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Preparation and Study of the Physical Properties of CdSe Films Deposited by a Chemical Bath Method and Exposed to Neutron Irradiation

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ABSTRACT

This study deals with the preparation of CdSe films using two sources of cadmium, (CdCl2) and (CdSO4), and studying the effect of neutron irradiation on their optical and structural properties. Using CBD method, the films were prepared on glass substrates at a temperature of 50 •C, with a deposition time of 3 hours. These films were exposed to the neutron beam from the radioactive source (Am241-Be10) with a neutron flux (3*105 n/cm2.s) and an energy of 5 MeV for 7 days. It was noted that neutron irradiation has a significant effect on the physical properties of the films. Using a UV-V spectrophotometer, the optical properties of the films were studied. It was found that the absorption coefficient (α) and the energy gap increase with irradiation, and from the following XRD, FESEM and EDX measurements, the shape and structure of the prepared and irradiated films were determined. X-ray measurements have shown that there are preferred directions for grain growth [111], [220], and [311]. It was also observed that the grain size increases, while the relative density decreases with irradiation. As for FESEM measurement, it was noted that the surface shape of the films is greatly affected when exposed to neutron radiation.

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1. INTRODUCTION

Semiconductors are considered one of the most important compounds that have attracted researchers' attention, as most of them possess a direct energy gap [10]. One of the most important binary semiconductors is group II-VI compounds in the periodic table. Cadmium selenide is a semiconductor compound that belongs to group II-VI in the periodic table. CdSe is very common in optoelectronics because it has a wide and direct energy gap of 1.74 eV [6,20], which allows it to be used in applications of solar cells, photodetectors, transistors, lasers, optoelectronic devices, and others [17]. Cadmium films have physical properties that are affected by irradiation, and many studies dealt with the study and improvement of physical properties by irradiating them with different rays and at different doses [19]. Thin films have been prepared using a variety of chemical and

physical methods such as coating, DC magnetic spraying, atomization, thermal evaporation, pulsed laser, and Sol-gel technology [5], all of these methods require sophisticated and expensive tools. Of all the thin-film deposition methods, CBD chemical bath deposition, or what is known as the solution growth process, is the simplest method that provides a large scope for manufacturing a large area of films [15] with low cost and low deposition temperature of less than 90°C [10]. The control of the sedimentation rate is by controlling the following parameters: bath temperature, the complex factor, pH, sedimentation time, and concentration of the reactants [16]. The following properties improve the size, shape, and homogeneity of the crystals. One of the disadvantages of this method is that it cannot be used to deposit thick materials because the repeated immersion does lead to a thickness of not more than a few microns. Also, repeated immersion of the sample may cause a high separation rate of the formed film. The restriction in choosing the appropriate substrate where there is a possibility of the substrate interacting with the reaction mixture, and it cannot be used in the deposition of high temperatures because this may lead to burning the CdSe inside the solution.

A neutron is a neutral particle, and because of its neutral charge, it is difficult to stop it, but it can be slowed down by using hydrogen, so it does not interact with matter by the Coulomb force, but it can penetrate atomic electrons without interaction. When a neutron beam falls on a certain material, its intensity decreases as a result of the neutrons colliding with the nuclei of the material, and this is done either by scattering (elastic or inelastic) or can be captured by the nuclei or materials with the emission of gamma rays [14].

The study of the effect of radiation began in 1962 when the satellite failed to work, due to the damage of the transistors in the driving circuits as a result of exposure to radiation during the transit of the moon through the Van Allen Belt. It is necessary to understand the mechanism by which radiation affects these devices to design devices that have the ability to work [1,7]. Radiation damage in semiconductors occurs either as a result of the displacement of the lattice atoms from their original positions when exposed to radiation and this is known as displacement damage or as a result of the formation of a gap-electron pair and this is known as ionizing damage [12].

This study aims to investigate the effect of neutron irradiation on CdSe thin films prepared using two cadmium sources in terms of optical, structural, and surface morphological properties.

2. Experimental Details

2.1 CdSe thin film preparation

A glass slide (CITOPLUS) of dimensions (7.5×1.3×0.1) cm was used as the substrate, washed with running water and one of the cleaning powders, the clean slide was placed in a solution of hydrochloric acid for 15min, then put in deionized water, immersed in a hot alcohol solution, then in acetone, and then it is kept in a vacuum place to keep it from the air and the factors affecting it**.** The cadmium selenide films were prepared by chemical bath deposition technique (CBD) using Na_2SeSO_3 as a source of Se ions and $CdCl_2$ and $CdSO_4$ as a source of Cd ions. Selenium was mixed with sodium sulfate in 10 ml of deionized water in a Reflux system and heated in a magnetic stirrer for 2 hours, $CdCl_2$ was dissolved in 10 ml of deionized water and white turbidity appeared with the addition of ammonia NH_3, then a few drops of Triethanolamine (TEA) added. While $CdSO_4$ is dissolved 10 ml of deionized water is added then the solution is placed on the magnetic stirrer for 5 minutes to dissolve the substance, then 2 ml of ammonium hydroxide NH_4OH is added, then a few drops of Triethanolamine TEA are added. When ammonium hydroxide is added, white turbidity appears in the solution. Then the first solution is added to the second solution in a glass beaker with a volume of 100 ml and deionized water is added to about 100 ml, then the slides are placed vertically inside the solution at 50 °C for 3 hours to complete the deposition process.

