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Full Length Article

# High thermoelectric properties of (Sb, Bi)$_2$Te$_3$ nanowire arrays by tilt-structure engineering

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ABSTRACT

In this paper, we present an innovative tilt-structure design concept for (Sb, Bi)$_2$Te$_3$ nanowire array assembled by high-quality nanowires with well oriented growth, utilizing a simple vacuum thermal evaporation technique. The unusual tilt-structure (Sb, Bi)$_2$Te$_3$ nanowire array with a tilted angle of 45° exhibits a high thermoelectric dimensionless figure-of-merit $ZT = 1.72$ at room temperature. The relatively high $ZT$ value in contrast to that of previously reported (Sb, Bi)$_2$Te$_3$ materials and the vertical (Sb, Bi)$_2$Te$_3$ nanowire arrays evidently reveals the crucial role of the unique tilt-structure in favorably influencing carrier and phonon transport properties, resulting in a significantly improved $ZT$ value. The transport mechanism of such tilt-structure is proposed and investigated. This method opens a new approach to optimize nano-structure in thin films for next-generation thermoelectric materials and devices.

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## 1. Introduction

Owing to the increasing concern on the global energy crisis, the thermoelectric (TE) technology has been paid much attention in recent years as an alternative energy source to reduce the conventional oil and fossil-fuel consumption. The ability of a TE material to convert heat into electricity is determined by the figure-of-merit $ZT = (S^2\sigma/\kappa)T$, where $S$, $\sigma$, $\kappa$ and $T$ are Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively [1–5]. There exists a strong coupling of TE parameters $\kappa$, $\sigma$ and $S$. Many research efforts to overcome the conventional $\sigma$-$S$ and $\kappa$-$\sigma$ trade-off have been made in attempts to obtain a high $ZT$ value during recent years [6–9]. Theoretical and experimental analyses have shown that the low-dimensional structure can significantly optimize the transport properties of electrons and phonons, which are to break through the limitation of the electron-phonon coupling and provide an effective pathway past a low-dimensional structure material, such as, the record high efficiency of 2.4 was reported for the Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice, and a $ZT$ value of 3 was also reported for the PbSeTe/PbTe quantum dot superlattice. However, One-dimensional nanowires (NWs) are predicted to exhibit a better TE property than superlattices [10–12].

Bi-Sb-Te materials are the best TE materials near room temperature, which are anisotropic with a layered structure. Their thermal and electrical conductivities along the $a$-axis (in the $c$-plane) are approximately two and four times higher, respectively, than those along the c-axis of Bi$_2$Te$_3$-based materials. But Seebeck coefficients are less dependent on the crystallography [13–16]. Therefore, an improved $ZT$ value can be expected when utilizing anisotropic thermal and electrical transport properties. Our previous results show that the Sb$_2$Te$_3$ pillar array structure can selectively scatter phonon more than carrier, resulting in an improved in-plane $ZT$ value [17]. In addition, we also find that unique NW array structuring can induce a change of the Fermi level of the Bi$_2$(Te, Se)$_3$ and favorably influence the carrier and phonon transport properties, thus dramatically enhancing an in-plane $ZT$ result [18]. The previous studies have witnessed the feasibility of controlling novel microstructures to modify TE properties of Sb$_2$Te$_3$ and Bi$_2$Te$_3$-based alloys. However, it is noted that the Sb$_2$Te$_3$ pillar array and the Bi$_2$(Te, Se)$_3$ NW array are grown perpendicular to the substrates and possess relatively high densities of interspaces, which degrade the in-plane thermopower to some extent. Sun and Stranz reported that a wafer-scale vertical nanopillar arrays or NW arrays can be realized by lithography and anisotropic etching for improving the performance of TE cross-plane devices as proposed recently [19,20]. But it is hardly to overcome a problem of carrier and

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phonon transport along the in-plane direction and measure cross-plane TE properties for vertical nanopillar arrays or NW arrays films. These adverse factors need to be further improved in films, enabling films to show better in-plane properties. Some vertically aligned nanowire arrays or nanopillar arrays have been synthesized by the electrochemical deposition with templates or the anisotropic etching and lithography method, however, this kind of NW array with tilt-structure has never been reported, let alone the TE (Sb, $Bi)_2Te_3$ material. This motivates us to further explore the effect of tilt-structure on the (Sb, $Bi)_2Te_3$ NW array.

Hence, in this work, we aim to control the tilt-angle of (Sb, $Bi)_2Te_3$ NW array based on the construction of one-dimensional NWs. A simple thermal evaporation technique was carried out, to our best knowledge, for the first time on the tilt-growth of (Sb, $Bi)_2Te_3$ NW arrays. The unusual structure (Sb, $Bi)_2Te_3$ NW array with a tilted angle of 45° exhibits a greatly high in-plane $ZT = 1.72$ at room temperature. It is believed that the interrelationship between the tilt-structure and the properties of films uncovered by this work may help to better understand unique tilt structuring of this kind of material. Furthermore, it provides a new avenue to control the structural configuration of materials with possible relevance to improvement of their properties. It is also convenient to further fabricate cross-plane or in-plane devices by integrating the (Sb, $Bi)_2Te_3$ NW array with tilted structure using the anisotropic etching or lithography method or mask-assisted deposition technology.

