fresh slowly and quickly cooled CdSe film electrodes showed V_{onset} values (~ -1.11 V), (~ -1.10 V), respectively. for the non-annealed CdSe film V_{onset} value is (~ -1.07 V).

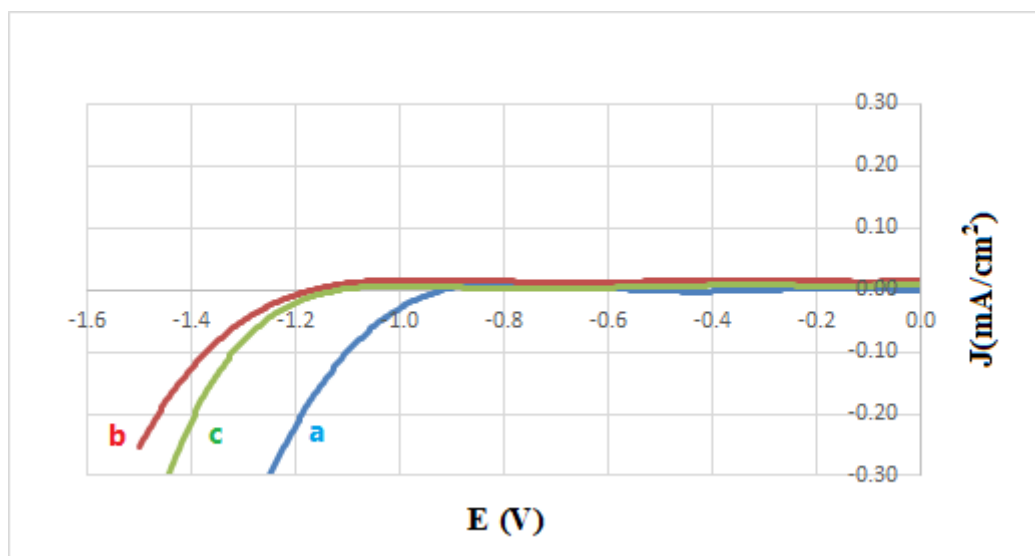


Figure (3.19): Dark J - V Plots for recycled ECD-CBD CdSe thin film electrodes *a*) non-annealed, *b*) annealed at 150 °C with slow cooling, *c*) annealed at 150 °C with fast cooling. Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

The dark J - V plot of recycled films showed nearly the same plot of fresh films. The recycled quickly and slowly cooled CdSe film electrodes gave V_{onset} (~ -1.19 V), and the non-annealed CdSe film gave V_{onset} (~ -0.95 V).

3.3.3.2 Photo J - V plots of CdSe thin film electrodes

Photo J - V plots were measured for ECD-CBD CdSe thin film electrodes with different controlled parameters (annealing process and cooling rate).

3.3.3.2.1 Effect of annealing and cooling rate on photo J - V plots

Photo J - V plots were measured for ECD-CBD CdSe thin film electrodes with different controlled parameters (annealing process and cooling rate). The photo J - V plots were measured for fresh and recycled ECD-CBD CdSe thin film electrodes before annealing and after annealing at 150°C with controlled cooling. Figure (3.20). Table (3.8) summarizing the results of the Figure (3.20).

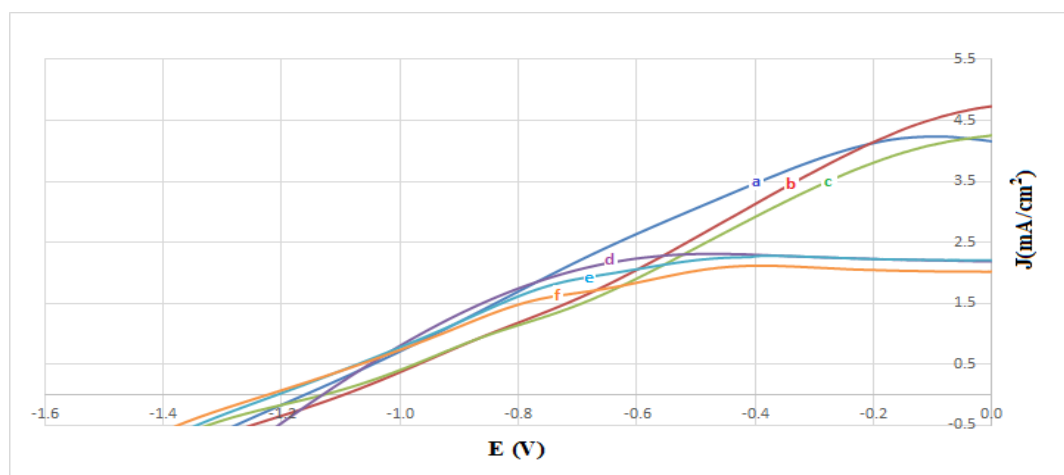


Figure (3.20): Photo J - V plots for ECD-CBD CdSe thin film a) non-annealed fresh, b) after annealing at 150°C and slowly cooled fresh, c) after annealing at 150°C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150°C and slowly cooled recycled, f) after annealing at 150°C and quickly cooled recycled. Using $\text{S}^{2-}/\text{S}_x^{2-}$ redox solution at $25 \pm 1^\circ\text{C}$.

Table (3.8): The PEC characteristics of ECD-CBD CdSe electrodes based on of annealing and cooling rate.

	sample	description	V_{oc} (V)	J_{sc} (mA/cm ²)	^a η %	^b FF%
fresh	a	Non-annealed	-1.16	4.16	12.8	33
	b	Slowly cooled	-1.10	4.73	10.4	25
	c	Fast cooled	-1.13	4.25	9.8	25
recycled	d	Non-annealed	-1.13	2.19	11.6	58
	e	Slowly cooled	-1.21	2.21	10.8	50
	f	Fast cooled	-1.22	2.02	9.7	50

$$^a\eta(\%) = [(\text{maximum observed power density})/(\text{reach-in power density})] \times 100\%.$$

$$^bFF = [(\text{maximum observed power density})/J_{sc} \times V_{oc}] \times 100\%.$$

V_{oc} for the annealed recycled films higher than other ones, and J_{sc} values for fresh films higher than recycled ones. The fresh and recycled films gave close percent conversion efficiencies. For fresh and recycled films, non-annealed films showed the highest conversion efficiency. And the annealed quenched film gave lowest percent conversion efficiency than the slowly cooled ones.

The non-annealed film gave higher electronic absorption and better PEC characteristics than the films annealed at 150 °C, this is consistent with results observed for ECD-CdSe films. Annealing was reported to enhance the particle properties, giving more orderly and compact surface, in addition to give more homogenous and higher crystallinity. Annealing lowers crystal defects, enhances the contact between particles, decreases surface harshness and eliminates surface states [20].

Annealing may enhance ECD-CBD thin films by increasing homogenizing the ECD and CBD layers in the ECD-CBD matrix [36]. In this study, annealing is unfavorable for both ECD-CdSe and ECD-CBD CdSe films. This is due to negative effect of annealing on the ECD-CdSe layer, which is more distorted by annealing, as confirmed in Section 3.1.3.2.

Fast cooling is preferred for CBD-CdSe and ECD-CdSe films, while slow cooling is preferred for ECD-CBD films. This because ECD-CBD CdSe film has higher thickness and disorder than CBD-CdSe. It needs extra time for the metastable atoms/ions to retain to their original order. Also, slow cooling may give CdSe nano-particles enough time to contact very well.

3.3.3.2.2 Effect of coating recycled CdSe thin film electrode with carbon

Photo J - V plots were measured for recycled ECD-CBD CdSe thin film electrodes with carbon and without carbon coating process before annealing and after annealing at 150°C with slow cooling, Figure (3.21). Table (3.9) summarizing the results of the Figure (3.21).

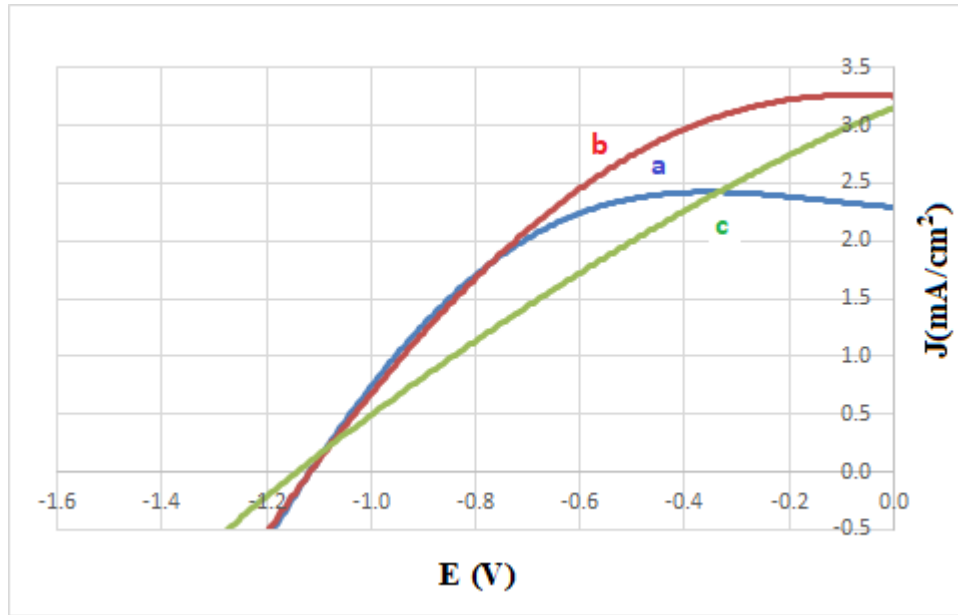


Figure (3.21): Photo J-V plots for ECD-CBD CdSe thin film a) non-annealed without carbon, b) non-annealed with carbon, c) annealed with carbon.

V_{oc} for the annealed coated film was higher than other ones, and J_{sc} values for non-annealed coated films higher than other ones. The non-annealed coated film showed highest percent conversion efficiency, the annealing process reduce percent conversion efficiency.

Table (3.9): Effect of coating ECD-CBD CdSe thin film electrodes with carbon on its PEC characteristics.

sample	description	V_{oc} (V)	J_{sc} (mA/cm ²)	^a η %	^b FF%
a	Non-annealed without carbon	-1.12	2.3	11.3	54.4
b	Non-annealed with carbon	-1.12	3.3	12	40.6
c	Annealed with carbon	-1.17	3.2	8.5	28

$$^a\eta(\%) = [(\text{maximum observed power density})/(\text{reach-in power density})] \times 100\%.$$

$$^bFF = [(\text{maximum observed power density})/J_{sc} \times V_{oc}] \times 100\%.$$

3.3.4 Stability of the CdSe thin film electrodes

The stability of ECD-CBD CdSe electrodes under PEC conditions was conducted, Figure (3.22). The current density values vs. time were measured, the applied potential was 0.0 V with respect of Calomel electrode.

Effect of annealing and cooling rate on J_{sc} vs. time plots has been studied. The fresh films showed higher J_{sc} vs. time than recycled films. The fresh non-annealed CdSe film showed higher J_{sc} vs. time than fresh annealed CdSe films. Slowly cooled fresh film showed higher J_{sc} vs. time than quenched film. Recycled films gave similar behavior. This indicates relative stability of non-annealed films compared to annealed CdSe thin films under PEC conditions. Stability study showed no much difference between recycled and fresh ECD-CBD CdSe electrodes.

