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Enhancement the Sensitivity of Zinc Sulfide Nanostructure Against NO_2 Toxic Gas by Loading Graphene

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Abstract
Nanocrystal-ZnS-loaded graphene was synthesized by a facile co-precipitation route. The Graphene was affected on the characterization of ZnS which has been investigated. XRD results reveal that ZnS has a cubic system while the hexagonal structure has been observed by loading graphene during preparation ZnS. D.c-conductivity proves that ZnS and ZnS/Gr have semiconductor behavior. The sensing properties of ZnS/Gr against NO_2 gas were investigated as a function of operating temperature and time under optimal condition. The sensitivity, response time and recovery time were calculated with different operating temperatures (100, 150, 200)^{o}C.

Keywords: ZnS, Graphene, Nanocrystals, Structural and Electrical Properties, Gas sensor.

تحسين حساسية كبريتيد الزنك ضد الغاز السامNO_2 بواسطة اضافة الكرافين

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الخلاصة
تم تحضير كبريتيد الزنك مع الكرافين بواسطة الترسيب الكيميائي. اكدت دراسة حيود الأشعة السينية (XRD) تكون ZnS بطوره المكعب وبعد اضافه الكرافين تم تكوين الطور السداسي بالاضافه الى المكعب . اكدت نتائج التوصيلية المستمرة سلوك شبه موصل لكل من الكرافين و كبريتد الزنك. تم دراسة خصائص الاستشعار (ZnS / Gr) ضد غاز NO_2 كدالة بين درجة حرارة التشغيل والوقت. تم حساب التحسسية وزمن الصعود والنزول مع درجات حرارة مختلفة.

1. Introduction

Nano particle analysis is presently a vicinity of the intense research project, in a large sort of potential applications in medical specialty, optical, and electronic fields. Nano particles have a scientific interest as they're effectively a bridge between bulk materials and atomic or molecular structures. The properties of material modification as their volume approaches the nano scale [1]. The layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness is called thin film. Zinc sulfide (ZnS) is extremely vital semiconductor material that belongs to the cluster of II–VI wide band gap semiconductors. ZnS exists in 2 crystallographic forms having cubic (zinc blende) or hexagonal (wurtzite) crystal structure. ZnS has a direct transition sort band structure. The cubic type features a band gap of 3.72eV, whereas the band gap of hexagonal type is higher being 3.77eV [2,3]. Graphene (Gr) consists of one atomic layer of sp^2 hybridized carbon atoms that outcome in a hexagonal lattice [4]. Gr has revolutionized the scientific boundary in nano science,

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engineering technology and condensed matter physics because of its essential and extrinsic physical and chemical properties [5].

Gas sensor devices are based on the variation in conductivity by interaction with gas molecules. This property depends on the operating temperature. Sensors are prepared to detect harmful or poisonous gases require to be accurate, sensitive and rapid. Gas sensor is a chemical sensor designed to detect matter in its gaseous phase. Gas sensors are serious for detecting and/or monitoring hazardous gases that subsist in small concentrations. Recent studies have converged on detecting gases such as CO, CO_2, SO_2, O_3, H_2 and NH_3 in the atmosphere [6].

In this work, the sensing properties of ZnS will be improved by loading Graphene to detect NO2 toxic gas.

2. Experimental Details

2.1 synthesis of ZnS and ZnS/Gr

ZnS nanoparticles were synthesized by co-precipitation chemical method**.** A stock solution of Zn^{2+} was prepared by adding 0.1 M of $Zn(NO_3)_2.6H_2O$ into 50mL of distilled water. A stock solution of S^{2-} was prepared by adding 0.2 M of Na_2S into 50mL of distilled water. Then put the first solution on magnetic stirrer at temperature of 80^oC for 1 hr, then the second solution is added drop wise and the whole solution is stirred for 30 min. Milky precipitation will be observed that indicates ZnS formation, then filtered and washed several times using distilled water, ethanol and finally by acetone then dried using oven at 100 ^oC for 5 hr. For preparing ZnS/Gr, graphene with different graphene volume ratios (10, 20) % was added to the stock solution of Zn^{2+} and stirred together at 80^oC for 1 hr, then solution of S^{2-} is added drop wise and the whole solution is stirred for 30 min. Grey color precipitation will be observed that indicates ZnS/Gr formation, then filtered and washed several times using distilled water, ethanol and finally by acetone then dried using oven at 100 ^oC for 5 hr.

