Research Article

The Synthesis of Highly Aligned Cupric Oxide Nanowires by Heating Copper Foil

Jianbo Liang,¹ Naoki Kishi,¹ Tetsuo Soga,¹ and Takashi Jimbo²

¹ Department of Frontier Materials, Nagoya Institute of Technology, Nagoya 4668555, Japan
² Department of Electrical and Electronics Engineering, Nagoya Institute of Technology, Nagoya 4668555, Japan

Correspondence should be addressed to Jianbo Liang, liangjienbo1980@yahoo.co.jp

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We have investigated the effects of grain size and orientation of copper substrates for the growth of cupric oxide nanowires by thermal oxidation method. Long, less-roughness, high-density, and aligned cupric oxide nanowires have been synthesized by heating (200) oriented copper foils with small grain size in air gas. Long and aligned nanowires of diameter around 80 nm can only be formed within a short temperature range from 400 to 700°C. On the other hand, uniform, smooth-surface, and aligned nanowires were not formed in the case of larger crystallite size of copper foils with (111) and (200) orientation. Smaller grain size of copper foil with (200) orientation is favorable for the growth of highly aligned, smooth surface, and larger-diameter nanowires by thermal oxidation method.

1. Introduction

Nanostructured materials have attracted much scientific attention due to their interesting size-dependent chemical and physical properties and potential technological applications. One-dimensional (1D) nanostructures such as nanowires, nanobelts, nanorods, and nanotubes have become the focus of intensive research as a result of their unique properties and potential usages [1]. Nanowires and nanorods of various semiconductor materials including Si, Ge, GaN, ZnO, and so forth, have been the focus of intense studies in the past years. Different approaches, such as vaporliquid-solid [2], vapor-solid [1], and template-mediated [3] growth methods, have been used for the preparation of 1D nanostructures of semiconducting materials.

Cupric oxide (CuO) with a known band gap of 1.2 eV has an interesting monoclinic crystal structure belonging to the Mott insulator material class whose electronic structure cannot be described by conventional band theory [4]. There has been increasing interest in developing 1D nanostructures of CuO for device applications such as gas sensor [5, 6], magnetic storage media [7], catalysts [8–10], and field emitters [11]. During the last couple of years, 1D nanowires, nanorods, nanowhiskers, and nanosheets of CuO have been synthesized by various growth techniques such as thermal decomposition of CuC₂O₄ precursors [12], hydrothermal decomposition route [13], self-catalytic growth processes [14], and so forth. Important factors in synthesizing 1D nanostructure are control of composition, size, and crystallinity. Moreover, from the point of view of studying fundamental properties of nanowires as well as their applications, the method of preparation of the 1D nanostructures should be simple for producing bulk quantities and amenable to control diameter and length. In comparison to complex chemical methods, thermal annealing or thermal oxidation of copper foil is a simple, convenient, and fast method for synthesizing CuO nanowires. This method is becoming an increasingly attractive method for synthesizing nanostructures. Many studies on synthesizing CuO nanowires by thermal annealing of the copper foils in oxygen atmosphere have been reported up to now [15-26]. However, recent studies on CuO nanowires have focused on the influence of growth time, temperature, and oxidative environment on the growth rate, size distribution, and a real density of CuO nanowires [11, 22]. It has been shown that the growth time can be used to control nanowire length distribution [11], the growth temperature can be used to control the nanowire diameter distribution, and the O₂ and H₂O partial pressures strongly affect areal density of nanowires [22]. The surface condition of the copper substrate was also shown to affect growth of nanowires significantly [14, 16]. But, the growth of long, high-density, and aligned cupric oxide nanowires has rarely been reported in the literature. It is due to the fact that the effects of copper substrates on the structure of cupric oxide nanowires have not studied until now. According to previous investigations, it seems very difficult to grow uniform and aligned vertical cupric oxide nanowires from pure metal thin films just by thermal oxidation, and very few approaches have been reported about this matter. In this study, we report a simple process for growing high-density, uniform, and vertically aligned cupric oxide nanowires by thermal oxidation. We have investigated the effects of the grain size, orientation of grains, and surface roughness of substrates for the growth of cupric oxide nanowires.

