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Structural properties of Ag-CuO thin films on silicon prepared via DC magnetron sputtering

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Abstract

In this paper, 3% and 5 % of Ag doped copper oxide (CuO) deposited onto silicon substrates as thin film using the DC magnetron sputtering process under Ar gas. The sputtering deposition was performed by using a power of 75 W. XRD results conformed a good crystallinity of the synthesized Ag/CuO nanoparticle thin films. SEM analysis indicated to all the prepared samples are having a quasi-spherical shape. Based on AFM analysis, the roughness of prepared samples determined and found the high roughness of 3% Ag/CuO sample that attitude to have it a less mean crystal size compated with 5% Ag/CuO, which calculated using Scherrer equation. The EDX spectra indicated the high purities for the prepared sample befor and after deposted on Si as substrate.

Keywords Ag/CuO; FE-SEM; Magnetron Sputtering; CuO; Nanoparticle; EDX; Thin film
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1. Introduction:

Copper oxide (CuO), whether it's bulk or nanomaterial, is regarded as a useful metal oxide with numerous applications in various fields. Copper oxide nanoparticles are of special relevance because of their efficiency as nanofluids in heat transfer applications. [1]. CuO is a semiconducting material with a relatively narrow bandgap (1.3 eV)[2]. It's conceivable to use it for photoconductive, photothermal, or antimicrobial purposes. [3]. CuO nanoparticles have biological properties such as wound dressings and biocidal properties [4], and antibacterial properties [5]. The semiconductor materials are particularly interesting because of their practical usefulness in electronic and optoelectronic devices such as electrochemical cells [6], gas sensors [7], magnetic storage devices [8], nanofluids [9], and catalysts [10]. Over the last decade, magnetron sputtering has advanced fast to the point where it has established itself as the procedure of choice for the deposition of a wide range of industrially relevant coatings. As a result, magnetron sputtering is currently widely employed for hard, wear-resistant coatings, low friction coatings, corrosion-resistant coatings, decorative coatings, and coatings with specialized optical or electrical properties [11].A thin film is a tiny coating of material that can be fractions of a nanometer-thick (monolayer) to several micrometers thick (multilayer). Electronic semiconductor devices and optical coatings are two of the most common applications that benefit from thin-film fabrication[12]. A well-known application of thin films is the home mirror, which typically comprises a thin metal coating on the back of a sheet of glass to generate a reflecting surface. Making mirrors with silvering was previously a widespread practice. An extremely thin film coating is employed to create two-way mirrors (less than 50 nanometers thick). When a thin-film coating consists of several layers with variable thicknesses and refractive indices, the performance of optical coatings (e.g., antireflective, or AR, coatings) has often been improved. A superlattice is a periodic arrangement made up of alternating thin films of various materials that uses quantum confinement to limit electronic processes to two dimensions[13]. The use of ferromagnetic and ferroelectric thin films as computer memory is being researched. Pharmaceutical companies gain from it as well, thanks to thin-film drug delivery.

The goal of this work is Preparation of copper oxide inlaid with silver and preparation of thin films of copper oxide as a nanostructure using a magnetic atomization deposition method on silicon as asubstrate at power 75W and pressure 3.6 mTorr. Following the preparation process, characterizations were carried out utilizing XRD, FTSEM-EDX analysis.

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2-Experimental detail:

A- Materials

All materials used were supplied by Merck without any purification.

B- Procedure

The preparation method was performed after modification depending on the reported in[14]. A simple co-precipitation approach was employed to make Ag-doped copper oxide nanoparticles (Ag/CuO NPS). As a starting material, copper sulfate heptahydrate and silver nitrate were utilized. (2.5 g) of copper sulfate $CuSO_4$ and different quantities of (3 percent, 5 percent (w/w) of $AgNO_3$) were dissolved in 100 mL deionized water and agitated for 1 hour in a typical synthesis of Ag/CuO NPs. With continual stirring at 60 °C, exact 1.2 g from SDS was added to each percentage of the aforementioned solution, followed by the dropwise addition of (5 M) NaOH until the pH reached to 14. This solution was stirred continuously for 24 hours, resulting in the production of white Ag/CuO NP precipitates. The precipitates were filtered and rinsed with deionized water and ethanol (1:1) multiple times until the pH reached 7. To ensure all SO_4^{2-} and Cl^{-1} as a negative ions of used precurcer salts removed from prepared material by chemical common idntification method. In a vacuum oven, the Ag/CuO NPs precipitates were dried overnight at 50 °C. The dried Ag/CuO NPs were calcined in a muffle furnace at 800 °C for 5 hours at a rate of 4 °C per minute. The Ag/CuO NPs were processed and stored in a piston mortar.

