Synthesis and characterization of radial structure cupric oxide microspheres

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This paper reports that the radial structure cupric oxide microspheres are synthesized by thermal oxidation of copper thin films. The films are deposited on indium tin oxides conducting glass by electric plating. The radial structure cupric oxide microspheres are characterized using the scanning electron microscope. The results show that the nanowires are about 60 nm in diameter and 2 μm in length. The diameter of the microspheres is about 4 μm. Among the conditions tested, the best condition for preparing the radial structure cupric oxide microspheres is 350 ^{o}C for 4 hours. Furthermore, the possible growth mechanism of the radial structure cupric oxide microspheres is discussed.

1. Introduction

Since the first discovery of carbon nanotubes in 1991, a window to new technological areas has been opened [1]. Nanostructures have received steady growing interest because of their fascinating properties and various applications as compared with the bulk or microsized counterparts.

Recently, cupric oxide (CuO) has been widely used in many fields such as in anode electrodes for batteries, gas sensors, FE emitters, catalysts and high temperature superconductors [2-4]. Based on these applications, many methods have been used to prepare one-dimensional CuO. Thermal decomposition of CuC_2O_4 precursor was also used to synthesize CuO nanorods [5]. Li et al. synthesized CuO nano-shuttle by the hydrothermal route [6]. Hsieh et al. synthesized CuO nanofiber by a self-catalytic process [7]. Sahooli et al. used precipitation method to synthesized CuO nanopaticles [8]. In the electrodeposition field, there are not reports of CuO nanostructure fabricated on the indium tin oxides (ITO) conducting glass. We try to synthesize radial structure CuO microspheres (RSMSs) on ITO conducting glass.

In this paper, the RSMSs were synthesized by annealing the copper-coated ITO conducting glass (Cu/ITO) in air. We investigated the effect of annealing temperature on the growth of RSMSs. The possible growth mechanism was investigated.

2. Materials and methods

The ITO conducting glass was washed in distilled water and acetone–ethanol mixture solution under ultrasonic bath for 20 minutes, respectively. After dried in air, the copper plating was completed in the electro bath for 10 minutes. The current intensity was 20 mA. Table 1 lists the electro bath conditions. The Cu/ITO was obtained. The thickness of copper thin films were measured with an advanced development profiler (Dektak 8M). The average thickness of copper film was about 1.217μm.

Table 1. Bath compositions and operation conditions for plating.

Chemical	Concentrations
Cupric subcarbonate $(Cu_2(OH)_2CO_3 \cdot H_2O)$	40~50 g/l
Citric acid $(C_6H_8O_7 \cdot H_2O)$	250~300 g/l
Potassium sodium tartrate $(C_4H_4O_6KNa \cdot 4H_2O)$	30~40 g/l
Sodium hydroxide (NaOH)	120~130 g/l
PH	10~12
Temperature	15~30 ^{o}C

The Cu/ITO was washed with distilled water followed by absolute alcohol. After dried in air, they were annealed at 300 ^{o}C, 350 ^{o}C and 400 ^{o}C for 4 hours in air, respectively. The heating rate was about 10°C/min. After cooled down naturally to room temperature, RSMSs were obtained. In order to investigate the structure and the morphology, CuO nanowires were characterized using X-ray diffraction (XRD, Philips X′ per pro), field emission scanning electron microscope (FESEM, JSM 6701F), and transmission electron microscope (TEM, JEM-2010).