2.2 Experimental Techniques

The samples were irradiated using the radioactive neutron source (Am^{241}-Be^{10}) for 7 days to obtain the best neutron flux from the radioactive source, producing a source of fast neutrons (α,n), but when the source is surrounded by paraffin wax, the speed of the neutrons slows down and converted them into thermal neutrons with an energy of (0.025 eV), because of their small mass number and high cross-sectional area. The samples were placed at a distance of 4 cm from the neutron source [13]. The interaction of neutrons with matter differs from the interaction of charged particles, as it was observed when fast neutrons whose energy is within the range of 2 MeV pass through the film, many collisions occur that cause the neutrons to deviate from their direction, and in each collision, they lose part of their energy and move away from the source of their emission and their intensity decreases in the incident ray. According to the following law [14].

$$I = I_{\circ} e^{\sigma n x}$$

where $I_\circ$: is the intensity of the initial neutrons before they enter the material, σ: is the total cross-section that represents the absorption and scattering of neutrons by the material it passes through, n: is the number of atoms in a unit volume of a substance, x: thickness of the distance traveled by the neutron inside the material.

Neutrons interact with matter in several ways, depending on the energy of the neutron and the type of reactant. Fig. (1) shows the interaction of neutrons with matter [21].

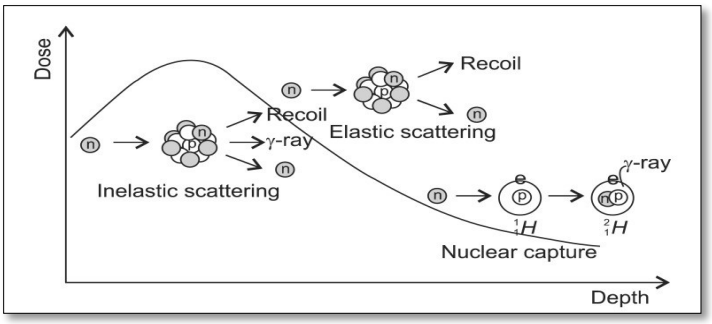

Fig. 1: Scheme of the interaction of neutrons with matter

The optical properties of CdSe films were measured using (UV-VIS-NIR) spectrophotometer. The transmittance and absorption were measured as a function of the wavelength of the range from (340-1000)nm and the optical absorption coefficient was calculated from the relationship: α = 2.303 A/t, where A: the absorption coefficient, and t: the thickness of the film. The gravimetric method was used to determine the thickness of the prepared films. If this method depends on the weight of the glass substrates before and after deposition, and from the following relationship, the thickness of the film was calculated: $t = \frac{\Delta m}{\rho A}$ where t: is the thickness of the film, Δm: is the difference between the weight of the glass substrate before and after deposition, ρ: is the density of the deposited material, and A: the surface area of the deposited film.

The relationship between the square of the absorption coefficient and the energy of the incident photon was plotted to calculate the energy gap (E_g) of the film. The extinction coefficient represents the amount of energy absorbed in the thin film or the inertia that occurs in the electromagnetic wave inside the film and can be found from the following relationship; $K = \frac{\alpha\lambda}{4\pi}$ [11].

Urbach energy lies in the exponential absorption region, and its value increases with increasing photon absorption. Optical absorption is associated with transitions from the secondary levels that lie above the valence band to the extended levels in the conduction band and is an indicator of the presence of random levels and defects that arise according to the method used in preparing the film, which causes irregularity of photons inside the thin film.

The Urbach energy can be calculated by taking the reciprocal of the slope resulting from plotting the relationship between (lnα) and (hν) [9]:

$$E_U = \left[\frac{d(ln\alpha)}{d(h\nu)}\right]^{-1}$$

An XRD device was also used to identify the crystal structure of pure and irradiated films by comparing it with the standard card for X-ray diffraction (JCPDS).

2.3 The mechanism of chemical reaction

CdSe films were prepared using a chemical bath deposition CBD technique, which is based on the slow release of Se^{-2} and Cd^{+2} ions in solution and then condensed to deposition on a glass base placed inside the solution. The following equations represent the reaction mechanism to obtain CdSe films using two sources of cadmium :

1- using source $CdCl_2$

$Se + Na_2SO_3 \longrightarrow Na_2SeSO_3$

$Na_2SeSO_3 + 2OH^- \longrightarrow Na_2SO_4 + H_2O + Se^{-2}$

$2CdCl_2 + 4NH_3 \longrightarrow (Cd(NH_3)_4)^{+2} + CdCl_4^{-2}$

$(Cd(NH_3)_4)^{+2} \longrightarrow Cd^{+2} + 4NH_3$

$Cd^{+2} + Se^{-2} \longrightarrow CdSe \downarrow$ [4]

2- using source $CdSO_4$

$CdSO_4 + 2NH_4OH \longrightarrow Cd(OH)_2 + (NH_4)_2SO_4$

$Cd(OH)_2 + 4NH_4OH \longrightarrow Cd(NH_3)_4 + 2(OH) + 4H_2O$

$Cd(NH_3)_4 \longrightarrow Cd^{+2} + 4NH_3$

$Cd^{+2} + Se^{-2} \longrightarrow CdSe \downarrow$ [3]

3. Results and discussion

The effect of neutron irradiation on the physical properties of these films was discussed by studying the structural, optical, and morphological properties.

