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Improving Properties of Cdse Thin Film Working as Gas Sensor by Using Cu Atom Dopping

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Abstract.
We investigated the impacts of Cu doping on the optical, structural, and gas sensitivity related to oxide carbon for CdSe semiconductors in this paper. CdSe and CdSe: Cu thin films that have been deposited on a glass substrate with the vacuum thermal evaporation. The X-ray diffraction (XRD) has been utilized in order to analyze samples, and XRD data has been utilized for the quantification of crystalline size regarding the CdSe thin film. Cu doping also leads to a reduction in crystalline size. In the spectral range 250-850 nm, changes in optical characteristics (absorption coefficient and optical band gap) after Cu doping were evaluated. After doping thin films, optical band gap is observed to be reduced. By using gas sensor system, gas sensitivity of oxide carbon has been investigated. Also, it was discovered that when the Cu doping pair was used; the sensitivity increased while thin film resistance has been reduced.

Keywords: Gas sensor, CdSe thin films, Cu doping, Thermal evaporation.

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تحسين خصائص CdSe فيلم الرقيق الذي يعمل كمستشعر للغاز عن طريق التشويب بذرة النحاس

اسامة اسماعيل خضير[1] , اشواق عبد الحسين[2] .

الخلاصة
لقد درسنا تأثيرات منشطات النحاس على الحساسية البصرية والهيكلية والغازية المتعلقة بأكسيد الكربون لأشباه موصلات CdSe في هذا البحث CdSe. و CdSe: أغشية رقيقة من النحاس تم ترسيبها على ركيزة زجاجية مع التبخر الحراري الفراغي. تم استخدام حيود الأشعة السينية (XRD) من أجل تحليل العينات ، وقد تم استخدام بيانات XRD لتقدير الحجم البلوري فيما يتعلق بالغشاء الرقيق CdSe. يؤدي تعاطي المنشطات بالنحاس أيضًا إلى تقليل الحجم البلوري. في النطاق الطيفي 250-850 نانومتر ، تم تقييم التغيرات في الخصائص البصرية (معامل الامتصاص وفجوة النطاق البصري) بعد تعاطي النحاس. بعد تنشيط الأغشية الرقيقة ، لوحظ أن فجوة النطاق البصري تقل. باستخدام نظام استشعار الغاز ، تم فحص حساسية غاز أكسيد الكربون. كما تم اكتشاف أنه عند استخدام زوج منشطات النحاس ، زادت الحساسية بينما تقل مقاومة الأغشية الرقيقة.

الكلمات المفتاحية: متحسس الغاز ، الأغشية الرقيقة CdSe ، تشويب بالنحاس ، التبخر الحراري.

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Introduction

Currently, gas sensing materials could be divided into two categories: namely, inorganic and organic [1]. Radiation, smoke, and gas detection are critical for a modern healthy lifestyle, and gas sensors have an important impact at the thaws. As gas sensors, a variety of semiconducting materials, particularly oxides, have been used. Using oxides of some of the elements such as zinc, tin, indium, and mixed oxides for identifying gas types in the

atmosphere has a lot of information. Co_2 and Co are hazardous pollutants that are created during partial oxidation of fossil fuels in combustion processes. Also, they were linked to automotive exhaust. The major goal of measuring Co_2 and Co was for the prevention of the intoxication from the incomplete burning in household appliances [2]. Sankarasubramanian, et al. have reported that the sensitivity of CuO gas sensor enhanced with doping by Cu atom [3]. Al-Hilli, have reported that to improve CdSe gas sensor properties, the reducing its crystalline size will be very convenient the sensitivity of CdSe gas sensors enhanced [4].

We prewired the CdSe: Cu gas sensor in this project and investigated the impact of copper doping on CdSe thin film properties.