3. Results and discussion

XRD measurements were carried out using Cu K_α radiation ($\lambda = 1.54056$) from a sealed tube operated at 45 kV and 40 mA. Fig. 1 shows the XRD pattern of RSMSs synthesized at 300 °C and 350 °C for 4 h in air, respectively. The results show that RSMSs are obtained by annealing Cu/ITO at different temperatures. It is found that the produced materials are mixtures of CuO (JCPDS: 45-0937) and Cu_2O (JCPDS: 65-3288), After Cu/ITO was annealed at 350 °C, the pure RSMSs were obtained.
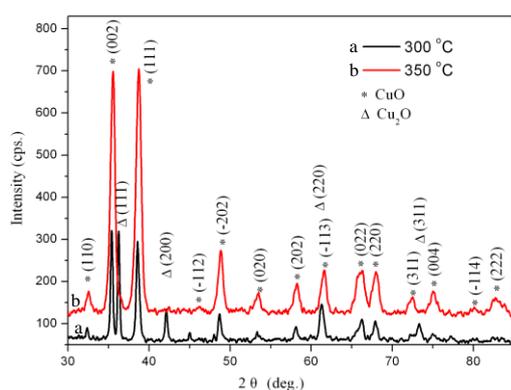
Fig. 1. XRD pattern of RSMSs prepared at 300 °C and 350 °C for 4 hours in air, respectively.

It is generally accepted that CuO belongs to the C_{2h}^6 space group symmetry with two molecules per primitive cell [10]. There are twelve zone-center optical-phonon modes, $4A_u + 5B_u + A_g + 2B_g$, three of which $A_g + 2B_g$ are Raman active [11]. Fig. 2 shows the micro-Raman scattering spectra of RSMSs prepared at 350 °C for 4 hours in air. The result shows that there are three Raman peaks at 291 cm^{-1}, 341 cm^{-1} and 636 cm^{-1}. In comparison with the vibrational spectra of a CuO single crystal [12], we can assign the peak at 291cm^{-1} to the Ag mode and the peaks at 341 cm^{-1} and 636 cm^{-1} to the Bg modes. This indicates that there is not Cu_2O modes [13]. Only the single phase property of CuO is exhibited.
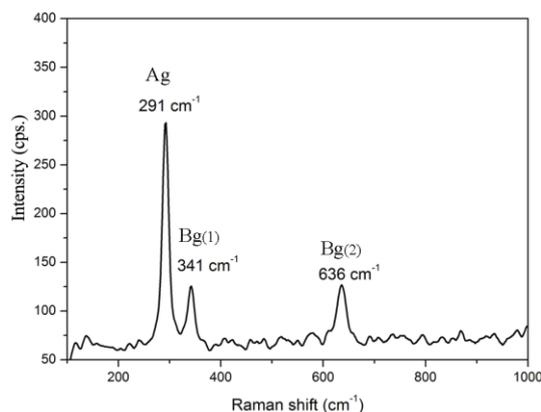
Fig. 2. Micro-Raman scattering spectra of RSMSs prepared at 350 °C.

The formation of copper thin film has been interpreted by following two consecutive reactions:

$$Cu^{2+}(aq) + e^- = Cu^{1+}(aq) \qquad (1)$$

$$Cu^{1+}(aq) + e^- = Cu^0(s) \qquad (2)$$
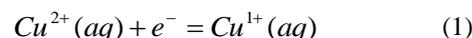
Further details of the process, particularly related to the initial stages of the copper phase growth, have been investigated by means of non-stationary techniques and surface microscopy [14]. The joining mechanism of electric plating of copper on glass is explained by mechanical bonding. The internal stress is stored between the CuO and glass. The internal stress plays an important role in the formation of the CuO nanowires and it is discussed below.

In order to obtain an optimal annealing temperature to prepare RSMSs, the surface morphology SEM images of samples prepared at different temperatures were shown in Fig. 3. Fig. 3a and b show FESEM images of Cu/ITO after annealed at 300 °C for 4 hours in air. It can be found from Fig. 3a, a few nanowires and some protuberances are observed in the sample surface. Fig. 3b shows the high magnification images of the sample annealed at 300 °C for 4 hours. The results show that the protuberance around appears some nanowires on the sample surface. The diameter of protuberance is about 1 μm.

