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ENHANCEMENT OF GAS SENSITIVITY FOR ZNO:SiO₂ THIN FILMS PREPARED BY PULSED LASER DEPOSITION TECHNIQUE

Zuheer. N. MAJEED¹, Abdul-Majeed.E. AL-SAMARAI², and Ghuson. H.MOHAMMED³

Abstract

In this paper, ZnO was mixing by various concentrations of SiO₂ (5,10,15) w%. The mixture was deposited on glass substrate by Pulsed Laser Deposition (PLD) technique under high vacuum (10⁻² Torr) using constant prepared conditions such as: Nd:YAG wavelength 1064nm, Laser Pulse energy (100-1000) mJ, Pulse duration=10ns and Repetition frequency 6 Hz. The thickness of the prepared films was about (250) nm. The structure of the thin films was examined by using (XRD) analysis. The results showed that there was a decrease in the peaks of zinc oxide with gradual peaks of the zinc silicate compound at angles 2 θ (25,38,49,66) due to increase in silicon oxide concentrations rates. The optical properties of thin films include the spectral absorption and transmission recording were studied at the wavelength range (200-1100) nm. Some of the optical constants, including absorption coefficient, and energy gap are calculated. The results show that an increases in the absorption coefficient after and decreases in the energy gap after the doping with SiO₂ particles. In this paper we studied the effect of SiO₂ ratio on the sensitivity of (NO₂) gas sensor. It is found that the increase in the sensitivity after doping process with SiO₂ particles.

Keywords: Pulsed Laser Deposited, Structural Properties, Optical Properties, Gas Sensor.

¹ Tikrit University, Iraq, Zuheeralbayaty2017@gmail.com

² Tikrit University, Iraq, majeedsa2004@gmail.com

³ Baghdad University, Iraq, ghuson1975@gmail.com

1-Introduction:

Zn₂SiO₄ (willemite) is a long known material which still retains its place among the best inorganic phosphors [1]. Having different crystal phases and being sensitive to doping by transition metals and rare earths, it can emit light at different wavelengths in the visible and near IR range. In the past years there were successful attempts to synthesize nano-phase of Zn₂SiO₄ using both solid state techniques [2,3] and wet chemistry aimed at the development of novel low voltage phosphors having high efficiency and chemical stability. One of the advanced methods for solid state synthesis of nanoparticles is ion implantation with subsequent annealing, which allows creation of nanoparticle-host matrix composites with high chemical stability. Many research groups have studied the ZnO nanostructure formation in SiO₂ matrices using ion beam synthesis and thermal oxidation [4].

2- Experiment part:

Zinc oxide powder and silicon oxide powder with purity of 99.999% were mixed according to concentration of (5,10,15)% wt. The proportions of the powders were weighed using a sensitive electronic balance Sensitive 10-4. The powders were then mixed into mixing machine Type of Spex mixer for(5) minutes and then the powders were blended by hydraulic press. Then the tablets were sintering in a tube electric furnace at a temperature of (1000°C) for two hours and after the process of sintering left the tablets to cool to room temperature. The process of deposition was accomplished within a vacuum chamber in the laser system under pressure 10⁻³ torr with laser energy 1000 mJ using (Nd-Yag) laser, which is the appropriate energy for deposition.

3-Results and discussion

1-X- ray diffraction:

X- ray diffraction was used to characterize the crystalline of the films. The dhkl spacing between crystal planes can be calculated using Bragg's law [5].

$$n\lambda = 2d\sin\theta \text{ --- (1)}$$

Where (θ) is diffraction angle and (λ) is the used XRD wavelength. Debay Scherrer equation, formula used to calculate crystalline size(D) utilize the peaks broadening [6].

$$D = K\lambda / B \cos\theta \text{ --- (2)}$$

Where(λ) is the x-ray wavelength for α transition from Cu target (1.5406 Å), B is full width at half maximum and (θ) is the angle of diffraction. We observe from Figure (1) that the peaks of the zinc silicate complex begin to appear with the reduction of the zinc oxide peaks by increasing the doping ratio which reveals that crystallization of the membranes is improving, as it can be seen that the height of the peaks increases with the increase of the doping ratio indicating an increase in the crystallization rate. It is also possible to observe that the width of the peaks decreases with an increase in the percentage of doping, which indicates an increase in particle size, where the particle size is inversely proportional to the width of the top, this corresponds to the results in the literature [7-8]

