Study on the Effect of Annealing on Structural and Sensing Properties of CdO Thin Films for (CO_2, H_2S) Gases

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ABSTRACT

Cadmium oxide (CdO) thin films have been deposited by Successive Ionic Layer Adsorption and Reaction (SILAR) method by using cadmium acetate at concentration 0.03 M and based solution from ammonium hydroxide on glass substrate. The structural and sensing properties of the as-deposited and annealed films are studied in details. The XRD and AFM analysis for its structural characteristic has been preformed .The average grain size of deposited film are increased after annealing . The sensing properties also are calculated and it is found that the sensitivity are increasing after annealing, and for CO_2 gas are better than the sensitivity for H_2S gas . The I-V properties are calculated for the films before and after annealing for the two gases.

دراسة تأثير التلدين على الخصائص التركيبية والتحسسية
لأغشية CdO للغازات (CO_2, H_2S)

الخلاصة

تم في هذا البحث ترسيب أغشية رقيقة من اوكسيد الكادميوم CdO باستخدام طريقة الطبقة الأيونية المتعاقبة التكتفية (SILAR) على قواعد زجاجية باستخدام خلات الكادميوم وبمولارية 0.03 مولاري مع محلول من هيدروكسيد الامونيوم . الخصائص التركيبية والتحسسية للاغشية المرسبه والملدنة تم دراستها . حيود الاشعة السينية XRD وفحص مجهر القوى الذرية AFM تم تشخيصها ، معدل الحجم الحبيبي للاغشية ازداد بعد التلدين . الخصائص التحسسية ايضا حسبت وقد وجد ان التحسسية تزداد بعد التلدين لغاز ثاني اوكسيد الكاربون اكثر من تحسسية غاز كبريتيد الهيدروجين . خصائص الفولتية -تيار حسبت للاغشية قبل وبعد التلدين للغازين.

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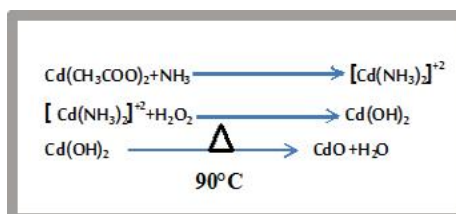(CO$_2$, H2S)   Gases**

INTRODUCTION

As a result from a scientific development , thin films preparing methods have developed   and they became   with a high degree of accuracy to the thickness determining of the thin films and homogeneity. These methods became more and each method has properties to serve their purpose, which used for it **[1].** Because of the industrial progress with the gaseous pollutants increases have focused the efforts of many researchers to get to the gas sensors at few cost , sensitivity properties and high selectivity with an operator simple technique . The large use of semiconductor oxides as gas sensing in all areas of life because the individual health and safety of the topics scientific important class basis **[2-3].** Where we see it is necessary to the subject synchronize of security and safety with every aspect of the work and the appropriate method selection for the thin film preparation depends on factors several. There are several reported methods for the preparation of the CdO nanostructure, but most of these methods only describe the thin film formation of CdO **[4**]. The use of the thin film especially of material type that is used in the preparation. The CdO thin films were prepared by Successive Ionic Layer Adsorption and Reaction (SILAR) on the glass substrate type – p. the formation of CdO nano-particles using the thermal treatment of cadmium acetate has been described by Ristic et al. **[5].**These thin films were used in the field of gas sensors considering to their wide energy gap and the high adsorption ability of CO$_2$ and H$_2$S .

EXPERIMENTAL WORK
Preparation of CdO Thin

When we prepare a used solution to precipitate the CdO thin film, cadmium acetate was used Cd (CH$_3$COO)$_2$. (cation) is a white powder and the concentration of 0.03 M and by melting 7.98gm of Cd (CH$_3$COO)$_2$ in a solution consisting of 100 ml of distilled water with ammonium hydroxide NH$_4$OH and the gradually solvent to the solution to reach the PH of the solution 8.3.