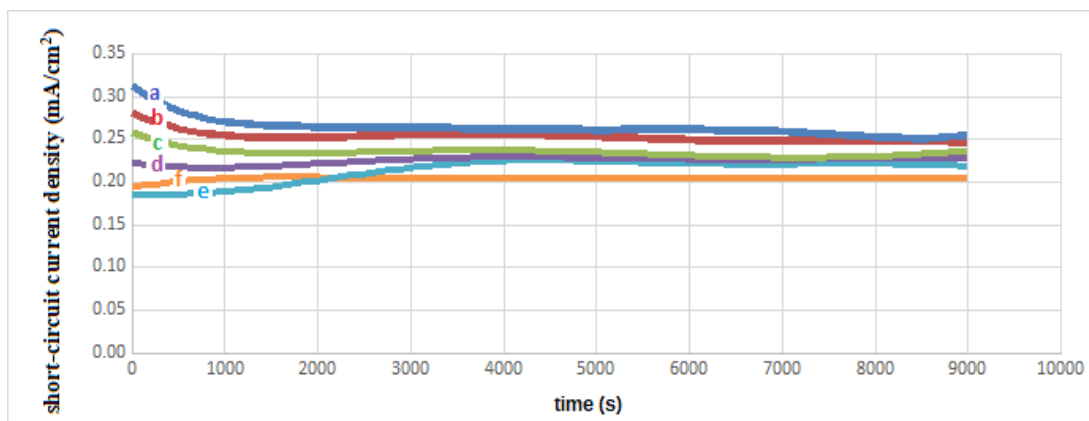
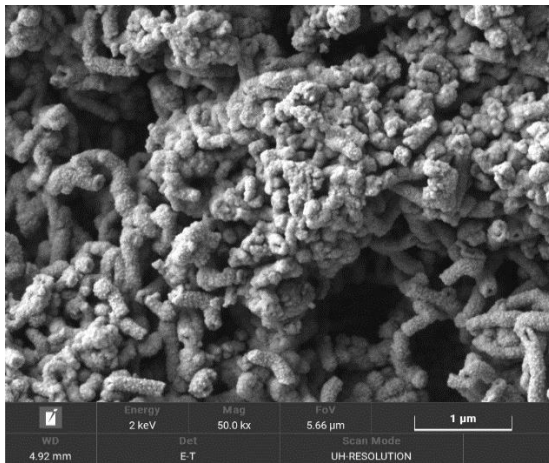


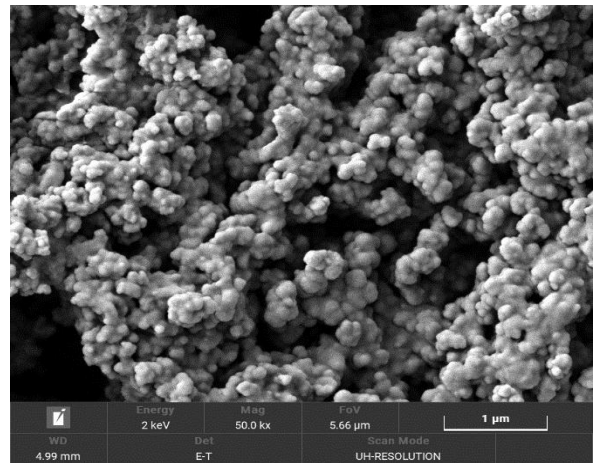
Figure (3.22): J_{sc} vs. time measurements for ECD-CBD CdSe electrodes a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled. Using S^{2-}/S_x^{2-} redox solution at $25 \pm 1^\circ\text{C}$.

3.3.5 SEM Images for CdSe Thin Film Electrodes

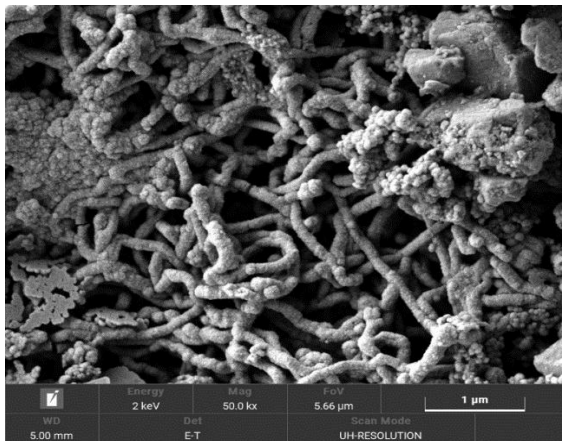
Surface quality of semiconductors has been made by SEM. SEM surface images have been obtained for recycled and fresh CdSe thin films before and after annealing to see the uniformity and quality of the surfaces, Figure 3.23 summarizes these results.



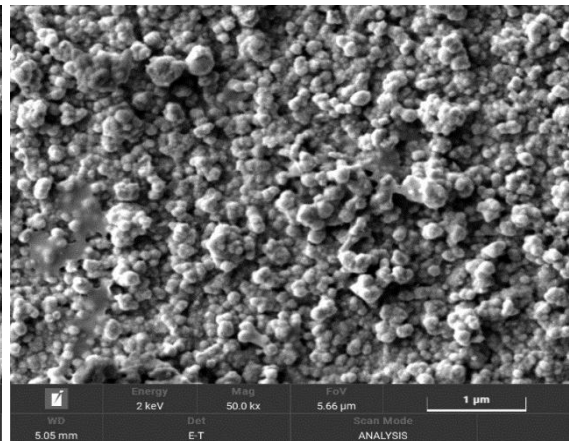
(a)



(d)



(b)



(e)

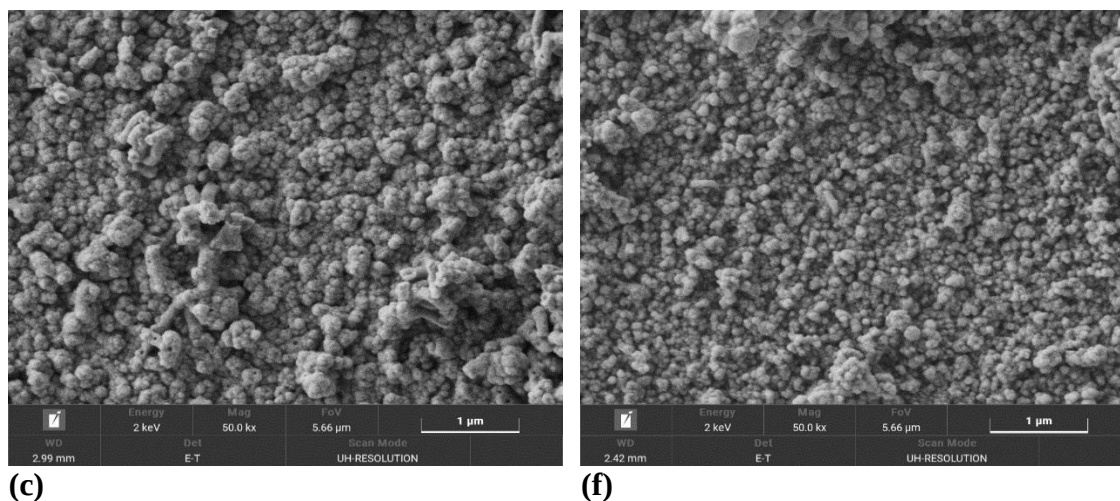


Figure (3.23): Scanning electron microscope images for ECD-CBD CdSe electrodes surface a) non-annealed fresh, b) after annealing at 150 °C and slowly cooled fresh, c) after annealing at 150 °C and quickly cooled fresh, d) non-annealed recycled, e) after annealing at 150 °C and slowly cooled recycled, f) after annealing at 150 °C and quickly cooled recycled.

SEM micrographs for different ECD-CBD CdSe films are summarized in Figure (3.23). The non-annealed fresh film shows agglomerates around 100 nm. Long fibers of agglomerates (~90 nm in diameter) also exist at the film. After annealing, the slowly cooled film involves interconnected agglomerates of less than 100 nm with a lot of fibers. The quickly cooled sample involves agglomerates of less than 100 nm with no fibers. All agglomerates exist inside random lumps.

The recycled non-annealed film involves agglomerates (of less than 100 nm). The slowly cooled film shows agglomerates of less than 100 nm with no fibers. The quickly cooled film involves agglomerates of less than 100 nm with no fibers.

3.3.6 EDX Spectra for CdSe Thin Film Electrodes

Energy-dispersive X-ray spectra measurements were performed for recycled and fresh ECD-CBD CdSe electrodes considering before and after annealing. EDX patterns are attached in appendix B. Cadmium to selenium with different atom ratios are assigned by EDX analysis results. The results are presented at Table (3.8). The Table showed that cadmium ratio was more than selenium.

Table (3.10): Effect of annealing and cooling rate on cadmium and selenium atom ratio.

technique	type	sample	description	Cd	Se
ECD-CBD	fresh	a	non-annealed	1.64	1
		b	slowly cooled	1.98	1
		c	fast cooled	1.92	1
	recycled	d	non-annealed	1.64	1
		e	slowly cooled	1.89	1
		f	fast cooled	1.8	1

Conclusions

1. This work confirmed the recycling of CdSe electrode-based solar cells.
2. ECD, CBD and ECD-CBD techniques can be performed to prepare CdSe electrodes from fresh Cd^{2+} ions. Cd^{2+} solutions recycled from waste CdSe cells can also be used.
3. Changing chemical bath solution, in the CBD method, affects PEC characteristics.
4. ECD-CBD CdSe electrodes showed higher stability and PEC efficiency than chemical bath deposition CdSe and electrochemical deposition CdSe electrode counterparts. Non-annealed recycled and fresh ECD-CBD CdSe electrode showed increasing in conversion efficiency in PEC cells than annealed counterparts.
5. Annealing enhanced PEC cell efficiency and stability of CBD-CdSe thin film electrodes, but is unfavorable for ECD and ECD-CBD CdSe thin film electrodes.
6. Covering recycled ECD-CBD CdSe films with carbon enhanced its PEC characteristics.

Suggestions for Future Work

1. CdTe, CuSe and many other types of semiconductors can be tested for recycling.
2. Modification of recycled electrode with different electro-active species embedded inside different matrices is worth to study.
3. Studying the effect of other experimental conditions and other types of redox on the electrode stability and efficiency is recommended.

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Appendix

Appendix A

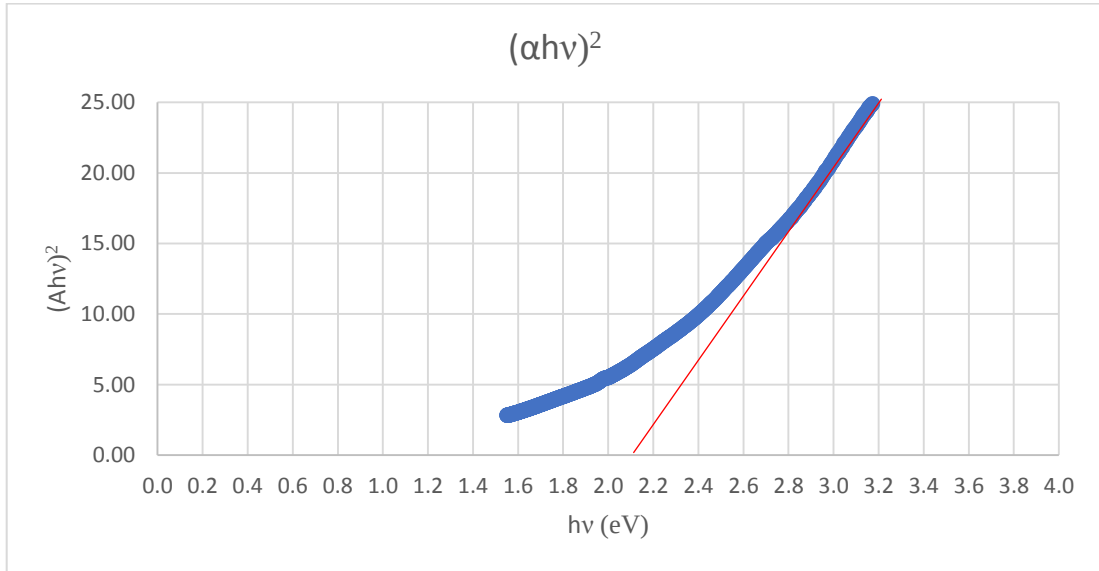


Figure 1: Tauc Plot from UV-Vis analysis of fresh non-annealed ECD-CdSe thin film.

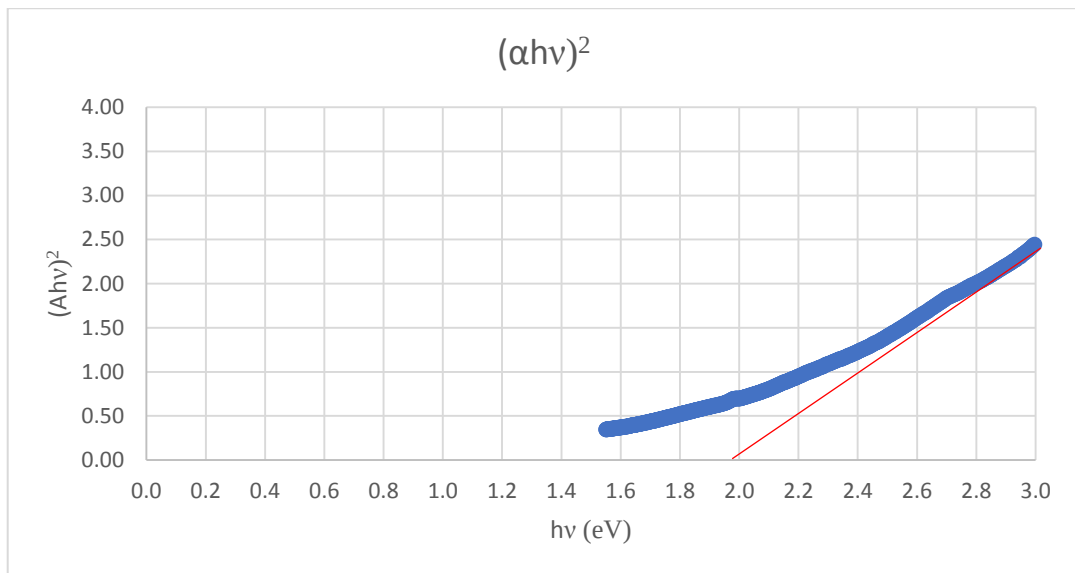


Figure 2: Tauc Plot from UV-Vis analysis of fresh slow cooled ECD-CdSe thin film.