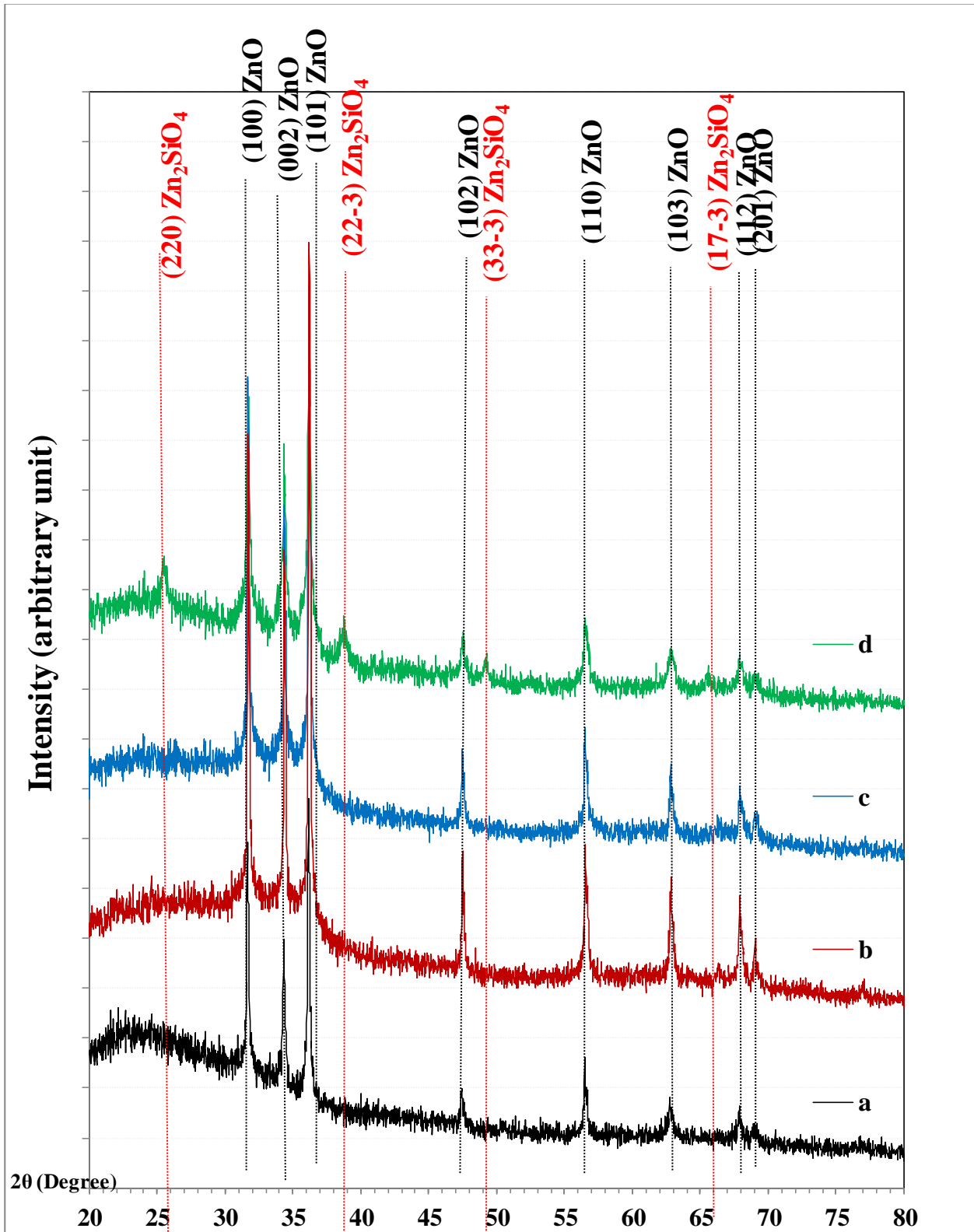


Fig (1) XRD for ZnO with different ratio of SiO2 (a)Pure ZnO, (b)5%, (c)10%,(d) 15%

2-Absorption Coefficient.

The absorption coefficient, which is denoted by the symbol α , is defined as the percentage of the decrease in the energy of the radiation relative to the unit of distance towards the propagation of the wave within the center and the absorption coefficient of the relationship was calculated [9]. $\alpha = 2.303 A / t$ ----- (3)

Where A is the absorption and t is the thickness.

Fig(2) declare that the doping result lead to increase in the absorption coefficient due to the generation of secondary levels within the energy gap near the conduction band, which increased the probability of low photon absorption.. this results agree with references [10].