Experimental

CdSe and CdSe:Cu thin films have been deposited on clean glass at room temperature with the use of the approach of thermal evaporation. A vacuum of 10^{-5} mbar order has been maintained in chamber throughout evaporation. Silver paste was used for ohmic contacts. CdSe and CdSe: Cu thin films gas sensors were variable resistance sensor type with the resistivity changing in presence of the Co and Co_2 gases. The test chamber's outer wall has been painted by a dark colour for the purpose of avoiding effects of the light upon thin films throughout measurements of the resistance was measured using a digital high multimeter. The evaluation of CdSe and CdSe: Cu thin films gas sensor properties and sensitivity has been performed a in normal environment. Under the normal atmospheric pressures, variations in resistance of CdSe and CdSe: Cu thin films gas sensors with Co and Co_2 gases.

Result and discussion

3.1. XRD Studies

Figure1 illustrates XRD of the CdSe thin films. The intensity of peak that corresponds to the orientation of (002) has been located at (002) plane at 2 θ =25.447º. A different peak of small intensity at 2 θ = 46.0801º at a (103) plane. The structure type has been found hexagonal wurtzite (W) that has been in agreement with standard value [5].

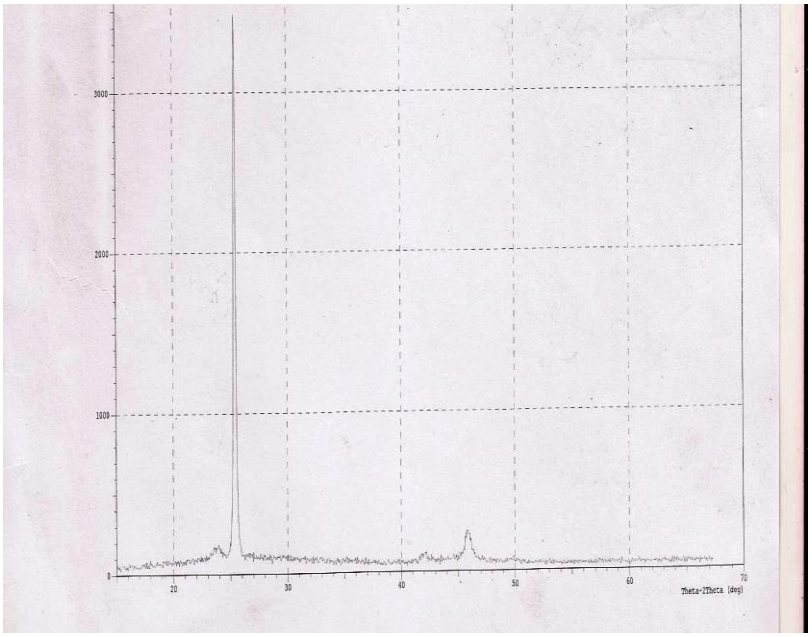

Figure (1): XRD of CdSe thin film

Figure 2 illustrates CdSe: Cu thin film XRD. Peak that corresponds to (002) plane was at 2 θ = 25.452º and the structure type was the hexagonal wurtzite (W) that was in agreement with standard value [6]. The size of the crystallite (D) of thin films may be calculated with the use of Scherrer's formula from full width at half maxima (FWHM) β [Schottmiller, et al, 1980],

$$D = 0.94\lambda / \beta \cos\theta \quad \text{.....(1)}$$

In which λ represents wave-length of utilized X-ray, β represents the FWHM, and θ (i.e. Bragg's angle) represents angle between scattered and incident X-rays. The values of the strain ε could be calculated with the use of the equation,

