

## Electrochemical Deposition of Well-ordered Single-crystal PbTe Nanowire Arrays

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Thermoelectric PbTe nanowire arrays have successfully been fabricated by dc electrodeposition in conjunction with porous anodic alumina templates prepared via a two-step anodization process. X-ray diffraction, high-resolution transmission electron microscopy, and selected-area electron diffraction results indicate that the as-deposited samples are single crystal with a NaCl-type structure. The morphology and the structure of PbTe nanowires have been investigated using scanning electron microscopy and transmission electron microscopy. The results show that the PbTe nanowire arrays have a high-filling rate and in large area are dense and continuous.

In recent years, quasi-one-dimensional nanomaterials, such as nanowires or nanotubes, have attracted much attention owing to their novel physical properties and potential applications in various areas, such as materials science, electronics, optics, magnetics, and energy storage.<sup>1-4</sup> Much effort has been made to fabricate one-dimensional nanomaterials using a variety of nanofabrication techniques and crystal growth methods.<sup>5-7</sup> Among various approaches to preparing nanowires, much attention has been paid to the anodic alumina membrane (AAM)-based fabrication in conjunction with electrochemical deposition.<sup>8,9</sup> Since the AAM template has several unique structural properties, such as controllable diameters, extremely narrow size distribution of pore diameters and their intervals, and the ideally cylindrical shape of pores. Thus, the AAM templates have been used to fabricate highly ordered nanowires arrays.

Lead telluride, an intermediate thermoelectric power generator, has attracted a considerable interest.<sup>10-13</sup> Having widely been used in commercial and military purposes, the bulk PbTe has a high melting point, a good chemical stability, and a high figure of merit. Investigations on PbTe have mainly been focused on the films, but few interests have been put on the studies of PbTe nanowires<sup>12</sup> to date. Theoretical studies, however, have shown that thermoelectric nanoscaled materials will have a high figure of merit in comparison with the corresponding bulk materials,<sup>14,15</sup> which is verified by Vankatasubramanian et al.<sup>16</sup> in Bi<sub>2</sub>Te<sub>3</sub> films. Therefore, it is worth trying to prepare high-quality and single-crystal PbTe nanowire arrays. On the other hand, electrodeposition of PbTe nanowires is still a challenge because of a negative electrode potential for Pb<sup>2+</sup>/Pb. In this paper, large-area, high-filling, ordered, and single-crystal PbTe nanowire arrays with a high aspect ratio have successfully been prepared using electrochemical deposition into the nanoholes of the AAM.

The AAM used in this work was prepared in a two-step anodization process as described in the literature.<sup>17,18</sup> After the second anodization, the central part of the remaining aluminum was etched off in 1 M CuCl<sub>2</sub> solution. The alumina barrier layer was then dissolved, and pores were widened using

5 wt % H<sub>3</sub>PO<sub>4</sub> solution at room temperature for 1–2 h. After that, a Au layer was sputtered onto one side of the through-hole AAM template to serve as the working electrode. Electrodeposition was performed in a conventional two-electrode electrochemical cell using a graphite plate as the counter electrode. The electrolyte solution consisted of 0.05 M Pb(AC)<sub>2</sub> and 0.05 M HTeO<sub>2</sub><sup>+</sup> originating from the reaction of Te powder to 5 M HNO<sub>3</sub>. The pH of the solution was adjusted to 1 by adding 1 M HNO<sub>3</sub> solution, which would keep Pb<sup>2+</sup> and HTeO<sub>2</sub><sup>+</sup> stable in aqueous solution. And the sparse concentration would decrease electrodeposition rate, so the crystallization would be fine. Before electrodeposition, the AAM template was immersed in the electrolyte solution and evacuated using a pump to release the bubbles within the nanoholes. PbTe nanowires were electrochemically deposited at room temperature for 2 h under a constant current density of 2.0 mA/cm<sup>2</sup>, which was strictly controlled by a potentiostat/galvanostat (HDV-7C). After deposition, the AAM template with PbTe nanowires was rinsed with absolute ethanol and then dried in air at room temperature.

X-ray diffraction (XRD) of the as-deposited sample was performed on an X-ray diffractometer (D/MAX- $\gamma$ A) with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) in the range of  $10^\circ \leq \theta \leq 70^\circ$ . The morphologies of the as-prepared AAM template and the PbTe nanowire arrays were observed using a field emission scanning electron microscope (FE-SEM, JSM-6700F) and a transmission electron microscope (TEM, H-800). A high-resolution transmission microscope (HRTEM, JEOL-2010) and an electron diffractometer (ED) attached to the HRTEM were employed to characterize the crystal structure of the nanowires.