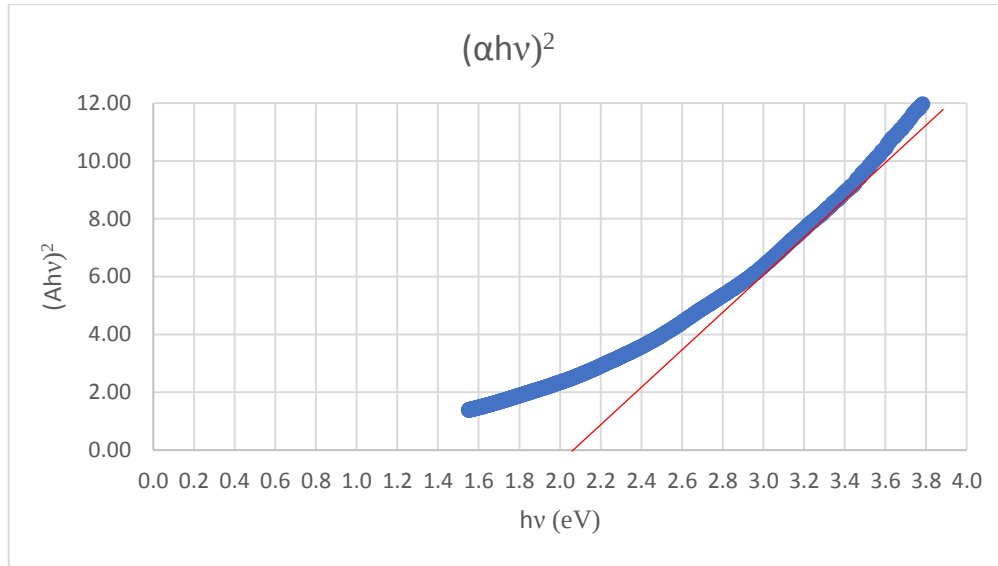


Figure 3: Tauc Plot from UV-Vis analysis of fresh quickly cooled ECD-CdSe thin film.

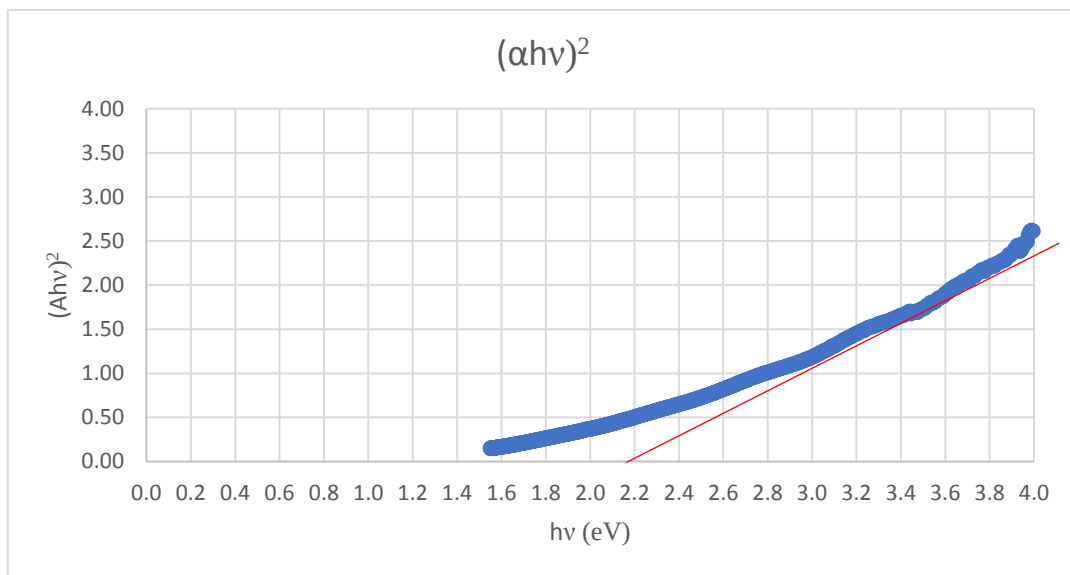


Figure 4: Tauc Plot from UV-Vis analysis of recycled non-annealed ECD-CdSe thin film.

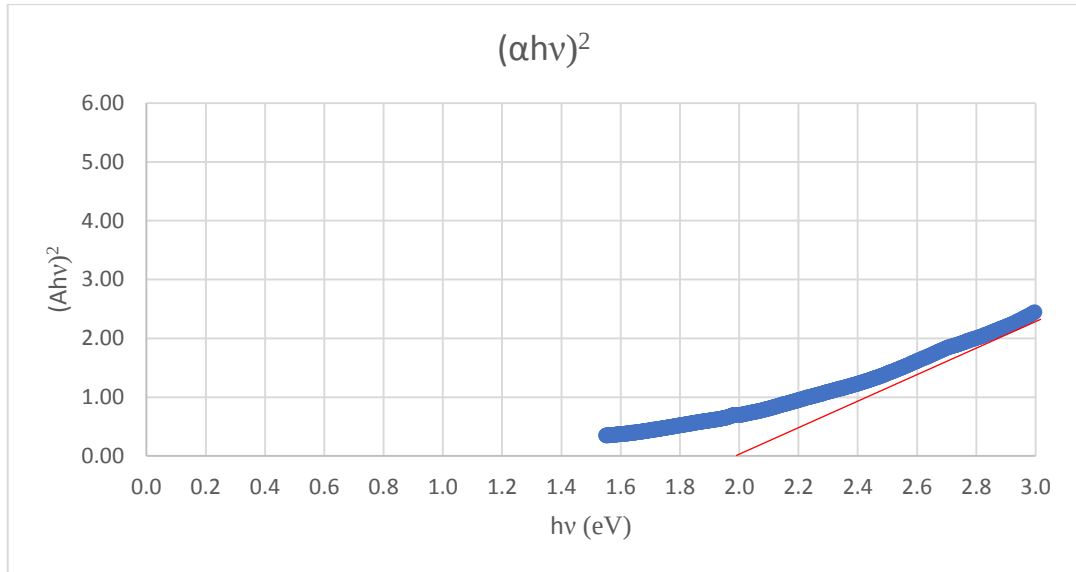


Figure 5: Tauc Plot from UV-Vis analysis of recycled slowly cooled ECD-CdSe thin film.

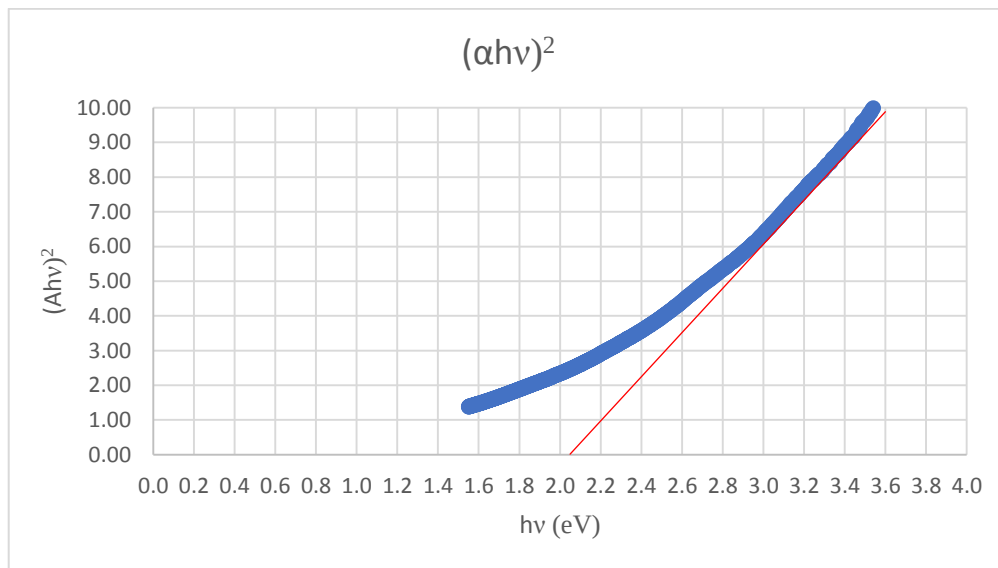


Figure 6: Tauc Plot from UV-Vis analysis of recycled quickly cooled ECD-CdSe thin film.

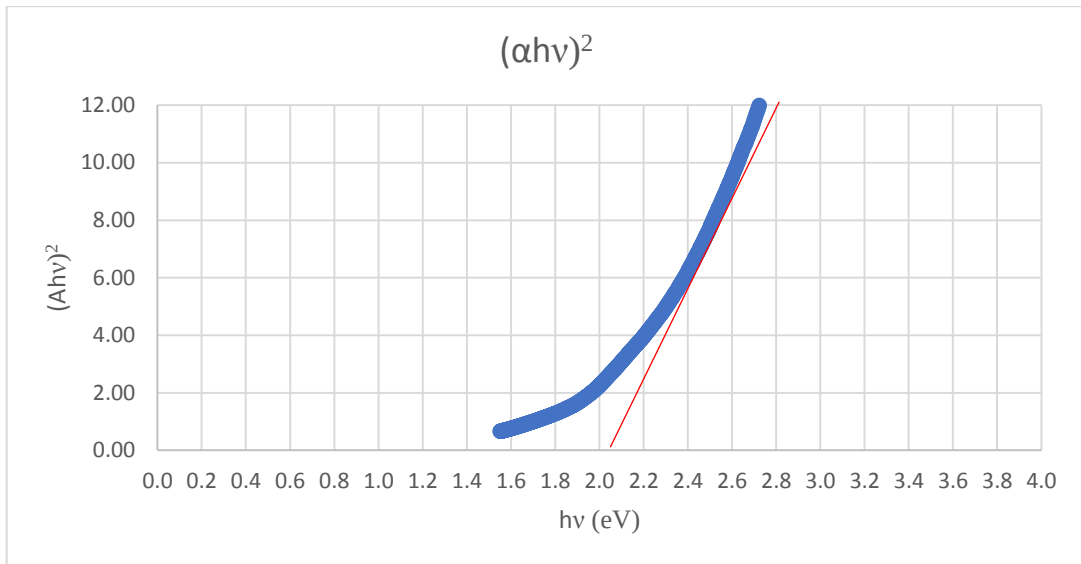


Figure 7: Tauc Plot from UV-Vis analysis of fresh non-annealed CBD-CdSe thin film.

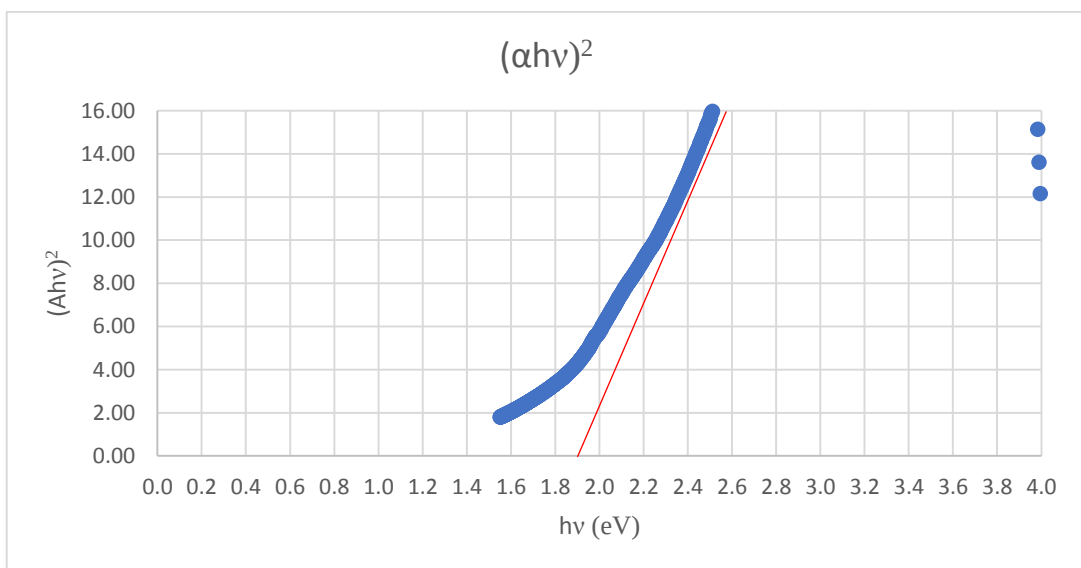


Figure 8: Tauc Plot from UV-Vis analysis of fresh slowly cooled CBD-CdSe thin film.

