Study the effect of thermal annealing on some physical properties of thin Cu_2SiO_3 films prepared by pulsed laser deposition

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Abstract

The Cu_2SiO_3 composite has been prepared from the binary compounds (Cu_2O, and SiO_2) with high purity by solid state reaction. The Cu_2SiO_3 thin films were deposited at room temperature on glass and Si substrates with thickness 400 nm by pulsed laser deposition method. X-ray analysis showed that the powder of Cu_2SiO_3 has a polycrystalline structure with monoclinic phase and preferred orientation along (111) direction at 2θ around 38.670^o which related to CuO phase. While as deposited and annealed Cu_2SiO_3 films have amorphous structure. The morphological study revealed that the grains have granular and elliptical shape, with average diameter of 163.63 nm. The electrical properties which represent Hall effect were investigated. Hall coefficient is negative which means that the films are n-type, and the electrical conductivity decreases with heat treatment.

The sensing properties of the Cu_2SiO_3 sensors for NO_2 gas have been studied, and the result revealed that the Cu_2SiO_3 films have low sensitivity at room temperature, and it's improve with increasing the operation temperature. The response time increase while the recovery time decrease with increasing operation temperature.

Key words

Cu_2SiO_3 films, structure and morphological properties, optical properties, sensing behavior.

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دراسة تأثير التلدين الحراري على بعض الخصائص الفيزيائية لأغشية Cu_2SiO_3 الرقيقة المرسبة بالليزر النبضي

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الخلاصة

تم تحضير متراكب Cu_2SiO_3 من المركبات الثنائية (SiO_2,Cu_2O) وبنقاوة عالية بطريقة تفاعل الحالة الصلبة. إن أغشية Cu_2SiO_3 رسبت عند درجة حرارة الغرفة على أساسات من الزجاج و Si وبسمك 400 نانومتر بطريقة الترسيب بالليزر النبضي. أوضحت تحليلات الأشعة السينية بان المسحوق يمتلك تركيب متعدد البلورات وبطور أحادي الميل وباتجاه مفضل (111) عند 2θ حوالي 38.670^o والتي تعود الى طور اوكسيد النحاس. بينما الأغشية المرسب والملدنة تمتلك تركيب عشوائي. أظهرت دراسة السطح بان الحبيبات تمتلك شكل حبيبي واهليجي، مع معدل قطر 163.63 نانومتر. الخصائص الكهربائية والمتمثلة بتأثير هول تم بحثها وكانت.إشارة معامل هول سالبه وهذا يعني إن الاغشيه من النوع الواهب، وان التوصيلية الكهربائية قلت مع المعاملة الحرارية. تم دراسة الخصائص التحسسية لمتحسس لغاز ثنائي اوكسيد النتروجين وان النتائج أوضحت إن أغشية تمتلك تحسسيه منخفضة عند درجة حرارة الغرفة وتتحسن مع زيادة درجة حرارة التشغيل.
زمن الاستجابة يزداد بينما زمن التغطية يقل مع زيادة درجة حرارة التشغيل.

Introduction

Silicon dioxide thin films are widely used in semiconductor device technology as gate insulators, for passivation and as intermetal dielectric layers [1]. These films are obtained either by thermal oxidation of silicon or by chemical vapor deposition processes, including both thermal and plasma-assisted ones [2]. SiO_2 properties like stability, amorphous nature, high density, adjustable refractive index, and low particulate contamination, led to use SiO_2 in many typical applications, including in high-reflection coatings, antireflection coatings, all-dielectric mirrors, beam dividers, band pass filters, and polarizers [3, 4].

SiO_2 has low refractive index and absorption that can be used in combination with high refractive index oxide layer coatings that operate in the UV (~200 nm) to near-IR (~3 μm) regions [5].

