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Morphology control of nickel oxide nanowires

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ABSTRACT

Nickel oxide (NiO) nanowires are synthesized by the hydroxylation and dehydration of nickel. We investigated how the morphology of NiO nanowires can be controlled by controlling parameters such as annealing temperature, pressure, and rate of temperature increase. It was found that nanowires were longest (2 μm) after annealing at approximately 700 °C at a pressure of 1.0×10^4 Pa in our process. We also discuss the growth mechanism of NiO nanowires by characterizing them by scanning electron microscopy observation and Raman spectroscopy.

1. Introduction

One-dimensional nanomaterials with a high aspect ratio and large surface area are expected to be used for advanced applications such as high-efficiency emission devices, the electrodes of electric cells, and chemical sensors because of their unique physical, electrical, and chemical properties. Nickel oxide nanowires are considered to be applicable to electronic devices [1–3] and gas sensors [4–7]. Furthermore, when the nanowires are reduced, Ni nanostructures can be obtained that may be used for advanced devices such as battery cells and solid-oxide fuel cells because Ni has a catalytic function [8–11]. To date, various fabrication methods for NiO nanowires have been reported: an aqueous solution method [12,13], an electrochemical deposition method [14,15], a vapor-based metal etching oxidation method [16], and a dehydration method [17,18]. In this study, we focus on the dehydration method and investigate the effects of parameters of annealing temperature and pressure on the resultant morphology of Ni nanowires. The morphology was observed by scanning electron microscopy (SEM) and the crystal geometry was characterized by Raman spectroscopy.

2. Experimental

First, a Ni foil (thickness: 40 μm) was soaked in a 20 gL LiOH solution bath at room temperature for one day. In this process, Ni was hydroxylated and a $Ni(OH)_2$ layer was formed on the Ni foil. The foil changed color from silver to green. The chemical equation for the hydroxylation of Ni is

$$Ni + 2H_2O(aq) \rightarrow Ni(OH)_2(s) + H_2(g) \quad (1)$$

Second, the foil was annealed in a furnace at 250 °C for 3 min to make $Ni(OH)_2$ layer anhydrous. This process also has the function of dehydration, given by the equation [17],

$$Ni(OH)_2 \rightarrow NiO + H_2O \quad (2)$$

Finally, the foil was annealed again in the furnace with a rate of temperature increase of 2.5 °C/s and maintained at a temperature of 300–900 °C for 20 min. The air pressure was varied from 1.0×10^1 to 1.0×10^5 Pa by a rotary pump. The rate of air flow was maintained at 2.5 l/min. As a result, the NiO nanowires grew from the $Ni(OH)_2$ layer [18]. The mechanism of NiO nanowires fabrication is shown at Fig. 1. After the samples were cooled to room temperature, we removed them from the furnace and observed them by SEM. Furthermore, the crystal geometry was investigated by Raman spectroscopy. The Raman spectra were analyzed with the data base of minerals and inorganic materials [19].

3. Results and discussion

3.1. Effect of temperature

The annealing temperature was varied under a constant pressure (1.0×10^5 Pa, atmospheric pressure). Fig. 2(a–f) show SEM images of the surface of the foils annealed at 700, 600, and 300 °C, respectively. When annealed at 625 °C and above, no NiO nanowires were obtained as shown in Fig. 2(a and b). Instead, particles with diameters of 100–200 nm were observed with a density of 10–20 μm^{-2}. It is considered that NiO condensed and formed nanoparticles at higher temperatures. When annealed at 500–600 °C, dark islands with a width of 10–20 μm were observed as shown in Fig. 2(c). Although there were no nanowires on the dark islands, nanowires with a width of 50 nm and a length of 100–500 nm grew densely in the bright flat areas as shown in Fig. 2(d).

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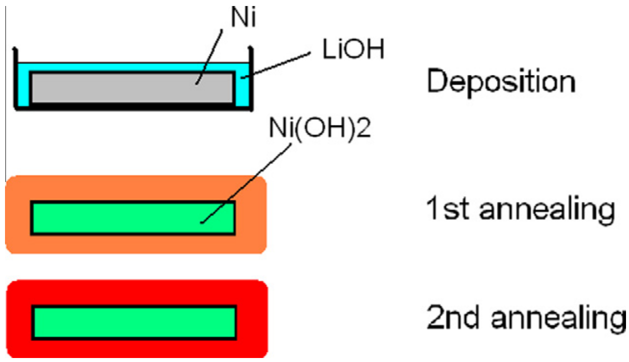

Fig. 1. The illustration of methodology of NiO naowires fabrication.