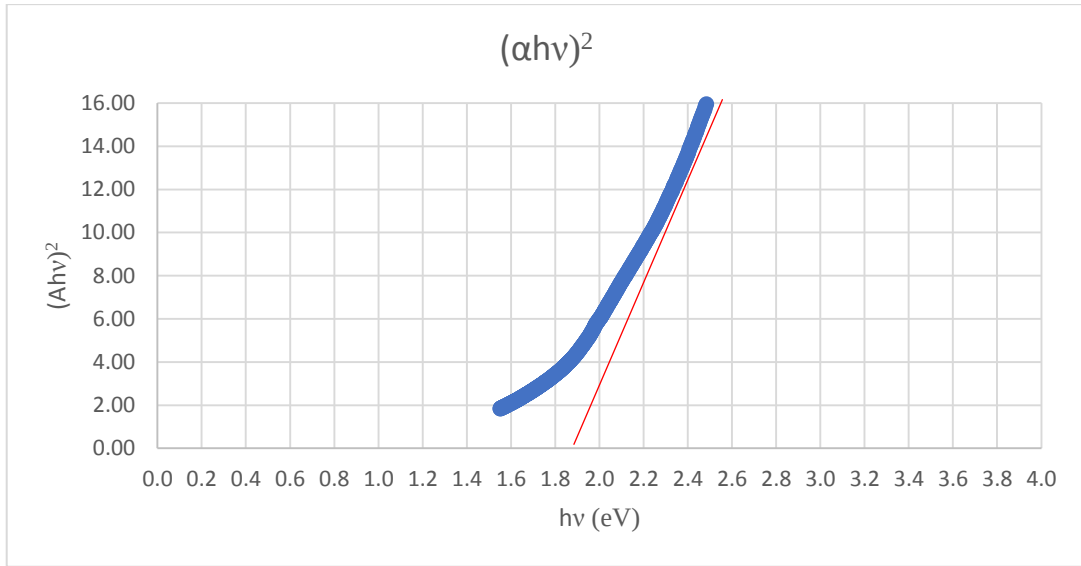


Figure 9: Tauc Plot from UV-Vis analysis of fresh quickly cooled CBD-CdSe thin film.

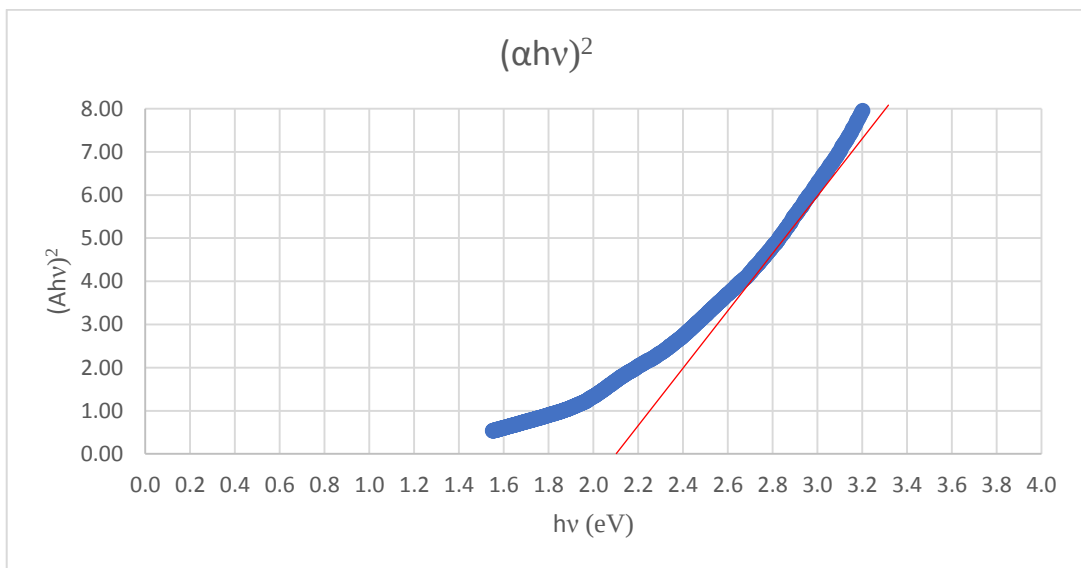


Figure 10: Tauc Plot from UV-Vis analysis of recycled non-annealed CBD-CdSe thin film.

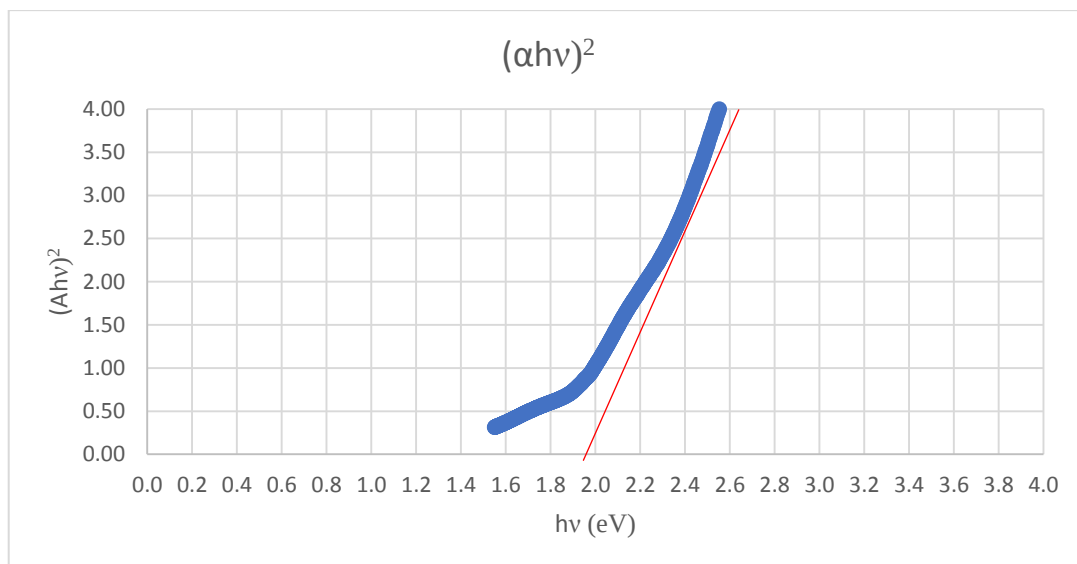


Figure 11: Tauc Plot from UV-Vis analysis of recycled slowly cooled CBD-CdSe thin film.

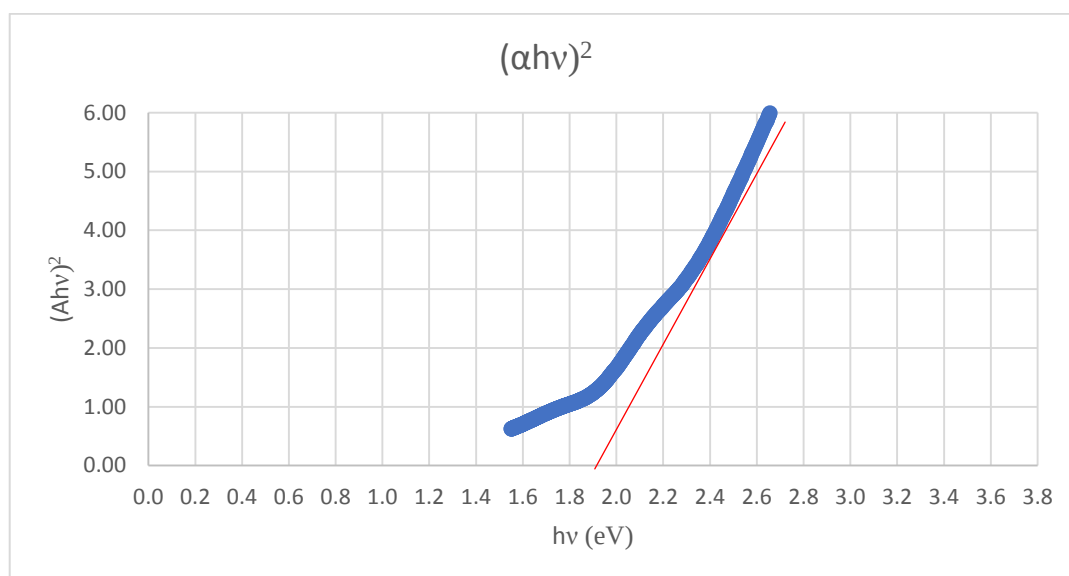


Figure 12: Tauc Plot from UV-Vis analysis of recycled quickly cooled CBD-CdSe thin film.

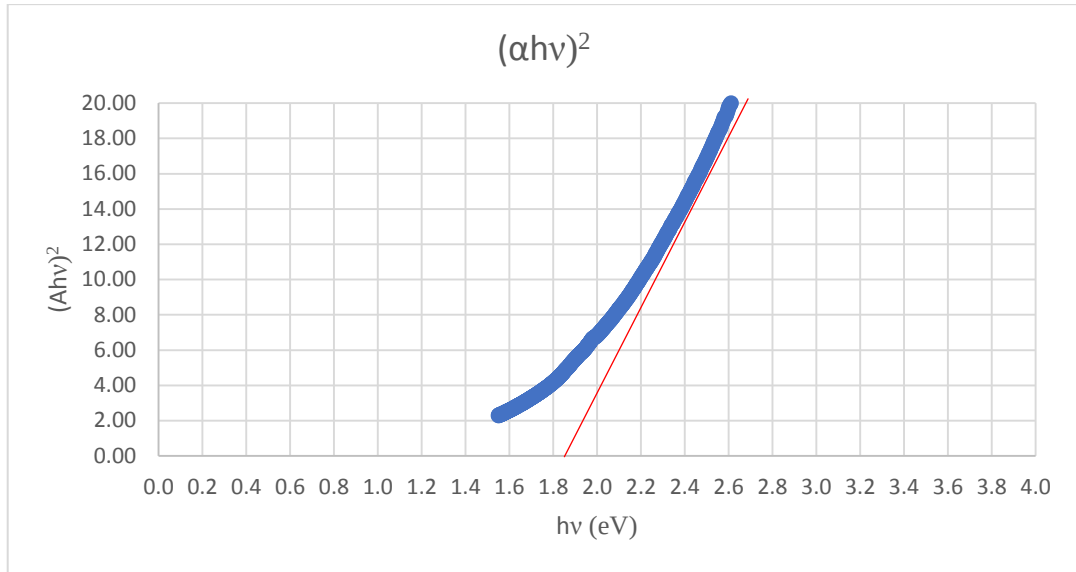


Figure 13: Tauc Plot from UV-Vis analysis of fresh non-annealed ECD-CBD CdSe thin film.

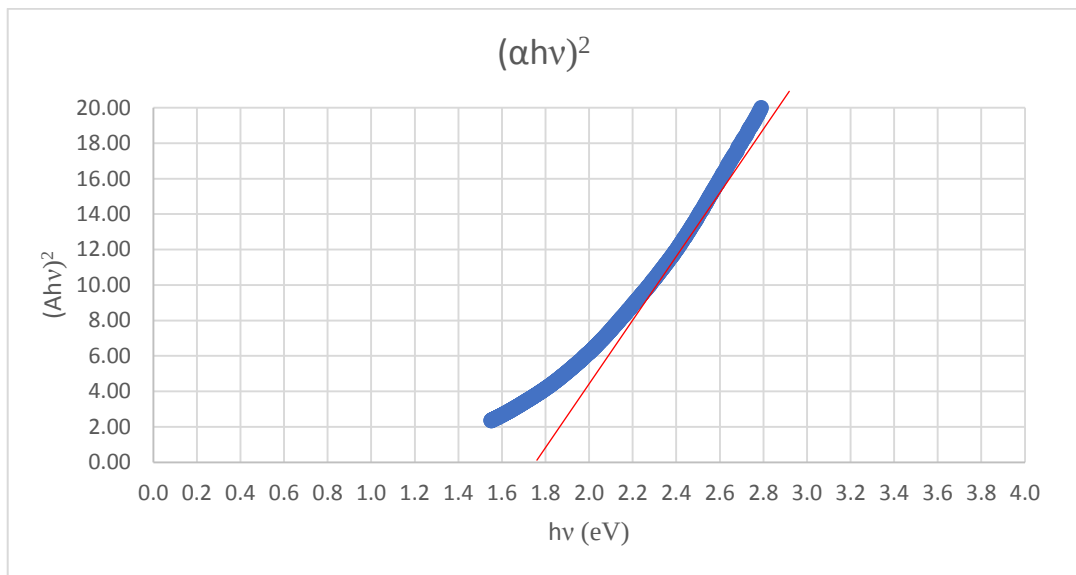


Figure 14: Tauc Plot from UV-Vis analysis of fresh slowly cooled ECD-CBD CdSe thin film.

