

Alternatingly Stacked Low- and High-Resistance PtSe₂/PtSe₂ Homostructures Boost Thermoelectric Power Factors

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2D transition-metal dichalcogenide (TMDC) materials are promising candidates with excellent thermoelectric (TE) properties owing to their low dimensionality in electronic and phonon transport. However, the considerable coupling of the Seebeck coefficient and electrical conductivity in such TE materials eventually results in the limit of the TE power factor increase, which severely hinders potential TE device applications. Herein, an alternative approach is demonstrated for breaking the strong coupling between the Seebeck coefficient and electrical conductivity in single TE materials by adopting a novel stacked PtSe₂/PtSe₂ homostructure. By alternately piling low-resistance (LR) PtSe₂ (3 nm) onto high-resistance (HR) PtSe₂ (2 nm) as one unit, the Seebeck coefficient and electrical conductivity of such stacked homostructures can be greatly enhanced with slightly improved electrical conductivity, ultimately resulting in a TE power factor in three-unit-stacked homostructures that is $\approx 1,648\%$ higher than that of a single PtSe₂ (15 nm) layer with the same thickness. This enhancement is attributed to an independent increase in the Seebeck coefficient, which depends on the interface among the LR and HR PtSe₂ layers. The findings pave the way for a method that, unlike power factor optimization in conventional thermoelectric materials, can only utilize the Seebeck coefficient and electrical conductivity of each layer in a stacked homostructure.

to apply them to irregular heat sources.^[4] Thus, 2D TE materials have been attracted in recent years. Among 2D TE materials, platinum diselenide (PtSe₂) has exhibited several excellent properties, such as a thickness-dependent energy band gap, high carrier mobility, high stability in ambient air, and high photoelectrical coupling; therefore, 2D PtSe₂ shows potential for application in field-effect transistors, photodetectors, gas sensors, spintronics, and thermoelectric devices.^[5–14] Since PtSe₂ has a typical layered structure and belongs to the D_{3d}⁵ (P3ml) space group, the molecular layer of PtSe₂ is composed of three atomic layers of Se-Pt-Se, i.e., the Pt layer is sandwiched between two Se layers.^[15,16] In addition, their electronic band structure is quite sensitive to the number of layers in atomic scale.^[17–20] For instance, monolayer PtSe₂ is a semiconductor with a band gap of 1.2 eV that is converted into a semimetal in the bulk state with increasing thickness up to three layers in the resultant of the theoretical calculation.^[20] With

thickness-modulated band engineering, i.e., the semimetal-to-semiconductor transition in an ultrathin bilayer of PtSe₂ via conventional semiconducting gating modulation, Moon et al. observed extremely high thermopower values of $\approx 1 \text{ mV K}^{-1}$.^[14] Moreover, the electrical and TE properties of 2D PtSe₂ materials are summarized in Tables S1 and S2, respectively (Supporting Information). When we investigated these results, there has

1. Introduction

Various thermoelectric (TE) materials have been studied to convert the waste heat from the human body, microchips, and exhaust gas into useful electricity.^[1–3] In the case of state-of-the-art bulk TE materials, such as GeTe, Cu₂Se, PbTe, and SnSe, show high-performance but limited applications because it is difficult

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been little research on the TE performance, including the thermopower (i.e., Seebeck coefficient) and power factor, of large-area 2D TMDC materials. The TE efficiencies of semi-conducting materials can generally be characterized by the dimensionless figure of merit, $ZT = S^2\sigma T/(\kappa_p + \kappa_E)$, where S , σ , T , κ_p , and κ_E represent the Seebeck coefficient, electrical conductivity, absolute temperature, and lattice and electronic thermal conductivity, respectively.^[21–23] Thus, higher ZT values can be achieved by minimizing the lattice thermal conductivity by microstructure engineering to enhance phonon scattering in low-dimensional structures, as well as by obtaining intrinsically low lattice thermal conductivity of the materials.^[22,24–27]

Most studies in which high ZT values were obtained were focused on reducing lattice thermal conductivity via phonon scattering and defect engineering.^[28,29] For example, Zhou et al. reported hole-doped SnSe polycrystalline materials with $ZT = 3.1$ and an extremely low lattice thermal conductivity of $\approx 0.07 \text{ W m}^{-1} \text{ K}^{-1}$ at 783 K.^[29] However, there has been little research on the improvement of the power factor ($S^2\sigma$) in the TE materials without a trade-off relationship between the S and σ . This is mainly because of the inverse intrinsic coupling between the Seebeck coefficient and the electrical conductivity, i.e., an increase in one promotes a decrease in the other. Consequently, this generally makes it extremely difficult to substantially enhance the power factor. Thus, to ensure effective enhancement of the TE power factor and the overall TE performance, an alternative method is strongly desirable for breaking this trade-off in TE materials with two TE parameters.

In this study, we demonstrate an alternative approach to enhancing the TE Seebeck coefficient and the power factor, in which we adopt a stacked 2D PtSe₂/2D PtSe₂ homostructure to effectively decouple the Seebeck coefficient and electrical conductivity. By alternately stacking low-resistance (LR) PtSe₂ (3 nm) onto high-resistance (HR) PtSe₂ (2 nm) as one-unit ($N = 1$) on a sapphire substrate by wet-transfer stacking, we successfully overcame the strong coupling of the Seebeck coefficient and electrical conductivity in stacked LR-PtSe₂ (3 nm)/HR-PtSe₂ (2 nm) homostructures. Furthermore, we confirmed that the interface formed between the LR and HR-PtSe₂ homostructures plays a key role in increasing the power factor in stacked LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm) homostructures.

