Ultra-high Thermoelectric Performance in SrNb$_{0.2}$Ti$_{0.8}$O$_3$ Oxide Films at a Submicrometer-Scale Thickness

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Supporting Information

ABSTRACT: Localized refrigeration and power generation via thermoelectric technology rely on efficient thermoelectric materials with high performance at room temperature. Although the two-dimensional electron gas (2DEG)-related materials exhibit ultra-high thermoelectric performance near room temperature, such performance is only preserved at thicknesses within subnanometer scales, limited by the requirement of two-dimensional size confinements. Here we report ultra-high thermoelectric performance similar to 2DEG-related materials but achieved in SrNb$_{0.2}$Ti$_{0.8}$O$_3$ oxide films with a submicrometer-scale thickness by regulating strain-induced lattice polarizations and interfacial polarizations. A large figure of merit, $zT$, and power factor ($\sim 10^5$–$10^7$ $\mu$W cm$^{-1}$ K$^{-2}$) were achieved near room temperature, and the maximum $zT$ is estimated to be $\sim 1.6$ for a 49 nm thick film. These performances exceed those of the existing n-type thermoelectric materials for room-temperature uses and the reported best oxide materials beyond subnanometer scales. The earth-abundant elemental composition of the oxide film paves the way toward potential applications in thermoelectric thin film devices with a microscale thickness.

Thermoelectric (TE) materials achieve localized conversion between thermal and electric energies, and the conversion efficiency is determined by a figure of merit $zT$ ($zT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ the electrical conductivity, $T$ the absolute temperature, and $\kappa$ the thermal conductivity). Efforts to raise the $zT$ value have been focused on two aspects: reducing the lattice thermal conductivity ($\kappa_{\text{Latt}}$) and improving power factors (PF = $S^2\sigma$). Since the 1990s, the $\kappa_{\text{Latt}}$, for many TE material systems has been reduced near the amorphous limit by using phonon scattering approaches, such as fabricating nanostructures, point defects, and rattling filler ions within cage structures. Therefore, it draws more potential to optimize the electronic component: PF = $S^2\sigma$. To date, two-dimensional electron gas (2DEG)-related TE materials hold the record for $zT$ and PF near room temperature. The generation of 2DEGs is driven by spatial confinement along the direction of thickness by making superlattice (or quantum dot) structured Bi$_2$Te$_3$/Sb$_2$Te$_3$, PbSeTe$_2$, or SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$ or is observed at the interface of TiO$_2$/SrTiO$_3$ and LaAlO$_3$/SrTiO$_3$. When the thickness of these TE materials is spatially confined within a subnanometer scale, the two-dimensional confinement of carriers enlarges the density of states near the Fermi energy and triggers electron phonon coupling (EPC). This overcomes the conventional $\sigma$–$S$ trade-off to more independently increases $S$ and thereby further increases $zT$. The generation of 2DEGs is driven by spatial confinement along the direction of thickness by making superlattice (or quantum dot) structured Bi$_2$Te$_3$/Sb$_2$Te$_3$, PbSeTe$_2$, or SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$ or is observed at the interface of TiO$_2$/SrTiO$_3$ and LaAlO$_3$/SrTiO$_3$. When the thickness of these TE materials is spatially confined within a subnanometer scale, the two-dimensional confinement of carriers enlarges the density of states near the Fermi energy and triggers electron phonon coupling (EPC). This overcomes the conventional $\sigma$–$S$ trade-off to more independently increases $S$ and thereby further increases
Nevertheless, the preserved large $S$ at a high carrier concentration ($n$) in 2DEG-related materials is strongly dependent on two-dimensional (2D) spatial confinement of carriers. As observed for the SrNb_{0.2}Ti_{0.8}O_{3}/SrTiO_{3} superlattice, the Seebeck coefficient is reduced sharply when the thickness of SrNb_{0.2}Ti_{0.8}O_{3} exceeds three unit cells $(\sim 1.2 \text{ nm})$. The prerequisite of spatial confinement largely impedes practical applications of the present 2DEG materials for high power energy conversions as the amount of TE material is insufficient. How to break through the limitation of the size confinement and increase the effective thickness past a nanometer scale are critical issues to address.

Using the polarizations and polar discontinuity in materials with asymmetric charge centers provides an alternative direction to regulate 2DEGs that does not strongly rely on spatial confinement. As typical examples reported for wurtzite AlGaN/GaN heterostructures, the direction of spontaneous lattice polarization was ordered by binding with the interfacial polarization charge using appropriate epitaxy strategies. The polarization- and polar discontinuity-induced internal electrostatic field significantly influences the distribution, density, and mobility of 2DEGs. Similarly, polarization-associated planar charge localizations within LaAlO_{3}/SrTiO_{3} and La_{0.5}Sr_{0.5}TiO_{3}/SrTiO_{3} interfaces were also recognized as important factors to achieve electronic confinement of 2D carriers to form 2DEGs. The observed phonon drag enhancement in $S$ was reported as a benchmark of 2DEGs that are their X-ray diffraction patterns shown in Figure S1. The film composition was measured as SrNb_{0.2}Ti_{0.8}O_{2.7} by Rutherford backscattering (RBS).