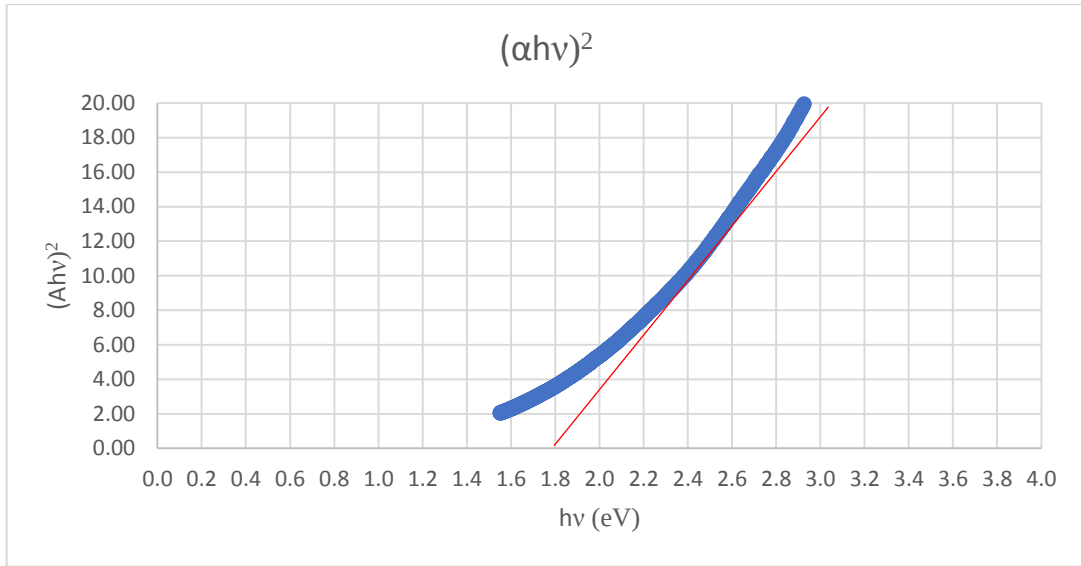


Figure 15: Tauc Plot from UV-Vis analysis of fresh quickly cooled ECD-CBD CdSe thin film.

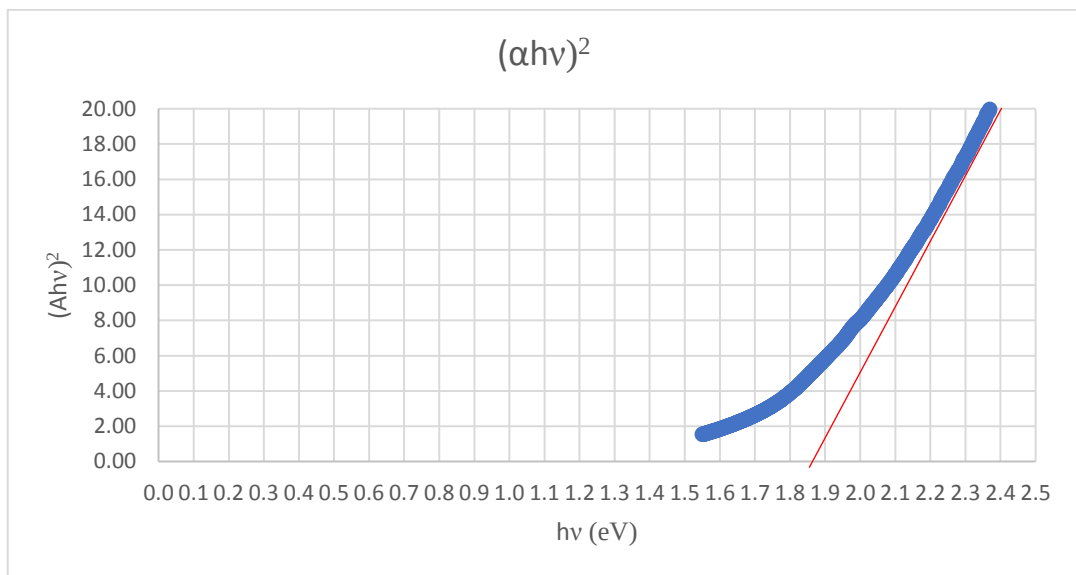


Figure 16: Tauc Plot from UV-Vis analysis of recycled non-annealed ECD-CBD CdSe thin film.

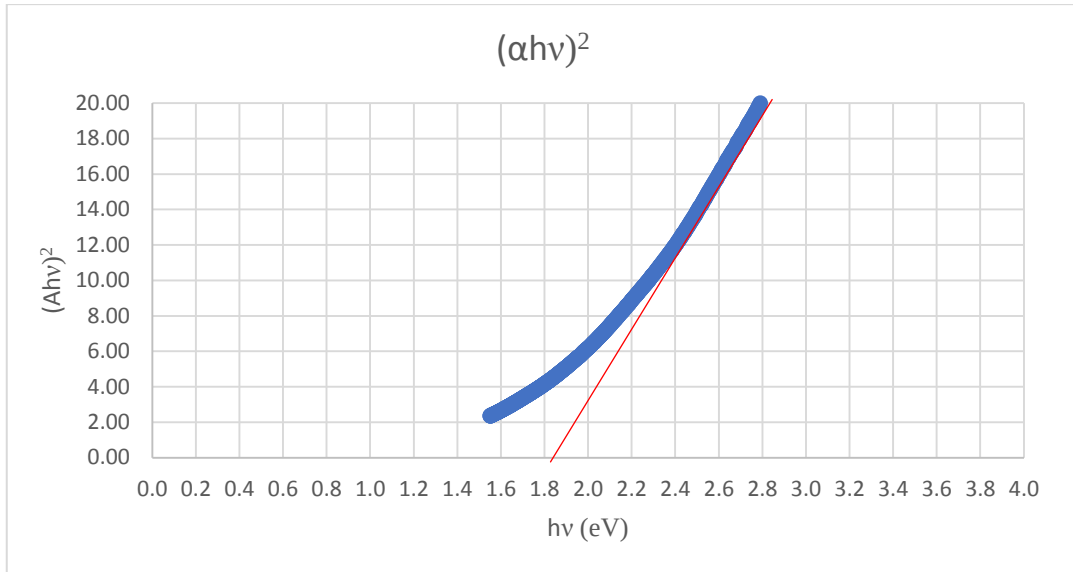


Figure 17: Tauc Plot from UV-Vis analysis of recycled slowly cooled ECD-CBD CdSe thin film.

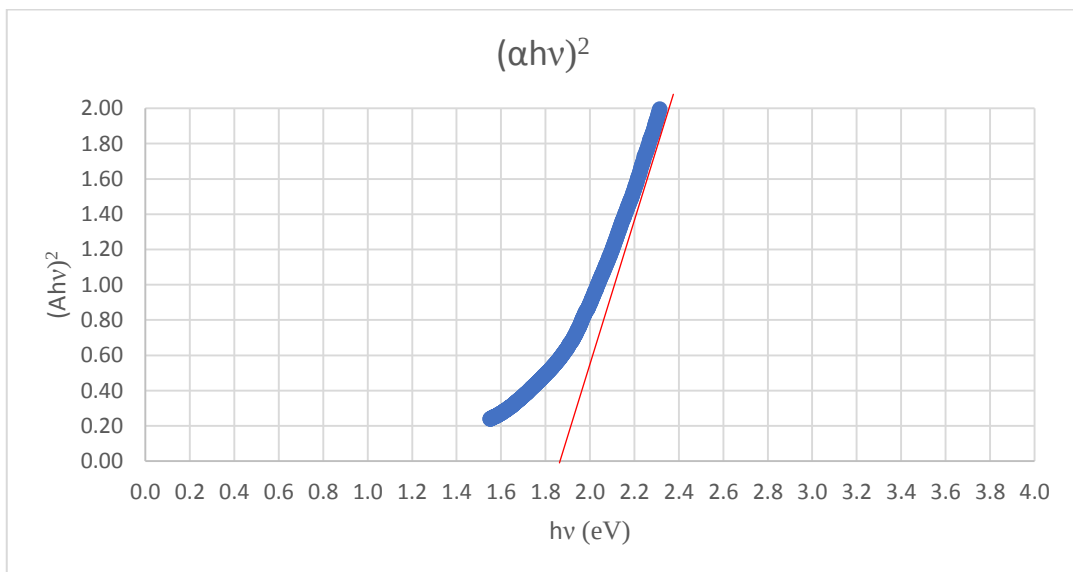


Figure 18: Tauc Plot from UV-Vis analysis of recycled quickly cooled ECD-CBD CdSe thin film.

Appendix B

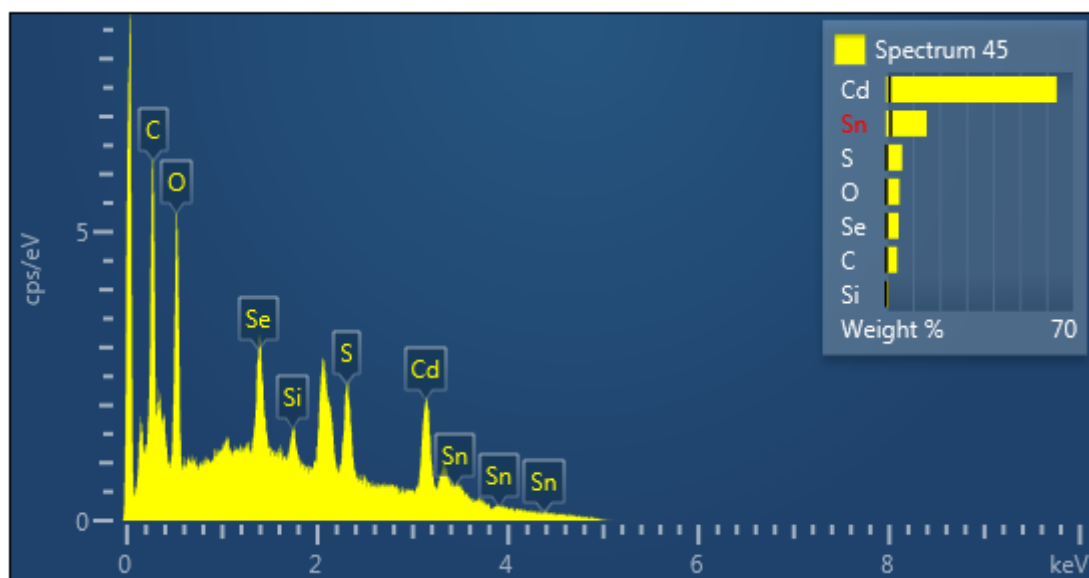


Figure 1: EDX for fresh non-annealed ECD-CdSe thin film.

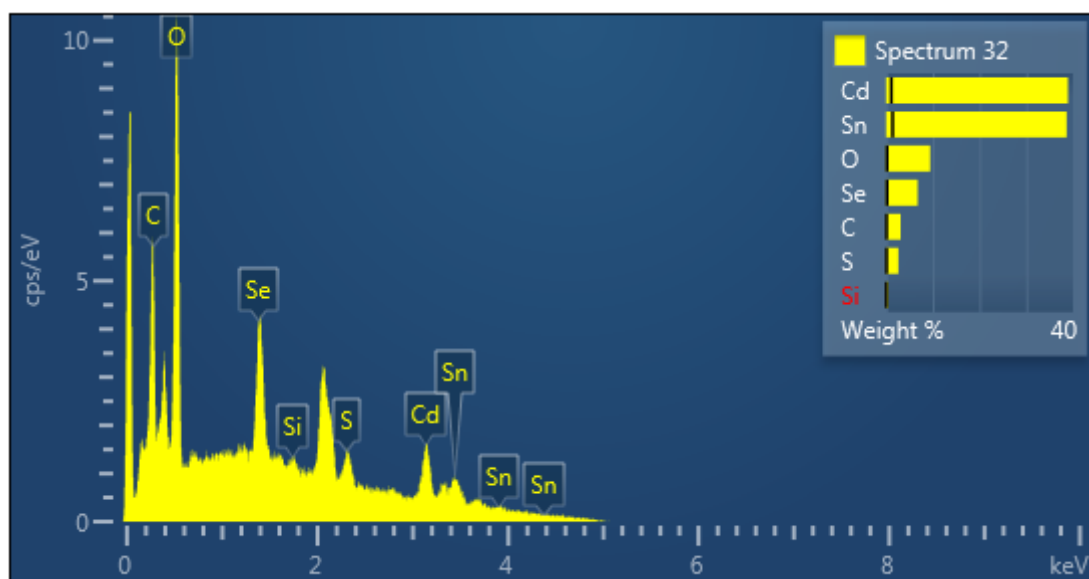


Figure 2: EDX for fresh slowly cooled ECD-CdSe thin film.

