Local Synthesis of Tungsten Oxide Nanowires by Current Heating of Designed Micropatterned Wires

Keisuke Nagato[1,2*], Yusuke Kojima[1], Keigo Kasuya[3], Hiroki Moritani[1], Tetsuya Hamaguchi[1], and Masayuki Nakao[1]

[1] *Department of Engineering Synthesis, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[2] *Research Fellow of the Japan Society for the Promotion of Science, 8 Ichibancho, Chiyoda-ku, Tokyo 102-8472, Japan*
[3] *Central Research Laboratory, Hitachi, Ltd., 1-280 Higashi-koigakubo, Kokubunji, Tokyo 185-8601, Japan*

Received December 4, 2007; accepted December 15, 2007; published online January 17, 2008

We locally synthesized tungsten oxide nanowires at predetermined positions by current heating of designed micropatterned wires. The current wires were fabricated from tungsten thin film and had two different widths in the same wire, and the narrower sections were heated more than the wider sections due to the difference in electric resistance. The temperature of the narrower sections was controlled to be optimal for nanowire synthesis in an O_2 atmosphere in a vacuum chamber. We demonstrated the synthesis of nanowires over an area of approximately 1 × 1 μm^2 and successfully synthesized nanowires on a regular 20 by 20 array with narrow sections with 10 μm pitch.

DOI: 10.1143/APEX.1.014005

Tungsten oxide nanowires have interesting electrical, chemical, and mechanical properties, and are promising materials for use in various nanodevices such as field emitters,[1–3] gas sensors,[4,5] electrochromic devices,[6] and high-aspect-ratio probes for scanning probe microscopy. Tungsten oxide nanowires have generally been synthesized by the evaporation of tungsten or tungsten oxide onto flat substrates,[1,2,7–9] or by annealing tungsten crystalline substrates,[10] powders,[11,12] wires,[13] or tips[14,15] in vacuum. Because of their high-aspect-ratio structure, the field-emission properties of nanowires synthesized on flat surfaces[1–3] or tips[14,15] have been widely investigated. To date, it has been reported that straight tungsten oxide nanowires with diameters of 10–100 nm and lengths of 100–1000 nm can be synthesized from sputtered tungsten films by annealing them in a vacuum furnace.[3,16,17] We have also demonstrated that the nanowires obtained from sputtered tungsten films have good field-emission properties.[3] The number density of nanowires was discovered to be an important parameter for determining the field-emission properties:[3] a suitably low density resulted in good field-emission properties due to the concentration of the electric field.[18] It has also been reported that regularly arrayed carbon nanotubes provide good field-emission properties.[19] Thus, the positional control of the nanowires is very important for the large-scale manufacture of field-emission devices. In this study, we propose another simple method of locally synthesizing nanowires by position-controlled current heating using designed micropatterned wires (Fig. 1). For the fabrication of nanodevices involving tungsten oxide nanowires, synthesis using patternable base materials is considered to be the most useful method. Furthermore, compared to global annealing in a furnace, current heating method is a more practical synthesis technique because temperatures as high as 800 °C are required. The patterned current wires can also be used as cathode electrodes.

The joule heat power q obtained when current I passes through a thin-film current wire with length l, thickness t, and width w is expressed by

$$q = I^2R = I^2\rho_e[l/(tw)], \tag{1}$$

where the electric resistance is R and the resistance ratio

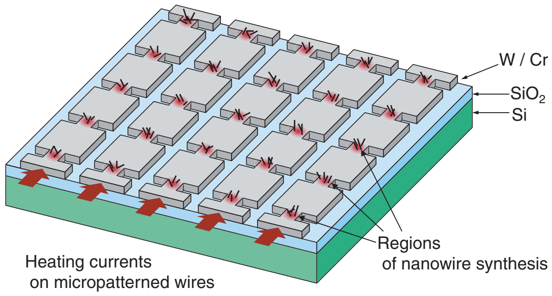

Fig. 1. Schematic of array of tungsten oxide nanowires grown on micropatterned wires by current heating.

