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Direct Growth of Copper(II) Oxide (CuO) Nanostructures Films via One-Step Chemical Bath Deposition by pH Variation

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Abstract. An aqueous solution was prepared by mixing the copper(II) sulfate pentahydrate ($CuSO_4$), lactic acid, sodium hydroxide (NaOH) and de-ionized (DI) water. Direct deposition of copper(II) oxide (CuO) nanostructures films on glass substrates was achieved by a simple, inexpensive and one-step chemical bath deposition method. The pH of the solution was varied at 11.7, 12.0, 12.3 and 12.6 and immersed at low temperature (90 °C). The influences of the pH solution towards the surface topography, morphology and thickness were investigated by a field emission scanning electron microscopy (FESEM), an atomic force microscope (AFM) and a surface profiler. Meanwhile, an X-ray diffractometer (XRD) was used to examine the structural properties of CuO films. The optical properties were measured by a UV-Vis spectroscopy. It was found that the grain size of the films decreases and the surface becomes smoother and more uniform by increasing the pH solution. The CuO nanostructures have high crystallinity with monoclinic structure which is preferentially grown along ($\bar{1}11$) and (200) directions. Therefore, the film has great potential for gas sensor device.

Introduction

The outstanding properties of metal oxide nanostructures in different fields and applications of catalysts, sensors, optoelectronics, batteries and semiconductors have attracted much attention, recently. As a p-type semiconductor with a narrow band gap of ~1.2 eV at room temperature, copper(II) oxide (CuO) have received much attention for its diverse uses which are semiconductors, biosensors, gas sensors, magnetic storage media, electronics, varistors, field transistors, capacitors, catalysis, batteries and solar cells [1-2]. There are several important advantages of CuO films such as low cost, non-toxicity in nature, easy to prepare, high-Tc superconductors and its constituents (Cu) are abundance on earth that become significant in device architectures and applications [3].

Reasoned from its high optical and electrical properties, some interest have been build up to study the surface structure of CuO films which is grown under variety of conditions in solar cell applications, nowadays [4]. In addition, it becomes attractive as it is a selective solar absorber reflects from its high solar absorbency [3]. The properties of CuO films depend sensitively on the surface morphology which in turn is determined by the growth process and also controlled by the surface structure [5]. The physical and chemical properties of CuO films which quite and strictly dependant on its morphology and size has cause many attempt to synthesis various of CuO nanostructures films since few decades earlier.

The morphology and size of the CuO nanostructures has been controlled by a number of different techniques. For instance, quick-precipitation [6], thermal oxidation [7], thermal evaporation [8], hydrothermal treatment [9], electrodeposition [10] and solution synthesis [11] have been used to control the morphology and size of the CuO nanostructures. Among these techniques, quick-precipitation, solution synthesis and hydrothermal are the promising techniques because they are environmental friendly, safe, simple, suitable to mass production and cost-effectiveness. By applying these methods, considerable powder samples of CuO nanostructures have been reported [12]. However, the CuO nanostructures thin films that were grown on a glass substrate have been reported seldomly. For this reason, we report a simple route to synthesize the dense, continuous and stable CuO nanostructures films by a simple route of one-step chemical bath deposition technique on the glass substrates. Besides, the crystal structure, growth mechanism, topographical surface and morphology of the CuO nanostructures films were investigated.