The introduction of transition metals in a SiO_2 glass matrix has a strong influence on the optical visible absorption spectrum. Various materials embedded in the glass matrix produce quantum and non linear optical effects when the particles have some critical size [6]. The wide range of applications of Silicate systems, especially synthetic ones, is a consequence of their specific properties. In laboratory conditions it is possible to obtain many more silicate-based systems with specific physicochemical parameters [7]. Orthosilicates of many bivalent metals (M_2SiO_4) are widely applied in various technologies, such as, Zn_2SiO_4 as luminescent materials and ultraviolet absorbers, while Mg_2SiO_4, Fe_2SiO_4, Zn_2SiO_4 are dielectric and corrosion protective coating materials [8]. Copper or copper oxides in oxide matrixes have attracted sustained interest due to their unusual properties [9]. Literature of copper silicates ($CuO.SiO_2$) composites synthesis is rather modest, in contrast to other oxide composites such as $MoSiO_2$ type, where M most often stands for aluminum, calcium, zinc, magnesium or titanium [7].

In this paper, Cu_2SiO_3 films were deposited on glass and silicon substrates by pulsed laser deposition technique. The effects of thermal treatment on the physical properties of these films were investigated.

Experimental

Copper metasilicate (Cu_2SiO_3) powder was synthesized by solid state reaction. In this case, astoichiometric mixture of SiO_2, and Cu_2O (Fluka AG, Buchs SG, Made in Switzerland, 99%) were mixed for an hour, and pressed under 5 ton to from a target with a pellet shape with (13 mm) diameter and (8mm) thickness, then treated at temperature equal to 950 $^{\circ}$C for two hours. The Cu_2SiO_3 thin films were deposited on glass and Si substrates at room temperature with 400 nm thickness by pulsed laser deposition (PLD) method. The laser type was Nd:YAG SHG Q-switching laser beam with a wavelength 1064 nm (pulse width 10 nsec and repetition frequency 6Hz) which incident on the target surface with an angle equal to 45^{o}at a vacuum chamber (10^{-2} mbar). The films annealed at 100 and 200°C. The X-ray diffractometer type (Miniflex II Rigaku company, Japan) with CuK_{α} target of wavelength 0.154 nm and $2\theta = 10^{o} – 80^{o}$ was used to determine the crystal structure of these films. Surface morphology measurement was done by using atomic force microscopy (AFM) CSPM-AA 3000 contact mode spectrometer, Angstrom Advanced Inc. Company, USA. The optical transmittance of the films was recorded using UV-VIS. spectrophotometer type (SP8001 Metertech, USA) over the wavelength range (190-1100) nm. Electrical properties were carried out by using Hall effect measurement system (3000 HMS, VER 3.5, supplied with Ecopia company). Electrical properties were carried out by using Hall effect measurement system (3000 HMS, VER 3.5, supplied with Ecopia company).

The gas sensing properties were performed in the specially designed gas sensor test rig. The test rig was used with stainless steal cylindrical test chamber. The chamber had an inlet for the test gas to flow in and an air a admittance valve. The changes in the resistance values of sensor which result from interaction with the target NO_2 gas were recorded using a data acquisition system consisting of multi-meter interfaced with a computer.

Results and discussion

X-ray diffraction pattern of Cu_2SiO_3 composite powder shows a polycrystalline structure and exhibited sharp peaks with preferential orientation in the [111] direction at 2Ө equals to 38.6700° which related to monoclinic phase of CuO as shown in Fig. 1. The data compared with JCPDS card number 96-900-8962. The high concentration of CuO in the Cu_2SiO_3 composite at 950C indicated to the practical absence of the chemical binding of CuO to any silicate structure. These results are agreement with the rustles of Maliavski et al. [8]. Table 1 Illustrates all structure parameters of Cu_2SiO_3 powder.

X-ray diffraction patterns for as deposited and annealed Cu_2SiO_3 thin films at 100 and 200 ^oC which deposited on glass substrates and prepared by Pulsed laser deposition method are shown in Fig. 2. The results reveals that the as deposited and annealed Cu_2SiO_3 films have amorphous structure. This result agree with the results of Tohidi [6] and Homaunmir et al. [10].

It is clear from the same figure that the heat treatment at 100 and 200 ^oC does not improve the structure of this film and the structure become more amorphous. This may be attributed to binding more CuO with silicate.

