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Investigation of C-V and Gas Sensor Characteristics of $Cd_{1-x}Zn_xS$/n-Si Heterojunction Fabricated by Spray Pyrolysis Technique

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Abstract: In this research, Cd_{1-x} Zn_xS thin films were prepared by spray pyrolysis technique on silicon substrate at a temperature 360°C. The reverse bias capacitance for $Cd_{1-x}Zn_xS$/n-Si heterojunciton was measured as a function of bias voltage at frequency 1MHz . The capacitance decreases with increasing of reverse bias voltage and increase with vol. of (x), it increases from 334-577 pF with increase of the (x) while the depletion width decreasing with increasing (x). We noted that these heterojunction are abrupt and the value of built-in potential decreases from 0.7-0.27 V with increasing of the ZnS vol.%. The sensitivity as a function of operating temperature in the range 100-300°C for $Cd_{1-x}Zn_xS$ thin films were prepared by spray pyrolysis technique on glass substrate at 360°C. It is obvious that the sensitivity of all films increases with increasing of the operating temperature.

Key words: Spray pyrolysis, cadmium sulfide, zinc sulfide, C-V measurements, sensitivity, operating temperature

INTRODUCTION

CdS and ZnS are an p-type semiconductor materials. Because of its good adsorptive properties and chemical stability, it can be deposited onto glass, ceramics, oxides and substrate materials of other types. It has a high melting point and good transmission and does not easily react with oxygen and water vapor in the air, so, it has a high specific volume and good cycling performance. In addition, CdS and ZnS thin films are also used for film resistors, electric conversion films, heat reflective mirrors, Semiconductor-Insulator-Semiconductor (SIS) heterojunction structures and surface protection layers of glass. At present, its most common application is as the anode material of solar cells (Vidhya *et al*., 2010; Hassan and Ghazi, 2016a, b).Varieties of methods like dc reactive sputtering, chemical bath deposition (Lisco *et al*., 2015) activated reactive evaporation (Reddy *et al*., 1998) solution growth (Varkey and Fort, 1994) self-organized arrested precipitation (Khot *et al*., 2014) sol-gel (Supothina and Guire, 2000) and spray pyrolysis have been reported in the preparation of CdS and ZnS thin films (Hasan and Ghazi, 2016a, b). The electro optical properties of CdS make this material very convenient as a solar cell material. In attempts to improve the properties of CdS, it is being tried out to mix with other Sulfides. In this study, the focus is on capacity measurements effort films prepared as one of the important measurements which we can determine the type of heterojunction (abrupt or graded), built in voltage (V_{bi}), carrier concentration and finally the width of depletion layer.

A gas sensor can be defined as a device that informs about the composition of its ambient atmosphere. Particularly, upon interaction with chemical species (adsorption, chemical reaction and charge transfer) the physicochemical properties of the metal oxide sensitive layer (such as its mass, temperature and electrical resistance) reversibly change. These changes are translated into an electrical signal such as frequency, current, voltage or conductance which is then read out and subjected to further data treatment and processing (Cattrall, 1997). Many metal oxides are suitable for detecting explosive, reducing or oxidizing gases by the variation in the electric conductivity measurements. Response time is the time interval over which the resistance of the sensor material attains a fixed percentage (usually 90%) of final value when the sensor is exposed to the full scale concentration of the gas. While recovery time is the time interval above which sensor resistance reduced to 10% of the saturation rate when the target gas is switched off and the sensor sited in artificial (or reference) (Mishra *et al*., 2009).