Another used solution is hydrogen peroxide (anion) H$_2$O$_2$, with a concentration of 0.005 M. Distilled water at a temperature 90°C. We used (SILAR) technique as shown in figure (1), the substrate was immersed first in cadmium acetate 0.03M and ammonium hydroxide solution for 40 s, and then immersed in double distilled water at 90°C for 30s and then immersed in a solution of hydrogen peroxide concentration of 0.005 M and then immersed in distilled water degree of 90°C with repeated immersion. The equations below show the chemical reaction for the preparation of CdO thin films.

$$Cd(CH_3COO)_2 + NH_3 \longrightarrow [Cd(NH_3)_2]^{+2}$$
$$[Cd(NH_3)_2]^{+2} + H_2O_2 \longrightarrow Cd(OH)_2$$
$$Cd(OH)_2 \xrightarrow{\Delta} CdO + H_2O$$
$$90°C$$

RESULTS AND EXAMINATIONS.
Measurements of Structural Properties .
A: Atomic Force Microscope (AFM) .

   The results of AFM examination for CdO thin films as in figure.(2- a) and (2- b), in figure(2-a) we obsrve the primitive growth stages that they may occur   of the CdO thin films before annealing respectively . The disappearance of most of the holes, surface defects and the appearance of granules borders was clear.   These results indicates that crystalline structure improvement of the CdO thin films that it means the improvement in the deposited films properties .

   The average grain size of the deposited CdO thin film is calculated to be 19.3 nm and 38.3nm   before annealing and after annealing 400°C respectively. The sharpness of the peaks show that film has good crystalline nature. The AFM shows the surface topography of CdO nano crystalline thin film in figure (2-**a**) and (2- **b**). The film shows the polycrystalline nature and uniform distribution of spherical grains.

Examination of X-ray diffraction (XRD)

   The results of XRD indicated that most of the prepared thin films that have polycrystallization structure of a cubic phase. The observation of the film shows smooth surface and well adhesive nature of the film with substrate. The peaks at plan (111),(200) and (220) refers to cubic phase formation as compared with standard X-ray diffraction data file [N 1997 JCPDS prevalent]. It has been observed that increasing the annealing temperature of the CdO thin films increasing intensity as in figure(3-a),(3-b). Grain size was calculated by compensation values that were obtained from the results of X-ray diffraction in earlier forms in the Shearer's equation **[6]** based on the (FWHM) as in the Tables (1) and (2).

$$G.S = \frac{0.94\lambda}{\beta cos\theta} \dots \dots \dots \dots (1)$$

G.S : is the grain
K: is a constant (0.94)
λ: is the wavelength of Cu Kα
θ: is the Bragg's angle and
β : is Full width at half Maximum

   We note that the values of grain size were calculated from equation (1) and intensity after annealing than before annealing. The reason is the annealing higher temperature of CdO films improved structural properties of the prepared thin films because of the improved crystallization of decreased structural defects**.** Generally with an increase in annealing temperature, structure of the film changes from amorphous to crystalline and grain growth occurs with increase in mobility **[7].**

EXAMINATION OF (CO₂, H₂S) SENSITIVITY
Measurement of Gases Sensitivity:
   The shown system in figure (4) has been used to measure prepared CdO thin films sensitivity for the (CO₂, H₂S). After connecting the deposited aluminum poles on the CdO thin films with wires. The sample was fixed on a base inside a chamber, the gases were pumped and recording the change in thin films resistance

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with time (per 10 seconds) and measure the current corresponding to the voltage in absence and presence of the gases to determine the impact of them on CdO thin films **.**

Calculation of Sensitivity

We can Calculation of Sensitivity (S) from equation (2) the following **[8,9]**:

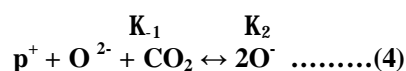$$S = (R_g - R_a) / R_a \times 100\% \ldots\ldots\ldots\ldots.(2)$$

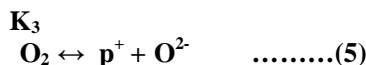R_g: Electric resistive of the thin film with gas
R_a :Electric resistive of the thin film without gas

The sensitivity of CdO thin films have been calculated by using CO_2 after measuring the thin films resistance in absence and presence of the gas as a function of time by applied of equation (2) shows the figure (5: a, b) sensitivity of thin films CO_2 and observe the effect of annealing on the sensitivity of thin films CdO where leads to the sensitivity decrease. This reason is ascribed to the annealing that leads to crystallization improvement which means a large granular size and granular borders decrease in which occur interaction between the gas and adsorbed oxygen; therefore the sensitivity will decrease which means sensitivity is a proportion inversely with grain size as shown in figures **.**

These thin films suffer from the height of potential barrier in the reducer gas such as H_2S and H_2; therefore ions (charge carriers) required a substantial amount of energy to cross that barrier ,that means increase in conductivity, as well as a decrease in potential barrier in the oxidizing gas such as CO and CO_2 because of the adsorption of oxygen and the formation of pair (hole - electron) that increase the conductivity.**[10],** as it shown in Table (3) as a values of resistivity and its behavior.

