Asian Journal of Chemistry; Vol. 23, No. 5 (2011), 2295-2298

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Preparation of CuO Thin Film with Corncob-Like Morphology *via* Chemical Solution Processing†

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AJC-9553

Uniform and crack-free cupric oxide (CuO) films have been prepared by chemical bath deposition method simply using $Cu(NO_3)_2$ and ammonia. Crystal structure and morphology of the deposited CuO films were characterized by XRD and SEM. The results illustrate that well defined nanostructured CuO thin film with unique morphologies can be deposited onto glass slide substrate at 40-80 ºC for 1-5 h with pH value ranging from 8.5-10. Unique elliptic sheet-like morphology can be obtained at higher temperature (≥ 70 ºC), while interesting corncob-like nano-structured CuO film can be obtained at lower temperature (≤ 60 ºC). Ammonia is the key parameter to the film deposition. It has much effect on morphology of the obtained film in the range of 2.6-3.0 mL, as well as not on deposition duration.

Key Words: Nanostructure, Chemical bath deposition, CuO, Thin film.

INTRODUCTION

Cupric oxide, as one of most popular *p*-type semiconductor oxides, is a versatile material with a narrow band gap of "1.4 eV due to an excess of oxygen[1,2] and excellent thermal stability[3]. Cupric oxide crystallizes in a monoclinic structure with the lattice parameters a = 4.684 Å, b = 3.425 Å, c = 5.129 Å and β = 99.28º in which CuO units are chained and Cu forms four coplanar bonds with O[4]. Cupric oxide is unique amongst the monoxides of 3*d* transition elements having a square planar coordination of copper by oxygen in the monoclinic structure[5]. Cupric oxide material in pure condition with good stoichiometry is almost like an electrical insulator. But during the preparation processing, a lot of defects like constitutional faults, point defects, impurities from the reactants and from substrate materials are associated with the otherwise pure crystalline state of the material and cause deviation from stoichiometry. This deviation although is not deliberate but it leads to important semiconducting characteristics of the prepared CuO samples and are interesting to study. Therefore, it is a promising semiconductor for solar cell fabrication due to its suitable optical properties[6]. It also attractive as a selective solar absorber since it has a high solar absorbency and a low thermal emittance[7]. Furthermore, it possesses unusual antiferromagnetic properties with an incommensurate antiferromagnetic structure existing below the Neel temperature of 230 K[8]. Recently, it has been discovered that CuO also shows high-temperature superconductivity, in which the specific coordination between Cu and O atoms is believed to play a crucial role[3,6,9]. The synthesis and the application study of CuO have both theoretical and practical importance. Cupric oxide nanosturctures including nanoellipsoids[10], nanoribbons[11], nanorods[12,13], nanotubes[14], nanorings[11], 3D hierarchical butterflies[15], nanospheres[16], nanocages[17], hollow nanospheres[18], nanoflowers[19], aligned nanowires[20], dandelion[21] and urchin[22] *etc*., have been successfully synthesized through different methods with or without the assistance of templates. Moreover, CuO films have also been prepared by various deposition techniques such as PLD[23], CVD[24], sputtering[25,26], thermal oxidation[27,28], evaporation[29,30], molecular beam epitaxy[31] and electrodeposition[32], spray-pyrolysis[33] and sol-gel[34], *etc*. CuO films have been reported to show native *p*-type conductivity due to copper vacancies in the structure[35] and has a band gap reported between 1.2 and 1.7 eV with a black colour and a partial transparency in the visible range[4]. An important advantage of using CuO in device applications is that it is non-toxic and its constituents are available in abundance.

In this work, well defined nanostructured CuO thin films with unique morphologies on glass slide substrate have been fabricated simply by using $Cu(NO_3)_2$ and $NH_3 \cdot H_2O$ instead of any toxic and dangerous reagents *via* a low-temperature and environment-friendly chemical bath deposition method. Morphology of the obtained film is sensitively affected by processing temperature.

†Presented to the 4th Korea-China International Conference on Multi-Functional Materials and Application.

EXPERIMENTAL

Film deposition: Films were obtained on the commercial microscope glass slide substrates. Before deposition, the substrates were cleaned by ultrasonic treatment in toluene, acetone and ethanol in turn, rinsed with distilled water and etched in HF (20 %) for about 1-3 min, then washed with denionized water and dried in air. All reagents were of analytical grade and used without further purification. Under continuous stirring, appropriate ammonia was added into $Cu(NO_3)_2$ solution (0.1 mol/L). After stirring, this clear and homogeneous aqueous solution was used as the precursor solution for CuO thin film. The pre-treated substrates were floated on the surface of the precursor solution to prevent particles formed in the solution from accumulating on the substrate surface. The beakers containing the precursor solution were maintained at desired temperature for different deposition duration in order to obtained proposed films. During the deposition process, the substrates were floated on the surface of the precursor solution. This is different from conventional method in which the substrates were placed vertically in the solution. The floating substrate on the surface of the solution is easier to prevent the particles from accumulating on the substrate surface, which is in favour of ion-by-ion heterogeneous processing to produce the high quality film[30].