2.2 Gas sensor measuring

The testing system for the proposed gas sensor consists of cylindrical stainless steel test chamber with a diameter of 18cm and height of 8cm. It has an inlet for allowing the tested gas to flow in and an air admittance valve to allow the flow of atmospheric air after evacuation. A multi pin feed through at the base of the chamber allows the electrical connections to be established to the heater, K-type thermocouple and sensor electrodes, as shown in the Figure-1.

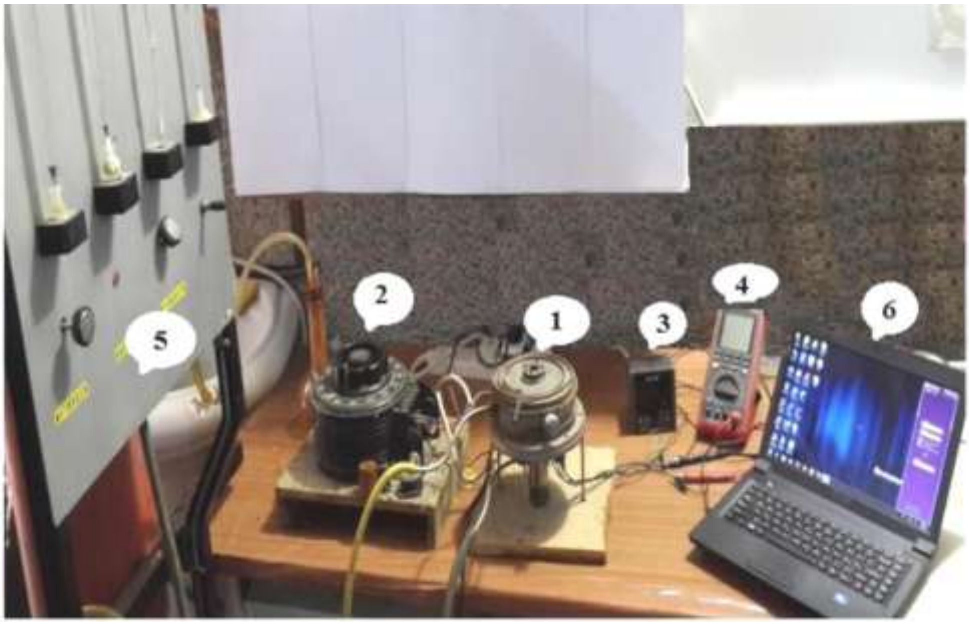


Figure 1-Gas Sensing Measurement System (1) system chamber, (2) variac, (3) reader, (4) multimeter, (5) gauge of gas, (6) laptop to connect with multimeter.

2.2.1 Steps of Gas Sensor Testing

The test chamber is opened and the gas sensor is placed on the heater. The electrical connections between the digital multimeter pins and the sensor sample were done utilizing conductive aluminum sheet, then test chamber is closed. Rotary pump was used to evacuate the test chamber for about 1 mbar. The gas sensor is set to the desired operating temperature using a temperature controller. The resistance variation is measured utilizing the PC- interfaced digital multimeter. The above measurements are repeated for another operating temperature.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis Results

Figure-2 shows the x-ray diffraction of the powder ZnS/Gr at different volume ratios of Gr which are 0, 10 and 20 %. From Figure-(2a) it has been observed that pure ZnS has cubic zinc blende structure with comparison to the standard card ICDPDS (96**-110-1051)**. The three main peaks are observed in the diffractrogram at 2Θ equal 28.3549^o, 47.5354^o, 56.195^o corresponds to (111), (220) and (311) planes respectively. After addition of graphene which are (10, 20) % as shown in Figure-(2b and c), new phase for ZnS appeared that is hexagonal structure with comparison to the standard card ASTM (I2-688) because Gr sheet has Hexagon structure (honeycomb lattice), so the graphene sheet becomes as a template to ZnS growth on this sheet. The data of peaks positions and miller indices of the diffracted planes, FWHM and crystallite size are shown in Table-1.

