

Effect of thickness and temperature on strain in a copper oxide nano film for gas sensing applications

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Abstract: In this study copper oxide nano film is synthesized on glass substrate by thermal evaporation technique for gas sensing applications. While deposition the distance between source and substrate is kept constant and the pressure of the chamber is kept at 2.5×10^{-5} torr. The rate of deposition is varied from 6 to 10°A. The thickness of the film is kept constant. The film is heat treated at varying temperature to get the optimum result. Structural study is done by using the Debye-Scherrer formula. From XRD graph, strain analysis is carried out which is useful to study gas sensing of different gases. The thickness of the film and annealed temperature can be varied further to obtain the optimum results.

keywords: Thermal Evaporation, Copper Oxide, Spectrophotometer, XRD.

1. Introduction

Copper is a soft metal with high thermal and electrical conductivity. Copper is used as good conductor of heat and electricity. It is one of the few metals that can occur in nature in a directly usable metallic form. Copper nanoparticles with great catalytic activities can be applied to sensors. Copper is one of the most essential in latest technologies and is easily accessible. From the recent years environment pollution has been increasing day by day due to industries and air pollution has become a serious damage to world. To prevent air pollution, it is vital to control the safety measures of dangerous gases. In the process of air pollution management dangerous gas detection becomes very important. There are different methods for gas detection like IR spectroscopy, gas chromatography, solid state gas sensing and many others. Among them solid state semiconducting gas sensors are having more advantages due to many factors. Fabrication of semiconducting gas sensors is very simple, reduced cost and can be designed to work at various temperatures. Different semiconducting metal oxides have been used as gas sensing material, among them copper nano film is a reliable material. Copper nano films can be used in applications such as transistors, gas sensors, photo chemical and photo conductive devices. Copper oxide is also known as tenorite oxide which is an inorganic substance and generally an p-type semiconductor. Copper oxide thin films can be synthesized by different techniques such as Thermal Evaporation, DC sputtering, R.F. Magnetron, Co-sputtering, Spray Pyrolysis, Laser Pulse Evaporation, Chemical Vapor Deposition, Sol-Gel, Vapor deposition technique, etc. Thermal evaporation technique has advantages for production of non-doped thin films as concern for homogeneous deposition, easy control over thickness, and overall its cost effective. Copper nano films synthesized on tin oxide film have been using for detection of gases like NO₂, CO, H₂S, NH₃ etc. Aparna et al. [1] illustrated that CuO nanoparticles have potential applications for solar energy transfer, sensors, storage devices and in

super conductors. CuO nanoparticles act as a good catalyst in chemical reactions. CuO nanoparticles are fabricated by sol gel technique and concluded that XRD pattern revealed CuO nanoparticles have monoclinic structure. Kannaki et al. [2] proposed the hydrothermal route for the production of copper oxide nano particles. XRD analysis is carried out to calculate the grain size and strain analysis is done. Darezereshki and Bakhtiari [3] described that CuO nanoparticles are fabricated by a thermal decomposition method with mean diameter of 170 ± 5 nm. This method does not require organic solvents, expensive raw materials and complicated equipment. So, it is concluded that the presented method is better to the other methods for the synthesis of CuO nanoparticles from dilute CuSO₄ solution. Ooi et al [4] studied the effect of oxygen percentage on the structural properties of cupric oxide (CuO) thin films and found the state of the three different phases of copper oxide thin films namely: Cu₂O, Cu₄O₃, and CuO. The presence of these phases controlled strongly to the oxygen percentage. At lower oxygen percentage a pure Cu₂O thin films with cubic structure are deposited with increasing the oxygen percentage a pure CuO thin films with monoclinic structure are elaborated. Singh et al [5] investigated the deposition of CuO films by ultrasonic spray deposition at different substrate temperature from 300 to 400°C and show that the CuO films are polycrystalline in nature with presence of two most prominent peaks corresponding to atomic planes (002) and (111), whereas growth along atomic planes (110), (020) and (220) are also observed. Akaltun et al. [6]. observed a decrease in films band gap from 2.03 eV to 1.79 eV related to the increase in film thickness from 120 to 310 nm for CuO films prepared by successive ionic layer adsorption and reaction (SILAR) method. Nithya et al. [7] investigated Copper oxide nanoparticles are prepared by modified sol-gel technique using sodium dodecyl sulphate as a surfactant. Effect of calcination temperature on particle size, band-gap, crystallinity and morphology of the nanoparticles are studied with the help of particle size analysis, UV-Spectroscopy, powder X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) studies. Gas sensitivity is carried out for sensing of different gases. Wongpisutpaisana et al. [8] described that CuO nanoparticles are fabricated by a sono-chemical synthesis by the aid of ultrasound with the reaction time up to 30 min and calcination at 600-700 °C. It is revealed that its crystallization and particle size can withstand the reaction time and calcination temperature.