Experimental Details

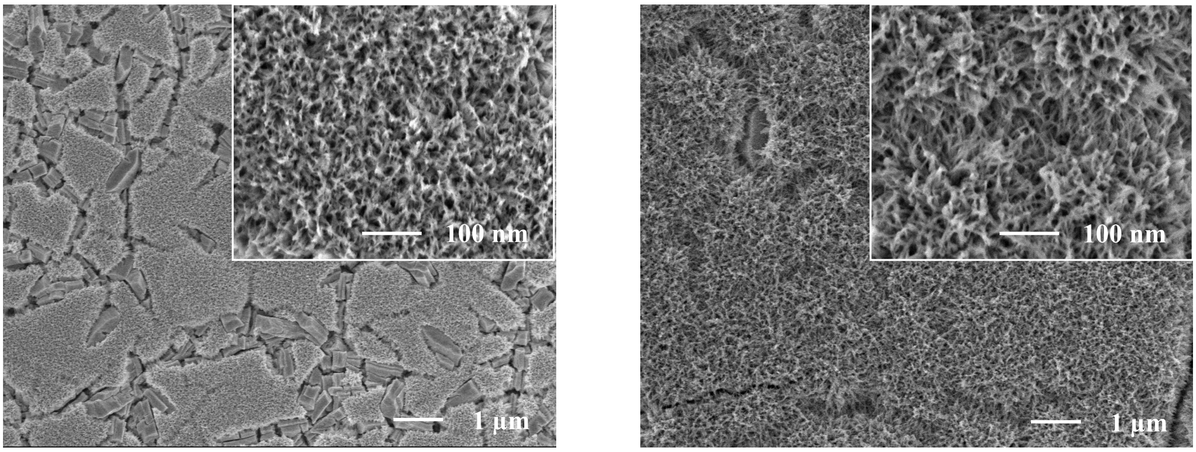
The substrate preparation was done by cleaning process of the glass substrates which are consists of three main steps cleaning such as in absolute acetone, absolute ethanol and de-ionized (DI) water for 10 min each in an ultrasonic bath to remove the impurities. Then, the glass substrates were dried in ambient. A catalyst (gold) was deposited by a d.c. sputter coater at 20 mA for 30 sec in order to adherent the deposition of CuO films. Synthesis of the CuO films was described as follows: the 2.497 g copper(II) sulfate pentahydrate ($CuSO_4$) was mixed with 50 ml de-ionized (DI) water in order to obtain 0.2 M $CuSO_4$ solution. After 5 minutes, 1.5 M lactic acid was added into the aqueous solution and stirred until it dissolved and completely mixed. Sodium hydroxide (NaOH) was added in a specific quantity which were shown in Table 1 to control the pH of the aqueous solution. Then, the aqueous solution were stirred and kept at room temperature for 24 hours. An addition of NaOH in the solution changed the colour of the solution to bluish and rise up the pH and temperature [13]. Previously, cleaned glass substrate with a gold catalyst was attached horizontally in a reagent bottle. An aqueous solution was poured into the reagent bottle and heating process was employed for 4 h at 90 °C using annealing furnace. The glass substrates were taken out from the bath solution after 4 h deposition and rinsed with DI water for several times to remove the unwanted deposition on the sample. Then, the sample was annealed on a hot plate at 250 °C for 2 h. The annealing process was commenced to removed the residual and improve the crystallographic structure of the samples. The crystal structures of the CuO fillms were analyzed by X-ray diffractometer system (Bruker Advance D8). Surface morphological study was carried out using FESEM (JEOL JSM-7600) and AFM (XE-100 Park System) was used to investigate the surface topology of the films. The optical properties of the samples were analyzed using UV-Vis spectrophotometer (Shimadzu 1800).

Results and Discussions

Fig. 1(a-b) indicates the morphology and structure of CuO films which were employed by a FESEM at pH 12.3 and 12.6. However, there is no deposition of CuO films presence on the glass substrates at pH 11.7 and 12.0 as shown in Table 1. It can be seen that the growth of CuO nanostructures in Fig. 1(a) were stacking each other on the same planar while CuO nanostructures in Fig.1(b) exhibits a uniform and nearly homogenous films. The stacking films may happens due to the high surface energy produced when deposited the CuO nanostructures films at pH 12.3. As observed, the substrates are fully covered by clusters of CuO nanowires. It can be concluded that the increasing of pH solution will affects the grain size and homogeneity of the films. Consequently, the mechanisms of both CuO nanostructures films were present in Fig. 2(a-b).

