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Scalable Preparation of $SrTiO_3$ Submicro-wires from Layered Titanate Nanowires

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Abstract

$SrTiO_3$ submicro-wires were prepared by the reaction of layered titanate nanowires with $Sr(OH)_2$ powder in an autoclave. The wires were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), Ultra-violet visible (UV-vis), photoluminescence (PL) and Raman spectroscopy. The XRD measurement shows that the prepared $SrTiO_3$ submicro-wires hardly have impurity phases. The SEM and TEM images demonstrate that the scalable wires, which need to be processed at the reaction temperature of 180 ℃ for about 48 hours, are not composed of single crystals. The PL shows that the wire-like $SrTiO_3$ has emission peaks at the wavelengths of 568 and 585 nm. Further, the Raman spectroscopy reveals structural changes in the products through different reaction time.

Keywords: oxide; titanate nanowires; strontium titanate; $SrTiO_3$ wires

1 Introduction

Ferroelectronic oxides are an important kind of technical materials widely applied in the fields of nonlinear optics, thin-film capacitors, pyroelectric detectors, optical memories and electro-optic modulators[1-4]. Strontium titanate ($SrTiO_3$) is one of the most well-known ferroelectrics among all perovskite-structural oxides. However, because its properties have a strong dependence on structure and finite sizes, much attention is paid to controllable preparation of crystalline sizes and thin films in order to improve device quality[5].

One-dimensional (1D) structure makes it possible to investigate the effects of crystalline size, which also should be considered in application of micro/nano-device, wherefore so far various 1D materials have been synthesized and widely studied[6-9]. However, few researchers managed to obtain $SrTiO_3$ submicro/nanowires except for Lee et al., who prepared these nanowires using TiO_2 nanoparticles and $Sr(OH)_2$ precursor in a hydrothermal process[10]. This paper proposes a new preparation method, in which layered titanate nanowires are used to synthesize $SrTiO_3$ submicro-wires in a Teflon-coated autoclave without any water or other organic solvents in it.

2 Experimental Procedure

Layered titanate salt nanowires (NTO-nws) were prepared using metatianic acid in strong alkaline with hydrothermal method similar to that reported in the Ref.[11].

$SrTiO_3$ submicrowires were synthesized by the reaction of the NTO-nws with $Sr(OH)_2$ in a hydrothermal process. A typical preparation procedure was as follows: an amount of powder of NTO-nws

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was put into a beaker, and, at the same time, strontium acetate $Sr(Ac)_2$ was dissolved into distilled water in another beaker. After having mixed up the contents of these two beakers, a certain quantity of NaOH was added into the mixture. Finally, the white precipitates were centrifuged and washed with anhydrous ethanol twice, and then the obtained was put into two Teflon-lined autoclaves (12 mL) and loaded into an oven at 180 ℃ for different durations of 10 h (TS-01) and 48 h (TS-02), respectively. After the autoclaves were cooled naturally down to the room temperature, the white powder was filtered, washed with diluted acetic acid and distilled water for several times.

The reacted products were identified by various measurement techniques. X-ray diffraction (XRD) was performed on a Rigaku D/MAX-PC2200 diffractometer using CuKα radiation (λ = 0.154 056 nm). Scanning electron microscope (SEM), transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) were carried out on JEOL-JSM 5800, JEM-2010 and JEOL JEM-2010F, respectively. Photoluminescence (PL) spectra were measured on a Shimadzu RF-5301 PC using a UV-vis spectrophotometer with Xe lamp as an excitation light source. Raman spectroscopy was measured on HR 800 with 633 nm radiation having an output power of 8 mW.

3 Results and Discussion

Fig.1 shows the TEM image, XRD pattern and Raman spectrum of the prepared NTO-nws. The TEM image in Fig.1(a) demonstrates that the NTO-nws turn out nanowires rather than nanotubes. The electron diffraction (ED) pattern reveals that the NTO-nws belong to a kind of layer-structured material having relatively high crystallinity.

