Sodium Niobate Nanowire and Its Piezoelectricity

Tsung-Ying Ke,† Hsiang-An Chen,‡ Hwo-Shuenn Sheu,‡ Jien-Wei Yeh,‡ Heh-Nan Lin,‡ Chi-Young Lee,*†,§ and Hsin-Tien Chiu‡

Department of Materials Science and Engineering and Center of Nanotechnology, Materials Science, and Microsystem, National Tsing Hua University, Hsinchu, Taiwan, 30043, R. O. C., Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, 30050 R. O. C., and National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30077, Taiwan, R.O.C.

Received: December 10, 2007; Revised Manuscript Received: March 28, 2008

Nanowires of crystalline orthorhombic sodium niobate (NaNbO₃), with diameters of approximately 100 nm and lengths of several to hundreds of microns, as well as cubes with edges of lengths of hundreds of nanometers were obtained by reacting niobium oxide (Nb₂O₅) with 10 and 12.5 M NaOH solutions, respectively. The microstructures of the synthesized wiry and cubic piezoelectric materials were investigated, and the details of the reactions were elucidated as well. The piezoelectricity of individual NaNbO₃ (Pbma) nanowires was confirmed by piezoresponse force microscopy, and an effective piezoelectric coefficient along the vertical direction of around a few pm/V was obtained. To our knowledge, the present work is the first report of the preparation of NaNbO₃ nanowires as well as the determination of piezoelectricity.

Recently, Kasuga presented the preparation of TiO₂ nanotubes by hydrothermal treatment using alkaline solutions, which have generated great interest. One-dimensional metal oxides, nanotubes and nanowires have been extensively investigated in recent years. There have been some studies on the piezoelectricity of nanowires about BaTiO₃, ZnO, GaN, and PZT in recent years. Additionally, lead-free piezoelectric ceramics have received increasing interest because of their potential usefulness in environmental protection. Among the alkali metal niobate ceramics, potassium niobate (KNbO₃) and NaNbO₃ have been studied as promising Pb-free piezoelectric ceramics. However, there are two different phases of NaNbO₃, antiferroelectric (Pbma, JCPDS Card Files, No. 89–8957) and ferroelectric (P2₁ma, JCPDS Card Files, No. 82–0606), at room temperature. To get a ferroelectric phase NaNbO₃ is thus an important task. NaNbO₃ has attracted substantial interest among researchers and equipment designers because of its unique physical properties and its capacity to form the basis of a class of environmentally friendly materials. This investigation describes a simple wet chemical approach for preparing crystalline orthorhombic NaNbO₃ nanowires in a reaction between Nb₂O₅ and concentrated NaOH solution. The morphology, structure, piezoelectric property, and formation pathway of the crystalline nanowires were studied in detail by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffractometry (XRD), thermogravimetry (TGA), and piezoresponse force microscopy (PFM).

In this study, Nb₂O₅ was mixed with various concentrations of NaOH solution in a Teflon reaction flask, refluxed at 120 °C for 3 h, and then cooled to room temperature. After the unreacted alkali solution had been removed, the obtained powders were washed many times using DI water before they were dried at 100 °C. Some of the powders were further annealed at 400 °C to examine their microstructure in detail before and after calcination.

The morphologies of the powders were examined using a JEOL JSE-6500F field emission SEM equipped with an energy dispersive X-ray spectrometric (EDS) system to detect elements. Furthermore, crystallinity and morphological analyses were performed using a JEOL 2010 TEM. Phase detection and analysis were performed using a MAC SCIENCE MXP-3 type diffractometer with Cu Kα radiation.

Figure 1 shows the XRD study of the microstructure of the as-prepared powders and the powders after annealing. All the

Figure 1. The XRD pattern of the powders obtained by reaction of Nb₂O₅ in various concentrations of NaOH solutions and then annealed at various temperatures. (a) The powder prepared in 12 M NaOH, and (b) the as-prepared powder obtained in 10 M NaOH. Variable temperature XRD measurement of the powder obtained in 10 M NaOH at (c) 400 °C, (d) 600 °C, (e) and cooling down to 300 °C and measured.
diffraction peaks of the as-prepared powder in 12.5 M NaOH solution (Figure 1a) are associated with orthorhombic sodium niobate. The intensities and positions of the peaks are consistent with the values expected for orthorhombic NaNbO3. The peak spacing values were measured to be about 3.83 and 2.93 Å, consistent with the orthorhombic NaNbO3 structure. Additionally, as the sample was cooled to 300 °C, tetragonal NaNbO3 re-emerged. These observations reveal that the phase transformation between orthorhombic and tetragonal NaNbO3 occurred at 400~600 °C, corresponding to TGA/DSC observations.

Figure 2 displays the morphologies and microstructures of the powder obtained by reacting Nb2O5 with 10 M NaOH solution. Figures 2a and 2b present weakly and highly magnified SEM images of the as-synthesized powder. Many nanowires with a uniform diameter of around 100 nm and lengths of several to hundreds of microns were obtained. Figure 2c shows selected area electron diffraction (SAED) patterns that reveal the single crystalline nature of the as-synthesized powder. The pattern is associated with a [201] zone axis, and the nanowire direction was determined to be along the [010] axis. Figure 2d displays an HRTEM image, which includes distinct fringes. The spacing values were measured to be 3.83 and 2.93 Å and were assigned to plane directions {112} and {204}, respectively. These results reveal that a singly crystalline wiry SOMS was obtained by reacting Nb2O5 with 10 M NaOH solution without further annealing.

