Available online at www.sciencedirect.com
SciVerse ScienceDirect
Scripta Materialia 66 (2012) 81–84
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Stress-induced growth of well-aligned Cu_2O nanowire arrays and their photovoltaic effect

Yumei Yue, Mingji Chen, Yang Ju* and Lan Zhang

Department of Mechanical Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Received 15 July 2011; revised 29 September 2011; accepted 29 September 2011
Available online 6 October 2011

A well-aligned Cu_2O nanowire array was fabricated by the stress-induced method. A new stress-redistribution phenomenon related to the cooling procedure was observed and a creative growth procedure was demonstrated. High-quality Cu_2O nanowires with an aspect ratio up to 300 and a growth density higher than 10^9 cm^{-2} can be derived under the optimum condition of cooling gradually for 4 h after heating for 5 h. A typical photovoltaic effect was demonstrated to exist in the Cu_2O/Cu junction.

Keywords: Nanostructure; Whiskers; Thin films; Diffusion; Stress-induced growth

Cuprous oxide (Cu_2O) and cupric oxide (CuO) nanowires are known to have many interesting physical properties and extensive applications [1,2]. Compared with traditional semiconductor materials, such as Si and GaAs, copper oxide is more plentiful and low-cost with low toxicity and good environmental acceptability. Thus, the synthesis and applications of Cu_2O and CuO nanowires are of particular interest for researchers.

The most common method to fabricate Cu_2O and CuO nanowires is the template-based synthesis in solution [3,4]. Although these template-based methods are effective in preparing nanowires with controllable diameters, they usually lead to complicated processes and the yield depends heavily on the density of channels. Reduction and dehydration of $Cu(OH)_2$ nuclei formed in solutions can also give birth to Cu_2O [1,5,6] and CuO [7] nanowires, respectively. However, the as-obtained copper oxide nanowires are always polycrystalline ones chaotically distributed in the solution.

A thermal annealing method for synthesis of CuO nanowires was proposed by Jiang et al. in 2002 [8]. This method takes advantage of a simple procedure and high-yield performance, and the as-obtained CuO nanowires are of orderly distribution, high quality and fine crystal structures such as bicrystal [8] and single crystal [9,10]. As a result, it has become one of the most popular methods for fabricating CuO nanowires [11–14]. However, to the best of our knowledge, synthesis of Cu_2O nanowires by the high-yield thermal annealing method has not yet been reported.

Recently, the growth of nanowires from electron beam (EB) evaporated Cu thin films on the SiO_2/Si substrate at 340 °C or even lower temperatures was reported, where the products were described as Cu nanowhiskers though no detailed investigation of their morphology and microstructures was performed [15]. Keeping the relatively low growth temperature in mind, we demonstrate in this paper the on-chip growth of Cu_2O nanowires by the thermal stress-induced method, with the emphasis on the effect of cooling procedure. Nanowires obtained under the optimum heating and cooling conditions can reach up to 10 μm long, about six times longer than those reported in Ref. [15].

The samples from which the Cu_2O nanowires grew were fabricated as follows. A Ta layer of 60 nm in thickness was deposited on a 280 μm thick Si [1 0 0] substrate covered with a thin SiO_2 layer by the EB evaporation technique. This Ta layer can enhance the adhesion between the SiO_2 layer and the subsequently deposited Cu film and prevent the diffusion of Cu atoms into other layers. A Cu film was then deposited on the Ta layer by EB evaporation to form the Cu/Ta/SiO_2/Si multilayer sample. The typical thickness of the Cu film is ~400 nm.

In order to produce thermal stress in the Cu film which is needed for stress-induced growth of nanowires, the sample was heated on a ceramic heater in air. The room temperature was kept at 25 °C. By controlling the voltage

---

* Corresponding author. E-mail: ju@mech.nagoya-u.ac.jp

1359-6462/$ - see front matter © 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.scriptamat.2011.09.041

of the power supply, the heating temperature can be adjusted to the required value. A large heating rate of ~63 °C $\min^{-1}$ was adopted in our experiment, by which the constant temperature of 340 °C was achieved 5 min after turning on the power of the heater. After being heated for 4–9 h at 340 °C, the samples were cooled in air either directly or gradually for 3, 4 or 5 h, respectively, to investigate the effect of cooling procedure on nanowire growth. In the gradual cooling process, the voltage of the power supply was decreased step by step to produce the gradually reduced temperature during a certain period. The temperature profile during the 5 h heating and cooling (either directly or gradually for 4 h) process is shown in Figure 1a. The cooling rate during the 4 h cooling process is 1.31 °C $\min^{-1}$.

