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Patterning of α-Fe_2O_3 nanowires by pressing a microstructured mold and their field-emission properties

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ABSTRACT

We patterned α-Fe_2O_3 nanowires by a simple pressing method and investigated their field emission properties. We synthesized α-Fe_2O_3 nanowires from a sputtered thin Fe film. Fe films (thicknesses: 150, 300, 650 and 1700 nm) were annealed from room temperature to 375 °C for 1 min and maintained at a temperature of 375 °C for 0–60 min. The length of the nanowires increased with the annealing time and thickness of the Fe films. We pressed a microstructured mold onto the nanowires and patterned the nanowires with an island array. The field-emission current of the nanowires patterned by pressing a mold was higher than that of nonpressed nanowires.

1. Introduction

Metal oxide nanowires are very interesting for diverse applications, such as field emission devices [1,2], gas sensors [3] and solar cells [4]. Metal oxide nanowires have been successfully synthesized by various methods. Since metal oxide nanowires have high aspect ratios and are easy to fabricate, they have attracted considerable attention as promising materials for field emitters in field-emission displays. We have investigated the effect of the dispersion degree of nanowires on their field-emission properties [5,6]. Fig. 1(a) and (b) shows schematics of electric fields around uniformly and discretely synthesized nanowires, respectively. An electric field at the tip of discretely synthesized nanowires is more concentrated than that at the tip of uniformly synthesized nanowires [7]. Concentrating an electric field at the tip of nanowires increases their emission current. We have indicated that discretely synthesized nanowires have high field-emission properties by performing an experiment using tungsten oxide nanowires synthesized on tungsten islands and electrostatic simulations [5]. However, it is very complicated to pattern the nanowires since it requires lithography and lift-off techniques.

In this study, we developed a very simple one-step method for patterning nanowires by pressing a microstructured mold onto nanowires and investigated the field emission properties of nanowires patterned by pressing. We used α-Fe_2O_3 nanowires which we successfully synthesized from sputtered films, and confirmed that they grew vertically from the surface of substrate [8]. Nanowires growing vertically are assumed to be suitable for patterning by pressing, since a mold is pressed parallel to the substrate. Thus we chose α-Fe_2O_3 nanowires for patterning in this study.

2. Experimental

2.1. Synthesis of α-Fe_2O_3 nanowires

We sputtered Fe and Cr thin films on Si substrates. The Cr thin film (100 nm) was sputtered to prevent the detachment of the Fe film from the substrate. The base pressure of the sputtering chamber was 1×10^{-2} Pa and the sputtering pressure was 5×10^{-1} Pa. To investigate the relationship between the Fe film thickness and the nanowire length, we prepared four Fe film samples with thicknesses of 150, 300, 650 and 1700 nm. The samples were placed in a vacuum furnace and annealed by infrared heating. The base pressure of the furnace was 2 Pa. Keeping a rotary pump on, we introduced air. The gas flow rate of was 2.5 L/min. We annealed the samples from room temperature to 375 °C for 1 min and then maintained them at a temperature of 375 °C for 0, 10, 30 or 60 min. After annealing, we cooled the furnace to room temperature while maintaining the air flow and removed the samples from the furnace. The surfaces of the samples were observed by scanning electron microscopy (SEM).

2.2. Patterning nanowires by pressing a mold

A microstructured mold was pressed onto the α-Fe_2O_3 nanowires, and the nanowires were patterned with an island array. We used a Si mold, and the pitch and depth of the pattern were 5 and 3 μm, respectively. The mold was pressed onto the nanowires by a pressing machine (VX-1000N-NN, SCIVAX Co.) for 10 s

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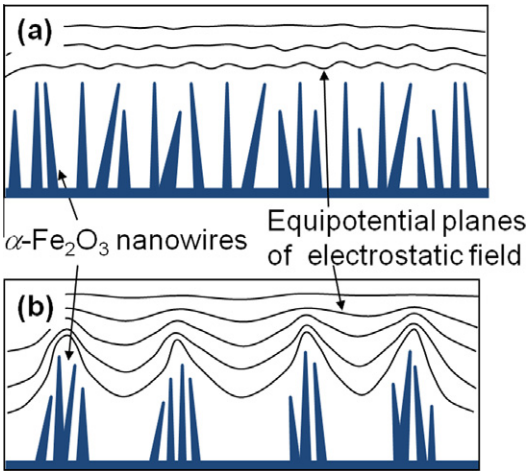

Fig. 1. Schematics of electric fields around (a) uniformly and (b) discretely synthesized nanowires.

at room temperature, and the press pressure was 5, 10, 20 or 30 MPa.