Characterization: The structure and overall crystallinity in the films were characterized through θ-2θ scans obtained on a Y-2000 X-ray diffractometer (XRD) with CuK_α radiation. Surface morphology was monitored through scanning electron microscopy (SEM) on a Sirion 200 field-emission SEM operated in a 5-10 kV voltage range.

RESULTS AND DISCUSSION

Effect of ammonia: The amount of ammonia is the key parameter to control the thin film deposition during the processing, since ammonia plays important role of chelating agent as well as adjusting pH value of the deposition solution. A series of experiments with using various amount of ammonia have been investigated. The results showed that the black CuO thin films have been obtained as deposition solution heating at 80 ºC for 1 h with ammonia volume varied from 2.7-3.0 mL, especially, the uniform and crack-free films without any pore obtained with ammonia volume of 2.7-2.9 mL. Obvious flaw on the surface of thin film can be observed by naked eye when ammonia volume goes up to 3.0 mL. There is no film deposited onto substrate if ammonia volume is less than 2.7 mL in this case. The pH value of deposition solution range between 8.5-10.0 as ammonia volume varies from 2.7-3.0. Fig. 1 shows the top-view SEM images of the obtained film. It can be seen that the uniform and dense films are constitute of elliptic sheets. These sheets have similar shape and thickness and sheet size is about 600 nm × 100 nm in length and wide. These sheets stack up tightly resulting in a certain orientation. Compare SEM images of two samples, it can be observed that variation of ammonia volume in the deposition system has not much effect on determination of micro-morphology of the deposited CuO thin film. These sheets on the sample obtained with ammonia volume of 2.7 mL show a little bit of random position and the grain size of these sheets is tiny smaller.

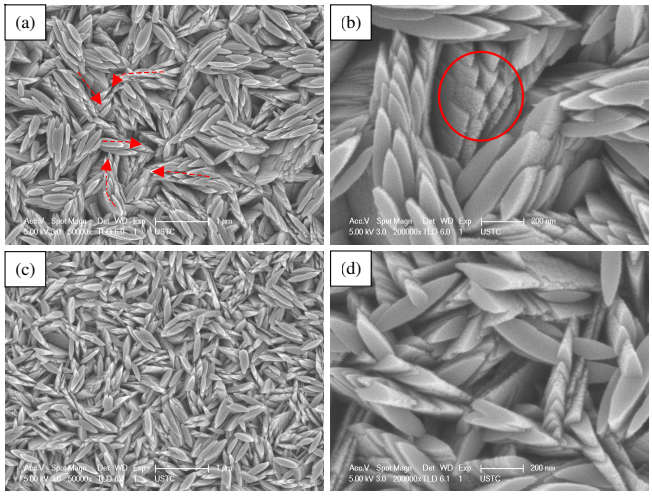

Fig. 1. SEM images of the obtained film with ammonia amount of (a), (b) 3.0 mL; (c), (d) 2.7 mL

Fig. 2 shows XRD patterns of the obtained thin film sample with different ammonia volume. Peaks on the three XRD patterns are corresponding to that of monoclinic CuO (PDF card No. 72-628). The XRD pattern of the powder collected from solution after film deposition processing indicates that the collected powder is phase-pure monoclinic CuO in good crystallinity (Fig. 3). These peaks with low density in the pattern of powder are not observed on the patterns of films, which would result from two kinds of possible reason, on one hand, the growth of grains on film has certain orientation, while that of powder is random; on the other hand, due to a quite thin layer of the film sample, the diffraction signal is definitely weaker than that of powder sample, which results in those peaks with low density could not be detected.

