



LPG Gas Sensor Sensitivity Optimizing of GeO₂ Mixed with SnO₂ Nanostructures Prepared by Pulse Laser Deposition

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Abstract:

Thin films of a mixture of germanium oxide (GeO₂) with tin oxide (SnO₂) by 50% weight were fabricated on silicon (Si) (111) substrate by pulsed laser deposition technique with different number of pulses, (300,500,700) pulses as a liquefied petroleum gas (LPG) sensor achieved in this paper. The identity of the compound and its structural properties were determined showing that the thin film has a hexagonal structure and the intensity of the peaks increases when the number of pulses increases and the crystal size decreases, the films are polycrystalline in nature, with (101) levels of Ge and (110) of Sn at one apex,. The decrease in the value of the absorption coefficient is inversely proportional to the energy gap. Therefore, an increase in the number of pulses leads to an increase in the gap value from (2.8 to 3.4 eV). Small spherical particles are formed upon deposition, and become more spherical with the increase in the number of pulses as shown in field scanning electron microscopy . The gas sensor sensitivity of (LPG) was measured to get the best results at 700 pulses.

Keywords: GeO₂ Nanostructures, PLD, XRD, spherical shapes , direct energy gap

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1. Introduction

Nanomaterials are widely used in a variety of scientific, medical, military and civil technologies, food and safety[1], and one of the safety applications is gas emissions monitoring, control and sensing of their presence. Over the past few decades, there has been a development and interest in gas sensors, including nanosensors. The operation of many existing gas sensors depends on the chemical absorption or chemical decomposition of gas molecules in their sensor materials. However, the non-specific nature of the absorber leads to poor selectivity of gas sensors, which may lead to false detection or false alarm. This weak selectivity is usually dealt with through the use of a group of gas sensors, the individual elements of which have different selectivity. The diverse selectivity of a range of sensors allows the creation of unique response

patterns for the detected gases, which can be used to identify different gases, making it more cost-effective and achieving better gas identification performance. In the past few decades, several types of sensors with different materials have been developed such as metal oxide semiconductor reagents, conductive composite polymers and metal oxide semiconductor field effect transistor (MOSFET) [2]. Pulsed laser deposition (PLD) is a widely used technology for thin-film development for academic research, industrial and other applications. Due to the increase in scientific development in the field of thin films, deposition methods have diversified and become more sophisticated and complex to obtain new characteristics and properties at lower economic costs, which constitute a major obstacle to obtaining thin films. Each method of preparing



films has its own advantages in terms of accuracy in determining thickness and homogeneity of the membrane that It serves the desired purpose [3][4]. Liquefied Petroleum Gas (LPG) is a mixture of gases that are produced from petroleum derivatives and consists mainly of butane gas, which has a proportion of approximately 68% with some other gases such as propane and other hydrocarbons. Petroleum gas is characterized by a high ignition temperature, and it is an absorbable gas, and pressure is applied to it to turn into a liquid gas. dry. Petroleum gas is characterized by higher temperatures than gasoline and less combustion residues when burning [5]. It is widely used in homes around the world in cooking and as a heat source as it is a highly flammable gas and is also used in the operation of some cars. Many violent explosions were recorded around the world due to leaks of this gas and the lack of attention to the presence of leaks in closed spaces, which increases the risks in the rescue process [6]. Germanium dioxide is a chemical compound that has some unique properties that characterize it, including the energy gap (2.66 eV) [7] and is used in the manufacture of gas sensors and as an important optical material in optical fibers [8][9] and is used as a nanoconductor in many important nano applications. It has a refractive index and almost constant thermal stability, and these properties make germanium oxide a promising material in many applications, nanotechnologies, optoelectronic devices and sensors [10][11]. Germanium oxide has some defects that have a significant role in its optical and electronic properties. Tin oxide (SnO₂) is one of the most prominent types of oxides and most common in catalysts, gas sensors, and photovoltaic applications, and has a low electrical resistance and a wide energy gap eV (4.1-3.5). (Two tin atoms and four oxygen atoms). The tin ion (Sn⁺⁴) is located in the center of the octahedron and is formed by six oxygen ions (O⁻²) and surrounded by each O⁻² three ions (Sn⁺⁴) [12], and it is chemically inert and mechanically solid, and it is a semiconductor of the type (n) is stable and has a high energy gap and conductivity when it is in nanopowder form and when deposited in layered form is approximately equal to (3.8)eV [13,14].