of the tungsten thin film is ρ_e. Therefore, the temperature increase of the tungsten film per unit time assuming a thermally isolated model is expressed by

$$\frac{\Delta T}{\Delta t} = \frac{q}{C} = \frac{q}{ctwl} = \frac{I^2\rho_m}{ct^2w^2}, \tag{2}$$

where the heat capacity is C, the specific heat is c, and the mass density is ρ_m. Thus, the temperature increase of the tungsten current wire is proportional to the square of its width. However, in the actual thermal model, the heated parts are conductively cooled by the neighboring patterns and the base substrate, and also lose heat in the form of light radiation. We carried out a finite element method (FEM) simulation of the surface temperature distribution generated by local heating in a single section of a current wire (Fig. 2, simulation software: ANSYS by ANSYS Inc.). It shows that the narrow section of the wire is strongly locally heated by the current. A center region of about 1 μm length is heated up to 800 °C. The temperature gradually decreases away from the center, and the points with a temperature of 700 °C are positioned at 1 μm either side of the center.

Here, we annealed tungsten thin films in a furnace up to various temperatures (700/750/800/850 °C) to compare the nanowires produced with those obtained by current heating (Fig. 3). We maintained each temperature for 10 min in an O_2 atmosphere of 4×10^{-2} Pa. Thin nanowires were synthesized by annealing at 800 °C. High-density short nanowires were synthesized on the substrate annealed at 700 and 750 °C. On the other hand, few nanowires were synthesized on the substrate annealed at 850 °C.

*E-mail address: nagato@hnl.t.u-tokyo.ac.jp

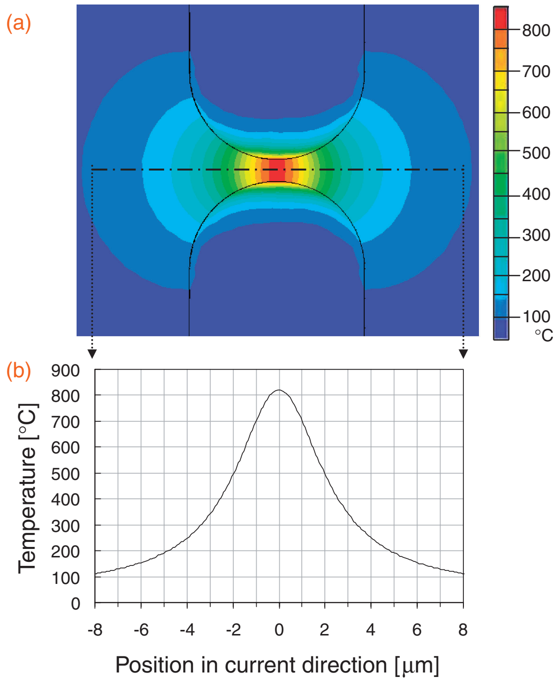

Fig. 2. FEM-calculated distribution of surface temperature of the micropatterned current wires (in the case of a single section). (a) Two-dimensional distribution and (b) distribution of the surface temperature along the center line.

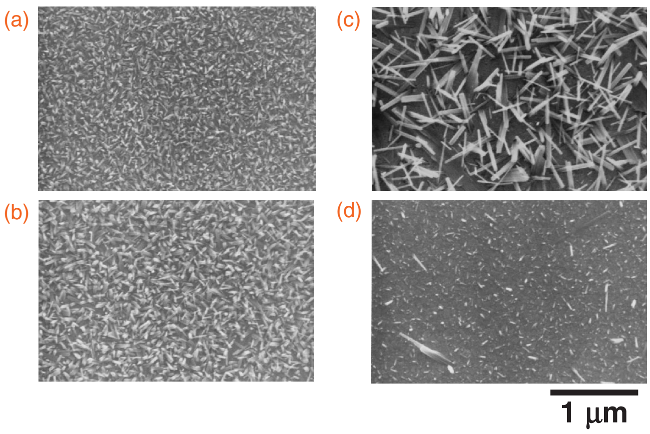

Fig. 3. SEM images of tungsten oxide nanowires synthesized in a vacuum furnace at various temperatures. (a) 700, (b) 750, (c) 800, and (d) 850 °C.