$$\varepsilon = \beta \cos\theta / 4 \quad \text{.....(2)}$$

Bragg's formula was used to calculate the lattice spacing 'd',

$$d = \lambda / 2\sin\theta \quad \text{.....(3)}$$

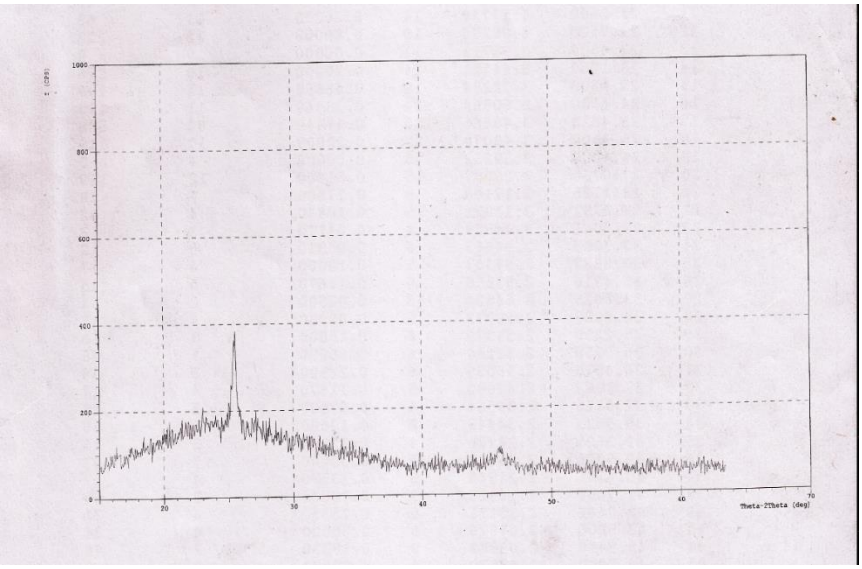

Figure (2): XRD of the CdSe: Cu thin film.

Lattice parameters 'a' & 'c' have been specified for hexagonal structure via the next formula:

$$1 / d^2 = 4 / 3 \{h^2 + hk + k^2) / a^2\} + (l^2 / c^2) \quad \text{.....(4)}$$

The lattice planes are represented by h, k, and l. Table 1 shows the findings of calculating crystallite size of thermally evaporated CdSe: Cu thin films. The XRD pattern's sharp and intense peaks demonstrate the films' good crystallinity and prove stoichiometric nature of the CdSe films. For thin films, peak's intensity has been observed to diminish with Cu, indicating that crystalline nature of a film was reduced. All of the films included the most dominating plane (002). The films had a hexagonal crystal structure and were nanocrystalline in nature. Schottmiller et al. [7] used Raman spectroscopy and Infrared to investigate the impact of several elements (Te, S, As, Bi, and Ge) on glassy Se structure. They

discovered that around 40% of the atoms in glassy Se had ring structure, while 60% of atoms have been bonded in the form of polymeric chains. The existence of an additive could cause an increase in charge carrier concentrations and a shift in Fermi levels. Table 1 shows crystallite size, 2θ, lattice spacing (d), strain (ε), (hkl) plane, lattice parameters (a) & (c), and structure type.

Table1: Crystallite size, Strain and 2 θ of the CdSe and Cd_xSe_{100-x} thin film

Sample	Crystallite size D (nm)	2θ	d-spacing Experimental d (Å)
CdSe	75	25.447º	3.497
CdSe:Cu	48	25.452º	3.496

3.2. Optical Study

The CdSe and CdSe: Cu thin film absorption spectra, which has been deposited onto glass substrate were evaluated at the temperature of the room in spectral range of 300nm–850nm as can be seen from Figure 3.

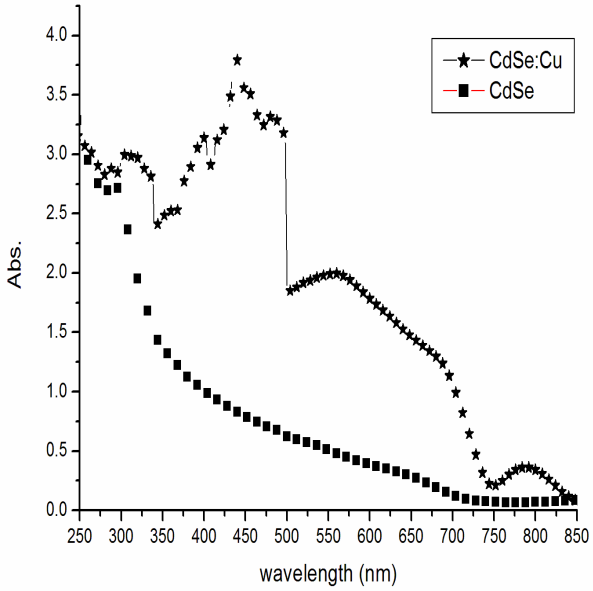

Figure (3): Spectral plots of the coefficient of absorption (α) vs. the wave-length (λ) for the CdSe and CdxSe: Cu thin film

