

# Synthesis and Characterization of Copper Oxide nanowires by Facile Heating under Static Air Condition

Tae-Ha Kwon, Hyek-Hwan Choi and Wan-Young Chung, *Member, KIMICS*

**Abstract**—Large-scaled area and aligned copper oxide nanowires have been synthesized by a vapor-phase approach to the facial synthesis of copper oxide nanowires supported on the surface of a copper gasket. The effects of annealing temperature and time were investigated. Long and aligned nanowires can only be formed within a narrow temperature range from 400 to 500 °C for 4 hrs. Annealing copper gasket in static air produces large-area, uniform, but not well vertically aligned nanowires along the copper gasket surface. The surface of copper gasket is converted into bicrystal CuO nanowires was observed after the copper gasket is annealed under static air condition.

**Index Terms**—nanowire, facial synthesis, CuO, annealing.

## I. INTRODUCTION

Nanostructured materials have received steadily growing interest because of their fascinating properties and various applications as compared to their bulk or micro-sized counterparts. Recently, one-dimensional (1D) nanostructures such as wires, belts, rods, and tubes have become one focus of intensive research as a result of their unique properties and potential usages [1]. Among the various 1D nanostructures, nanosized copper oxides, usually cupric oxide (CuO) and cuprous oxide (Cu<sub>2</sub>O), have attracted much attention due to their interesting applications. Copper oxides have been widely used in many areas such as in heterogeneous catalyst [2], anode electrodes for batteries [3], magnetic storage media [4], and high temperature superconductors [5]. More recently, nanosized copper oxide has been employed to realize nanoenergetic material because of the high energy release when combining with nanoaluminium [6].

Different approaches have been employed to synthesize 1D copper oxide. Xu *et al* manufactured CuO nanorods by thermal decomposition of CuC<sub>2</sub>O<sub>4</sub> precursor [7]. Cu<sub>2</sub>O nanowires were fabricated by reducing copper were fabricated by reducing copper sulfate with hydrazine in a

basic solution [8]. Nanowires containing both Cu<sub>2</sub>O and CuO were formed while Cu<sub>2</sub>S nanowires were heated under oxygen at and above 300 °C [9]. Hsieh *et al* proposed a self-catalytic process for the growth of CuO nanofibre arrays [10]. Chen *et al* realized CuO nanobelts by immersing a copper foil into a water solution composed of NaOH and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> [11]. Compared to the above-mentioned relatively complicated synthesis methods, a simple approach was demonstrated in, where CuO nanowires were prepared by direct heating copper substrates in air [12].

In this study, free-standing copper oxide nanowires grown on copper gasket. It will be interesting to realize aligned copper oxide nanowires that is a basic material for microelectronics and microsystems.

## II. APPARATUS

Different parameters that affect the growth of copper oxide nanowires are studied. The morphology of nanowires are characterized using scanning electron microscopy (SEM). SEM images were obtained FE-SEM (Hitachi S-4300) at an acceleration voltage of 10–20 kV. The wires could be removed from the original copper gasket by rinsing with ethanol, redeposition onto a carbon-coated transmission electron microscopy (TEM) grid, and used for high-resolution TEM (HRTEM). TEM, HRTEM images, selected area of electron diffraction patterns (SAED) were obtained from a JEOL transmission electron microscope (JEM 4010) operated at 400 keV. and X-ray diffraction (XRD) pattern of the products was recorded by employing a Rigaku D/MAX-2500 with CuK $\alpha$  radiation ( $\lambda = 1.54187 \text{ \AA}$ ).

## III. EXPERIMENTS

In a typical procedure, the copper substrate was cleaned for 20 s in a solution composed of 10 ml HCl (37%) and 120 ml DI water, followed by repeated rinsing with distilled water. After it had been dried under a N<sub>2</sub> gas flow, it was placed in an alumina boat (Al-23, Alfa Aesar, MA) and immediately heated to the set-point temperature (at ambient pressure) in a VWR box furnace. We have tested a copper substrate.

Manuscript received December 18, 2009; revised January 7, 2010; accepted January 21, 2010.