2.3. Field emission

To investigate the field emission properties of the patterned nanowires, the samples were set opposed to ITO glass in a vacuum chamber and connected to a high-voltage dc power supply. The gap between the samples and the ITO glass was set at 70 μm. The base pressure of the vacuum chamber was 1×10^{-3} Pa. We used the nanowires synthesized from Fe films with a thickness of 650 nm, annealed for 30 min and pressed at 30 MPa.

3. Results and discussion

Fig. 2 shows SEM images of the α-Fe_2O_3 nanowires synthesized from Fe films with thicknesses of 150, 300, 650 and 1700 nm. Vertical bladelike or wirelike nanostructures with sharp apexes and a greater width at the base were synthesized on the substrate. As the thickness of the Fe film increased, the nanowires became longer and wider. Fig. 3 shows the average length of the nanowires synthesized from Fe films thicknesses of 150, 300, 650 and 1700 nm as a function of annealing time (0, 10, 30 and 60 min). The length of the nanowires increased with the annealing time and thickness of the Fe films. Generally, the synthesis of metal oxide nanowires by the oxidation of a metal substrate is considered to follow the vapor–liquid–solid growth model [9] or the solid-phase growth model [10]. In these models, Fe atoms initially enter the liquid phase and are then oxidized, and FeO_x nanowires grow at the boundary between the liquid Fe and the oxidized Fe (solid). While the nanowires grow, the oxidation of the Fe film proceeds, and the nanowire growth may stop when the Fe film is completely oxidized. Therefore, the thicker the base metal (Fe film), the longer the nanowires grow.

Fig. 4 shows a SEM image of the mold and Fig. 5 shows SEM images of the nanowires patterned by pressing at 5, 10, 20 and 30 MPa. We observed that the nanowires pressed at 5 MPa were broken near the tip and the nanowires were slightly patterned with an island array. The nanowires pressed at 20 and 30 MPa were broken near the root and distinctly patterned with island array.

Fig. 6 shows current density versus electric field (I–V) plots and Fowler–Nordheim (F–N) [11] plots for α-Fe_2O_3 nanowires pat-

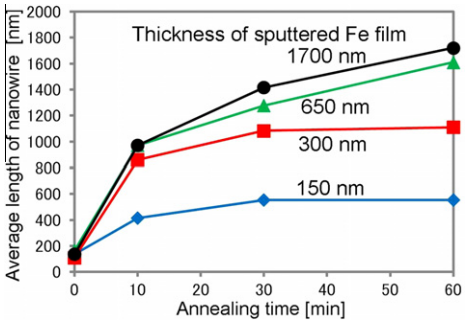

Fig. 3. Average lengths of α-Fe_2O_3 nanowires synthesized from Fe films with thicknesses of 150, 300, 650 and 1700 nm with annealing times of 0, 10, 30 and 60 min.

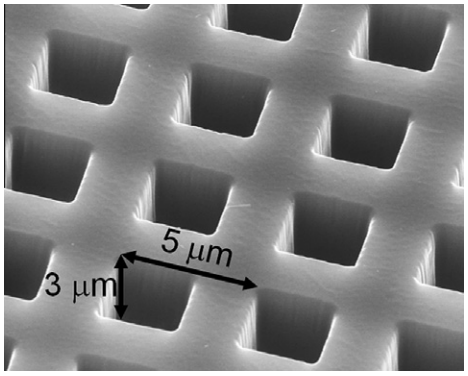

Fig. 4. SEM image of microstructured mold (tilt angle: 40°).