2. Results

2.1. Synthesis of PtSe₂ Films and Wet-Transfer Process

Figure 1a shows the schematics for the synthesis of PtSe₂ and the wet-transfer process of the samples on sapphire substrates. In the vertically stacked LR-PtSe₂/HR-PtSe₂ homostructures, each unit ($N = 1$) of the alternately stacked PtSe₂ homostructure consisted of two single PtSe₂ layers (2-nm and 3-nm layers). The 2-nm-thick PtSe₂, referred to as HR-PtSe₂, has a resistance greater than 10 M Ω inhibiting its detection of Seebeck coefficient due to the disturbance of heat carriers from the hot side to the cold side. Whereas the 3-nm-thick PtSe₂, referred to as LR-PtSe₂, has a lower resistance that allows the sample to be detected. One-unit ($N = 1$) was defined as one LR-PtSe₂ layer piled on top of one HR-PtSe₂ layer in a stacked LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm) homostructure. The thickness of the PtSe₂ layer was controlled

by varying the deposition time of the sputtered Pt thin film on the SiO₂/Si substrate. Then, the two well-controlled single PtSe₂ layers were alternately wet-transferred onto a sapphire substrate to obtain a vertically stacked LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm) homostructure comprising up to three units ($N = 3$) in a diluted HF solution.^[30] The growth and transfer procedure details are presented in the experimental section (Supporting Information). Figure 1b shows the schematic of the setup for measuring the in-plane Seebeck coefficient and electrical conductivity for single PtSe₂ layers and three-unit-stacked LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm) homostructures transferred onto sapphire substrates. In each unit ($N = 1$) of the PtSe₂ homostructure, LR-PtSe₂ and HR-PtSe₂ are separated by an interface and has different characteristics from the single PtSe₂ thin film with the same thickness. In Figure 1b, the Seebeck coefficient of the lower HR-PtSe₂ (2 nm) layer could not be measured because the internal resistance of this layer was too high ($>10 \text{ M}\Omega$), while that of the upper LR-PtSe₂ (3 nm) layer could be measured in a one-unit-stacked homostructure. As shown in the last image of Figure 1b, the LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm) homostructure was stacked up to three units ($N = 3$), and the Seebeck coefficients and electrical conductivities of these samples were measured. All TE measurements were performed using a homemade CAU system in a vacuum, as discussed in the experimental section (Supporting Information), and the measurement error was confirmed to be below 2% from our previous study.^[30]

2.2. Material Characterization of Single and Stacked PtSe₂/PtSe₂ Homostructures

To investigate the crystallographic characteristics of the single PtSe₂ films (thicknesses = 2, 3, and 15 nm) and alternately stacked LR-PtSe₂/HR-PtSe₂ homostructures, cross-sectional high-resolution transmission electron microscopy (HR-TEM) specimens were prepared by focused ion beam milling. The single HR-PtSe₂ (2 nm) and LR-PtSe₂ (3 nm) films represent large-area continuous uniformity and horizontally aligned configurations consisting of ≈ 3 and ≈ 5 2D layers, respectively (Figure S1, Supporting Information). On the other hand, the single 15-nm-thick PtSe₂ film possesses a relatively rough morphology caused by redirecting the 2D orientation in a vertical manner to relieve the strain along the grain boundaries.^[16,31] HR-TEM and Raman analyses (Figures S1 and S2, Supporting Information) revealed that pre-deposited Pt thin films were completely converted into single PtSe₂ 2D films by a simple selenization process in a low-pressure chemical vapor deposition (LPCVD) system. Representative HR-TEM images of one- and three-unit-stacked LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm) homostructures (Figure 2a–b and 2c–e) show alternately stacked LR-PtSe₂/HR-PtSe₂ homostructures with large-area continuous stacking morphologies and interface formation between the LR- and HR-PtSe₂ layers. The enlarged HR-TEM image of the three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructure (Figure 2e) shows that the LR-upper PtSe₂ (3 nm) layers exhibited a horizontally aligned van der Waals (vdW) structure comprising ≈ 5 layers, retaining the identical morphology and crystallography of the single LR-PtSe₂ film. The d-spacing of $\approx 0.54 \text{ nm}$ was consistent with the (002) interplanar distance of the 1T PtSe₂ crystal.^[31–33]