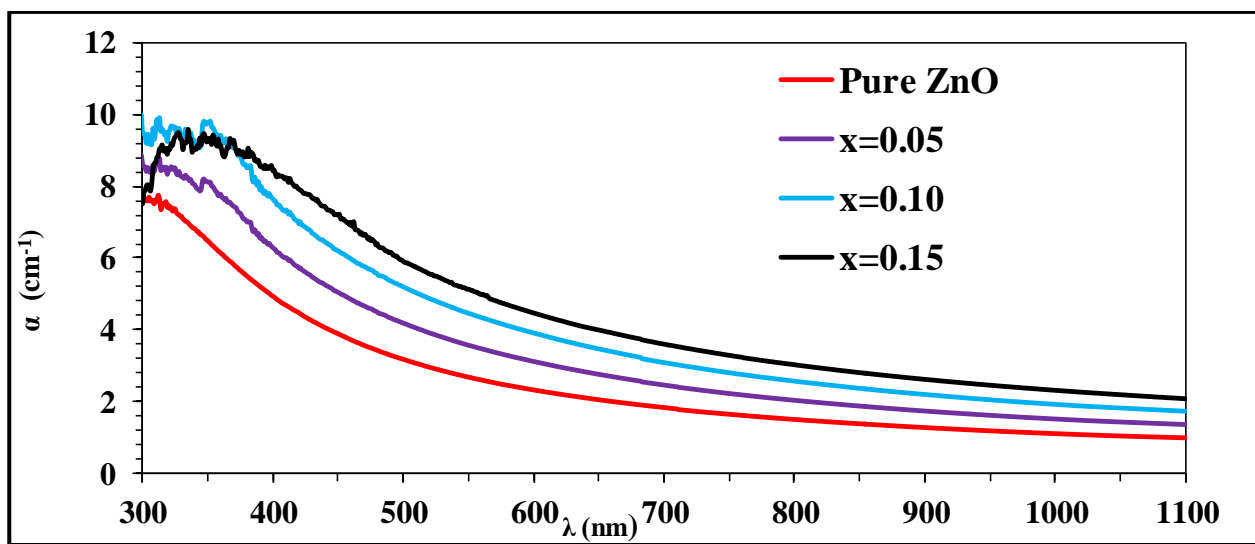


Fig (2) Absorption coefficient for ZnO with different ratio of SiO2 (a)Pure ZnO, (b)5%, (c)10%,(d) 15%

3 - Energy Gap

It is known as the energy needed to transfer an electron from the top of the valence band to the bottom of the conduction band. It is one of the most important optical constants that rely on semiconductor physics to manufacture many electronic devices. The value of the energy gap was calculated using the relationship [11].

$(\alpha h\nu) = B (h\nu - E_g)^r$ -----(4)

Where: $h\nu$ is the energy photon, B constant proportional inversely with the amorphousity, E_g energy gap, r exponential amount has value of $\frac{1}{2}$ for direct transition. Fig (3) shows as that the doping leads to decrease in the energy gap values with increasing doping rates. Increasing the doping rate leads to new topical levels below the conduction band. These levels are ready to receive electrons and generate tails in the optical power gap. These tails work toward reducing the energy gap. This results agree with references [12-13].

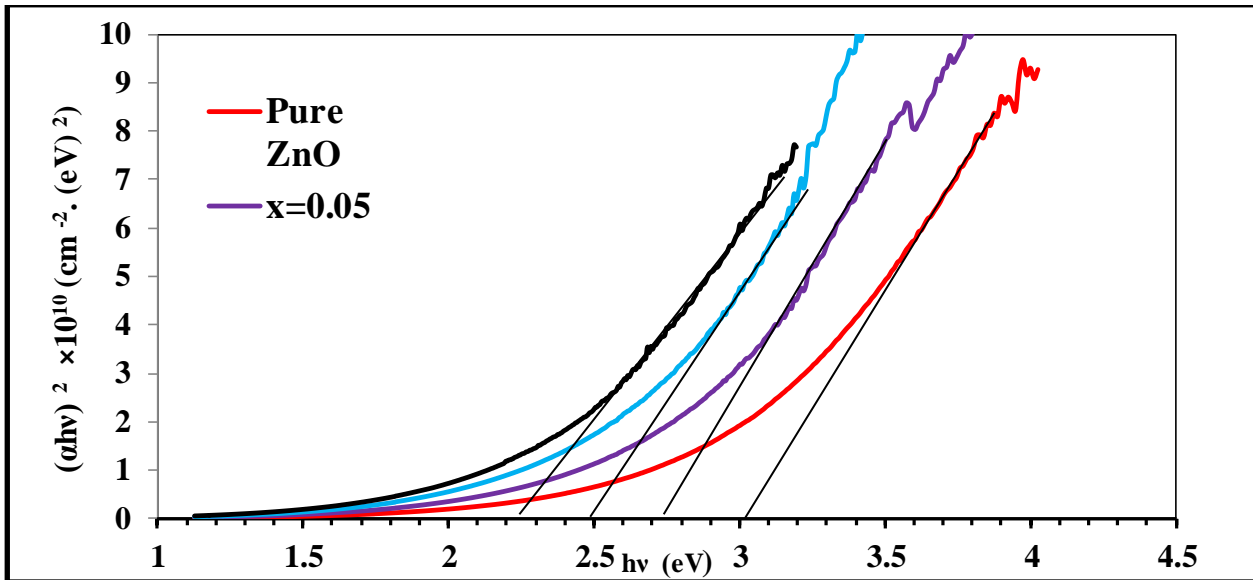


Fig (3) Energy gap for ZnO with different ratio of SiO2 (a)Pure ZnO, (b)5%, (c)10%,(d) 15%

