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Improving microstructural properties and minimizing crystal imperfections of nanocrystalline Cu_2O thin films of different solution molarities for solar cell applications

Alaa A. Akl[a,c], Safwat A. Mahmoud[a,d], S.M. AL-Shomar[e], A.S. Hassanien[b,f,*,1,2]

[a] Physics Department, Faculty of Science, Minia University, El-Minia, Egypt
[b] Math. and Eng. Physics Department, Faculty of Engineering (Shoubra-Cairo), Benha University, Egypt
[c] Physics Department, Faculty of Science and Humanities, Ad-Dawadmi, Shaqra University, Saudi Arabia
[d] Physics Department, Faculty of Science, Northern Border University, Saudi Arabia
[e] Physics Department, Faculty of Science, Hail University, Hail, Saudi Arabia
[f] Physics Department, Faculty of Education, Afif Governorate, Shaqra University, Saudi Arabia

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ABSTRACT

This article was devoted to synthesis nanocrystalline Cu_2O thin films using the spray pyrolysis technique, besides to study the influence of their solution molarity on crystallography, microstructure and crystal defects. X-ray diffraction analysis revealed that as-deposited Cu_2O films have the amorphous nature but after their annealing at 550 K for two hours they turned to have the polycrystalline cubic structure with a preferred orientation in $< 111 >$ direction. Williamson-Hall and Scherrer methods were utilized to determine the microstructural parameters using line profile analysis of X-ray diffraction. Obtained results revealed that when the solution molarity was increased from 0.01 to 0.12 M the crystallite size increased from 28.75 to 35.12 and from 16.92 to 26.22 nm, while the microstrain was found to decrease from 2.171×10^{-3} to 0.896×10^{-3} and from 5.321×10^{-3} to 3.699×10^{-3} according to Williamson-Hall and Scherrer methods, respectively. Moreover, increasing of the solution molarity of prepared Cu_2O film samples led to reduce the crystal defects, where, the lattice strain, the total internal stress, the interfacial tension and the elastic strain energy were found to decrease. Furthermore, increasing of the solution molarity led also to increase the X-ray mass-density from 6.081 to 6.099 g/cm^3.

1. Introduction

Copper (I) oxide, Cu_2O nanostructure has attracted a considerable attention due to its interesting chemical, physical, optical and electrical properties. It is used in several important fields as an antifouling agent for marine paints, as a fungicide and it is used also in the pigments [1–3]. It has been also industrially utilized in fabricating the rectifier diodes before using the silicon, Si. Cuprous oxide is considered also a promising transparent conductive oxide and good semiconducting material [4–8], because it has a narrow direct optical gap (E_g) ranged between 1.50 and 2.25 eV and it has also a cubic crystal structure [2,9–13]. Consequently, it was found that using of Cu_2O is widely common in the fabrication of photo-catalysis, printed electronics, optoelectronic devices like lithium ion battery, microdevices, biological sensors, gas sensing material and photo electrochemical cells [2–5,10–13]. This is due to its low consumption, non-toxic, the good photoelectric properties and its good photo-responsible characterization. As well as, it is used in solar cells, optical devices and in some medical uses [13–18].

On the other hand, Cu_2O thin films have been utilized for many modern applications, such as the resistive memories, the smart windows, infra-red detectors, thin film transistor, and biosensors solar cells as p-type absorber layer for the heterojunction solar cell because of its high-energy conversion efficiency [19–22]. Moreover, Cu_2O thin films are considered as the best choice films to be used as anodes for sodium-ion batteries owing to their high theoretical capacity [23,24].

Thin films of Cu_2O can be deposited by using many different techniques, among these techniques the radio frequency sputtering [14,25,26], the magnetron sputtering [27–29], facing target sputtering, FTS [15,30] pulsed laser deposition [31], chemical vapor deposition [32–34], electrodeposition technique [1,35–37]electrochemical deposition [38] thermal oxidation method [39,40], Sol-Gel method

* Corresponding author at: Math. and Eng. Physics Department, Faculty of Engineering (Shoubra-Cairo), Benha University, Egypt.
E-mail address: a.s.hassanien@gmail.com (A.S. Hassanien).
[1] Permanent address: Math. and Eng. Physics Department, Faculty of Engineering (Shoubra-Cairo), Benha University, Egypt.
[2] On leave to: Physics Department, Faculty of Education, Afif Governorate, Shaqra University, Saudi Arabia.

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[13,41,42], simple wet-chemical method [43,44] hydrothermal synthesis method, chemical reduction technique [45,46], chemical brightening, spraying, chemical vapor deposition, gas phase deposition, plasma evaporation, reactive sputtering, and molecular beam epitaxy [1,47–52]. In addition of these techniques, there is the spray pyrolysis technique, which has many advantages. This method is easy, simple, gentle, economical and inexpensive method. Moreover, it is a reliable method and can be also used to prepare the relatively large area of the metal oxide films [53,54]. The advantages of this method allow also to control the crystal growth and the crystallization process of deposited films. Therefore, it can thoroughly be used to synthesis metal oxides thin films like Cu_2O films.