It was discovered that thin film absorption spectra have been blue shifted as a result of the increases in optic band gap for those materials. The optical band gap value 'E_g' has been estimated with the use of equation below [8- 10],

$$\alpha = A\,(h\nu - Eg)^{n}/h\nu \quad \ldots\ldots\ldots\ldots(5)$$

where A represents constant value, and n has the value of 1/2 for the semi-conductors of the direct band gap. Plots of $(\alpha h\nu)^2$ vs. hν have been

illustrated by Fig. 4 for the CdSe and CdSe: Cu films. The E_g optical band gap has been obtained through intercept as an x-axis and values have been listed in Table 2. It has been noticed that optical band gap has been increased with the content of Cu. The optical band gap increases on additions of the Cu in CdSe films could be explained on bases of model of state density in the amorphous semi-conductors that have been suggested by Davas & Mott [11]. Based on that model, the width of the localized states near the edges of mobility is dependent upon the extent of the disorder and the defects that are presented in amorphous structures. Particularly, it has been known that the unsaturated bonds in combination with some of the saturated bonds have been created due to the inadequate amount of the atoms that have been deposited in amorphous films [12]. Localized state is decreased with the decrease of Cu and crystallite size is decreased, which has been responsible for increasing optic band gap [13- 14]. The coefficient of extinction k was estimated with the use of well-known equation [11],

$$\alpha = 4\pi\kappa/\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

λ represents incident beam wave-length. Those films' absorption coefficients have been high (approximately $10^4 cm^{-1}$). The values of extinction coefficient (k), absorption coefficient (α), and the energy band gap (E_g) obtained have been listed in Table 2.

Table 2: Optical parameters of the thin film at 600nm

(α:coefficient of absorption; E_g: optical band gap; k: coefficient of extinction)

Sample	$\alpha * 10^4 cm^{-1}$	K	E_g (eV)
CdSe	4.6	0.224	1.69 ± 0.001
CdSe: Cu	2.6	0.126	2 ± 0.001

The shift in optical energy gap with metal concentration is due to a change in the bonded atoms network that is linked to one another from Cd-Se and Se-Se bonds to small Se amounts and big Cd-Cd and Cd-Se amounts with an increased Cu doping. The change in stoichiometry was primarily responsible for the difference in optical characteristics with metal incorporation. Cu additives in CdSe should cause a compositional change in the Se–Se host network, which is known as the alloying effect [15]. As a result, the drop in Eg can be related to creation of additional centers of defect, which grow in order as Cu concentration rises [15]. The defects and disorder degree in the amorphous structure determine width regarding localized states along the edges of the mobility. As a result of the insufficient amount of the atoms in amorphous films, unsaturated bonds, as well as certain saturated bonds, were known to form. The creation of several defects in the films was caused by such unsaturated bonds. In amorphous solids, such defects cause localized states. The low value of Eg was a result of the existence of significant concentrations of the localized states in the structure of the band [16]. It was discovered that when Cu is added to the Cd-Se system, a Se-Cd-Cu bond is formed, carrier concentration rises, and the system's energy band gap lowers. The structural alterations

caused by the increased Cu doping can explain this type of the gap of energy behavior with an increase in the cadmium level in the glasses of Se-Cd.