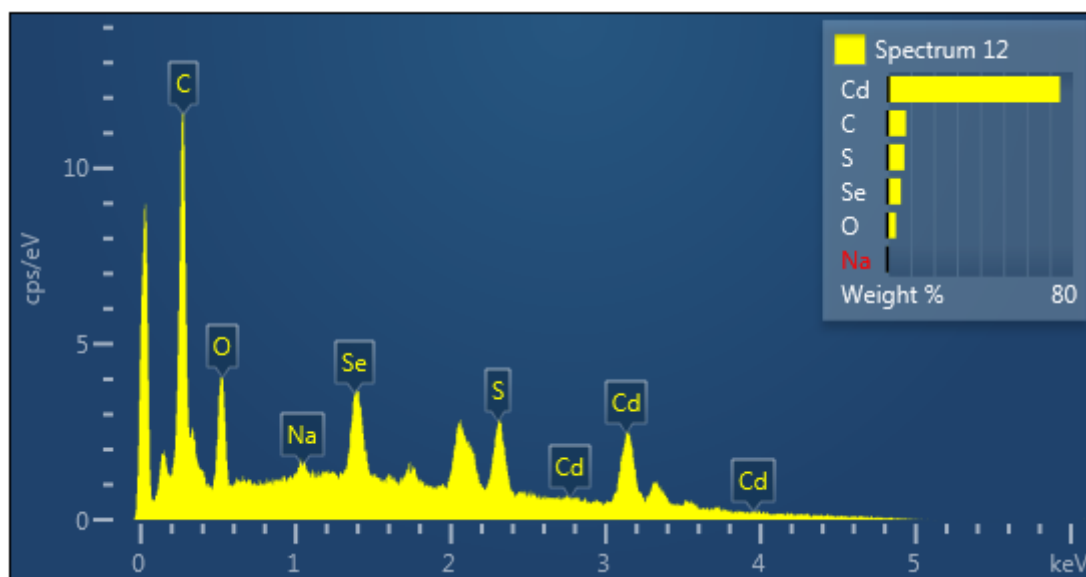


Figure 3: EDX for fresh quickly cooled ECD-CdSe thin film.

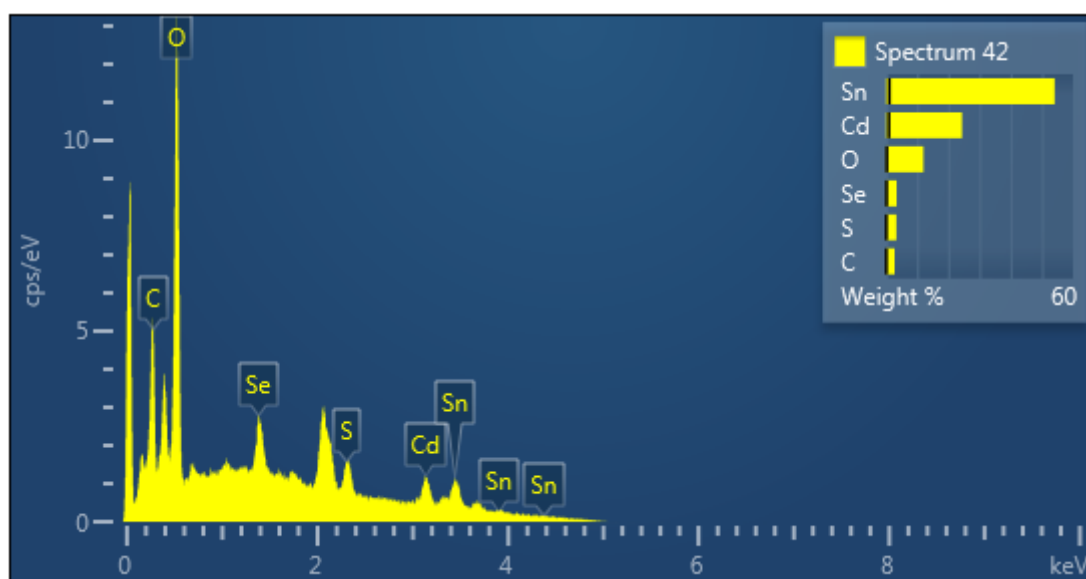


Figure 4: EDX for recycled non-annealed ECD-CdSe thin film.

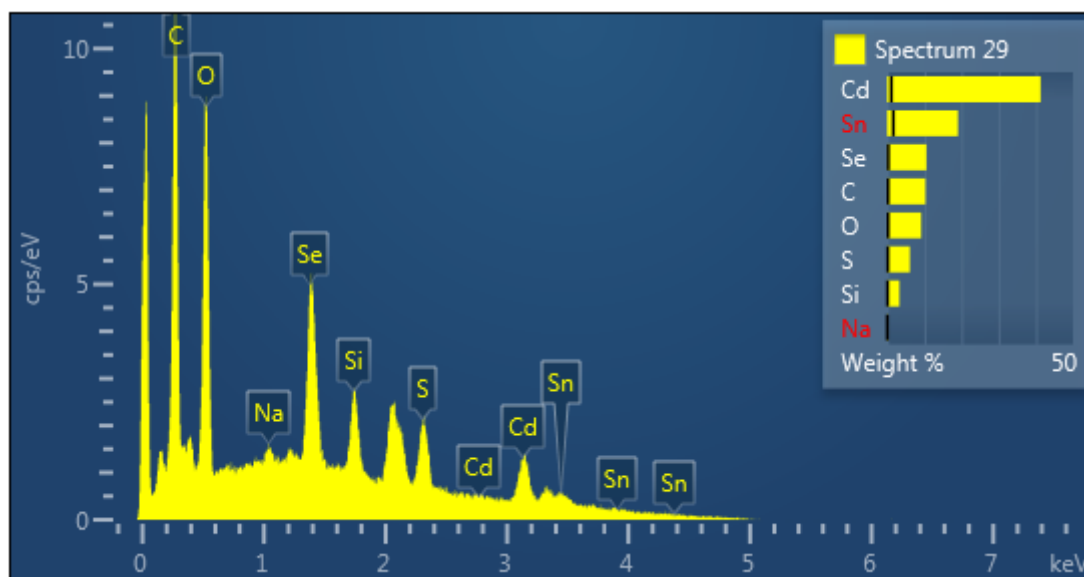


Figure 5: EDX for recycled slowly cooled ECD-CdSe thin film.

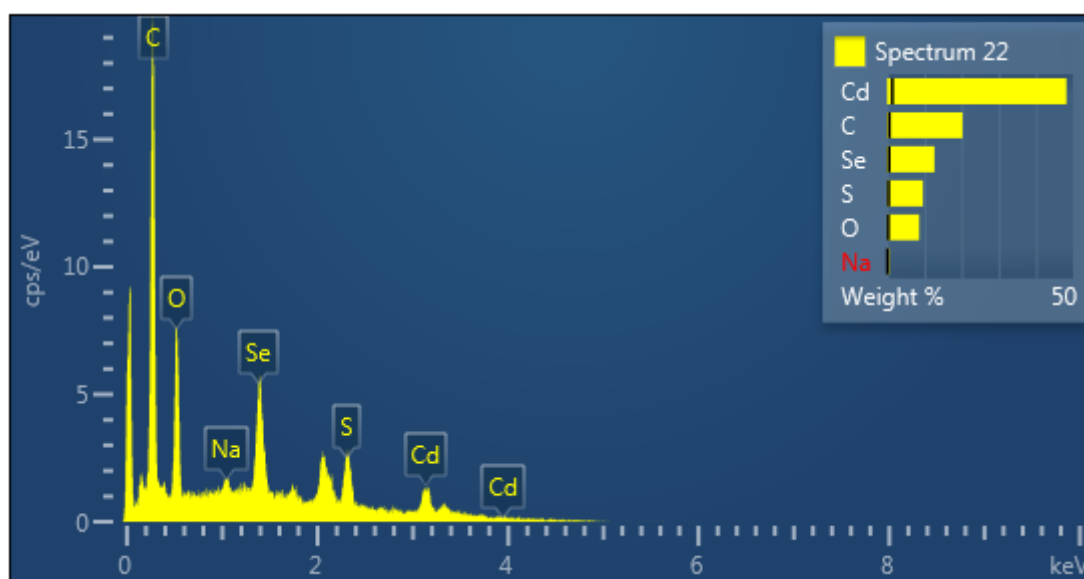


Figure 6: EDX for recycled quickly cooled ECD-CdSe thin film.

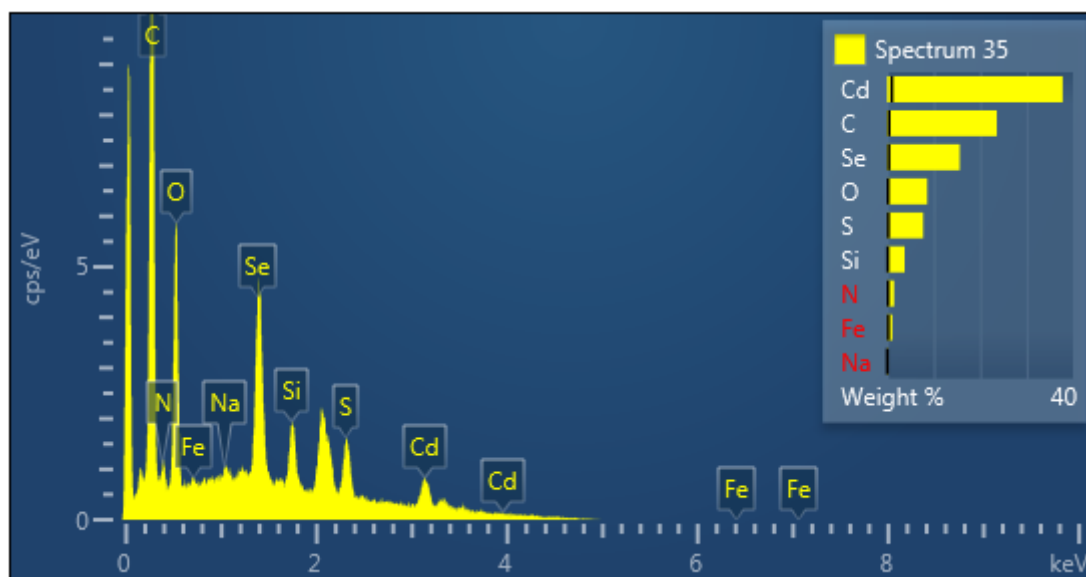


Figure 7: EDX for fresh non-annealed CBD-CdSe thin film.

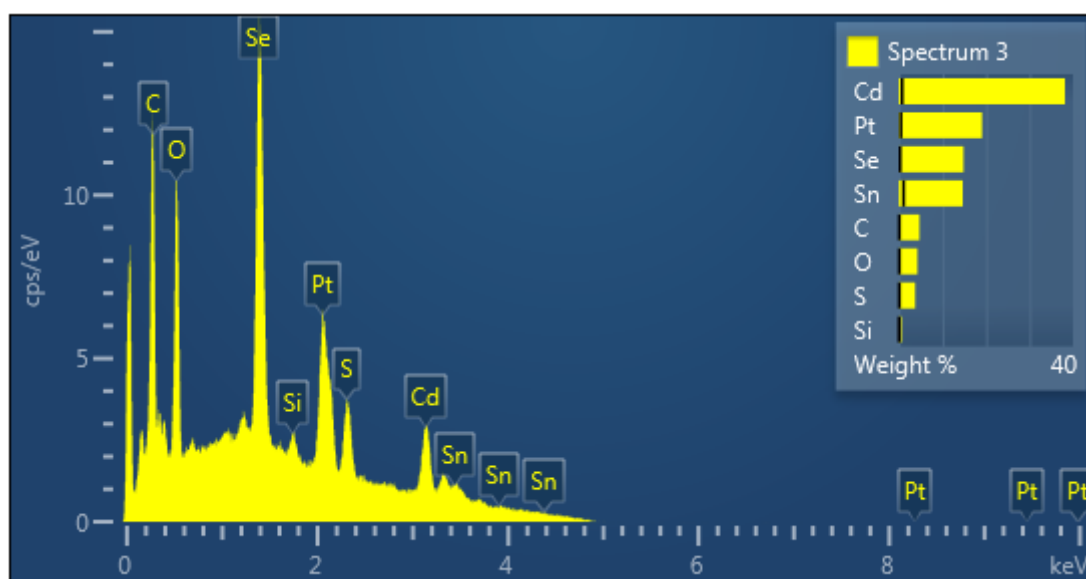


Figure 8: EDX for fresh slowly cooled CBD-CdSe thin film.