The macroscopic stress over the whole Cu film during the heating and gradual cooling process was measured by means of a wafer curvature system using interference between two laser paths split from the same laser beam ($\lambda = 632.8$ nm). The stress can be derived from the measured curvature using Stoney's formula.

The samples with nanowire arrays were observed by field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDXS) and X-ray diffraction (XRD). Then, the fabricated nanowires were dispersed onto a Cu grid and observed by the transmission electron microscopy (TEM), selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) to examine their microstructure and composition.

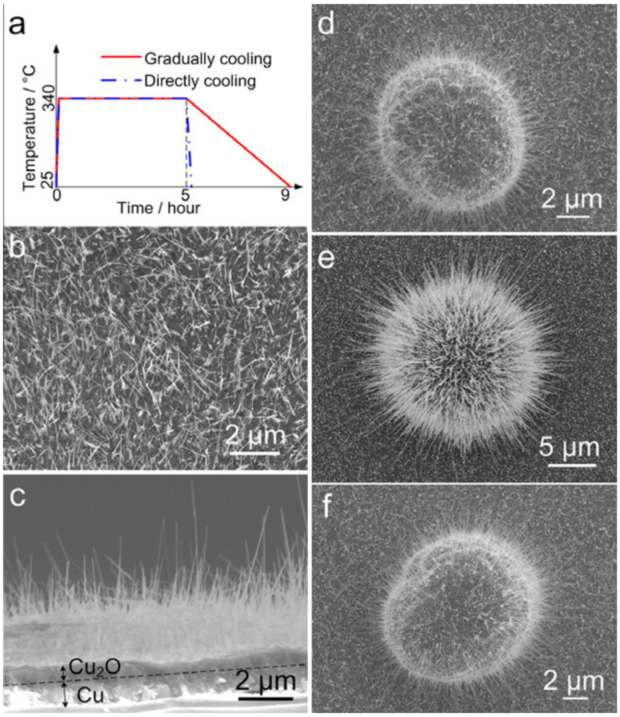

Figure 1. Growth of nanowires: (a) temperature profile during the 5 h heating and cooling (either directly or gradually for 4 h) process, (b) nanowires growing on the substrate in the experiment with direct cooling process, (c) side view of (b), (d)–(f) nanowires growing on hillocks during the gradual cooling process lasting for (d) 3 h, (e) 4 h and (f) 5 h, respectively.

The samples for the photovoltaic effect investigation were prepared as follows. First, a wire was connected to the top surface of the Cu/Ta/SiO_2/Si sample by the high-temperature conductive adhesive (Pyro-Duct 597A, Oludec Ltd.), immediately after the EB evaporation process. Then the sample endured a heating and gradual cooling treatment as shown in Figure 1a, and the on-chip Cu_2O/Cu multilayer structure with hillocks and Cu_2O nanowires formed. Another wire was then connected to the surface of the Cu_2O layer by the conductive adhesive.

After being heated at 340 °C for 4–9 h and cooled directly, the sample was observed to be covered with dense nanowires, as shown in Figure 1b. Figure 1c shows the side view of nanowires growing on the substrate. The average length of these nanowires is ~2 μm and their growth density is ~10^9 cm^{-2}.

For the samples that underwent the gradual cooling process, some randomly distributed hillocks with much longer nanowires on them were observed, as shown in Figure 1d–f. This phenomenon did not appear for samples under direct cooling, even though these samples were heated for 9 h and cooled directly. FE-SEM analysis showed that the nanowires growing on the hillocks were 10–50 nm in diameter. For samples treated by the optimum heating and cooling procedure (Fig. 1e), nanowires growing on the hillocks can reach up to 10 μm long, nearly five times longer than those growing on the substrate. The largest aspect ratio was not less than 300 and the growth density was even higher than 10^9 cm^{-2}. This phenomenon has not been reported elsewhere, and it provides a positive view for the fabrication of on-chip copper oxide nanowires with much higher aspect ratio.

The different growth mechanism of the nanowires on the substrate and the hillocks is discussed as follows.