## 2. Experimental section

In this work, in order to successfully grow the tilted and the vertical (Sb, $Bi)_2Te_3$ NW arrays on $SiO_2$ glass substrates by the thermal evaporation technique, the corresponding angles between the substrate holder plane and the horizontal plane are supposed to be about 45°, 30° and 0°, respectively. The compensation for Te deficiency and doping Bi element are expected to improve the transport properties in the (Sb, $Bi)_2Te_3$ films. The high purity (99.99%) $Sb_2Te_3$, Te and Bi powders (The mass rate of $Sb_2Te_3$:Te:Bi is 10:1:1) were mounted on the evaporating dish which is connected to the alternating current power supplies, and the evaporated current was 165A for all NW arrays. Before deposition, the common glass substrate was first cleaned by diluted nitric acid, and then acetone, and dried under the nitrogen gas flow. After the substrate was loaded onto the substrate holder, $N_2$ gas was introduced into the chamber and vacuumized three times to remove oxygen. The deposition temperature was set at 250 °C, the working pressure was maintained at $2 \times 10^{-6}$ Torr in the deposition process for the films. All TE films were grown to thickness of 1.5 μm by adjusting the deposition rate and deposition time in our experiments.

The crystal structure characterizations for the NW arrays were measured using X-ray diffraction (XRD, Rigaku D/MAX 2200) with Cu Kα radiation ($\lambda = 0.154056$ nm). The morphology and composition of the samples were investigated using a field emission scanning electron microscope (FE-SEM, Sirion 200) equipped with an energy dispersive X-ray spectroscope (EDX). Further structural analyses were performed using high-resolution transmission electron microscopy (HRTEM, FEI Company, Tecnai G2 F20S-Twin FEG TEM at 200 kV). Surface profilometry (Ambios XP-2, USA) was used to measure the film thickness. Electrical conductivity and Seebeck coefficient of the films were examined using a ZEM-3 (Ulvac Riko, Inc.) with a self-made test holder for film measurement in the in-plane direction. The in-plane thermal conductivity data was collected using a Laser PIT (Ulvac Riko, Inc.) at room temperature. The principle of the measurement method is described in detail in Ref. [21]. The carrier concentration and mobility were determined using a four-probe measurement based on the Hall effects (ECOPIA HMS-3000) at room temperature. All tests for transport properties were repeated at least 5 times. The errors are 4% for electrical conductivities, 5% for Seebeck coefficients, 5% for thermal conductivities, and 10% for *ZT* values.

## 3. Results and discussion

The morphologies of the (Sb, $Bi)_2Te_3$ NW arrays were studied by SEM, respectively. The SEM images (Fig. 1a and b) reveal that the (Sb, $Bi)_2Te_3$ NW array with a tilted angle of 45° has been perfectly prepared by a simple thermal evaporation technique. Seen from the cross-sectional image of the tilted film (Fig. 1a), a large number of (Sb, $Bi)_2Te_3$ NWs are densely grown tilted to the substrate, along their oriented growth direction. It clearly shows that the angle between the radial direction of NW and the substrate plane is about 45°. The diameters of tilt-growth NWs are estimated to be <20 nm, implying a large number of unique interfaces in the NW array. Some interspaces between NWs are found, but the adjacent NWs have been tilted and interconnected closely to give a very good contact each other, guaranteeing carriers transport in the in-plane direction of the film. Seen from the top view (Fig. 1b), the sizes of NWs are uniform in the tilt-structure film, which is composed of NW array based on the construction of one-dimensional NWs. By controlling growth parameter, NW arrays microstructures have obviously changed as shown in Fig. 1. With the angle between the substrate plane and the horizontal plane reduces to about 30°, the (Sb, $Bi)_2Te_3$ NW with a tilted angle of 60° has been successfully fabricated (Fig. 1c and d). From Fig. 1c, we note that numerous NWs are tilted growth on the substrate and the angle between the radial direction of NW and the substrate plane is approximately 60°. Seen from the surface SEM image (Fig. 1d), some nano-scaled open gaps between NWs can be found in the NW array. When the angle between the substrate plane and the horizontal plane is about 0°, that is, the substrate plane approximatively parallels to the horizontal plane. The NW array is uniformly grown perpendicular to the substrate, which exhibits that the angle between the radial direction of vertical NWs and the substrate plane is about 90° (Fig. 1e and f). This phenomenon is the same to the reported result for the vertically aligned $Bi_2(Te, Se)_3$ NW array [18].

In order to gain insight into the crystal structure, NW arrays were examined by XRD. Fig. 2 presents XRD patterns of all (Sb, $Bi)_2Te_3$ NW arrays. As shown in Fig. 2, a single $Sb_2Te_3$ phase, consistent with the standard card (JCPDS 71-0393) of the $Sb_2Te_3$, was obtained in NW arrays samples, implying Bi atoms enter into Sb vacancies or formation of other defects. A preferential orientation (0 1 5) peak (located at $2\theta = 28.13°$) was mainly observed in these NW arrays. Compared with the standard card, the major (0 1 5) diffraction peaks of (Sb, $Bi)_2Te_3$ films have slightly shifted toward lower angle. It seems reasonable to assume that the large Bi atom replacing Sb atom causes the lattice to expand. The intensity of (0 0 1 5) texture of the NW array with a tilted angle of 45° is dramatically strong. With increasing the tilted angle, the (0 0 1 5) peak becomes weak, while the intensity of (1 0 1 0) peak becomes strong in the NW array with a tilted angle of 60°. When the angle becomes large to 90°, the intensity of (1 0 1 0) peak of the NW array becomes greatly strong and the (0 0 1 5) peak is disappeared. This seems to indicate that the tilt-growth is associated with the (0 0 1 5) and (1 0 1 0) peaks of NW arrays. The atom lateral mobility increase on the surface due to a decrease in the angle between the deposition direction and the substrate plane may be responsible for the structure change. The growing grains can be sufficiently mobile to migrate to the preferred sites for crystallization growth.

The microstructure details of the special NW array with a tilted angle of 45° are observed in TEM and HRTEM images, as depicted in Fig. 3. A microstructure of (Sb, $Bi)_2Te_3$ NWs varies continuously

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