2. Experimental Procedure

In order to investigate the effect of grain size and orientation of copper substrates for cupric oxide nanowire formation during thermal oxidation, four copper foils (purchased from Nilaco Co. Ltd.) were used as substrates. Foils were cut into standard sizes of $1 \text{ cm} \times 1 \text{ cm}$. The substrates were washed by dilute hydrochloric acid to remove the native oxide layer and adsorbed impurities followed by cleaning with acetone, methanol, and deionized water under an ultrasonic bath for 5 min and, finally, dried by N₂ flow. The cleaned samples were placed in a quartz boat. The quartz boat was positioned in the center of a quartz tube, and the quartz tube was mounted in the middle of a horizontal tube furnace. The air humidity is unstable in ambient air; it may be affect the growth of nanowires, so we use stability cylinder air. The cylinder air was firstly introduced into the quartz tube at a flow rate of 1 L/min for 20 min to remove the ambient air from the system, and then it was adjusted to 0.5 L/min for oxidation of copper foils. The tube furnace was heated to the set-point temperature (300, 400, 500, and 600°C at atmospheric pressure). After reaching the set-point temperature, the air gas flow was stopped and the N2 gas flow was employed at a rate of 1 L/min. The film was allowed to cool naturally to room temperature to prevent the thin film from cracking by thermal stress and further oxidation by atmospheric air (arise due to rapid cooling). The substrate was pulled out of the furnace for further analysis.

The crystal structure and phase composition were identified by X-ray diffraction (XRD, Rigaku RINT-2100) using a 40 kV, 30 mA, Cu-K α X-ray. A scanning step of degree of 0.02° was applied to record the XRD patterns in the 2 θ range of degree of 40–55°. The morphology of the CuO nanowires were characterized by scanning electron microscope (SEM, Hitachi S-3000H) operated at 15 kV. Transmission electron microscopy (TEM) and electron diffraction observation were carried out using a JEOL JEM-4000 EXII.

3. Results

3.1. Effect of Crystallite Size. In order to know the crystal structure and the corresponding grain size of copper foils,

X-ray diffraction was performed immediately after cleaning the substrate. There were a set of Bragg peaks in the XRD that could readily be indexed to the *fcc* structure of metal copper (Fm $\overline{3}$ m, a = 3.615 Å, JCPDF no. 85-1326) (Figure 1). The diffraction profiles of the copper foil A, C and B, D show very distinctive features. In Figure 1 there are two peaks on the copper foil A and C at $2\theta = 50.50^{\circ}$ and $2\theta = 43.36^{\circ}$ corresponding to (200) plane and (111) plane of copper structures. Compared with the XRD pattern of the copper foil A and C, only the peak at $2\theta = 50.50^{\circ}$ corresponding to (200) reflection of the crystals in the sample B and D appeared. Such a feature indicates that copper crystals in the sample B and D are predominantly oriented with their a-axes perpendicular to the support surface. The average grain size can be calculated using the Scherrer equation [22]:

$$D = \frac{0.9\lambda}{W\cos\theta},\tag{1}$$

where λ is the X-ray wavelength, θ is the Bragg diffraction angle, and W is the full width at half maximum (FWHM) of the peak corresponding to θ . When calculated by using the peak corresponding to the (200) plane of copper, the resultant grain size in copper foil A is about 72.2 nm, in copper foil B is about 35.6 nm, in copper foil C is about 64.5 nm, and in copper foil D are about 34.3 nm. The size of the grain in the copper foil A and C is about two times larger than that in the copper B and D. So the number of grain in the copper foil B and D is larger than that in the copper A and C. The properties of copper foil A, B, C, and D are summarized in Table 1.