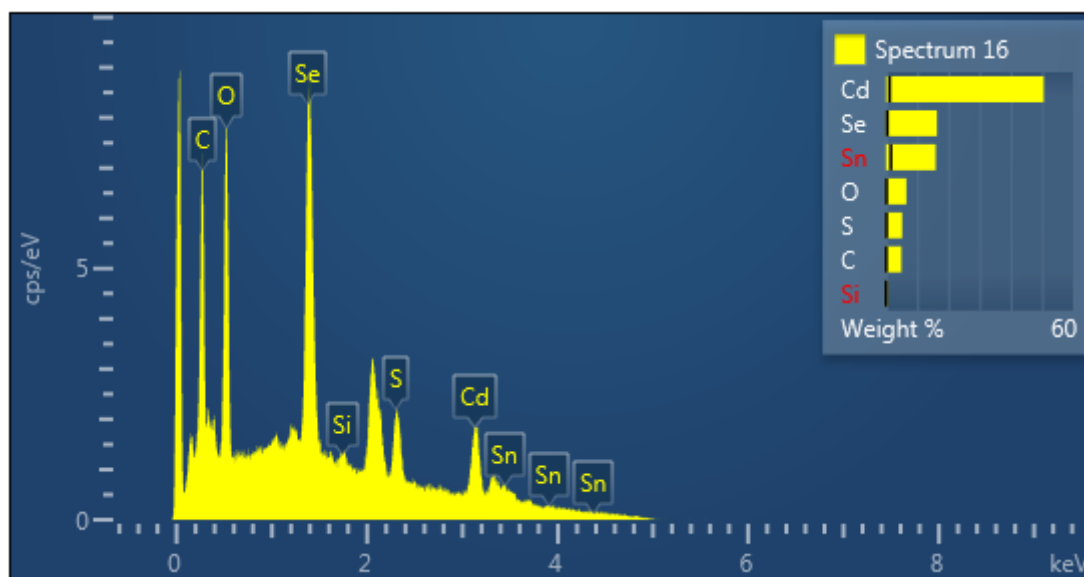


Figure 9: EDX for fresh quickly cooled CBD-CdSe thin film.

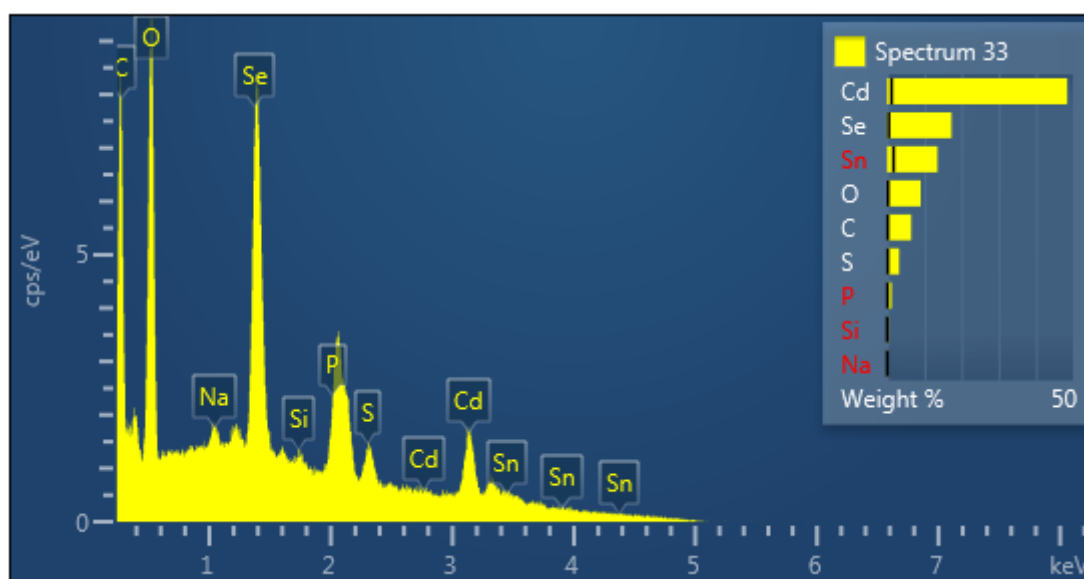


Figure 10: EDX for recycled non-annealed CBD-CdSe thin film.

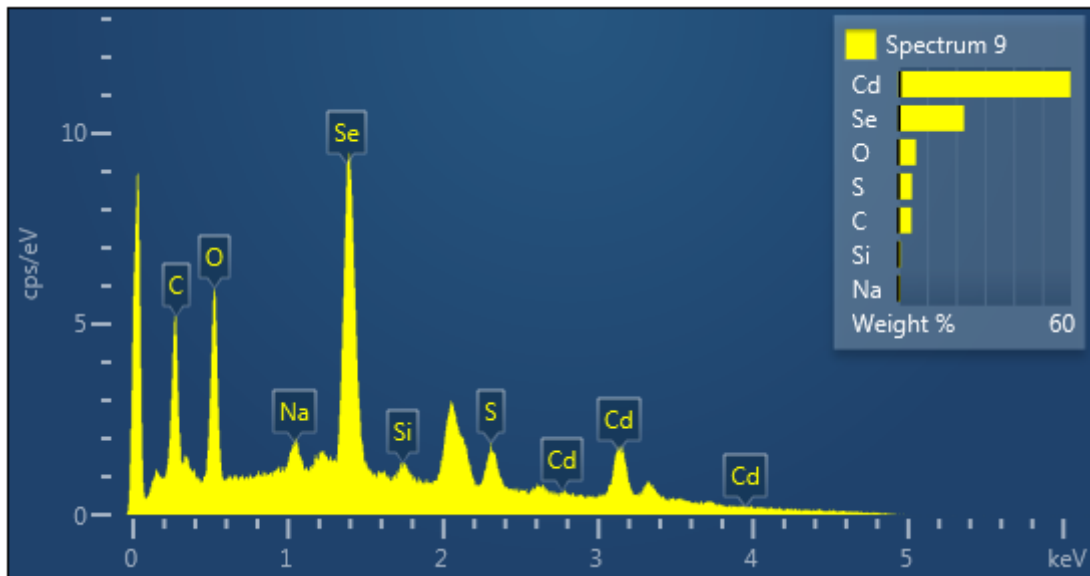


Figure 11: EDX for recycled slowly cooled CBD-CdSe thin film.

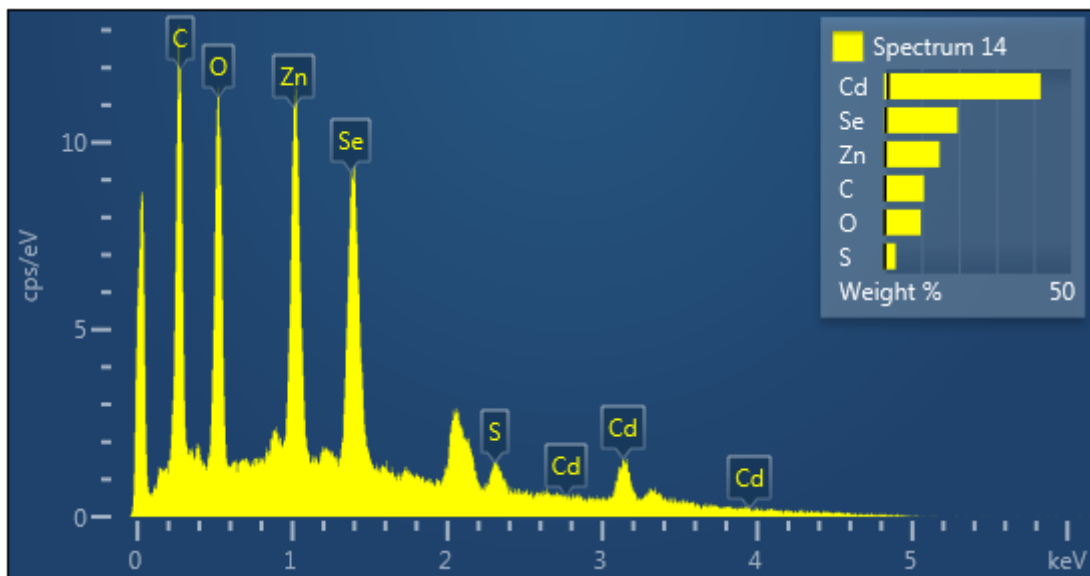


Figure 12: EDX for recycled quickly cooled CBD-CdSe thin film.

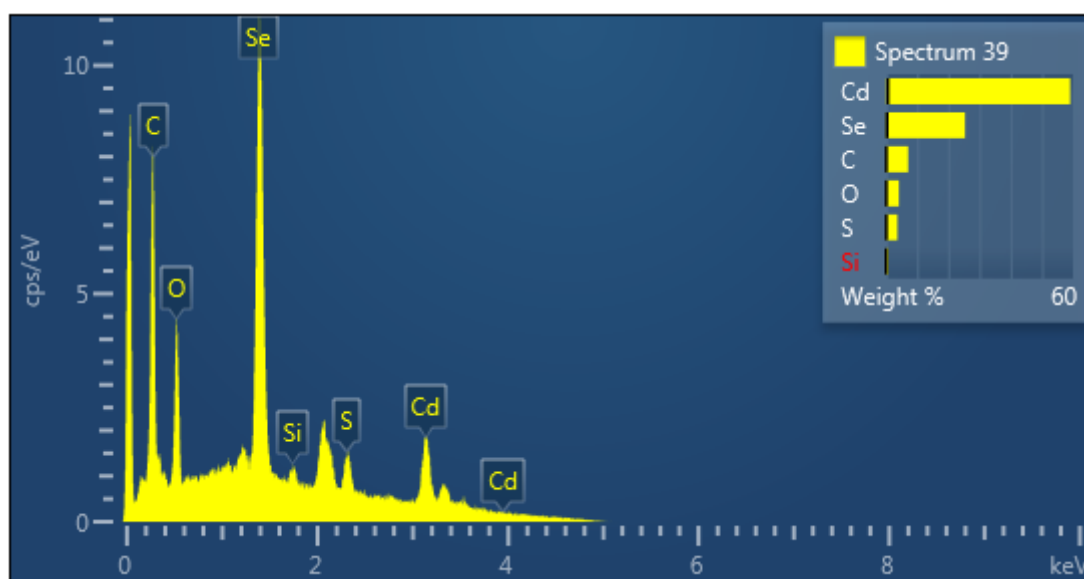


Figure 13: EDX for fresh non-annealed ECD-CBD CdSe thin film.

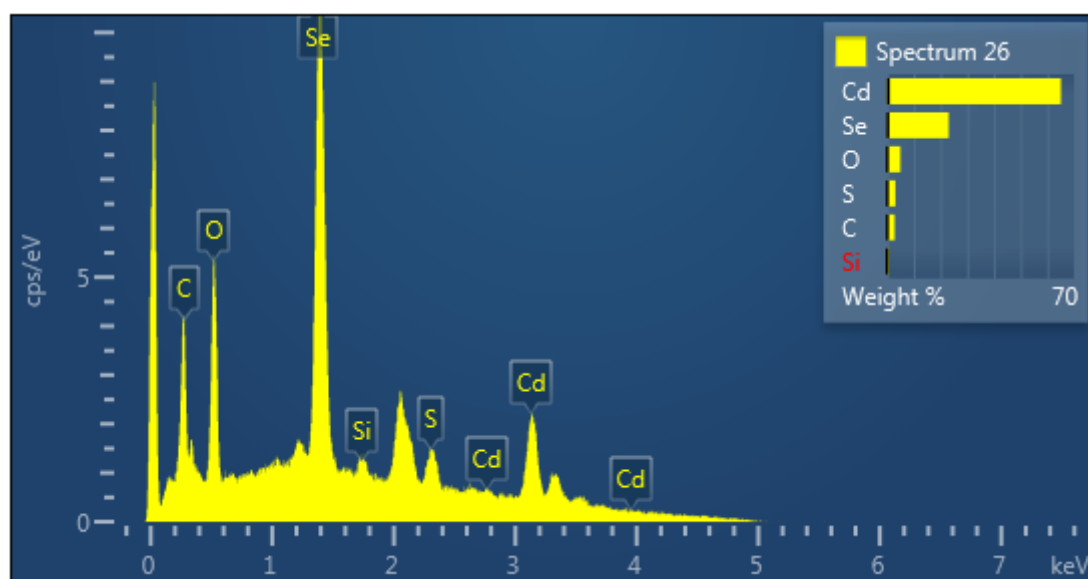


Figure 14: EDX for fresh slowly cooled ECD-CBD CdSe thin film.

