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The Effect of Cadmium Selenide Thin Film Thickness on Carbon Monoxide Gas Sensing Properties prepared by Plasma DC-Sputtering Technique

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Abstract
Cadmium Selenide (CdSe) thin films have been deposited on a glass substrate utilizing the plasma DC-sputtering method at room temperature at different deposition time in order to achieve different films thickness, and studied its sensitivity to the carbon monoxide CO gas which are show high response as the film thickness increases, the DC-conductivity and photoconductivity are also studied and which are increased too as the film thickness increases, that indicates the good semiconducting behavior at room temperature and light environments.

Keywords: Cadmium Selenide (CdSe), DC-Sputtering, gas sensor, photoconductivity.

دراسة تأثير السمك على تحسسية أغشية سيلينيد الكادميوم الرقيقة لغاز أول أوكسيد الكابون والمحضرة بتقنية الترذيذ المستمر

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الخلاصة
تم تحضير أغشية سيلينيد الكادميوم (CdSe) على قواعد زجاجية وبأسماك مختلفة تم الحصول عليها من زمن تحضير مختلفة عند درجة حرارة الغرفة مع ثبوت ظروف التحضير الأخرى. وتم دراسة تأثير سمك الغشاء على تحسسيته لغاز أول أوكسيد الكاربون CO، ووجد ان الغشاء ذو استجابة عالية لهذ الغاز، وان تحسسيتة للغاز تزداد مع زيادة سمك الغشاء. وكذلك تم دراسة خواص التوصيلية الكهربائية المستمرة والتوصيلية الضوئية للأغشية المحضرة ووجد ان لها خواص سلوك شبه الموصل المثالي وان لها استجابة عالية للضوء، مما يشير الى امكانية استخدامها في صناعة الكواشف الضوئية.

Introduction

The binary semiconductor thin films of II-VI group (CdS, CdSe, CdTe, ZnSe, ..) has rapid development because of their intrinsic direct energy gap of about 1.7eV, the excessive absorption coefficient, and photosensitive nature and frequently possesses n-type conductivity in thin films in addition to bulk state. Now a day semiconducting nano-crystalline materials are used for many interesting applications. [1]

CdSe thin films of crystalline size within the nano-scale have attracted scientific attention. Their characteristics deviate from the corresponding material in a size dependent manner due to the effect of confinement. The localization of charge carriers in a confined space (nano-crystal) is accompanied with quantization of electronic energy states. The consequences of confinement within the case of CdSe thin films are appears strongly whilst the crystal radius is less or closer to the Bohr's radius of

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bulk CdSe (i.e., 5.6 nm).[2] Quantum confinement, for example, allows the optical properties of the semiconductor to be adjusted in the nanocrystalline size, i.e. it leads to a widening the optical energy gap (blue shifting), making it of a great importance in many optoelectronic device applications.

A variety of deposition methods have been effectively implemented for production of high quality nano-crystalline CdSe thin films, which can be achieved by controlling some deposition parameters. Usually CdSe thin films have been prepared using physical and chemical methods such as thermal evaporation[3], chemical path deposition [4], sputtering[5], electron beam evaporation[6],spray-pyrolysis[7],electro-deposition[8],photoelectrochemical[9],SILAR[10] and photochemical deposition[11].

Large area thin films with closely spaced nano-crystals may be prepared by plasma sputtering. The nano-crystal size can be managed by controlling some deposition parameters.

In present paper, the effect of the film thickness on CO gas sensing of CdSe thin films prepared by means of plasma DC-sputtering method with Argon inert gas are studied.

Experimental

The CdSe thin film sample were previously prepared by DC- sputtering with various deposition time, and achieve different film thickness which are leads to various crystalline size and morphology characteristics shown in Table-1[12].

Table 1-The CdSe thin film thickness as a function of sputtering deposition Time, V=2000 Volt, $p=2\times10^{-2}$ mbar, D=4.6 cm: [12]

Sample no.	**1**	**2**	**3**	**4**
Deposition Time (Min)	**30**	**60**	**90**	**120**
Thickness (nm)	**350**	**400**	**500**	**600**
Crystalline size (nm)	**10.34 - 12.65**	**11 – 15.1**	**13.38 – 15.6**	**14.2 - 17.1**

Results and Disscussions:

1- Electrical properties:

The DC conductivity has been measured as a function of temperature over the range 300-453 K using digital electrometer type keithly (616) and oven. The conduction mechanism is due to carrier excited into localized states at the edge of the band [13].