The high-angle annular dark-field (HAADF) images of the interfaces between as-grown thin films and the underlying substrates are shown in Figure 2a. For the SrNb_{0.2}Ti_{0.8}O_{3}/SrTiO_{3} sample, co-lattice-matched lattice atoms from the film and substrate are seen at their interfacial regions, with no detectable diffusion of the Nb element observed (see Figure S5). Further demonstration of the coherent epitaxy is verified by the same in-plane vectors of the film and substrate diffraction patterns in reciprocal space mappings (RSMs), as shown in Figure 2c. Similar RSM patterns were observed for more SrNb_{0.2}Ti_{0.8}O_{3}/SrTiO_{3} samples with different film thicknesses varied from 49 nm to 2.2 $\mu$m, as shown in Figure S2. These results demonstrate that the lattice of the film was plane-locked by the substrate when further increasing the deposition thickness across a micrometer scale. Therefore, the compressive interfacial strain is effectively imposed upon the
film materials. This is in contrast to the SrNb0.2Ti0.8O3/LaAlO3 sample deposited under the same conditions, in which case the interfacial strain relaxed fast owing to a larger lattice mismatch (∼3.65%) between the film and substrate. The edge dislocations are clearly observed at the interfaces between the SrNb0.2Ti0.8O3 films and the underlying LaAlO3 substrates (see Figure 2a). From its RSM patterns shown by Figure 2c, the in-plane vectors are different for the films and substrates, indicating the relaxations of the interfacial strains.

On the basis of the RSM results, as shown in Figures 2b,c and S2, the averaged in-plane and cross-plane lattice displacements ($\varepsilon_{\parallel,\text{Avr}}$ and $\varepsilon_{\perp,\text{Avr}}$) are derived from the film pattern in the RSM by eq 1

$$
\varepsilon_{\parallel,\text{Avr}} = \frac{\int_{Q_1} \left( \frac{1}{Q_1^2} \right)^{1/a_{\text{film}}} dQ_1 \cdot \int_{Q_2} I_{\text{film}}(Q_1, Q_2) dQ_2}{\int_{Q_1} \int_{Q_2} I_{\text{film}}(Q_1, Q_2) dQ_1 dQ_2},
$$

where $Q_1$ and $Q_2$ represent the in-plane and cross-plane reciprocal vectors, respectively and $I_{\text{film}}(Q_1, Q_2)$ is the diffraction intensity of the film located at the specific reciprocal coordinate. As shown in Figure 2d, the biaxial compressive distortion of the film material is demonstrated by the negative $\varepsilon_{\parallel,\text{Avr}}$ and the positive $\varepsilon_{\perp,\text{Avr}}$ from the respective cross-plane transverse expansion. With an increased film thickness of SrNb0.2Ti0.8O3/SrTiO3(001) and the resultant strain relaxation,
both $e_{\text{film}}$ and $e_{\text{substr}}$ tend to be zero. The effective lattice distortion is absent for SrNb$_{0.2}$Ti$_{0.8}$O$_3$/LaAlO$_3$(001) owing to the complete relaxation of the interfacial strain. The distribution of in-plane lattice distortion was also derived from RSM by eq 2:

$$f(\epsilon) = \frac{1}{Q_{||}} \left[ \frac{1}{Q_{\perp}} - \frac{1}{Q_{\perp}} \right]$$

$$\epsilon_{\text{film}} = \int_{Q_{\perp}}^{Q_{\perp}} \int_{Q_{\perp}}^{Q_{\perp}} \left[ \frac{1}{Q_{\perp}} - \frac{1}{Q_{\perp}} \right] dQ_{\perp} dQ_{\perp}$$

The percentages of material distributed at each magnitude of in-plane lattice distortions $f(\epsilon)$ for SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$(001) with different deposition thicknesses are shown in Figure 2e. A more broadened material distribution is clearly observed with an increased deposition thickness.

Figure 3 shows the TE performance for SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$(001) and SrNb$_{0.2}$Ti$_{0.8}$O$_3$/LaAlO$_3$(001) grown under a comparable condition with varied thicknesses ($t_{\text{film}}$). Linear enhancements are observed for both sheet conductance ($\sigma_{xx}$) and sheet carrier density ($n_{\text{film}}$) with increased $t_{\text{film}}$ as shown in Figure 3a. It indicates a constant conductivity, $\sigma = d(\sigma_{xx})/dt_{\text{film}}$ and carrier concentration, $n = d(n_{\text{film}})/dt_{\text{film}}$ associated with the film deposition. Barely annealing the SrTiO$_3$ and LaAlO$_3$ substrates at the deposition atmosphere and temperature (650 °C) for 2 h without film depositions does not result in any detectable conductance. A large $n$ of $\sim 1.1 \times 10^{21}$ cm$^{-3}$ associated with deposition is observed for SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$(001). This number is much larger compared to the ones grown on a LaAlO$_3$(001) substrate under the same conditions ($\sim 6 \times 10^{17}$ cm$^{-3}$, with the carrier contributed by both the Nb dopant and oxygen vacancy) or the reported values at a similar doping content. Similar effects were attributed to both intrinsic and extrinsic reasons, as summarized in previous literature reports. The intrinsic one includes distortion or polaron-induced Ti-t$_{2g}$ orbital reconfiguration and formation of 2DEGs by interfacial polarization, while the extrinsic one is the deposition-associated generation of V$_{\text{O}}$ and free electron carriers within the SrTiO$_3$ substrate.