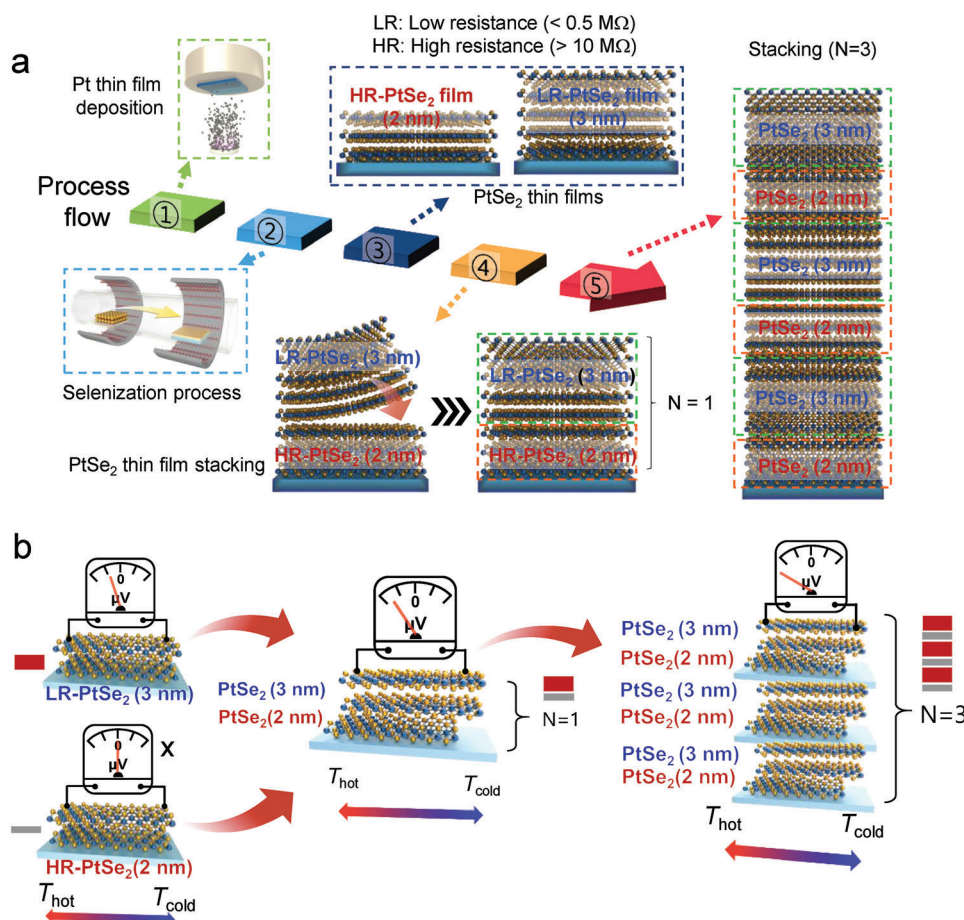


Figure 1. PtSe₂ growth and wet-transfer stacking process for in-plane Seebeck coefficient measurement. a) Schematic of the synthesis of the alternately stacked LR-PtSe₂ (2 nm)/HR-PtSe₂ (3 nm) homostructures. Each period of the repeatedly stacked PtSe₂ homostructure (N = 1) consisted of two PtSe₂ thin films: a LR-PtSe₂ (3 nm) and a HR-PtSe₂ (2 nm) film. Here LR-PtSe₂ and HR-PtSe₂ denote the low-resistance PtSe₂ (≈0.5 MΩ) and high-resistance PtSe₂ (>10 MΩ) layers, respectively. Each PtSe₂ thin film (2-nm and 3-nm films) was fabricated by a direct selenization process after deposition of the Pt thin film. Thus, the thickness of PtSe₂ films was controlled by varying the deposition time of the Pt thin film. b) Schematic of the setup for measuring the in-plane Seebeck coefficient and electrical conductivity for single PtSe₂ layers and three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures transferred on sapphire substrates.

Meanwhile, a slight deterioration of the (002) lattice planes was observed in the 2D layers of the HR-lower PtSe₂ (2 nm), which is attributed to the O₂ plasma treatment of the HR-lower PtSe₂ layers for fabricating wrinkle-free alternately stacked LR-PtSe₂/HR-PtSe₂ homostructures with good adhesive properties. Raman spectra of the pristine and O₂-plasma-treated HR-PtSe₂ layers (Figure S2b, Supporting Information) show significant suppression of two prominent in-plane (E_g) and out-of-plane (A_g) modes in the O₂ plasma-treated HR-PtSe₂ layers.^[32,33] Figure 2f–i shows the bright- and dark-field scanning TEM images of the three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructure and the corresponding elemental mappings of Pt (M-line, green) and Se (L-line, yellow), respectively. The Pt and Se distributions are consistent with the thickness of the alternately stacked homostructure, whereas apparently different Z-contrasts of the HR-PtSe₂ lattice fringes and low Pt and Se contents were observed in the HR-PtSe₂ layers between adjacent HR-PtSe₂ layers. These phenomena originate from the Pt- and Se-deficient atomic vacancies on the O₂-plasma-treated HR-PtSe₂ layers,^[30] lead-

ing to more insulator transitions than in the pristine HR-PtSe₂ layer.

2.3. Observation of In-Plane TE Properties of Single and Stacked PtSe₂/PtSe₂ Homostructures

We measured the output voltage (ΔV) in the *x*-axis direction (Figure 1b) when a temperature difference (ΔT) was applied along the same *x*-axis of the 2D structure using a strain gauge heater. Seebeck coefficients of all the samples were measured on a sapphire (Al₂O₃) substrate to prevent substrate effects from compromising the in-plane Seebeck coefficient measurement^[34] and were acquired by linear fitting the multiple (ΔV and ΔT) data points to obtain more accurate Seebeck coefficients of the PtSe₂ thin films. This slope method is able to exclude the offset voltage (the measured voltage at ΔT = 0 K) caused by differences in thermocouple wires, material inhomogeneity, and the cold finger effect.^[35] As a result, the measurement errors