3.2. Effect of Oxidizing Temperature. Figure 2 shows SEM images of surface morphologies after heating the copper foil A, B, C, and D at 300°C for 2 h in an air gas flow of 0.5 L/min., respectively. As can be seen, oxide grains are observed on four substrates. Oxide grains on copper A and C are less compact than the others on the copper B and D. The measured oxide grain size on copper A and C are about 250 and 300 nm. The grains on the copper foil B and D are denser, and the size is about 160 and 170 nm, without nanowires on the surface of the specimen. The oxide grains become larger as temperature increases. The oxide grains formed on copper foil B and D (smaller grain size) are much smaller than those formed on copper foil A and C (larger grain size) at the early stage of oxidation. It is due to a large number of nucleation sites on the smaller grain size of copper foils. From the morphology of the samples grown at 400°C (Figure 3), it is observed that nanowires formed at this temperature. Highdensity, more uniform, and longer nanowires are formed on copper foil B and D compared with copper foil A and C. As the temperature was increased to 500°C, a large amount of nanowires formed on the copper B and D (Figures 4(B) and 4(D)). It can be seen that long and uniform nanowires are formed on the entire surface, and nanowires are mostly vertical along the substrate surface. The average diameters of nanowires on copper foil B and D are about 80 and 100 nm, and average length of nanowires on the same substrates are about 7 and 8 μ m, respectively. Nevertheless, large-area



FIGURE 1: XRD patterns of (A) copper foil A, (B) copper foil B, (C) copper foil C, and (D) copper foil D.

and high density CuO nanowires can also grow from the copper A and C substrates under an air gas flow as shown in Figures 4(A) and 4(C). The as-prepared nanowires on the copper foil A and C were not well vertically aligned along the substrate surface with the lengths of about 4 and $5\,\mu m$ and the diameter of about 50 and 62 nm. It is desirable to grow large-area, uniform, and vertically aligned CuO nanowires along the copper substrate surface for the applications in field emission emitters [23] and realization of nanosized CuO/Albased energetic materials [24]. At 600°C, a high-density and uniform nanowires formed on copper foil B and D as shown in Figures 5(B) and 5(D). However, these nanowires are longer than those nanowires on copper foil A and C, with the length ranging from 5 to $15\,\mu$ m and the diameter about 180 nm as shown in Figure 5. A large amount of nanowires of low density were observed on copper foil A and C prepared at 600° C with the length of 3 to 6 μ m and the diameter from 100 to 400 nm. We can conclude that the grain size and crystal orientation of copper foil have a great effect on the growth of nanowires. The smaller grain size with (200) oriented copper foil is favourable for the growth of nanowires.

TABLE 1: Properties of four copper foils. The grain size and orientation of copper foils were characterized by XRD measurement.

	Grain size (nm)	Orientation of copper foils
Copper foil A	72.2	(111) and (200) orientation
Copper foil B	35.6	(200) orientation
Copper foil C	64.5	(111) and (200) orientation
Copper foil D	34.3	(200) orientation

3.3. Cross-Sectional Characterization of CuO Nanowire Samples. Figure 6 shows the SEM images of the cross sections of oxidized the copper foil A and B at 500° C for 2 h. In order to measure the oxide layer thickness, an oxide flake was carefully removed from a copper substrate. When copper foil is oxidized, at first the major product is Cu₂O, and it is expected that CuO is formed through a second step of oxidation of Cu₂O [15, 27]. In this case, Cu₂O serves as a precursor to CuO. The outmost layer is always of CuO if the oxide consists of both Cu₂O and CuO. In this bilayer



FIGURE 2: SEM images of copper foil (A) A, (B) B, (C) C, and (D) oxidized at 300°C for 2 h in an air gas flow of 0.5 L/min.

