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Electrical properties for cold sprayed Nano copper oxide thin films

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Abstract
This work is a Copper oxide (CuO) thin films were effectively produced using cold spray technique. The process take place in an inert gas (helium) without using catalyst. Nano CuO was deposited on a glass slide, using helium as carrier gas heated to 100, 200, 300, and 400 ºC, respectively on heated glass substrates at 300°C. The effect of structural and electrical properties was examined at each temperature for each film. AFM images show that the CuO thin film have different diameters ranging from 80 to 600 nm, and low surface roughness about 20.9 nm. The measured value of copper oxide resistivity was found to be decrease very much with the increasing temperature. All the result showed that copper oxide is suitable material for photovoltaic applications. This research is part of a larger work for the solar cells industry. Therefore, the aim of this research is to study the electrical properties of solar cells in the primary stages of manufacturing from available materials at low costs.

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1.1. Introduction

In recent years, the study of micro / Nano particles has gotten a lot of attention. The fascination in these microscopic particles stems from the unique qualities they possess as a result of their small size. Ceramics, thin films, electronics, fuel cells, data storage, and catalysis are only a few of the applications for these particles (Khan et al., 2020) Copper oxide is one of the most important material that used as thin film for solar cell application because of its narrow band gab which match the band gab of sun light spectrum, enabling it to take in more light (Jawad et al., 2011; Gao et al., 2012). Also it used in other application such as magnetic storage media, in the sensors as catalyst, battery electrodes for battery, transistors with a field effect, photo electrochemical Cells (Dhaouadi, 2018). The tenorite structure of cupric oxide CuO is substantially more complex. Four CuO molecules are found in the monoclinic unit cell (Wang et al., 2016). It has a unit cell parameter 4.6837A˚, 3.4226A˚, 5.1288A˚ which is a, b and c respectively with volume of the cell 81.08 $\mathbf{A}^{\circ 3}$ and density 6.315 g/cm^3 (Korzhavyi and Johansson, 2011). It is a toxic-free material with melting point 1201˚C (Zheng et al., 2018). CuO has native p-type conductivity due to the presence of vacancies for copper in the lattice (Choudhary et al., 2013). The most important thing is to find way to deposit the copper oxide to use in that application, the popularity of the cold spray technique has sparked a lot of research, both in terms of equipment design and strategies to make it easier and more efficient (Omar et al., 2020). Cold spray process is a one type of thermal spray process, it used to deposit various type of materials onto different type of substrates (Srikanth et al., 2019). It found out in the middle of eighty of the last century (Srikanth et al., 2019). Cold spray process has an important feature which is the use of low temperature compared with other thermal spray process that lead to prevent the stress generation because of the application of high temperature, it is consider a low cost spray method (Chakrabarty and Song, 2020). The principle of this process is that it used a carrier compressed heated gas that flow through a nozzle which design to make the gas and hence the particle of the material reach supersonic speed and then impact the substrate this supersonic speed causes a large amount of plastic deformation to the particles lead it to adhesion on the substrate as a thin film (Mason, 1999; Singh, et al., 2021).

