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Preparation and study of Cu_2O thin film at low temperature by Chemical vapor deposition (CVD) route

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ABSTRACT

In this study cuprous oxide (Cu_2O) nanoparticle has been synthesized at low temperature of 200^{o}C by chemical vapor deposition (CVD) route. The complex compound Cu $(acac)_2$ was used as precursor sublimated at temperature of 275^{o}C and deposited over a glass substrates. The synthesized films have been characterized by using X-ray diffraction (XRD) analysis, field emission electron microscope (FE-SEM), atomic force microscopy (AFM) and transmission electron microscope (TEM) analysis.

Keywords: Cu_2O nanostructures, CVD, AFM, FE-SEM, TEM.

1. INTRODUCTION

Nanotechnology is an attractive branch of science that interesting in the materials among the size of 1-100 nm with different shapes of spherical nanoparticles, nanorods, nanoribbons, nanobelts and nanoplatelets [1]. Cuprous oxide is a low-cost and non-toxic metal oxide with a cubic crystal structure [2]. It is naturally a p-type semiconductor due to negatively charged Copper vacancies with a direct band gap of approximately 2eV [3]. Cu_2O have been extensively investigated for various technological applications, such as field emission devices, batteries, solar energy conversion, photovoltaic materials, heterogeneous catalysts, gas sensors [4, 5]. Several methods have been used for the production of cuprous oxide such as thermal oxidation [6], chemical technique [7], sol-gel method [8], radio frequency reactive sputtering and chemical vapor deposition is a chemical process used to produce highly pure and high-performance solid state materials [9].

2. Experimental

Horizontal tube furnace, type GSL-1600X-80, was used in CVD technique to grown Cu_2O thin film nanostructure. A quartz tube (with external and internal diameters of 55 and 50 mm, respectively) inserted inside the furnace has been used as a reactor. A glass substrate (10×10×1 mm) dimensions with surface pre cleaning by acetone and distilled water, according to the well-known procedure have been done. The substrate has inserted into a position of temperature 200^{o}C, since there was a temperature gradient outside the constant area within 15cm at the center of the tube. A ceramic boat containing 0.2 gm powder of copper (II) acetylacetonate, Cu $(acac)_2$ as a precursor positioned inside the reactor at 275^{o}C. After reaching the decomposition temperature the Cu $(acac)_2$ was carried by argon carrier gas at flow rate of 14NL/hr controlled by mechanical flow meter at atmospheric pressure. Finally the film oxidized with 3NL/hr of Oxygen gas for half an hour, the carrier and oxygen gas were stopped after the deposition. The furnace was left to cool to 50^{o}C.

3. Characterization techniques

The structure analysis and phase diagnosis were determined by X-diffractometer equipped with Cu K1 (λ=1.54178 Å) using a generator voltage of 40 kV and a current of 40 mA. The morphology of Cu_2O thin films deposited has been worked out by FE-SEM. The surface roughness R_a and root mean square rms of the films were measured by Atomic force microscopy AFM device. TEM image analysis also has been applied for deep insight into the sample.

4. Results and discussion

4.1 Structure analysis

The Cu_2O nanostructure thin film synthesized at 200 ^{o}C, with color of yellowish to brown. The film is investigated by XRD analysis, figure (1). Which shows the cubic structure of lattice constant, a=4.267 Å. The resulted patterns were dominated by three diffraction peaks the most intense one located at 2θ = 36.44^o in the direction (111), the second peak

which has a very low intensity is at $2\theta = 42.32^{o}$ in the direction (200) while the third one is very small peak at $2\theta = 61.24^{o}$ from (220) plane according to the ICSD collection code (063281), which agrees with reported previously [10].

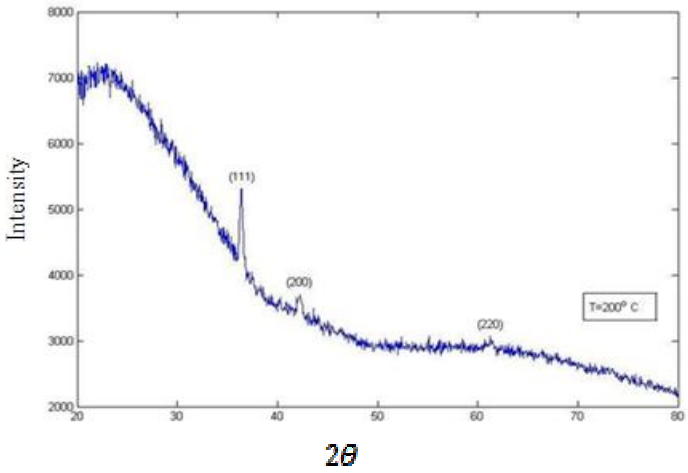

Figure 1: XRD reflection peaks of Cu_2O thin film synthesized by CVD route.

From the peaks shape it is clear that the film has polycrystalline structure with relatively good crystallinity as it is concluded from the shape of the peak and FWHM value of 0.29^{o}, the grain size diameters was 28.85nm and has a preferential direction (111) which concluded from the texture coefficient value of T_c=2.12. Table (1) below shows the most important data collected from the XRD analysis.