oxide, fractional thickness of outmost layer mainly depends on annealing temperature. In the Figure 6(A), the oxide layer is divided into the bottom layer of Cu₂O and the outermost layer of CuO [28]. By EDX measurement, the CuO layer was found about 0.9 μ m thick and Cu₂O layer about 4.2 μ m for copper foil A. For copper foil B, the outermost CuO layer is thicker than that of foil A which is about $1.8\,\mu\text{m}$ thick (Figure 6(B)). The bottom Cu₂O layer is evidently thicker (about 5.8 μ m). The total thickness of the layer on the copper substrate B is about 7.6 μ m, which is thicker than that of copper foil A (about 5.1 μ m). The thicker oxide layer on the copper foil B is due to the higher oxidation rate. In principle, the copper ions and oxygen ions can diffuse across the scales much faster along the grain boundaries than through the bulk. The high oxidation rate of copper foil B would be due to the smaller grain size, resulting in faster overall rates of scale growth.

3.4. TEM Characterization of CuO Nanowires. We further characterized the size, structure, and crystal of these nanowires using TEM and selected area diffraction (SAD) pattern. The selected sample was prepared at 500°C for 2 h. Figures 7 and 8 display TEM diffraction patterns of an individual nanowire of the copper foil A and B oxidized at 500°C for 2 h. In Figure 8(A), it is observed that the nanowire of the copper foil B has wire-like shape of very smooth surface with the diameter of about 70 nm. In comparison with the nanowires of foil B, the surface of nanowire of copper foil A has roughness and diameter of about 45 nm (Figure 7(A)). Larger diameter of nanowire (in Figure 8(A)) is observed for copper foil B compared to Cu foil A (Figure 7(A)), which may be due to larger number of grain boundaries of the copper foil B. Figure 7(B) shows a TEM diffraction pattern of an individual nanowire from copper foil A. It would be typically observed when the electron beam was focused on an individual nanowire along the [001] direction. The double diffraction is due to the twin plane within a nanowire. Figure 8(B) also shows a TEM diffraction pattern of an individual nanowire from copper foil B prepared at 500°C. Similarly, the double diffraction is caused by the twin plane within the nanowire, each set diffraction spot is a single crystal and corresponds to monoclinic structure of CuO with the lattice constants, a = 0.469 nm, b = 0.343 nm, c = 0.513 nm, and $\beta = 99.55^{\circ}$.

4. Discussion

The formation of nanowires occurs when two layers of copper oxides are gradually formed by oxidation of copper [15, 26–28]. We examine our results based on mechanisms of nanowire growth reported in the literature. Goņalves et al. suggested that CuO nanowires growth occurs via grain boundary diffusion of copper ions through the Cu₂O layer and the oxygen ions through the outmost CuO layer [25]. Xu et al. also suggested that nanowire growth is via grain boundary diffusion [26]. This idea shares similarities with the model proposed recently for Fe₂O₃ nanowire formation [29]. However, Park et al. and Shao et al. reported that the mechanism of nanowires growing in this case is due to the relaxation of compressive stress [27, 28]. Here, we



FIGURE 3: SEM images of copper foil (A) A, (B) B, (C) C, and (D) oxidized at 400°C for 2 h in an air gas flow of 0.5 L/min.