2. Fabrication of Thin Film

Thermal evaporation unit model – 12A 4D is used for the fabrication of Copper oxide thin films deposited on glass substrates (75mm x 25mm). Organic particles are removed on the surface of the glass plate by using ultrasonic cleaner with acetone and water before deposition .Later on washed with distilled water and dried. Now place the cleaned substrates were placed inside the vacuum chamber of Thermal Evaporation unit (model 12A 4D). Copper in the form of small particles taken into a tungsten boat and connected between the electrodes. The pressure of the chamber is maintained at 2.5×10^{-5} torr and rate of deposition can be varied. During the process the distance between source and substrate kept constant.

2.1 Annealing

After deposition, the substrates were taken out from vacuum chamber and placed in a furnace (Indfurr muffle furnace). Here the samples were annealed at constant temperature i.e 200°C for three hours. Experimental setup is shown in fig1.



Fig 1: Experimental setup

3. Results and Discussions

3.1 Optical Characterization

Optical properties of copper oxide thin films were characterized from the transmission% vs wavelength graph by using the equipment ELICO UV/VIS spectrophotometer (model SL-210) in the range of 190nm to 1100nm. Refractive index, thickness of the film and band gap energy were calculated.

Refractive index is given,

$$n = \{N + (N^2 - \mu^2)^{1/2}\}^{1/2} \quad [9] \quad (1)$$

Where

$$N = 2\mu \frac{T_u - T_l}{T_u T_l} + \frac{\mu^2 + 1}{2} \quad [9] \quad (2)$$

And n is the refractive index of thin film.

μ is the refractive index of the glass substrate, T_u and T_l are the transmission maximum at upper limit and transmission minimum at lower limit for a certain wavelength. From Fig.2, for maxima $\lambda_1=824\text{nm}$, $T_u=0.5643$, $T_l=0.4$ and $\mu=1.5$ by substituting in (2) we get $N_1=3.808678$ from this by equation (1) $n_1=2.703615$.

for minima:

$\lambda_2= 924\text{nm}$, $T_u=0.5843$, $T_l= 0.4780$ and $\mu=1.5$ by substituting in (2) we get $N_2=2.7668018$ from this by equation (1) $n_2=2.25648150$. Thickness of the film is calculated from transmission spectra data. Thickness of the film d is given by,

$$d = \frac{\lambda_1 \lambda_2}{4(n_1 \lambda_2 - n_2 \lambda_1)} \quad [9] \quad (3)$$

where n_1 and n_2 are refractive index of thin film at maxima and minima i.e at wavelengths λ_1 and λ_2 . Using the values of n_1 and n_2 we calculated thickness of the film as 300nm.