2. Experimental

In this part, a mixture of GeO₂ powder (99.99 purity) 50% by weight with 50% weight tin dioxide powder SnO₂ was deposited on a directional N-type silicon (111) substrate via PLD technique using a pulsed laser device. Nd: YAG with a wavelength of (1064 nm) after bombing the target with a laser, the amount of energy is (200 mJ). The deposition was done using a different number of pulses (300,500,700) and frequency of 6 Hz. The deposited films were examined by XRD. The type of X-ray diffractometer system (Philips PW 1710, USA) is used to test the properties of the structure, which included crystal structure and size. Crystal. Field emission electron microscopy (FESEM, NOVA NANOSEM 450, USA) was used to test the morphological properties of the deposited films. Moreover, the optical properties were fully investigated by UV-Vis spectrometer (Shimadzu, UV-3600).The contact was Al It is vapor deposited in a vacuum at a pressure of ~ 10⁻⁵ Pa using the E306A Edwards thermal evaporation system Figure (1) shows a working system for measuring the sensitivity of the deposited films as a gas sensor (LPG) after the pulsed laser deposition process.

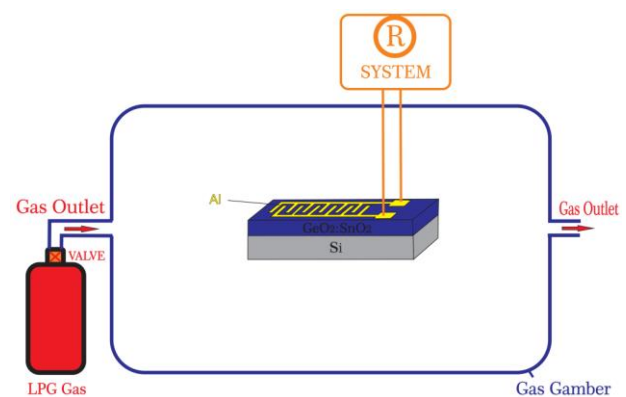


Figure. 1. Schematic illustrations of sensor structure and measurement set-up.

3. Results

3.1. XRD analysis

Figure 2 shows the X-ray diffraction method of mixed GeO₂ and SnO₂ nanostructured GeO₂ thin films deposited on Si with different proportion (50%) of SnO₂, at different (300,500,700) laser pulses.) . The result showed that the crystal structure and diffraction peaks of the mixture are polycrystalline in nature, with the appearance of a number of characteristic diffraction peaks belonging to both materials with the appearance of the (101) plane of germanium with plane (110) of tin at the top One and as shown in Table (1), which means the formation of new nucleation centers due to the presence of the mixture atoms resulting from a decrease in the nucleation energy barrier [15]. SnO₂ become as a random substance on the surfaces of the films. It is clear from the XRD diagrams that the mixing ratios did not change the crystal growth direction to the prevailing levels, as the growth continues towards (101), which is attributed to the competitive growth model Drift, which is called the survival model of the fastest growing atoms. This model assumes that the nucleation process takes several directions in the early stages of membrane development, then begins to compete during growth, and the faster nuclei continue to grow while the other nuclei stop growing. It may also be caused by self-crystalline arrangement, which leads to a decrease in the free energy of the crystal surface, and therefore, the nucleus with a lower value of the free energy of the crystal surface will dominate [16].

From Table (1), an increases in the full width at half maximum (FWHM) with the increased in the number of pulses was observed which consequently leads to a decrease in the size of

the crystals, compared to the films of pure tin dioxide, and according to Scherer's equation (2-3), where the relationship between Crystal size and inverse (FWHM). The decrease in crystal size after the addition of tin is evidence of the improvement of the nanocrystals, indicating that the atoms precipitated from these films are moving towards the nanostructure.

The size of the crystals was calculated using the Debye-Scherrer equation[17].

$$D = k\lambda / (\beta \cos\theta) \dots (1)$$

where λ , β , FWHM and: represent the wavelength and full width half maximum diffraction peak in radians and Bragg angle respectively. From the diffraction peaks, the full width of the FWHM becomes larger compared to the number of pulses. It increases and shows a low level of crystallization, which leads to a decrease in the crystal size.