MATERIALS AND METHODS

A simple spray pyrolysis experimental setup was employed to prepare mixed $Cd_{1-x}Zn_xS$ thin films on silicon substrate (n-type (111) orientation and (1×1 cm^2) diameter) at temperature of 360°C. The difference in ZnS vol..% (x) was achieved by mixing the aqueous solutions of 0.1 M of cadmium and znic acetates to pre-determined volume ratio. The value of (x) in the solution was varied from 0-1 (x = 0, 0.2, 0.4, 0.6, 0.8 and 1). The mixed solutions which

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were then diluted with water formed the final spray solution and a total volume of 25 mL was used in each deposition. The deposition parameters such as spray nozzle-substrate distance (30 cm), spray time (4sec) and the spray interval (1 min) were kept constant. The carrier gas (filtered compressed air) flow rate was maintained at 6 l/min at a pressure of 6.5×10^4 Nm^{-2}. The capacitance of the heterojunction was measured as a function of the reverse bias voltage in the range 0-1 V with fixed frequency of 1 MHz by using WAYNE KERR 6500 P 1 multi-frequency LRC meter.

The sensing measurements were carried out by measuring the variation in resistivity resulting from exposing the thin film surface to the gas (NO_2), the temperature was recorded by a k-type thermocouple (XB 9208B). The bias voltage was supplied by (FARNELL E350) power supply.

RESULTS AND DISCUSSION

C-V measurement: The measurement of the junction capacitance as a function of reverse bias is often used as a powerful experimental technique for the analysis of the depletion region's potential and the charge distribution in a heterojunction. The variation of capacitance as a function of reverse bias voltage in the range of 0-1 V and at frequency equal to 1MHz has been studied for $Cd_{1-x}Zn_x$ S/n-Si heterojunction at different vol.% of (x) as shown in Fig. 1.

It is clear that the capacitance decreases with increasing of the reverse bias voltage and the decreasing was non-linear which demonstrates that the samples has an obvious space charge region and increase with increasing of vol. % of (x). Such behavior is attributed to the decreasing in the depletion region width which leads to decrease of the value of a built in voltage. An improvement of the capacitance of zero bias voltage (C_o) with the increasing of vol.% of ZnS could be shown in Table 1. This behavior attributed to

Table 1: The variation of the C_o, W, V_{bi} and N_D for $Cd_{1-x}Zn_xS$/n-Si hetrojunction at different vol.% of (x)

Sample	C_o (pF)	W (μm)	V_{bi} (V)	N_D (cm^{-3})
CdS_{pure}	334	0.05915	0.70	1.34×10^{10}
$CdS_{0.8}ZnS_{0.2}$	384	0.03817	0.50	2.12×10^{10}
$CdS_{0.6}ZnS_{0.4}$	410	0.02465	0.42	5.65×10^{11}
$CdS_{0.4}ZnS_{0.6}$	478	0.02258	0.35	1.45×10^{14}
$CdS_{0.2}ZnS_{0.8}$	532	0.01517	0.30	2.89×10^{16}
ZnS_{pure}	577	0.01227	0.27	2.76×10^{18}

