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INFLUENCE OF ANNEALING TEMPERATURE ON THE PHYSICAL PROPERTIES OF THIN Cu_2SiO_4 FILMS PREPARED BY PULSED LASER DEPOSITION

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The Cu_2SiO_4 compound have been prepared from the binary compounds (CuO, and SiO_2) with high purity by solid state reaction. The Cu_2SiO_4 films that deposited at room temperature with thickness 400 nm were prepared by pulsed laser deposition technique. X-ray analysis showed that the powders of Cu_2SiO_4 have a polycrystalline structure with monoclinic phase and preferred orientation along (111) direction at 2θ around 38.970^o which related to CuO phase .While for as deposited and annealedCu_2SiO_4 thin films which have a weak crystallinty with two peaks related to cubic phase of Cu_2O which appear with preferred orientation along (111)direction. The morphological study revealed that the grains have round and elliptical shape, with average diameter of 122.62 nm. The electrical properties which represent Hall effect were investigated. Hall coefficient is negative which means the films are n-type. The sensing properties of theCu_2SiO_4 sensors for NO_2 gas have been studied, and the result revealed that the Cu_2SiO_4films have low sensitivity, and its improve with increasing the operation temperature . The response time increase while the recovery time decrease with increasing operation temperature.

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Keywords: Cu_2SiO_4 films, Structure and morphological properties, Optical properties, Sensing behavior

1. Introduction

Silicon dioxide thin films play a relevant role in silicon device technology, being used for passivation, as gate insulators, and as inter metal dielectric layers. These films are obtained either by thermal oxidation of silicon or by chemical vapor deposition processes, including both thermal and plasma-assisted ones[1,2].

Silicon dioxide is a material with 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. Because of its stability, amorphous nature, high density, adjustable refractive index, and low particulate contamination, SiO_2 has many typical applications, including in high-reflection coatings, antireflection coatings, all-dielectric mirrors, beam dividers, band pass filters, and polarizers [3].SiO_2 is the most widely used dielectric material for optical and electronic applications. An ultra thin layer of SiO_2 is of advantage as interlayer between the Si substrate and high- dielectric constant material to prevent chemical reactions of the high- material with the silicon substrate[4].SiO_2 regarded irreducible oxides and it relatively inert. However, in certain cases, silica has been shown to exhibit a metal–support interaction following a high temperature treatment [5].In silicates, Si is coordinated almost exclusively to four oxygen ions forming a (SiO_4) tetrahedron. Although they may exist as isolated SiO_4^{4-} centers, like in olivine (Fe, Mg)$_2SiO_4$, in most cases the silicates are formed by corner-sharing (SiO_4) tetrahedra.

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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].

Orthosilicates of many bivalent metals (M_2SiO_4) are widely applied in various technologies, such as, Zn_2SiO_4 as luminescent materials, also as ultraviolet absorbers , while Mg_2SiO_4, Fe_2SiO_4, Zn_2SiO_4 are dielectric and corrosion protective coating materials [7].

Copper or copper oxides in oxide matrixes have attracted sustained interest due to their unusual properties[8] .Mohanan and Brock [9] have studied copper oxide silica aerogel composites by varying pH values, copper precursor salts, and treatment temperatures. They found that base-catalyzed gels underwent a gradual change from bonded Cu^{+2} to segregated CuO at different heating condition.

The aim of present work is understanding the effect of annealing temperature on the structure, optical and electrical properties of Cu_2SiO_4 thin films prepared by pulsed laser deposition method.

2. Experimental procedure

The Cu_2SiO_4 powder was synthesized by solid state reaction of SiO_2 , and CuO (Fluka AG, Buchs SG, Made in Switzerland, 99%) which sintered at temperature equal to 950 °C for two hours. The two binary compounds are mixed and crushed for an hour then pressed under 5 ton to from a target with a pellet shape with (13mm) diameter and (8mm) thickness. The Cu_2SiO_4 thin films were deposited on glass and Si substrates at room temperature with 400 nm thickness by pulsed laser deposition (PLD) method. The films annealed at 100 and 200°C. The laser type wasNd: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^oat a vacuum chamber (10^{-2} mbar). The crystal structure analysis of these films was obtained by using X-ray diffractometer type (Miniflex II Rigaku company, Japan) was used with CuK_α target of wavelength 0.154nm and $2\theta = 10^o – 80^o$. 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). 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.

3. Result and discussion

The X- ray diffraction was used to study the crystalline structure of powder and thin films of Cu_2SiO_4composite which deposited on glass substrate.