believe that the growth of nanowire occurs to reduce the stress generated during oxidation of copper by the grain boundary diffusion process [20]. Now, we shall discuss how the proposed model can be explained by our obtained results. Long, high-density and aligned cupric oxide nanowires observed in Figures 3, 4, 5(B), and 5(D) can be attributed to grain boundary and the crystal direction with the effective relaxation of compressive stress. It is well known that the initial oxidation rate of a metal at intermediate temperatures (300–600°C for copper) is too rapid to be attributed solely to lattice diffusion of the various ionic species in its oxide film [30]. The oxidation of copper at low temperatures is dominated by grain boundaries. The smaller grain size and the higher grain boundary energy can play an important role in increasing the effective diffusion coefficient of copper ions and oxygen in smaller crystallite size at intermediate temperatures as a result of grain boundary diffusion [31]. Oxidization of Cu foil to Cu₂O and Cu₂O to CuO leads to a compressive stress on the interface due to volume and structural change. The compressive stress drives outward diffusion of copper cations along grain boundaries, resulting in CuO nanowire growth on CuO grains [27]. Therefore, a high density of nanowires is observed in Figures 3, 4, 5(B), and 5(D) compared to Figures 3, 4, 5(A), and 5(C) as the large numbers of grain boundaries increase the relaxation of the compressive stresses at the CuO and Cu₂O layer interface. The oriented direction is favorable to the diffusion of copper cations along grain boundaries in the copper film. It may affect the surface of nanowire. The TEM images presented in Figure 8 indicate a large diameter of nanowire

and smooth-surface nanowire formed on copper foil B. This is also attributed to the relaxation of compressive stress by effective grain boundary diffusion. Depending on the oxidation temperature, the diffusion of the atoms or ions may take place within the lattice, through grain boundaries in the oxide layer. As a result nanowire density decreases as temperature increases, as seen in the sequence of SEM images of Figure 5. The oxide grains become larger as temperature increases in our experiment. Although we have tried to raise the heating temperature to 800°C, large oxide grains are observed, but no nanowires appeared on the surface of substrate. When the temperature is higher than 800°C, copper oxidation is dominated by lattice diffusion of copper ions; the influence of grain boundary diffusion would finally become small compared to lattice diffusion. This explains the absence of nanowires for oxidations at 800°C. The relative importance of grain boundary transport through a scale depends on the grain size of the oxide and on temperature and tends to become negligible at sufficiently high temperatures [32]. By heating the copper foil with the smaller grain size with (200) oriented in an air gas flow, the large numbers of grain boundaries are favorable to the relaxation of compress stress, resulting in the growth of highdensity and smooth-surface nanowires.

5. Conclusion

High-density, smooth-surface, and aligned cupric oxide nanowires have been synthesized by heating copper foils



FIGURE 4: SEM images of copper foil (A) A, (B) B, (C) C, and (D) oxidized at 500°C for 2 h in an air gas flow of 0.5 L/min.





FIGURE 5: SEM images of copper foil (A) A, (B) B, (C) C, and (D) oxidized at 600°C for 2 h in an air gas flow of 0.5 L/min.

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FIGURE 6: SEM images of the cross section of nanowires on (A) the copper foil A and (B) B. The nanowires were synthesized at 500°C for 2 h.



FIGURE 7: (A) TEM images and (B) SAD pattern of a single CuO nanowire of copper foil A prepared at 500° C for 2 h in air gas flow of 0.5 L/min.

FIGURE 8: (A) TEM images and (B) SAD pattern of a single CuO nanowire of copper foil B prepared at 500° C for 2 h in air gas flow of 0.5 L/min.

with the smaller grain size and (200) oriented in an air gas flow. On the other hand, uniform, smooth-surface, and aligned nanowires cannot be obtained by heating copper foils with the larger grain size and two crystal orientations. The difference is attributed to the faster relaxation of compress stress by outward diffusion of copper ions and inward diffusion of oxygen along the grain boundaries (both in the metal and in the layer for the smaller grain size of copper substrate). The small grain size of the copper foil B and C is favorable to the growth of nanowires due to the larger number of grain boundaries. Aligned cupric oxide and smooth-surface nanowires could be produced by heating the (200) oriented copper foil.

References

- Y. Xia, P. Yang, Y. Sun et al., "One-dimensional nanostructures: synthesis, characterization, and applications," *Advanced Materials*, vol. 15, no. 5, pp. 353–389, 2003.
- [2] R. S. Wagner and W. C. Ellis, "Vapor-liquid-solid mechanism of single crystal growth," *Applied Physics Letters*, vol. 4, no. 5, pp. 89–90, 1964.