Fig. 3c and d show low and high magnification FESEM images of Cu/ITO annealed at 350 °C for 4 hours in air. It can be seen from Fig. 3d that the RSMSs with 4 μm are observed on the sample surface. CuO nanowires with length of ~2 μm were shown on the microsphere surface. A large amount of needle-like CuO nanowires have nonuniform length and diameter on the microsphere surface. Further TEM observation in Fig. 4 indicated that the diameter of CuO nanowire was about 60 nm [15, 16]. Fig. 4b shows that the selected area electron diffraction (SAED) pattern of the CuO nanowire, indicating that the nanowires are single crystalline in structure. It was well known that, when they are in environment, gas sensors and catalysts based on radial structure cupric oxide microspheres with a high surface-to-volume ratio can provide more adsorption desorption sites comparing to traditional structures. Therefore, we believed that the RSMSs are potential materials for making gas sensors and catalysts. However, the application properties of the RSMSs needs further in-depth researched.
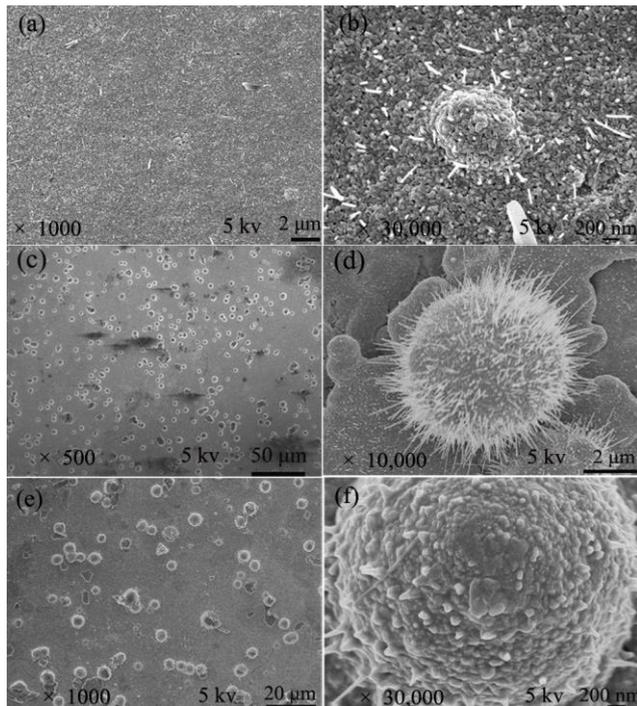
Fig. 3. The different magnification FESEM images of Cu/ITO annealed at different temperatures for 4 hours in air: (a) and (b) 300 °C , (c)   and (d) 350 °C, (e)   and (f) 400 °C, respectively.

Fig. 4. The TEM image and SAD pattern of single CuO nanowire.

The surface morphology of the sample obtained by annealing the Cu/ITO at 400 °C in air for 4 hours was exhibited by different magnification FESEM images. It was shown in Fig. 3e that the RSMSs had nonuniform diameter. A few CuO nanowires appeared on the microsphere surface. The microsphere surface in Fig. 3d was more density than that in Fig. 3f. Therefore, among the conditions tested, the best annealing temperature for obtaining the RSMSs was 350°C, which had better effect on the growth of nanowires.

Vapor-solid (VS) mechanism and vapor-liquid-solid (VLS) mechanism were used to explain the growth of CuO nanowires [17, 18]. In the VS mechanism, the precursors were evaporated in high temperature region, and then were condensed and grew to nanowires in low temperature region. In this experiment, the samples were annealed at 400 °C, which was much far less than the melting point of Cu (1083 °C) and the decomposition temperature of CuO (1124 °C) [19]. Therefore, VS mechanism is not adapted to explain the growth of CuO nanowires in our experiment. VLS mechanism was also introduced by researchers to explain the growth of CuO nanowires [20]. In the VLS mechanism, there is a metal catalyst (Fe, Co, Ni) at tip of the nanowires, and the diameter of the nanowires is limited by the size of the metal catalyst. However, the metal catalyst is not found in FESEM images, and the diameter of CuO nanowires is not uniform (Fig. 3e-f). Therefore, VLS mechanism cannot be used to explain the growth of CuO nanowires in our experiment too.

