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Effect of Grain Size on Strain in a Copper Oxide Nanofilm for Gas Sensing Applications

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In this study, copper oxide nanofilm is synthesized on glass substrate by thermal evaporation technique for gas sensing applications. During deposition, the distance between source and substrate is kept constant and the pressure of the chamber is kept at 1.0×10^{-4} torr. The rate of deposition is varied from 6 to 10 Å/s. The thickness of the film is kept constant at 150 nm. The film is heat treated at varying temperature and for different time interval to get the optimum result. Structural study is done by using the Debye-Scherrer formula. From XRD graph, strain analysis is carried out which reveals that strain increases with decrease in grain size which is useful to study gas sensing of different gases.

Keywords: Band gap, Thermal evaporation, XRD, Transmittance and optical characteristics.

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1. INTRODUCTION

Copper is a soft metal with high thermal and electrical conductivity. Copper is used as a 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, environmental 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, they have reduced cost and can be designed to work at various temperatures. Different semiconducting metal oxides have been used as gas sensing materials, among them copper nanofilm is a reliable material. Copper nanofilms 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 a *p*-type semiconductor. Copper oxide thin films can be synthesized by different techniques such as thermal evaporation, DC sputtering, RF 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 it is cost effective. Copper nanofilms synthesized on tin oxide film have been used for detection of gases like NO_2, CO, H_2S, NH_3, etc. Aparna et al. [1] illustrated that CuO nanoparticles have potential applications for solar energy transfer, sensors, storage devices and in superconductors. 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 nanoparticles. 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 $CuSO_4$ 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: Cu_2O, Cu_4O_3, and CuO. The presence of these phases controlled strongly to the oxygen percentage. At lower oxygen percentage a pure Cu_2O 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

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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 (75 mm×25 mm). 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.

3. 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.

4. 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. From this data refractive index, thickness and band gap were calculated by using the following formula [9]:

$$n = \left\{ N + \left(N^2 - \mu^2 \right)^{1/2} \right\}^{1/2},$$

where $N = 2\mu \dfrac{T_u - T_l}{T_u T_l} + \dfrac{\mu^2 + 1}{2}$, 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 $\lambda_1 = 824$ nm, $T_u = 0.5643$, $T_l = 0.4$ and $\mu = 1.5$ by substituting in (2) we get N1 = 3.808678 from this by equation (1) $n_1 = 2.703615$. for minima $\lambda_2 = 924$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 $d = \left| \dfrac{\lambda_1 \lambda_2}{4(n_1\lambda_2 - n_2\lambda_1)} \right|$ where n_1 and n_2 are refractive index of thin film at maxima and minima i.e at wavelengths λ_1 and λ_1. Using the values of n_1 and n_2 we calculated thickness of the film as 300 nm.

Fig. 1-Fig. 4 indicate the variation of transmittance with wave length for film annealed at different temperature and at different time interval.

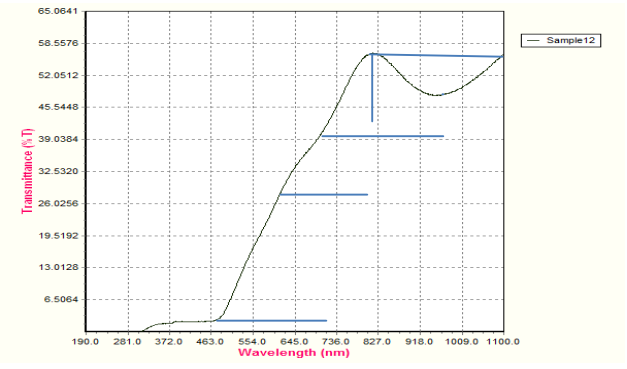

Fig. 1 – Transmittance vs. wavelength (200 ^{0}C and 2 hours)