The results show that there are decreases of DC conductivity (σdc) with increase thickness, this is caused from the forbidden band, and it has a specific localized energy states concentration which originates from the statistical disordering of atoms. During the film growing process, the degree of such disordering decreases or voids are eliminated, and this may cause a decrease in the number of unsatisfied bonds [14], this agrees with Chttick [15], Chik and Lim [16] studies.

We observe that the DC-conductivity increases at 500nm thick, because the degree of electrons localization increases with capturing concentrations increase, thereby increasing the donor centers. A large number of donor center concentrations effectively increase. The electrical conductivity which increases in thicker samples as shown in Figure-1, from these figures it is clear that there are two transport mechanisms, giving rise to two activation energy Ea_1&Ea_2. It is clear that the activation energies increase, while σ_{RT} decreases with increasing thickness as shown in Table-2.

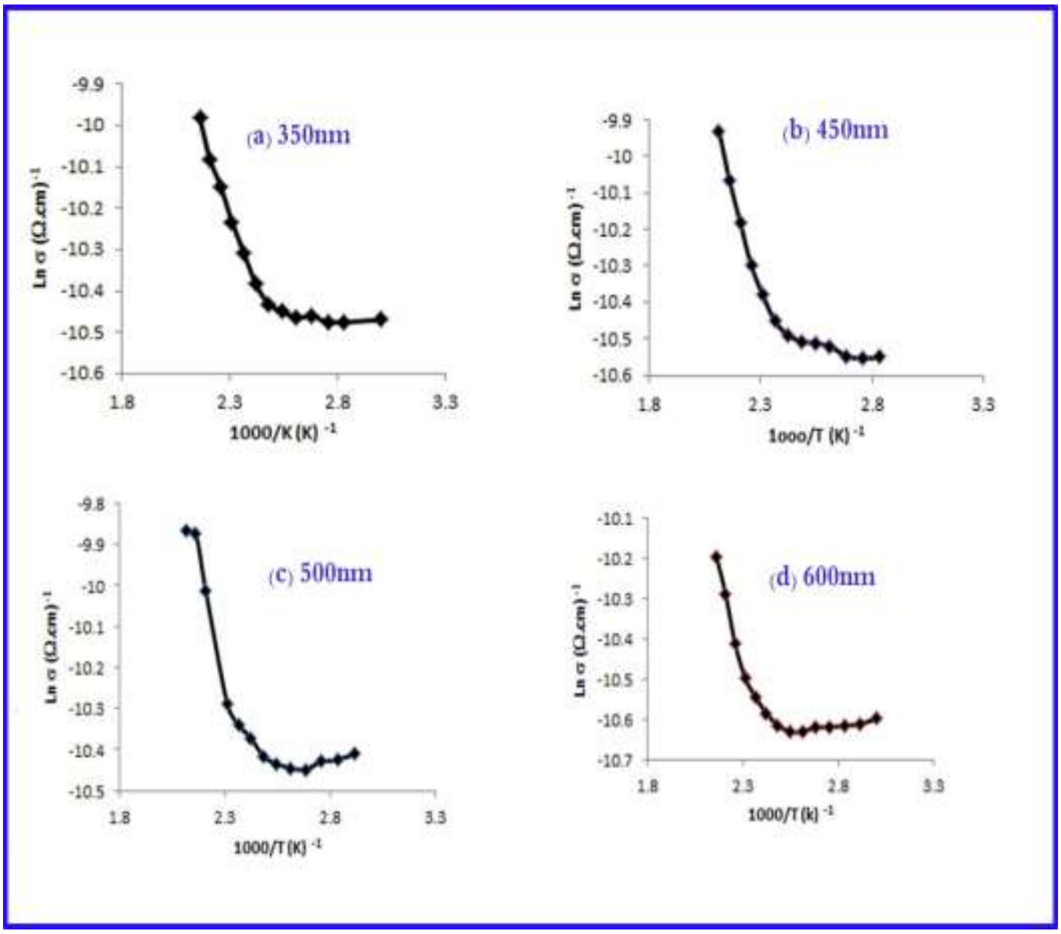

Figure1-Ln σ vs. 1000/T of thin films with different thickness

Table 2-DC conductivity parameters of CdSe thin films for different thickness

Thickness (nm)	(300 – 393)K	(393 –437)K	$\sigma_{dc}(\Omega.cm)^{-1}$
	E_{a1} (eV)	E_{a2} (eV)	
600	0.027	0.029	$7.18*10^{-6}$
500	0.018	0.054	$5.36*10^{-6}$
450	0.013	0.074	$4.42*10^{-6}$
350	0.03	0.083	$3.34*10^{-6}$

2- Photoconductivity

The presence of photoconductivity in semiconductor thin films on a glass substrate has been observed previously. Since the low size of nanocrystals increases the mobility significantly, one would expect similar improvements in photoconductivity. In order to study the photoconductivity of the CdSe thin films for different thickness (350-600 nm). The measurements are usually done in dark (Id) and under illumination (Il). Important device parameters can be extracted from (I-V) characteristic measurements. The CdSe films have measured current in a dark (I dark) and light (Iph) of thin films photocell photoconductivity as a function of applied voltage, when irradiated by a halogen lamp in combination (1840 LUX). We note the change of the lightening current in proportion to the darkness current as shown in Figure-2. The increase in falling photon energy from the illumination intensity leads to the increased mobility of charge carriers and the electrons travels from a valence package to the conduction package. These conduction electrons flowing from n-type semiconductor to surface. As illumination time increases, the anomalous behavior of photoconductivity in rise and decay is observed. All thickness of CdSe thin films is good but with improved photoconductivity with thickness. From these results it is obvious we can recommend that the CdSe thin films are good semiconductor for photoconductive detector, photovoltaic cell and other optoelectronic devices.

