Study the effect of thermal annealing on some physical properties of thin Cu₂SiO₃ films prepared by pulsed laser deposition

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Abstract

The Cu₂SiO₃ composite has been prepared from the binary compounds (Cu₂O, and SiO₂) with high purity by solid state reaction. The Cu₂SiO₃ 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 Cu₂SiO₃ has a polycrystalline structure with monoclinic phase and preferred orientation along (111) direction at 2θ around 38.670° which related to CuO phase. While as deposited and annealed Cu₂SiO₃ 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 Cu₂SiO₃ sensors for NO₂ gas have been studied, and the result revealed that the Cu₂SiO₃ 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.

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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]. SiO₂ properties like stability, amorphous nature, high density, adjustable refractive index, and low particulate contamination, led to use SiO₂ in many typical applications, including in high-reflection coatings, antireflection coatings, all-dielectric mirrors, beam dividers, band pass filters, and polarizers [3, 4]. SiO₂ 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 SiO₂ glass matrix has a strong influence on the optical visible absorption spectrum. Various materials embedded in the glass matrix produce quantum and nonlinear 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 (M₂SiO₄) are widely applied in various technologies, such as, Zn₂SiO₄ as luminescent materials and ultraviolet absorbers, while Mg₂SiO₄, Fe₂SiO₄, Zn₂SiO₄ 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.SiO₂) composites synthesis is rather modest, in contrast to other oxide composites such as MoSiO₂ type, where M most often stands for aluminum, calcium, zinc, magnesium or titanium [7].

In this paper, Cu₂SiO₃ 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 (Cu₂SiO₃) powder was synthesized by solid state reaction. In this case, astroichiometric mixture of SiO₂, and Cu₂O (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 °C for two hours. The Cu₂SiO₃ 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°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 CuKα target of wavelength 0.154 nm and 2θ = 10°–80° 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\textsubscript{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\textsubscript{2}SiO\textsubscript{3} composite powder shows a polycrystalline structure and exhibited sharp peaks with preferential orientation in the [111] direction at 2\(\Theta\) equals to 38.6700\(^\circ\) 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\textsubscript{2}SiO\textsubscript{3} composite at 950\(^\circ\)C 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\textsubscript{2}SiO\textsubscript{3} powder.

X-ray diffraction patterns for as deposited and annealed Cu\textsubscript{2}SiO\textsubscript{3} thin films at 100 and 200 \(^\circ\)C 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\textsubscript{2}SiO\textsubscript{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 \(^\circ\)C 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\textsubscript{2}SiO\textsubscript{3} powder.](image)
Table 1: X-ray diffraction data for Cu$_2$SiO$_3$ powder.

| Sample  | 2θ (Deg.) | FWHM (Deg.) | $d_{hkl}$ Exp.(Å) | G.S (nm) | hkl    | $d_{hkl}$ Std.(Å) | Phase   | Card No.          |
|---------|-----------|-------------|------------------|----------|--------|------------------|---------|------------------|
| Cu$_2$SiO$_3$ | 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$_2$SiO$_3$ films as deposited and annealed at (100, 200) °C.

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$_2$SiO$_3$ 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.
The optical transmittance spectra of as deposited and annealed Cu$_2$SiO$_3$ 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 °C and the decrease when annealing temperature reach to 200°. However the change in transmission indicates there are changes in film structure. The absorption coefficient ($\alpha$), was calculated using Lambert’s law [11]:
\[
\ln \frac{I_o}{I} = 2.303A = \alpha t
\]
where, A is the optical absorbance, t is the film thickness, $I_o$ 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. 3: 2D and 3D images for as deposited Cu$_2$SiO$_3$ thin films.

Fig. 4: (a) The transmittance (b) absorption coefficient versus the wavelength for Cu$_2$SiO$_3$ as deposited and annealed films at different annealing temperature.
The optical band gap \( (E_g) \) of \( \text{Cu}_2\text{SiO}_3 \) films has been determined from the optical absorption coefficient and photon energy \( (h\nu) \) data assuming the direct transmission occurs between valance and conduction band using Tauc’s relation [12].

\[
(\alpha h\nu) = B(h\nu - E_g)^{1/2}
\]

(2)

where B is a constant inversely proportional to amorphousity. Extrapolation of the linear portion of the plots of \((\alpha h\nu)^2\) versus photon energy to \( \alpha = 0 \) yields the direct optical band gap of the \( \text{Cu}_2\text{SiO}_3 \) films. Fig. 5 shows the plot of \((\alpha h\nu)^2\) versus photon energy \( (h\nu) \) of as deposited and annealed \( \text{Cu}_2\text{SiO}_3 \) films.

