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Strain-engineered allotrope-like bismuth nanowires for enhanced thermoelectric performance

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ABSTRACT

Allotropy is a fundamental concept that has been frequently studied since the mid-1800s. Although the bulk allotropy of elemental solids is fairly well understood, it remains challenging to reliably produce an allotrope at the nanoscale that has a different crystal structure and accompanies a change in physical properties for specific applications. Here, we demonstrate a "heterostructure" approach to produce allotrope-like bismuth nanowires, where it utilizes the lattice constant difference between bismuth and tellurium in core/shell structure. We find that the resultant strain of [100]-grown Bi nanowires increases the atomic linear density along the c-axis that has been predicted from theoretical considerations, enabling us to establish a design rule for strain-induced allotropic transformation. With our >400-nm-diameter nanowires, we measure a thermoelectric figure of merit ZT of 0.5 at room temperature with reduced thermal conductivity and enhanced Seebeck coefficient, which are primarily a result of the rough interface and the reduced band overlap according to our density-functional calculations.
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1. Introduction

Allotropy is the property of atoms or molecules in more than two different structural form, but with one physical state, which exhibits different chemical and physical behaviors. Although the bulk allotropy of elemental solids is fairly well understood, it remains challenging to reliably produce an allotrope that has a different crystal structure, and thus accompanies a change in physical properties. This difficulty of producing allotropes in bulk materials also extends to the low-dimensional materials, such as nanowire, where even local strain can significantly alter nanometer-scale crystal symmetry. In the context of crystal symmetry, bismuth nanowires possess an interesting crystal anisotropy that have a highly elongated crystal structure along the c-axis, which is directly associated with its anisotropic electrical properties [1,2]. In principle, the allotropic transformation from a rhombohedral to a near-cubic structure in bismuth has been predicted to occur under a high-pressure environment, which may potentially provide the ability to control and modulate the electronic band structure [3,4]. This effect can reduce the band overlap without the size reduction that causes unwanted surface states, a reduced mean free path, and an effective mass increase [5–8]. However, the high-pressure environment for strain-induced allotropic transformation practically limits the use of the allotropic forms of bismuth. Here, we demonstrate a “heterostructure” approach that utilizes the lattice constant difference between bismuth (Bi) and tellurium (Te) in core/shell (C/S) nanowires to produce allotrope-like Bi. We find that the resultant strain of [100]-grown Bi nanowires increases the atomic linear density along the c-axis that has been predicted from theoretical considerations, enabling us to establish a design rule for strain-induced allotropic transformation. In our Bi/Te C/S nanowires, thermoelectric figure of merit *ZT* is estimated to be 0.5 at room temperature with reduced thermal conductivity κ and

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enhanced Seebeck coefficient *S*, which are primarily a result of the rough interface and the reduced band overlap according to our density-functional calculations.

Owing to the highly anisotropic Fermi surface, long mean free path, and small effective mass, significant efforts have been placed on the study of unique properties of bulk Bi [1–12]. Individual nanowires have been proposed for investigating the fundamental physics as well as the potential applications of semimetal Bi using conventional nanoscale devices. Nanowire devices have been fabricated and tested to realize the potential uses of Bi using different nanowire growth means such anodic alumina templates [5,9], Ulitovsky [10], or on-film formation of nanowires (OFFON) [8,11] methods. These efforts have provided data supporting the importance of nearly defect-free high crystal quality and highly transparent electrical contacts. Because these prerequisites, which are central to studying the intrinsic behavior of charged carriers in Bi, have only been recently addressed experimentally, the realization of the unique capabilities of Bi such as thermoelectricity have been delayed [5,8–10,12].

While taking advantage of the large Bohr radius of Bi, the quantum size effects approach barely addresses the long-standing goal of creating a 'band gap', and then turns Bi into a semiconductor for potentially designing Bi-nanowire-based electronics and thermoelectrics. When the nanowire size is decreased, this limitation is hardly circumvented because of the additional surface states and the shorter mean free path [5]. Therefore, a new route for band engineering should be considered, where the size is not compromised to avoid surface state effects and to preserve a sufficient mean free path. However, few studies have succeeded in band engineering Bi nanowires without utilizing quantum size effects [13,14]. Here, we report an approach to band engineering in Bi nanowires by controlling the crystal anisotropy in the context of a lattice-mismatched heterostructure, where Te shells are incorporated onto the Bi core structures. The compressive strain associated with the different lattice constants between the Bi core and Te shell yield a reduction in the unit cell length along the trigonal axis of the Bi core (i.e., transition from rhombohedral to near-cubic structure) such that we can reduce the crystal anisotropy and thus the energy band overlap. Owing to the reduced band overlap, the thermoelectric figure of merit, *ZT*, is found to be 0.5 for the Bi/Te C/S nanowire.