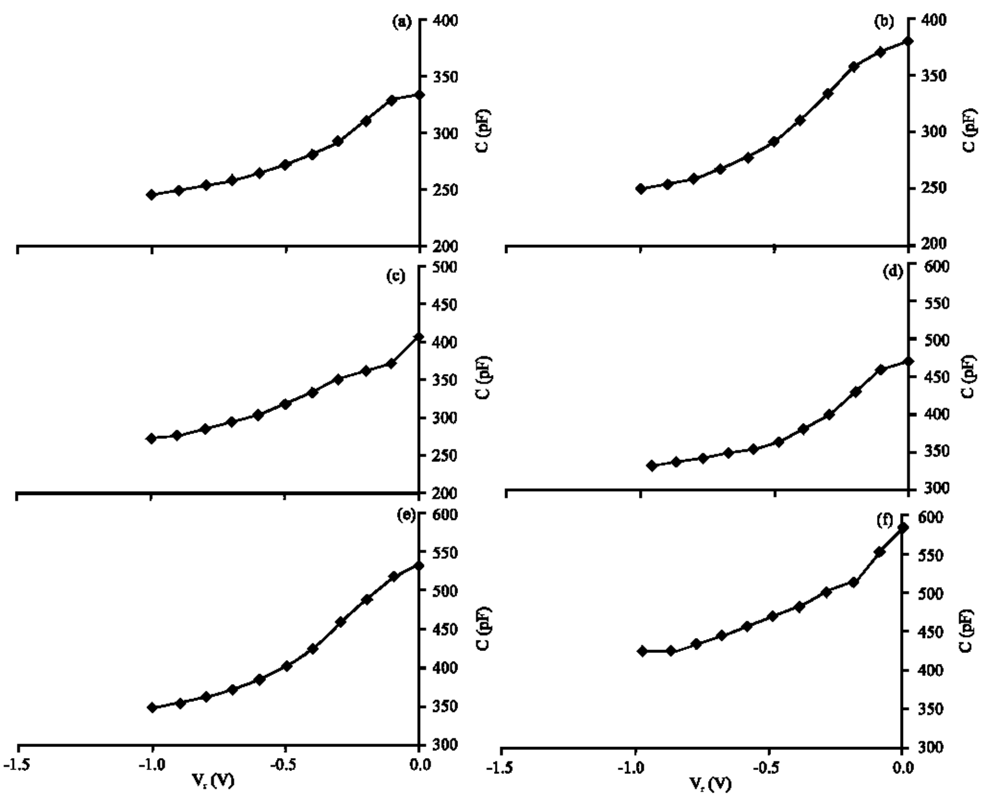

Fig. 1: The variation of capacitance as a function of reverse bias voltage for $Cd_{1-x}Zn_xS$ /n-Si hetrojunction at different vol.% of (x): a) CdS pure; b) 0.27 ZnS 0.8 CdS; c) 0.4 Zns 0.6 CdS; d) 0.6 ZnS 0.4 CdS; e) 0.8 ZnS 0.2 CdS and f) ZnS pure