Tae-Ha Kwon, Hyek-Hwan Choi, and Wan-Young Chung are with the Department of Electronics, Pukyong National University, Busan, 608-737, Korea (Tel: +82-51-629-6213, Fax: +82-51-629-6210, Email: thkwon@pknu.ac.kr)

#### IV. RESULTS AND DISCUSSION

The surface color of copper gasket was changed as tarnished through heat-treatment at 400 and 500 °C in air for 4 hrs. Further study using another measurement under an optical and electron microscope indicated the formation of 1D-wirelike copper nanostructures over the entire surfaces of gasket at 500 °C for 4 hrs. Figure 1 shows photograph of copper gasket (a) and large-area and uniform nanowires of a copper gasket by SEM images ((b) and (c)) after it had been heated in air at 400 and 500 °C for 4 hrs, respectively. At 400 °C, big grain's particles were synthesized on the surface of copper gasket. Otherwise, all nanowires were mainly grown in the plans to the surface of copper gasket at 500 °C. Because of the surface curvature of this substrate, each wire was grown in the direction essentially perpendicular to the support. The length and diameter of the synthesized nanowires are in the range of 2.5 μm and 40-80 nm, respectively. We further characterized the size, structure, and crystallinity of these nanowires by XRD, TEM, and SAED.

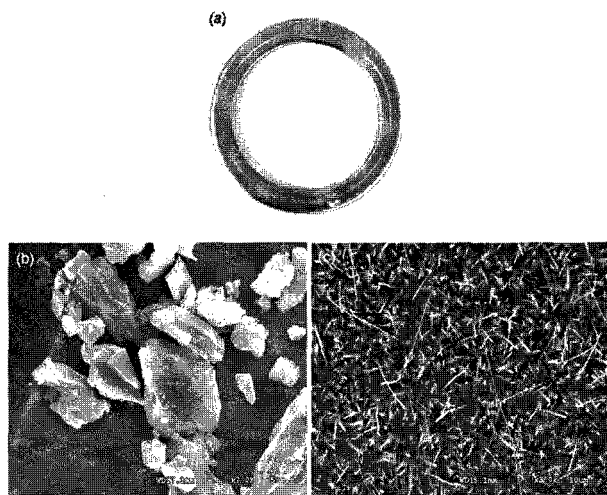


Fig. 1. Photograph of copper gasket (a) and SEM images of different annealed temperature at 400 °C (b) and 500 °C (c), respectively.

Figure 2 shows the XRD pattern of the copper gasket annealed at 400 °C and 500 °C for 4 hrs in static air. As shown XRD pattern, both  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  phases, which are in good agreement with the literature results ( $\text{Cu}_2\text{O}$ ; JCPDS Card 5-0661 and  $\text{CuO}$ ; JCPDS Card 45-0937), are present at different parameters.

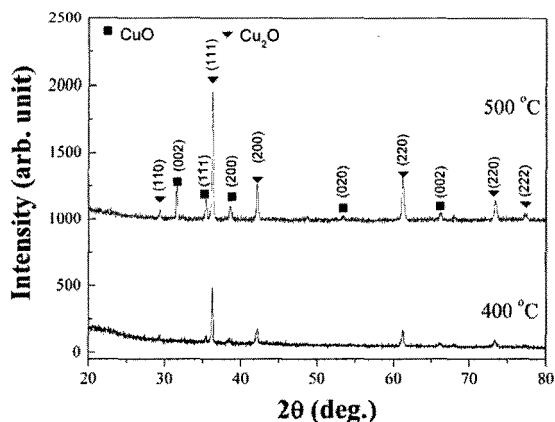


Fig. 2. XRD pattern of a copper gasket after it has been heated at 400 and 500 °C for 4 hrs.

Figure 3 (a) and (b) shows the TEM image of obtained nanowires from heated copper gasket. Some of these wires appeared to be thicker than they should be as a result of overlapping between wires at different levels. Figure 3 (c) displays individual nanowire whose middle is clearly divided by a twin plane along the longitudinal axis. This was confirmed by the bicrystallinity of this nanowire by a high-resolution