1.2. Literature review

Annealing the CuO coating has a higher hardness as comparing to the deposited CuO (Yu et al., 2013). Increasing the masking slide width would densely pack the CuO particles (Kim et al., 2013). Cuprous oxide (Cu_2O) and cupric oxide (CuO) are the two main semiconductor phases of copper oxide with narrow band gap (Iqbal Singh et al., 2011). Compared with Cu_2O, CuO is more stable and more easily prepared. Its band gap matches the spectrum of sunlight more closely, allowing it to absorb more sunlight. These characteristics make it more suitable for solar cell applications (Buppachat Toboonsunga and Pisith Singjai, 2011). Since CuO is a p-type semiconductor with a narrow band gap so it uses for photo-thermal and photoconductive applications (Zoolfakar, et al., 2014). Additionally, it is an effective catalyst and a useful component in the fabrication of sensors, magnetic storage media, solar-energy transformation, electronics, as a semiconductor (Michael and Iniyan, 2015). Polycrystalline cupric oxide (CuO) thin films was successfully deposited at various bath temperatures onto conducting indium tin oxide coated glass substrates using an alkaline solution bath employing cathodic electrodeposition method (Yu et al., 2013). Aqueous solution of cupric nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) was modified with cetyltrimetylammonium bromide (CTAB) to deposit CuO films on glass substrate by chemical spray pyrolysis technique (Singh et al., 2011). Copper oxide nanorods (NRs) and their bundles was deposited on glass substrates by an electrochemical dissolution and deposition proces (Buppachat Toboonsunga and Pisith Singjai, 2011). Copper oxide thin films was seccusfully deposited using chemical methods with thickness of 0.45 μm on glass substrates (Johan et al., 2011). In this research, copper oxide (CuO) thin films was generated using a cold spray unite in an inert gas without using catalyst, to study the electrical properties of CuO thin films. This research is a part of a work that will serve the process of manufacturing low cost solar cells in future.

2. Experimental and Materials

2.1. Powder preparation

Copper oxide (CuO) powder material was used, the purity of it is 98% with particle size (75μm) 200 mesh using sieving which pass through mesh screen, origin (Wenger materials for craft pottery). Copper oxide (CuO) was dispersed in ball miller (9VS, CAPCO test equipment Ltd. UK) for 8 hr.

2.2. Substrate preparation

The substrate used was transparent glass slides with dimensions (75mm, 25mm, 1 mm), with part No. (BS-50P-100S-22). The substrate was cut into small pieces (20×20mm), (10×10mm) and (10×20mm). The glass slide was cleaned ethanol alcohol and acetone then non-ionized water was used for washing it, finally a wet soft tissue was used to wipe it.

2.3. Cold spray unit

The cold spray unit were assembled in the college of material engineering – university of Babylon/ Iraq, schematic diagram showed in Figure (1). The typical parameters used for cold spray unit illustrate in Table (1).

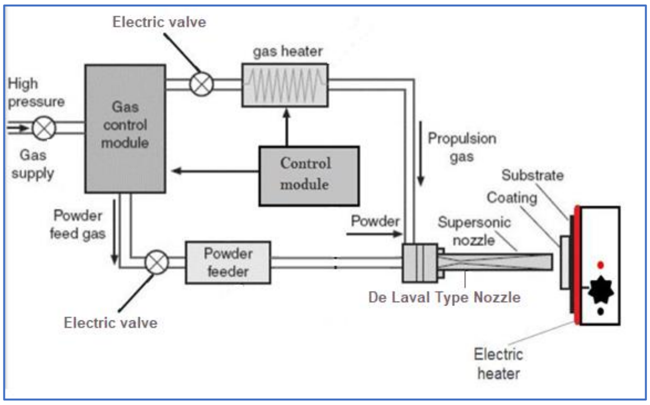

Fig. 1. Schematic diagram of a cold spray unit

Table 1. Typical parameters for cold spray process.

Parameters	Range
Operation gases	Helium gas
Substrate temperature (℃)	300
Gas pressure (bar), without catalyst	30
Gas temperature (℃)	100, 200,
Spray distance (mm)	40
Power consumption (for heat gas) (Kw)	3
Powder feed rate (g/s)	0.3
Deposition angles (°)	0, 30, 45

2.4. Thin film preparation

The prepared powder was fed on the glass substrate which placed onto heater powered by electricity with power consumption 3 kw that heated to 300^0C. The feeding operation held using cold spray apparatus then sprayed through De Laval nozzle (this type of nozzle lead the particle to reach supersonic speed) by using an inert atmosphere (helium gas) which then heated to temperatures 100, 200, 300, and 400 with a gas pressure 30 bar without the using of any catalyst. The Nano crystalline layer started to growth and develop on the glass substrate. Using vacuum furnace the deposited copper oxide thin films were annealed for a half hour at temperature 450°C with vacuum of about $0.6 \cdot 10^{-3}$ torr to avoid carburizing and nitridizing of the thin film at a rate of $25°C.min^{-1}$, the annealing process reduce the residual stresses introduced during the deposition.