The sputtering target was prepared using the (Hot Isostatic Pressing) method after 30 g of each composite ratio had been prepared. This method's operating information is as follows: Milled Ag-CuO powders were first compacted at 50 MPa and sintered at 1173 K for 2 hours before being hot pressed at 973 K under 30 MPa [15, 16]. Ag-CuO thin films were prepared by DC magnetron sputtering system on silicon slides as substrates. Firstly, the target was pre-sputtered under argon gas with purity 99.999% in order to remove the oxide layer. Moreover, the Ar gas was supplied as working gas through the mass-flow controller. The sputtering chamber was evacuated down to 3.6 mTorr by the turbomolecular pump. This procedure was modified from the references[14-16]. Microscope silicon slides were used as the substrates for thin films Prior to deposition,Film thickness of 3% Ag/CuO, 5% Ag/CuO (205.1, 141.3 nm) Straight. The silicon slides were sequentially cleaned in

Step1: using Ultrasonication in warm acetone (55) ºC for 10 mins

Step2: Blow-dried using dry nitrogen gas

Step3: The cleaning solution is made up of 5 parts deionized water, 1 part 30% hydrogen peroxide, and 1 part 27 % ammonium hydroxide then Ultrasonication in this solution for 15 mins.

Step4: Rinse/dip in de-ionized water twice.

Step5: Blow-dried using dry nitrogen gas

Step6: The cleaning solution is made up of 100 mL de-ionized water and 4 mL Hydrofluoric Acid, and then the substrate (Si) is immersed inside for two minutes.

Step7: Blow-dried using dry nitrogen gas

3.Results and discussion:

3.1 Structural Properties

XRD spectrum has been obtained for the synthesized 3% Ag: CuO nanoparticle thin films in **Figure 1** and 5% Ag: CuO nanoparticle thin films in **Figure 2.**

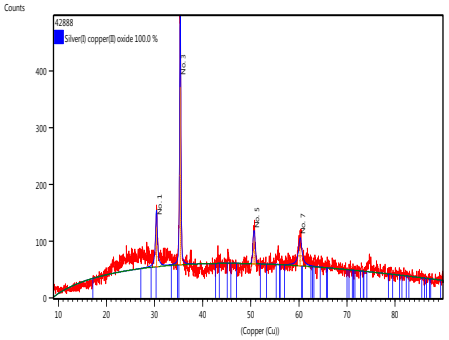

Fig. 1: XRD patterns of 3% Ag/CuO nanopartical thin film on silicon.

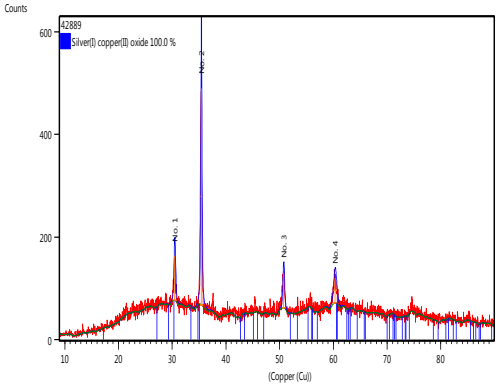

Fig. 2: XRD patterns of 5%Ag/CuO nanopartical thin film on silicon.

The multidiffraction peaks were 2θ diffraction of planes demonstrated at 30.38 º, 35.316 º, 50.780 º and 60.230 º in figure 1 for 3% Ag /CuO and 2θ equal to

30.476 º, 35.410º , 50.731º and 60.298º in figure 2 for 5% Ag /CuO, which were assigned to the main planes 110, 002, 112, and 022 respectively(JCPDS card: 45-0937 and JCPDS card: 80-0076)[17,18]. That ensure the momoclinic CuO and Ag/ CuO are really prepared .

The low percentage of Ag that doped on CuO, leads to low change in position of peaks but increased in intensity with increasing the amount of Ag from 3 % to 5%. The mean crystal size(D or L) in nm for 3% and 5% Ag/CuO can be calculated using Scherer's equation [19-25].

$$L = \frac{k\,\lambda}{\beta\,Cos\,\theta} \qquad (1)$$

where λ is the wavelength of the instrument source (Cu k_α) in (0.15406 nm), β is the full width at half maximum intensity in (mathematically transfer from degree to radian) [26], θ is the Bragg diffraction angle and k is shaped constant (0.94-0.85)[27], here using 0.9 for quiasi-spherical shape.

