Ordered nickel oxide nanowire arrays and their optical absorption properties

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Abstract

Ordered NiO nanowire arrays embedded in anodic alumina membranes have been prepared by using an electrochemical deposition method. After annealing at 300 °C, the NiO nanowire arrays were characterized using SEM, TEM, SAED, and XRD. SEM and TEM observations reveal that these nanowires are dense, continuous and arranged roughly parallel to one another. XRD and SAED analysis together indicate that these NiO nanowires crystallize with a polycrystalline structure. The optical absorption band gap of NiO nanowire arrays is 3.74 eV, and no obvious blue shift or red shift with respect of that of the bulk NiO can be observed.
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1. Introduction

Recent progress in the synthesis and characterization of nanowires has been driven by the need to understand the novel physical and chemical properties of one-dimensional nanoscale materials, and their potential applications in constructing electronic and optoelectronic nanodevices. Template synthesis provides a possibility to control both size and shape of nanomaterials, and has been proved to be a versatile and simple approach for the preparation of one-dimensional nanomaterials since the pioneering work of Martin's group [1,2]. In particular, anodic alumina membranes (AAMs) grown in acid electrolytes possess hexagonally ordered porous structures with pore diameters ranging from 10 to 200 nm, pore lengths from 1 to over 100 μm, and pore density in the range from 10^{10} to 10^{12} cm^{-2}. These unique structure properties and their thermal and chemical stability make AAMs ideal templates for the fabrication of one-dimensional nanomaterials. An attractive synthesis method, electrochemical deposition (ECD) is controllable and inexpensive, and provides great opportunities for the preparation of new materials and nanostructures. In particular, by ECD of materials within the nanochannels of a template [2,3], such as track-etched polymeric membrane or AAM, various one-dimensional nanomaterials such as metals [4–6],

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semiconductors [7,8], and metal multilayers [9,10] have been prepared.

In recent years, there is considerable scientific and technological interest in developing nanostructured metal oxides with p-type semiconductivity. There are, however, relatively few metal oxides that tend to be p-type. Nickel oxide, NiO, is a stable wide band gap material and can be used as a transparent p-type semiconducting layer [11]. In particular, nickel oxide has attracted much attention as a promising elecrochromic material due to its high coloring efficiency, low material cost, and high stability as a counterelectrode in actual electrochromic devices [12,13], and are being studied for application in smart windows, electrochemical supercapacitors [14], and dye-sensitized photocathodes [15]. Various methods such as evaporation [16], sputtering [17], electrodeposition [18], and sol–gel techniques [19] have been adopted to prepare thin films containing nanocrystalline NiO. However, to the best of our knowledge, there have been no reports on the fabrication and optical properties of NiO nanowire arrays embedded in ordered AAM. In this Letter, the fabrication of NiO nanowires with diameter of about 80 nm embedded in AAM by ECD was reported. The optical absorption spectra of these ordered NiO nanowire arrays were investigated.

2. Experimental

AAMs were formed by a two-step anodization process. Briefly, high purity (99.99%) aluminum plate was annealed in vacuum at 500 °C for 3 h and degreased in acetone. Al plate was anodized in 0.3 M oxalic acid solutions under constant voltage 40 V. The remaining aluminum layer was removed in saturated aqueous $HgCl_2$ solution, and a subsequent etching treatment was carried out to remove the barrier layer on the bottom side of the AAM. The nanohole diameter (40–90 nm) was adjusted by the pore-widening treatment of immersing the substrates in 5 wt% phosphoric acid for different times. A gold layer was sputter-deposited onto one side of the through-hole AAM template to provide a conductive contact.

NiO nanowire arrays were prepared using the same procedure as reported previously [20,21]. Briefly, electrodeposition was carried out in a bath containing 1.8 M $Ni(NO_3)_2$ and 0.075 M $NaNO_3$ in a solvent of 50 volume percent (v/o) ethanol. The pH of the solution was adjusted in the range from 3.0 to 3.5 by adding nitric acid solution. Prior to immersion in the electrolyte, the AAMs were dipped in purified water under ultrasonic agitation for 2 min to ensure wetting of the nanopores. For the ECD, a carbon sheet was used as the anode, and an AAM with Au substrate attached to Cu foil was used as the cathode. NiO nanowire arrays were deposited at voltage 2–5 V using a dc power supply. Then, the sample was annealed at 300 °C for 24 h in order to crystallize the NiO nanowires.

Scanning electron microscope (SEM, JEOL JSM-6300), transmission electron microscope (TEM, JEM 200CX) assisted with selected area electron diffraction (SAED), X-ray diffraction (XRD, Philips PW 1710 with Cu Kα radiation), and UV–Vis absorption spectra (Cary 5E spectrophotometer) were employed to analyze the sample obtained. For SEM observation, a piece of AAM with ordered NiO nanowire arrays sample was eroded by an aqueous solution of 5 wt% NaOH for 20 min in order to remove the upper part of AAM of sample and then washed with distilled water several times. The sample for TEM was treated by 5 wt% NaOH solution for 40 min, and then ultrasonically dispersed in ethanol.