However, as the concentration of the NaOH solution increased to 12.5 M, the morphology of the product changed markedly. Figure 3a presents an SEM image of the powder obtained by reacting Nb2O5 with 10 M NaOH solution. The main products were large, sharp-edged cubes and thick plates with depths and widths of hundreds of microns and a wide range of lengths. Figure 3c shows selected area electron diffraction (SAED) patterns of the [101] zone axis, revealing the single crystalline nature of each cube. An HRTEM image in Figure 3d presents distinct fringes in the area that is marked in Figure 3b. Two planes, {040} and {101}, were identified. The spacing values were measured to be about 3.88 and 3.91 Å, equal to the values expected for orthorhombic NaNbO3.
the morphologies and the microstructure of the wiry SOMS following annealing at 400 °C. Figures 4a and 4b present the SEM and TEM images of the heated powder. Many nanowires with a uniform diameter of about 100 nm and lengths of several to hundreds of microns were observed. The white powders obtained before and after annealing were comprised of oxygen and approximately equal molar amounts of sodium and niobium, as revealed by EDS. These results show that calcination did not change the morphology and composition of the powder. According to XRD, the diffraction of the wiry SOMS following annealing at 400 °C (Figure 2c) revealed orthorhombic sodium niobate.

Figure 4c presents the SAED patterns that were marked in Figure 4b. The pattern was associated with the [001] zone axis, and the nanowire direction was determined to be [010]. Figure 4d shows an HRTEM image with distinct fringes. The d spacing values were measured to be 3.88 Å and were assigned to the (040) plane.

The above discussion indicates that the NaOH concentration strongly affects the morphologies and microstructures of the resulting powders obtained in the reaction of NaOH solution with Nb2O5. When the NaOH concentration was low (∼10 M), one-dimensional sodium niobate hydrate was the first major product, and then wiry orthorhombic NaNbO3 was obtained as the powder was heated to 400 °C. When the NaOH concentration exceeded 12.5 M, cubes of orthorhombic NaNbO3 were formed. Further heating of the orthorhombic sodium niobate nanowires or cubes caused a phase transformation from orthorhombic to tetragonal. The results are summarized below (Scheme 1).

To measure the effective piezoelectric coefficient $d_{zz}$ along the vertical direction of an individual NaNbO3 nanowire, piezoresponse force microscopy (PFM) was employed. The experiment was performed under ambient conditions using a...
commercial atomic force microscope (AFM; Smena-A, NT-MDT). The nanowires were first dispersed on an Au film. As shown in Figure 5a, a nanowire was then found, and the AFM tip was held at various locations on the nanowire. A small alternate current (AC) voltage was applied between the Au-coated tip (NSC36/Cr−Au, MikroMasch) and the bottom Au film. The nanowire and, consequently, the tip, vibrated at the same frequency and with the same amplitude due to the converse piezoelectric effect. The $d_{zz}$ can be determined by eq 1

$$d_{zz} = \frac{\Delta l}{V_{ac}} = \frac{D \cdot V_{pr}}{V_{ac}}$$

where $\Delta l$ is the root-mean-square (rms) amplitude of the tip deflection, $V_{ac}$ is the rms amplitude of the applied voltage, $V_{pr}$ is the rms amplitude of the tip deflection voltage, and $D$ is the AFM detector sensitivity. Details of the measurement procedure and parameters can be found elsewhere.$^{30}$

The topographic images of two nanowires with widths of 200 and 100 nm and heights of 80 and 120 nm, respectively, are shown in Figure 5, panels b and c, respectively. The relationships between the tip deflection and the applied voltage amplitude at the locations A, B, and C marked in panels b and c in Figure 5 are shown in Figure 5, panels d−f, respectively. As expected, a linear behavior is observed in all curves. The average $d_{zz}$ values are 0.85, 0.95 and 4.26 pm/V, respectively. As can be seen, the $d_{zz}$ of the nanowire in Figure 5c is about four times as large as those of the nanowire in Figure 5b. The outcome suggests that a nanowire with a larger height-to-width ratio vibrates more easily under an applied electric field. Also, these values are much smaller than the piezoelectric coefficients of polarized and doped bulk NaNbO₃, which are about 30−40 pm/V. $^{20,21}$ Nevertheless, it should be stressed that the smaller $d_{zz}$ values are mainly due to the fact that the electric field is applied in an unknown and unfavorable crystal direction. With proper control of the crystal orientation of the nanowires and the applied electric field, much higher values of $d_{zz}$ can be expected. Such investigations are currently underway.

In conclusion, crystalline orthorhombic NaNbO₃ nanowires and cubes were synthesized by the simple base treatment of Nb₂O₅ with 10 and 12.5 M NaOH solutions. The initial major products of the reaction of Nb₂O₅ with 10 M NaOH solution were monoclinic SOMS nanowires, formed by the intercalation of NaOH to Nb₂O₅. Heating the nanowires to 400 °C yielded wiry orthorhombic NaNbO₃ by the removal of H₂O from the layers. The effective piezoelectric coefficient along the vertical direction of an individual NaNbO₃ (Pbma) nanowire measured by PFM is about a few pm/V. When the reaction proceeded in concentrated alkaline solution, orthorhombic NaNbO₃ cubes were obtained. This selective and efficient method yields specific products of the base treatment, which were perovskite materials of various shapes.

Acknowledgment. The authors like to thank the National Science Council of the Republic of China, Taiwan, for
financially supporting this research under contract Nos. NSC 93-2213-M-007-035, NSC 93-2213-M-009-003, and NSC 96-2221-E-007-100.

References and Notes