Table 1: Synthesis parameters and morphologies of CuO nanostructures at different pH solution

Sample	**Time (h)**	Temp. (˚C)	**NaOH (g)**	**pH solution**	**Morphology**	**Thickness (μm)**	**Colour**
1	24	24	2.83 g	11.7	None	None	Green (glass)
2	24	24	2.91 g	12.0	None	None	Green (glass)
3	24	24	2.93 g	12.3	CuO nanowire	3.53	Black
4	24	24	3.13 g	12.6	CuO nanowire	1.42	Black



(a) (b)

Fig. 1: FESEM micrographs of CuO films at different pH solution: (a) 12.3 at 10 K magnification; and (b) 12.6 at 10 K magnification; (inset is the magnification at 100 K)

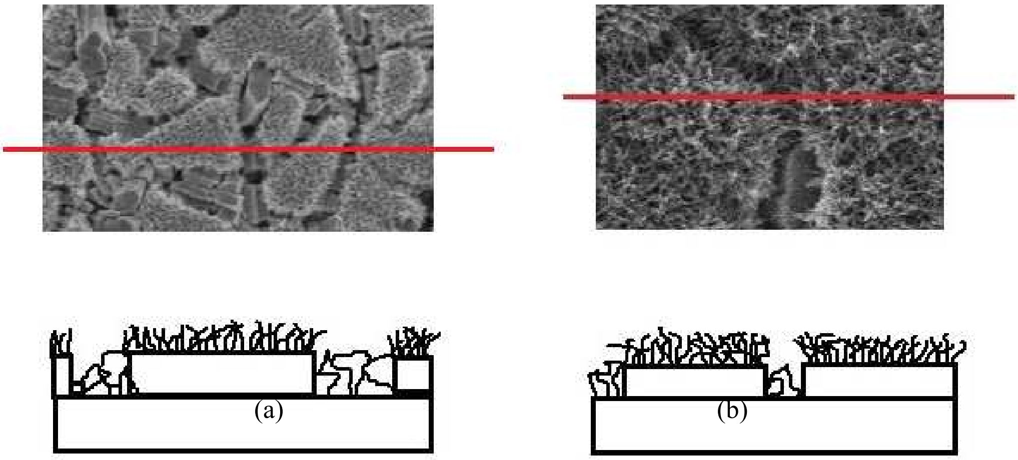
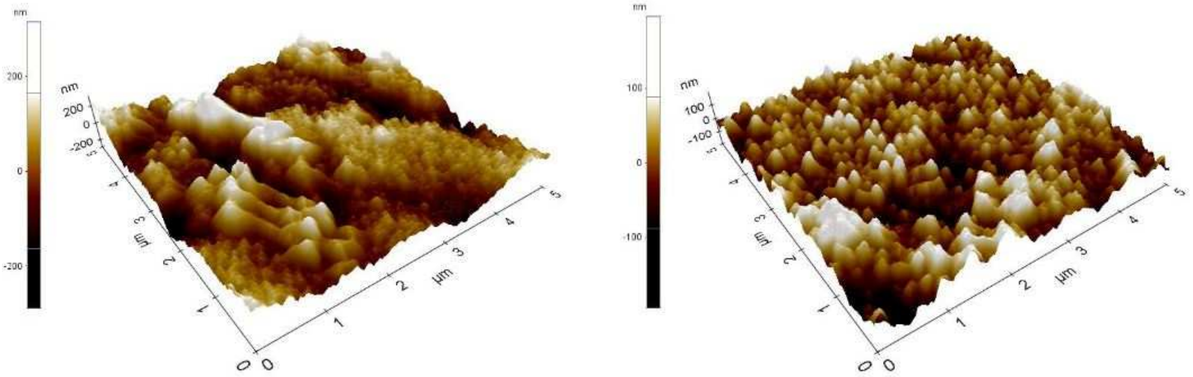


Fig. 2: The mechanisms of CuO nanostructures films with: (a) high stacking structure at pH 12.3 and (b) less stacking structure at pH 12.6



(a) (b)

Fig. 3: AFM topography of CuO films at different pH solution: (a) 12.3; and (b) 12.6