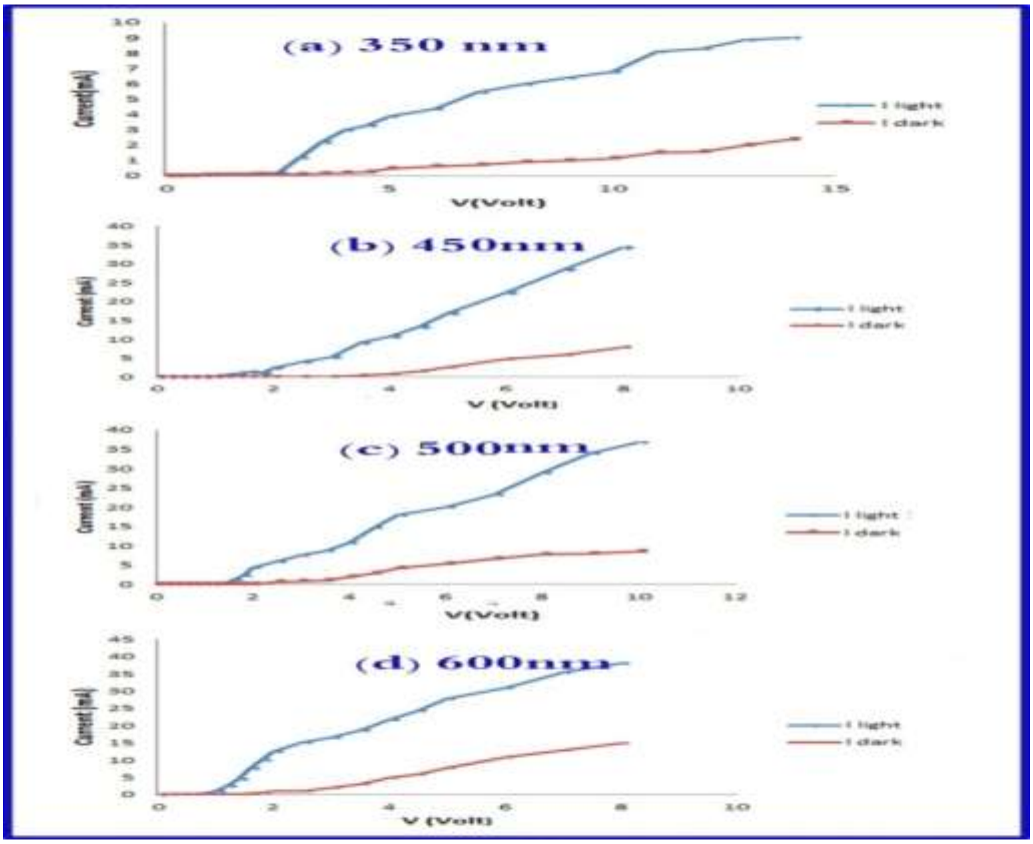

Figure 2-the I-V characteristics of CdSe thin films with different thickness

3- Gas Sensitivity

Cadmium Selenide can be employed as an electronic nose, however its resistance varies in the presence of gas. The experimental setup prepared to investigate the sensitivity as well as the dynamic response for Carbon monoxide CO gas is shown in Figure-3. The inner chamber wall is dark color painted in order to ensure no light affect the CdSe films resistance during the gas sensing measurements. Aluminum electrodes with specific mask using thermal evaporation machine deposited on the CdSe thin films, and a connecting wires are welded on the electrodes using silver paste then the samples are fixed on the base inside the chamber.

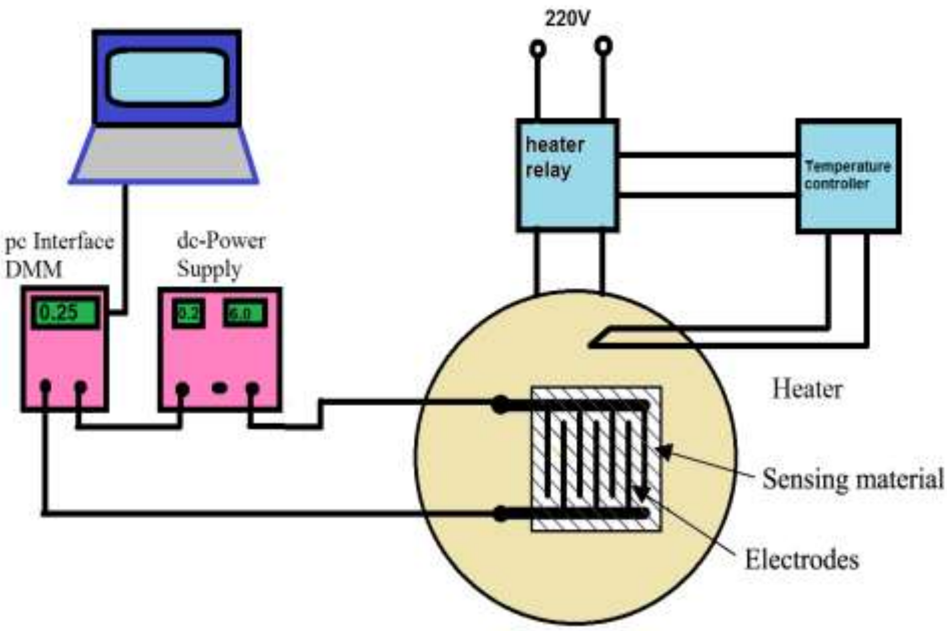

Figure 3-scheme of the gas sensing study used system

The CO gas has been prepared in laboratory and achieved according to the following equation:

$$HCOOH + 30\% \xrightarrow{60\ ^{o}C} CO + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

And the concentrations of the gas inside the chamber are approximately collected according to the general gas constant relation:

$$PV=nRT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The CO gas is injected into the test chamber with a constant mass flow rate while the resistance of the films were recorded with time (per 10 second) using the digital electrometers (KEITHLEY 614). The evaluation of CdSe gas sensor characteristics and sinsitivity is achieved in normal atmospheric pressure and in room temperture by the change in resistance of the CdSe thin film using the following relation [17]:

$$S = \frac{\Delta R}{R} = \frac{R_{gas}-R_{air}}{R_{air}} \times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$Response = Rs/Ra \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

In which: R_{air} is the film resistance in the absence of test gas, and R_{gas} is the final film resistance in presence of test gas (CO).