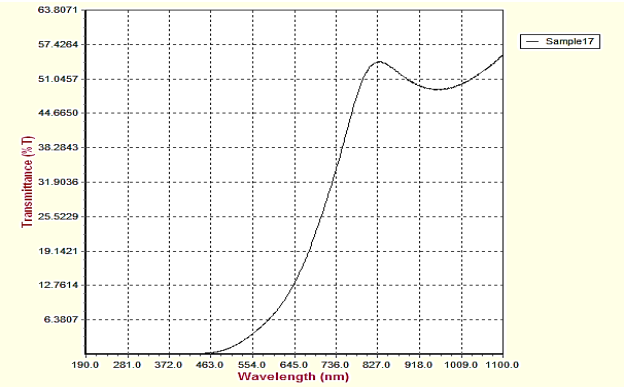

Fig. 2 – Transmittance vs. wavelength (200 ^{0}C and 3 hours)

Fig. 3 – Transmittance vs. wavelength (300 ^{0}C and 2 hours)

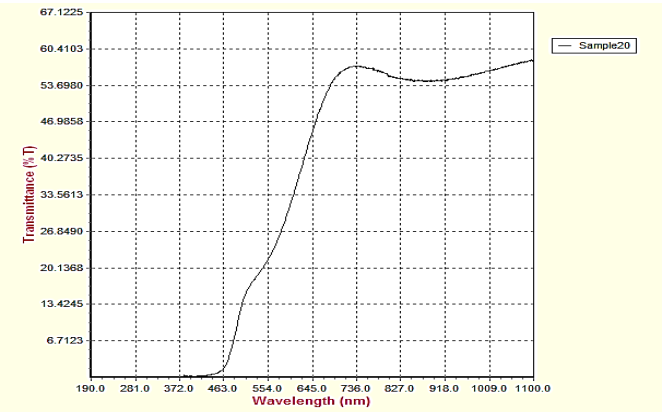

Fig. 4 – Transmittance vs. wavelength (300 ^{0}C and 3 hours)

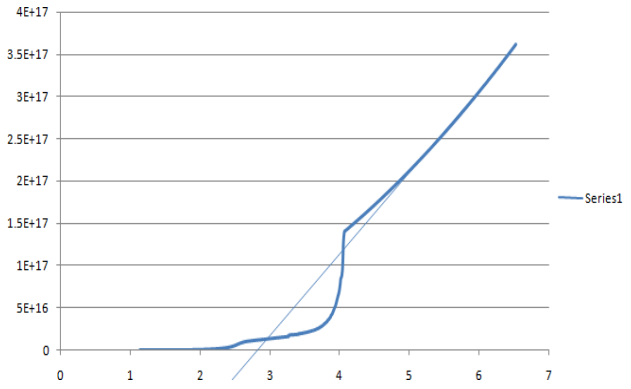

Fig. 5 – $(\alpha h\nu)^2$ vs. photon energy

The band gap energy of copper thin film was calculated from the graph $(\alpha h\nu)^2$ vs. $(h\nu)$ i.e. from Fig.5. When the linear portion of the graph is extended back it intersect eV axis and this intercept is the energy band which is measured as 2.54 eV.

The absorption coefficient (α) was calculated from the expression

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right),$$

where d is thickness of the film and T is optical transmission. The calculated absorption co-efficient was about 10^5 cm^{-1}. The calculated absorption co-efficient data was fitted to the relation given by Davis and Mott [10].

$$\alpha h\nu = A(E - E_g)^2,$$

where A is a constant which is almost independent of the chemical composition of the semiconductor, $E = h\nu$ is the photon energy, E_g is the optical band gap.

5. STRUCTURAL ANALYSIS

The structural analysis of the film is carried out by using SIEMENS diffractometer model (1275) using copper having the wavelength range $\lambda = 1.540$ Å.