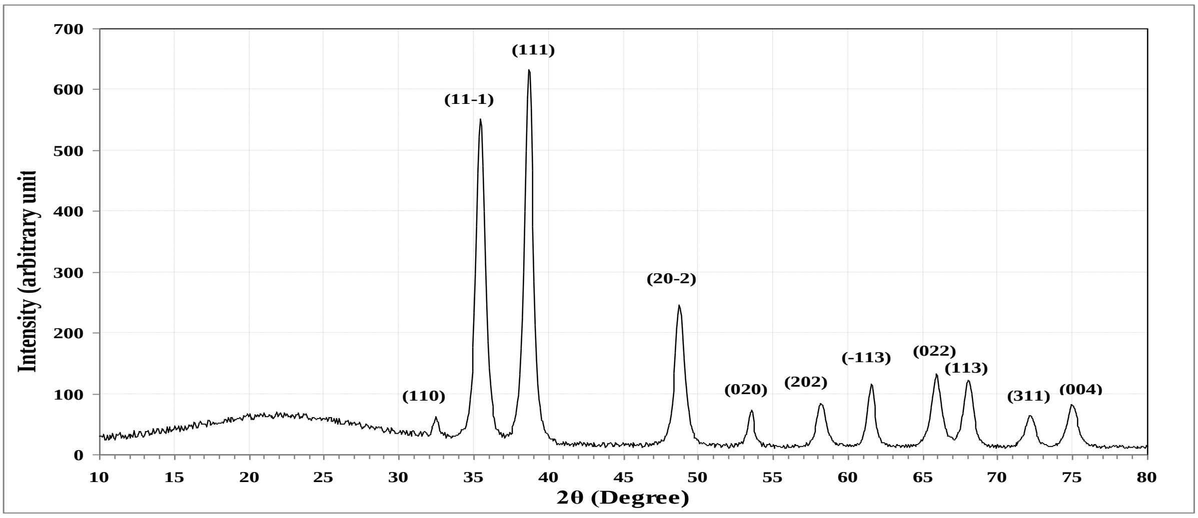

Fig. 1: X-ray diffraction patterns for Cu_2SiO_3 powder.

Table 1: X-ray diffraction data for Cu_2SiO_3 powder.

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	Phase	Card No.
Cu_2SiO_3	32.4500	0.4700	2.7569	17.6	(110)	2.7372	Mono. CuO	96-900-8962
	35.4500	0.6800	2.5301	12.3	(11-1)	2.5108	Mono. CuO	96-900-8962
	38.6700	0.6500	2.3266	13.0	(111)	2.3118	Mono. CuO	96-900-8962
	48.7500	0.7400	1.8665	11.8	(20-2)	1.8553	Mono. CuO	96-900-8962
	53.4900	0.4900	1.7117	18.2	(020)	1.7050	Mono. CuO	96-900-8962
	58.2100	0.7100	1.5836	12.8	(202)	1.5724	Mono. CuO	96-900-8962
	61.5300	0.5800	1.5059	15.9	(-113)	1.4986	Mono. CuO	96-900-8962
	65.8900	0.7700	1.4164	12.3	(022)	1.4120	Mono. CuO	96-900-8962
	68.0300	0.7200	1.3770	13.3	(113)	1.3726	Mono. CuO	96-900-8962
	72.1500	0.7500	1.3082	13.1	(311)	1.2960	Mono. CuO	96-900-8962
	74.9700	0.7930	1.2658	12.6	(004)	1.2596	Mono. CuO	96-900-8962