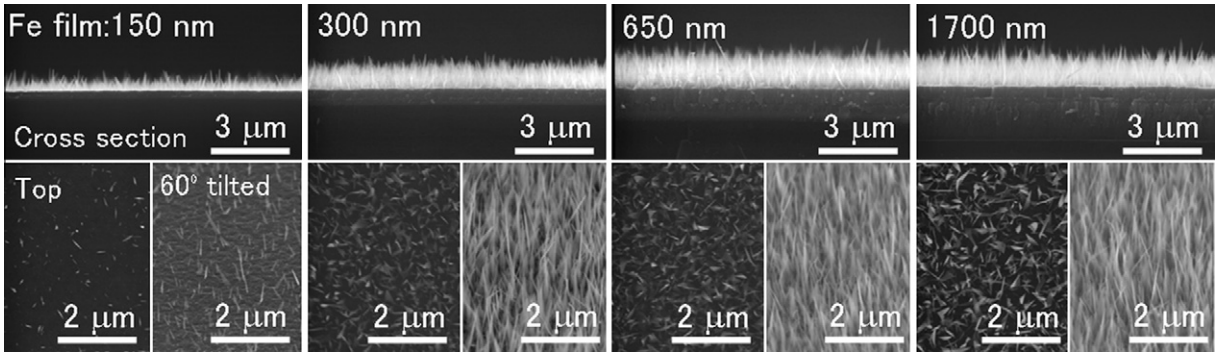

Fig. 2. SEM images of α-Fe_2O_3 nanowires synthesized from Fe films with thicknesses of 150, 300, 650 and 1700 nm. The annealing time was 30 min. Upper panels show cross-sectional images. Lower panels show top-view and tilted (60°) images.

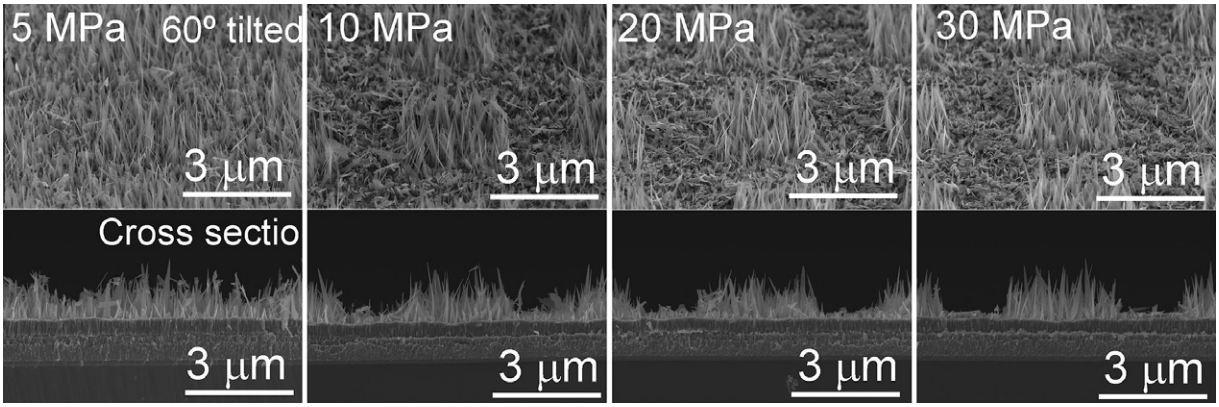

Fig. 5. SEM images of patterned α-Fe_2O_3 nanowires pressed at 5, 10, 20 and 30 MPa. Upper panels show tilted (60°) images and lower panels show cross-sectional images.