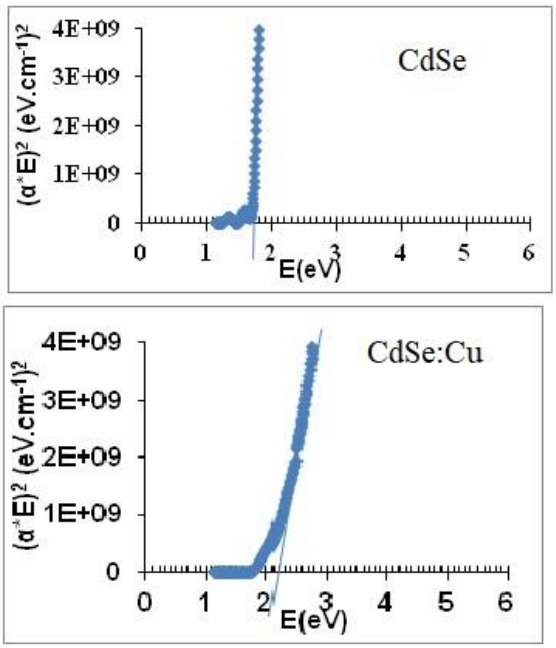

Figure (4): Plots of (α hν) 2 vs. hν for the thin films of CdSe and CdSe: Cu.

Copper introduces the homopolar bonds of Cd-Cd and the hetero-polar bonds of Cd-Se-Cu in Se_8 rings when copper is added to the CdSe system. It's worth noting that the Cd-Cd bond was longer than the Se-Se bond, potentially increasing the system's volume and lowering the effective molecular weight. Many authors have documented an increase in the frequency of In-In bonds when metal content in the selenium is increased (for example, indium in selenium system). The CdSe system's volume shrinks while its molecular density rises. Therefore, the system's carrier density falls, leading to a rise in the energy band gap [17-18].

3.3. Sensitivity of CdSe and CdSe: Cu thin films on Co and Co_2 gases

S= R_{air}/ R_{gas} was used to calculate the gas sensitivity, in which R_{air} represents the film's background resistance in absence of the test gas and R_{gas} represents final film resistance in presence of the testing gas. Figure 5 demonstrates the sensitivity differences between the four CdSe and CdSe samples: Cu thin films have been deposited at room temperature on glass substrate with a thickness of 200 nm. It was discovered that when thin films were doped with copper duo, the response of gas sensitivity rose while thin film resistance has been reduced. When put to comparison with Co gas, the thin film's response is increased with Co_2. One of the possible mechanisms for reduction thin film resistance in test gas Co_2 has been presented [17]. It was feasible that an adequate Co_2 orbital would be overlapping with orbital carrying valence band electron in the CdSe, resulting in production of 2 new orbitals, one of them with a greater energy than the previous orbitals and the other with a lower

energy. It's possible that a higher energy orbital is located right under conduction band, improving conductivity.

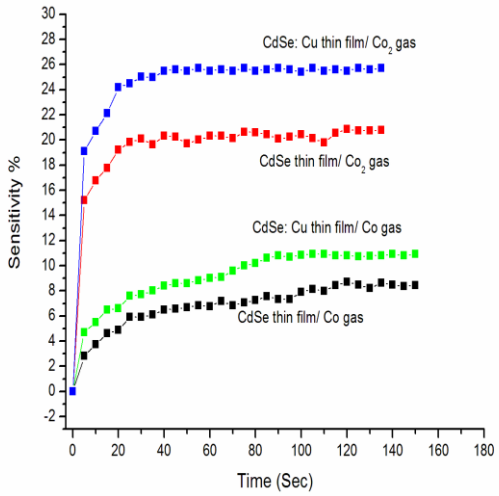

Figure (5): variations of the gas sensitivity as function of Co andCo2 gases with CdSe and CdSe: Cu thin films respectively.

4. Conclusions.

The pure and Cu doped CdSe thin films were deposited on glass substrates at room temperature by using thermal evaporation technique. The effect of Cu doping on structural, optical, electrical and Co2 sensing properties of CdSe thin films was systematically analyzed and discussed. All deposited films exhibited hexagonal wurtzite (W) structure. The slight variation in lattice parameter of CdSe film and the crystalline nature decreases due to the replacement of Cd by Cu atom in structural of CdSe. Furthermore, the band gap energy increases with an increase in Cu concentration. This is attributed to the decreased of grain size of the thin films with Cu doping. Gas sensing parameters indicate that the doping process significantly improves the sensitivity. The thin films could be used to monitor the levels of the pollutant CO_2. When thin film doping with copper, the sensitivity of the gas has been discovered to depend upon thin films' resistance. Copper doping with CO_2 gas yielded the highest sensitivity in thin films.

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