The response and recovery time of the CdSe thin films to CO gas concentration close to 6ppm at room temperature (300 ^{o}K) have been tested, and the successive tests carried out at 5 Volt bias voltages, and it analyzed as the tracing signal shown in Figure-4.

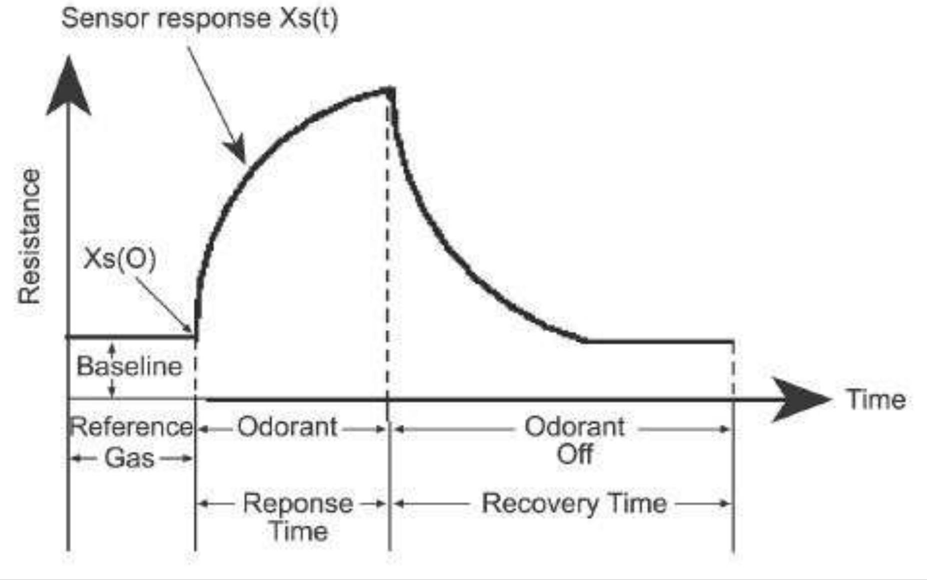

Figure 4-an ideal signal trace show the analysing gas sensor response with respect to the baseline [18].

From the gas sensing measurements, it is obvious that all the CdSe thin films obey the role of decreasing in films resistivity as exposed to CO gas, which can be explained by Molecular Orbital (MO) theory [19].

Table-3 indicates the response and the recovery time of the CdSe gas sensor with films thicknesses, which are increase with increasing film thickness, this is come from the reason that increasing film thickness will increase more sample crystallization Table-1. As a result, the shortest response and recovery time are coming from smallest grain size of the sample. This agrees with Korotcenkov[20].

Table 3-The response and recovery time of the CdSe gas sensor

Film thickness (nm)	Response time (Sec)	Recovery time (Sec)
350	-	-
450	10	-
500	25	30
600	35	65

The gas sensitivity is determined as a function of time period using equation (4). Figure-5 shows the sensitivity dynamics with operation time at various CdSe films thickness are (350,450, 500 and 600) nm, respectively keeping constant CO gas concentration close to 6 ppm calculated according to the general gas constant relation (2) at room temperature (300 K). The figure shows the impact of film thickness on the sensitivity, which reveals that the increase in the film thickness led to increasing in sensitivity. This agrees with previous studies of smyntyna. et al [21] which is shows the dependence of the concentration of chemisorbed oxygen on the surface of cadmium selenide films on their thickness. The results attributed to the cadmium surface concentration (Coming from self-doped with Cd atoms during the growth of CdSe films) increase causes the chemisorbed oxygen concentration raising which results an increase of electrons captured at the surface centers of the oxygen chemisorption. Figure-6 shows that the sensor's response to CO gas decreases at film thickness larger than 600 nm, these film thickness, and the gas sensitivity decrease because of the entry of the grain size effect which plays the dominant role, and the gas sensitivity of CdSe gas sensor depends upon its grain size. This can be attributed to the effect of Debay length. When the thickness of the film decreases and will becomes close to the Debay length, the conduction charge of the whole film is stricken by oxygen vacancies, and O_2 and/or CO chemisorption at the surface of CdSe film and the grain boundary to become larger than that in 500nm, as a result the sensitivity decreases[22].