- [3] K. S. Shankar and A. K. Raychaudhuri, "Fabrication of nanowires of multicomponent oxides: review of recent advances," *Materials Science and Engineering C*, vol. 25, no. 5-8, pp. 738–751, 2005.
- [4] P. A. Cox, Transition Metal Oxides: An Introduction to Their Electronic Structure and Properties, Oxford University Press, New York, NY, USA, 1992.
- [5] A. Cruccolini, R. Narducci, and R. Palombari, "Gas adsorption effects on surface conductivity of nonstoichiometric CuO," *Sensors and Actuators, B*, vol. 98, no. 2-3, pp. 227–232, 2004.
- [6] V. R. Katti, A. K. Debnath, K. P. Muthe et al., "Mechanism of drifts in H2S sensing properties of SnO₂:CuO composite thin film sensors prepared by thermal evaporation," *Sensors* and Actuators, B, vol. 98, no. 1-2, pp. 245–252, 2003.
- [7] H. Fan, L. Yang, W. Hua et al., "Controlled synthesis of monodispersed CuO nanocrystals," *Nanotechnology*, vol. 15, no. 1, pp. 37–42, 2004.
- [8] A. Santos, P. Yustos, A. Quintanilla, G. Ruiz, and F. Garcia-Ochoa, "Study of the copper leaching in the wet oxidation of phenol with CuO-based catalysts: causes and effects," *Applied Catalysis B*, vol. 61, no. 3-4, pp. 323–333, 2005.
- [9] A. A. Ponce and K. J. Klabunde, "Chemical and catalytic activity of copper nanoparticles prepared via metal vapor

- [10] G. Larsen and S. Noriega, "Dendrimer-mediated formation of Cu-CuOx nanoparticles on silica and their physical and catalytic characterization," *Applied Catalysis A*, vol. 278, no. 1, pp. 73–81, 2004.
- [11] C. T. Hsieh, J. M. Chen, H. H. Lin, and H. C. Shih, "Field emission from various Cuo nanostructures," *Applied Physics Letters*, vol. 83, no. 16, pp. 3383–3385, 2003.
- [12] F. Lanza, R. Feduzi, and J. Fuger, "Effects of lithium oxide on the electrical properties of CuO at low temperatures," *Journal* of Materials Research, vol. 5, no. 8, pp. 1739–1744, 1990.
- [13] D. Chen, G. Shen, K. Tang, and Y. Qian, "Large-scale synthesis of CuO shuttle-like crystals via a convenient hydrothermal decomposition route," *Journal of Crystal Growth*, vol. 254, no. 1-2, pp. 225–228, 2003.
- [14] C. T. Hsieh, J. M. Chen, H. H. Lin, and H. C. Shih, "Synthesis of well-ordered CuO nanofibers by a self-catalytic growth mechanism," *Applied Physics Letters*, vol. 82, no. 19, pp. 3316– 3318, 2003.
- [15] J. Liang, N. Kishi, T. Soga, and T. Jimbo, "Cross-sectional characterization of cupric oxide nanowires grown by thermal oxidation of copper foils," *Applied Surface Science*, vol. 257, no. 1, pp. 62–66, 2010.
- [16] K. Zhang, C. Rossi, C. Tenailleau, P. Alphonse, and J.-Y. Chane-Ching, "Synthesis of large-area and aligned copper oxide nanowires from copper thin film on silicon substrate," *Nanotechnology*, vol. 18, no. 27, article 275607, 2007.
- [17] R. C. Wang and C. H. Li, "Improved morphologies and enhanced field emissions of CuO nanoneedle arrays by heating zno coated copper foils improved morphologies and enhanced field emissions of CuO nanoneedle arrays by heating ZnO coated copper foils," *Crystal Growth and Design*, vol. 9, no. 5, pp. 2229–2234, 2009.
- [18] K. Zhang, Y. Yang, E. Y.B. Pun, and R. Shen, "Local and CMOS-compatible synthesis of CuO nanowires on a suspended microheater on a silicon substrate," *Nanotechnology*, vol. 21, no. 23, p. 7, 2010.
- [19] J. Chen, B. J. Hansen, and G. Lu, "Direct oxidation growth of CuO nanowires from copper-containing substrates," *Journal* of Nanomaterials, vol. 2008, no. 1, Article ID 830474, 7 pages, 2008.
- [20] A. M.B. Gonalves, L. C. Campos, A. S. Ferlauto, and R. G. Lacerda, "On the growth and electrical characterization of CuO nanowires by thermal oxidation," *Journal of Applied Physics*, vol. 106, no. 3, article 34303, 5 pages, 2009.
- [21] X. Jiang, T. Herricks, and Y. Xia, "CuO Nanowires Can Be Synthesized by Heating Copper Substrates in Air," *Nano Letters*, vol. 2, no. 12, pp. 1333–1338, 2002.
- [22] C. H. Xu, C. H. Woo, and S. Q. Shi, "The effects of oxidative environments on the synthesis of CuO nanowires on Cu substrates," *Superlattices and Microstructures*, vol. 36, no. 1–3, pp. 31–38, 2004.
- [23] C. T. Hsieh, J. M. Chen, H. H. Lin, and H. C. Shih, "Field emission from various Cuo nanostructures," *Applied Physics Letters*, vol. 83, no. 16, pp. 3383–3385, 2003.
- [24] C. Rossi, K. Zhang, D. Esteve et al., "Nano energetic materials for MEMS: a review IEEE/ASME," *Journal of Microelectromechanical Systems*, vol. 16, no. 4, pp. 919–931, 2007.
- [25] A. M. B. Goņalves, L. C. Campos, A. S. Ferlauto, and R. G. Lacerda, "On the growth and electrical characterization of CuO nanowires by thermal oxidation," *Journal of Applied Physics*, vol. 106, no. 3, Article ID 034303, 2009.