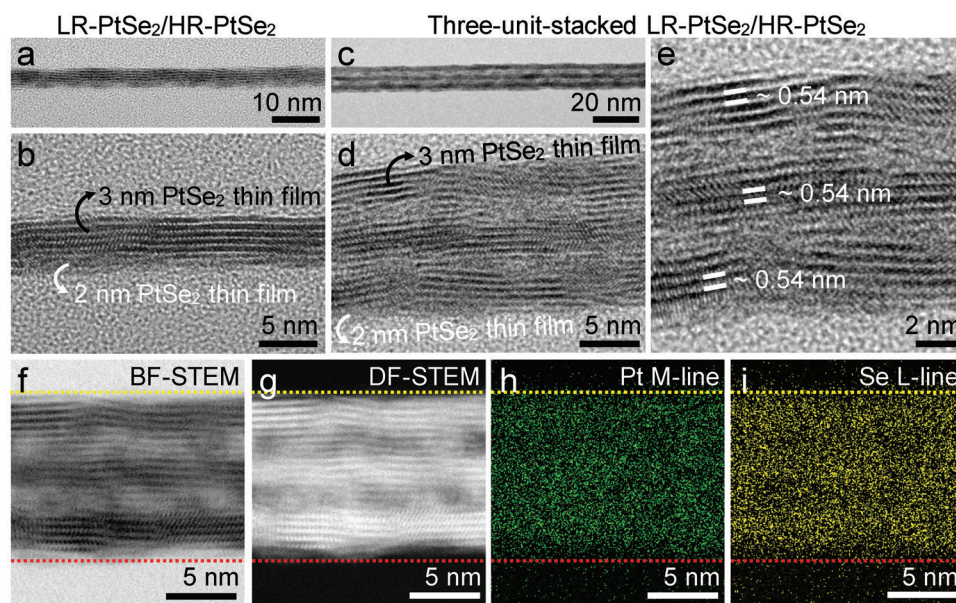


Figure 2. Structural and morphological analyses of alternately stacked LR-PtSe₂/HR-PtSe₂ homostructures. a–e) Cross-sectional HR-TEM images of the one- and three-unit-stacked 2D LR-PtSe₂/2D HR-PtSe₂ homostructures on the SiO₂/Si substrate, respectively. Here LR-PtSe₂ and HR-PtSe₂ denote the low-resistance PtSe₂ (≈ 0.5 M Ω) and high-resistance PtSe₂ (> 10 M Ω) layers, respectively. f–i) Dark-field and bright-field STEM images of the three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructure, and corresponding elemental mappings of Pt (M-line, green) and Se (L-line, yellow).

were estimated to be $\leq 2\%$ for the CAU system, as we have proved previously.^[30] The measurement details can be found in our previous report.^[30] Thus, in-plane Seebeck coefficients for the samples from these results (Figure 3a,b), where the Seebeck coefficient is defined as $S = -\Delta V/\Delta T$, are measured across the sample at fixed ambient temperature.^[36] Figure 3b shows in-plane TE voltage differences for single PtSe₂ layers (thicknesses = 2, 3, and 15 nm), one-unit-stacked LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm)/sapphire ($N = 1$), and three-unit-stacked LR-PtSe₂/HR-PtSe₂/LR-PtSe₂/HR-PtSe₂/LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm/3 nm/2 nm/3 nm/2 nm)/sapphire ($N = 3$) homostructures as functions of the temperature difference up to $\Delta T = 5$ K at 300 K. The error bars at each point (Figure 3b) were determined by the measured ΔV and ΔT , which were recorded in a vacuum chamber for at least 10 minutes. The in-plane Seebeck coefficients of the samples were then determined at 300 K (Figure 3c), and no Seebeck coefficient was observed in the single HR-PtSe₂ (2 nm) layer at a temperature gradient of up to 5 K owing to the extremely high resistance (> 10 M Ω) of the samples (Figure 3b). On the other hand, we observed an in-plane Seebeck coefficient of $+71.5$ $\mu\text{V K}^{-1}$ for the 3-nm-LR-PtSe₂ layer at 300 K (Figure 3c). This enhancement in the Seebeck coefficient in the single LR-PtSe₂ layer compared to those in 3D bulk PtSe₂ materials (≈ 40 $\mu\text{V K}^{-1}$) is due to the quantum confinement effect in 2D systems with polycrystalline properties, as reported previously.^[30,37] For a thicker single PtSe₂ (15 nm) layer, we obtained a relatively lower Seebeck coefficient (≈ 34 $\mu\text{V K}^{-1}$) at 300 K than that for the single 3-nm-LR-PtSe₂ layer, which is attributed to the semiconductor-to-semimetal transition as thickness was increased to 15 nm. In addition, this indicates that the Seebeck coefficient depends strongly on the thickness of the PtSe₂ layer, which is in good agreement with the results of previous studies.^[14,30] On the other hand, the See-

beck coefficients of the one-unit ($N = 1$) and three-unit-stacked LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm, $N = 3$) homostructures were measured to be ≈ 137 and ≈ 198 $\mu\text{V K}^{-1}$, respectively, at 300 K, which are correspondingly $\approx 192\%$ and $\approx 277\%$ higher than that for a single LR-PtSe₂ (3 nm) layer (Figure 3c). Additionally, the Seebeck coefficient increased by $\approx 145\%$ in the stacked structure, in which the number of layers of LR-PtSe₂/HR-PtSe₂ (3 nm/2 nm) in the homostructure were increased up to three. Finally, it was confirmed that the Seebeck coefficient of three-unit-stacked structures was $\approx 582\%$ higher than that of the single PtSe₂ (15 nm) layer even though they have almost the same thickness of 15 nm. The difference in the Seebeck coefficient is caused by the formation of interfaces in the three-unit-stacked structures (Figure 2c–e), despite the fact that these thin films have the same thickness (Figure S1c, Supporting Information). This will be discussed in more detail in the discussion section.