The temperature is an important parameter for gas sensing materials and designing of the sensor. The sensing materials have to appropriate temperature to achieve crystallization and structural evaluation. A sufficient degree of crystalline is required to attain the desired electronic properties necessary for gas sensor application. A number of experiments have been carried out to measure the sensitivity as a function of operating temperature. All the time sensitivity of the sensor element has approximately constant value indicating the repeatability of the sensor. The sensing mechanism of H_2S and CO_2 are quite complex and it proceeds through several intermediate steps. It is based on the changes in the resistance of the CdO, which is controlled by gas species. It is known that a certain amount of oxygen from air is absorbed on the surface of the CdO thin film. The CdO thin film interacts with the oxygen, by transferring the hole (p+), from the conduction band to adsorbed oxygen atoms, resulting into the formation of ionic species such as O^{2-} or O^-. The reaction kinematics may be explained by the following reaction **[11].**

$$O_2 \overset{K_1}{\leftrightarrow} p^+ + O^{2-} \qquad \ldots\ldots\ldots\ldots.(3)$$

$$p^+ + O^{2-} + CO_2 \overset{K_{-1} \quad K_2}{\leftrightarrow} 2O^- \quad \ldots\ldots\ldots(4)$$

$$\overset{K_3}{O_2 \leftrightarrow \ p^+ + O^{2-}} \qquad \text{.........(5)}$$

A simple model for the response of a p-type sensor is demonstrated by Equations (3) and (4), showing the adsorption of an oxygen atom to the surface of the material, causing ionization of the atom and yielding a positive hole (p+), demonstrated by (1). The positive hole and the ion can then react with a reducing gas such as CO_2, forming CO_2, (k_2) or be removed through interaction with each other (k_{-1}) [12] (2) The difference in charge carrier concentration (in this case the positive hole) is manifest in a resistance change between the sensor's electrodes, and read by the measurement circuitry assumes that the absorbed species on the surface of the metal oxide is the O^{2-} species; a species that is unlikely to be included as it is energetically unfavorable (Equation 5) . Describes a relationship where the change in resistance is proportional to the concentration of the gas (in this example CO_2) and a sensitivity parameter *A* (the sensitivity parameter is constant for a given material at a given temperature) where R_a is the resistance after exposure to analyte gas and R_g the baseline resistance (Equation 6):

$$R_a / R_g = 1 + A[CO_2] \qquad \text{............(6)}$$

The effect of chemisorptions is discussed in details by V. S. Vaishnav et al. [13]. The gas sensitivity of as deposited CdO thin film for H_2S and CO_2 has been performed at gas concentration 6 ppm as it shown in figures (5(a), 5(b)) before and after annealing , the annealing was at 400 ^{o}C. It has been observed that the sensitivity of the film is quite large for CO_2 as compared to the H_2S. The sensitivity of CdO thin film for CO_2 gas is maximum   values at 400°C. The type of semiconductor (p- or n-type) is not only a function of doping and material extrinsic properties, but is also dependent on the concentration of oxygen exposed to the semiconductor [14].

Thin film interacts with oxygen by transferring the positive hole (p+)from the conduction band to adsorbed oxygen atoms. The response to H_2S can be explained as a reaction of gas with the $O_2(ads)^-$ (Equation7) .

$$H_2S + 3O \ (ads)^- \ + P^+ \rightarrow H_2O(g) + 3p^+ \ \text{........... (7)}$$

With this reaction, many positive hole (p^+) could be released to thin film surface. This could make the Schottky surface barrier decrease. the sensitivity decreases at higher operating temperature, as the oxygen adsorbates are desorbed from the surface of the sensor [15]. Also, at higher temperature, the carrier concentration hole (p^+) increases due to intrinsic thermal excitation and the Debye length decreases. This may be one of the reasons for decreased gas sensitivity at higher temperature [16].