Table (1): XRD data for Cu_2O thin film prepared at 200 ^{o}C.

Prepared condition	$(2\theta)^{\circ}$ XRD	(I/I_o) XRD	$d(\text{Å})$ XRD	FWHM XRD	$(2\theta)^{\circ}$ ICSD	(I/I_o) ICSD	$d(\text{Å})$ ICSD	hkl	ICSD Code Number
T_s=200^{o}C	36.35	100	2.46	0.29	36.44	100	2.46	111	063281
	42.16	27	2.14	0.6	42.32	34.7	2.13	200	063281
	61.24	14.4	1.51	0.3	61.40	26.5	1.50	220	063281

4.2 Morphology study

Figure 3 the depth insight into the surface morphology was provided by FESEM analysis at deposition temperature 200^{o}C, figure 3(a) the microstructure (2µm) morphology shows very smooth and dense surface and no individual particles have been recognized but on nanoscale (200nm), figure 3(b) the micrographs appears to be a densely packed Cu_2O with small particles, which distributed uniformly over entire glass substrate surface with particle mean size of 30 ± 5 nm.

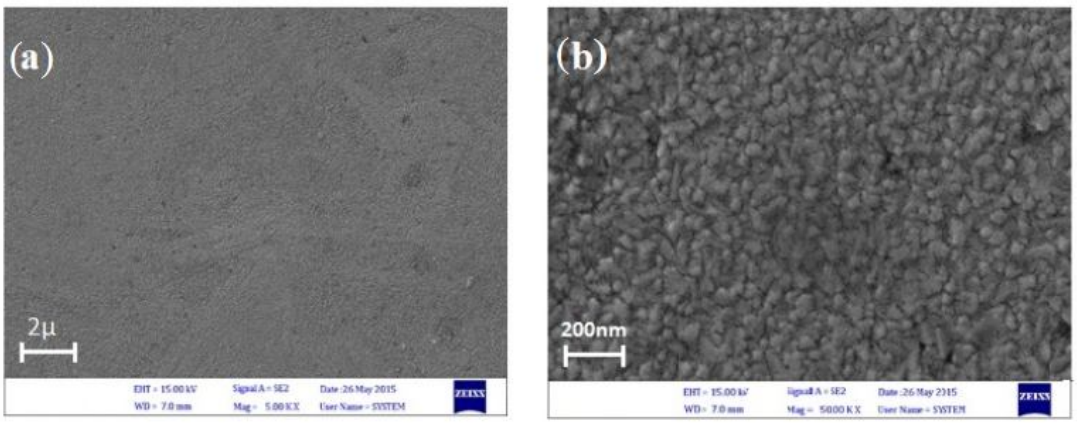

Figure 3: FE-SEM micrograph of Cu_2O thin film deposited at 200 ^{o}C by CVD route, magnified for a) 2µm b) 200nm.

The synthesized film figure 4 has showed the light brown color which refer to the formation of Cu_2O thin film. The SEM cross section have been used to measure the thickness of the film, which resulted of low deposition rate of (59.2 nm) for deposition time of half an hour. The substrate temperature was 200^{o}C the result become consistent with reaction in which $Cu(acac)_2$ and O_2 adsorb dissociatively on the surface. Oxygen reacts with adsorbed ligands to

produce volatile by products. Finally surface copper is oxidized by adsorbed O atoms with result that copper is transferred in very fast time to Cu_2O [11].

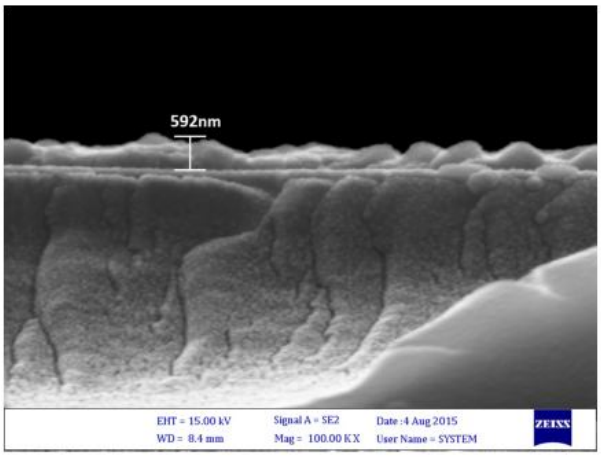

Figure 4: Thickness of Cu_2O thin films measured by SEM cross section resulted of 59.2 nm.

The factors which control the film thickness are oxygen flow rate, deposition temperature and the distance of the substrate from the sublimated precursor.

4.3 Topographical study

2D image (3µm×3µm) of Cu2O thin figure 5(a) film prepared at 200°C,which shows smooth surface with small particle size which are not recognized individually. The 3D image figure 5(b) shows particles with small pillar like shapes which have mean height of 30.39nm, average roughness of 5.80nm and root mean square roughness RMS of 7.5nm, the peak to valley Rp-v is also in agreement with mentioned data which has the value of 63.61nm. AFM study revealed small nanoparticles with pillar like shapes with average roughness of 5.8nm.