3.1 Optical measurements

This technique depends on the study and analysis of the results of the interaction of light with the material to be analyzed, as part of the incident UV ray is absorbed or permeated through the film. The absorbed energy causes disturbances in the electronic structure of the film, which results in the transfer of electrons from a lower energy level to a higher energy level.

Because of the importance of the energy gap in the possibility of determining the use of thin films in the makings of solar cells and hybrid junctions because it is a basic measure for spectrum selection, Therefore, the values of the direct energy gap of this film were calculated before and after irradiation.

To find the value of the energy gap of the film, a tangent to the curve is drawn, and the point of intersection of the tangent with the x-axis represents the energy gap E_g [8], As shown in figure (2). the energy gap is affected by irradiation, where an increase in the energy gap is observed when the films to neutron-irradiated

Fig. (2), shows the energy gap of CdSe films prepared from $CdCl_2$ for pure and exposed to neutron-irradiated films.

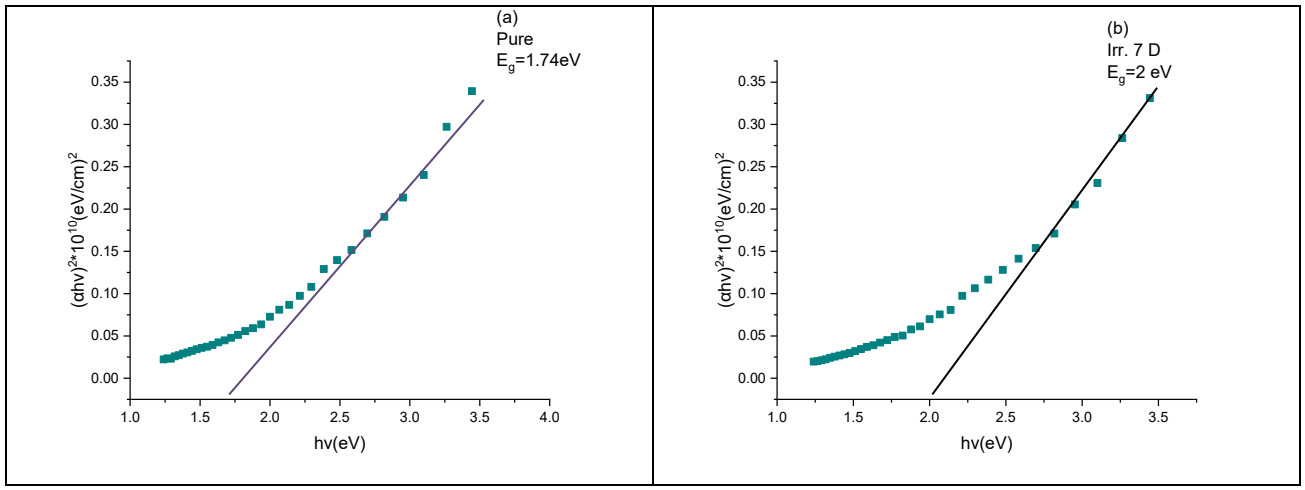

Fig. 2: energy gap of CdSe thin films :(a) pure (b) Irradiated

Fig. (3), shows the energy gap of CdSe films prepared from $CdSO_4$ for pure and exposed to neutron-irradiated films.

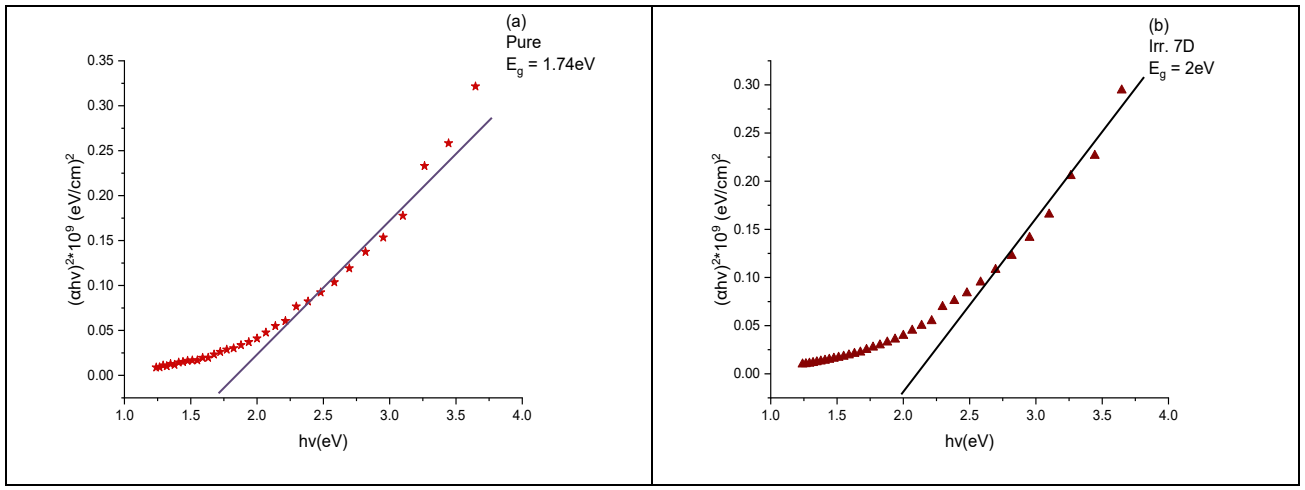

Fig. 3: energy gap of CdSe thin films :(a) pure (b) Irradiated

It was found that the values of the optical properties increase with the increase in the radiation dose, and the energy gap value increases as a result of the generation of additional energy levels within the region confined between the valence and conduction beams [2].