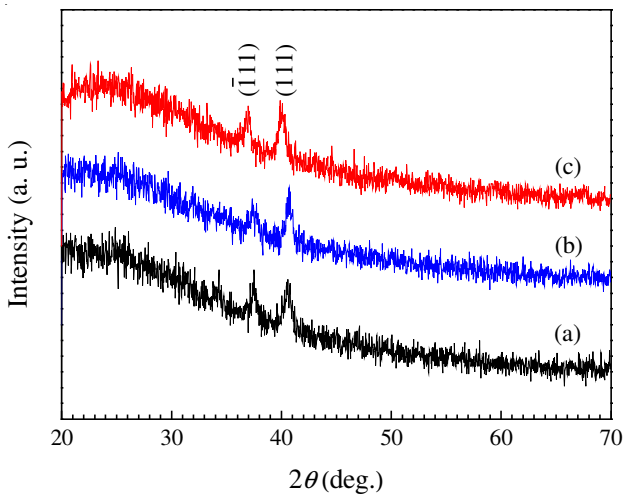

Fig. 2. XRD patterns of the films obtained with ammonia of (a) 2.7 mL, (b) 2.8 mL, (c) 2.9 mL

The effect of treatment temperature: Fig. 4 shows XRD patterns of the thin films obtained at different treatment temperature for 1 h with ammonia volume of 2.7 mL and pH value of 8.5. It can be seen from the patterns that the diffraction peak density increasing gradually with temperature raising from 40-80 ºC due to diffraction signal intensity is growing, which indicates that the films are thickening. The peaks are

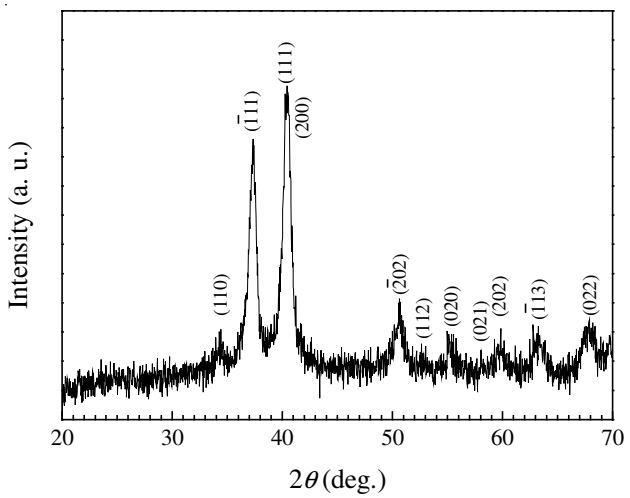

Fig. 3. XRD pattern of the powder collected from deposition solution

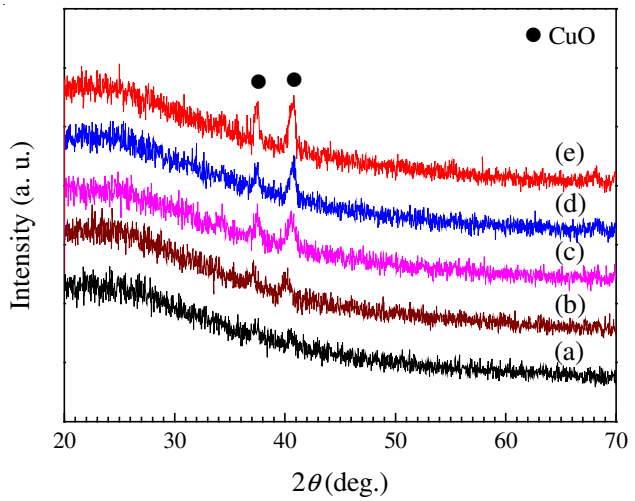

Fig. 4. XRD patterns of the thin films obtained at: (a) 40 ºC, (b) 50 ºC, (c) 60 ºC, (d) 70 ºC, (e) 80 ºC, respectively

more and more sharp, which means the crystallinity is also increased. When treatment temperature maintained at 30 ºC, there is no film deposited onto substrate, neither participated powder out. The deposited films are very thin obtained at 40 and 50 ºC as compared to those of at higher temperature. It is reasonable that increasing temperature favours thin film rapid formation as well as crystallinity enhancement.

Fig. 5 shows top-view SEM images of the thin films obtained at 60 ºC. It's obvious that the uniform and dense thin CuO films can both deposit at temperature ranging from 60-80 ºC. The detail observation in SEM images [Figs. 5 and Fig. 1(a-b)] finds that the film obtained at 60 ºC is constitute of corncob-like substructures with length of around 500 nm assembled by 20-30 nm fine grains in certain orientation. While the morphology of the film obtained at 80 ºC shows quiet different from that of 60 ºC. The film at 80 ºC is constituted of slice sheets single crystal with very smooth surface piled upin certain orientation. Treatment temperature is one of the most important parameter tune morphology of nano-materials due to its influence on nuclei and crystal growth velocity. The results of the rest experiments with various ammonia volumes indicate that treatment temperature should be properly decreasing with reducing ammonia amount in order to high quality film.