Fig. 3(a-b) shows the surface topography of the monoclinic CuO phase thin films realized at different pH solutions (12.3 and 12.6), analyzed using AFM at 5 µm × 5 µm scan size. It is clearly observed that the surface roughness for samples deposited at 12.3 pH solution is 2 times higher (88.77 nm) than the samples deposited at 12.6 pH solution (49.41 nm). The reason of high surface roughness is because of the stacking surface on the samples deposited at 12.3 pH solution are higher than the 12.3 samples. This is due to the surface energy of CuO films deposited at pH 12.3 is high. In addition, the surface morphologies of the CuO films changed with an increasing pH solution. It also can be seen that the surface of CuO films grown with densely packed and less stacks using 12.6 pH solution. Furthermore, the grain size decreases slightly when the pH solution was increased.

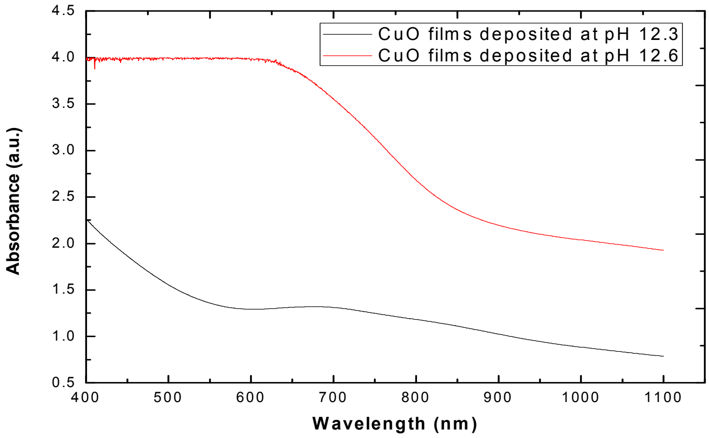


Fig. 4:Typical optical absorption of CuO films deposited at different pH solutions: (a) 12.3; and (b) 12.6

The optical absorption properties of the obtained CuO nanostructures films at pH 12.3 and pH 12.6 are shown in Fig. 4(a-b). From the results, the CuO films that deposited at pH 12.6 has broaden absorption spectra which is in 400-650 nm range while the band edge of CuO films deposited at pH 12.3 was obviously not appeared. It also can be seen that the absorption peaks of CuO films at pH 12.6 is higher than the pH 12.3 CuO films which is 4.0. This may happens due to the morphology of CuO films deposited at pH 12.6 is more uniform, dense and nearly homogenous. It also has reported that the size, morphology and crystallinity of the films would affect the optical absorption peak [11].

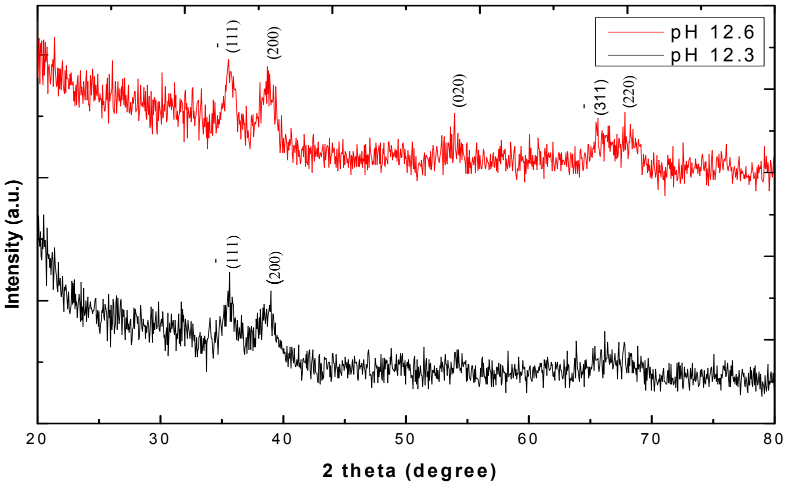


Fig. 5: The XRD patterns of CuO thin film with different pH solution: (a) 12.3; and (b) 12.6

Fig. 1(a-b) shows the XRD patterns of CuO nanostructures films. All the diffraction peaks can be clearly indexed to the monoclinic CuO phase and match with JCPDS card no. 05-0661. Besides, the grown films completely consists of CuO molecules and there was no XRD peaks referred to $Cu(OH)_2$. The defined peaks at 35.5° and 38.9° corresponding to the reflections from $(\bar{1}11)$ and (200) planes are observed in Fig. 1(a-b) while there are another three peaks which are (020), $(31\bar{1})$ and (220) were shown in the XRD pattern in Fig. 1(b). The reflections from the $(\bar{1}11)$ and (200) plane respectively attributed to tenorite CuO structure [5, 14].