The interplaner spacing **d** is calculated using the relation [7]

$$d_{hkl} = n\lambda / 2\sin\Theta$$

where λ is the X-ray wavelength (here λ = 1.54184 Å) and θ is the Bragg angle. The average crystallite size is calculated from Scherer formula

$$D=0.9\lambda/(\beta \cos\theta)$$

where β is the full-width at half-maximum (FWHM) measured in radian.

3.2 Electrical properties

3.2.1 DC-measurement of ZnS/Gr

The dc-conductivity ($\sigma_{d.c}$) for pure ZnS and ZnS/Gr at different volume ratios of Gr is studied as a function of temperature with the range of 303- 473 K as shown in Figures-3. The activation energy increases with increasing graphene, That's mean graphene improves the structure and canceled the defects inside the energy band gap. The value of activation energy for pure ZnS and ZnS/Gr are shown in Table-2.

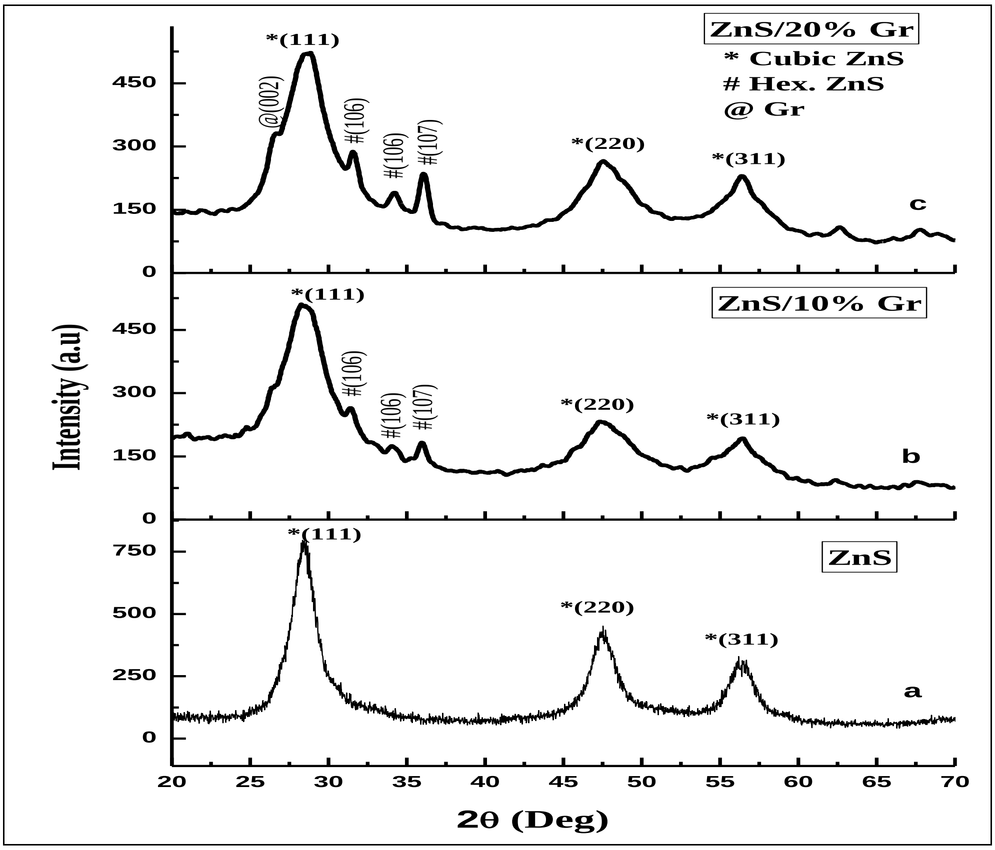


Figure 2-XRD patterns for ZnS/Gr at different volume ratios of Gr; a) 0%, b)10%, c) 20%