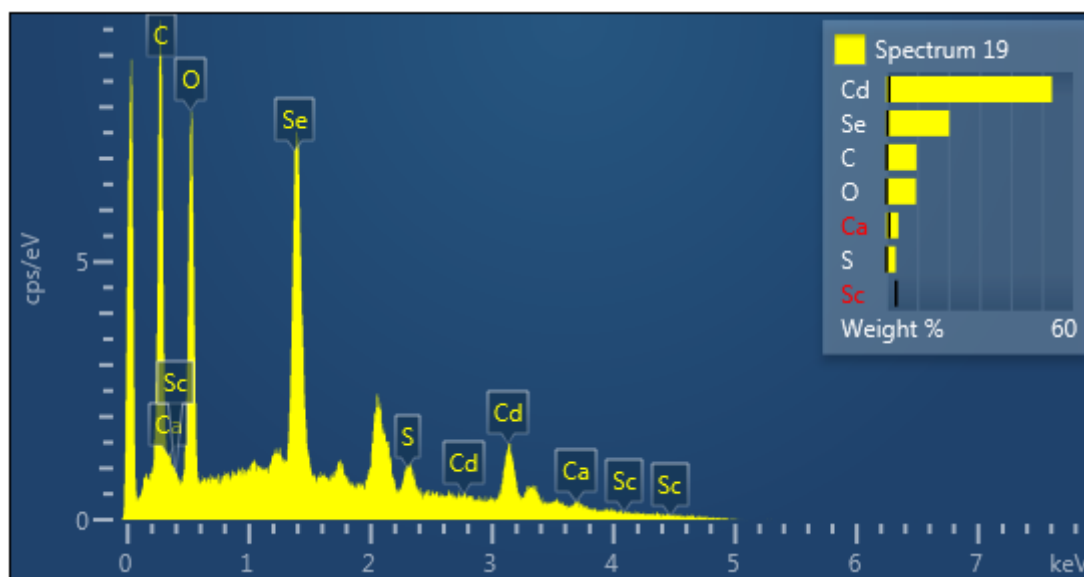


Figure 15: EDX for fresh quickly cooled ECD-CBD CdSe thin film.

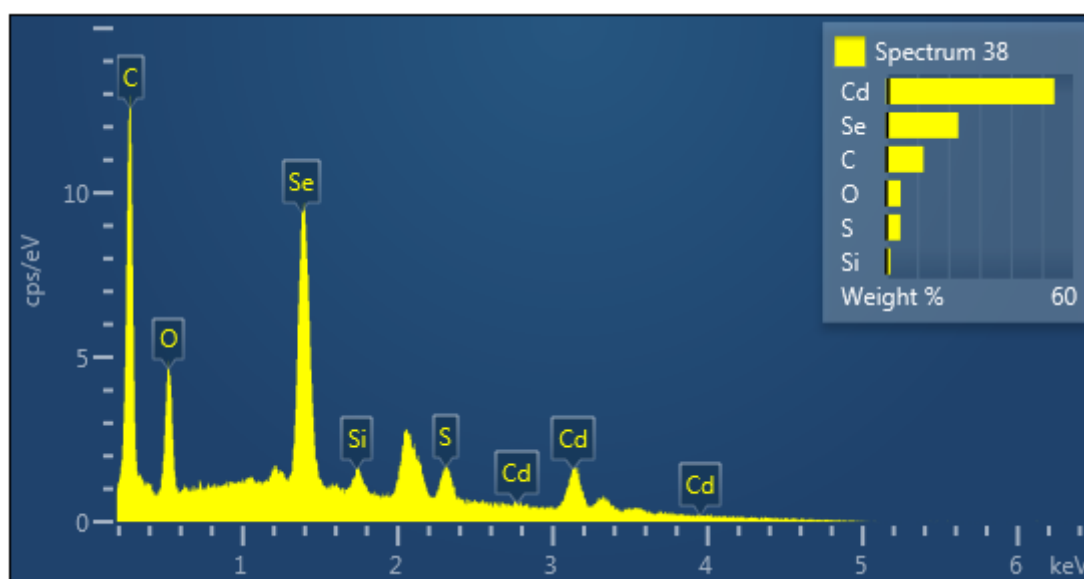


Figure 16: EDX for recycled non-annealed ECD-CBD CdSe thin film.

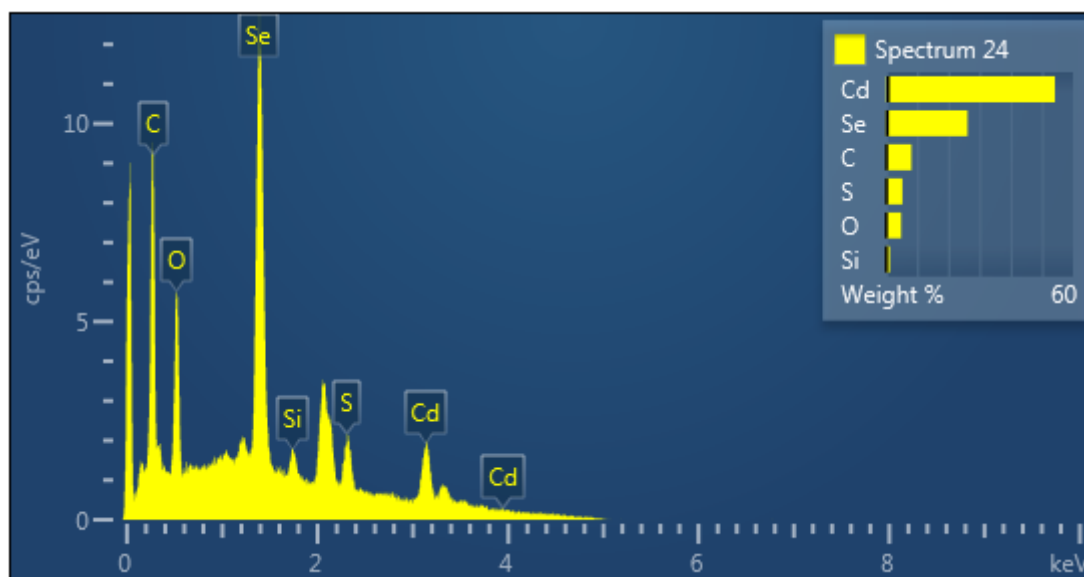


Figure 17: EDX for recycled slowly cooled ECD-CBD CdSe thin film.

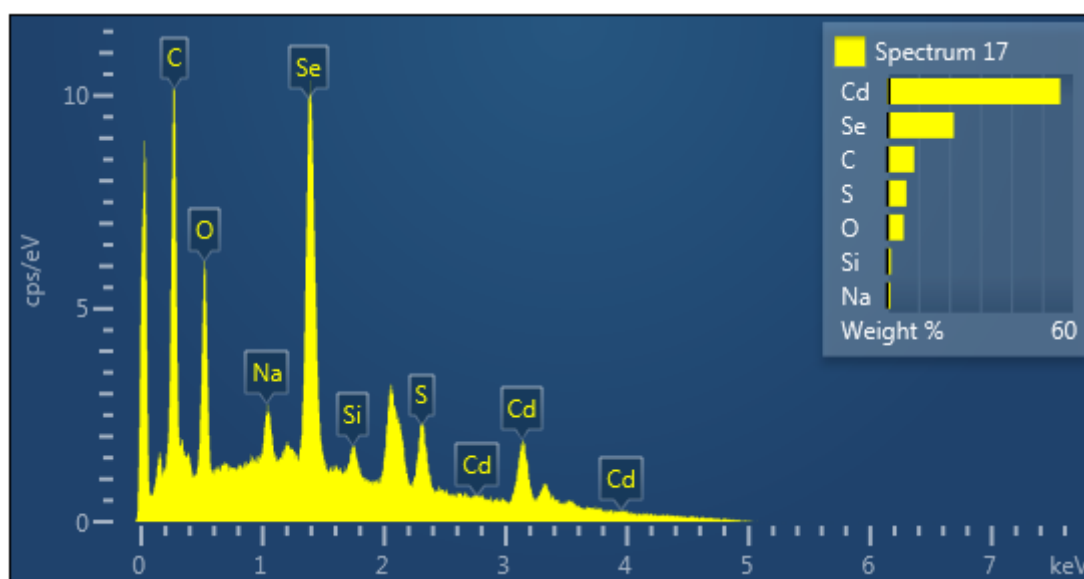


Figure 18: EDX for recycled quickly cooled ECD-CBD CdSe thin film.

جامعة النجاح الوطنية

كلية الدراسات العليا

إعادة تدوير الخلايا الشمسية المحضرة من أفلام CdSe الرقيقة

إعداد

صهيب محمد فيصل أبو الرب

إشراف

أ.د. حكمت هلال

د. عاهد زيود

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء، بكلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس - فلسطين.

2019

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الملخص

من أجل تجنب تلوث المياه بأفلام الخلايا الشمسية، ومن أجل الاستفادة من هذه الأفلام ثانية، تم في هذا البحث تحضير وإعادة تدوير أفلام CdSe الرقيقة باستخدام تقنيات مختلفة، الترسيب الكهروكيميائي (ECD)، والترسيب الكيميائي (CBD) وطريقة مشتركة تعتمد على الترسيب الكهروكيميائي تليها تقنية الترسيب بواسطة الحمام الكيميائي (ECD / CBD) على شرائح زجاجية مغطاة بطبقة رقيقة موصلة شفافة من أكسيد القصدير المزود بالفلور (FTO/glass). تم تعزيز خصائص أفلام CdSe الرقيقة المعاد تدويرها في الخصائص الكهروكيميائية الضوئية (PEC) بطرق علاج مختلفة مثل تغيير محلول الحمام الكيميائي في طريقة (CBD). وتم أيضا تغليف ECD-CBD CdSe بطبقة من الكربون لتعزيز خصائص PEC، تليها عملية الشي عند 150 درجة مئوية لمدة 1 ساعة، وبعد ذلك تم تبريد الأفلام إلى درجة حرارة الغرفة باستخدام طريقتين مختلفتين: التبريد السريع والبطيء. هذا وقد تمت المقارنة بين الأفلام المحضرة عن طريق المسح المجهر الإلكتروني (SEM)، حيود الأشعة السينية (XRD)، وطيف الامتصاص الإلكتروني.

ثم درست كفاءة الأفلام المحضرة في تحويل الضوء إلى كهرباء بالطريقة الفوتو كهروكيميائية لأقطاب الأفلام المختلفة من حيث عوامل مختلفة مثل منحنيات كثافة تيار الاضاءة (photo J-V) مقابل الجهد، منحنيات كثافة تيار الظلمة (dark J-V) مقابل الجهد، كثافة تيار الدارة القصيرة (J_{sc})، جهد الدارة المفتوحة (V_{oc})، وكفاءة التحويل، وعامل الملىء (FF). أجريت جميع القياسات في درجة حرارة الغرفة، بوجود النيتروجين باستخدام نظام بولي كبريتيد

$$NaOH / S^{-2} / S_x^{-2}$$

تظهر قياسات PEC أن أفلام CdSe الطازجة والمعاد تدويرها هي من النوع سلبي التوصيل الكهربائي. تبين قياسات الامتصاص الإلكتروني أن نطاق فجوة الشريط للأفلام الطازجة والمعاد تدويرها يقع في النطاق من (1.7-2.15 eV). تظهر نتائج XRD أن الأنظمة الثلاثة تضمنت جزيئات CdSe بحجم النانو مع بلورات من النوع المكعب. تظهر أفلام CBD / ECD المعاد تدويرها والحديثة أعلى قيم كفاءة تحويل PEC مع 11.6 % و 12.8 % على التوالي. يتميز فيلم CBD / ECD بأنه متفوق لأنه يجمع بين مزايا كل من فيلم ECD-CdSe (تمسك جيد بالطبقة السفلية FTO / الزجاجية) وفيلم CBD-CdSe (سماكة فيلم مناسب). الشواء (عند 150 درجة مئوية لمدة 60 دقيقة) حسن من الخواص الفوتو كهروكيميائية لأفلام CBD-CdSe، كذلك فإن التبريد السريع أفضل من التبريد البطيء. وأظهرت أفلام ECD-CdSe وأفلام ECD-CBD CdSe انخفاض في أداء PEC. لذلك، قد لا يكون الشيء مرغوباً فيه في هذا العمل، لأن التسخين قد يزيد من الطاقة الحركية للجزيئات وبالتالي قد يزيد من اضطرابها. كذلك فإن تغطية الأفلام المعاد تدويرها بطريقة ECD-CBD CdSe بالكربون يعزز كفاءتها.

وفي المجمل تبين النتائج أن أفلام CdSe المعاد تدويرها لا تقل كفاءة عن الأفلام المحضرة من كيمياويات تجارية حديثة، مما يؤكد إمكانية الاستفادة من الأفلام القديمة في تحضير أفلام مدورة وتجنب المياه من التلوث بها.