3. Results and discussion

During the ECD process, the $Ni(OH)_2$ deposit onto the cathode surfaces from the solutions, and grows in the form of wires owing to the confinement effect of the nanochannels.

As reported previously [20,21], in acid condition, the process for the electrodeposition of NiO in the ethanol solution containing $NiNO_3$ and $NaNO_3$ may be presented as follows:
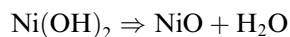
$$NO_3^- + 7H_2O + 8e^- \Rightarrow NH_4^+ + 10OH^-$$
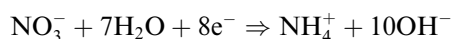
The production of OH^- increases the surface pH of the electrode, resulting in the precipitation

of $Ni(OH)_2$ at the electrode surface according to the following reaction:

$$Ni^{2+} + 2OH^- \Rightarrow Ni(OH)_2$$

After heated in 300 °C, NiO is formed according to the reaction

$$Ni(OH)_2 \Rightarrow NiO + H_2O$$

A typical top view of the NiO nanowires prepared by electrodeposition in AAM with diameters of about 80 nm is shown in Fig. 1. It is obvious that the NiO nanowires are arranged roughly parallel to one another, and highly uniform in diameters with an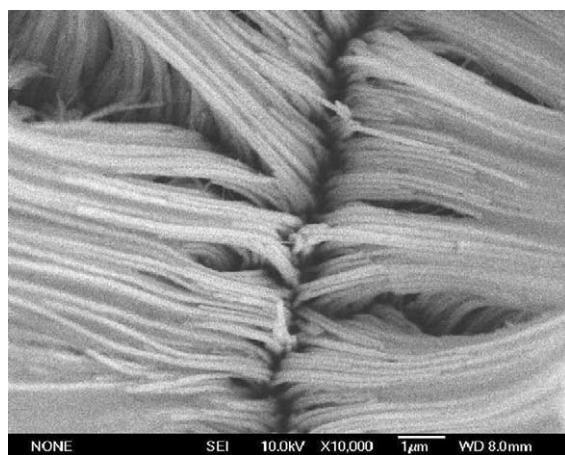 average of about 80 nm, the same as the pore sizes of the AAM used. Some broken nanowires can be seen, and this would be explained by the differences in thermal expansion coefficients of the membranes and nanowires, distortion of the membranes, and the preparation of samples.

TEM and SAED studies of the as synthesized products provide further insight into the NiO nanowire arrays. Figs. 2a, b show TEM images of the NiO nanowires that resulted from completely chemically dissolving the AAM template. The NiO nanowires are dense, continuous. The uniform diameters of 80 nm and smooth surfaces are clearly visible. A typical SAED pattern taken from the individual nanowire is shown in Fig. 2c, indicating that the NiO nanowire was polycrystalline structure.

The XRD technique was used to investigate the phase structure of the NiO nanowire arrays. Fig. 3 shows the XRD pattern of NiO nanowires with about 80 nm diameter. The diffraction peaks at 37.27°, 43.30°, 62.90°, 75.44°, and 79.43° can be indexed to (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) of face centered cubic NiO, respectively. These peak positions and their relative intensities are in good concordance with the standard diffraction data of powder cubic NiO, indicating that there is no preferred orientation and that the NiO nanowires are polycrystalline with face center cubic structure. The broadening of NiO peaks is due to the small particle size. Further, no obvious peaks for the amorphous AAM were observed.

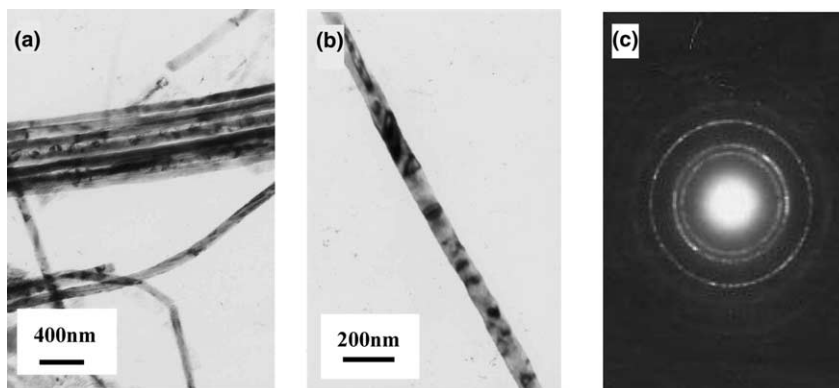Fig. 1. A typical SEM image of the fabricated NiO nanowires.