Table 1-Structural Parameters of ZnS/Gr which are diffraction angle (2θ), (hkl), d-spacing, and FWHM

% Gr	2Θ (deg)	Interplaner spacing d (Å)	FWHM (Rad)	Plane (hkl)	D Crystallite size (nm)	Phase	Card no.
0	28.3549	3.147897	0.043611	111	3.28	Cubic	96-110-1051
	47.5354	1.912953	0.034889	220	4.34	Cubic	5-0566
	56.1950	1.63712	0.027911	311	5.63	Cubic	96-110-1051
10	28.4358	3.138925	0.066289	111	2.41	Cubic	96-110-1051
	31.4505	2.844723	0.027911	106	5.16	Hex	I2-688
	34.0808	2.631126	0.020933	106	6.96	Hex	I2-688
	35.9826	2.496503	0.013956	107	10.45	Hex	I2-688
	47.4343	1.916758	0.087222	220	1.73	Cubic	5-0566
	56.3973	1.631577	0.095944	311	2.26	Cubic	96-110-1051
20	26.6351	3.34746	0.024422	002	5.83	Gr	23-64
	28.6179	3.11987	0.052333	111	2.73	cubic	96-110-1051
	31.5314	2.837394	0.020933	106	6.91	Hex	I2-688
	34.1819	2.623962	0.024422	106	5.94	Hex	I2-688
	36.0635	2.490856	0.017444	107	8.36	Hex	I2-688
	47.5354	1.912953	0.069778	220	2.17	Cubic	5-0566
	56.3367	1.633305	0.055822	311	2.82	Cubic	96-110-1051
	62.6492	1.482595	0.022678	227	7.16	Gr	22-1069
	67.7479	1.383312	0.017444	416, 228	7.97	Gr	22-1069

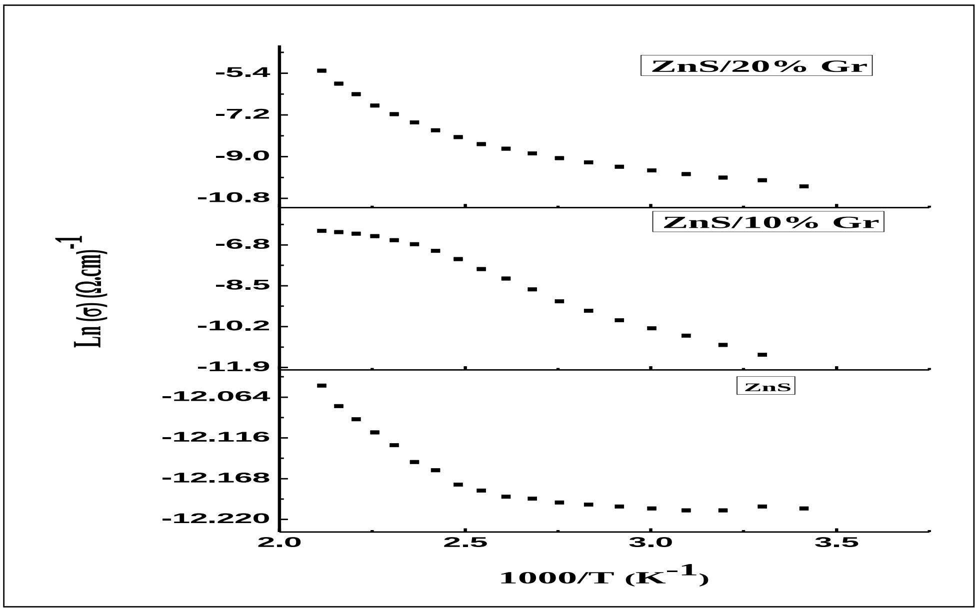


Figure 3-Temperature dependence of D.C. conductivity of the deposited ZnS/Gr thin films