Figure 3d,e shows the internal resistances and electrical conductivities of the single PtSe₂ structure and one- and three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures, respectively. As shown in Figure 3d, the internal resistances of both the one- and three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures do not increase significantly compared to that for a single 3-nm-PtSe₂ structure, which ultimately resulted in $\approx 117\%$ increase in electrical conductivity (Figure 3e). Remarkably, the power factor of the three-unit-stacked LR-PtSe₂/HR-PtSe₂ structure was determined to be ≈ 61.0 $\mu\text{W m}^{-1} \text{K}^{-2}$ at 300 K, which is $\approx 1638\%$ higher than that of a single PtSe₂ layer of the same thickness (15 nm), as shown in Figure 3f, and ≈ 2.9 times higher than that of a single-crystal PtSe₂ layer with a similar thickness (≈ 19.4 nm) reported previously.^[14] This excellent power factor performance in stacked PtSe₂/PtSe₂ homostructures can be explained by the additional Seebeck effect (i.e., interface-induced Seebeck effect), as well as the reduced effective thickness of the stacked

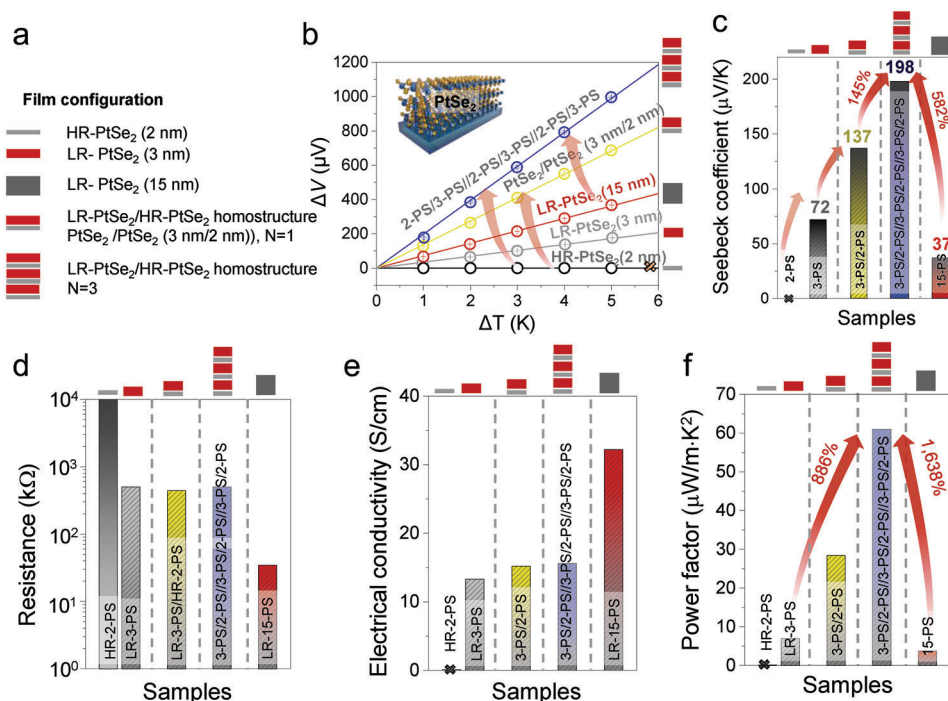


Figure 3. In-plane TE properties for single PtSe₂ layers and one- and three-stacked PtSe₂/PtSe₂ films. a) Schematics for pure and stacked PtSe₂/PtSe₂ homostructures. b) TE voltages for single PtSe₂ (thicknesses = 2, 3, and 15 nm) and one- and three-unit-stacked LR-PtSe₂ (3 nm)/HR-PtSe₂ (2 nm)//sapphire substrates with respect to a temperature difference of up to 5 K at 300 K. Here 2-PS and 3-PS denote 2-nm- and 3-nm-thick PtSe₂ layers, respectively. The inset shows the typical atomic structure of the PtSe₂ layer. c–f) Measured in-plane Seebeck coefficient, electrical resistance, electrical conductivity, and power factors for single PtSe₂ layers and alternately stacked LR-PtSe₂ (3 nm)/HR-PtSe₂ (2 nm) up to N = 3, respectively.

homostructure, owing to the contribution of the longitudinal temperature gradient and the HR-PtSe₂ lower layer in both one- and three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures, respectively. Additional details will be provided in the following section.

2.4. FEM Calculation of Stacked PtSe₂/PtSe₂ Homostructures

To confirm the longitudinal (z-direction) temperature gradient distribution of the stacked PtSe₂/PtSe₂ homostructures when applying a transverse (x-direction) temperature gradient, we conducted a finite-element method simulation (FEM) using the COMSOL Multiphysics simulator with a heat transfer module (Figure 4a–c). The detailed parameters of the materials used in the calculations are summarized in Table S3 (Supporting Information). Figure 4a shows the calculated results of the temperature distribution, assuming that the in-plane Seebeck coefficients of the PtSe₂ (5 nm)/PtSe₂ (5 nm)//sapphire substrate (430 μm) were measured using the CAU system. According to the heater power, we confirmed that a satisfactory transverse temperature difference (ΔT_x , temperature difference between $x = -3.5$ and $x = +3.5$ mm on the upper PtSe₂ thin film) was generated (Figure 4c) at $\Delta T_x = 5$ K. As shown in Figure 4a,b, a longitudinal temperature difference (ΔT_z) was formed at the edge of the stacked 2D PtSe₂/2D PtSe₂ homostructure and was $\approx 2\%$ of the ΔT_x . In particular, at the edge of the stacked PtSe₂/PtSe₂ (5 nm/5 nm) homostructure, the magnitude of the tempera-