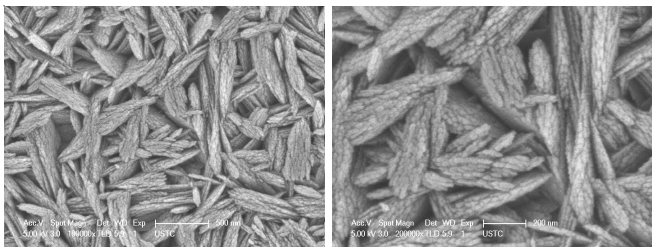

Fig. 5. SEM images of the thin film obtained at 60 ºC

Effect of deposition duration: The dynamic behaviour of thin film deposition at 50 ºC has been investigated. Fig. 6 shows XRD patterns of the film obtained at 50 ºC for different deposition duration. It can be seen from the patterns that diffraction peak density increases gradually with prolonging deposition duration, which indicates that the film is thickening. It is notable that the crystalline CuO thin film has been already formed with deposition processing for 1 h.

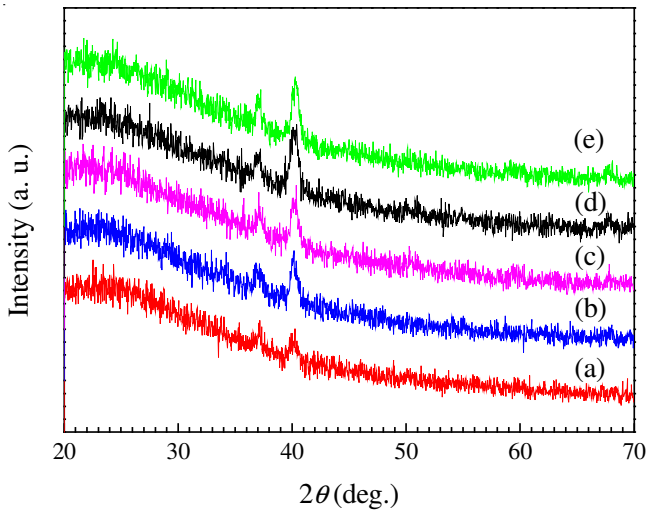

Fig. 6. XRD patterns of the thin film obtained at 50 ºC for: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, (e) 5 h, respectively

Fig. 7 shows SEM images of the film deposited at 50 ºC for 4 h. Comparing Fig. 7 with Figs. 1 and 5, a conclusion has been drawn that the corncob-like morphology thin film is easy to obtain at lower temperature and at the same time at lower temperature, the smaller grain size. The well crystalline perfect sheet-like morphology can be formed at higher temperature. However, prolonging deposition duration does not create fine grains grow up, which would be deduced from the restricted two-dimensional growth model, single grain could not grow continuously. Only some filaments around the corncobs are

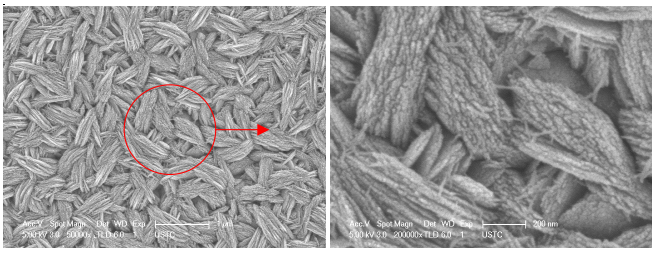

Fig. 7. SEM images of the thin film deposited at 50 ºC for 4 h

formed with prolong duration, which resembles the silk of corncobs. It is also clear that the thin film deposited for 4 h is more uniform and dense, which indicates that prolonging deposition duration is an advantage to high quality film in this case.

Conclusion

In summary, a low-temperature and environment-friendly chemical bath deposition technique has been successfully applied to fabricate CuO thin film. The results show that the dense and crystalline CuO thin films with unique architecture morphologis could be obtained under the processing parameters as following: $Cu(NO_3)_2$ as Cu^{2+} ion source, ammonia as complexing agent as well as pH adjustment agent, pH value of 8.5-10, processing temperature ranging from 40-80 ºC, deposition duration of 1-5 h. Ammonia is the key parameter to the film deposition. However, it has not much effect on the surface morphology of the film in the range of 2.6-3.0 mL, neither has deposition duration. Processing temperature has responsibility to the surface morphology evolution in this case. Elliptic sheet-like morphology can be obtained at higher temperature (≥ 70 ºC), while interesting corncob-like nanostructured CuO film has been obtained at lower temperature (≤ 60 ºC). The dense CuO thin film with unique morphology *via* a simple chemical solution route may have potential applications such as optical-electric functional materials, thin film catalysis and lithium ion batteries, *etc*.

ACKNOWLEDGEMENTS

This work was financially supported by the National Nature Science Foundation of China (No. 20901001), Education Department of Anhui Province (No. KJ2009B133 and KJ2010B291) and Anhui University of Architecture (No. 20081204).

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