We sputtered a W/Cr thin film (200/50 nm thickness)[3] on an Si chip with thermally oxidized film (1 μm thickness). The Cr film prevented the tungsten film from detaching from the chip. The thermally oxidized film insulated the current wires from Si substrate. The chip size was $25 \times 25 \times 0.625\,mm^3$. Micropatterned current wires were then formed by photolithography and acid wet etching. We used AZ 1500 (20 cP, AZ Electric Materials) as the ultraviolet-light positive photoresist. The etchant for W consisted of 3.1% KH_2PO_4, 1.2% KOH, 3.1% $K_3Fe(CN)_6$, and 92.6% H_2O. The etchant for Cr consisted of 17% $Ce(NH_4)_2(NO_3)_6$, 6% $HClO_4$, and 77% H_2O. After this patterning process, the samples were carefully cleaned using a resist remover (AZ Remover 100) and acetone. Figure 4(a) shows a scanning electron microscopy (SEM; Hitachi S-4160s) image of a patterned current wire. The final width of the narrower section was 1 μm.

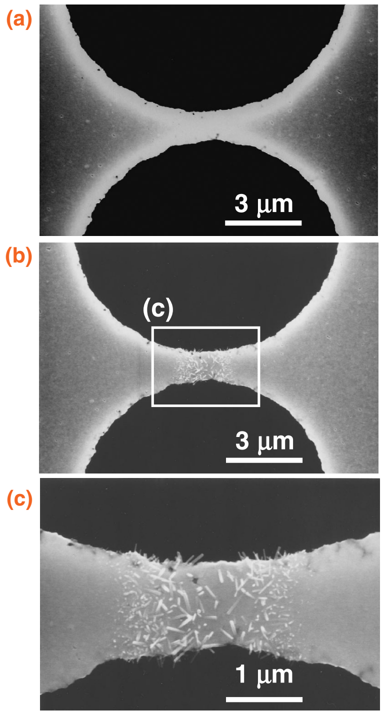

Fig. 4. SEM images of micropatterned wire (a) before synthesis of tungsten oxide nanowires and (b) after tungsten oxide nanowires were locally synthesized. (c) Magnified image of (b).

Because of the scaling limit of wet etching, the corners were rounded. Then, the sample was placed in a vacuum chamber, and the chamber was evacuated to 2×10^{-3} Pa using a turbomolecular pump. We heated the micropatterned wire by a current flow, while observing the radiated light from the heated section using an objective lens and a cooled charge-coupled-device (CCD) camera (Apogee U47) through a glass view port. The signals of the CCD were calibrated using the optimal temperature for synthesizing the nanowires (800 °C). We maintained this temperature (by adjusting the CCD signals from the current wire) at the synthesis section for 3 min, and we introduced a flow of O_2 gas at 0.5 sccm; accordingly, the pressure of the vacuum chamber became 4×10^{-2} Pa. We then maintained the temperature of 800 °C for another 10 min while adjusting the current. The current and voltage were about 1.5 V and 40 mA, respectively. The resultant nanowires are shown in Figs. 4(b) and 4(c). Approximately 20 thin nanowires were synthesized in the center region of the narrow section of the current wire over an area of about $1 \times 1\,\mu m^2$. The structure of the thin nanowires at the center is similar to that of the nanowires synthesized by annealing in the furnace at 800 °C [Fig. 3(c)]. On the other hand, the synthesized nanowires at the edge of the locally heated section were short and of high density, closely resembling those obtained by annealing at 700 °C. No nanowires were synthesized further than 1 μm from the center of the heated section. This nanowire distribution agrees well with the results of the FEM simulation and the furnace synthesis. A finer pattern (submicron-sized or sub-100-nm-sized pattern) will result in synthesis of fewer nanowires per section.