Fig. (1)shows the XRD pattern of Cu_2SiO_4powder which have a polycrystalline structure and indicated the presence of unique crystalline phase of CuO with monoclinic structure with preferred orientation along (111) direction at 2Ɵ around 38.970^o .The data compared with JCPDS card number 96-900-8962 . The high concentration of CuO in the Cu_2SiO_4 powder at 950C corresponds 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 [7].

Table 1 illustrates all structure parameters of Cu_2SiO_4 powder.

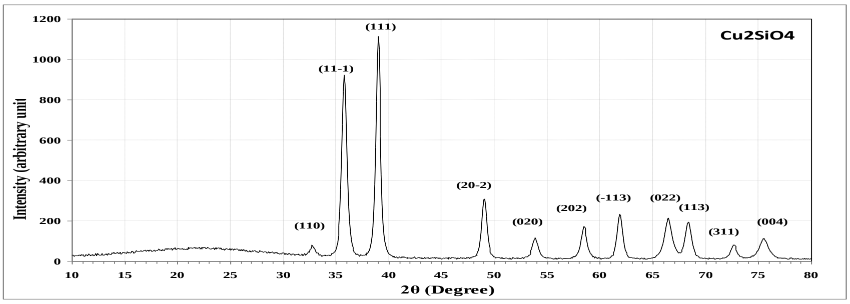


Fig. 1. X-ray diffraction patterns for Cu_2SiO_4 powder

Table 1. X-ray diffraction data for Cu_2SiO_4 powder

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	Phase	Card No.
Cu_2SiO_4	32.7500	0.5400	2.7323	15.3	(110)	2.7372	Mono. CuO	96-900-8962
	35.7700	0.5320	2.5082	15.7	(11-1)	2.5108	Mono. CuO	96-900-8962
	38.9700	0.4940	2.3093	17.1	(111)	2.3118	Mono. CuO	96-900-8962
	49.0100	0.5342	1.8572	16.4	(20-2)	1.8553	Mono. CuO	96-900-8962
	53.8300	0.6320	1.7017	14.1	(020)	1.7050	Mono. CuO	96-900-8962
	58.4500	0.6310	1.5777	14.4	(202)	1.5724	Mono. CuO	96-900-8962
	61.8500	0.5650	1.4989	16.4	(-113)	1.4986	Mono. CuO	96-900-8962
	66.4300	0.8430	1.4062	11.3	(022)	1.4120	Mono. CuO	96-900-8962
	68.3300	0.6530	1.3717	14.7	(113)	1.3726	Mono. CuO	96-900-8962
	72.6300	0.6350	1.3007	15.5	(311)	1.2960	Mono. CuO	96-900-8962
	75.4700	0.9860	1.2586	10.2	(004)	1.2596	Mono. CuO	96-900-8962

X-ray diffraction pattern for as deposited and annealed Cu_2SiO_4 thin films which deposited on glass substrates and prepared by Pulsed laser deposition are shown in figure (2). The results reveals that the as deposited Cu_2SiO_4 films have weak crystallity with two peaks related to cubic phase of Cu_2O which appear with preferred orientation along (111) direction at 2θ around 36.58°,and 36.46° and another orientation along (200) direction at 2θ around 42.34° and 43.02° for as deposited and annealed films respectively. The data compared with JCPDS Card number 96-100-0064.The Cu_2O phase appearance may be related to high concentration of CuO which decompose and converted to Cu_2O .these results agree with the result of Tohidi[6] and Homaunmir et al [10].

The peak intensity of Cu_2SiO_4 films increases as the annealing temperature increase which mean increase the crystallite size of this film. This may be due to the improvement of crystallinity. It is important to say, that there are two possibilities to improve the crystalline of the films: an increase in grain size to decrease the number of grain boundaries and a decrease in barrier height at the grain boundaries. The comparison of (XRD) data also shows that the full-width at half-maximum (FWHM) values of the (XRD) peaks decrease with increasing annealing temperature, which indicates that the crystalline of these films enhanced as the annealing temperature increases. Table (2) shows the structural properties of as deposited and annealed Cu_2SiO_4 film at (100 and 200)^{o}C.