4- Gas sensor

A gas sensor is defined as a device or device, one or more of its properties, such as (conductivity or electrical capacitance) that changes when exposed to a specific gas. Moreover, any change in these properties can be measured or determined directly or indirectly, ie a typical gas sensor that includes a sensor layer A sensor integrated with the transformer platform that is in direct contact with the flowing gas and the chemical reaction between the gas molecules and the sensitive sensor layer which leads to a change in the physical or chemical properties can be measured and analyzed by the transformer as an electrical signal outside [14].Characteristics of gas Sensor

A -The Sensitivity

Sensitivity can be defined as the ability of the sensor to detect the difference in chemical or physical properties of sensitive materials when exposed to detection under the influence of a particular gas. [15] The manufacture of semiconductors from microstructure structures is required to improve the sensitivity of the sensor and also to deal with nanomaterial structures provides a large surface area for exposure to the gas passing through the sensor. The control and control of particle size in semiconducting materials has a major impact in improving the sensitivity of the sensor, in the case of oxidation of the gas, the sensitivity is given by relationship (6) [16]. In the event that gas is reduced, it is given by relationship (7) [17].

$$S = R_g / R_a \times 100\% \dots\dots\dots (6)$$

$$S = R_a / R_g \times 100\% \dots\dots\dots (7)$$

The sensitivity of the device R_a , (R_g) represents the electrical resistance of the membrane with air and the presence of gas

B- Response and Recovery Times:

The response time (τ_{res}) can be defined as the time when the sensor reaches a value (90%) of the highest value from the oxidation or reduction reactions of the gas. Likewise, the recovery time (τ_{rec}) can be defined as the time required to recover 10% of the original value recovered by the sensor at the baseline rule in the diagram shown in Figure (4) when oxidation and reduction processes decrease due to the isolation of the

gas flow from the sensor [18]. From the figures (5) - (7) that represent the change of electrical resistance over time for the samples of the nitrogen dioxide gas sensor N02 from the prepared and deposited films on the purified and porous silicon according to the value of X(5,10,15 wt) respectively and at different temperatures we note that the amount of resistance It changes with the time needed to reach the state of stability in the case of opening and closing the gas (in the case of gas opening response time in the case of turning off the gas recovery time) It varies and varies from one sample to another according to the percentage of deformation where the nitrogen dioxide gas is oxidized and when oxidized The gas by evaporating the surface of the semiconductor membrane of the type (n-type), the concentration of charge carriers (electrons) on the surface of the membrane will decrease, which causes an increase in the membrane resistance. Using the relationship (6), the sensitivity has been calculated and from Figure (8) that represents a change Allergic reactions with deformation ratios according to the value of X(5,10,15 wt) , we note that the allergic reactions increase with the percentage of deformation and temperature, and the reason is due to the homogeneity of the membrane surfaces and the lack of crystalline defects, including granular limits on the membrane surface, which increased the gas adsorption and its interaction with the membrane surfaces and the best sensitivity was p Peer Score (300Co).