We also simultaneously synthesized nanowires locally on a regular 20 by 20 array consisting of 20 designed wires, each with 20 narrow sections with a pitch of 10 μm (Fig. 5).

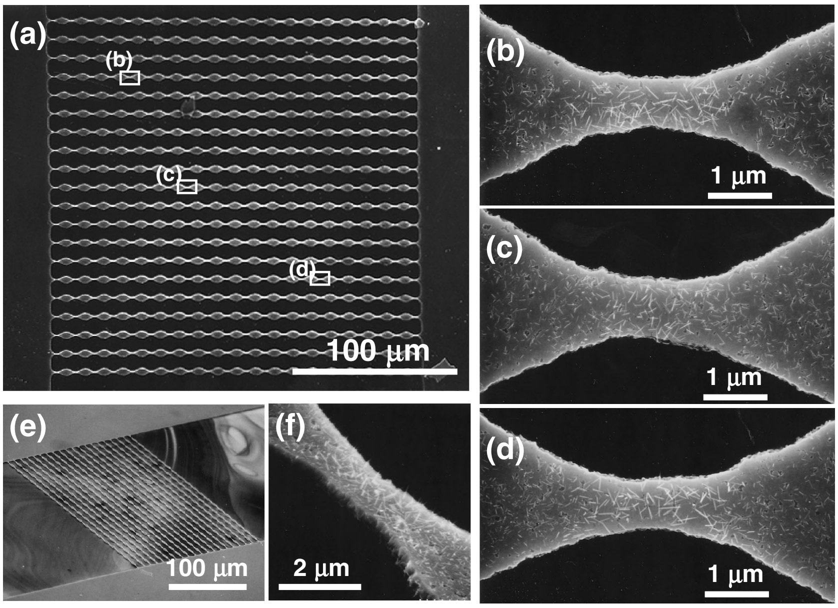

Fig. 5. SEM images of regular array of tungsten oxide nanowires (20 by 20 array with pitch of 10 μm). (a) Whole image of the micropatterned wires, (b–d) magnified images of the synthesized regions, and (e, f) tilted images.

In this experiment, a voltage of 19 V and a current of 0.49 A were required to synthesize the nanowires. The joule heat power was not proportional to the number of sections where nanowires were synthesized. This is because the heat is transferred to neighboring sections; thus, the total heat efficiency increases with the number of heated sections. For this reason, thin nanowires were synthesized over a greater distance (about 2 μm) in the current wire direction than those synthesized at a single section. In addition, short nanowires were synthesized at the wider sections of the nanowires. This indicates that the wider sections might have been heated to approximately 700 °C.

In summary, we designed a micropatterned current wire on a tungsten thin film and locally synthesized tungsten oxide nanowires in the narrow sections of the wire by current heating. The size of the region where thin nanowires were synthesized was approximately $1 \times 1\,\mu m^2$. We successfully simultaneously synthesized nanowires on a 20 by 20 array with a narrow-section pitch of 10 μm. This method is expected to be particularly suitable for the fabrication of field-emission displays, which require arrayed synthesis and a high-concentration electric field.

This local heating method can also be applied to the synthesis of other nanowires such as Si nanowires[20] or carbon nanotubes[21] by catalytic chemical vapor deposition (CVD). Our group has reported the local synthesis of carbon nanotubes by laser-assisted CVD.[22] In comparison with laser heating, local heating using micropatterned wires has an advantage of being able to simultaneously heat multiple sections. Furthermore, the local synthesis of nanowires by current heating in a designed micropatterned wire will lead not only to the realization of large-scale surface devices but also to that of other devices such as nanomechanical probes and nanowire transistor devices.[23)]

Acknowledgement The photomasks used for patterning of the tungsten film were fabricated using the electron-beam writer at the University of Tokyo Very Large Scale Integration (VLSI) Design and Education Center (VDEC) (F5112+VD01), donated by Advantest Corporation. We would like to thank Dr. Tetsuo Kan (The University of Tokyo) for his technical lecture on the photolithographic patterning of tungsten wires.