Table 2- D.C. Conductivity Parameters for pure ZnS and ZnS with different volume ratio (0, 10, 20)% of Gr

% Gr	$E_{a\,1}$ (eV)	$E_{a\,2}$ (eV)
0	**0.001**	**0.026**
10	**0.088**	**0.553**
20	**0.167**	**0.623**

3.3 Gas Sensing Measurement

3.3.1 Measurement of NO_2 Gas

Thin films specimens are examined for gas sensing using NO_2 at different operating temperatures. The sensitivity factor (S%) is calculating by equation [8]

$S=|(R_g-R_a) / R_a|*100\%$

where S is the sensitivity, R_a and R_g are the electrical resistance of the film in the air and electrical resistance of the film in the presence of gas, respectively**.** Figure-4 shows the variation of resistance as a function of time with on/off gas valve for pure ZnS.

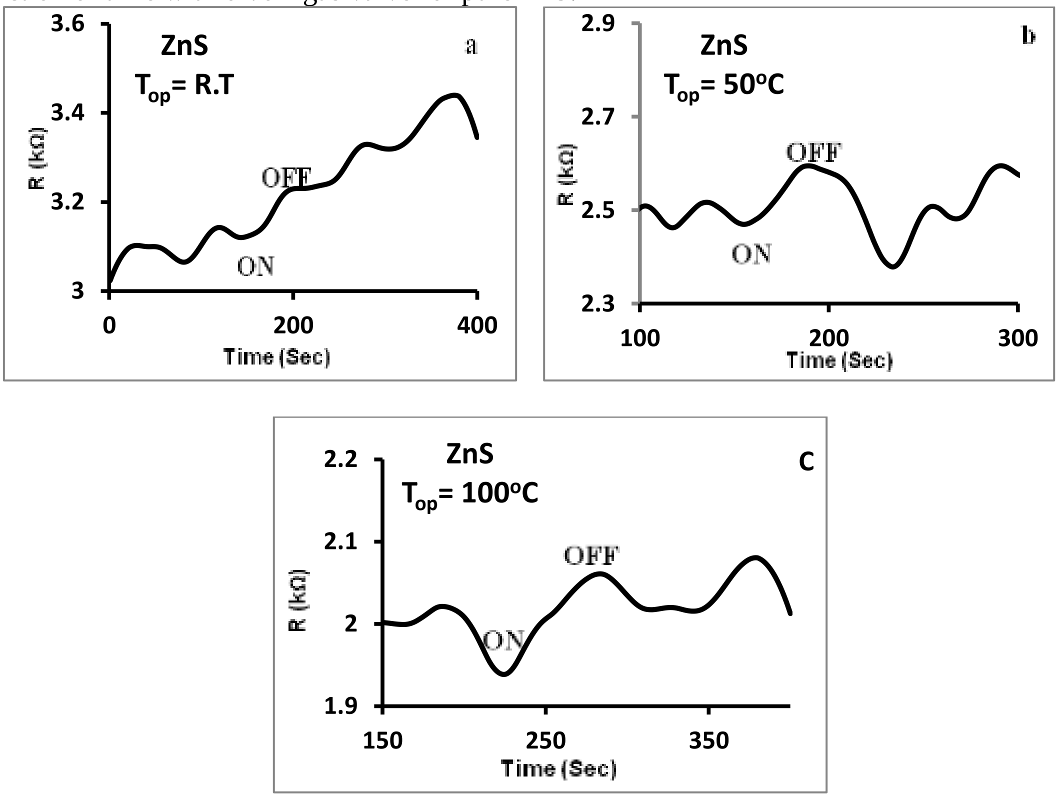


Figure 4-The variation of resistance with time for pure ZnS against NO_2 gas at operating temperatures: a) R.T c) 50^{o}C and b) 100^{o}C.