Literature research showed that Cu_2O thin films are extensively used in several modern applications, such as the optoelectrical, photochemical devices, and solar cells. Although, the microstructural parameters and the crystal imperfections strongly influence upon the physical, optical and electrical properties of the thin films, they have not been adequately studied and did not give their attention to these important and crucial parameters. The authors therefore devoted this manuscript to study these serious subjects. In the present paper, the authors used the X-ray diffraction, XRD to study the crystallographic and microstructural parameters, as well as the crystal defects of nanocrystalline Cu_2O thin films prepared with different solution molarities ranged between 0.01 and 0.12 M. They applied Williamson-Hall and Scherrer methods to estimate the microstructural parameters (crystallite size and average microstrain). In addition, these methods were utilized to investigate and study some other crystal defects after determining the correct broadening values, β using the integral breadth method. The estimated parameters have been correlated with each other.

Consequently, the aim of the present work is firstly to prepare nanocrystalline Cu_2O thin films of different solution molarities (different film thicknesses) by using the spray pyrolysis technique. In addition, their aim is to synthesize these films with high quality and homogeneous nature. Secondly, the goal of this work is to study the effect of the solution molarity, SM on the synthesis of the films, their crystallographic properties, the preferred direction of the crystal growth, microstructural parameters and the crystal defects. The authors also have tried to obtain the optimum conditions to get good film samples have high quality and of homogeneous nature, in addition to reduce crystal defects as possible to be used in the potential optoelectrical application and devices.

2. Experimental details

2.1. Chemical materials

Cupric acetate monohydrate of the linear formula [Cu $(COOCH_3)_2 \cdot H_2O$] and has the molecular weight 199.65 g/mole was supplied by Sigma-Aldrich Chemical Company. Double distilled water as a starting solution was used. All the reagents had of analytical grade and had been used without further purification. It is worthy to mention that the reducing agent material that used in this work was the ethanol.

2.2. Synthesis of Cu_2O thin films

Cupric acetate monohydrate aqueous solution, $[Cu(COOCH_3)_2 \cdot H_2O]$ was used to prepare the cuprous oxide thin-film samples. The spray pyrolysis technique was used to deposit Cu_2O thin films on pre-cleaned glass substrates (microscopic glass slides). The substrate was thoroughly cleaned by chromic acid for 5 h and then rinsed by the running water for 20 min. Subsequently, it was placed in an ultrasonic bath filled with ethanol for 15 min. Thereby, the glass substrate has become ready for its uses for the deposition process. The spray pyrolysis system was described before in previous works [53–55]. Different solution molarities, SM (0.01, 0.03, 0.05 0.09 and 0.12 M) were prepared to get the aqueous solutions. The aqueous solutions were sprayed on a preheated glass substrate of constant temperature at 400 K for all samples. The deposition time was fixed also at 10 min for all films. All as-deposited Cu_2O film samples were annealed at 550 K for 2 h, to obtain polycrystalline thin-film samples and to get rid of the thermal stresses, as possible. The film thickness of as-deposited and annealed samples was determined by the weight method and then it has been confirmed by using the mechanical stylus method, MSM-Sloan Dektak of model 11-A [55].

2.3. Samples identifications

The crystal structure of the prepared as-deposited and annealed samples was identified by using X-ray diffraction, XRD at the room temperature. The used diffractometer is JEOL and has this model (JSDX-60PA). This diffractometer was operated at 40 kV and 35 mA to well investigate the prepared film samples. The used source of this diffractometer was Cu of K_α-radiation. The wavelength of this source is $\lambda = 1.54184$ Å and its energy was 8.042 keV, while the used filter was Ni. During the X-ray examination of as-deposited and annealed film samples, the following operating conditions have been applied and fixed for all samples: (a) the continuous counting speed was 1°/min, (b) the time constant was fixed at 1 s (c) the diffraction angle (2θ) was changed from 10° to 80°. These powerful conditions are sufficient to well examine and investigate the prepared Cu_2O thin-film samples. Therefore, all the diffraction peaks could be detected [56–58]. Line profile analysis method of X-ray diffraction employed to study the microstructural parameters and crystal imperfections of the annealed Cu_2O thin films [53,54,56,59]. The energy dispersive X-ray spectrometry, EDX has been used to analyze and know the compositional elements of the Cu_2O thin-film sample of a SM 0.12 M as a typical sample. An attachment of model Oxford instruments, England was superimposed on a field emission scanning electron microscope FE-SEM, Zeiss - SIGMA VP, Germany was used.

3. Results and discussions

3.1. Thickness measurements

The film thickness of as-deposited and annealed Cu_2O film samples was measured by using the weight method and confirmed by the mechanical stylus method, MSM. It was found that the determined values using the two methods are in good agreement with each other. Fig. 1 depicts the behavior of the film thickness versus SM, of the prepared as-deposited and annealed thin films. It can observe that the increasing of the solution molarity led to increase the film thickness for both as-deposited and annealed samples. This is simply due to that if there is more

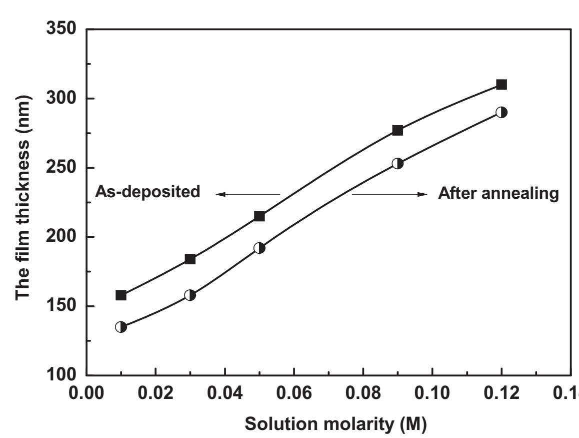

Fig. 1. The film thickness of as-deposited and annealed Cu_2O thin films as functions of the solution molarity.