FORMATION OF Cu_xO (x=1, 2) NANOWIRES BY THERMAL ANNEALING COPPER FILM DEPOSITED ON Ti/Si SUBSTRATE

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Introduction

Since carbon nanotubes were discovered by Iijima[1], one-dimensional (1D) nanomaterials such as nanowires, nanobelts, nanotubes, and nanorods have become one focus of intensive research with their large surface area and possible quantum-confinement.

In recent years, CuO and Cu_2O have been received extensive investigations for its prospective applications in many fields such as such as gas sensor[2], and high temperature superconductors[3]. Based on these applications, many methods have been developed to prepare copper oxides with various morphologies. Hish[4] et al produced well-ordered CuO nanofibers by a self-catalytic growth mechanism. Well-aligned Cu_2O nanowire arrays were prepared by an ethylene glycol-reduced process[5]. Methods mentioned above cannot be departed from complex chemical reactions or process. Nowadays, more studies for developing CuO nanowires by directly heating copper substrates (foils, grids, and wires) have been reported[6,7]. Thermal annealing of copper substrate is a simple, fast and convenient methods to get Cu_xO (x=1, 2) nanowires, in comparison to the above-mentioned complicated methods.

The present work reports the preparation of Cu_xO (x=1, 2) nanowires by directly heating copper thin films deposited by electron beam evaporation on Si substrate. Different parameters which affect the growth of Cu_xO(x=1, 2) nanowires are investigated.

Experimental

Cu_xO (x=1, 2) nanowires were fabricated by directly heating copper thin films at set-point temperature. Copper thin films deposited onto Si substrate by electron beam evaporation. Firstly, a 30 nm thick titanium should be deposited onto silicon by magnetron sputtering to prevent copper thin film cracking during thermal oxidation. After this stage, copper films were deposited by electron beam evaporation with the thickness of 1000 nm onto the Ti/Si substrate. All of the samples were cut into small chips for further investigation. The chip was placed into the center of pipe furnace with a different set-point temperature (300, 350, 400, 450, 500, 600 and 700 ℃) in air. The pipe furnace was arranged into different thermal oxidation time (2, 4, 5, and 6 h) after getting the set-point temperature with heating rate of 8℃/min. After thermal oxidation, the whole system was allowed to cool from set-point temperature to room temperature with a rate of 2℃/min. The microstructure of nanowires grown on silicon substrates was characterization by a field-emission scanning electron microscope (FESEM) (ZEISS ULTRA PLUS GEMINI) and the identification was evaluated by D8 ADVANCE X-ray diffraction (XRD).

Results and Discussion

Cu_xO(x=1, 2) nanowires were grown on the Cu films deposited by electron beam evaporation by thermal oxidation in air. At first, the samples were oxidized at 400 ℃ in air for different time in order to obtain an optimal annealing time to prepare nanowires. Fig. 1 shows the morphology of the sample obtained by annealing Cu films at 400 ℃ in air for 2, 4, 5 and 6 h. From Fig. 1(a), it is apparent that it is sufficient to fabricate a large number of nanowires for just 2 h of thermal annealing. But when the annealing time comes to 6 h, the nanowires are gone (Fig. 1(d)). The average diameter of nanowires is 50 nm, the length varies between 1 and 2 μm for annealing time of 2 h. when the growth time is prolonged to 4 h (Fig. 1(b)), more nanowires with length of 2-3 μm can be seen on the surface. While prolonging the growth time to 5 h, the length of most nanowires are in the range of 0.6-1 μm (Fig. 1(c)). But one more thing should be noticed that the average diameter of nanowires keep constant (50 nm), independent of annealing time.

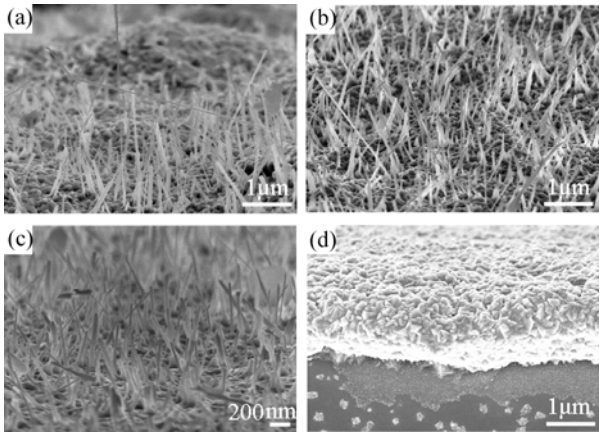

Fig. 1 SEM cross-sectional images of 1μm thick copper films annealed at 400℃ in air for different annealing time: (a) 2h, (b) 4h, (c) 5h, and (d) 6h.

The samples were oxidized for 4 h in air at different temperatures for studying the effect of the time on the morphology as shown in Fig. 2. It can be seen from Fig. 2(a), large spherical grains with the average diameter of 300 nm are found in the sample without nanowires annealed at 300 ℃. When the temperature

is increased to 350 ℃, the morphology of the samples obtained by annealing Cu films has changed into fluey surface with a lot of pores (Fig. 2(b)). The growth of nanowires is only observed at 400 ℃, as is apparent from Fig. 2(c). The nanowires not only cover almost the complete area of the substrate but are also almost directional. On further increasing the temperature to 450 ℃, almost negligible creation of nanowires is observed, as is revealed by the SEM image shown in Fig. 2(d). When the temperature comes to 500, 600, 700 ℃ respectively, large grains are the only formation instead of nanowires (Figs. 2(e)-(g)). Fig. 3 shows the XRD results of 1 μm thick copper film annealed at 400 ℃ for 4 h in air. It confirms that the product is only composed of two phases, namely, Cu_2O and CuO.

