Hydrothermal Production of $SrTiO_3$ Nanotube Arrays

Jaturong Jitputti, Patcharee Charoensirithavorn, and Susumu Yoshikawa*
Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011

(Received August 15, 2007; CL-070871; E-mail: s-yoshi@iae.kyoto-u.ac.jp)

Strontium titanate ($SrTiO_3$) nanotube arrays were produced through a simple hydrothermal process from amorphous TiO_2 nanotubes arrays. The resulting samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). During the hydrothermal treatment, the TiO_2 nanotube arrays retained their shape to produce $SrTiO_3$ nanotube arrays. The formation mechanism can be explained by the nanoscale Kirkendall effect.

Because of its high-charge-storage capacity, good insulating properties, and chemical stability, strontium titanate ($SrTiO_3$) has been extensively studied and widely used in modern electronic devices and catalytic materials.[1–3] Generally, $SrTiO_3$ is prepared by solid-state reaction of strontium carbonate and titanium dioxide, typically at temperature higher than 900 °C.[4,5] However, the $SrTiO_3$ powders obtained from this traditional method are generally microstructural variations due to lack of control over the physical and/or chemical characteristics, which always lead to poor properties optimization and reproducibility.[6] Many different methods and techniques have been developed for the preparation of $SrTiO_3$ powders, including sol–gel technique,[6] sonochemical method,[7] coprecipitation method,[8] and hydrothermal method.[9–11] In contrast to other techniques, the hydrothermal method offers an inexpensive and environmentally friendly route and the ability to control chemical, homogeneity, purity, morphology, shape, and phase composition of the powder under moderate conditions.[10,11] Recently, there were some new techniques for the preparation of special morphologies of $SrTiO_3$, such as preparation of eight-pod star-shaped particles by sol–gel technique,[6] $SrTiO_3$ thin film by liquid-phase deposition (LPD) method,[12] $SrTiO_3$ nanotubes by hydrothermal method,[13] and spherical $SrTiO_3$ prepared by hydrothermal method.[11,14] However, the preparation method of $SrTiO_3$ nanotube arrays has not been reported yet. In this communication, we report a simple hydrothermal approach for preparation of $SrTiO_3$ nanotube arrays by a novel method combining the ZnO nanorod arrays (core material) using a low-temperature hydrothermal growth, the TiO_2 by LPD,[15,16] and the $SrTiO_3$ by hydrothermal process.

The amorphous TiO_2 nanotube arrays on the fluorine-doped SnO_2 transparent conducting oxide (FTO) were prepared by a templating method describe elsewhere.[15] In details, the strategy involves two steps: firstly, the ZnO nanorod arrays (core material) were grown on FTO substrate using hydrothermal method. Secondly, TiO_2 nanotube arrays were prepared by LPD by using ZnO nanorod arrays as a template. After amorphous TiO_2 nanotubes preparation, the $SrTiO_3$ nanotubes were then prepared by hydrothermal treatment. The resulting amorphous TiO_2 nanotube arrays was added into an 80-mL Teflon-lined stainless steel autoclave containing 50 mL of aqueous $Sr(OH)_2$ solution (0.025 M) and then placed in an oven at 120 °C for 15 h. The resulting sample was then washed by 0.1 M aqueous acetic acid solution and ethanol and finally dried at 60 °C. XRD, SEM, and TEM studies were performed on the samples.

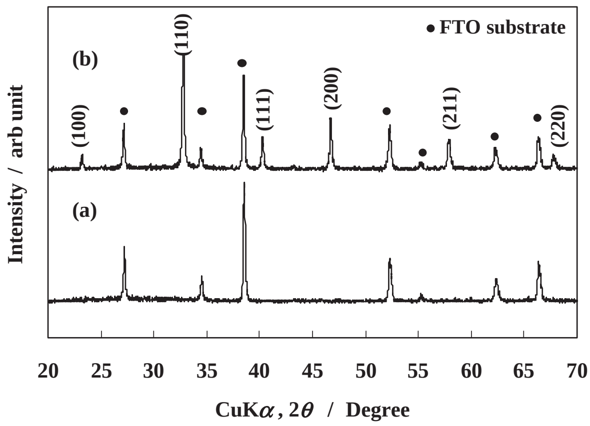

Figure 1. The representative XRD patterns of a) amorphous TiO_2 nanotubes and b) crystalline $SrTiO_3$ nanotubes.

Figure 1 shows XRD patterns of amorphous TiO_2 nanotube arrays on FTO and hydrothermally prepared $SrTiO_3$. No diffraction peaks of starting TiO_2 nanotubes were found (Figure 1a), indicating that the sample obtained by LPD is amorphous phase. Figure 1b shows the XRD pattern of crystalline $SrTiO_3$ nanotubes on FTO. The XRD patterns (Figure 1b) can well be indexed to cubic strontium titanate (JCPDS No. 73-0661). From the XRD results, it can be concluded that crystalline $SrTiO_3$ can be obtained through a simple hydrothermal process from amorphous TiO_2.