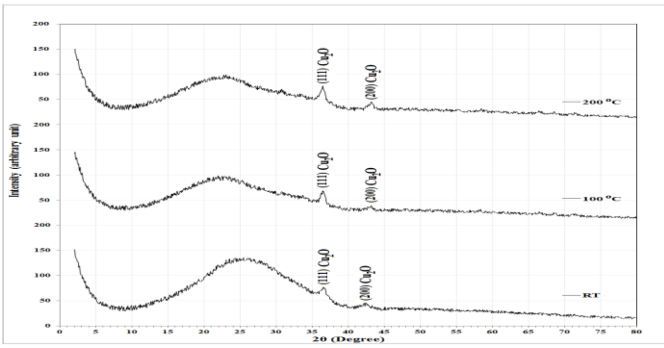


Fig.2. X-ray diffraction pattern for Cu_2SiO_4 films as deposited and annealed at (100,200)^oC

Table 2. X-ray diffraction data forCu_2SiO_4 films as deposited and annealed at (100,200)^oC

Annealing	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	Phase	Card No.
RT	36.5800	1.1200	2.4545	7.5	(111)	2.4549	Cub. Cu_2O	96-100-0064
	42.3400	1.2650	2.1330	6.7	(200)	2.1260	Cub. Cu_2O	96-100-0064
100	36.4600	0.6880	2.4623	12.2	(111)	2.4549	Cub. Cu_2O	96-100-0064
	43.0200	0.7600	2.1008	11.2	(200)	2.1260	Cub. Cu_2O	96-100-0064
200	36.4600	0.5640	2.4623	14.8	(111)	2.4549	Cub. Cu_2O	96-100-0064
	43.0200	0.9540	2.1008	9.0	(200)	2.1260	Cub. Cu_2O	96-100-0064

An atomic force microscopic (AFM) allowed to get the microscopic information of the surface structure and to plot topographies of the surface relief. This technique offered the digital images, which gave quantitative measurements of surface features, such as the average diameter and the average roughness. The surface roughness of the thin films are an important parameter which beside describing the light scattering at the surface, gives a significant indication about the quality of the surface under investigation. The increase in surface roughness of the films leads to increase in efficiency for sensing properties, therefore, it is very important to investigate the surface morphology of the films.

The two and three dimensional AFM images of Cu_2SiO_4thin film prepared by pulsed-laser deposition, which acquired over an area 2.5x 2.5 μm^2 in contact mode are shown in figure (3). It is clear that the nanoparticles are round and elliptical in shape, with average grain size of 122.62 nm , and the surface has a small roughness value 2.6 nm.

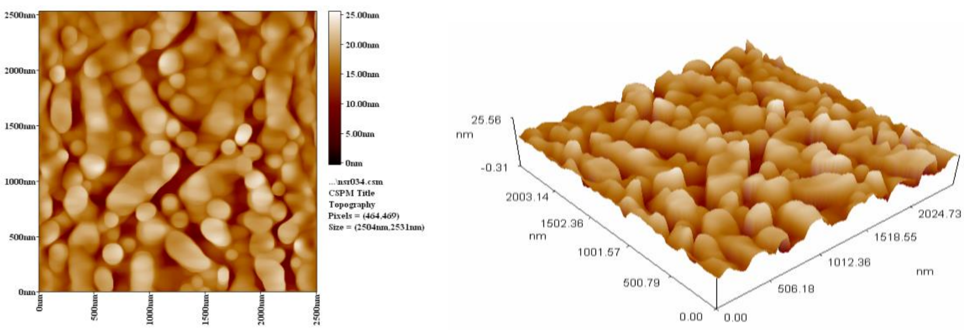
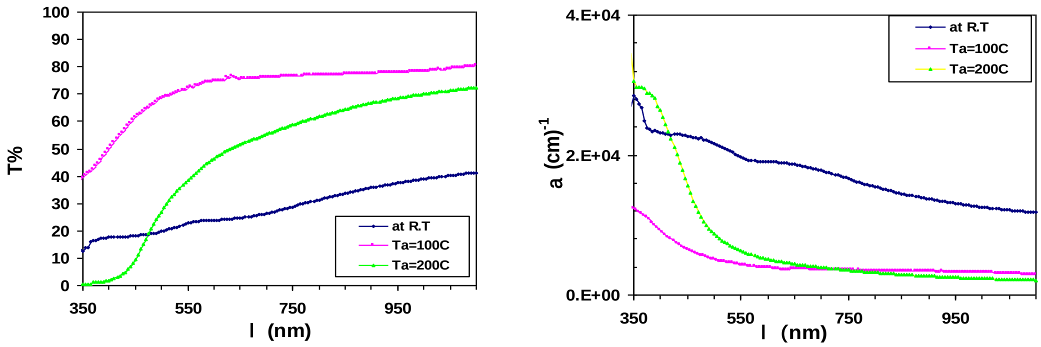


Fig. 3. AFM picture and histogram for as deposited Cu_2SiO_4 thin films

The optical transmittance spectra of the Cu_2SiO_4 films were measured at wavelength range (300-1100)nm for as deposited and annealed films as show in figure (4a). It is clear that the film transmission increase with increasing wavelength, and the optical transparency of the films increases with increases annealing temperature to 100^{o}C and then decrease when annealing temperature reach to 200^{o}C.