The XRD pattern in Fig.1(b) is similar to the one published in Bruce's Ref.[12]. In Fig.1(c), Raman spectrum shows that, in close agreement with the results found in the Ref.[13], there are four main broad bands of round 203, 283, 464 and 672 cm^{-1}. Here comes a conclusion that these NTO-nws have a structure of lepidocrocite titanate ($H_xTi_{2-x/4}\square_{x/4}O_4$ (x-0.7,□:vacancy))[14].

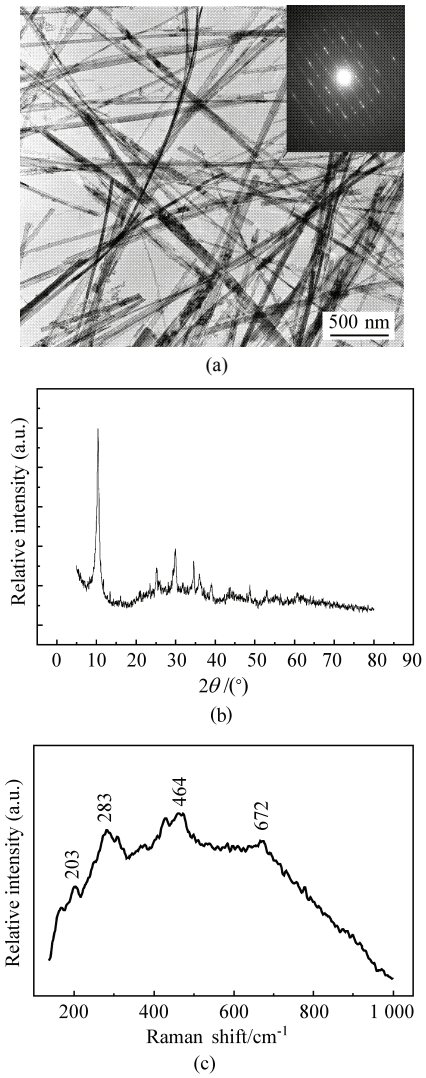


Fig.1 Morphology and structure of prepared NTO-nws precursor. (a) TEM image, inset: electron diffraction pattern of one nanowire; (b) XRD pattern; (c) Raman spectrum.

X-ray diffraction (XRD) analysis was used to determine the phases between the NTO-nws and $SrTiO_3$ powder (Fig.2). As an XRD pattern of the sample TS-01, the pattern (a) has seen many sharp peaks, but what the pattern is remains unknown. With the reaction time prolonged to 48 hours, as shown in Fig.2(b), the patterns of $SrTiO_3$ phase crop up (JCPDS No. 73-0661). The absence of any peaks of other phases attests to the products to be a relatively pure strontium titanate compound.

In order to investigate the growing process of the wire-like $SrTiO_3$ material (TS-02) during the

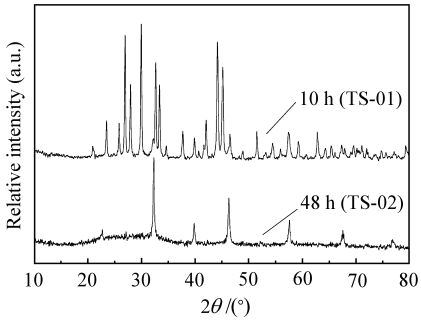


Fig.2 XRD patterns of products prepared under the reaction of NTO-nws with $Sr(OH)_2$ for different reaction times.

reaction between the NTO-nws and $Sr(OH)_2$, the SEM images of the two samples were further measured as shown in Fig.3. When the reaction time extends to 10 hours (TS-01), a great number of NTO-nws has transferred into particles (Fig.3(a)). Under the same condition, only the $Sr(OH)_2$ is replaced by Sr $(Ac)_2$ but the morphology of the products remains almost unchanged, which means OH^- anions responsible for the formation of the particles. For the TS-02, after reaction for 48 h, scalable $SrTiO_3$ wires with diameters ranging from tens to hundreds of nanometers can be produced. Such formation of the wires from particles may be Osward ripening process.