3. Characterization

3.1. Atomic Force Microscope (AFM)

Atomic Force Microscopy (AFM) type (CSPM-AA3000, Angstrom Advanced Inc. USA), was used to characterize the CuO, to give information on the structural morphology, the diameter and the height of the CuO thin films that could be reveal after deposition. Gwyddion software was used for images data analysis.

3.2. Electrical measurements

The electrical properties were measured using hall effect measurement type (HMS 3000 Ecopia, Poland). The hall effect should provide a clear view for how well the CuO film conducts electrical current.

4. Results and discussion

4.1. AFM Images of prepared CuO Thin films

The three dimensional (3D) and two dimensional (2D) images of CuO thin films using AFM are shown in Figures (2-5). The data from these images will provide information about roughness, feature height, and grain analysis. As noticed from Figures (2-3), the surface roughness has a surface uniformity and the distribution of the coated spray. Increasing the images magnification for the same spot, Figure (4-5), shows that the coating has low roughness with evenly distribution along the surface. From the four figures, it can be noticed that deposited thin film was compact and uniformly distributed over the entire structure surface. The surface of the deposited films is smooth where (the average surface roughness is 20.9 nm) this low value of surface roughness will reduce scattering of light when strike the surface.

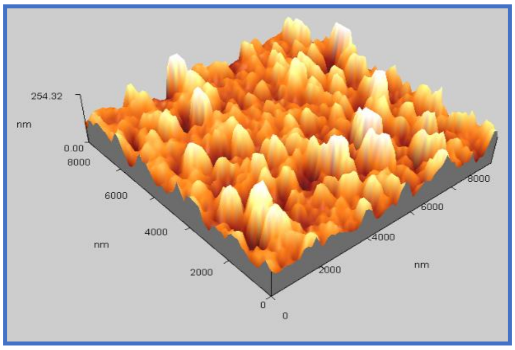

Fig. 2. 3D AFM image size = (10000 nm, 10000 nm, 10000 nm) of CuO thin film deposited onto glass substrate at deposition temperature 200°C.

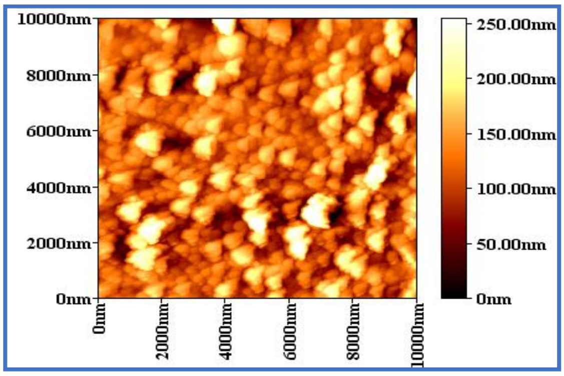

Fig. 3. 2D AFM image size = (10000 nm ,10000 nm) of CuO thin film deposited onto glass substrate at deposition temperature 200°C.

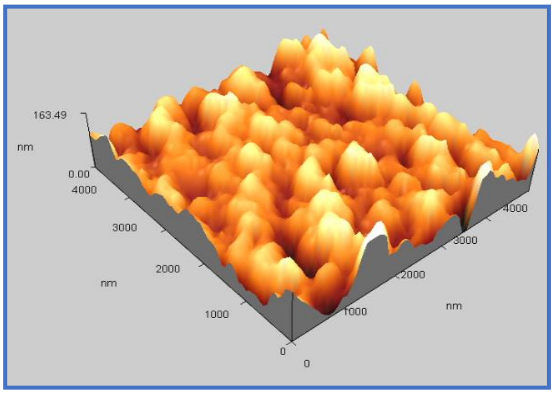

Fig. 4. 3D AFM image size = (5000 nm ,5000 nm, 5000 nm) of CuO thin film deposited onto glass substrate at deposition temperature 200°C.