Figures-(5 and 6) show the variation of resistance as a function of time with on/off gas valve. Loading Gr with different volume ratios which are 10%, 20% to ZnS that make thin films being sensitive for input gas. The increasing sensitivity after addition graphene to ZnS. Graphene nanosheets have large surface area and ZnS nanoparticles well dispersed in Gr surface area that make these nanoparticles responses to input gas. The ZnS/graphene nanostructure exhibits improved sensing properties and compared to pure ZnS due to the incorporation of graphene which acts both as a buffer to alleviate the volume changes and as a separator to refrain the aggregating of the particles. Furthermore, the introduced graphene offers a conducting channel for ZnS and increases the specific surface area, enhancing the gas detecting. The values of Sensitivity at different temperatures for ZnS and ZnS/Gr are tabulated in Table-3.

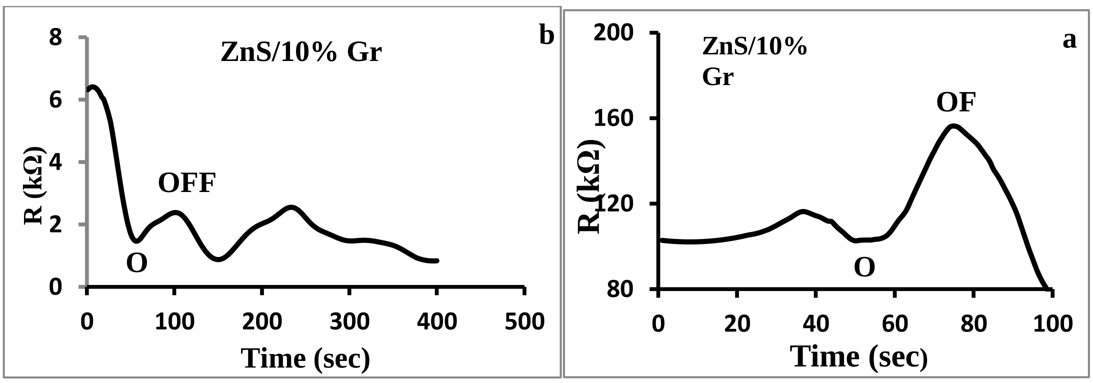


Figure 5- The variation of resistance with time for ZnS with 10% Gr against NO_2 gas at operating temperatures: a) 100^{o}C and b) 150^{o}C