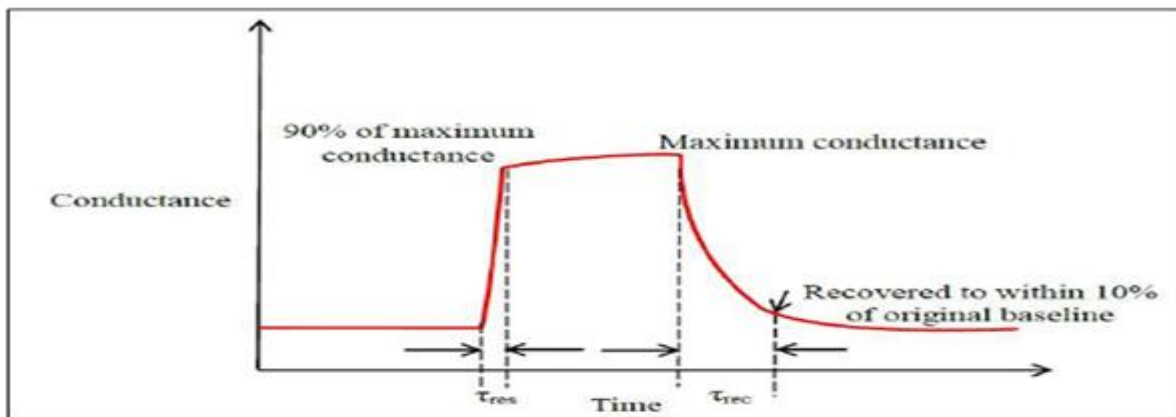


Fig (4) Response time and recovery in the gas sensor

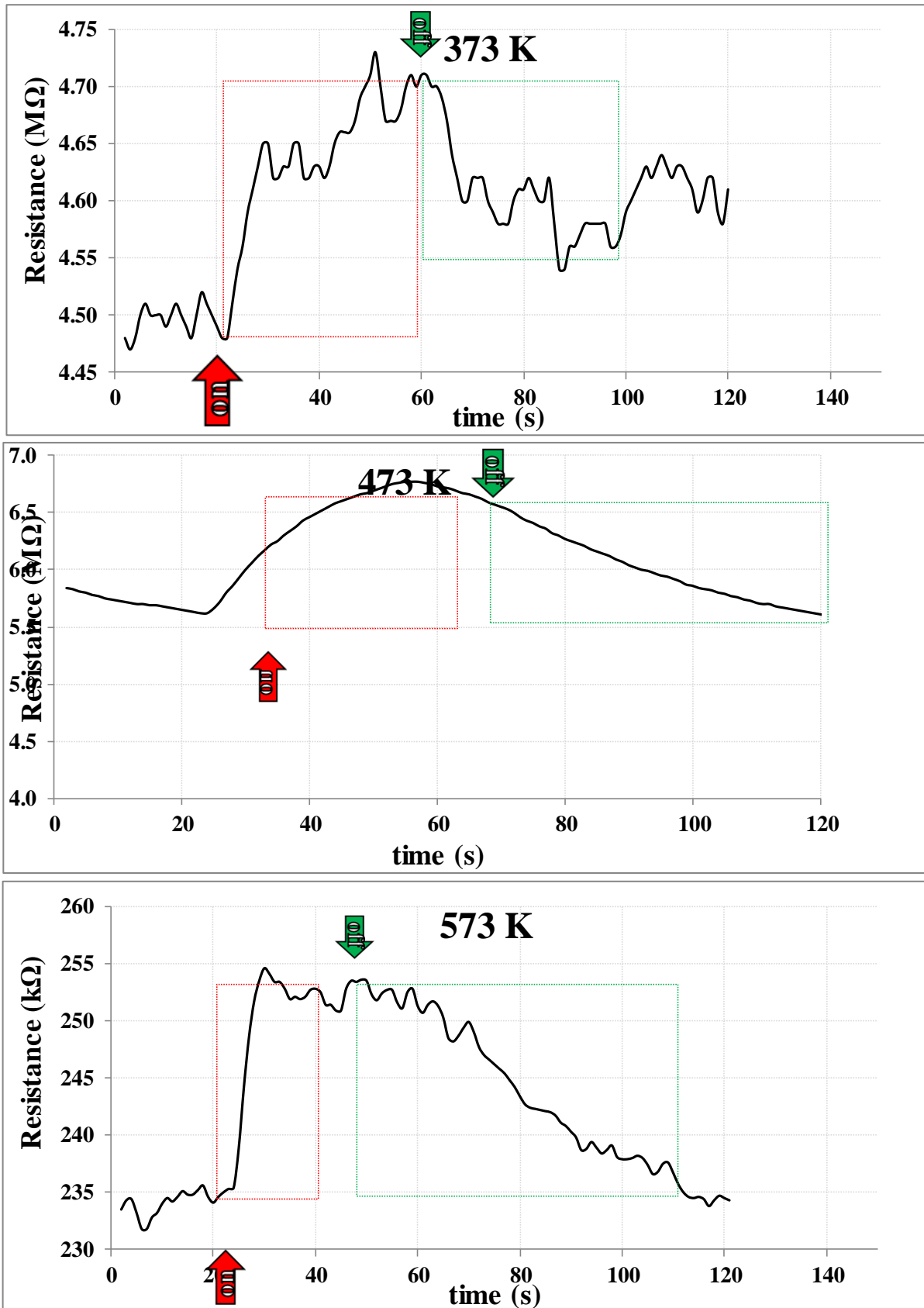


Figure (5) Change of resistance with time for 5% doping.