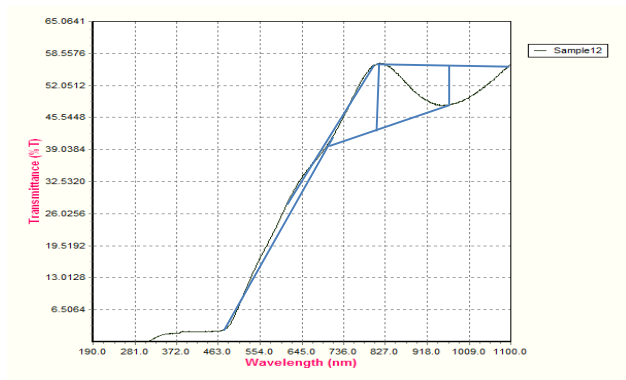


Fig.2- Transmittance % vs Wavelength

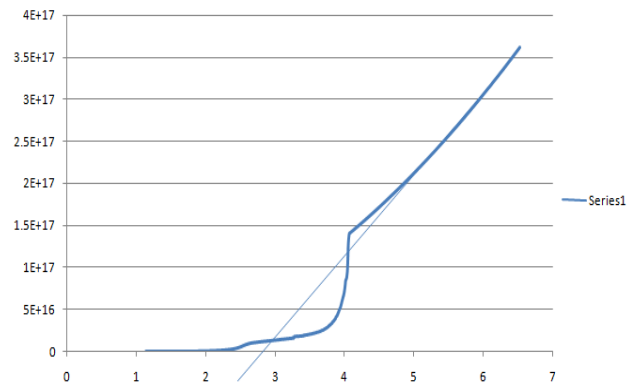


Fig.3- $(\alpha h\nu)^2$ vs. photon energy

The band gap energy of copper thin film was calculated from the graph $(\alpha h\nu)^2$ vs. $(h\nu)$ i.e from fig.3. When the linear portion of the graph is extended back it intersects the eV axis and this intercept is the energy band which is measured as 2.54 eV.

3.2 Structural Analysis

From fig.4 The structural analysis of the film is carried out by using SIEMENS diffractometer model (1275) using copper having the wavelength range $\lambda = 1.540 \text{ \AA}$. From XRD analysis, mean grain size (D) and strain (ϵ) are calculated.

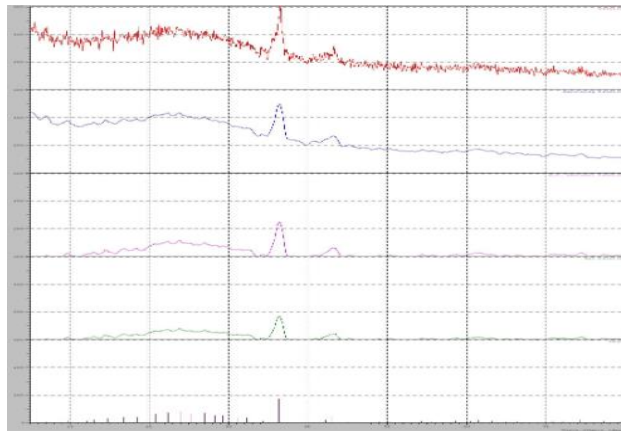


Fig.4- XRD pattern of copper thin film

Table1-XRD data with strongest peaks

No	Peak no	2 Theta(deg)	FWHM
1.	18	36.3617	1.12350
2.	10	23.900	0.00
3.	9	22.400	0.00

Mean grain size(D):

By using Debye-Scherrer formula

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad [9] \quad (4)$$

$$\beta \cos\theta = \frac{0.9\lambda}{D} + \varepsilon \sin\theta \quad [9] \quad (5)$$

Where D is mean grain size, λ is the wavelength of X-ray is 1.54\AA , θ is the angle of diffraction, ε is the strain and β -Full Width Half Maximum (FWHM) of observed peaks. By using the formulas (4) and (5) and by taking the mean values of the strongest peaks we calculate average grain size as 12.9nm and strain as 3.2×10^{-5} .

4. Conclusion

Copper oxide thin films were fabricated by thermal evaporation technique. From optical measurement the band gap was measured as 2.54 eV . XRD revealed the grain size as 12.9nm and strain as 3.2×10^{-5} . The film was under studied for gas sensing of different gases and further sensitivity of the film is measured.

5. Acknowledgment:

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