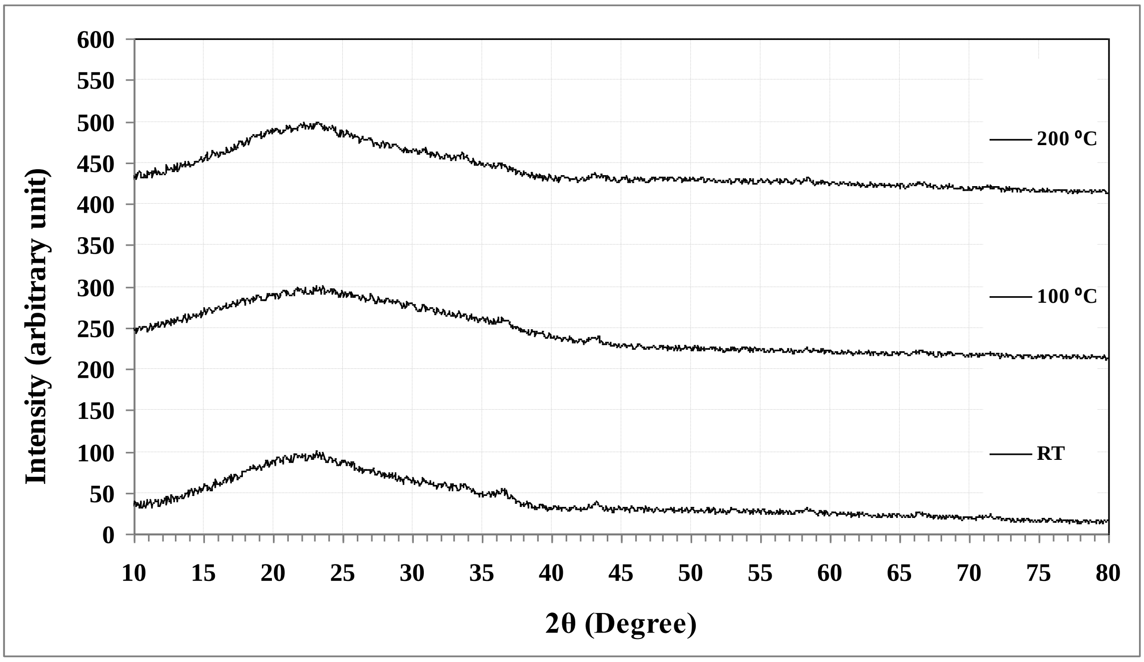

Fig. 2: X-ray diffraction pattern for Cu_2SiO_3 films as deposited and annealed at (100, 200) ^oC.

Atomic Force Microscopic (AFM) is a convenient technique to study the morphological characteristics and surface roughness semiconductor thin films, and is one of the most effective ways for the surface analysis due to its high resolution and powerful analysis software.

The two and three dimensional AFM images of Cu_2SiO_3 thin films prepared by pulsed-laser deposition which acquired over an area 2.5x 2.5 μm^2 in contact mode are shown in Fig. 3.

It is clear that the shape of grains are round and elliptical, with big average grain size about 163.63 nm, and the surface roughness about 15 nm.

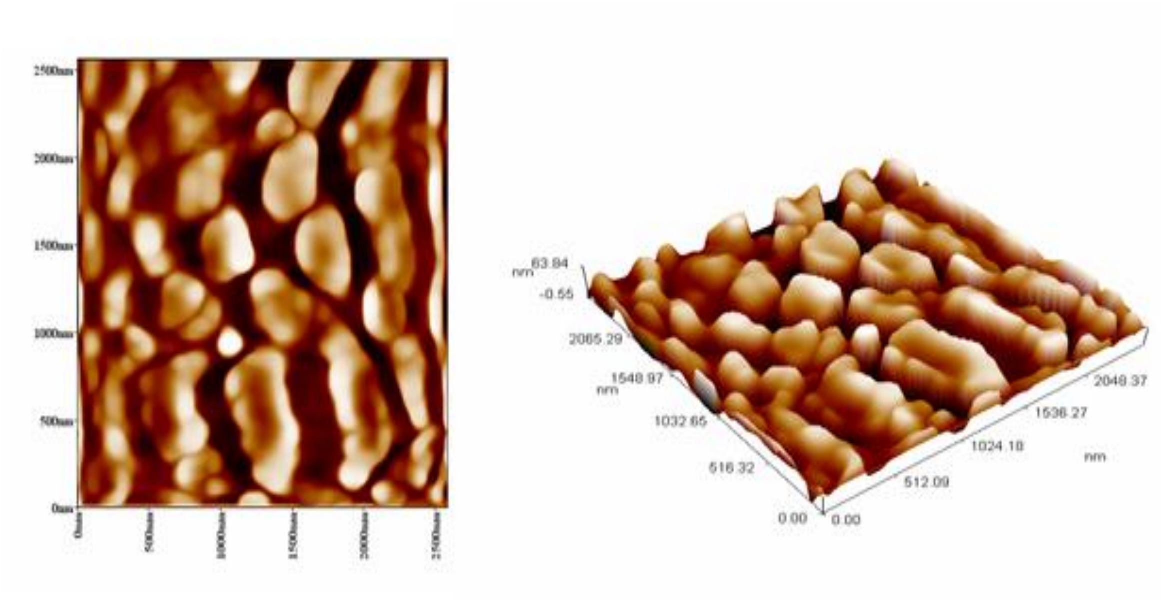

Fig. 3: 2D and 3D images for as deposited Cu_2SiO_3 thin films.