ture gradient in the z-axis direction (∇T_z) was determined to be ≈ 150 K m⁻¹ when ΔT_x was fixed at 5 K (Figure 4c). The most important finding of the FEM simulation conducted herein was an unusual temperature gradient in the out-of-plane (longitudinal) direction (z-direction) when the in-plane (transverse) temperature gradient was applied along the samples (Figure 4a–c), which is a key driving force for accelerating and transferring the high-energy hot carriers in the HR-lower layer to the LR-upper PtSe₂ layers via the interface-induced effect, as we observed in the stacked LR-PtSe₂/HR-PtSe₂ homostructure (Figure 3).

3. Discussion

Figure 5a,b shows the schematics of single LR and HR-PtSe₂ layers, the stacked LR-PtSe₂/HR-PtSe₂ homostructure, their electronic transports, and equivalent circuit diagrams. First, for the single HR-PtSe₂ (2 nm) layer, its high internal resistance prevents the heat carrier transport in the transverse direction even though the in-plane ΔT was generated up to ≈ 5 K (first-row image Figure 5a), which leads to a result that the thermopower of the HR-PtSe₂ (2 nm) was not measured in the nanovoltmeter. Assuming we turn this state into an equivalent circuit, the HR-PtSe₂ (2 nm) can be expressed as a voltage source placed on an open-circuit state (first-row image in Figure 5b). This explanation seems to be more appropriate because the S of the 2-nm-thick PtSe₂ thin film has not been measured in our previous study.^[30] The HR property of the PtSe₂ layer (2 nm) is attributed to the insulator transition caused by the Pt- and Se-deficient atomic

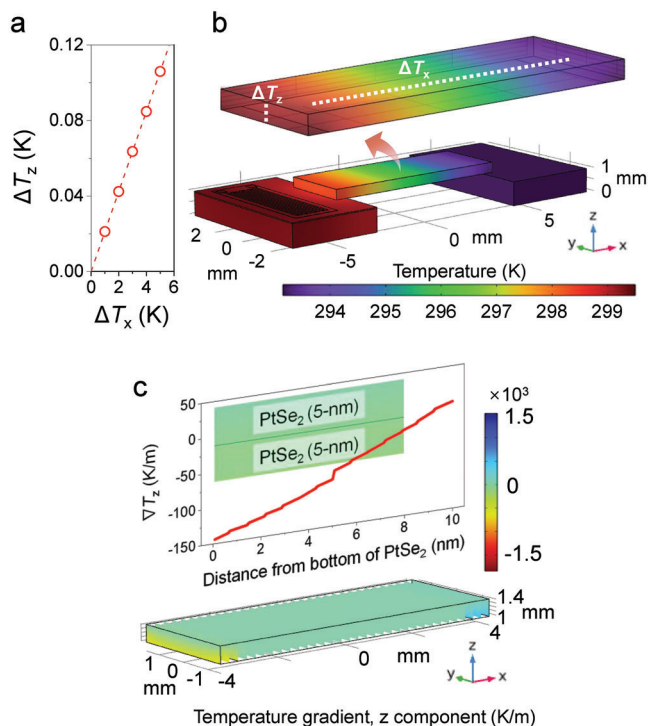


Figure 4. COMSOL simulation in 2D single PtSe₂ and 2D PtSe₂/2D PtSe₂ homostructures. COMSOL simulation result for calculating the temperature distribution of the PtSe₂ (5 nm)/PtSe₂ (5 nm)/sapphire substrate structure, when measuring the in-plane Seebeck coefficient using the CAU system at 300 K. We define the transverse temperature difference (ΔT_x) as the temperature difference on the surface of the upper PtSe₂ layer (dotted line). When measuring ΔT_x , the longitudinal temperature difference (ΔT_z) was generated at the edge of sample. a) Longitudinal ΔT_z for the stacked sample as a function of the transverse temperature difference ΔT_x . b,c) Calculated temperature gradient (z component) for the stacked PtSe₂ (5 nm)/PtSe₂ (5 nm)/sapphire substrate at $\Delta T_x = 5$ K. The results were calculated using COMSOL Multiphysics software (V5.6) with the heat transfer module.

vacancies after O₂ plasma treatment, as evidenced by the HR-TEM and Raman spectra (Figure 2; Figure S2, Supporting Information). On the other hand, we could measure the Seebeck coefficient of the LR-PtSe₂ (3 nm) structure because a closed circuit was formed in this structure (second-row images in Figure 5a,b). These results reveal that the formation of a closed circuit facilitates the evaluation of the Seebeck coefficient in 2D TMDC materials. Following a similar mechanism, the in-plane Seebeck coefficient in stacked LR-PtSe₂/HR-PtSe₂ homostructure (third-row images) are observed as shown in Figure 5a,b because a closed circuit was formed on the upper LR-PtSe₂ layer in the stacked homostructure. In this case, even though the closed circuit for Seebeck coefficient measurement is formed on the PtSe₂ layer, as same as the LR-PtSe₂ (3 nm) thin film, the measured TE properties differ from the other homo- or heterostructure reported previous studies as well as the LR-PtSe₂ (3 nm) thin film. In terms of the previous studies on TE characteristics of the homo- or heterostructure so far,^[38–42] two parallel conductor model is widely used for determining the overall Seebeck coefficient of the hetero- or homostructure, consisting of multiple conducting channels that are connected in parallel. If we assume that the TE properties