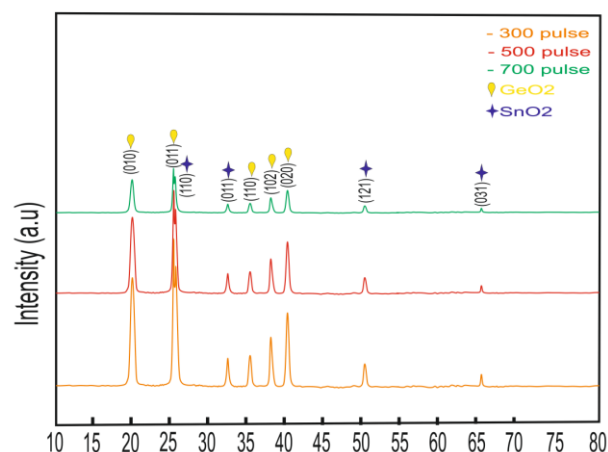


Figure .2 X-ray diffraction of a GeO₂, and SnO₂-mixed 50% on a silicon base at various pulses (300,500,700)

Table.1 Crystal structure parameters of GeO₂, and SnO₂- mixed 50% on a silicon base at various pulses (300,500,700)

Pulsed No.	Pos. [°2Th.]	FWHM Le ft [°2Th.]	D nm	h	k	l	d-spacing Stan.	d-spacing Exp.	Crystal system	Code No.
300	20.634	0.296	27.26925	0	1	0	4.3324	4.3048	Hex.GeO ₂	98-020-0731
	26.0743	0.468	17.41731	0	1	1	3.42042	3.42043	Hex.GeO ₂	98-020-0731
	26.738	0.523	15.60686	1	1	0	3.34957	3.36179	Tetra.SnO ₂	98-001-6635
	33.91	0.399	20.80715	0	1	1	2.6407	2.64871	Tetra.SnO ₂	98-001-6635
	36.234	0.357	23.40456	1	1	0	2.49252	2.4814	Hex.GeO ₂	98-020-0731
	38.165	0.352	23.87201	1	0	2	2.365763	2.35632	Hex.GeO ₂	98-020-0731
	41.902	0.421	20.19806	0	2	0	2.1622	2.1514	Hex.GeO ₂	98-020-0731
	51.91	0.367	24.06542	1	2	1	1.76236	1.7608	Tetra.SnO ₂	98-001-6635
	66.03	0.378	25.05397	0	3	1	1.41412	1.41267	Tetragonal	98-016-0667
500	20.634	0.345	23.39623	0	1	0	4.3324	4.3048	Hex.GeO ₂	98-020-0731
	26.07	0.472	17.26971	0	1	1	3.42042	3.42043	Hex.GeO ₂	98-020-0731
	26.741	0.529	15.42984	1	1	0	3.34957	3.36179	Tetra.SnO ₂	98-001-6635
	33.92	0.399	20.80715	0	1	1	2.6407	2.64871	Tetra.SnO ₂	98-001-6635
	36.225	0.357	23.40456	1	1	0	2.49252	2.4814	Hex.GeO ₂	98-020-0731
	38.167	0.359	23.40654	1	0	2	2.365763	2.35632	Hex.GeO ₂	98-020-0731
	41.91	0.425	20.00796	0	2	0	2.1622	2.1514	Hex.GeO ₂	98-020-0731
	51.9	0.369	23.93498	1	2	1	1.76236	1.7608	Tetra.SnO ₂	98-001-6635
	66.05	0.386	24.53471	0	3	1	1.41412	1.41267	Tetra.SnO ₂	98-016-0667
700	20.634	0.345	23.32865	0	1	0	4.3324	4.3048	Hex.GeO ₂	98-020-0731
	26.07	0.472	17.19685	0	1	1	3.42042	3.42043	Hex.GeO ₂	98-020-0731
	26.741	0.529	15.34347	1	1	0	3.34957	3.36179	Tetra.SnO ₂	98-001-6635
	33.92	0.399	20.24412	0	1	1	2.6407	2.64871	Tetra.SnO ₂	98-001-6635
	36.225	0.357	22.9571	1	1	0	2.49252	2.4814	Hex.GeO ₂	98-020-0731
	38.167	0.359	23.14952	1	0	2	2.365763	2.35632	Hex.GeO ₂	98-020-0731
	41.91	0.425	19.8222	0	2	0	2.1622	2.1514	Hex.GeO ₂	98-020-0731
	51.9	0.369	23.49138	1	2	1	1.76236	1.7608	Tetra.SnO ₂	98-001-6635
	66.05	0.386	24.36209	0	3	1	1.41412	1.41267	Tetra.SnO ₂	98-016-0667