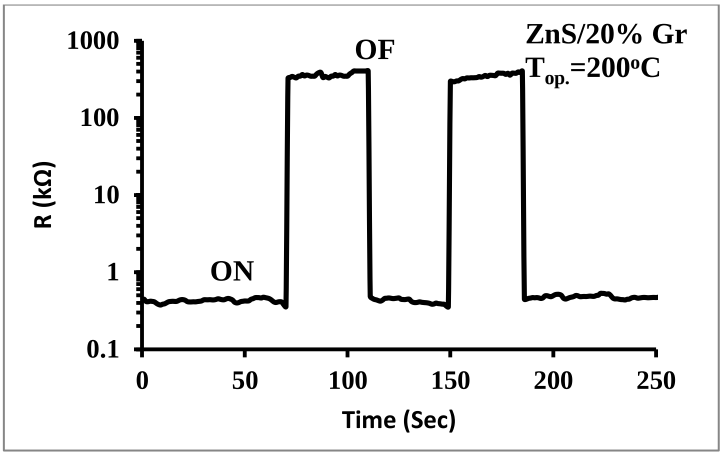


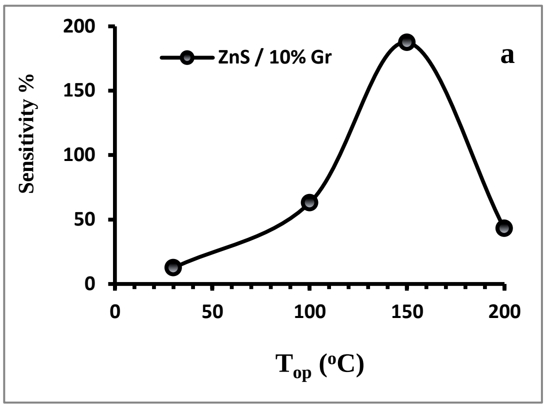
Figure 6-The variation of resistance with time for ZnS with 20% Gr against NO_2 gas at 200°C operating temperatures

Table 3-Sensitivity% for pure ZnS, Gr and ZnS/Gr with different volume ratios (0, 10, 20) % of Gr against NO_2 gas

Sample	Sensitivity % at				
	30°C	50°C	100 °C	150 °C	200 °C
ZnS	0.320513	8.695652	1.99005	- - -	- - -
ZnS / 10% Gr	12.5	- - -	63	187.5	43.03797
ZnS / 20% Gr	7.692308	14.51613	15	25	75069.3
Gr	9.090909	11.11111	4.347826	- - -	- - -

3.3.2 Operating Temperature

Maximum value for sensitivity is observed to be shifted to higher operating temperatures with increasing graphene contents as shown in Figure-7, so increasing graphene in the film need higher temperature in response to input gas.



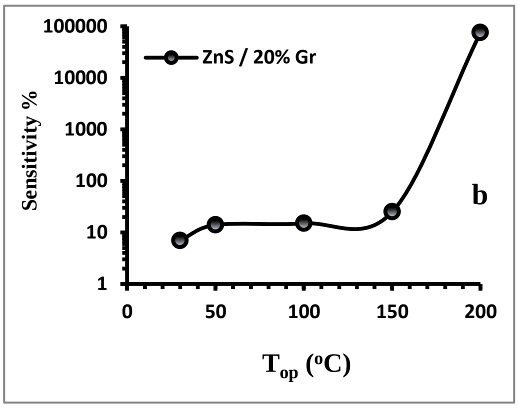


Figure 7-The variation of sensitivity with operating temperature for ZnS / Gr system against NO_2 gas with different Gr volume ratios; a) 10% Gr and b) 20% Gr

3.3.3 Response and recovery times

Fabricated gas sensors have fast response as shown in Table-4. For ZnS / 20% Gr gas sensor at 200°C, there is square pulse with fast response and recovery times which is 0.8s and 0.7s respectively. Also, its sensitivity is greater than 75000 %. So this sample is challenged to work as fast response NO_2 gas sensor.

Table 4-Response and Recovery times for pure ZnS, Gr and ZnS/Gr with different volume ratios (10, 20) % of Gr against NO_2 gas

Sample	**Res. time (s) / Rec. time (s) at**				
	30°C	**50°C**	**100 °C**	**150 °C**	**200 °C**
ZnS	**15 / 18**	**10 / 11**	**13 / 19**	**x / x**	**x / x**
ZnS / 10% Gr	**15 / 21**	**16 / 10**	**8 / 7**	**30 / 27**	**34 / 15**
ZnS / 20% Gr	**10 / 14**	**22 / 16**	**7 / 21**	**16 / 22**	**0.7 / 0.8**
Gr	**14 / 16**	**14 / 28**	**8 / 17**	**x / x**	**x / x**

Conclusions

The pure ZnS and ZnS/Gr have been prepared successfully by a novel method using chemical co-precipitation. X-ray diffraction patterns proved that crystalline system for ZnS is changed from cubic zinc blende structure to hexagonal structure after graphene addition. For gas sensor device, the maximum sensitivity to NO_2 gas was for ZnS/10%Gr of 187.5% at operating temperatures 150°C and ZnS/20%Gr of 75069.3 % at operating temperatures 200 °C.

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