From XRD analysis, mean grain size (D) and strain (ε) are calculated deposited glass substrates. XRD measurement was carried out by Siemens Diffractometer Model D 5000 using CuKα having wavelength $\lambda = 1.540$ Å radiation with a diffraction angle 10° to 70°. XRD spectra were analyzed with Gaussian function where FWHM was determined. By using Debye-Scherrer formula [9]

$$D = \frac{0.94\lambda}{\beta\cos\theta} \text{ and } \beta\cos\theta = \frac{0.94\lambda}{D} + \varepsilon\sin\theta,$$

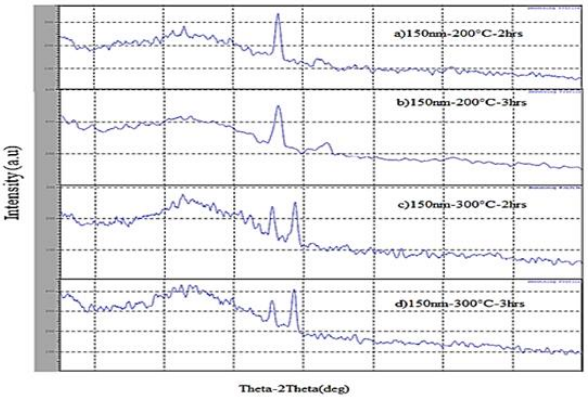

Fig. 6 – XRD pattern of Cu film

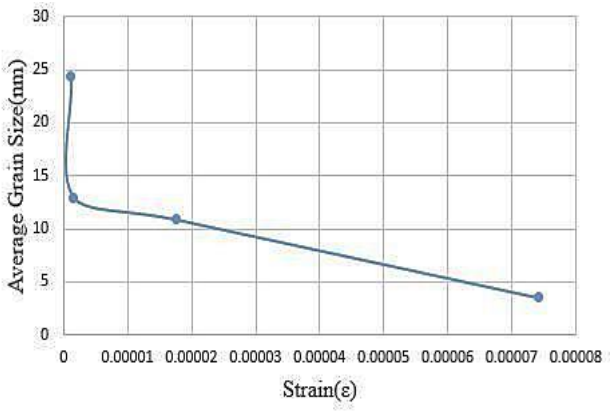

Fig. 7 – Strain vs. average grain size (nm)

where D is mean grain size,β is FWHM (full width at half maximum) of the observed peak, λ is wavelength of X-ray used for diffraction, θ is angle of diffraction, ε is strain. By using the formulas and by taking the mean values of the strongest peaks we calculate the average grain size at different annealing temperature and different time interval which is shown in Table 1.

From Fig. 7 it is clear that strain is inversely proportional to the grain size which is very useful for gas sensors.

6. CONCLUSIONS

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 which varies from 3.52 nm to 24.34 nm. The variation of strain is from 7.413×10^{-5} to 1.149×10^{-5} which indicates that strain is inversely proportional to grain size. The film was under studied for gas sensing of different gases and enhancement of sensitivity.

Table 1 – Variation of strain on grain size

Sample No	Thickness of copper nanothin film, nm	Temperature, °C	Time, h	Average grain size D, nm	Strain ε
1	150	200	2	3.52	7.413×10^{-5}
2	150	200	3	10.88	1.757×10^{-5}
3	150	300	2	12.97	1.532×10^{-5}
4	150	300	3	24.34	1.149×10^{-5}

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Вплив розміру зерна на деформацію в наноплівці оксиду міді для застосувань у газовій сенсориці

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У дослідженні наноплівка оксиду міді синтезується на скляній підкладці методом термічного випаровування для застосувань у газовій сенсориці. Під час осадження відстань між джерелом та підкладкою підтримується постійною, а тиск у камері становить $1{,}0\times10^{-4}$ Тор. Швидкість осадження коливається від 6 до 10 Å/с. Товщина плівки підтримується постійною на рівні 150 нм. Плівку піддавали термічній обробці при різній температурі та протягом різного часового інтервалу, щоб отримати оптимальний результат. Структурне дослідження проводиться за допомогою формули Дебая-Шеррера. Рентгенодифракційний аналіз виявляє, що деформація збільшується зі зменшенням розміру зерна, що корисно для вивчення зондування різних газів.

Ключові слова: Заборонена зона, Теплове випаровування, Рентгенівська дифракція, Пропускні та оптичні характеристики.