The optical transmittance spectra of as deposited and annealed Cu_2SiO_3 thin films were recorded in the wavelength range of 350 nm to 1100 nm, at normal incidence as shown in Fig. 4a. It is clear that the film transmission increase with increasing the wavelength and the optical transparency of the film increases with increases annealing temperature to 100 ^{o}C and the decrease when annealing temperature reach to 200^o. However the change in transmission indicates there are changes in film structure.

The absorption coefficient (α), was calculated using Lambert's law [11]:

$$\ln \frac{I_o}{I} = 2.303A = \alpha t \qquad (1)$$

where, A is the optical absorbance, t is the film thickness, Io and I are the intensities of the incident and the transmitted light, respectively. Fig. 4b shows the relation between absorption coefficient and wavelength. It is clear that the absorption coefficient exhibits higher values within the range of 10^4 cm^{-1}, these values means that there is a large probability of the allowed direct transition.

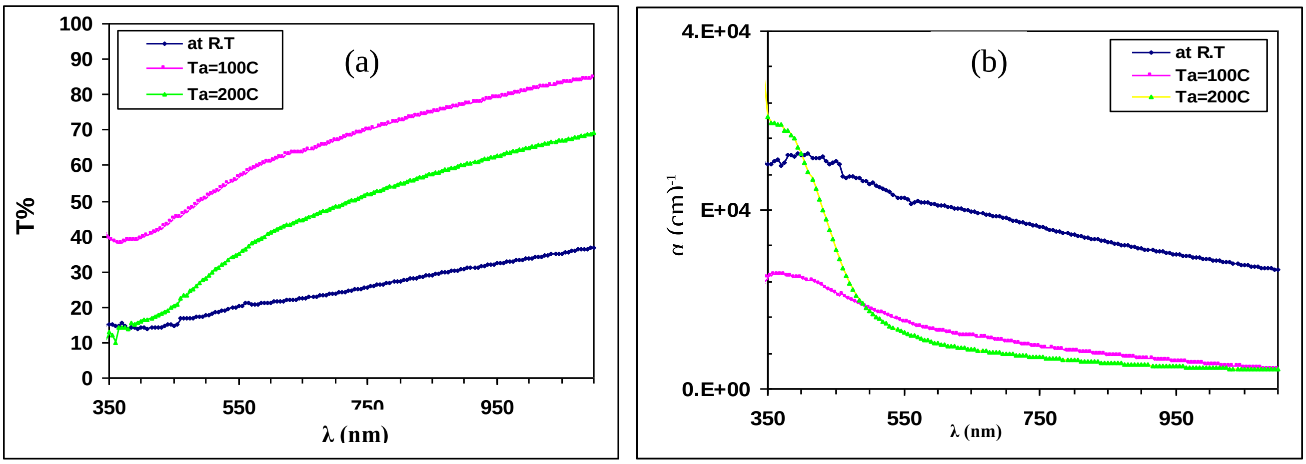

Fig. 4: (a) The transmittance (b) absorption coefficient versus the wavelength for Cu_2SiO_3 as deposited and annealed films at different annealing temperature.

The optical band gap (E_g) of Cu_2SiO_3 films has been determined from the optical absorption coefficient and photon energy (hυ) data assuming the direct transmission occurs between valance and conduction band using Tauc's relation [12].

$$\alpha h\upsilon = B\left(h\upsilon - E_g\right)^{1/2} \tag{2}$$

where B is a constant inversely proportional to amorphousity. Extrapolation of the linear portion of the plots of $(\alpha h\upsilon)^2$ versus photon energy to $\alpha = 0$ yields the direct optical band gap of the Cu_2SiO_3 films. Fig. 5 shows the plot of $(\alpha h\upsilon)^2$ versus photon energy (hυ) of as deposited and annealed Cu_2SiO_3 films.