Here, the above results are discussed. Generally, Ni is oxidized when it is annealed in air by the reaction

$$Ni + 1/2O_2 \rightarrow NiO \quad (3)$$

However, in this route, NiO is not formed as nanowires but as a film. At 500–600 °C, both the dehydration of $Ni(OH)_2$ (Eq. (2)) and oxidation of Ni (Eq. (3)) are occurred in the annealing process. The dehydration route resulted in the generation of NiO nanowires and the oxidation route resulted in the generation of dark islands, i.e., NiO film.

When annealed at 500 °C or less, no nanostructure were produced as shown in Fig. 2(e and f). This is because the temperatures were not enough high to occur the dehydration reaction.

3.2. Effect of pressure during annealing

We varied the pressure during annealing at constant temperatures (700 and 600 °C). Fig. 3(a and b) show SEM images of the surface of the foils annealed at 700 and 600 °C at 1.0×10^4 Pa, respectively. When the annealing temperature was 700 °C, NiO nanowires grew to a length of 2 μm at 1.0×10^4 Pa, which is longer than those grown at 1.0×10^5 Pa. However, the number density of nanowires was only 10 μm^{-2}. On the other hand, when the annealing temperature was 600 °C, the length and density of the nanowires were similar to those obtained at 1.0×10^5 Pa.

Fig. 4 shows the length and number density of nanowires obtained by annealing at 1.0×10^5 and 1.0×10^4 Pa as a function of annealing temperature. Note that the number density was counted in the dense area if the nanowires grew sparsely as Fig. 2(c). The temperature ranges in which nanowires grew at pressures of 1.0×10^5 and 1.0×10^4 Pa were 500–600 and 550–750 °C, respectively. At the both pressures, the nanowires grew longer with lower number densities as the annealing temperature was higher. At lower pressures of 1.0×10^3 and 1.0×10^2 Pa, the results were the same as those obtained at 1.0×10^5 Pa. At 10 Pa, no nanowires grew. At a pressure of 1.0×10^5 Pa, Ni remaining on the $Ni(OH)_2$ surface may be oxidized by oxygen in the air and the route for nanowire synthesis (Eq. (2)) might become no longer available. On the other hand, at a pressure of 1.0×10^4 Pa, the oxidation of Ni is stopped and the dehydration of $Ni(OH)_2$ can proceed.

From the results that the nanowires obtained at a pressure of less than 1.0×10^4 Pa were the same as those obtained at atmospheric pressure and that no nanowires were obtained at 10 Pa,