of the one-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructure can be explained by this model, the total Seebeck coefficient (S_{homo}) can be calculated from the Seebeck coefficient and sheet electrical conductance of the upper LR-PtSe₂ and lower HR-PtSe₂ using two parallel conductor models. It is defined as

$$S_{\text{homo}} = \frac{S_{u,PS}\sigma_{u,PS} + S_{l,PS}\sigma_{l,PS}}{\sigma_{u,PS} + \sigma_{l,PS}} \approx S_{u,PS} \quad (1)$$

where $S_{u,l}$ and $\sigma_{u,l}$ are the Seebeck coefficients and sheet conductances of the upper and lower PtSe₂ films, respectively, and the subscript PS represent the PtSe₂. According to Equation (1), the total Seebeck coefficient depends strongly on the Seebeck coefficient of the upper LR-PtSe₂ films, because the lower HR-PtSe₂ layer has a significantly lower sheet electrical conductance than the upper LR-PtSe₂ layer. A similar parallel conductor model can be applied to a three-unit-stacked alternating LR-PtSe₂/HR-PtSe₂ homostructure by expanding the components for the increased layer. Consequently, the total Seebeck coefficient should be simply evaluated to be that of the upper LR-PtSe₂ layer, as indicated in Equation (1). However, the measured Seebeck coefficients for the one- and three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures were ≈ 192 and $\approx 277\%$ higher than that of the single LR-PtSe₂ (3 nm) layer. Thus, another approach is required to explain the total Seebeck coefficient in the stacked LR-PtSe₂/HR-PtSe₂ homostructure.

Through the cross-sectional TEM observation (Figure 2), we confirmed that a clear interface was formed between the LR-PtSe₂ and HR-PtSe₂ layers in the one- and three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures. This results in a little change in the σ (Figure 3e), implying that the total σ of the homostructures is determined by the LR-PtSe₂. Simultaneously, the S of the homostructures has independently increased as shown in the out-of-plane temperature difference calculated in the COMSOL simulation results (Figure 4). As in the case of the σ , the heat carriers generated by the in-plane temperature difference could not be transferred along the sample (transverse direction) due to the high resistance of the HR-PtSe₂ layer. Instead, the distinct temperature gradient in the longitudinal direction (∇T_z), it is sufficient for these heat carriers to affect in the out-of-plane direction since the thickness of the HR-PtSe₂ (2 nm) is shorter than the typical mean free path of carriers in 2D TMDC materials at room temperature.^[43,44] This condition causes the momentum transfer of heat carriers from the HR-PtSe₂ layer to the LR-PtSe₂ layer through the interface, leading to an increase the total Seebeck coefficient compared to that of the single LR-PtSe₂ (3 nm) layer. What further supports this argument is that while these mechanisms and results are almost identical in the phonon drag effect, but the contribution of the phonon drag effect is negligible at room temperature.^[45–47] As a result, we defined the extra Seebeck coefficient by the momentum transfer of heat carriers as the interface-induced Seebeck coefficient (S_{int}), and the total Seebeck coefficient in the stacked LR-PtSe₂/HR-PtSe₂ homostructure can be expected to be a sum of the conventional Seebeck coefficient and the S_{int} , $S_{\parallel} = S_{\parallel}^c + S_{\text{int}}$, where $S_{\parallel}^c$ is the conventional Seebeck coefficient of the single PtSe₂ thin film. In Figure 3e, the electrical conductivities of the single PtSe₂ (3 nm), one-unit-stacked LR-PtSe₂/HR-PtSe₂, and three-unit-stacked LR-PtSe₂/HR-PtSe₂ have almost same value. This result not only