2. Experimental

2.1. Sample preparations

The Bi core of Bi/Te C/S nanowires was fabricated using OFFON [11]. Bi thin films were deposited on an oxidized Si substrate using a custom-made radio-frequency (RF) sputtering system, which was evacuated to 10^{-7} Torr prior to deposition, and the vacuum was maintained during sputtering under a 2-mTorr Ar environment. The deposition of the Bi thin films was performed at 300 K with a growth rate of 44 Å/s. To grow Bi nanowires, the Bi thin films were subsequently placed in a custom-made vacuum furnace for thermal treatment. The annealing process was performed in a vacuum of 10^{-7} Torr at 250 °C for 5–10 h. The Te shell was deposited on the as-grown Bi nanowires on the substrate by RF sputtering [15]. All processes were performed in situ in a high vacuum environment to prevent oxidation.

2.2. Microstructure investigations

Structural characterization and strain analysis were performed using a transmission electron microscope (FE-TEM JEM-2100F JEOL). The Bi/Te C/S nanowires were sliced perpendicular to the growth direction by a focused ion beam (FEI Quanta 3D FEG system) for the TEM analysis.

2.3. Transport measurements

For measuring the electrical transport properties, thermoelectric devices based on an individual Bi/Te C/S nanowire were fabricated using typical electron-beam lithography (JSM-7001F JEOL and ELPHY Quantum Raith) and metallization (custom-made DC sputtering system) as shown in Fig. S1. To obtain electrical contact between the Bi core and the electrodes, the Te shell was removed using Ar plasma, followed by a Cr (5 nm)/Au (250 nm) metallization. The electrical conductivity and Seebeck coefficient were measured by nano-voltmeter (2182A KEITHLEY) and a lock-in amplifier (SR850 Stanford Research Systems), respectively. The details of the device fabrication and measurement technique have been described in Ref. [8]. For thermal conductivity measurements of nanowires, an individual Bi/Te C/S nanowire was transferred onto the two suspended membranes (silicon nitride) of the microdevice using a micro-manipulator. The two suspended membranes played a role of hot and cold junctions, respectively, which were connected by the nanowire as shown in Fig. S2. Thermal contacts between the nanowires and membranes were formed by Pt layers, which were deposited for three minutes using a FIB (FEI Quanta 3D FEG system, 2 kV/67 pA). Following the Fourier law, the thermal conductance of the nanowire was measured in a steady state of heat flow before and after removal of the nanowire. The thermal conductivity was calculated from the thermal conductance using the length and cross-sectional area of the nanowires. The detailed procedure of thermal conductivity measurement cab be found in the previous report [16,17].

2.4. DFT and BTE calculations

The band structure of Bi with strain was calculated using first-principles calculations within the density functional theorem. The anisotropic strain was applied to each c and a-axis, resembling experimental observation. We used the Vienna ab initio simulation package (VASP) [18,19] to perform total-energy calculation and structural optimization. Projector augmented-wave pseudopotentials were used [20]. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) was employed to describe the exchange and correlation [21]. A cutoff value of 350 eV and gamma centered k-mesh of $11 \times 11 \times 11$ in the Bi primitive cell were used to ensure better than 1 meV convergence of the total energy better. Internal atomic positions were relaxed with a conjugated gradient routine in which the forces were within 0.01 eV/Å for each atom. The spin-orbit interaction (SOI) was incorporated in all calculations. The Seebeck coefficient and electrical conductivity were estimated by solving the Boltzmann transport equation (BTE) implemented in the BoltzTraP code [22] in which the rigid band approach was used. The dense k-mesh of $41 \times 41 \times 41$ was used to obtain the converged transport properties. Eigenenergies of the electronic structures without and with strain were utilized to obtain the transport properties. The relaxation time was assumed to be constant in the considered doping range. The Seebeck coefficient can be obtained without any fitting parameter from the electronic structure and BTE within the constant relaxation time approximation, whereas the calculated electrical conductivity was fitted to the experimental conductivity to estimate the value of the relaxation time. This approach proves to be good approximation (Supplementary data) [23,24].

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