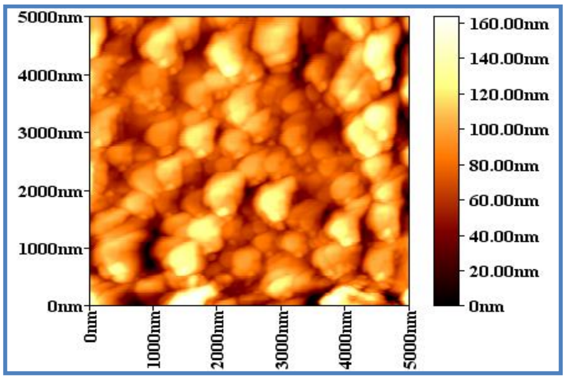

Fig. 5. 2D AFM image size = (5000 nm ,5000 nm) of CuO thin film deposited onto glass substrate at deposition temperature 200°C.

The collected data of diameter versus volume and granularity cumulation distribution are summarized in Table (2), this data shows an average grain diameter 257.09 nm. From Figure (6), it can be notice that the diameter increases with the amount of cumulation, which indicates that the distribution is consistent on the glass slide. Since AFM volume is highly proportional to the grain mass (Fuentes-Perez et al. 2013), the variation of volume % versus grain diameter was plotted, this allowed the determination of the mass of deposited coating (Fuentes-Perez et al. 2013), Figure (7).

Table 2. Statistical analysis of CuO thin film grain diameters by using AFM

Avg. Diameter:257.09 nm						<=10% Diameter:100.00 nm		
<=50% Diameter:220.00 nm						<=90% Diameter:420.00 nm		
Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
40.00	0.52	0.52	260.00	6.25	57.29	460.00	2.08	92.19
80.00	1.04	1.56	280.00	4.17	61.46	500.00	2.08	94.27
100.00	3.65	5.21	300.00	6.77	68.23	520.00	1.56	95.83
120.00	5.73	10.94	320.00	4.69	72.92	540.00	1.04	96.88
140.00	10.42	21.35	340.00	3.65	76.56	560.00	1.04	97.92
160.00	8.33	29.69	360.00	1.04	77.66	600.00	1.04	98.96
180.00	6.77	36.46	380.00	3.65	81.25	620.00	0.52	99.48
200.00	4.69	41.15	400.00	3.13	84.38	640.00	0.52	100.00
220.00	4.17	45.31	420.00	2.08	86.46			
240.00	5.73	51.04	440.00	3.65	90.1			