Absorption coefficient of the films as a function of wavelength showed in figure (4b) which is characterized by strong absorption at shorter wavelengths region, and as deposited film has less sharp edge and the edge becomes sharper with increasing annealing temperature. This is attributed to improve the structure. The absorption edge shifted to higher energy however its indicates that it is related to changes in film structure.



(a) (b)

Fig.4. (a)The transmittance (b) absorption coefficient versus the wavelength for Cu_2SiO_4 as deposited and annealed films at different annealing temperature

The optical energy gap values (E_g^{opt}) for as deposited and annealed Cu_2SiO_4 films can be calculated using the Fundamental absorption, which corresponds to electron excitation from the valance band to conduction band as a direct transition. Extrapolation of the linear portion of the plots of $(\alpha h\upsilon)^2$versus photon energy to α =0 yields the optical band gap of the Cu_2SiO_4 films. Figure (5) shows the plot of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) of as deposited and annealed Cu_2SiO_4 films annealed at different annealing temperature .

The direct band gap value of the Cu_2SiO_4 films increases from 1.80eV to 2.72eV when film annealed at 100^{o}C and change to 2.55eVwhen annealed at 200^{o}C. This means the optical energy gap increases with heat treatment. This is related to eliminate the defect and decreasing the defect state in energy gap.

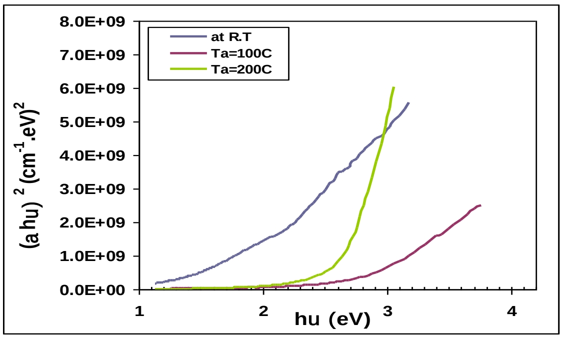
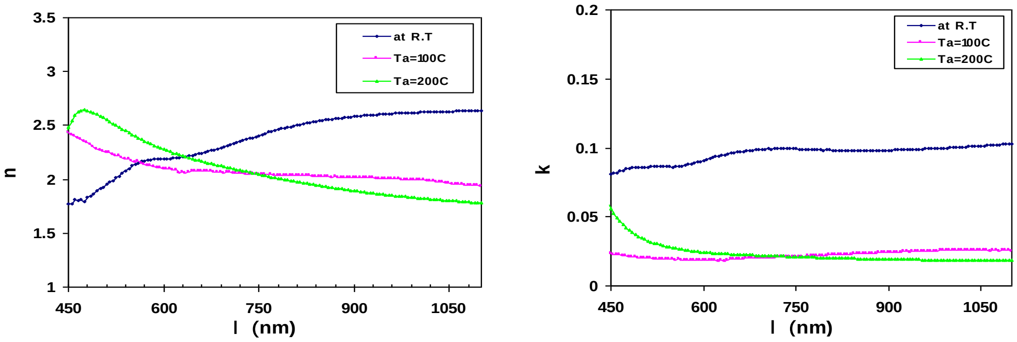


Fig.5. Energy gap of Cu_2SiO_4 films as deposited and annealed films at different annealing temperature

The variation of the refractive index versus wavelength in the range of 450–1100 nm for as deposited and annealed Cu_2SiO_4 films are shown in figure (6a).It is interesting to see that refractive index decreases with increasing annealing temperatures. This behavior is due to decrease in the reflection which the refractive index depend on it.

The behavior of the extinction coefficient of as deposited andannealed Cu_2SiO_4 films are shown in figure (6b).The behavior of extinction coefficient (k) is nearly similar to the corresponding absorption coefficient as shown in Table(3) at different T_a, we can see from this Table that k decreases with increasing T_a from RT to 200°C. This attributed to the same reason, which mention previously in absorption coefficient .



(a) (b)

Fig.6. The variation of (a) refractive index and (b) extinction coefficient with wavelength for as deposited and annealed Cu_2SiO_4 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_4 films as deposited and annealed at different annealing temperature

Sample	Temperature	E_g^{opt}(eV)	α(cm^{-1}) *10^4	n	k	ε_r	ε_i
Cu_2SiO_4	R.T	1.80	1.26	2.620	0.100	6.859	0.524
	100	2.75	0.32	1.994	0.025	3.975	0.1029
	200	2.55	0.23	1.827	0.018	3.340	0.069

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 obtained by Hall Effect measurements for Cu_2SiO_4thin films deposited at room temperatures and annealed at (100,200)°C. 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 1.32×10^{-5} to 1.59×10^{-7} $(\Omega.cm)^{-1}$ when film annealed at 200°C, as illustrate in Table (4).