When the as-fabricated multilayer sample was placed in air at room temperature, the surface of the Cu film was oxidized, forming a thin layer of Cu_2O. During the heating process, all layers experienced thermal expansion. Since the thermal expansion coefficients of different layers are quite different ($2.6 \times 10^{-6}\ K^{-1}$ for Si and $16.5 \times 10^{-6}\ K^{-1}$ for Cu at 25 °C), circumferential tensile or compressive stresses occurred in all the layers to keep the deformation compatibility of the whole sample. Therefore, macroscopic compressive stresses were generated in the Cu layer, as shown in Figure 2a and d. In the early stage of the heating process, the surface diffusion of Cu atoms near the Cu_2O/Cu interface was caused by the stress concentrations which occurred at the grain boundaries due to material singularities. When the diffusion rate was high enough and the accumulation of Cu atoms at the Cu_2O/Cu interface attained a critical value, the accumulated Cu atoms started to penetrate the Cu_2O layer via any weak spots, after which the nanowires were nucleated, as shown in Figure 2b. The growth of nanowires relieved parts of compressive stresses near the Cu_2O/Cu interface and the stress gradient between the top (Cu_2O side) and bottom (Si side) faces of the Cu film was generated.

During the cooling process, the stresses induced in the sample due to the thermal expansion tended to disappear and the sample tended to recover to the state

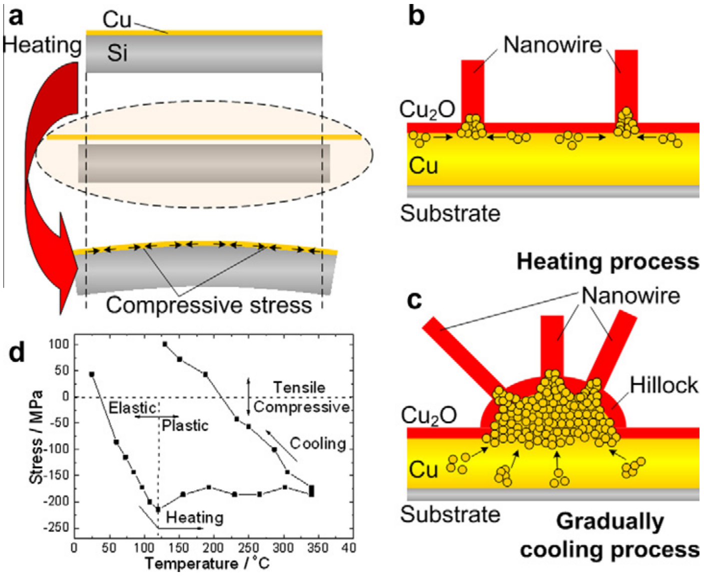

Figure 2. Schematics and supporting data for the growth of nanowires: (a) the compressive stresses generated in the Cu film by heating, (b) growth of nanowires on the substrate, (c) growth of hillocks and nanowires on them, (d) the macroscopic stresses over the whole Cu film measured by laser interference during the heating and gradual cooling process.

before it was heated, as shown in Figure 2d. However, since the growth of nanowires had relieved a lot of the compression stresses in the Cu film from the Cu_2O/Cu interface, a local tensile stress was generated in the Cu film near the Cu_2O/Cu interface in the contraction process of the Cu film. Consequently, a larger stress gradient was formed between the top and bottom faces of the Cu film, which might further increase the diffusion rate of Cu atoms moving from the bottom to top faces of the Cu film.

During the gradual cooling process, which lasted for a long time, a huge diffusion of Cu atoms was realized and the hillocks were formed, as shown in Figure 2c. When the growth rate of hillocks was too high, which corresponded to a relatively high cooling rate, the formation of surface oxide layers cannot catch up with the growth of hillocks, and thereby little nanowires grew on the hillocks, as shown in Figure 1d. When the cooling rate was too low, the stress gradient might not be large enough for the rapid diffusion of Cu atoms and the growth of hillocks cannot match with the formation of thick surface oxide layer, thereby, fewer nanowires were obtained (Fig. 1f). Only when the gradual cooling was held in a proper rate, can dense and long nanowires grow on the hillocks, as shown in Figure 1e. This stress-redistribution phenomenon, which can promote the growth of Cu_2O nanowires, has not been reported elsewhere. After many experiments, the optimum growth condition of heating for 5 h and cooling gradually for 4 h was proposed. On the other hand, when the sample was cooled directly, more cracks instead of hillocks were formed on the sample surface due to the extremely high cooling rate.