The mean crystal size for 3% Ag/CuO is found to be 24.247 nm and for 5% Ag/CuO is equal to 27.8894 nm. The elevated in size with increasing the amount of Ag is expected result that due to the large ionic radius of Ag^{+}(1.06 Å) compared with Cu^{2+} (0.615Å), hence, the size will elevate via incorporated it in CuO Matrix[28].

3.2 FTSEM-EDX analysis

Figures 3 and 4 show the surface morphology of prepared samples after annealing at a specific temperature which was investigated using field emission scanning electron microscopy (FESEM). The images of (FESEM) for 3% Ag/CuO, 5%Ag/CuO samples that uniform pattern and confirms the formation of uniform porous structures on the (silicon) wafer. Images on the left at (15.00) kx and images on the right at (5.00) kx magnification of top view.

The results demonstrate the quasi-spherical for prepared samples and the size of the nanoparticles started to grow with increasing the preparation from 3% to 5%. The average particle widths (diameters) for the samples 3%Ag/CuO and 5%Ag/CuO are micro-size that attituded to the high ability for this prepared particals to agglomerate as polycrystals.

Figures 5,6 represent EDX spectra of Ag/CuO nanoparticles for (3%Ag/CuO, 5%Ag/CuO,) samples. The EDX analysis clarifies that the substances are actually prepared and the summation of atom percentage for (Cu, O, and Ag)% is 100 % as listed in table1, which ensure they prepared without impurities.

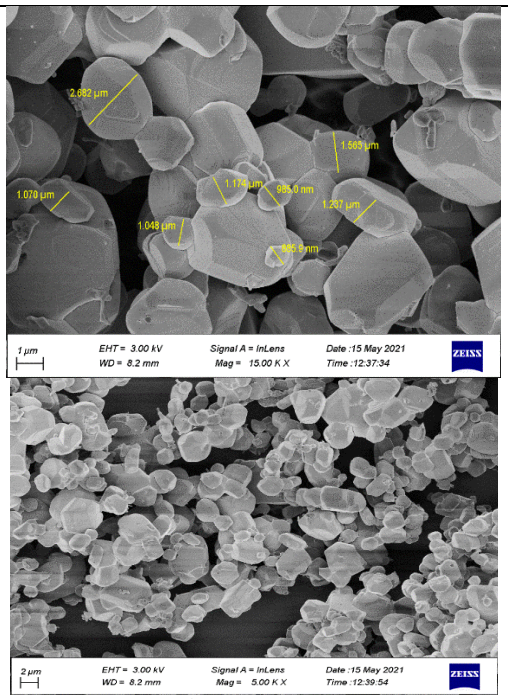

Fig.3: FESEM images for 3%Ag/CuO sample

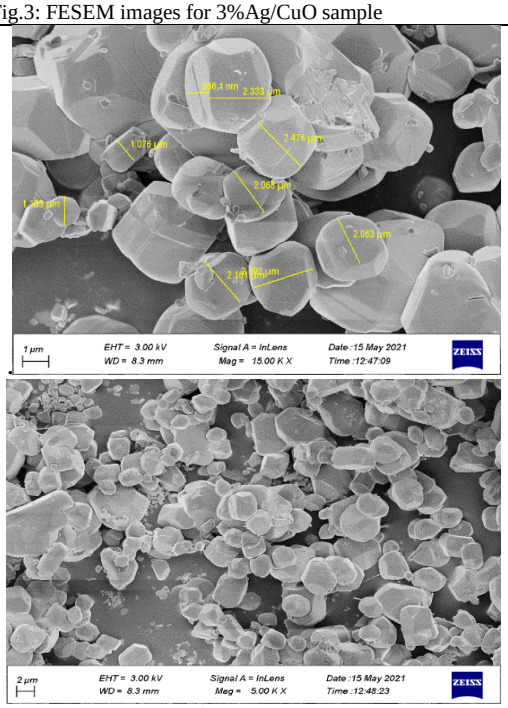

Fig.4: FESEM images of 5%Ag/CuO sample

The FESEM images in **figures 7** shows that the structure of the samples has a non-uniform distribution and they involves either several polycrystals or cluster of particles with an average size of (7.734 – 34.25) nm diameter for the samples 3%Ag/CuO and (5.156 - 7.734) nm for 5%Ag/CuO. A closer view of the FESEM images showed rough surface and high pore size which caused high specific surface areas for the samples Before sedimentation and after sedimentation.