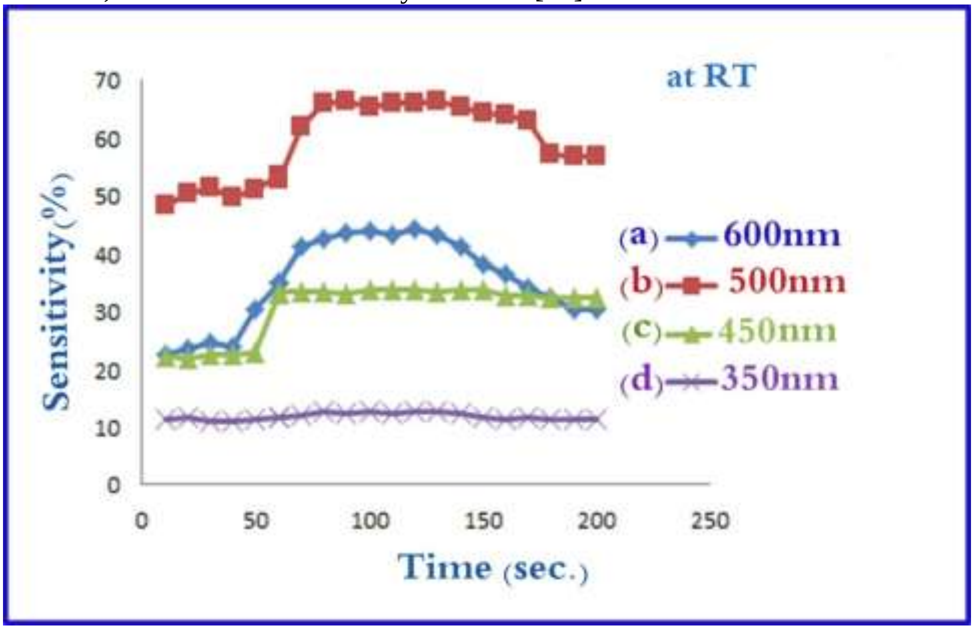

Figure 5-CdSe thin film sensitivity for CO gas at room temperature with different thickness

The data in the table above shows that the response and recovery time are decreased with increased film thickness. Increasing the film thickness, reduces oxygen adsorption of electrons extracted from the vicinity of the surface, forming an electron – depleted surface layer, increasing the number of active adsorption sites and achieving a rapid response time, this agrees with. Ebothe et.al. [23].

The most common defects of most semiconductor gas sensors are the high operating temperature required (200-500) ^{o}C. For this reason, the effect of the operating temperature on the sensitivity of the films is studied.

The sample is located on a controlled heated base and the resistance measured as the temperature raised to (423 ^{o}K), Figure-7 indicates the variation of sensitivity with time for different thickness, it is obvious that the resistance of the film decreases as the temperature increases showing negative temperature coefficient of resistance (NTCR) as a result of thermal excitation of the charge carriers in semiconductor, this confirm the common semiconductor behavior, The variation of the resistance value within the expectance of CO gas is so little which mean its sensitivity to the gas is almost nothing.