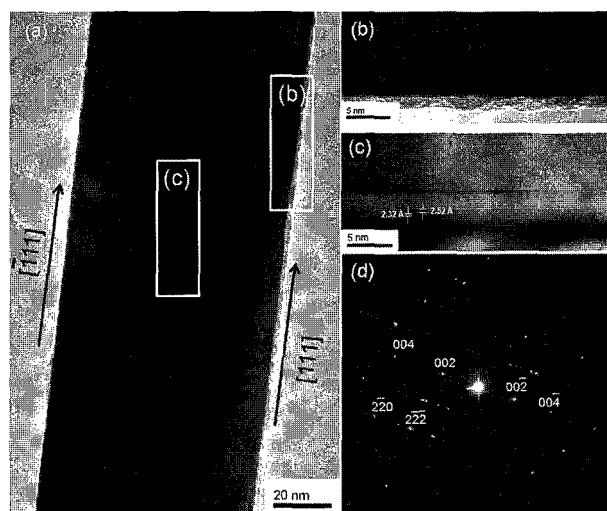
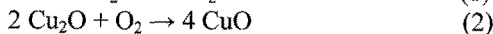
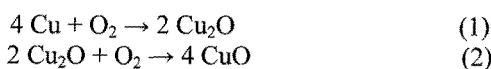


Fig. 3. (a) TEM images of copper oxide nanowires prepared by heating a CG at 500 °C for 4 hrs. (b) High-resolution TEM image showing the one side of a  $\text{CuO}$  nanowire (c) High-resolution TEM image showing the twin boundary of a nanowire. (d) Electron diffraction pattern recorded from an individual  $\text{CuO}$  nanowire. Indices without subscript refer to the upper side of the nanowire shown in (C), and indices with subscript refer to the other side. The electron beam was parallel to the  $[110]$  axis. These results indicated that each  $\text{CuO}$  nanowire was bicrystal: the grown directions were  $[\bar{1}11]$  and  $[111]$ , respectively.

Each side of this wire was, indeed, a single crystal with a well-defined fringe space pattern, and a twin defect could be observed in the middle. The interplanar spacings for each side were 2.52 and 2.32 Å, respectively. There two values corresponded well with the spacing calculated for  $\{\bar{1}11\}$  and  $\{111\}$  planes in monoclinic CuO (cell =  $4.69 \text{ \AA} \times 3.43 \text{ \AA} \times 5.13 \text{ \AA}$ ,  $\beta = 99.55^\circ$ ). Figure 3 (d) shows a diffraction pattern that would be typically observed when the electron beam was focused on an individual nanowire along the  $[110]$  direction. The mirror image relationship between the two sets of diffraction spots confirmed the formation of a bicrystalline structure within each wire. The growth direction for each side of this twinned nanowire could be derived from the diffraction spots as  $[\bar{1}11]$  and  $[111]$ , respectively.

Two mechanisms – vapor liquid solid (VLS) and vapor solid (VS) – have been most commonly used to account for the growth of nanowires in the gas phase. On the basis of our results, the VLS mechanism could be excluded because none of our copper oxide nanowires was terminated in particles. We suggested that the VS mechanism seems to be responsible for the growth of CuO nanowires observed in the present study. We note that this mechanism has recently been explained as the formation of nanowires from a variety of metal oxides. The present procedure for forming cupric oxide nanowires differs from other systems in that a precursor (rather than the direct oxidation of copper). When copper is oxidized in air, the major product is  $\text{Cu}_2\text{O}$  and CuO is formed slowly only through a second step of oxidation. In this case,  $\text{Cu}_2\text{O}$  served as a precursor to CuO. The reaction involved in the entire synthesis can be summarized as the following, with the second one functioning as the rate-determining step for the formation of CuO vapor [12].



The slow rate for the formation of CuO ensures a relatively low vapor pressure for this material in the reaction chamber and thus a continuous growth mode and uniform diameter for the CuO nanowires. On the basis of these arguments, the surface of the copper gasket shown in Figure 1 (c) should be mainly covered by a dense film of  $\text{Cu}_2\text{O}$ , with only small amount of CuO in the form of nanowire. This speculation was confirmed by the XRD pattern shown in Figure 2. The temperature effect could also be understood by taking into account the dependence of the Gibbs free energy of reaction 2 on the temperature. Since the change in free energy ( $\Delta S$ ) for reaction 2 has a negative sign, the change in free energy ( $\Delta G$ ) for this reaction will be from negative to positive when the temperature is sufficient high [12]. At this point, the formation of CuO will be terminated, and thus no nanowires will be observed. On the basis of the standard thermodynamic data from the Handbook [13], this transition temperature was estimated to be around  $964^\circ\text{C}$ .