- [26] C. H. Xu, C. H. Woo, and S. Q. Shi, "Formation of CuO nanowires on Cu foil," *Chemical Physics Letters*, vol. 399, no. 1–3, pp. 62–66, 2004.
- [27] Y. W. Park, N. J. Seong, H. J. Jung, A. Chanda, and S. G. Yoon, "Growth mechanism of the copper oxide nanowires from copper thin films deposited on CuO-buffered silicon substrate," *Journal of the Electrochemical Society*, vol. 157, no. 6, pp. K119–K124, 2010.
- [28] P. Shao, S. Deng, J. Chen, and N. Xu, "Large-scale fabrication of ordered arrays of microcontainers and the restraint effect on growth of CuO nanowires," *Nanoscale Research Letters*, vol. 6, no. 86, pp. 1–4, 2011.
- [29] A. G. Nasibulin, S. Rackauskas, H. Jiang et al., "Simple and rapid synthesis of α-Fe2O3 nanowires under ambient conditions," *Nano Research*, vol. 2, no. 5, pp. 373–379, 2009.
- [30] J. M. Perrow, W. W. Smeltzer, and J. D. Embury, "The role of structural defects in the growth of nickel oxide films," *Acta Metallurgica*, vol. 16, no. 10, pp. 1209–1218, 1968.
- [31] Z. Han, L. Lu, H. W. Zhang, Z. Q. Yang, F. H. Wang, and K. Lu, "Comparison of the oxidation behavior of nanocrystalline and coarse-grain copper," *Oxidation of Metals*, vol. 63, no. 5-6, pp. 261–275, 2005.
- [32] Y. Niu, F. Gesmundo, G. Farnè, Y. S. Li, P. Matteazzi, and G. Randi, "The air oxidation of a nanocrystalline Cu-10 we%Ni alloy at 800°C," *Corrosion Science*, vol. 42, no. 10, pp. 1763–1777, 2000.