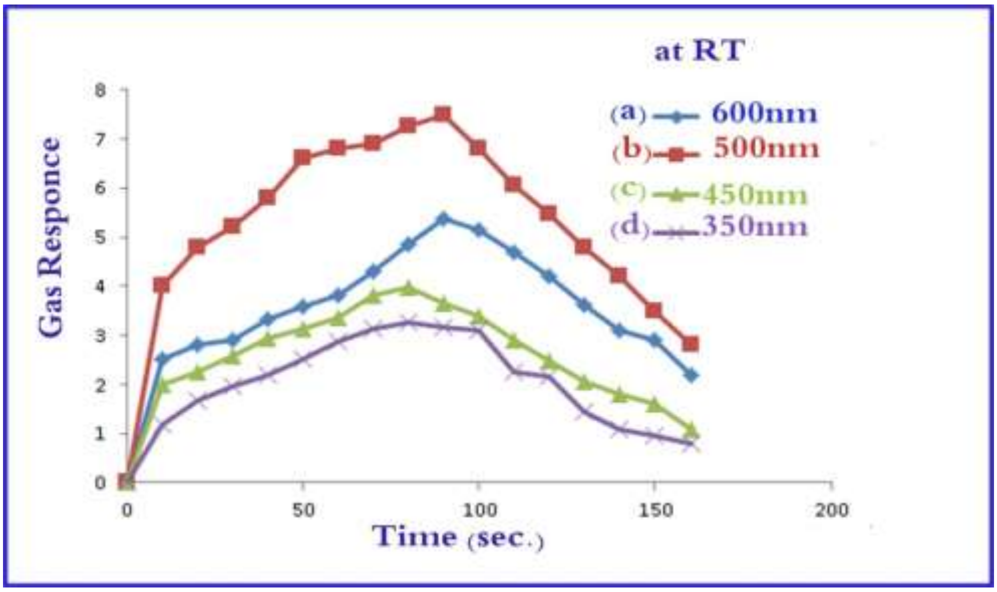

Figure 6-CdSe thin film gas response of sensitivity for CO gas at room temperature with different thickness**.**

For the purpose of reducing the optimum operating temperature can be related to the decrease the particle size. As the particles in the nano-scale number increase, the surface to volume ratio increase, in other words, reducing grain size allows for large area coverage, and a wide variety of grain boundaries that provide a wide adsorption area O^-, O^{-2}. Thus, the large variation in the barrier and resistance can enhance reactivity at low temperature. Also, the density of surface states will increase with a decrease in particle size, or the density of surface states can assist to reduce optimum operating temperature.

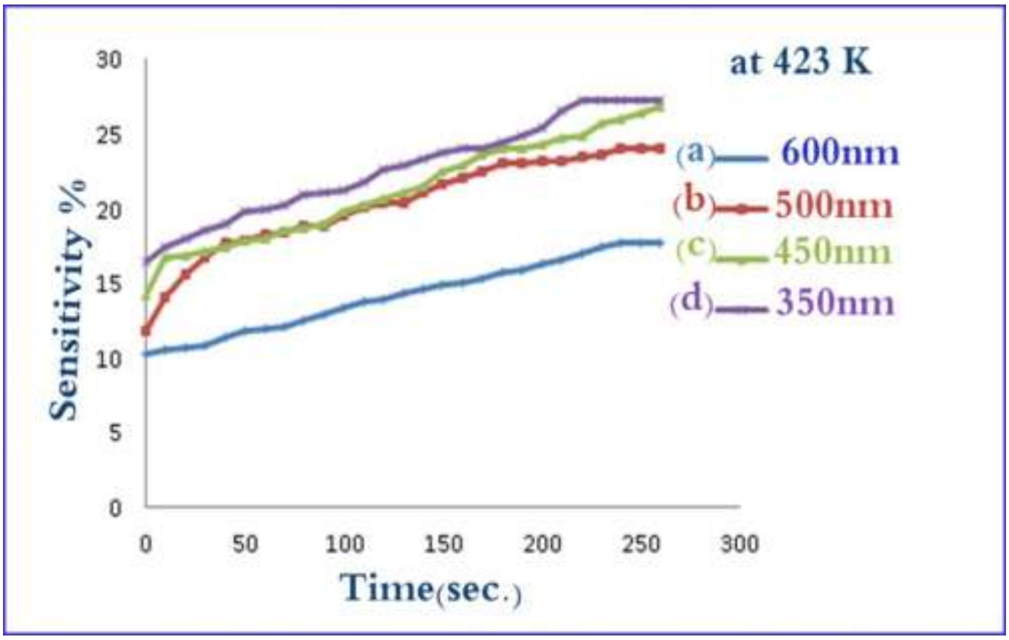

Figure 7-CdSe thin film sensitivity at 423 0K for CO gas with thickness : (a) 350 nm, (b) 450 nm, (c) 500 nm and (d) 600 nm.

Conclusions

Cadmium Selenide Semiconductor is recommended devices for gas sensing for its good characteristics such as high sensitivity, fast response and stability as well as photoconductivity. Besides, in order to improve its properties, the reducing its crystalline size will be very convenient.

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