Figures 8 shows the EDX analysis for sample with silicon as substrate, the elemental percentages of interpretation of copper(Cu), oxygen (O), and silver (Ag) deposited on Si for the most appropriate (3,5), respectively, were found to be (25.78, 4.08)% for (Cu), while elemental percentages of oxygen (O) were found to be (17.66, 20.46), and silver (Ag) (0.78, 0.79), in (3% Ag, 5% Ag) doped CuO respectively. The high percentage for Si occurs in both sample that due to use it as substrate for prepared samples. The quantitative details about the EDX analysis are listed in table 2.

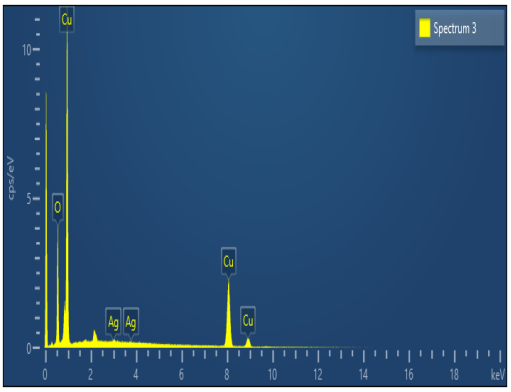

Fig.5: EDX spectrum of 3%Ag/CuO nanoparticles sample.

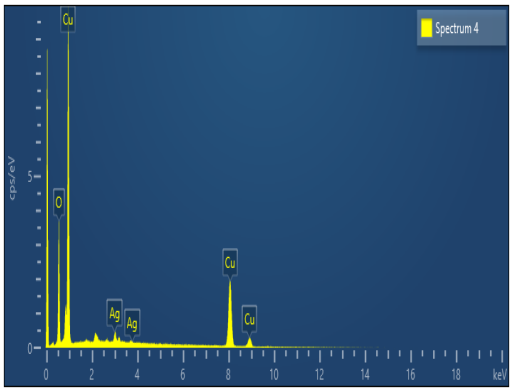

Fig.6: EDX spectrum of 3%Ag/CuO nanoparticles sample.

Table 1. The quantitative details about the EDX analysis of Ag/ CuO with substrate.

Sample	Oxygen elemental percentage %	Copper elemental percentage %	Silver elemental percentage %	Total %
3% Ag/CuO	25.27	71.87	2.86	100
5% Ag/CuO	25.59	70.37	4.03	100

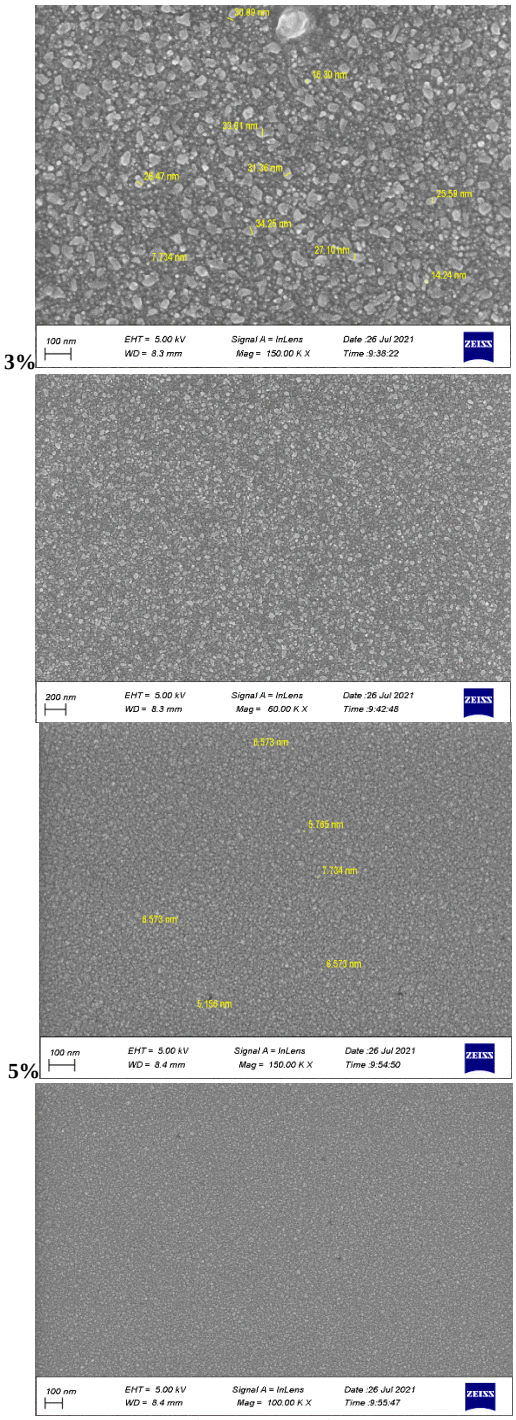

Fig.7: FESEM images of Ag/CuO thin-film Si sample.