Figure 3a shows the TEM image of an individual nanowire with the smooth surface and the uniform diameter along the axis. From the SAED pattern taken from a random assembly of the nanowires, as shown in Figure 3b, the compositions can be deduced to be Cu_2O and CuO, of which the former is the main composition. Figure 3c shows the HRTEM image of a single-crystal area with clear lattice fringes. The lattice fringe spacing is ~0.30 nm, which corresponds to the {1 1 0} plane of Cu_2O crystal. As shown in Figure 3d, the EDXS spectrum from the surface of a hillock indicates that the main chemical elements are Cu and O, the percentages of which are 67.3% and 32.4% (nearly 2:1), respectively. This result is in accordance with the SAED pattern that the composition of the as-obtained nanowire is mainly Cu_2O. XRD analysis on the surface of a sample that had undergone gradual cooling also shows that the main composition of the sample surface and nanowires covering on it is Cu_2O (Fig. 3e). It should be noted that since Cu_2O is a metastable phase, some of the nanowires growing on the substrate which experienced the annealing process at 340 °C may be further oxidized to be CuO. This is the reason why some CuO was observed in Figure 3b and e. However, since the nanowires growing on hillocks are generated during the cooling process at relatively low temperatures, they can hold the metastable phase of Cu_2O.

Cu_2O is a typical semiconductor, predicted to be promising for photovoltaic applications [16]. The Schottky barrier forming on the Cu_2O/Cu interface can play a similar role as the p–n junction to generate the photovoltaic effect [17]. Thus, to further verify the composition of the as-obtained nanowires, the photovoltaic effect of the multilayer sample with nanowires was investigated.

The rectifying behavior in the dark current curve indicates that a Schottky barrier is formed on the Cu_2O/Cu interface, as shown in the inset of Figure 4. To obtain the photovoltaic current density–voltage (J–V) curve, the sample was illuminated by a lamp. The open circuit voltage (V_{oc}) and the short circuit current density (J_{sc}) can be read from the photovoltaic J–V curve shown in Figure 4 to be 7.5 mV and 2.67 μA cm^{-2}, respectively. The fill factor $FF = (J \times V)_{max}/(J_{sc} \times V_{oc}) \approx 0.25$ can also be

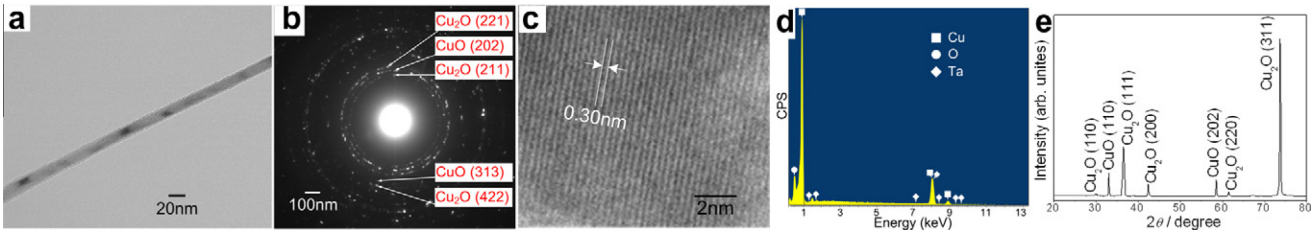

Figure 3. Microstructures and compositions of the Cu_2O nanowires: (a) TEM image of an individual nanowire, (b) SAED image taken from a random assembly of the nanowires, (c) HRTEM image of part of an individual nanowire, (d) the EDXS pattern taken from the surface of a hillock, (e) XRD analysis on the surface of a sample that had undergone gradual cooling.

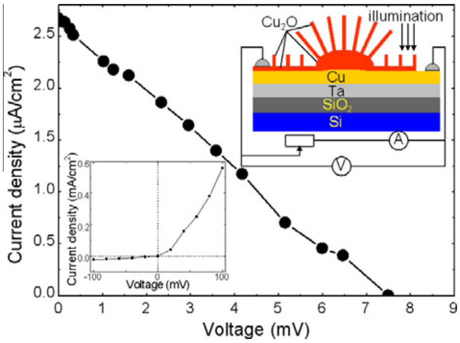

Figure 4. Measured photovoltaic properties of a multilayer sample with Cu_2O nanowires. The inset shows the structure of the sample and the measurement circuit, as well as the dark current curve.

calculated from the *J–V* curve. As shown in Figure 4, the shape of the *J–V* curve is similar to that of the Cu_2O/n-ZnO nanowire photovoltaic sample [18]. The typical photovoltaic effect further demonstrates that the main composition of the nanowires and the sample surface is Cu_2O rather than Cu [15] or CuO [13,14]. It should be mentioned that the photovoltaic current density and voltage of the present sample are relatively low. This may be due to the presence of some microcracks on the sample surface after the heating and cooling process, which brings up the inner resistance of the sample and leads to smaller photovoltaic current. It was also observed that, when the focused light scanned on the sample surface from one point to the others, the photovoltaic voltages were different. The area with more hillocks and well-growing Cu_2O nanowires always corresponded to higher photovoltaic voltage. The direct cooling sample (without hillocks and well-growing nanowires) and the sample heated at a relatively low temperature (without nanowires) were also studied, but no obvious photovoltaic effect was observed. Therefore, the observed photovoltaic effect of the sample is mainly contributed by the well-growing Cu_2O nanowires.