XRD pattern of the as-prepared sample is shown in Figure 1. It can be seen from Figure 1 that all the peaks can be indexed to the face-centered cubic (fcc) PbTe with a lattice constant of  $a = 0.6461$  nm in good agreement with the JCPDS data (770246). The intensity for the (222) is much higher than the others, which indicates that the PbTe nanowires have a preferred orientation along the [111] direction. It is confirmed by the HRTEM observation. No diffraction peaks from the elemental Pb and Te are detected.

The surface morphology and the structure of the as-prepared

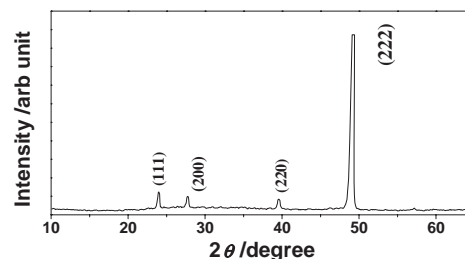
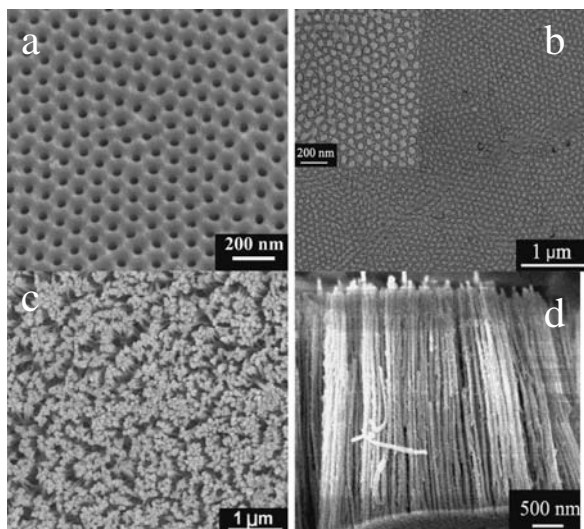
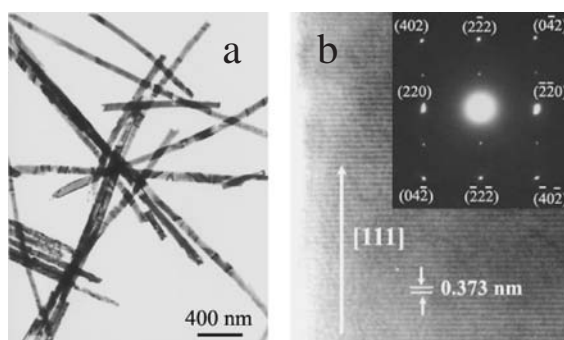


Figure 1. XRD pattern of PbTe nanowire arrays.



**Figure 2.** SEM photographs of AAM template and PbTe nanowire arrays. (a) A typical SEM photograph of AAM, (b) and (c) the top views of the nanowires array, (d) the cross section of nanowires array.



**Figure 3.** TEM image of PbTe nanowires.

AAM template and the PbTe nanowires array are displayed in Figure 2. Figure 2a reveals that the AAM template has highly ordered pores with a diameter of about 60 nm and an interpore distance of around 70 nm. Figures 2b and 2c are the surface views of the PbTe nanowire arrays after etching in 1 M NaOH solution for different times (Figure 2b: 3 min; Figure 2c: 10 min). Apparently, almost every pore is filled with a nanowire, and the exposed parts of the nanowires increase as the etching lasts longer. Figure 2d is the cross-sectional view of the PbTe nanowire array with a length as long as several micrometers.

A typical TEM image of the PbTe nanowires and a typical HRTEM image of a single PbTe nanowire are presented in Figure 3. A large amount of nanowires has smooth and clean surfaces, and a high aspect ratio can be seen in Figure 3a. The nanowires are dense and uniform with a diameter of about 60 nm consistent with the nanochannels of the AAM template used. The HRTEM lattice fringes of a single PbTe nanowire

are displayed in Figure 3b, and the inset in Figure 3b is the corresponding ED pattern. The diffraction spots in the ED pattern are attributed to the single-crystal fcc PbTe. It can be seen from Figure 3b that the lattice fringes are parallel to each other and perpendicular to the axis of the nanowires. The interplanar spacing between two neighboring fringes is about 0.37 nm in good agreement with the interplanar distance of the (222) planes ( $d = 0.373$  nm) of the fcc PbTe. The HRTEM and ED results show that the PbTe nanowires are single crystals. The energy dispersive spectrometer (EDS) reveals that the nanowires consist of Pb and Te elements and that their chemical composition is close to the stoichiometric PbTe (Pb:Te = 1:1).

In conclusion, high-filling, uniform, and single-crystal PbTe nanowires arrays have been prepared via the AAM template-assisted dc electrodeposition technique at room temperature. The optimum conditions for fabricating high-filling, uniform, and single-crystal PbTe nanowires arrays are discussed. If we understand the electrochemical deposition process well, it will help us fabricate other metal, semimetal, or semiconductor single-crystal nanowire arrays using the same technique.

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