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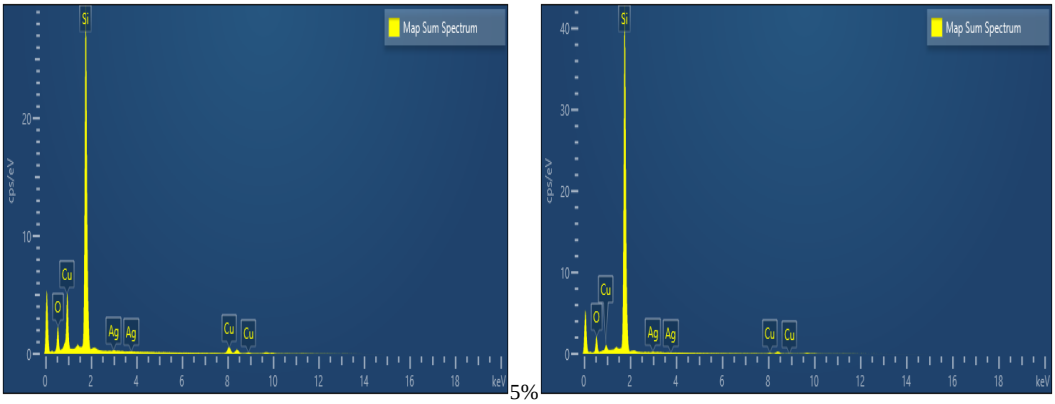


3% 5%

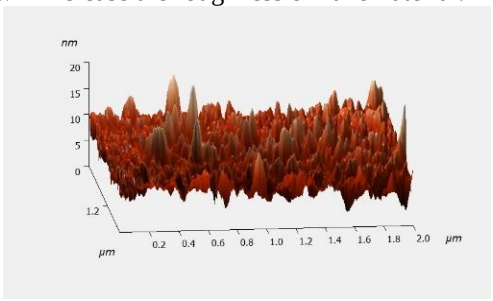
Fig.9: EDX spectra of Ag/CuO deposited on Si

Table 2. the quantitative details about the EDX analysis.

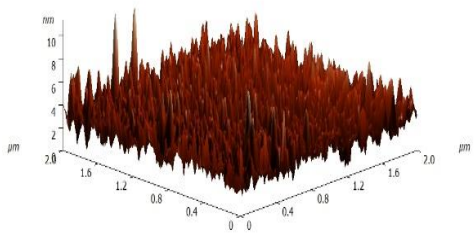
Sample Silicon	Oxygen elemental percentage %	Copper elemental percentage %	Silver elemental percentage %	Silicon %	Total %
3%Ag/CuO	17.66	25.78	0.78	55.78	100.00
5%Ag/CuO	20.46	4.08	0.79	74.66	100.00

3-3 Analysis of atomic force microscope (AFM)

Figure 10 shows the surface shape and topography of Ag/CuO layers observed from an AFM analysis. The result in table 2, the Ag/CuO thin film nanoparticle that prepared using magnetron sputtering and deposition on a (Si) a high roughness at 3% silver and a precipitate on silicon, that due to mean crystal size of 3% Ag /CuO is less than that value for mean crystal size of 5% Ag/CuO. This behavor is inagrement with the principle of the depress of mean crystal size will increase the roughness of nanomaterial.



3%



5%

Figure10. 3-dimension images of AFM analysis for Ag/CuOdeposited on Si.

Table 3: The values of Root mean square and Average roughness for 3% and 5% Ag/CuO deposite on Si

Sample Si	Root mean square (nm)	Average roughness (nm)
3%Ag/CuO	23.5233	3.1955
5%Ag/CuO	6.27456	0.780815

4-Conclusion

Preparation of copper oxide grafted with silver in (3 anf 5)% proportion and deposition on a silicon substrate using DC reactive sputtering method. The XRD analysis indicated to prepared both nanomaterials. AFM analysis ensured the 3% Ag/CuO has a high roughness with less mean crystal size. SEM analysis refered to the all prepared samples are quasi-spherecal FE-SEM photos proved that also.

Conflicts of interest

There are no conflicts to declare.

Formatting of funding sources

Self

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