3.2 FE-SEM analysis

Figure 3 shows the scanning electron microscope (FESEM) images of the surface morphology of the deposited film of a mixture of germanium oxide with 50% of tin oxide as in the oxidizer at room temperature prepared by the pulsed laser deposition method at energy (200mJ) The number of pulses is 300, annealed at 600 °C. Celsius temperature, where it gives an upper image of the thin film of the compound. The images in Figure (3a) show the particles deposited on the silicon substrate. While the images in Figure 3 (b,c) indicate that some particles are agglomerated in large groups up to 100 nm when the number of pulses increases to 500, which is a phenomenon generally observed in nanomaterials to reduce energy surface [18]. The addition of tin oxide leads to a decrease in

the size of the particles and their arrangement in a regular spherical shape, and this is important for the gas sensor, and the shape and size of the nanostructures of the prepared mixture can be greatly affected by their electronic properties. The preliminary analysis of nanostructures of the mixture with different concentrations of tin was examined using EDX Their precipitated compositions at different pulses are illustrated as in Fig. (3). The presence of Ge, Sn, O, Si, Au elements was confirmed by EDX analysis. Table (4-6). Which led to an increase in the percentage of oxygen, and perhaps this explains the increase in the energy gap by increasing the number of pulses of the mixture, as in the visual examinations.