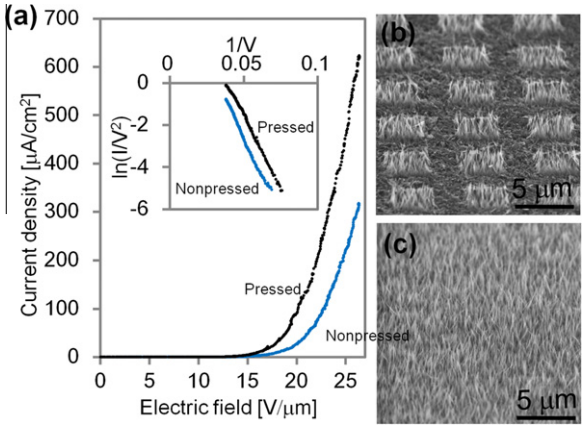

Fig. 6. (a) Current density versus electric field (I–V) plots for α-Fe_2O_3 nanowires patterned by pressing and nonpressed α-Fe_2O_3 nanowires. The inset shows their Fowler–Nordheim (F–-N) plots. (b) A SEM image of nanowires patterned by press (tilt angle: 60°). (c) A SEM image of as non-pressed nanowires (tilt angle: 60°).

terned by pressing and nonpressed α-Fe_2O_3 nanowires. The area used to calculate the current density of the patterned nanowires is the overall emission area, i.e., the area including pressed and remained area. The plots show typical field-emission current density versus applied electron field characteristics for a nanowire cathode in the diode configuration. The linear F–N plot indicates that the electron emission of the nanowires proceeded from a field-emission process, such as the tunneling of electrons through a potential barrier. The field-emission current of the nanowires patterned by pressing is about twice that of the nonpressed nanowires. Since the nanowires became discrete upon patterning, the electric field at the tip of the nanowires is more concentrated than that at the tip of the nonpatterned nanowires. Therefore, the field-emission current is increased by patterning.

4. Conclusions

We synthesized α-Fe_2O_3 nanowires from sputtered thin Fe films, patterned the α-Fe_2O_3 nanowires by pressing, and investigated their field-emission properties. Fe films (thicknesses: 150, 300, 650 and 1700 nm) were annealed from room temperature to 375 °C for 1 min and maintained at a temperature of 375 °C for 0, 10, 30 or 60 min. The length of the nanowires increased with the annealing time and thickness of the Fe films. We pressed a microstructured mold onto the nanowires at a pressure of 5, 10, 20 or 30 MPa, and the nanowires pressed at 20 and 30 MPa were distinctly patterned with an island array. The field-emission current of the nanowires patterned by pressing was higher than that of nonpressed nanowires.

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References

[1] Y.B. Li, Y. Bando, D. Golberg, Adv. Mater. 15 (2003) 1294.
[2] Y.W. Zhu, T. Yu, C.–H. Sow, Y.J. Liu, A.T.S. Wee, X.J. Xu, C.T. Lim, J.T.L. Thong, Phys. Lett. 87 (2005) 023103.
[3] J. Chen, L. Xu, W. Li, X. Gou, Adv. Mater. 17 (2005) 582.
[4] M. Law, L.E. Greene, J.C. Johnson, R. Saykally, P. Yang, Nat. Mater. 4 (2005) 455.
[5] M. Furubayashi, K. Nagato, H. Moritani, T. Hamaguchi, M. Nakao, Microelectron. Eng. 87 (2010) 1594–1596.
[6] Y. Kojima, K. Kasuya, T. Ooi, K. Nagato, K. Takayama, M. Nakao, J. Appl. Phys. 46 (2007) 6250.
[7] L. Nilsson, O. Groning, C. Emmenegger, O. Kuettel, E. Schaller, L. Schlapbach, H. Kind, J.-M. Bonard, K. Kern, Appl. Phys. Lett. 76 (2000) 2071.
[8] K. Nagato, M. Furubayashi, T. Hamaguchi, M. Nakao, J. Vac. Sci. Technol. B28 (2010) C6P11.
[9] Y.Q. Zhu, W. Hu, W.K. Hsu, M. Terrones, N. Grobert, J.P. Hare, H.W. Kroto, D.R.M. Walton, H. Terrones, Chem. Phys. Lett. 20 (1999) 327.
[10] Y. Kojima, K. Kasuya, K. Nagato, T. Hamaguchi, M. Nakao, Vac. Sci. Technol. B 26 (2008) 1942.
[11] O. Gloning, O.M. Kuttel, Ch. Emmengger, P. Groning, L. Schlapbach, J. Vac. Sci. Technol. B 18 (2000) 665.