The direct band gap value of the Cu_2SiO_3 films varies between 1.87, 2.35 and 2.28 eV for as deposited and annealed at 100 and 200 ^oC respectively. It can be found from that the band gap value increases with annealing temperature. This is due to increase the amorphousity when the films annealed at different annealing temperatures.

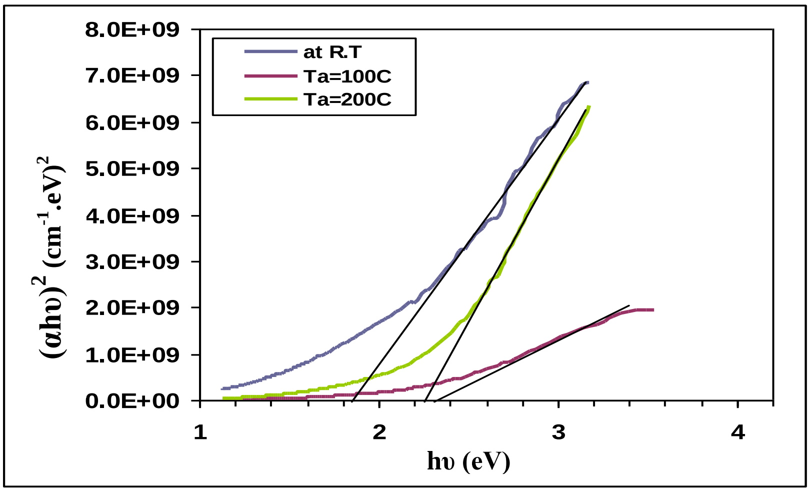

Fig.5: Energy gap of Cu_2SiO_3 films as deposited and annealed films.

The variation of the re fractive index versus wavelength in the range of 400–1100 nm for as deposited and annealed Cu_2SiO_3 films are shown in Fig.6a. In general it is obvious that the refractive index decreases with increasing annealing temperatures. This behavior is due to decrease in the reflection which the refractive index depend on it. The relation between the extinction coefficient and wavelength of as deposited and annealed Cu_2SiO_3 films are shown in Fig. 6b. The behavior of extinction coefficient (k) is nearly similar to the corresponding absorption coefficient as shown in Table3, we can see from this table that k decreases with increasing T_a. This attributed to the amorphous structure of film which formed with heat treatment.

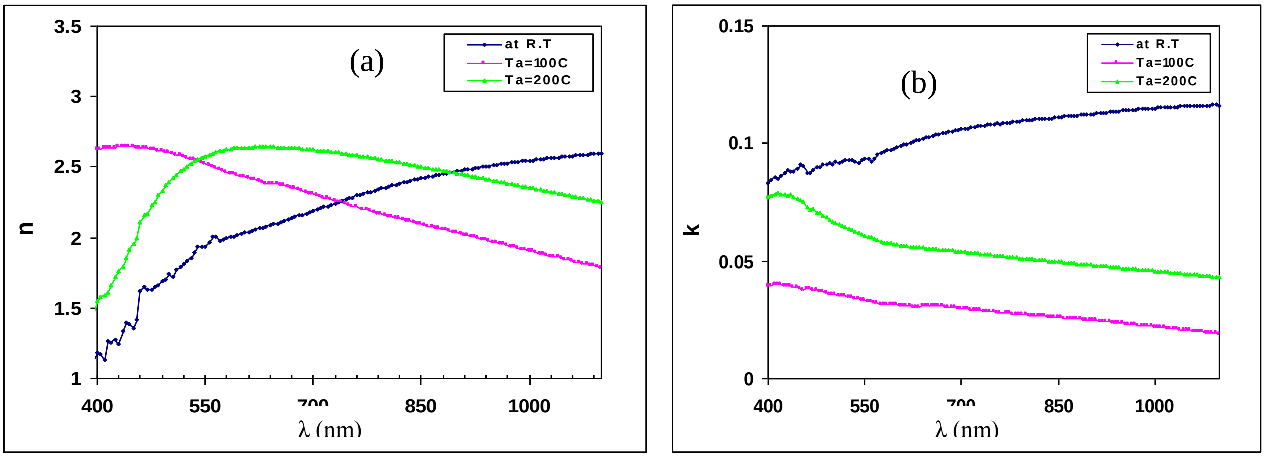

Fig. 6: The variation of (a) refractive index and (b) extinction coefficient with wavelength for as deposited and annealed Cu_2SiO_3 films at different annealing temperature.