The possible growth mechanism of RSMSs is discussed. This mechanism consists of several stages. The schematic diagram of the growth mechanism is shown in Fig. 5. The formation of oxide hillocks leads to the relaxation of the internal stress, and the reaction-diffusion proceeds under the internal stress [21, 22]. The energy is stored in a film or cold-worked metals by the internal stress. Kumar et al. reported that the growth of CuO nanowires was the result of the accumulation and relaxation of the stress in annealing process [23]. In addition, Chen et al. also reported that the growth of CuO nanowires on the copper foil was due to the accumulation and relaxation of the stress [24]. In this experiment, due to the different thermal expansion coefficient of copper films and ITO conducting glass and the volume expansion effect of the combination of Cu and O, the internal stress is accumulated in the interface between copper films and ITO conducting glass. The compress stress is induced in oxide layer [25]. Under the electrodeposition, the copper was deposited on the ITO conducting glass surface by mechanical bonding (eqs. 2) because of the low solubility of glass in copper. As the copper thin film grew, the stress was accumulated between copper and glass interfaces. In addition, due to oxygen atoms in the atmosphere reacting with copper film during the annealing process and the difference in density between Cu and the growing CuO, the compress stress was resulted in oxide layer. Therefore, at lower temperature, accumulated stress impacted copper thin films at 300 °C, and the part of stress was released by excluding the nanowires and diffusing the grain boundaries. A few short CuO nanowires and protuberances appeared on film surfaces (Fig. 3b). Additionally, the more accumulated energy was released when the annealing temperature was raised to 350 °C, and the larger number of length CuO nanowires were shown. Further, the copper film substrate supplied continuously the copper atoms and internal stress as the driving force promoting the growth of CuO nanowires along the lower energy plane [24]. Owing to the outer energy of the copper film was lower than that of the internal, the CuO nanowires grew normal to the film surface to form radial structure CuO nanowires (Fig. 3). In the previous reports [9, 16, 26 and 27], the growth directions of the CuO nanowires prepared by thermal oxidation were [-111] and [111]. These results indicated that the growth of CuO nanowires prepared by thermal oxidation was due to a crystalline preferential growth.

Meanwhile, a lot of protuberances on the copper thin film surface changed into microspheres, and RSMSs were obtained (Fig. 5c). With the annealing temperature increasing to 400 ^{o}C, the length CuO nanowires became short and massive, and the micro-spheres were distorted after annealing treatment for 4 hours (Fig. 5d). During annealing treatment, copper was oxidized first on the copper thin film surface, and then the inner copper films. This process was achieved by the atomic diffusion. Therefore, we consider that the growth of CuO nanowires is the result of accumulated energy release and the preferential orientation. However, the detailed growth mechanism of the RSMSs needs further in-depth researched.
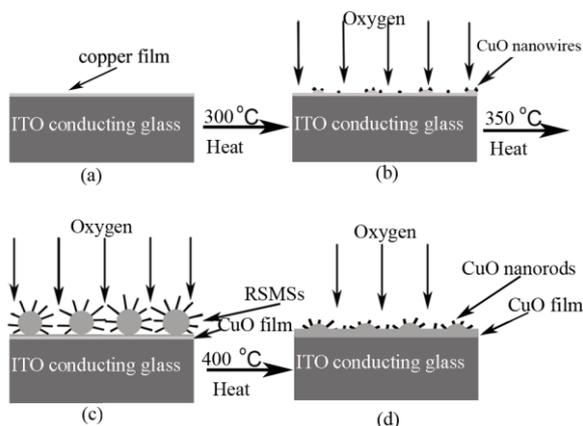
Fig. 5. Schematic illustration of the growth process of the RSMSs: (a) Cu/ITO; (b) formation of CuO nanowires; (c) formation of RSMSs; (d) formation of short and massive CuO nanrods.

4. Conclusions

RSMSs are synthesized by annealing the Cu/ITO at 350 ^{o}C for 4 hours in air. The Cu/ITO is prepared by electric plating. The CuO nanowires of RSMS are about 60 nm in diameter and 2 μm in length. The diameter of the microspheres is about 4 μm. The growth mechanism of CuO nanowires may have some relationship with the released energy of the internal stress in the copper film by the atomic diffusion.