Table 1, shows the E_g value for CdSe thin film before and after exposure to neutron irradiation at 50°C temperatures.

Table 1: Thickness, energy gap, and Urbach energy for pure and n-exposed CdSe films

Cadmium source	T	Before irradiation	After irradiation	Before irradiation	After irradiation
	(μm)	E_g(eV)	E_g(eV)	E_U(meV)	E_U(meV)
$CdCl_2$	0.3	1.74	2	740	800
$CdSO_4$	0.3	1,74	2	909	769

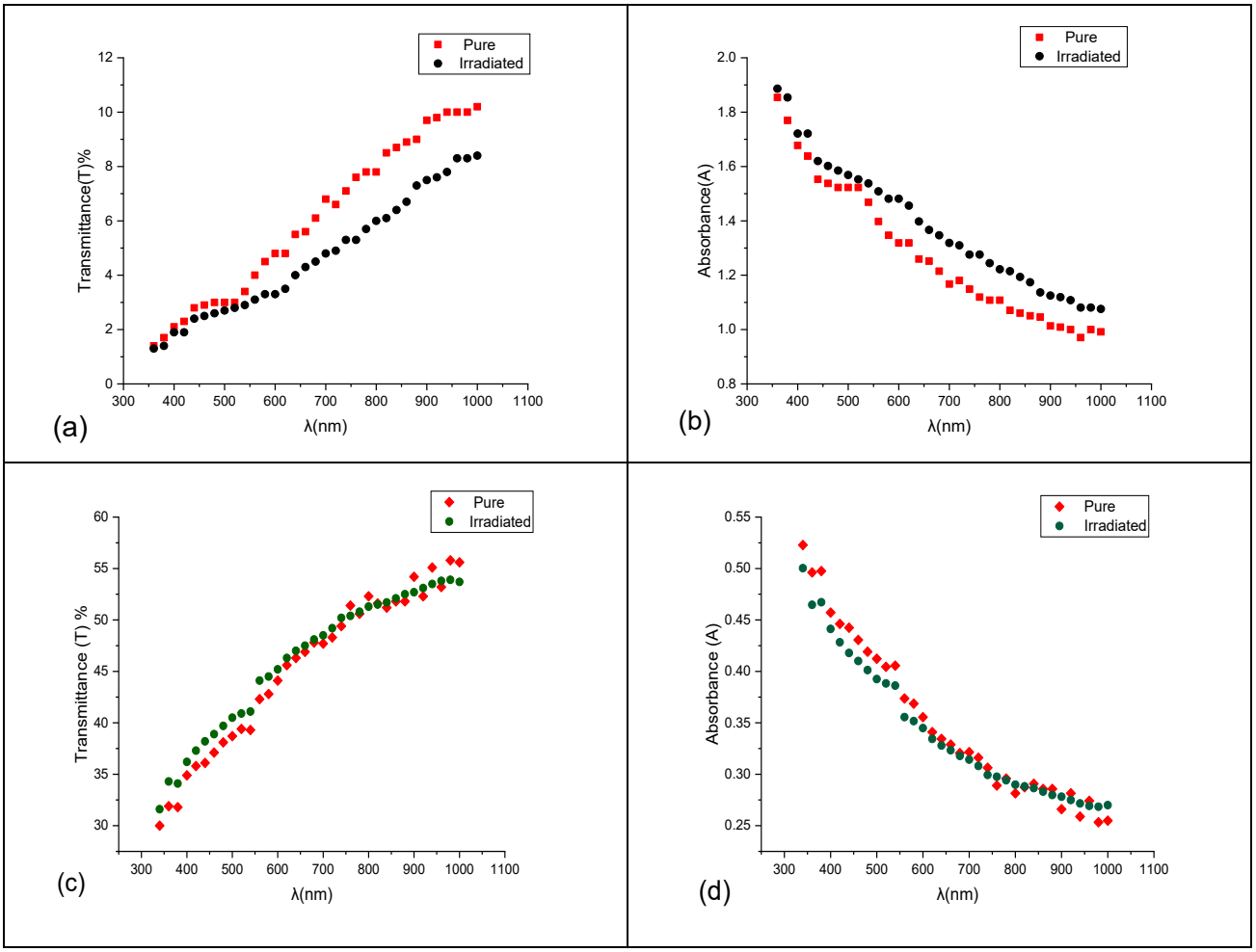

Fig. 4: Transmittance (T) and absorbance (A) as a function of wavelength (λ) for pure and irradiated CdSe films:(a&b) for material $CdCl_2$ and (c&d) for material $CdSO_4$

From fig. (4) we note that the transmittance decreases and the absorbance increases for the CdSe film prepared from $CdCl_2$, as the change in the absorption coefficient of these films came as a result of the change in their absorption, Therefore, we expect the appearance of energy levels centered within the energy gap resulting from the method of preparing the films**.** While for the film prepared from $CdSO_4$, we note that there is a very slight change in the transmittance spectrum and the absorbance spectrum, as the transmittance spectrum increases and the absorbance spectrum decreases.