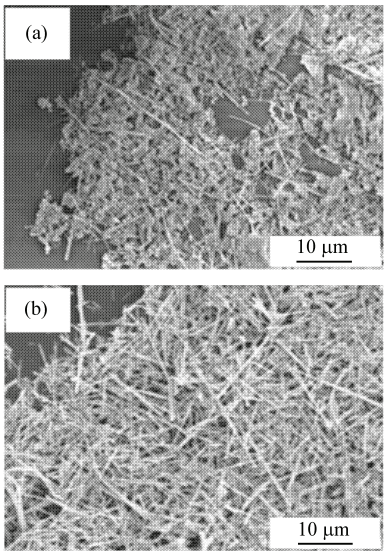


Fig.3 SEM images of two products. (a) TS-01; (b) TS-02.

As shown in Fig.4, Raman spectroscopy was used to measure lattice vibrational spectra of the two samples prepared through different reaction time. The spectrum of the TS-01 in Fig.4(a) is completely different from that of the TS-02. In Fig.4(b), the $SrTiO_3$ has four distinct photon lines of 195, 274, 543 and 726 cm^{-1}. The lines of 195 and 543 cm^{-1} are attributed to the degenerated TO_2-longitudinal optical (LO_1) phonon and TO_4 modes, while the line of 274 cm^{-1} corresponds to the mixed TO_3-LO_2 phonon mode, and the line of 726 cm^{-1} is assigned to the LO_4 photon mode[15,16]. It reiterates the possession of much high crystallinity by the nanowires thus prepared.

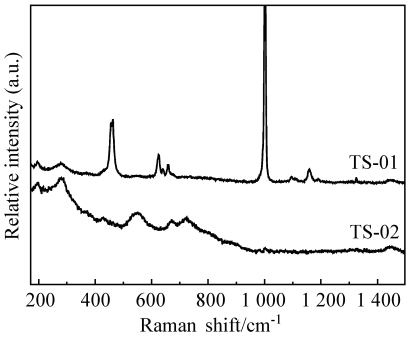
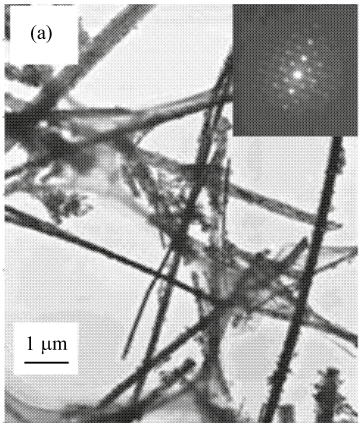


Fig.4 Raman spectra of two samples.

Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images provide an insight into the structure of the $SrTiO_3$ wires (Fig.5). Fig.5(a) exhibits the rough surface of the rods. The Fig.5(b) of HRTEM image of the individual rod shows its structure not composed of a single crystal keeping which is in line with the results from the electron diffraction (ED) measurement in Fig.5(c) where the diffraction points are irregular. In Fig.5(d), the EDX result demonstrates that the sample only consists of Sr, Ti and O elements.