The direct band gap value of the \( \text{Cu}_2\text{SiO}_3 \) films varies between 1.87, 2.35 and 2.28 eV for as deposited and annealed at 100 and 200 °C 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.

The variation of the refractive index versus wavelength in the range of 400–1100 nm for as deposited and annealed \( \text{Cu}_2\text{SiO}_3 \) 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 \( \text{Cu}_2\text{SiO}_3 \) films are shown in Fig. 6b. The behavior of extinction coefficient \( (k) \) is nearly similar to the corresponding absorption coefficient as shown in Table 3, 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.
The real \((\varepsilon_r)\) and imaginary \((\varepsilon_i)\) parts of dielectric constant were also calculated. The behavior of \(\varepsilon_r\) similar to refractive index because the smaller value of \(k^2\) comparison of \(n^2\), while \(\varepsilon_i\) 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 \(\text{Cu}_2\text{SiO}_3\) films are listed in Table 3.

**Table 3: The values of \(E_g^{\text{opt}}\) and Optical constants for \(\text{Cu}_2\text{SiO}_3\) films as deposited and annealed films of different annealing temperature.**

| Sample   | Temperature | \(E_g^{\text{opt}}\) (eV) | \(\alpha\) \((\text{cm}^{-1})\times10^4\) | \(n\)  | \(k\)  | \(\varepsilon_r\) | \(\varepsilon_i\) |
|----------|-------------|-----------------------------|------------------------------------------|-------|-------|-------------------|-------------------|
| \(\text{Cu}_2\text{SiO}_3\) <br> 100 | 1.87        | 1.45                        | 2.546<sub>1000 nm</sub>                 | 0.115 | 6.469 | 0.085             |
|         | 2.35        | 0.27                        | 1.907<sub>1000 nm</sub>                 | 3.636 | 0.57  | 0.215             |
|         | 2.28        | 0.57                        | 2.352<sub>1000 nm</sub>                 | 5.532 | 0.045 |                   |

The type of charge carriers, concentration \((n_H)\) and Hall mobility \((\mu_H)\), have been estimated from Hall measurements. Table 4 illustrates the main parameters estimated from Hall Effect measurements for \(\text{Cu}_2\text{SiO}_3\) thin films deposited at room temperatures and annealed at \((100, 200)\) °C. It is clear from this table that all films have negative Hall coefficient \((n\text{-type})\), the majority carriers are electrons while the minority carriers are holes.

The value of conductivity for as deposited films decreases from \(1.32\times10^{-5}\) to \(3.27\times10^{-9}\) \((\Omega\cdot\text{cm})^{-1}\) when film annealed at 100°C and then increases to \(6.26\times10^{-6}\) for film annealed at 200 °C, 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 \((\mu_H)\) 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$_2$SiO$_3$ films as deposited and annealed films at different annealing temperature.

| sample    | Temperature(°C) | type | $\sigma_{RT}$ (Ω.cm)$^{-1}$ | $n_H$ (cm$^3$) | $\mu_H$ (cm$^2$/V.sec) |
|-----------|-----------------|------|-----------------------------|----------------|------------------------|
| Cu$_2$SiO$_3$ | R.T             | n    | $1.12 \times 10^{-5}$       | $1.01 \times 10^{11}$ | $6.92 \times 10^{2}$  |
|           | 100             | n    | $3.27 \times 10^{-9}$       | $5.86 \times 10^{11}$ | $3.48 \times 10^{-2}$ |
|           | 200             | n    | $6.26 \times 10^{-6}$       | $1.22 \times 10^{12}$ | $3.18 \times 10^{1}$  |

The sensing properties to NO$_2$ gas of the as deposited Cu$_2$SiO$_3$ 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$_2$SiO$_3$ 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]:

$$S = \frac{(R_g - R_{air})}{R_{air}}$$

(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$_2$SiO$_3$ 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 °C.

![Fig.7: The variation of sensitivity with the operating temperature for Cu$_2$SiO$_3$ films.](image)

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$_2$SiO$_3$ film.

Table 5: Sensing characteristics of Cu$_2$SiO$_3$ films at different operating temperatures.

| Sample   | Temperature °C | Sensitivity | Response time | Recovery time |
|----------|----------------|-------------|---------------|---------------|
| Cu$_2$SiO$_3$ | 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$_2$SiO$_3$ films deposited by pulsed laser deposition technique were investigated.

The x-ray analysis showed that the as deposited and annealed Cu$_2$SiO$_3$ 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$_2$SiO$_3$ 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$_2$SiO$_3$ films is increase with operation temperature, and the response time increase while the recovery time decrease with increasing temperature.

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