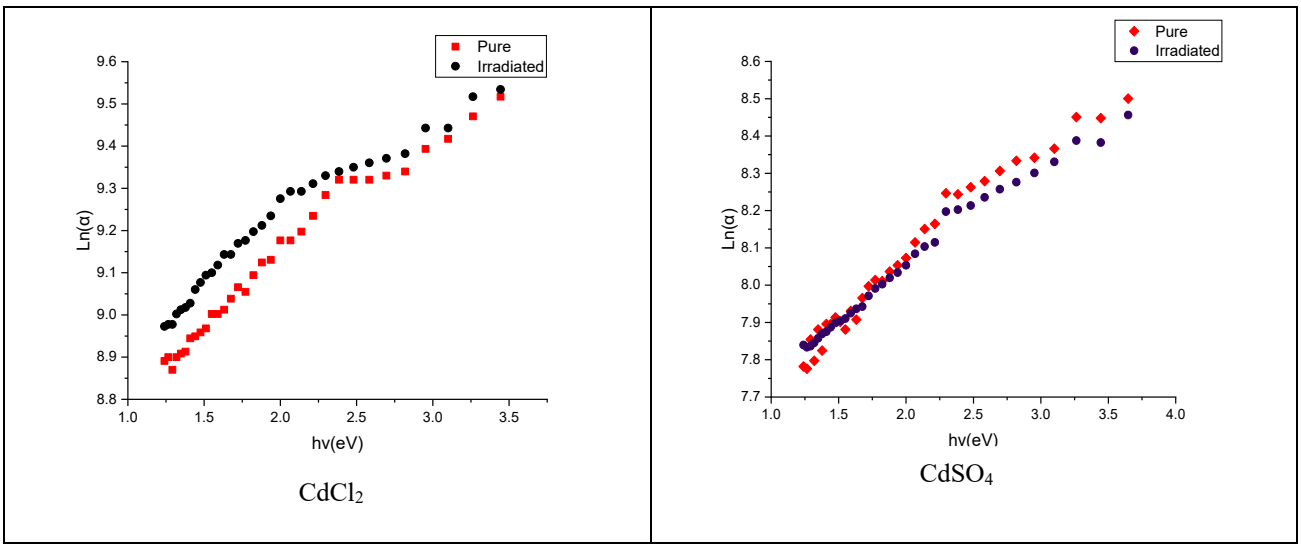

Fig. 5: Urbach energy for pure and irradiated CdSe films

Fig. (5) shows that the Urbach energy increases significantly with neutron irradiation for the CdSe film prepared from $CdCl_2$, and the Urbach energy decreases slightly for the film prepared from $CdSO_4$. The increase in Urbach energy indicates the presence of a high density of levels within the energy gap resulting from the appearance of crystalline defects inside the film.

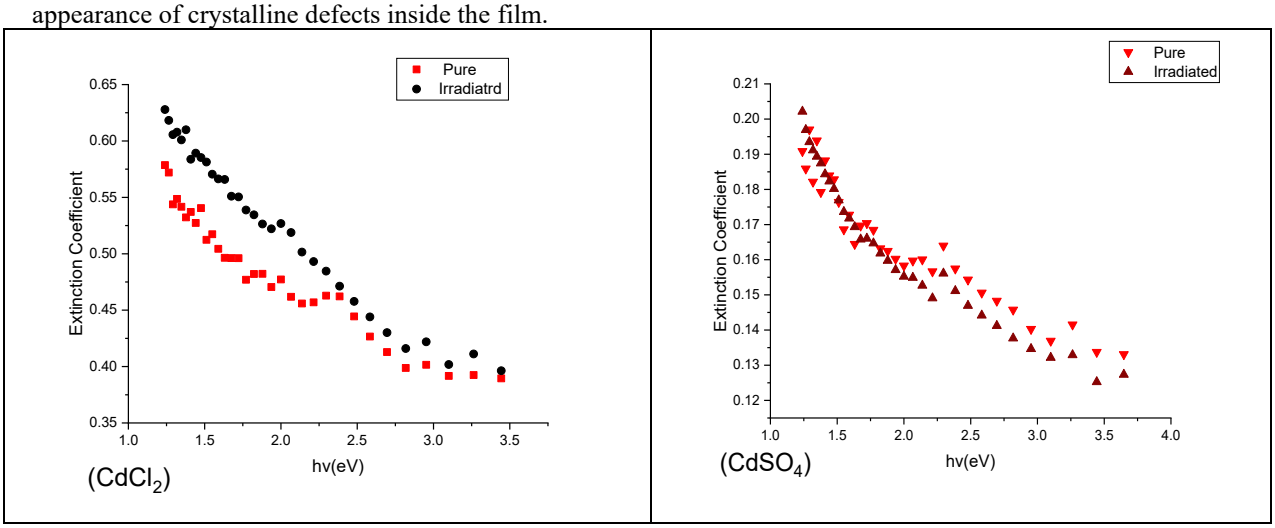

Fig. 6: The extinction coefficient (K) of CdSe films as a function of the photon energy before and after irradiation

Fig. (6) shows that the extinction coefficient increases significantly with neutron irradiation for the CdSe film prepared from $CdCl_2$ and decreases slightly for the film prepared from $CdSO_4$. It can be seen that the neutron irradiation had a clear effect on the surface of the films, which indicates that the total dose absorbed by the film increases, and thus the defects left by the radiation on the film increase, which may lead to a defect in the crystals, and this is evident in the FESEM technique.