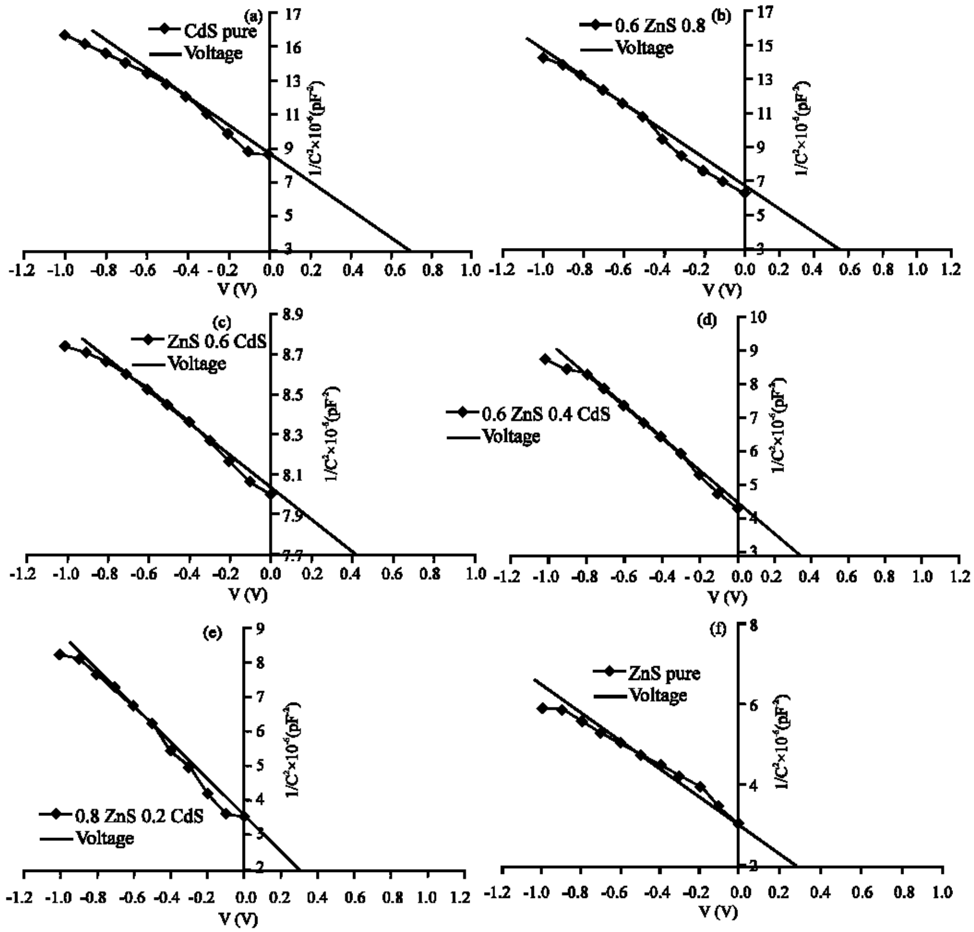

Fig. 2: The variation of $1/C^2$ as a function of reverse bias voltage for $Cd_{1-x}Zn_xS$/n-Si hetrojunction at different Vol.% of (x) and its built-in voltages: a) CdS pure; b) 0.27nS 0.8 CdS; c) ZnS 0.6 CdS; d) 0.6 ZnS 0.4 CdS; e) 0.8 ZnS 0.2 CdS and f) ZnS pure

the surface states which leads to a decrease in the depletion layer and an increasing of the capacitance which is due to the increasing in the carrier concentration. The width of depletion layer can be calculated using Eq:

$$W = \frac{\varepsilon_s A_j}{C_o} \quad (1)$$

Where:

- C_o = The capacitance at zero biasing voltage
- A_j = The effective area of the junction
- ϵ_s = The permittivity of semiconductor calculated from the following Eq. 2 (Piprek, 2003)

$$\varepsilon_s = \frac{(\varepsilon_1 \varepsilon_2)}{(\varepsilon_1 + \varepsilon_2)} \quad (2)$$

where, ϵ_1 and ϵ_2 is the semiconductor permittivity of the two semiconductor materials. The inverse capacitance square is plotted against applying bias voltage for $Cd_{1-x}Zn_xS$/n-Si heterojunction at different vol.% of (x) as shown in Fig. 2. The plots revealed straight line relationship which means that the junction was of an abrupt type .

The interception of the straight line with the voltage axis at ($1/C^2$ = 0), represents the built-in voltage (Soleimanpour *et al*., 2013). We observed from Table 1 that the built-in voltage decreases with increasing of vol.% of ZnS.

From Fig. 2, we have deduced the carrier's concentration of the abrupt $Cd_{1-x}Zn_xS$/n-Si heterojunction at different vol.% of (x), from the slope of the straight line by using Eq. 3 (Sze and Ng, 2006):

$$C^2 = \frac{qN_D N_A \varepsilon_1 \varepsilon_2}{2(N_A \varepsilon_1 + N_D \varepsilon_2)} \cdot \frac{1}{(V_{bi} - V)} \quad (3)$$

Where:

N_D = The donor density in p-type thin films
N_A = The acceptor density in n-Si substrate
ε_1 and ε_2 = The dielectric constants of p-type and n-Si, respectively
V_{bi} = The built-in junction potential
V = The applied voltage

Sensing measurement: Sensitivity can be defined as response of a gas sensor per unit change in the gas concentration in the case of resistive gas sensors is defined as the relative change in resistance or conductivity of the thin film. It is the ratio of the change in the resistance (approximately to 90%) of the thin film in air to the change in resistance in particular gas atmosphere. The sensitivity is given by Miller *et al.* (2006):

$$\text{Sensitivity} = \frac{\Delta R}{R_a} = \left|\frac{R_a - R_g}{R_a}\right| \times 100\% \quad (4)$$

$$\text{Sensitivity} = \frac{\Delta R}{R_g} = \left|\frac{R_g - R_a}{R_g}\right| \times 100\% \quad (5)$$

Where:

R_a = Resistance of the film sensor in air presence
R_g = Resistance of the film sensor in a gas presence

Although, it can be calculated from current as in the relation (Garde, 2010):

$$S = \frac{I_g - I_a}{I_a} \times 100\% \quad (6)$$

Where:

I_a = The sample current measured at ambient environment
I_g = Under the test gas. The sensitivity is highly dependent on film thickness, operating temperature, presence of additives and crystallite size