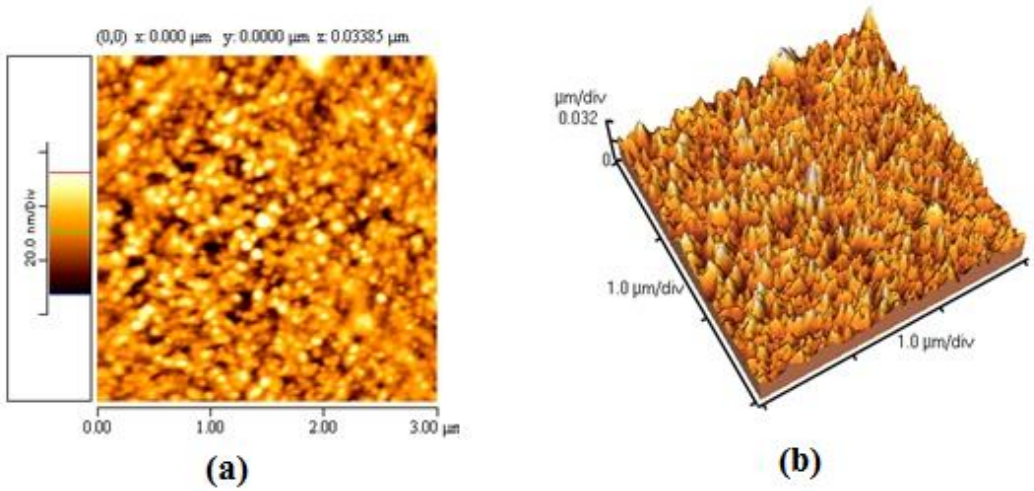

Figure 5: 2D and 3D AFM image of Cu2O thin film synthesized at 200°C.

4.4 TEM image analysis and particle size distribution

TEM microscopy investigation carried out on the particles of Cu_2O thin film obtained by CVD method, to see the size and shape of the particles. Figure 6 (a to d) show the nanoparticles of Cu_2O, which appears to have a variable flat, semispherical and some aggregate shapes, with dimensions of individual nanoparticles are between 5nm and 60nm.

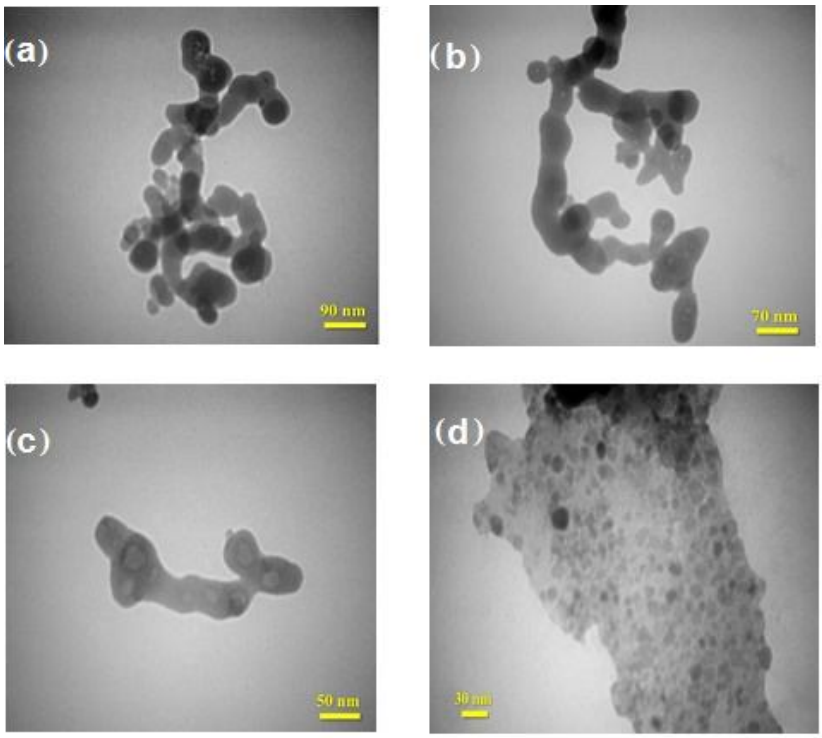

Figure 6: Different TEM images of Cu_2O synthesized at 200°C.

5. Conclusion

Deposition and properties of copper oxide Cu_2O thin films prepared by chemical vapor deposition CVD on glass substrate at 200°C have been studied. From the obtained results these points can be drawn. Single phase Cu_2O thin films with cuprite structure can be synthesized by CVD technique at low temperature. The film structure has mainly (111) and (200) crystalline orientations. The FE-SEM images showed uniform films with mean particle size of about 30 nm, and low deposition rate of 59.2 nm has been measured, the AFM image showed the average roughness for the film about 5.8nm. TEM images showed the formation of individual nanoparticles in the range of 5nm to 60nm in size.

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