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Decoupling of thermal and electrical conductivities by adjusting the anisotropic nature in tungsten diselenide causing significant enhancement in thermoelectric performance

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ABSTRACT

A polycrystalline WSe_2 nanocompound was produced via a brief thermal reaction between the atomic elements. It should grow along the in-plane direction with covalent bonds rather than along the through-plane direction with van der Waals forces, leading to both crystallographic and morphological anisotropies. Not only the anisotropies should structurally induce strong phonon scattering but they alleviate possible electron scattering at the van der Waals forces; thus, we greatly reduced thermal conductivity while minimizing electrical conductivity loss. The decoupled conductivities resulted in enhancement in figure of merit, by approximately 70% at 350 °C, thus affording a promising material for mid-temperature thermoelectric operations.

Introduction

Tungsten diselenide (WSe_2) is one of the most investigated compounds among transition metal dichalcogenide families with MX_2 formula (M = transition metal, Mo and W; X = chalcogen, S and Se) because it shows various distinctive material properties [1–12]. For example, because of the outstanding chemical and physical properties of WSe_2, it has been often used as a solid lubricant [13–15]. In addition, WSe_2 is known to have a small bandgap energy (i.e., ~1.35 eV) that enables it to be applied to electrodes in photovoltaic devices or photoelectrochemical cells [16–25]. Recently, researchers have investigated the application of WSe_2 as a thermoelectric material [26–28]. The comprehensive performance of such materials is evaluated via the dimensionless figure of merit Z ($=\alpha^2\sigma/\kappa$), where α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity [26–30]. To obtain an excellent thermoelectric material, a high ZT value should be achieved through low thermal conductivity (κ) as well as high electrical conductivity (σ), indicative of phonon glass electron crystal (PGEC) characteristic [26–29]. Researchers have developed single crystalline WSe_2 compounds (bulk phase) because they exhibit low thermal conductivity along the through-plane direction, which results from the typical anisotropic nature in WSe_2. WSe_2 generally has a chemical structure in which the atoms are connected by covalent bonds along the in-plane direction while the atoms interacted via van der Waals forces along the through-plane direction [31–35]. This structural anisotropy results in the anisotropic thermal transport phenomenon, in which thermal conductivity is much smaller along the through-plane direction than along the in-plane direction because of the possible phonon scattering at the van der Waals interactions [36–38]. Recently, some researchers attempted to randomly stack two-dimensional crystalline WSe_2 sheets along the through-plane direction, and thus they obtained the in-plane ordered and through-plane disordered WSe_2 films, showing a remarkable anisotropic property; the disordered structures induced great phonon localization, which resulted in much lower thermal conductivity along the through-plane direction than along the in-plane direction [39,40]. This through-plane thermal conductivity is the lowest one ever reported for a dense solid to this date. However, the electrical conductivity should also decrease along the through-plane direction because of these obvious anisotropic characteristics; such a reduction can seriously decrease thermoelectric performance, as captured by the figure of merit, Z ($=\alpha^2\sigma/\kappa$). Most researchers have focused on decreasing the

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thermal conductivity by utilizing the anisotropic characteristics without considering the possible serious loss in electrical conductivity caused by the anisotropy.

We endeavored to decouple the thermal and electrical conductivities by developing polycrystalline WSe_2 and consider its morphology to obtain a promising thermoelectric material. A polycrystalline WSe_2 nanocompound was prepared via a thermal reaction between tungsten and selenium and then was packed by using spark plasma sintering equipment. The nanocompound should grow preferentially along the in-plane direction with covalent bonds instead of along the through-plane direction with van der Waals forces during the sintering process, leading to crystallographic anisotropy in a polycrystalline bulk specimen. However, the specimen showed much lower degree of crystallographic anisotropy than that of single crystalline WSe_2. This finding indicates that the specimen has fewer van der Waals interactions along the through-plane direction, thereby considerably reducing the loss in electrical conductivity along this direction caused by possible interruption for electron transport at the van der Waals interfaces. The growth behavior of the nanocompound should also give rise to different morphological aspects in the specimen along the directions, in which many thin layers were observed along the through-plane direction and irregularly shaped grains were found along the in-plane direction. Because of the lower degree of crystallographic anisotropy, the specimen was not expected to have great phonon scattering because of the van der Waals interaction along the through-plane direction, as expected in single crystalline WSe_2. However, phonons should scatter at the thin layers when they transport along the through-plane direction; as a result, we attained a significantly low thermal conductivity along this direction. We confirmed that the Seebeck coefficient (α) showed no considerable change when we dealt with the specimen's anisotropic nature. The decoupling of the conductivities should result in the great enhancement in the figure of merit.