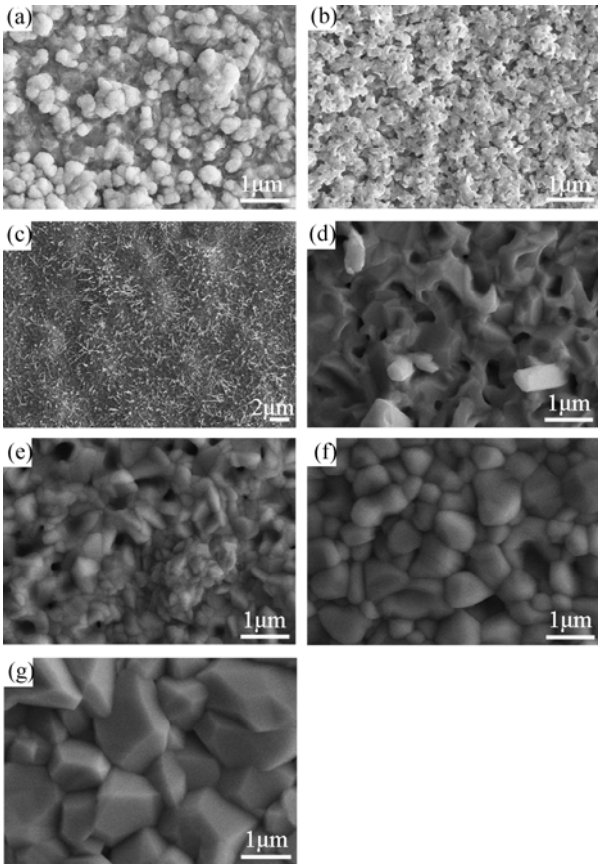

Fig. 2 SEM images of 1μm thick copper films annealed for 4h in air at various temperatures: (a) 300℃, (b) 350℃, (c) 400℃, (d) 450℃, (e) 500℃, (f) 600℃, and (g) 700℃.

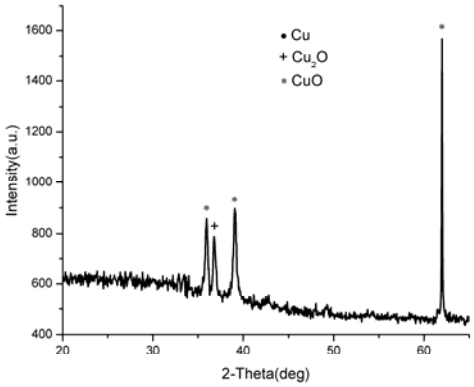

Fig. 3 XRD pattern of 1μm copper film annealed at 400℃ in air for 4h.

Conclusion

Uniform and large-area Cu_xO (x=1, 2) nannowires have been successfully fabricated by thermal annealing of copper film deposited by electron beam evaporation on silicon substrate in air. The as-deposited copper thin film has to be annealed at 400 ℃ in order to synthesize nanowires. It is observed that the annealing time does affect the length of nanowires, while the average diameter of nanowires keeps constant to 50 nm. The thermal annealing time, and the annealing temperature will be set to 4 h, 400 ℃ to grow large-area, and uniform Cu_xO(x=1, 2)nanowires.

References

1. S. Iijima, Helical microtubules of graphitic carbon. *Nature* **354**, (1991) 56-58.

2. N. Duc Hoa, N. Van Quy, M. A. Tuan, and N. Van Hieu, Facile synthesis of p-type semiconducting cupric oxide nanowires and their gas-sensing properties. *Physica E* **42**, (2009) 146-149.

3. J. B. Reitz and E. I. Solomon, Propylene oxidation on copper oxide surfaces: electronic and geometric contributions to reactivity and selectivity. *J. Am. Chem. Soc.* **120**, (1998) 11467-11478.

4. C. Hsieh, J. Chen, H. Lin, and H. Shih, Synthesis of well-ordered CuO nanofibers by a self-catalytic growth mechanism. *Appl. Phys. Lett.* **82**, (2003) 3316-3318.

5. X. Liu, R. Hu, S. Xiong, Y. Liu, L. Chai, K. Bao, and Y. Qian, Well-aligned Cu_2O nanowire arrays prepared by an ethylene glycol-reduced process. *Mater. Chem. Phys.* **114**, (2009) 213-216.

6. A. Kumar, A. K. Srivastava, P. Tiwari, and R. V. Nandedkar, The effect of growth parameters on the aspect ratio and number density of CuO nanorods. *J. Phys.: Condens. Matter* **16**, (2004) 8531.

7. X. Jiang, T. Herricks and Y. Xia, CuO nanowires can be synthesized by heating copper substrate in air. *Nano. Lett.*, **2**, (2002) 1333-1338.