Figure 3 shows that sensitivity as a function of operating temperature in the range 100-300°C for $Cd_{1-x}Zn_xS$ thin films which are deposited on silicon substrates at an air mixing ratio the bias voltage of 5 V were applied on all the samples, Fig. 3 is obvious that the sensitivity of all films increases with increasing of the operating temperature. This is attributed to increase in the rate of surface reaction of the target gas. The optimal temperature that have maximum values of temperature is 200°C for all films, at this temperature the activation energy may be enough to complete the chemical reaction. We can note that the sensitivity of films for gases decreases with increases the concentration of ZnS because the sensitivity depends on grain size and grain boundary. The distance between the grains are large and including the interaction between oxygen absorbed and gases occurs when any grain boundary that will decrease interaction and decreasing sensitivity.

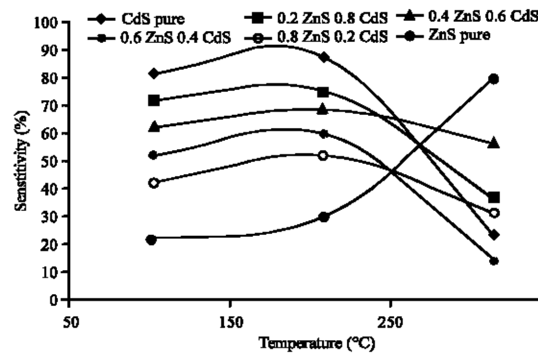

Fig. 3: The variation of sensitivity with the operating temperature of the $Cd_{1-x}Zn_xS$ thin films with different vol.% of (x) for mixing ratio (NO_2 gas)

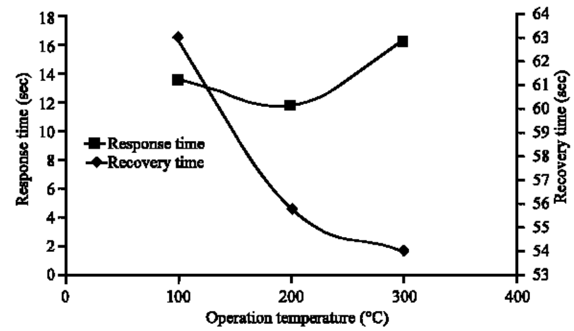

Fig. 4: The variation of response time and recovery time with operating temperature for (CdS_{pure}) sensor

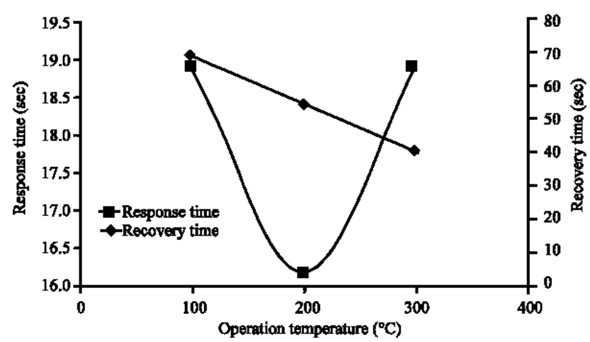

Fig. 5: The variation of response time and recovery time with operating temperature for ($CdS_{0.8}$ $ZnS_{0.2}$) sensor

Figure 4-9 show the relation between the response time and the recovery time with the operating temperature of the $Cd_{1-x}Zn_xS$ thin films for NO_2 gas and bias voltage

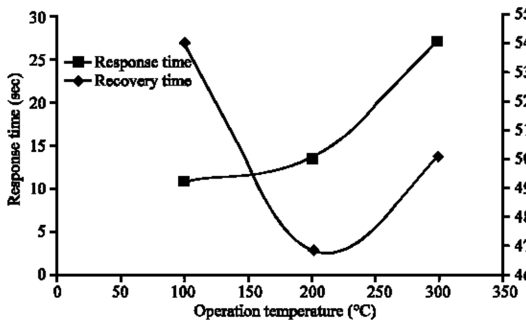

Fig. 6: The variation of response time and recovery time with operating temperature for ($CdS_{0.6}$ $ZnS_{0.4}$) sensor