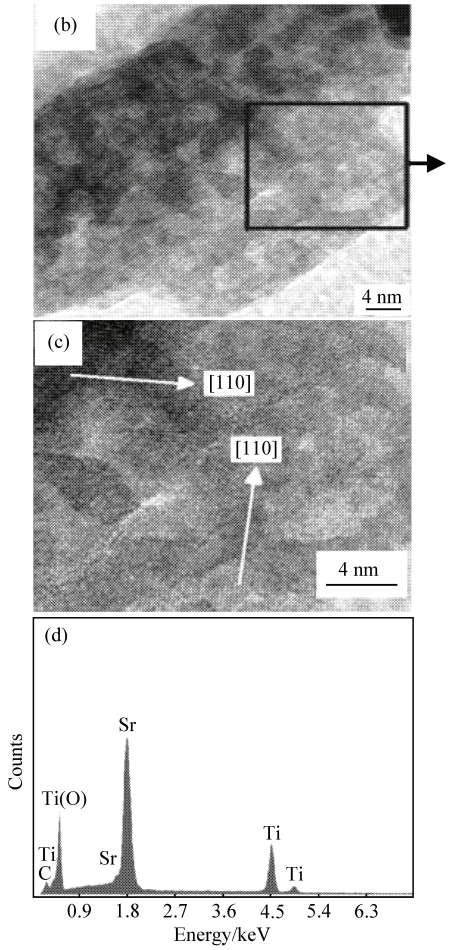


Fig.5 Morphology and structure of the TS-02. (a) TEM image; (b) HRTEM image; (c) HRTEM image; (d) EDX.

In summary, $SrTiO_3$ powder can be synthesized in an autoclave using the NTO-nws precursor and $Sr(OH)_2$ at 180 ℃ for a reaction time of 48 h. The reaction time strongly affects the morphology of the $SrTiO_3$ powder. When the reaction takes about 48 h, wire-like products will be obtained. The PL of this wire-like $SrTiO_3$ displays existence of a lot of oxygen defects in the structure.

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References

[1] Wilson J M, Parma D L C. Method of precipitating metal titanate powders, US patent 4,670,243, 1987.

[2] Lines M E, Glass A M. Principles and applications of ferroelectrics and related materials. Oxford: Oxford University Press, 2001.

[3] Hill N A. Why are there so few magnetic ferroelectrics. J Phys Chem B 2000; 104(29): 6694-6709.

[4] Schrott A G, Misewich J A, Nagarajan V, et al. Ferroelectric field-effect transistor with a $SrRu_xTi_{1-x}O_3$ channel. Appl Phys Lett 2003; 82(26): 4770-4772.

[5] Fong D D, Stephenson G B, Streiffer S K, et al. Ferroetectricity in ultrathin perovskite films. Science 2004; 304(5677): 1650-1653.

[6] Nelon S F, Lin Y Y, Gundlach D J, et al. Temperature-independent transport in high-mobility pentacene transistors. Appl Phys Lett 1998; 72(15): 1854-1856.

[7] Dimitrakopoulos C D, Malenfant P R L. Organic thin film transistors for large area electronics. Adv Mater 2002; 14(2): 99-117.

[8] Ji T H, Tang M Y, Guo L, et al. Scalable synthesis of $Sb(III)Sb(V)O_4$ nanorods from Sb_2O_5 powder via solvothermal processing. Solid State Commun 2005; 133: 765-769.

[9] Ji T H, Liu G R, Qi X Y, et al. Scalable synthesis of A_2S_3 (A=Sb, Bi) submicro/nanowires using their powders via solvothermal proceeding. Chin Sci Bull 2006; 51(6): 655-660.

[10] Joshi U A, Lee J S. Template-free hydrothermal synthesis of single-crystalline barium titanate and strontium titanate nanowires. Small 2005; 1(12): 1172-1176.

[11] Kasuga T, Hiramatsu M, Hoson A, et al. Titania nanotubes prepared by chemical processing. Adv Mater 1999; 11(15): 1307-1311.

[12] Armstrong A R, Armstrong G, Canales J, et al. TiO_2-B nanowires. Angew Chem Int Ed 2004; 43: 2286-2288.

[13] Mao Y, Kanungo M, Hemraj-Benny T, et al. Synthesis and growth mechanism of titanate and titania one-dimensional nanostructures self-assembled into hollow micrometer-scale spherical aggregates. J Phys Chem B 2006; 110(2): 702-710.

[14] Sasaki T, Nakano S, Yamauchi S, et al. Fabrication of titanium dioxide thin flakes and their porous aggregate. Chem Mater 1997; 9(2): 602-608.

[15] Zhang M S, Yin Z, Chen Q, et al. Study of structural and photoluminescent properties in barium titanate nanocrystals synthesized by hydrothermal process. Solid State Commun 2001; 119(12): 659-663.

[16] Sun X, Li Y D. Synthesis and characterization of ion-exchangeable titanate nanotubes. Chem Eur J 2003; 9: 2229-2238.

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