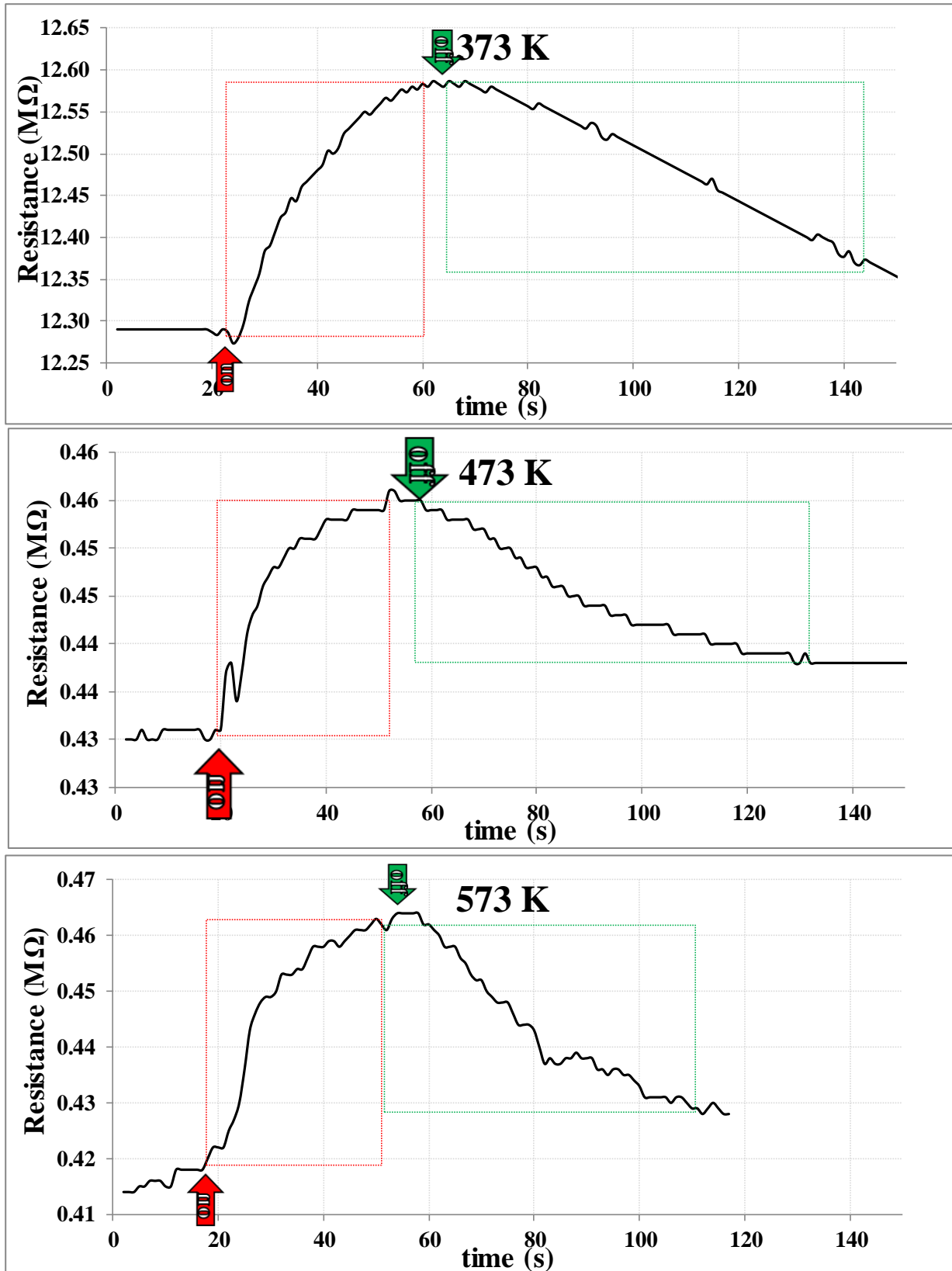


Figure (6) Change of resistance with time for 10% doping

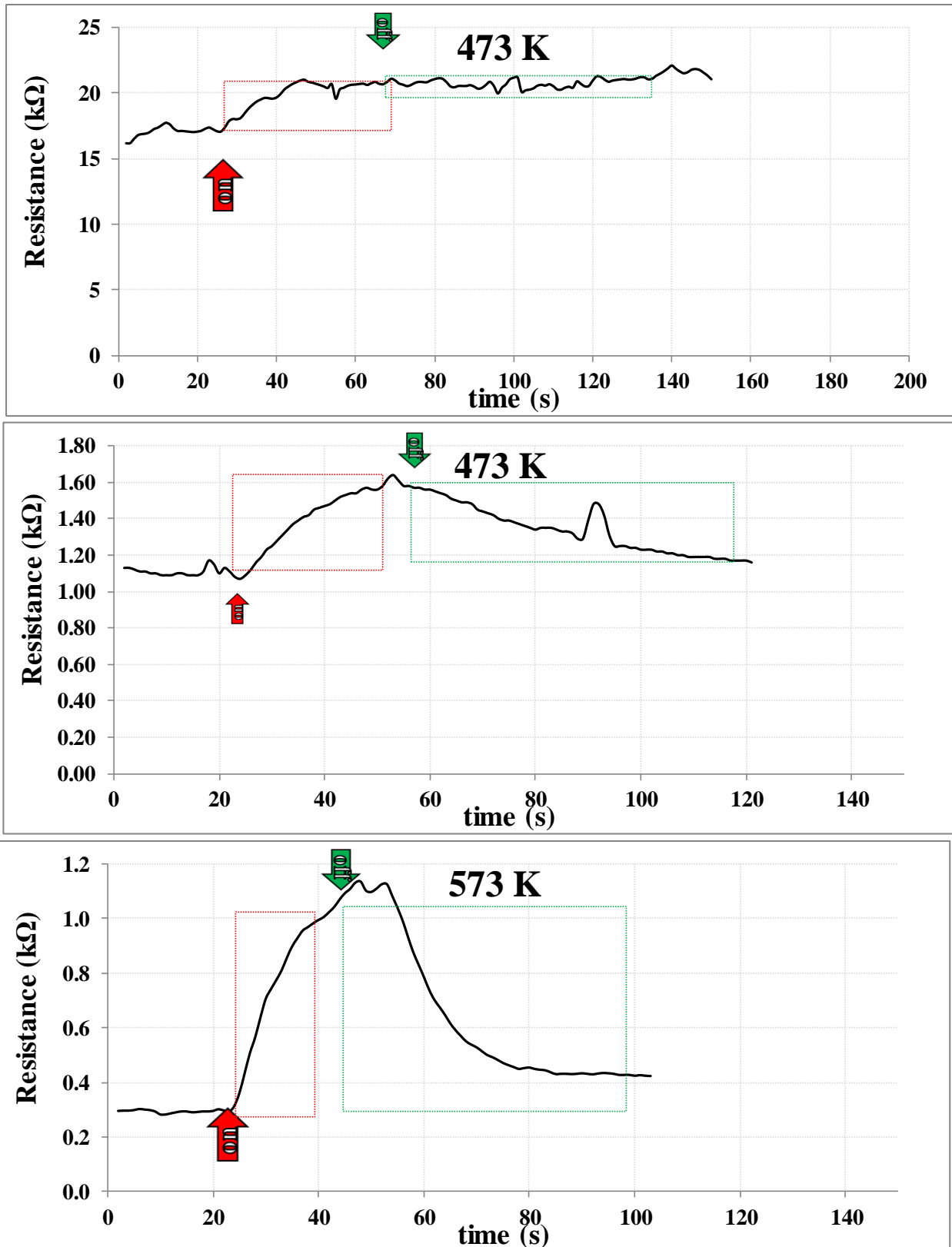


Figure (7) Change of resistance with time for 10% doping

Table (1)The(Sensitivity, response time, recover time) for different ratio of SiO2 (5, 10, 15)%

373K	SiO2%	Sensitivity (%)	response time (s)	recover time (s)
	5	2.44	40.00	40.00
	10	4.44	37.00	80.00
	15	17.65	40.00	65.00
473	SiO2%	Sensitivity (%)	response time (s)	recover time (s)
	5	5.49	30.00	50.00
	10	6.98	32.00	73.00
	15	45.45	30.00	60.00
573	SiO2%	Sensitivity (%)	response time (s)	recover time (s)
	5	0.80	20.00	60.00
	10	10.71	32.00	60.00
	15	266.67	27.00	38.00