3.2 X-ray diffraction measurements (XRD)

The X-ray diffraction (XRD) technique was used to investigate the crystal structure of CdSe films deposited on a glass substrate by analyzing the X-ray diffraction spectrum of the film. By examining the diffraction spectrum of the pure and irradiated films, It turns out that there are several peaks at levels [111], [220], and [311]. This shows that the film is polycrystalline and has a cubic structure and the presence of a distinct peak with high relative intensity at level [111], where the results were matched with the standard card numbered JCPDS 19-0191.

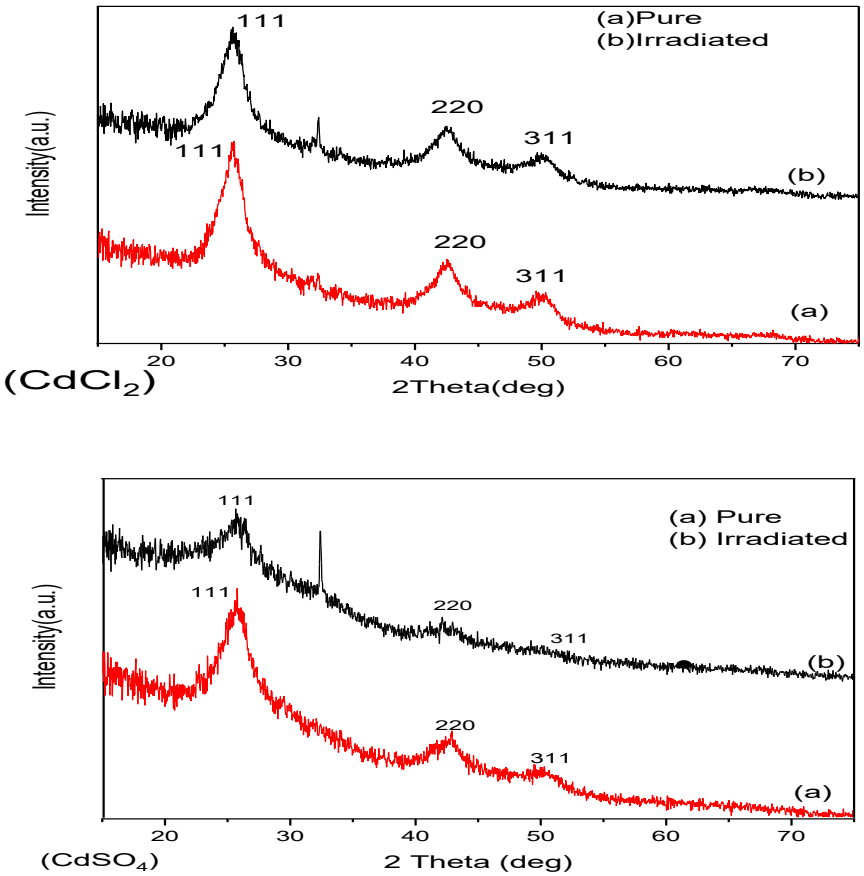

Fig. 7: X-ray spectrum of pure and irradiated CdSe films of two cadmium sources

Table 2, show the properties of the XRD spectrum obtained for pure CdSe films and the exposure by neutron irradiation.

Table 2: Some of the factors obtained from the results of XRD of CdSe films pure and exposed to neutron irradiation

Cadmium source	Model type	2θ	Peaks no.	Rel. Intensity	Hight	d-spacing	β	Crystallite Size	
		(deg)	(hkl)	(counts)		A°	deg	(nm)	
$CdCl_2$	Pure	25.59	(111)C	100	885	3.47797	2.10	4.19	CdSe
		42.50	(220)C	35.04	310	2.12528	2.5	4.29	CdSe
		50.14	(311)C	19.24	170	1.81805	2.7	4.58	CdSe
	Irradiated	25.62	(111)C	100	750	3.47418	2.26	3.88	CdSe
		31.94	(002)	15.27	115	2.80006	0.21	46	Cd
		32.364	ambiguous	38.40	288	2.76398	0.16	62.72	ambiguous
		42.45	(220)C	37.57	282	2.12780	2.36	4.55	CdSe
		49.98	(311)C	17.23	129	1.82344	2	6.18	CdSe
		67.7	(331)C	3.03	23	1.38214	3	6.96	CdSe
$CdSO_4$	Pure	25.74	(111)C	100	514	3.45767	2.6	3.38	CdSe
		42.60	(220)C	31.08	160	2.12119	2.9	3.71	CdSe
		50.40	(311)C	16.44	85	1.80958	3	4.14	CdSe
	Irradiated	25.61	(111)C	72.28	247	3.47533	2.2	4	CdSe
		32.365	(002)	100	341	2.76388	0.13	76.66	Cd
		42.54	(220)C	19.07	65	2.12335	1.8	5.97	CdSe
		50.11	(311)C	8.82	30	1.81891	1.1	11.31	CdSe