As the temperature dropped below  $400^\circ\text{C}$ , the formation of CuO became too slow to maintain a sufficiently high vapor pressure for CuO, and thus no nanowire growth would occur on the copper substrate.

## V. CONCLUSIONS

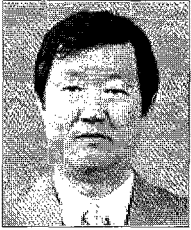
In summary, We have demonstrated a simple and convenient route for the facial synthesis of 1D copper oxide nanostructure (40 nm – 80 nm in diameter) supported on solid copper gasket. TEM, HRTEM, SAED, and XRD results show that these 1D copper oxide nanostructures were bicrystals with a (111) twin plane sitting, each 1D nanostructures could be grown up to 2.5 micrometers in length without branching or entanglement. In addition to their direct use as a heterogeneous catalyst and as a class of semiconducting nanostructures for device fabrication, these nanowires can also serve as templates from which to prepare 1D nanostructures made of copper based materials and also employed to grow other metal oxide nanowires, which can integrate electronic device to lead nanobased functional structures.

## ACKNOWLEDGMENT

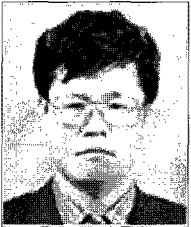
This work was supported by the Pukyong National University Research Abroad Fund in 2008(PS-2008-034).

## REFERENCES

- [1] Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F. Yan, H. *Adv. Mater.* (2003), 15, 353.
- [2] Reitz, J. B.; Solomon, F. I. *J. Am. Chem. Soc.* (1998), 120, 11467.
- [3] Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon J. M. *Nature* (2000), 407, 496.
- [4] Kumar, R. V.; Diamant, Y.; Gedanken, A. *Chem. Mater.* (2000), 12, 2301.
- [5] MacDonald, A. H. *Nature* (2001), 414, 409.
- [6] Subramaniam, S. *Mater. Res. Soc. Symp. Proc.* (2006), 896, 0896-1101-051-6.
- [7] Xu, C. K.; Liu, Y. K.; Xu, G., D.; Wang, G., H. *Mater. Res. Bull.* (2002), 37, 2365.
- [8] Wang, W.; Wang, G.; Wang, X.; Zhan, Y.; Liu, Y.; Zheng, C. *Adv. Mater.* (2002), 14, 67.
- [9] Wang, S.; Huang, Q.; Wen, X.; Li, X.; Yang, S. *Phys. Chem. Chem. Phys.* (2002), 4, 3425.
- [10] Hsieh, C. T.; Chen, J. M.; Lin, H. H.; Shih, H. C. *Appl. Phys. Lett.* (2003), 82, 3316.
- [11] Chen, J.; Deng, S. Z.; Xu, N. S.; Zhang, W. X.; Wen, X. G.; Yang, S. H. *Appl. Phys. Lett.* (2003), 83, 746.
- [12] Xuchuan Jiang, Thurston Herricks, and Younan Xia, *Nano Lett.* 2002, 2, 1333.
- [13] CRC Handbook of Chemistry and Physics, 67th ed; Weast, R. I., Ed.; CRC Press: Boca Raton, FL, 1979.



**Tae-Ha Kwon** received B.S., M.S, and the Ph.D. degrees in electronic Engineering from KyungPook National University in 1975, 1979, and 1986, respectively. His research interests include semiconductor sensors, nano-devices, and RF circuit design.



**Hyek-Hwan Choi** received B.S., degree in electronic engineering from KyungPook National University in 1979, and the M.S. and Ph.D. degree in electronic engineering from Arizona State University, USA, in 1990 and 1993, respectively. His research interests include semiconductor device modeling, digital system design, and VLSI design.



**Wan-Young Chung** received B.S. and M.S. degree in electronic engineering from KyungPook National University in 1987 and 1989, respectively and Ph.D. degree in sensor engineering from Kyushu University, Fukuoka, Japan in 1998. His research interests include silicon sensor and system, ubiquitous healthcare, wireless sensor network and embedded system.