References

[1] R. H. Baughman, A. A. Zakhidov, W. A. de Heer, Science 297, 787 (2002).
[2] L. Wang, Y. Kang, Y. Wang, B. Zhu, S. Zhang, W. Huang, S. Wang, Mater. Sci. Engin. C **32**, 2079 (2012).
[3] J. Zhai, X. Tao, Y. Pu, X. F. Zeng, J. F. Chen, Mater. Res. Bull. **46**, 865 (2011).
[4] A. A. Ponce, K. J. Klabunde, J. Mol. Catal. A **225**, 1 (2005).
[5] C. K. Xu, Y. K. Liu, G. D. Xu, G. H. Wang Mater. Res. Bull. **37**, 2365 (2002).
[6] S. Li, H. Zhang, Y. Ji, D. Yang, Nanotechnology **15**, 1428 (2004).
[7] C. T. Hsieh, J. M. Chen, H. H. Lin, H. C. Shih, Appl. Phys. Lett. **82**, 3316 (2003).
[8] M. Sahooli, S. Sabbaghi, R. Saboori, Mater. Lett. **81**, 169 (2012).
[9] K. L. Zhang, C. Rossi, C. Tenailleau, P. Alphonse, J. Y. Chane-Ching, Nanotechnology **18**, 275607 (2007).
[10] X. R. Ye, D. Z. Jia, X. Q. Xin J. Solid State Chem. **147**, 516 (1999).
[11] J. Chrzanowski, J. C. Irwin, Solid State commun. **70**, 11 (1989).
[12] X. K. Chen, J. C. Irwin, J. P. Franck, Phys. Rev. B **52**, R 13130 (1995).
[13] K. Reimann, K. Syassen, Phys. Rev. B **39**, 11113 (1989).
[14] B. L. Rivas, E. D. Pereira, I. Moreno-Villoslada, Prog. Polym. Sci. **28**, 173 (2003).
[15] H. Q. Liang, L. Z. Pan, Z. J. Liu, Mater. Lett. **62**, 1797 (2008).
[16] Q. L. Shou, J. P. Cheng, L. Zhang, B. J. Nelson, X. B. Zhang, J. Solid Stat. Chem. 191 (2012).
[17] C. Geng, Y. Jiang, Y. Yao, X. Meng, J. A. Zapien, C. S. Lee, Y. Ifshitz, S. T. Lee, Adv. Funct. Mater. **14**, 589 (2004).
[18] Z. Wang, Q. Zhao, Y. Zhang, B. Xiang, D. P. Yu, Eur. Phys. J. D **34**, 303 (2005).
[19] F. García-Labiano, L. F. Diego, J. Adánez, A. Abad, P. Gayán, Chem. Eng. Sci. **60**, 1401 (2005).
[20] X. F. Duan, C. M. Lieber, Adv. Mater. **12**, 298 (2000).
[21] S. Aggarwal, A. P. Monga, S. R. Perusse, R. Ramesh, V. Ballarotto, E. D. Williams, B. R. Chalamala, Y. Wei, R. H. Reuss, Science **287**, 2235 (2000).
[22] S. R. Shinde, A. S. Ogale, S. B. Ogale, S. Aggarwal, V. Novikov, E. D. Williams, R. Ramesh, Phys. Rev. B **64**, 035408 (2001).
[23] A. Kumar, A. K. Srivastava, P. Tiwari, R. V. Nandedkar, J. Phys. Condens. Matter. **16** ,8531 (2004).
[24] J. T. Chen, F. Zhang, J. Wang, G. A. Zhang, B. B. Miao, X. Y. Fan, D. Yan, P. X. Yan, J. Alloy Compd. **454**, 268 (2008).
[25] J. Zeng, P. Tao, S. Wang, J. C. Xu, Appl. Surf. Sci. **255**, 4916 (2009).
[26] X. C. Jiang, T. Herricks, Y. Xia, Nano lett. **2**, 1333 (2002).
[27] Y. W. Zhu, T. Yu, F. C. Chenong, X. J. Xu, C. T. Lim, V. B. C. Tan, J. T. L. Thong, C. H. Sow, Nanotechnology **16**, 88 (2005).

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