It is noted from a table (2) that there is an increase in the particle size upon neutron irradiation and the emergence of additional peaks, some of which are due to the element cadmium. As for the relative intensity, the intensity decreases with neutron irradiation, and this is due to the energy acquired by the granules that changed the direction of the granule, which led to changes in the limits of the darling and its location.

3.3 Compositional Analysis

The initial analysis of the CdSe films deposited on a glass substrate was carried out using EDX technology, and the fig. shows (8) elemental analysis of the pure and irradiated films. It is noted the appearance of some elements such as carbon, oxygen, and other elements can be attributed to the surface contamination of the film from the environment and conditions of the experiment [18].

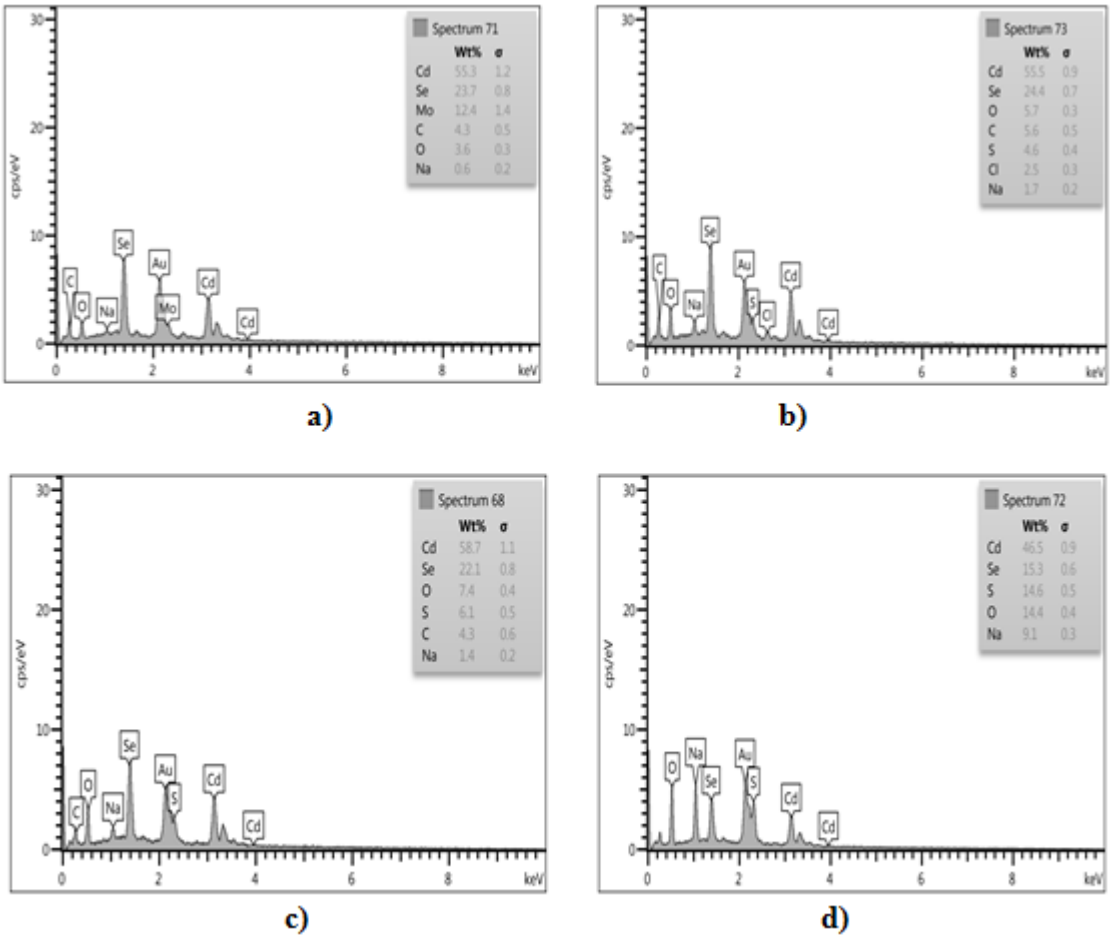

Fig. 8: The EDX pattern of CdSe films on the glass substrate for $CdCl_2$ material (a) pure (b) irradiated, for $CdSO_4$ material (c) pure (d) irradiated

3.4 Morphological Surface

Fig. (9) shows pure CdSe films and exposed to neutron irradiation, for the film prepared from $CdCl_2$ the pure film consists of homogeneous semi-spherical granules with some distances between them, but after exposure to neutron irradiation, the shape of its surface changes and the shape of the semi-spherical granule disappears with the appearance of cracks in the film, due to exposure of the film the high energy of the falling neutrons caused it to change its shape, due to the interaction of the neutrons with the matter, as the neutrons give their high energy to the crystals, which leads to a rise in their temperature, and the formation of in situ fluidity of crystals, which transform crystals into random crystals and cause damage to the crystal lattice. For the film prepared from $CdSO_4$, we note that the pure film has quasi-spherical structures with nanoneurocytes, but after exposure to the film to irradiation, the shape of the granule completely disappears as shown below.