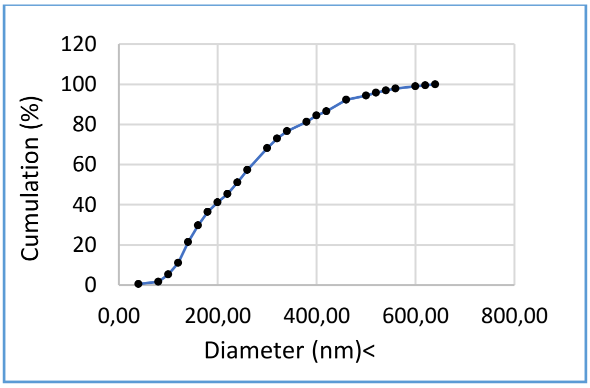

Fig. 6. Variation of Granularity Diameter and Cumulation %

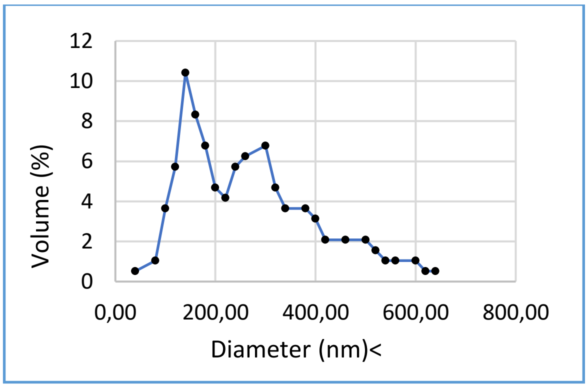

Fig. 7. Variation of Granularity Diameter and Volume %

4.2. Effect of the temperature on the electrical properties

The electrical properties (Electric resistivity, mobility, carrier concentration) for copper oxide thin films are shown in Table 3. Revealing that the coatings are semiconducting and implying a thermally induced conduction mechanism. The decrease in resistivity with increase the temperature can be understood from the increase in grain size. The growth of grains with temperature leads to reduction in grain boundary scattering thus decreases the film resistivity. The behavior of the electrical resistivity of the films as a function of temperature is quite similar to that of the crystallite size as a function of temperature. It is believed that as the temperature rises, the crystallization process accelerates, resulting in fewer flaws and, as a result, less charge carrier scattering at the defect.

The height of the barrier at the grain boundary decreases as crystallite size increases with temperature. This enhances the mobility of the charge carrier and thus decreases film resistivity. It is widely recognized that p-type conductivity in copper oxide is because of the existence of cation vacancy, this is because of the hole density is proportion to electric conductivity for copper oxide. The hole formed by the interstitial oxygen and cation vacancy will affect the electrical conductivity. Increases in cation vacancy or interstitial oxygen may also contribute to the increase in hole concentration, resulting in a significant reduction in activation energy. The electrical characterization of the films revealed that as the grain size was raised, the activation energy and strain in the films decreased. It's worth noting that temperature is regarded as a key determinant of carrier concentration, which is boosted by an increase in cation vacancy in the films as the films develop.

Table 3. The effect of temperature on electrical properties of CuO thin film

Temperature (℃)	Carrier type	Resistivity (Ω cm)	Mobility ($\frac{cm^2}{Vs}$)	Carrier concentration ($\frac{1}{cm^3}$)
100℃	P	2.098 x 10^8	5.156 x 10^{-2}	5.771 x $\mathbf{10^{11}}$
200℃	P	1.013 x 10^8	1.431 x 10^{-1}	4.305 x $\mathbf{10^{11}}$
300℃	P	3.958 x 10^5	4.047 x 10^1	3.898 x $\mathbf{10^{11}}$
400℃	P	8.369 x 10^3	9.063 x 10^2	8.230 x $\mathbf{10^{11}}$

5. Conclusion

Cold spray process was successfully formed copper oxide film on glass substrate. The AFM results show that the average surface roughness is 20.9 nm, this low value of surface roughness will reduce scattering of light when strike the surface. The CuO thin film have an average diameter 257.09 nm. Finally, the electric resistivity decrease as the temperature increased because the growth of grains with temperature leads to reduction in grain boundary scattering, thus decreases the film resistivity, the value of electric resistivity obtain at 400℃ is very low 8.369 x 10^3.

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Conflict of interest

The authors declare that they have no conflict of interest.

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冷喷涂纳米氧化铜薄膜的电性能

關鍵詞
关键词
氧化铜
冷喷射
电学性质
纳米薄膜
光伏

摘要
本研究采用冷喷射技术有效地制备了铜氧化物（CuO）薄膜。该过程在惰性气体（氦气）中进行，不使用催化剂。采用加热至100、200、300和400˚C的氦气作为载气，在300˚C的加热玻璃基底上沉积纳米CuO薄膜。在每个温度下检查了每个薄膜的结构和电学性质的影响。原子力显微镜图像显示，CuO薄膜的直径范围从80到600纳米不等，并且表面粗糙度低，约为20.9纳米。测量得到的氧化铜电阻率随温度升高而大幅降低。所有结果都表明，氧化铜是光伏应用的合适材料。这项研究是太阳能电池行业的大型工作的一部分。因此，本研究的目的是研究从低成本可获得材料中制造太阳能电池的电学性质的初级阶段