Experimental section

Reagents

Tungsten (powder, Kojundo Chemical, 99.99%, 2–4 μm) and selenium elements (powder, Kojundo Chemical, 99.9%, 75 μm) served as the raw materials. The elements were used without further purification.

Sample preparation

We mixed 120 mmol of tungsten with 240 mmol of selenium in an agate mortar by hand. The mixed elements were transferred into a cylindrical graphite mold (55 mm × 60 mm) with an inner hole of 15 mm in diameter to obtain a cylindrical pellet. The resulting pellet was thermally treated at 900 °C for 6 hours under an argon atmosphere to induce a reaction between the elements. This procedure produced a powder phase sample. We placed approximately 15 g of the powder product into the graphite mold for compaction at 1150 °C under a pressure of 50 MPa in an argon atmosphere using spark plasma sintering equipment (SPS, SPS-632Lx, Fuji Electronic Industrial Co.). The heating rate was ca. 100 °C min^{-1}, and the period during which the sample was maintained at this sintering temperature was 10 min. This process resulted in the production of a cylindrical sintered specimen (15 mm (w) × 20 mm (h)).

Characterizations

We characterized the powder product and the sintered specimen. To examine the anisotropic nature of WSe_2, we measured various properties of those faces of the sintered specimen both perpendicular and parallel to the SPS pressurizing direction. Field-emission scanning electron microscopy (FE-SEM) micrographs were obtained using an S-4800 Microscope (Hitachi). Powder X-ray diffraction (XRD) patterns were recorded using a D/MAX-2500 Diffractometer (Rigaku) using CuK_α radiation (λ = 1.5406 Å) and a scintillation counter detector; the relevant patterns were recorded over a 2θ range of 10–80°. The electrical conductivity (σ) and Seebeck coefficient (α) were measured simultaneously in the temperature range between 25 and 400 °C using a commercial instrument (ZEM-3, Ulvac-Rico). The Hall coefficient was measured with the van der Pauw method at room temperature using a Hall Effect measurement system (HMS-3000, Ecopia) to obtain the carrier concentration (n). Carrier mobility was calculated with the equation: $\mu = \sigma/(ne)$, where e is electric charge, 1.6×10^{-19}C. The thermal conductivity (κ) is related to the thermal diffusivity (λ) through the equation $\kappa = \lambda C_p d$, where d and C_p denote the physical density and specific heat of the sample, respectively. The thermal diffusivity was measured between 25 and 400 °C using a laser flash tool (LFA447, Netzsch). The density was determined by using the Archimedes immersion method. We measured the specific heat capacity using a differential scanning calorimeter (DSC200, Netzsch). We used these measured values to calculate the thermal conductivity through the equation given above. The carrier thermal conductivity (κ_c) was estimated using the Wiedemann–Franz law, $\kappa_c = L_0 \sigma T$, where L_0 and σ are the Lorenz number and the electrical conductivity, respectively. We used the Lorenz number of 1.5×10^{-8} WΩK^{-2} for a non-degenerate semiconductor [41]. Because the thermal conductivity can be approximately determined by summing the carrier thermal conductivity and lattice thermal conductivity (κ_l), the lattice contribution was also estimated. The figure of merit was calculated by the following equation: $Z = \alpha^2 \sigma/\kappa$.

Results and discussion

As explained in the Experimental section, a pellet was made using the mixture of tungsten and selenium elements, and then it was thermally treated at 900 °C for the desired reaction (see details in the Experimental section). At the high reaction temperature, selenium should actively evaporate in the reaction system; the resulting gaseous selenium was expected to diffuse to the neighboring tungsten grain, which is relatively stable at the reaction temperature. The gaseous selenium possibly reacted with tungsten atoms in the grain surface to form WSe_2 nuclei, which

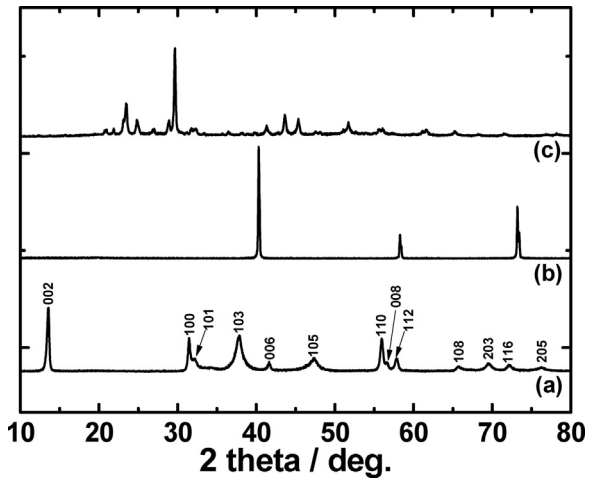

Fig. 1. XRD patterns of the product and raw elements: WSe_2 compound (a), tungsten (b), and selenium (c).

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