Properties of the current and voltage

Darkness and light currents were measured to describe of operating voltage function on both sides of the sample at room temperature, as in figure. (6: a , b) When the lighting intensity capacity (470LUX), we note the change of the lighting current in proportion to the darkness current . When the light intensity at a capacity (800LUX) a current increases , we note that the light current increasing with the

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incident light intensity. The increase in falling photon energy from the light intensity leads to the increased mobility of charge carriers gaps type -p or electrons type- n . The gaps hunt electrons or the electrons transmit from a valence package to the conduction package. When we measure the darkness current of the non-annealed CdO thin films, we found the current was less than the current of annealed CdO thin films, as in the form figure (6: a, b). We conclude that the increasing of the annealing temperature will increase the crystalline grains size , that leads to improving the thin films quality by improving the crystalline structure and consequently the resistivity increases to reach to a maximum value

CONCLUSIONS
 1- The results of the X-ray examinations XRD had indicated the prepared CdO thin films with a poly-crystallization structure of a cube type before and after annealing, and that the annealing led to an increase range of a granular size. Semiconductors oxides were used to detect few concentrations a of the dangerous gases in the atmosphere, which depend on concept of the process of gases adsorption on the semiconductor oxide surface based on the defects size presence and a crystalline structure of a thin film, where oxygen atoms appear in the ions O_2 form on the thin film surface , that work to form the depletion layer and the barrier potential growth at the granular borders and it also represents a source of gas molecules hunting which are adsorbed on the surface.
2- The CdO thin film deposited through Successive Ionic Layer Adsorption and Reaction (SILAR) method on glass substrate shows better sensitivity in CO_2 atmosphere at temperature $400^{o}C$. The average grain size of CdO thin film has been calculated 19.3nm and 38.3 nm before and after annealing respectively .
3- This method for preparing CdO composite thin films is thought to be of low cost and capable of achieving reproducible and sensitive thin film gas sensors for detecting H_2S and CO_2gases.

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Table (1) : The structure properties of films before annealing.

2 θ degree	d(A°)	I(a.u)	FWHM	hkl	G.S(nm)
33.01940	2.7107630	100	0.45080	111	19.2071
38. 31051	2.3475800	63	0.4500	200	19.529
55.34011	3.3458	8	0.4510	200	19.112

Table (2): The structure properties of films after annealing 400°.

2θ degree	d(A°)	I(a.u)	FWHM	hkl	G.S(nm)
33.05200	2.70790	100	0.22380	111	38. 704
38.03385	2.34584	65	0.27240	200	32.236
55.85900	2.35980	6	0.15000	220	44.413

Table (3). Sign of resistance change (increase or decrease) to change in gas atmosphere[10].

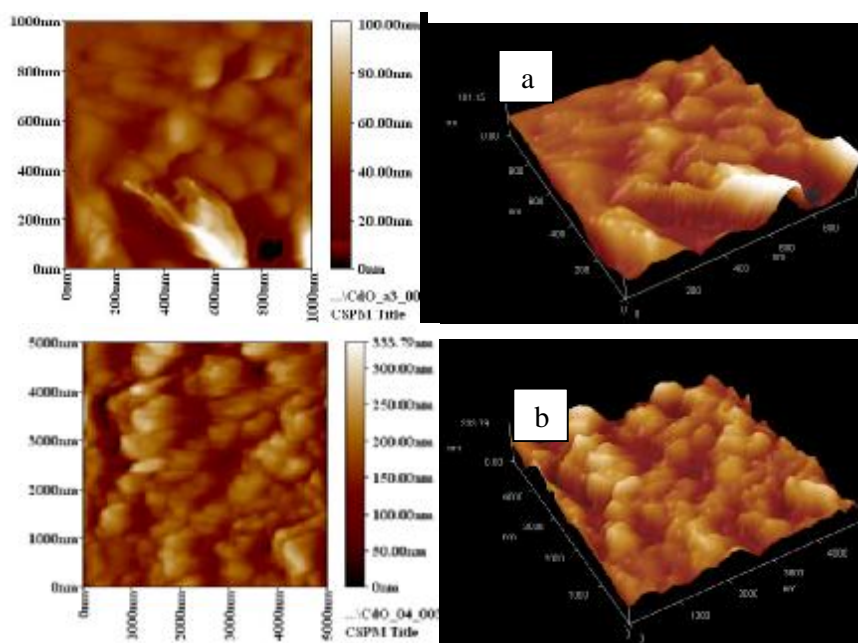| Classification	Oxidising Gases	Reducing Gases
p-type	Resistance decrease	Resistance increase
n-type	Resistance increase	Resistance decrease

Figure (1): SILAR system.