This decreasing in the conductivity with annealing temperature can be explained by the decrease in carrier concentration and 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 forCu_2SiO_4films as deposited and annealed Film sat different annealing temperature

Sample	Temperature(^oC)	type	σ_{RT} $(\Omega.cm)^{-1}$	n_H (cm^{-3})	$\mu_H(cm^2/V.sec)$
Cu_2Sio_4	R.T	n	$1.32X10^{-5}$	4.329E+11	1.909E+2
	100	n	$4.95X10^{-6}$	1.180E+12	2.622E+1
	200	n	$1.59X10^{-7}$	4.563E+10	2.320E+1

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. To measure gas sensing properties of the Cu_2SiO_4 thin films we prepared these films by PLD. 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_4films are 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:

$$S = (R_g – R_{air}) / R_{air} \tag{1}$$

where S represents sensitivity, R_g and R_{air} were the electrical resistances in NO_2 and synthetic air, respectively. To observe dynamic and repetitive responses. Figure (7) shows the relation between sensitivity with the operating temperature for Cu_2SiO_4 films. 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.

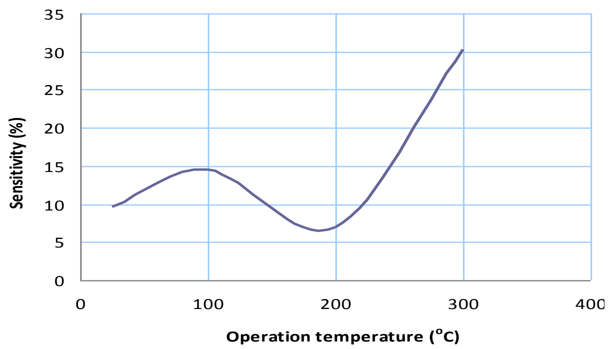


Fig.7. The variation of sensitivity with the operating temperature for Cu_2SiO_4 films

Fig. (8) shows the relation between the response and the Recovery time as a function of operation temperature deposited on silicon wafer (111) for NO_2 gas. 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).

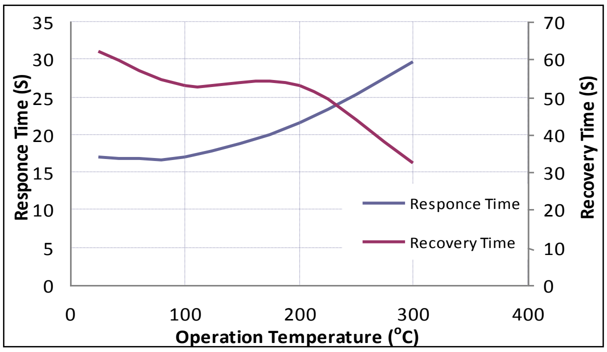


Fig. 8.The variation of response and recovery time with operation temperature of Cu_2SiO_4 films.

Table 5.Sensing characteristics of Cu_2SiO_4 films at different operating temperatures.

Sample	Temperature °C	Sensitivity	Response time	Recovery time
Cu_2SiO_4	R.T	9.67	17.1	62.1
	100	14.51	17.1	53.1
	200	6.94	21.6	53.1
	300	30.19	29.7	32.4

4. Conclusions

Effect of annealing temperature on structural, optical and electrical properties of thin Cu_2SiO_4 films deposited by pulsed laser deposition technique were investigated.

XRD patterns show that the deposited Cu_2SiO_4 films have weak crystallity with two peaks related to cubic phase of Cu_2O which appear with preferred orientation along (111) direction and another orientation along (200) direction . AFM measurements revealed that the grains have round and elliptical shape, with average diameter of 122.62 nm. The effect of annealing temperature on optical properties shows that the increasing in T_a shifts absorption edge to the shorter wavelength compared to the as deposited film. The optical energy gap are direct transitions, and the heat treatment lead to increase the energy gap, whereas in general the optical constants decreases. Hall effect measurement reveals that the sign of the Hall coefficient for Cu_2SiO_4 films is negative. This confirms that these films have n-type charge carriers. The gas sensor characteristics revealed that the Cu_2SiO_4 films have low sensitivity, and its improve with increasing the operation temperature . The response time increase while the recovery time decrease with increasing operation temperature.

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