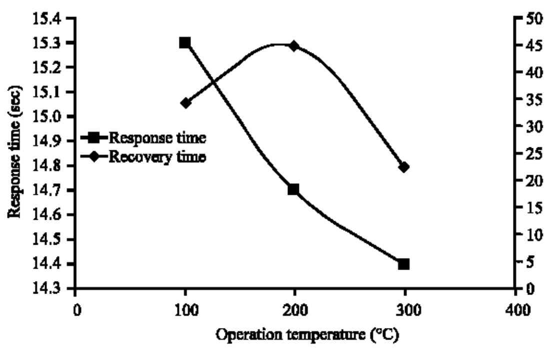

Fig. 7: The variation of response time and recovery time with operating temperature for ($CdS_{0.4}$ $ZnS_{0.6}$) sensor

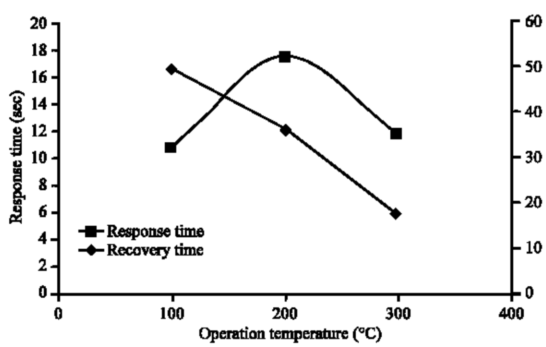

Fig. 8: The variation of response time and recovery time with operating temperature for ($CdS_{0.2}$ $ZnS_{0.8}$) sensor

Table 2: The response time and the recovery time with the operating temperature of $Cd_{1-x}Zn_xS$ thin films with different vol.% of (x)

Sample	Response time at 200°C	Recovery time at 200°C
CdS_{pure}	11.7	55.8
$CdS_{0.8}$ $ZnS_{0.2}$	16.2	54.9
$CdS_{0.6}$ $ZnS_{0.4}$	13.5	46.8
$CdS_{0.4}$ $ZnS_{0.6}$	14.7	44.8
$CdS_{0.2}$ $ZnS_{0.8}$	17.3	36.0
ZnS_{pure}	18.0	29.0

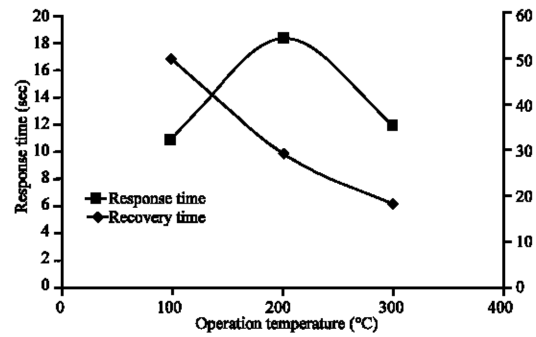

Fig. 9: The variation of response time and recovery time with operating temperature for (ZnS_{pure}) sensor

5 V. From Table 2 note that the increasing vol.% of (ZnS) due to increase in response time and decrease in recovered time at optimal temperature (200°C).

CONCLUSION

$Cd_{1-x}Zn_xS$ mixed films were deposited on silicon and glass substrates at 360°C and studied as a function of ZnS vol.%, x ($0 \leq x \leq 1$). The C-V measurements of this film show that the capacitance decrease with increasing of the reverse bias voltage and the decreasing was non-linear, the decreasing was sharply. The depletion width decreasing with increasing (x) which is due to the increasing in the carrier concentration which leads to a increasing of the capacitance. The buil in voltage decreases with increasing of vol.% of ZnS.

Gas sensor measurements for $Cd_{1-x}Zn_xS$ films that deposited on glass substrates obvious that the sensitivity of all films increases with increasing of the operating temperature. The optimal temperature that have maximum values of temperature is 200°C for all films, also, sensitivity of films for gases decreases with increases the concentration of ZnS, response time and the recovery time with the operating temperature also found.

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