Conclusion

In summary, we have synthesized a dense, continuous and stable CuO nanostructures films with good crystallinity by a low temperature, simple and cost effective solution method. It was found that the films with high pH 12.6 solutions produced more uniform, dense and nearly homogenous morphology than films deposited at pH solution of 12.3. Besides, the grain size of the films also decreases with an increasing in pH solution. The films has good crystallinity with monoclinic CuO phase crystal structure which preferentially growth along $(\bar{1}11)$ and (200) directions. In this work, we show a great improvement on the absorption properties by increasing the pH of the solution.

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References

[1] F. Bayansal, *et al.*, "Growth of homogenous CuO nano-structured thin films by a simple solution method," *Journal of Alloys and Compounds,* vol. 509, pp. 2094-2098, 2011.

[2] F. Bayansal, *et al.*, "Nano-structured CuO films prepared by simple solution methods: Plate-like, needle-like and network-like architectures," *Ceramics International,* vol. 38, pp. 1859-1866, 2012.

[3] A. Y. Oral, *et al.*, "The preparation of copper(II) oxide thin films and the study of their microstructures and optical properties," *Materials Chemistry and Physics,* vol. 83, pp. 140-144, 2004.

[4] S. C. Ray, "Preparation of copper oxide thin film by the sol–gel-like dip technique and study of their structural and optical properties," *Solar Energy Materials and Solar Cells,* vol. 68, pp. 307-312, 2001.

[5] Q. Zhang, *et al.*, "CuO nanostructures: Synthesis, characterization, growth mechanisms, fundamental properties, and applications," *Progress in Materials Science,* vol. 60, pp. 208-337, 2014.

[6] J. Zhu, *et al.*, "Highly dispersed CuO nanoparticles prepared by a novel quick-precipitation method," *Materials Letters,* vol. 58, pp. 3324-3327, 2004.

[7] J. T. Chen, *et al.*, "CuO nanowires synthesized by thermal oxidation route," *Journal of Alloys and Compounds,* vol. 454, pp. 268-273, 2008.

[8] V. R. Katti, *et al.*, "Mechanism of drifts in H2S sensing properties of SnO2:CuO composite thin film sensors prepared by thermal evaporation," *Sensors and Actuators B: Chemical,* vol. 96, pp. 245-252, 2003.

[9] Q. Liu, *et al.*, "Hydrothermal synthesis of CoFe2O4 nanoplatelets and nanoparticles," *Materials Chemistry and Physics,* vol. 108, pp. 269-273, 2008.

[10] J. Yang, *et al.*, "A highly sensitive non-enzymatic glucose sensor based on a simple two-step electrodeposition of cupric oxide (CuO) nanoparticles onto multi-walled carbon nanotube arrays," *Talanta,* vol. 82, pp. 25-33, 2010.

[11] Z. Yang, *et al.*, "Controlled synthesis of CuO nanostructures by a simple solution route," *Journal of Solid State Chemistry,* vol. 180, pp. 1390-1396, 2007.

[12] L. Cheng, *et al.*, "Preparation, characterization, and electrochemical application of mesoporous copper oxide," *Materials Research Bulletin,* vol. 45, pp. 235-239, 2010.

[13] K. Lew, *Chemical reactions*: Infobase Publishing, 2009.

[14] M. R. Johan, *et al.*, "Annealing effects on the properties of copper oxide thin films prepared by chemical deposition," *Int. J. Electrochem. Sci,* vol. 6, pp. 6094-6104, 2011.