**Figure (2): (AFM) images Of CdO thin films, a: Before annealing,
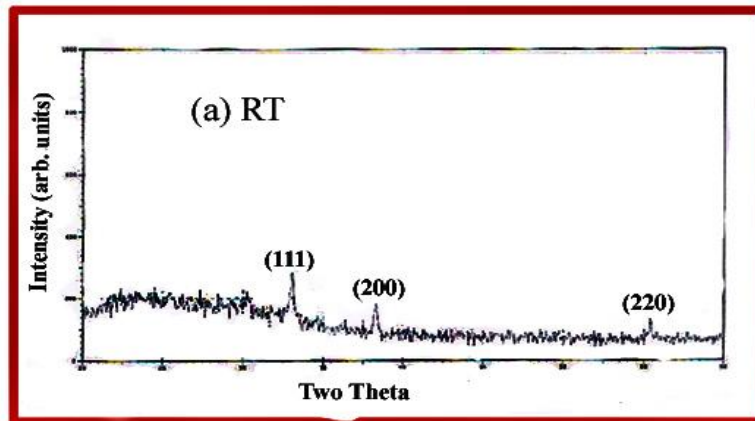b: After annealing.**

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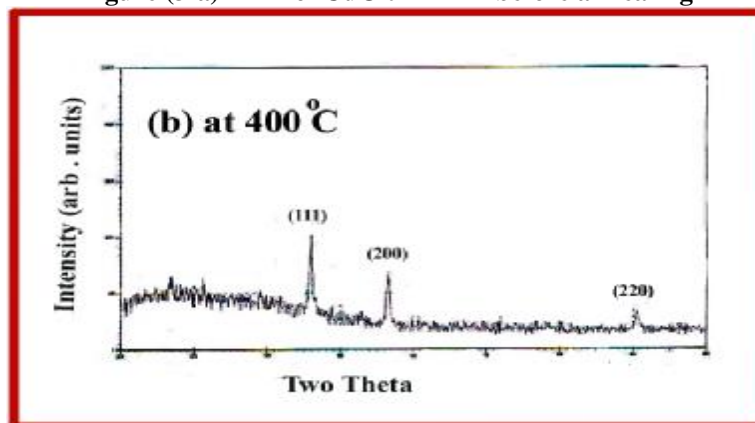**Figure (3-a) XRD of CdO thin film before annealing**

Figure (3-b): XRD of CdO thin film after 400°C annealing temp.
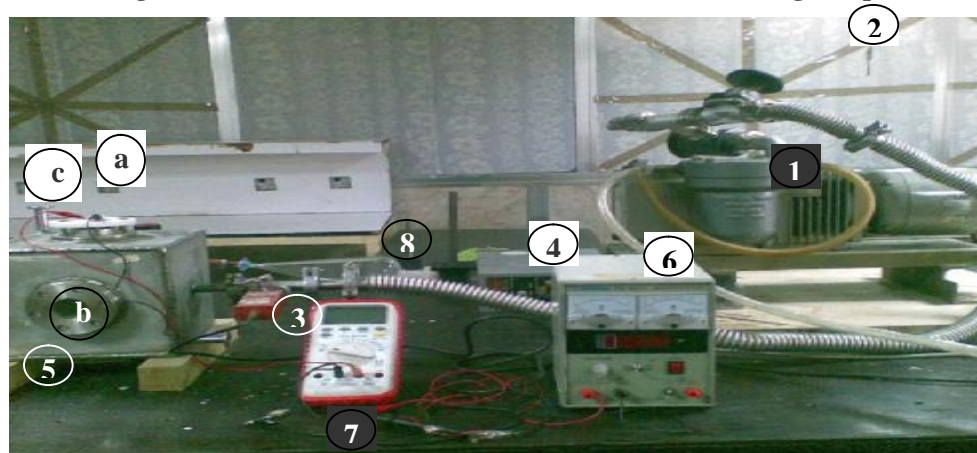