The real (ε_r) and imaginary (ε_i) parts of dielectric constant were also calculated. The behavior of ε_r similar to refractive index because the smaller value of k^2 comparison of n^2, while ε_i is mainly depends on the k values, which are related to the variation of absorption coefficient. In general the dielectric constants decrease with increasing annealing temperature.

The optical properties parameters including, energy gap, absorption coefficient, refractive index, extinction coefficient, real and imaginary part of the dielectric constant at wavelength equals to 1000 nm for as deposited and annealed Cu_2SiO_4 films are listed in Table 3.

Table 3: The values of E_g^{opt} and Optical constants for Cu_2SiO_3 films as deposited and annealed films of different annealing temperature.

Sample	Temperature	E_g^{opt}(eV)	$\alpha(cm^{-1})*10^4$	n	k	ε_r	ε_i
			at λ=1000 nm				
Cu_2SiO_3	R.T	1.87	1.45	2.546	0.115	6.469	0.585
	100	2.35	0.27	1.907	0.022	3.636	0.084
	200	2.28	0.57	2.352	0.045	5.532	0.215

The type of charge carriers, concentration (n_H) and Hall mobility (μ_H), have been estimated from Hall measurements. Table 4 illustrates the main parameters estimated from Hall Effect measurements for Cu_2SiO_3 thin films deposited at room temperatures and annealed at (100, 200) ^oC. It is clear from this table that all films have negative Hall coefficient (n-type), the majority carriers are electrons while the minority carriers are holes.

The value of conductivity for as deposited films decreases from $1.32x10^{-5}$ to $3.27X10^{-9}$ $(\Omega.cm)^{-1}$ when film annealed at 100^oC and then increases to $6.26X10^{-6}$ for film annealed at 200 ^oC, as shown in Table 4.

This decreasing in the conductivity with heat treatment can be explained by the decrease in mobility of the charges, or perhaps the resistivity increases as a result of decreased electron density by reducing the oxygen content with annealing. It is also found that mobility decreases with the increase of annealing temperature. The explanation of decreasing in (μ_H) with T_a is due to increase of the scattering of the carrier from the surface as well as grain boundaries.

Table 4: Hall Effect measurements for Cu_2SiO_3 films as deposited and annealed films at different annealing temperature.

sample	Temperature(^oC)	type	σ_{RT} $(\Omega.cm)^{-1}$	n_H (cm^{-3})	μ_H $(cm^2/V.sec)$
Cu_2SiO_3	R.T	n	$1.12X10^{-5}$	1.01E+11	6.92E+2
	100	n	$3.27X10^{-9}$	5.86E+11	3.48E-2
	200	n	$6.26X10^{-6}$	1.22E+12	3.18E+1

The sensing properties to NO_2 gas of the as deposited Cu_2SiO_3 thin film which prepared by PLD method was performed, where nitrogen dioxide (NO_2) is a toxic compound with a pungent odor that is harmful to the environment as a major cause of acid rain and photochemical smog. NO_2 is mainly produced by power plants, combustion engines and automobiles. The room temperature sensitivity observed here is most likely to be due to the high surface-to-volume ratio of the one-dimensional nanostructures. Meanwhile, since Cu_2SiO_3 is an n-type semiconductor, the oxidizing NO_2 molecules adsorbed on the oxide surface may capture electrons from the conduction band and the electrical response of the sensor was measured with a computer-loaded analytic system. A voltage detecting method was used to calculate the sensitivity of the sensor, and it was defined as [13]:

$$S = (R_g - R_{air}) / R_{air} \quad (3)$$

where S represents sensitivity, R_g and R_{air} were the electrical resistances in NO_2 and synthetic air, respectively. Fig. 7 shows the variation of sensitivity with the operating temperature for as deposited Cu_2SiO_3 thin film. In general it is clear that the sensitivity increase with increasing the operation temperatures and it have maximum value at operation temperature equal to 300 ^oC.