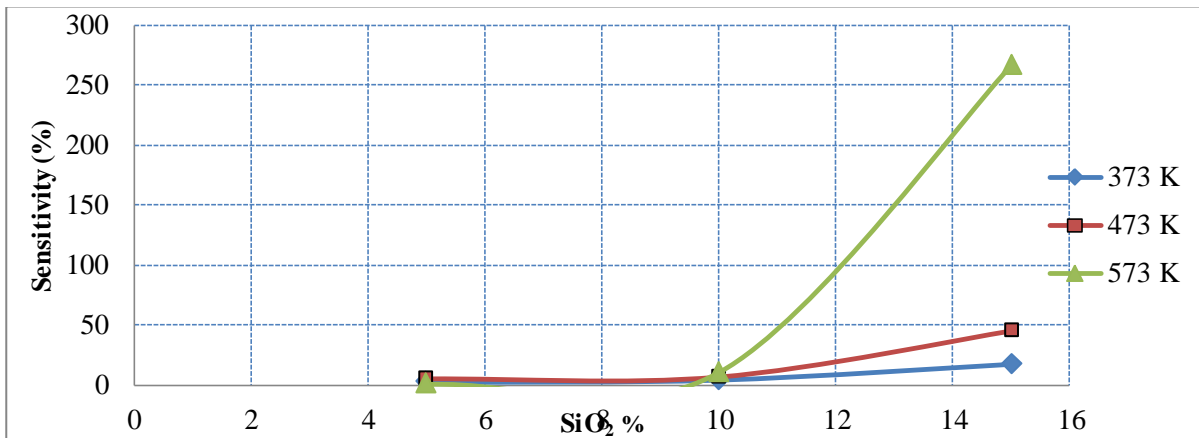


Fig (8) The Sensitivity with different ratio of SiO2

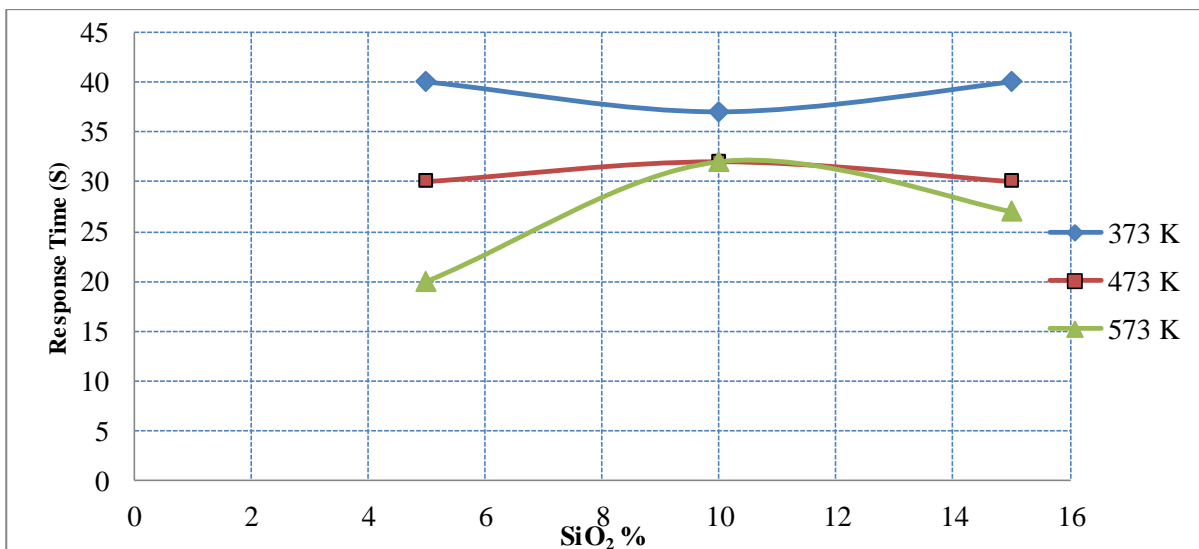
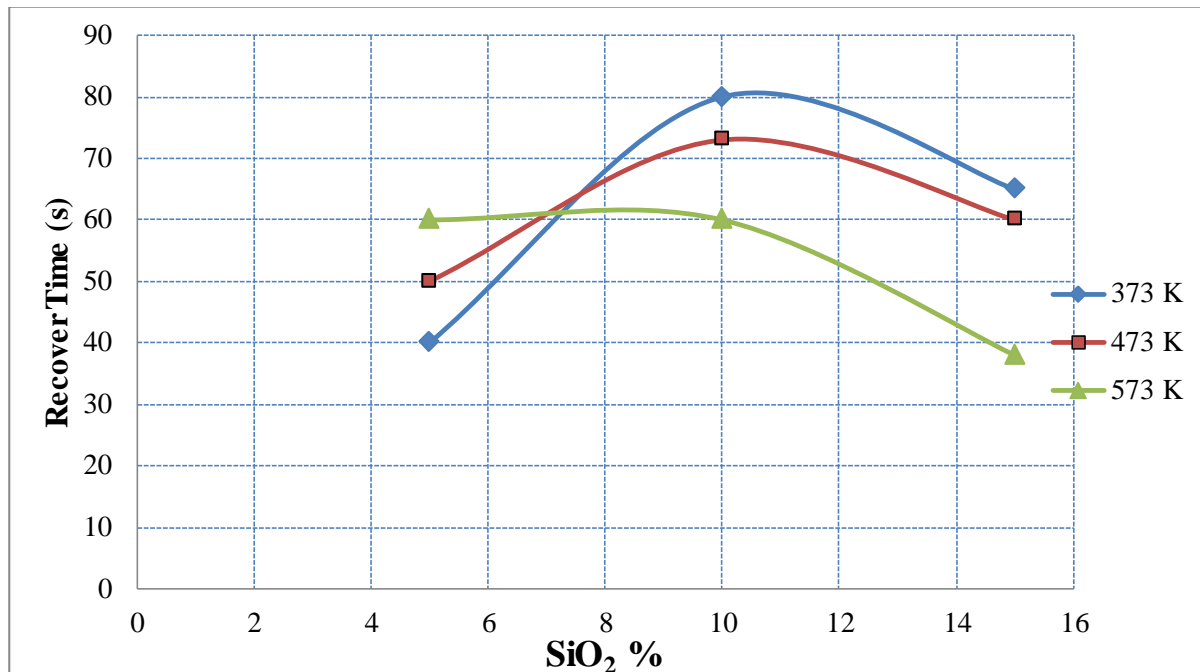


Fig (9) The Response time with different ratio of SiO2

Fig (10)The Recover time with different ratio of SiO₂

4-Conclution:

The appearance of a hexagonal structure through the compound used, as well as a clear reduction in particle size with increasing concentrations. And Absorption increases by increasing of doping ratios. The energy gap decreases from (3) eV to (2.2) eV by increasing of SiO₂ ratio. we note that the Sensitivity increases with increasing of SiO₂ ratio.

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