1) Y. B. Li, Y. Bando, and D. Golberg: Adv. Mater. **15** (2003) 1294.
2) J. Zhou, L. Gong, S. Z. Deng, J. Chen, J. C. She, N. S. Xu, R. Yang, and Z. L. Wang: Appl. Phys. Lett. **87** (2005) 223108.
3) Y. Kojima, K. Kasuya, T. Ooi, K. Nagato, K. Takayama, and M. Nakao: Jpn. J. Appl. Phys. **46** (2007) 6250.
4) Y. S. Kim, S.-C. Ha, K. Kim, H. Yang, S.-Y. Choi, Y. T. Kim, J. T. Park, C. H. Lee, J. Choi, J. Paek, and K. Lee: Appl. Phys. Lett. **86** (2005) 213105.
5) B. Deb, S. Desai, G. U. Sumanasekera, and M. K. Sunkara: Nanotechnology **18** (2007) 285501.
6) S. Gubbala, J. Thangala, and M. K. Sunkara: Sol. Energy Mater. Sol. Cells **91** (2007) 813.
7) Y. Q. Zhu, W. Hu, W. K. Hsu, M. Terrones, N. Grobert, J. P. Hare, H. W. Kroto, D. R. M. Walton, and H. Terrones: Chem. Phys. Lett. **309** (1999) 327.
8) J. Zhou, Y. Ding, S. Z. Deng, L. Gong, N. S. Xu, and Z. L. Wang: Adv. Mater. **17** (2005) 2107.
9) Y. B. Li, Y. Bando, D. Golberg, and K. Kurashima: Chem. Phys. Lett. **367** (2003) 214.
10) F. Xu, S. D. Tse, J. F. Al-Sharab, and B. H. Kear: Appl. Phys. Lett. **88** (2006) 243115.
11) Y. Z. Jin, Y. Q. Zhu, R. L. D. Whitby, N. Yao, R. Ma, P. C. P. Watts, H. W. Kroto, and D. R. M. Walton: J. Phys. Chem. B **108** (2004) 15572.
12) K. Hong, M. Xie, R. Hu, and H. Wi: Appl. Phys. Lett. **90** (2007) 173121.
13) Z. Liu, Y. Bando, and C. Tang: Chem. Phys. Lett. **372** (2003) 179.
14) Y. Baek, Y. Song, and K. Yong: Adv. Mater. **18** (2006) 3105.
15) R. Seelaboyina, J. Huang, J. Park, D. H. Kang, and W. B. Choi: Nanotechnology **17** (2006) 4840.
16) M. H. Cho, S. A. Park, K. D. Yang, I. W. Lyo, K. Jeong, S. K. Kang, D. H. Ho, K. W. Kwon, J. H. Ku, S. Y. Choi, and H. J. Shin: J. Vac. Sci. Technol. B **22** (2004) 1084.
17) C. H. Chen, S. J. Wang, R. M. Ko, Y. C. Kuo, K. M. Uang, T. M. Chen, B. W. Liou, and H. Y. Tsai: Nanotechnology **17** (2006) 217.
18) L. Nilsson, O. Groening, C. Emmenegger, O. Kuettel, E. Schaller, L. Schlapbach, H. Kind, J.-M. Bonard, and K. Kern: Appl. Phys. Lett. **76** (2000) 2071.
19) S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassel, and H. Dai: Science **283** (1999) 512.
20) O. Englander, D. Christensen, and L. Lin: Appl. Phys. Lett. **82** (2003) 4797.
21) J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate, and H. Dai: Nature **395** (1998) 878.
22) K. Kasuya, K. Nagato, Y. Jin, H. Morii, T. Ooi, and M. Nakao: Jpn. J. Appl. Phys. **46** (2007) L333.
23) X. Duan, C. Niu, V. Sahi, J. Chen, J. W. Parce, S. Empedocles, and J. L. Goldman: Nature **425** (2003) 274.