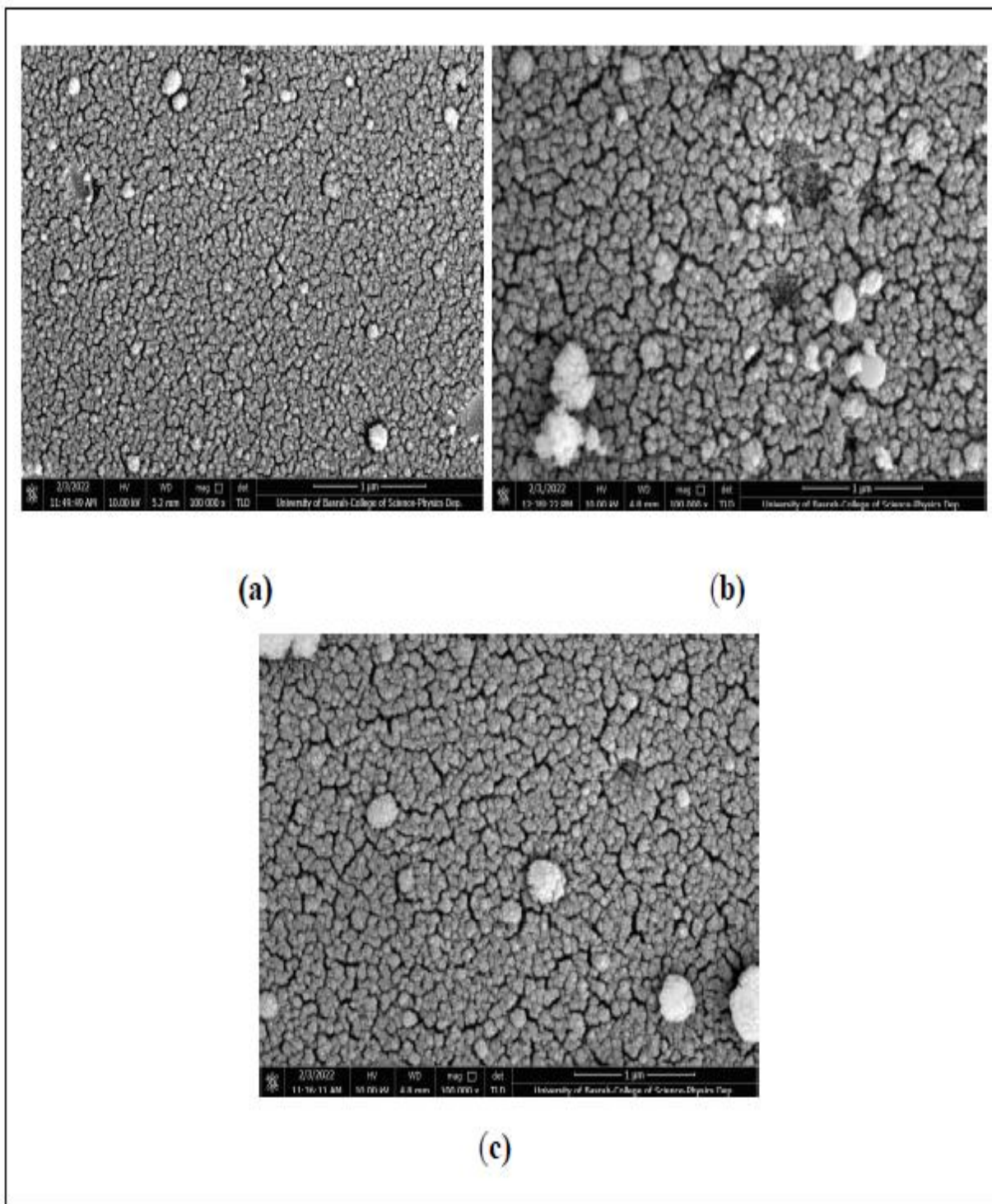


Figure .3 FE-SEM of GeO₂, and SnO₂- mixed 50% (a) 300 pulse (b) 500 pulse (c) 700 pulse

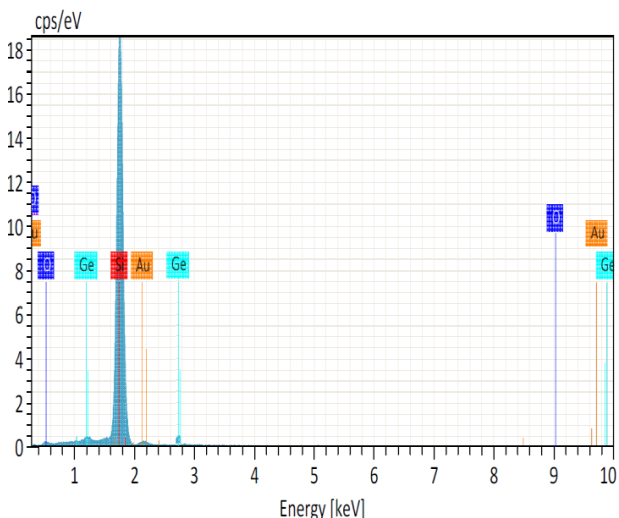


Figure .4 EDX of (a) GeO₂ SnO₂50%

3.3 UV-Vis analysis

The absorption coefficient (α) was calculated for the precipitated films consisting of germanium dioxide GeO₂ and SnO₂ and a mixture of 50% and deposited on silicon bases after annealing at a temperature of 600°C by pulsed laser deposition method. The absorption coefficient depends on the energy of the incident photons and on The energy gap of the oxides The results of (UV-VIS) measurements showed in Figure (5) (change of absorption coefficient of the prepared thin films as a function of wavelength) that the values of the absorption coefficient (α) of the mixture: SnO₂ (GeO₂ decreases with increasing number of pulses due to the change in the microstructure of the films) And thus leads to a change in the energy gap, and that all the values of the absorption coefficient of the membrane all have values greater than (10^4 cm^{-1}) (and the value of $r = 1/2$, and this indicates that the value of the energy gap is direct and this is consistent with what the researcher found [19]. It is noted from the mentioned figure that the absorption coefficient (α) of the prepared thin films decreases with increasing wavelength because the absorption coefficient increases with increasing photon energy due to the formation of new (donor) levels inside the energy gap [20], and this value decreases with the increase in the number of pulses. We note the energy gap values for germanium oxide Mixed with tin oxide in percentages (50%), the energy gap values

increase when the number of pulses increases due to the decrease in crystal size . Figure (6) shows that the film has an energy gap of 2.9 eV and increases with the increase in the number of pulses to 3 and 3.4 respectively, and this may be due to reducing the crystal size, the Fermi level shifts towards the conduction plane and the gap increases energy. The increase in the amount of the energy gap is called due to the so-called displacement (Borstein-Mohs) [20].