The morphologies of the resulting samples were investigated by scanning electron microscopy. Figure 2a shows an SEM image of oriented ZnO nanorod arrays (core material) grown on FTO substrate. A highly uniform and densely packed array of ZnO nanorods with an average diameter of ca. 50 nm and length of ca. 3 µm could be observed over the entire substrate. The morphology of the TiO_2 arrays obtained by LPD is shown in Figure 2b. According to our previous work,[15] the tube length of TiO_2 nanotubes could be controlled by changing length of ZnO nanorods and LPD reaction time.[15] The morphology of crystalline $SrTiO_3$ obtained by hydrothermal treatment is shown in Figure 3a. After hydrothermal treatment, the resulting sample retained their nanotube shape perpendicular to the substrate. However, some broken nanotubes, which believed to be broken during the sample cutting step, could be observed. The microstructure of the sample was further investigated by transmission electron microscopy (TEM). Figure 3b shows the TEM image of crystalline $SrTiO_3$. Obviously, crystalline $SrTiO_3$ nanotubes were composed of nanosized primary particulates of several nanometers in size. The nanotubes have an outer diameter of

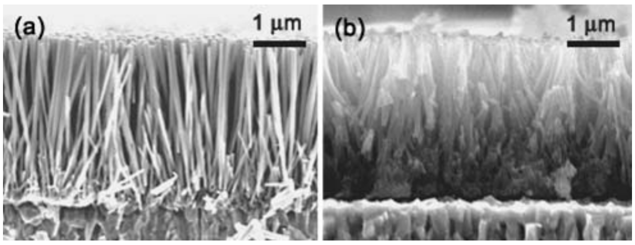

Figure 2. SEM images of a) ZnO nanorod arrays and b) amorphous TiO_2 nanotube arrays.

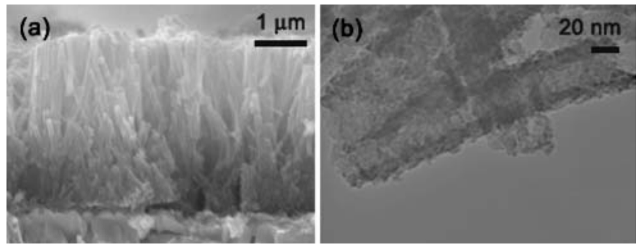

Figure 3. a) SEM and b) TEM images of crystalline $SrTiO_3$ nanotube arrays prepared by hydrothermal method.

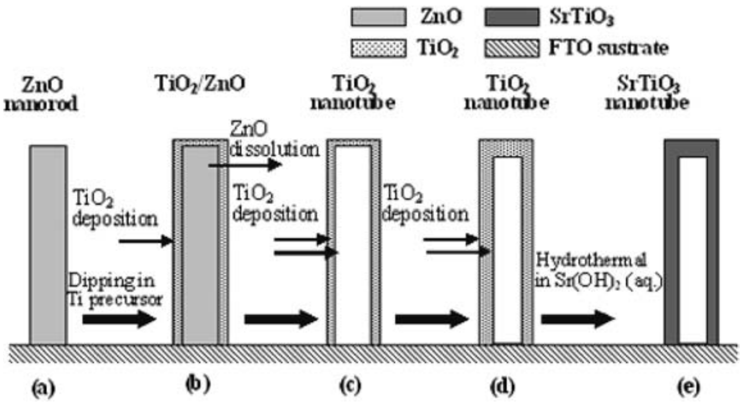

Figure 4. Schematic diagram of the formation process of crystalline $SrTiO_3$ nanotube arrays.

ca. 54 nm and a wall thickness of ca. 10 nm.

Figure 4 schematiclly illustrates the formation of crystalline $SrTiO_3$ nanotube arrays. The aligned ZnO nanorods are first prepared on the FTO substrate by low-temperature hydrothermal process (Figure 4a) and the TiO_2 is then deposited on the ZnO nanorods by LPD process (Figures 4b, 4c, and 4d).[16] The crystalline $SrTiO_3$ are then synthesized from amorphous TiO_2 by hydrothermal method in the distilled water and strontium hydroxide solution (Figure 4e), respectively.

Generally, there are two kinds of mechanisms, which have been used to illustrate the hydrothermal synthesis of perovskite: (1) a dissolution–recrystallization mechanism and (2) an in situ transformation mechanism.[1,9] Very recently, Wang et al.[11] reported the formations of hydrothermally synthesized $SrTiO_3$ illustrated by a mechanism analogous to the Kirkendall effect. In this study, on the basis of characterization results, we believe that the formation of crystalline $SrTiO_3$ nanotube structure could be explained in term of Kirkendall effect according to Wang et al.[11]

The present study has demonstrated the fabrication method for the crystalline $SrTiO_3$ nanotube arrays. The method consists of three steps: (1) preparation of well-aligned ZnO nanorod arrays (core material), (2) preparation of TiO_2 nanotube arrays by LPD process, and (3) hydrothermal conversion of amorphous TiO_2 nanotube arrays into crystalline $SrTiO_3$ nanotube arrays. This study provides a new route for fabrication of crystalline $SrTiO_3$ nanotube arrays. This resulting $SrTiO_3$ nanotube arrays may find applications in the fields of catalysis, photoelectrics, and so forth. Furthermore, it is expected that the preparation procedure could also be applied to other one-dimensional nanostructured materials, such as $BaTiO_3$ and $PbTiO_3$, via a simple hydrothermal process.

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