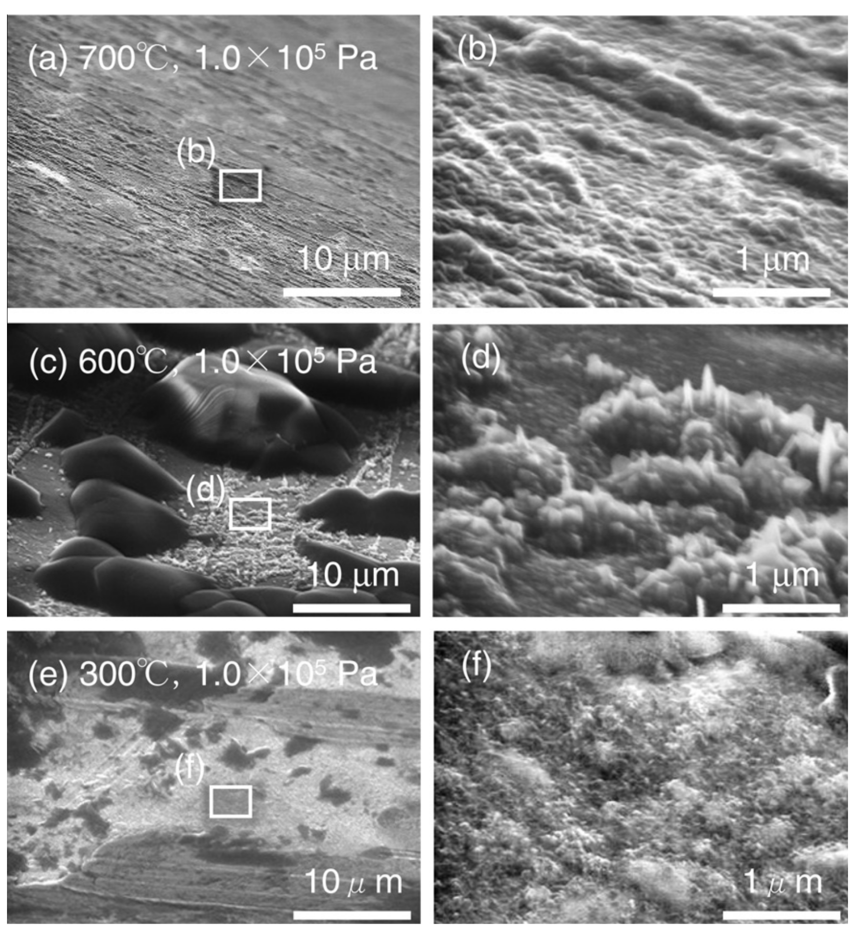

Fig. 2. SEM images of foil surfaces after annealing at 1.0×10^5 Pa with temperatures of (a and b) 700, (c and d) 600, and (e and f) 300 °C. (Tilt angle: 55°).

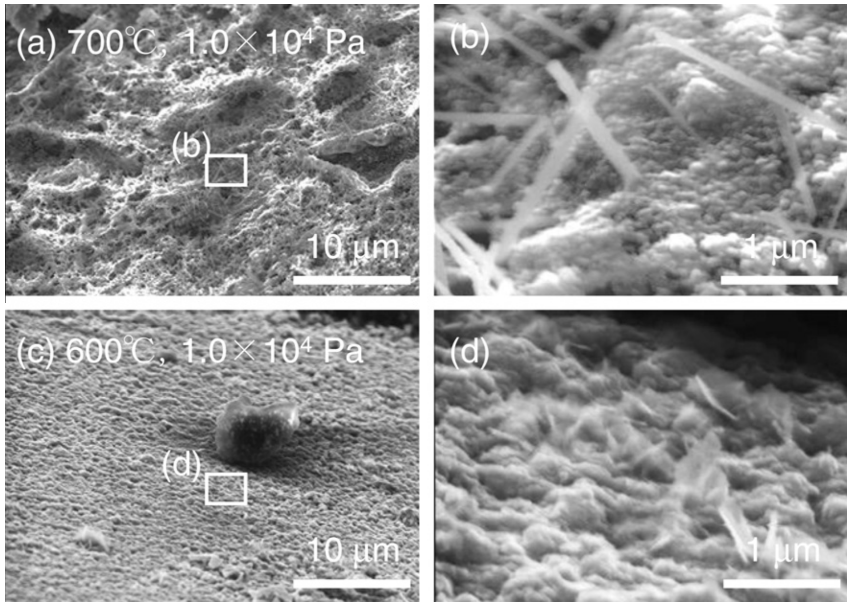

Fig. 3. SEM images of foil surfaces after annealing at 1.0×10^4 Pa with temperatures of (a and b) 700 and (c and d) 600 °C. (Tilt angle: 55°).

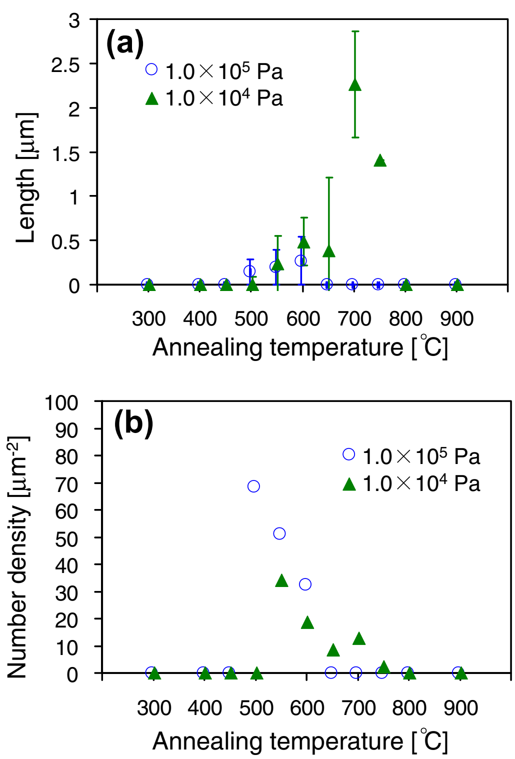

Fig. 4. (Color online). (a) Average length and (b) number density of NiO nanowires as a function of annealing temperature at pressures of 1.0×10^5 and 1.0×10^4 Pa.