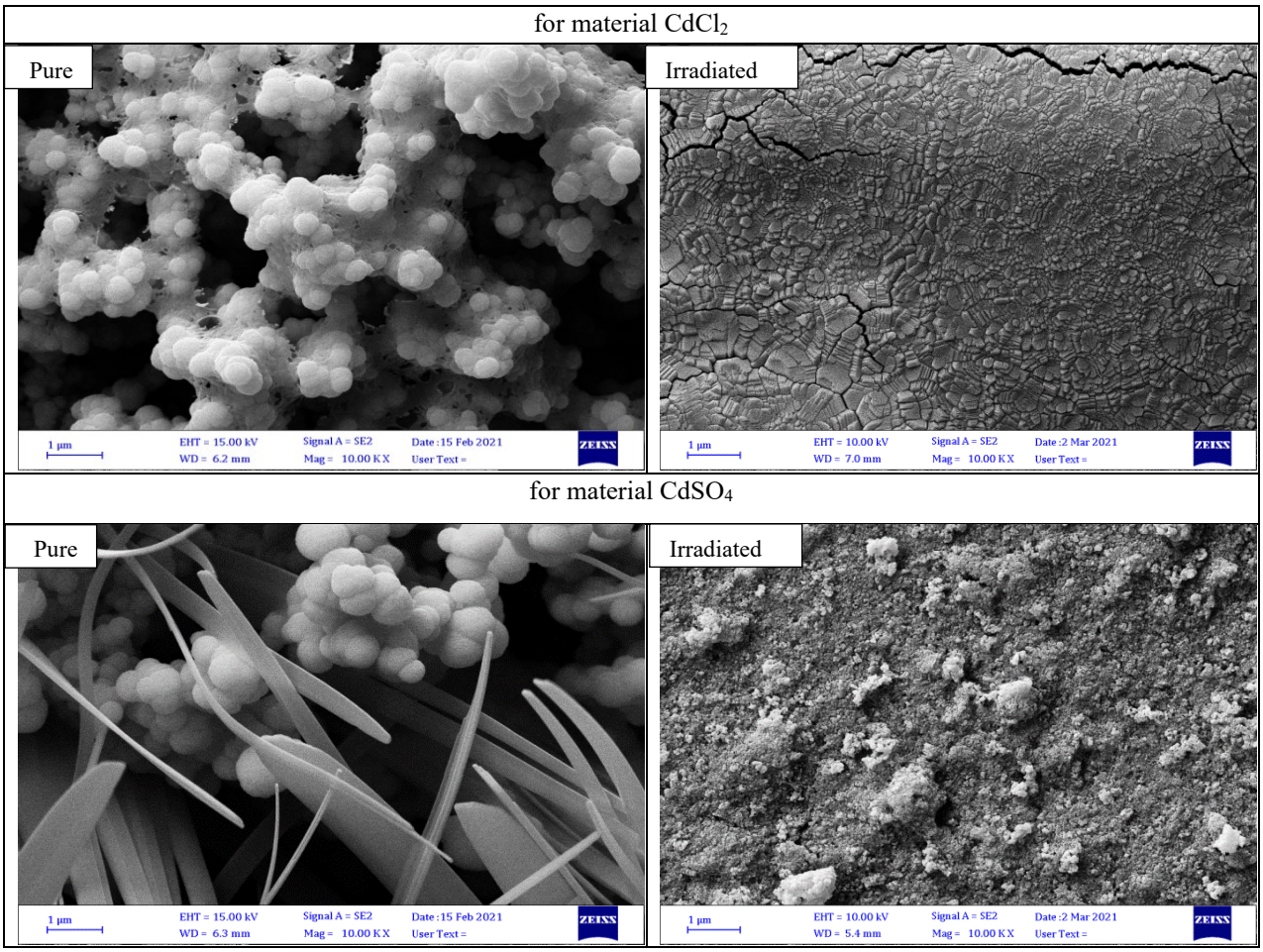

Fig. 9: FESEM image of as-synthesized CdSe nanoparticles by CBD

4. Conclusion

From this work, we can reach the following conclusions: CdSe films have favored grain growth directions, which are [111], [220], [311] for both materials. The energy gap increases after exposure to neutron irradiation, as well as the particle size increases, but the relative intensity decreases after exposure to irradiation. In optical measurements, there is a clear decrease in the transmittance spectrum and an increase in the absorption spectrum for $CdCl_2$, but for $CdSO_4$, there is a very slight change, and the Urbach energy also increases. The extinction coefficient also increases after exposure to irradiation for films prepared from $CdCl_2$, but for films prepared from $CdSO_4$, there is a very slight change. As for the FESEM measurements, the surface shape is semi-spherical for the films prepared from $CdCl_2$, but for the films prepared from $CdSO_4$, we notice the appearance of nanoparticles with the semi-spherical shape, and the surface shape changes completely after exposure to neutron irradiation.

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