Fig. 2. (a) A typical TEM image of several NiO nanowires; (b) a typical morphology of one of the NiO nanowires; (c) showing the SAED pattern taken from it.
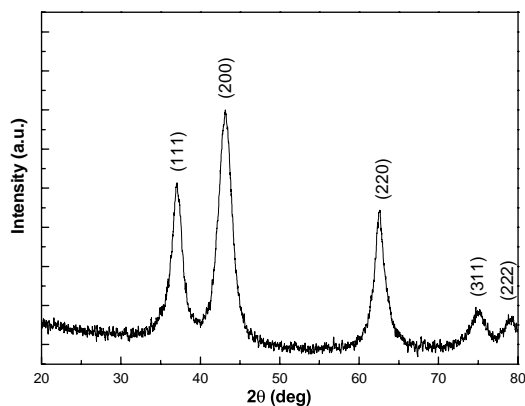
Fig. 3. The XRD spectrum of the fabricated NiO nanowires.

Optical absorption spectra were obtained on a Cary-5E spectrophotometer at room temperature. Fig. 4 shows the optical absorption spectra of the bland AAM and the NiO/AAM assembly system annealed at 300 °C. The strong absorption in the UV region is attributed to band gap absorption in NiO [22]. It is obvious that the spectra of the annealed NiO/AAM assembly system are quite different from that of the blank AAM. It is known that the correlation between absorption coefficient α and optical band gap E_g can be determined by the following equation:

$$(\alpha h\nu)^n = A(h\nu - E_g),$$

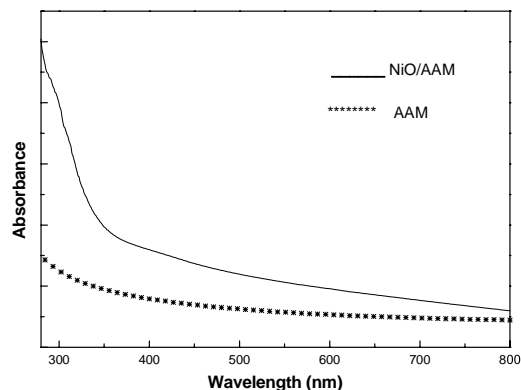where A is the edge-width parameter, $h\nu$ is the photon energy, and n is either 2 for direct inter-band transitions or 1/2 for indirect interband transitions [23]. Hence, the optical band gap for the absorption peak can be obtained by extrapolating the linear portion of the plot of $(\alpha h\nu)^n$ versus $h\nu$ to $\alpha = 0$. Fig. 5 shows $(\alpha h\nu)^2$ versus $h\nu$ plots for the sample annealed at 300 °C. For all samples, the optical absorption in the edge region can be well fit by the relation $(\alpha h\nu)^2 \sim h\nu - E_g$, which shows that NiO nanowires embedded in AAM have the direct band gap. The band gap of NiO nanowires embedded in AAM is about 3.74 eV, which is bigger than the value (3.55 eV) reported by Boschloo and Hagfeldt [24], and is similar to the normal NiO (3.6–4.0 eV) [22,25]. The optical band edge does not exhibit obvious blue shift or red shift.

There are many reports concerned with quantum size effects in low dimensional semiconductor system. It is well known that the semiconductor nanoparticle energy gap increases with decreasing the grain size, which leads to a blue shift of the optical absorption edge and have been observed in many semiconductor nanoparticle systems [26–28]. Compared to the range of nanoparticle sizes reported in the literature [26–28], the diameter (80 nm) of NiO nanowires is larger, so the blue shift of the optical absorption edge is very weak. It is a possible reason of the absence of blue shift. However, the optical properties of a semiconductor can also be modified by mechanisms other than the quantum size effect. For example, the NiO nanowires can interact with surrounding walls of the AAM and this interaction can also alter the

Fig. 4. Optical absorption spectra of the NiO nanowire arrays in AAM.
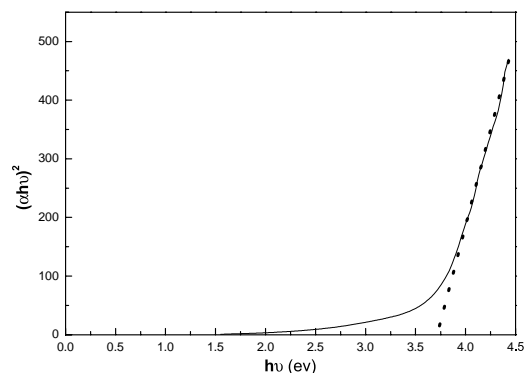

Fig. 5. $(\alpha h\nu)^2$ versus $h\nu$ plot for the NiO nanowire arrays in AAM.

optical properties. Determining the exact nature of the optical absorption edge will require further detail study.

4. Conclusions

Ordered polycrystalline NiO nanowire arrays embedded in AAM were prepared by using an electrochemical deposition method. The individual NiO nanowires (diameter ∼80 nm) were dense, continuous. The optical absorption band gap of the NiO nanowires was 3.74 eV, and no obvious blue shift or red shift of the optical band edge was observed.

Acknowledgements

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