Figure (4): System of Gas Sensor 1- Rotary, 2- conductivity tubes, 3-measure of vacuum sensor,   4-reader of pressure, 5- Chamber contain (a- aperture for evacuation, and pump gas   b- Glass window c- Lead throw) 6- DC . Power supply ,   7- measure
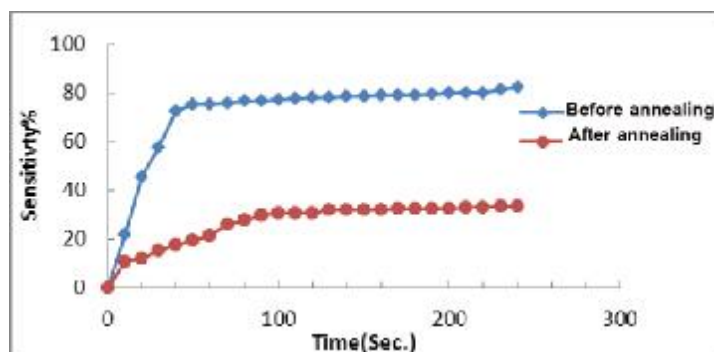
Figure (5-a): CdO thin film sensitivity to CO$_2$ gas after And before annealing.
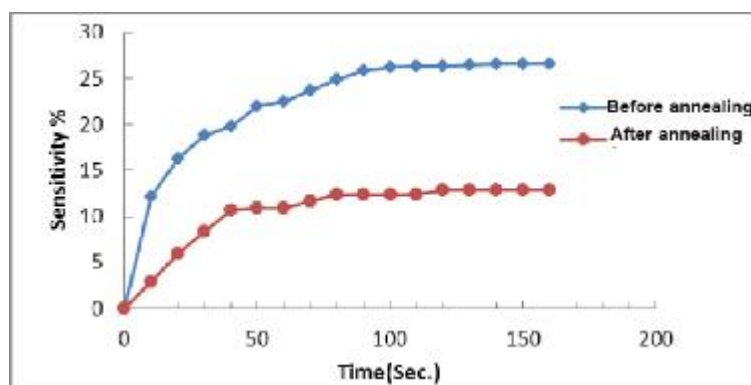

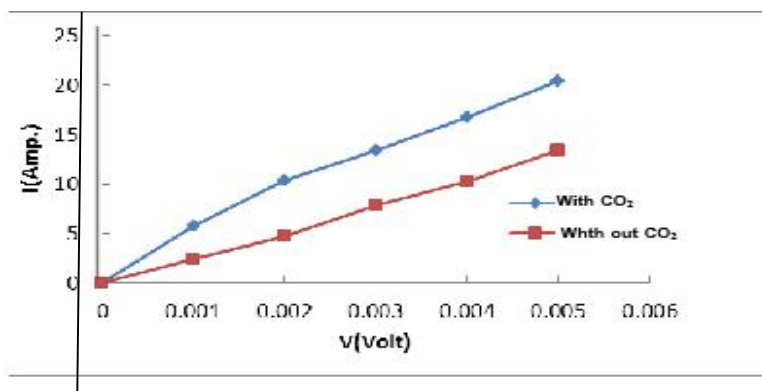**Figure (5-b): CdO thin film sensitivity to H$_2$S gas after and before annealing.**

Figure (6-a): Properties of the voltage - current in the absence and presence of CO$_2$ gas after and before annealing.
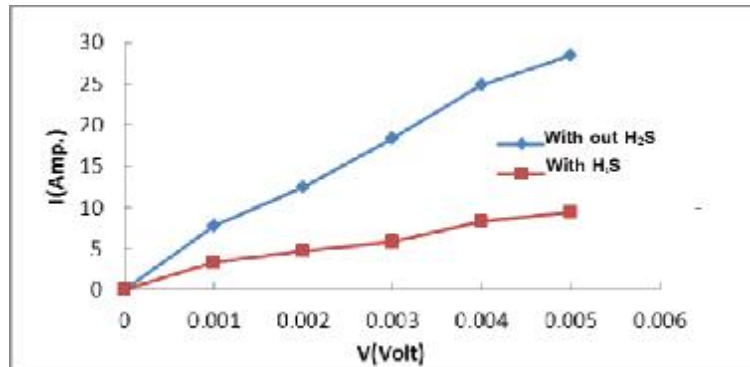
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Figure (6-b): Properties of the voltage - current in the absence
and presence of H$_2$S gas after and before annealing.