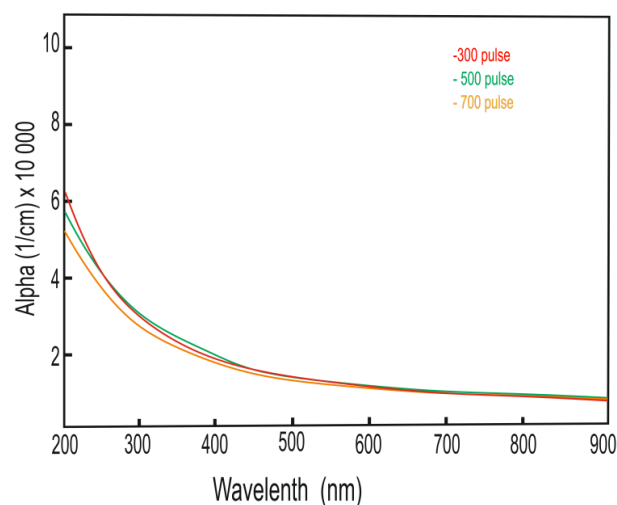


Figure 5. absorption coefficient of a GeO₂, and SnO₂- mixed GeO₂ at 50%.

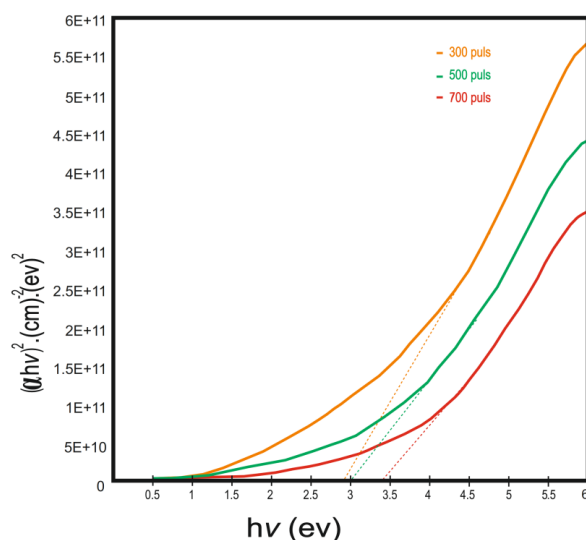


Figure 6. energy gap of a GeO₂, and SnO₂- mixed GeO₂ at 10%, 30%, and 50%.



3.4 (LPG)gas sensor based SnO₂- mixed GeO₂

The gas sensor was tested as a LPG sensor at room temperature (RT) and the gas quantity was gradually increased until the gas quantity became twice the amount of air ratio (2:1) based on the mixture GeO₂ and SnO₂ deposited on Si substrate At 700 pulses is the best selected pulse as shown in Figure 7. The current increase was obvious to increase the resistance of the sensor due to the adsorption process when exposing the gas, which leads to a decrease in resistance. Figure 7 shows the increasing current of the films sensor, which contrasts with the behavior of n-type oxides towards reducing gases. Sensor sensitivity was 62.7%

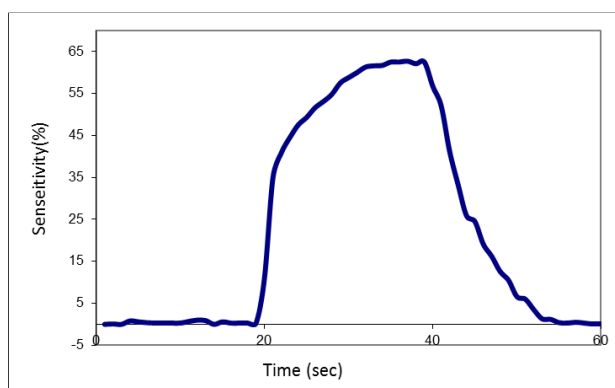


Figure 7. Sensitivity of a GeO₂, and SnO₂-mixed GeO₂ as a function of time for LPGgas at 700 pulse.

5. conclusion

Spherical GeO₂:SnO₂ nano porous thin films were deposited on silicon substrates by pulsed laser deposition with a ratio of (50%) by weight.. The XRD patterns indicated a decrease in the particle size with an increase in the number of pulses and also due to the addition of tin oxide at 50% by weight. The addition of tin oxide led mainly to a change in the nanostructure of the films and thus leads to a change in the energy gap. On the other hand, it was found that increasing the number of pulses reduces the particle size and reduces the value of the absorption coefficient, the optical bandgap energy E_g has shifted to the medium - UV rays , expected to make it suitable for use in a gas sensor. Addition of SnO₂ to GeO₂ has been found to be useful for effective detection of LPG.

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