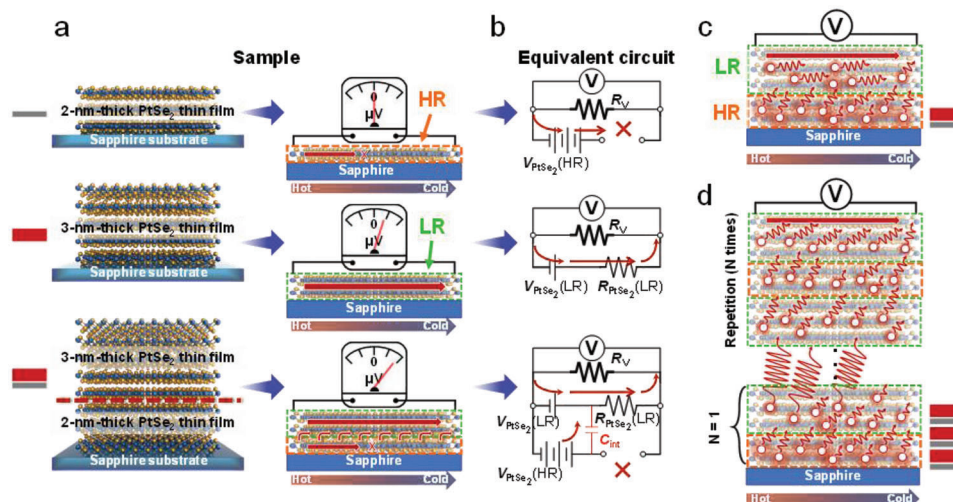


Figure 5. Interface-induced Seebeck effect in 2D single PtSe₂ and 2D PtSe₂/2D PtSe₂ homostructures. a, b) Schematics and corresponding equivalent circuits for the HR-PtSe₂ (2 nm), LR-PtSe₂ (3 nm), and one-unit-stacked LR-PtSe₂ (3 nm)/HR-PtSe₂ (2 nm) homostructure, respectively. Third-row image in b) shows that the LR-PtSe₂ and HR-PtSe₂ are connected in series, indicating an additional Seebeck effect (i.e., interface-induced Seebeck effect), which in turn increases the overall Seebeck coefficient in alternately stacked LR-PtSe₂/HR-PtSe₂//sapphire substrate. Here R_V denotes the internal resistance of the voltmeter ($>G\Omega$). Heat carrier transport behavior for c) one-unit-stacked and d) three-unit-stacked LR-PtSe₂ (3 nm)/PtSe₂ (2 nm) homostructures under a transverse temperature gradient along the samples.

means that the flow of charge carriers is restricted in the PtSe₂ top layer of the LR-PtSe₂/HR-PtSe₂, but also that the magnitude of the measured $S_{\parallel}^c$ should be the same as that of the single PtSe₂ (3 nm) thin film. Thus, the S_{int} mainly contributes to the increased ΔV in the stacked homostructure. Based on this result, we can be replaced with a capacitor in an equivalent circuit (third-row in Figure 5b) because the interface-induced voltage, $V_{\text{int}} = S_{\text{int}} \times \Delta T_z$, was generated by the out-of-plane temperature different (ΔT_z).

In the proposed model for electronic carrier transport in one-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures (Figure 5c), the momentum transfer from the high-energy carriers in the lower HR-PtSe₂ layer was occurred through the interface between the upper LR-PtSe₂ and lower HR-PtSe₂ layers in the stacked homostructure as a result of the longitudinal temperature gradient at the edge of the samples (Figure 4c) under a transverse temperature gradient. With an increase in stacking units up to three ($N = 3$), we can propose a similar mechanism for the electronic carrier transport in the samples under the transverse temperature gradient along the sample owing to the longitudinal temperature gradient (Figure 5d). Accordingly, we obtained a high transverse Seebeck coefficient exceeding $198 \mu\text{V K}^{-1}$ at 300 K for the three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures. Another noticeable feature of the stacked PtSe₂/PtSe₂ homostructure is that theoretically, there is no energy barrier between the two PtSe₂ layers owing to the nature of the homojunction structure, which eventually results in improved carrier transport in the stacked LR-PtSe₂/HR-PtSe₂ homostructure.

More importantly, the electrical conductivity increases with increasing carrier concentration ($n = \sigma/e\mu$), where e and μ are the elementary charge and carrier mobility, respectively, while the Seebeck coefficient, which is proportional to the $n^{-2/3}$ for metal or degenerated semiconductors, decreases with increasing carrier

concentration. Accordingly, such strong coupling between the Seebeck coefficient and electrical conductivity limits further enhancement of the TE performance of TE materials. In this study, we confirmed that the stacked LR-PtSe₂/HR-PtSe₂ homostructure is a novel and challenging scheme for increasing both the Seebeck coefficient and electrical conductivity simultaneously, while breaking the strong coupling of the Seebeck coefficient and electrical conductivity because of extra interface-induced Seebeck effect and reduced effective thickness of the stacked homostructures. Consequently, we obtained high TE power factors of $\approx 61.0 \mu\text{W m}^{-1} \text{K}^{-2}$ at 300 K in the three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures (Figure 3f). Since this approach can only take advantage of the high electrical conductivity of the LR layer and the high Seebeck coefficient of the HR layer, a very high power factor that exceeds conventional thermoelectric materials can be expected depending on the material selection of each layer.

4. Conclusion

In summary, we experimentally demonstrated a novel method for breaking the strong coupling between the Seebeck coefficient and electrical conductivity of 2D PtSe₂ materials by stacking homo-PtSe₂ layers in the form of LR-PtSe₂/HR-PtSe₂ homostructures. We observed that the exceptionally high TE power factor of the three-unit-stacked LR-PtSe₂/HR-PtSe₂ homostructures reached $\approx 61 \mu\text{W m}^{-1} \text{K}^{-2}$ at 300 K compared to the single PtSe₂ thin film. Our findings provide a novel paradigm for designing high-performance TE devices via alternately stacked 2D TMDC materials and offer insight into the electronic and thermal transport in single and alternately stacked 2D/2D TMDC materials at the atomic level.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

W.-Y.L. and M.-S.K. contributed equally to this work. S.-K.L. conceived and designed the research project and performed part of experiments. W.-Y.L., M.-S.K., and G.-S.K. performed the device fabrication and analysis of pure PtSe₂ films and stacked PtSe₂/PtSe₂ homostructures. G.-S.K., J.W.C., S.-H.K., N.-W.P., and Y.-H.K. measured the material properties and in-plane thermoelectric characteristics of PtSe₂ films. S.-H.K. supervised all the experiments. S.-K.L., W.-Y.L., and G.-S.K. wrote the paper. All authors contributed to the discussion.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords

decoupling phenomenon, interfacial Seebeck effect, parallel conduction models, transition metal dichalcogenide, van der Waals, platinum diselenide

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