In summary, high-quality Cu_2O nanowires have been fabricated on SiO_2/Si substrate by a thermal stress -induced method. A new stress-redistribution phenomenon has been observed and the effect of the cooling procedure is demonstrated to be a key factor for obtaining Cu_2O nanowires with aspect ratios higher than 300 and for further improving the growth density of nanowires. An optimum growth condition of heating for 5 h and cooling gradually for 4 h is proposed. The as-obtained Cu_2O nanowires are mainly single-crystal ones with smooth surfaces and uniform cross-sections along their axes. A typical photovoltaic effect is demonstrated to exist in this Cu_2O/Cu multilayer structure with Cu_2O nanowire array, which makes it a potential option for cheap and low-toxicity photovoltaic devices with good environmental acceptability.

[1] X.Y. Liu, R.Z. Hu, S.L. Xiong, Y.K. Liu, L.L. Chai, K.Y. Bao, Y.T. Qian, Mater. Chem. Phys. 114 (2009) 213.
[2] C.M. Tsai, G.D. Chen, T.C. Tseng, C.Y. Lee, C.T. Huang, W.Y. Tsai, W.C. Yang, M.S. Yeh, T.R. Yew, Acta Mater. 57 (2009) 1570.
[3] Y.F. Mei, G.G. Siu, Y. Yang, Ricky K.Y. Fu, T.F. Hung, P.K. Chu, X.L. Wu, Acta Mater. 52 (2004) 5051.
[4] A.S. Walton, M.L. Gorzny, J.P. Bramble, S.D. Evans, J. Electrochem. Soc. 156 (2009) K191.
[5] W.Z. Wang, G.H. Wang, X.S. Wang, Y.J. Zhan, Y.K. Liu, C.L. Zheng, Adv. Mater. 14 (2002) 67.
[6] X.G. Wen, Y.T. Xie, C.L. Choi, K.C. Wan, X.Y. Li, S.H. Yang, Langmuir 21 (2005) 4729.
[7] D.J. Shang, K. Yu, Y.S. Zhang, J.W. Xu, J. Wu, Y. Xu, L.J. Li, Z.Q. Zhu, Appl. Surf. Sci. 255 (2009) 4093.
[8] X.C. Jiang, T. Herricks, Y.N. Xia, Nano Lett. 2 (2002) 1333.
[9] Y.L. Huang, M.H. Chou, S.Y. Wu, C.L. Cheng, Jpn. J. Appl. Phys. 47 (2008) 703.
[10] J.J. Chen, K. Wang, L. Hartman, W.L. Zhou, J. Phys. Chem. C 112 (2008) 16017.
[11] G. Cheng, S.J. Wang, K. Cheng, X.H. Jiang, L.X. Wang, L.S. Li, Z.L. Du, G.T. Zou, Appl. Phys. Lett. 92 (2008) 223116.
[12] A.M.B. Goncalves, L.C. Campos, A.S. Ferlauto, R.G. Lacerda, J. Appl. Phys. 106 (2009) 034303.
[13] K.L. Zhang, C. Rossi, C. Tenailleau, P. Alphonse, J.Y. Chane-Ching, Nanotechnology 18 (2007) 275607.
[14] S. Sahoo, S. Husale, B. Colwill, T.M. Lu, S. Nayak, P.M. Ajayan, ACS Nano 3 (2009) 3935.
[15] M. Saka, F. Yamaya, H. Tohmyoh, Scripta Mater. 56 (2007) 1031.
[16] A.E. Rakhshani, Solid-State Electron. 29 (1986) 7.
[17] J.A. Assimos, D. Trivich, J. Appl. Phys. 44 (1973) 1687.
[18] T.J. Hsueh, C.L. Hsu, S.J. Changa, P.W. Guo, J.H. Hsieh, I.C. Chen, Scripta Mater. 57 (2007) 53.