the oxidation of Ni is considered to have provided the nuclei for nanowire growth. In other words, the annealing temperature and air pressure may determine the number of nucleation sites of NiO nanowires synthesized through the dehydration of a $Ni(OH)_2$ film. On the other hand, a NiO film synthesized through the oxidation of Ni remaining on the $Ni(OH)_2$ surface may inhibit the generation of nucleation sites for NiO nanowires; as a result, long NiO nanowires with a low density are synthesized.

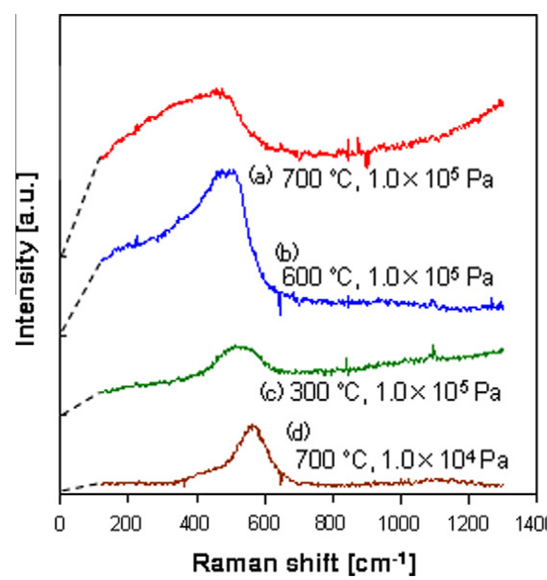

Fig. 5. Raman spectra of annealed foils. The annealing temperature and air pressure were (a) 700 °C, 1.0×10^5 Pa, (b) 600 °C, 1.0×10^5 Pa, (c) 300 °C, 1.0×10^5 Pa, and (d) 700 °C, 1.0×10^4 Pa, respectively.

3.3. Raman spectroscopy

Fig. 5 shows the Raman spectra of the samples annealed at (a) 700, (b) 600, and (c) 300 °C at 1.0×10^5 Pa; (d) annealed at 700 °C at 1.0×10^4 Pa, corresponding to Figs. 2(a, c and e), and 3(a), respectively. The peak between 400 and 600 cm^{-1}, which was observed in all four spectra, is from NiO. From the results in Fig. 5(a–c), the amount of NiO increased as the annealing temperature increased. In the spectra in Fig. 5(a and c), the intensity gradually increased with the Raman shift. The gradual increase in intensity in Fig. 5(a) originates from Ni_2O_3, which was formed by the further oxidation of NiO at the high temperature of 700 °C and the comparatively high pressure of 1.0×10^5 Pa. The reaction equation is

$$2NiO + 1/2O_2 \rightarrow Ni_2O_3 \qquad (4)$$

On the other hand, the gradual increase in intensity in Fig. 5(c) is considered to originate from LiOH remaining on the foil.

Comparing the spectra in Fig. 5(a and d), the peak height of NiO in Fig. 5(d) is approximately the same as that in Fig. 5(a); therefore, the amount of NiO at 1.0×10^4 Pa that originated from the nanowires and film is the same as that originated from the NiO nanoparticles and film at 1.0×10^5 Pa.

4. Conclusions

We synthesized NiO nanowires by the hydroxylation of Ni followed by two-step annealing to dehydrate the $Ni(OH)_2$ formed by hydration. We investigated the changes in morphology as parameters of temperature, and air pressure during annealing. We found that the NiO nanowires were longest (2 μm) after annealing at 700 °C at a pressure of 1.0×10^4 Pa. In the case of annealing at atmospheric pressure, the nanowires were longest at a temperature of 600 °C; however, they were much shorter (300 nm) than those obtained at 700 °C and 1.0×10^4 Pa. And island-shape NiO films with a width of 10–20 μm were formed and there were no nanowires on them. From this result, both the dehydration of $Ni(OH)_2$ and the oxidation of Ni may be occurred during the annealing process. Furthermore, we characterized the amounts of NiO and Ni_2O_3 formed during the synthesis by using Raman spectroscopy. The oxidation of Ni may contribute to the nucleation and subsequent growth of NiO nanowires with the dehydration route.

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