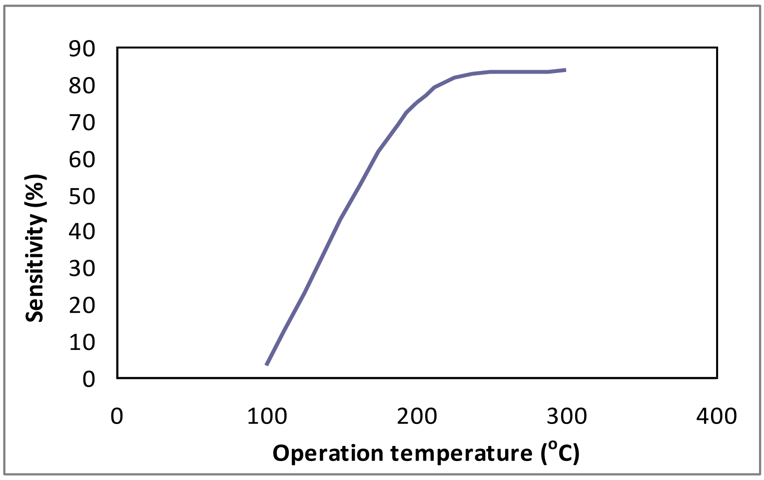

Fig.7: The variation of sensitivity with the operating temperature for Cu_2SiO_3 films.

Fig. 8 shows the relation between the response time and the Recovery time as a function of operation temperature deposited on silicon wafer (111) for 3 % NO_2: air, and bias voltage of 6 V. The figure reveals that the response time increase while recovery time decrease with increasing temperature. In real situations a fast response time is usually required, but a fast recovery time is not so important. All sensing parameter were illustrate in Table 5.

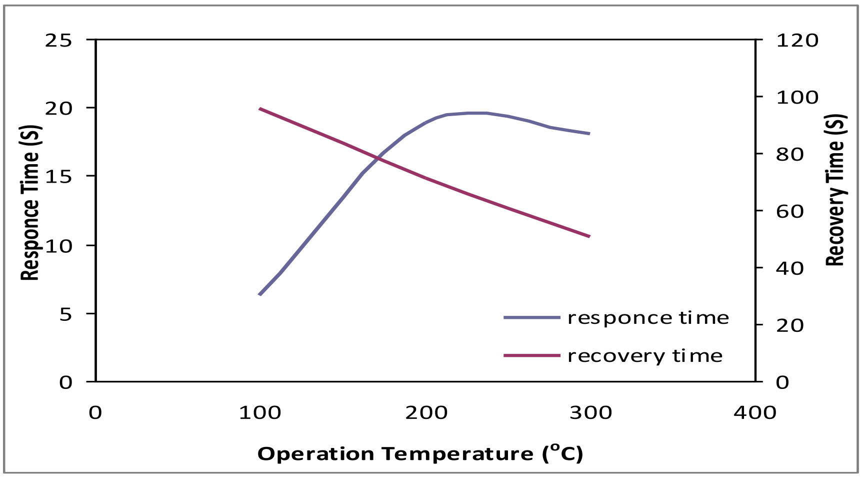

Fig.8: The variation of response time and recovery time of Cu_2SiO_3 film.

Table 5: Sensing characteristics of Cu_2SiO_3 films at different operating temperatures.

sample	Temperature °C	Sensitivity	Response time	Recovery time
Cu_2SiO_3	R.T	1.30	5.6	82.5
	100	3.21	6.3	95.4
	200	74.89	18.9	71.1
	300	83.53	18	50.4

Conclusions

The post deposition heat treatment effect on the structural, optical and electrical properties of Cu_2SiO_3 films deposited by pulsed laser deposition technique were investigated.

The x-ray analysis showed that the as deposited and annealed Cu_2SiO_3 films have amorphous structure and the structure becomes more amorphous with heat treatment. Topography study shows that films have granular grains with high average diameter of 163.63 nm. The optical transition in the Cu_2SiO_3 film is observed to be direct transition, and the optical energy gap broadens with heat treatment. Hall measurement showed that all the films are n-type.

The NO_2 gas sensitivity of Cu_2SiO_3 films is increase with operation temperature, and the response time increase while the recovery time decrease with increasing temperature.

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