Figure 3b shows the directly measured Seebeck coefficient of the SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$(001) and SrNb$_{0.2}$Ti$_{0.8}$O$_3$/LaAlO$_3$(001) samples ($S_{\text{film/substr}}$), compared with the previously reported 2DEGs. As-measured $S_{\text{film/substr}}$ is the averaged Seebeck coefficient of the film ($S_{\text{film}}$) and substrate ($S_{\text{substr}}$) weighted by their proportion in contributed electrical conductance. By attributing the net increase in $n$ of SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$(001) compared to that of SrNb$_{0.2}$Ti$_{0.8}$O$_3$/LaAlO$_3$(001) completely to the extrinsic conductance of the SrTiO$_3$ substrate, the Seebeck coefficient of the thin film ($S_{\text{film}}$) was calculated. This prohibits the overestimation of $S_{\text{film}}$ and more details on derivations are provided in the Supporting Information (ST), section C. It is worth noting that if there is any intrinsic enhancement in $n$ or the depth distribution of V$_{\text{O}}$ is smaller than the thickness of the substrate, the practical $S_{\text{film}}$ will be larger than the calculated ones shown in Figure 3b, as detailed in more discussions given in Figure 3b,c. Despite the potential underestimation, significant enhancements in $S_{\text{film}}$ are found in SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$(001) compared with SrNb$_{0.2}$Ti$_{0.8}$O$_3$/LaAlO$_3$(001) and the reported bulk SrNb$_{0.2}$Ti$_{0.8}$O$_3$. Increasing $t_{\text{film}}$ from 45 nm to 2.2 μm reduces $S_{\text{film}}$ by $\sim 200 \mu \text{V K}^{-1}$, while the 2.2 μm thick film maintains $S_{\text{film}}$ approaching to be $\sim 170 \mu \text{V K}^{-1}$. This is in contrast to a much sharper decrease in $S$ by $\sim 400 \mu \text{V K}^{-1}$ reported in SrNb$_{0.2}$Ti$_{0.8}$O$_3$ 2DEGs when the $t_{\text{film}}$ was only increased from one to three unit cells ($S_{\text{film}}$ similar to the bulk...
Figure 4. (a) Seebeck coefficient and sheet conductance of a 49 nm thick SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$(001) measured with a raising temperature up to 200 °C followed by a cooling down technique with a constant speed of 0.3 °C min$^{-1}$ in vacuum. (b) Sheet conductance of a 2.2 μm thick SrNb$_{0.2}$Ti$_{0.8}$O$_3$ film grown on a 1 mm thick SrTiO$_3$(001) substrate and a 2 μm thick SrNb$_{0.2}$Ti$_{0.8}$O$_3$ film grown on a 100 μm thick SrTiO$_3$(001) substrate as a function of temperature. The contributions from both the film and substrate to the sheet conductance are separated for the SrNb$_{0.2}$Ti$_{0.8}$O$_3$ (2.2 μm)/SrTiO$_3$ (1 mm) sample (details are provided in the SI, section D). (c) Seebeck coefficients and electrical conductivities and (d) PFs of the SrNb$_{0.2}$Ti$_{0.8}$O$_3$ (2 μm)/SrTiO$_3$ (100 μm) sample measured as bulk material (accounting for the thicknesses of the film and substrate), compared with conventional TE materials for low-temperature applications, such as Bi$_2$Te$_3$ and CsBi$_4$Te$_6$. The achieved TE performance exceeds the one measured for a 800 nm thick SrTiO$_3$ (001) substrate under the same condition, a 49 nm thick SrTiO$_3$ film measured in bulk by accounting for the thicknesses of the substrate. Similar to the reported SrNb$_{0.2}$Ti$_{0.8}$O$_3$ single-crystalline materials, the temperature enhancement $S$ and decreases $\sigma$. The two discontinuous steps observed in the $S$–$T$ curve at ~40 and 150 K are confirmed to be intrinsic associated to the present sample, which may be associated with the phonon drag contributed by the film and substrate at different carrier concentrations reported previously by ref 3. Even taking the thickness of the substrate into account, a bulk PF (integrating the thicknesses of both the film and substrate) of 78 μW cm$^{-1}$ K$^{-2}$ is achievable at low temperatures, as shown in Figure 4d.

In contrast to the previous 2DEG-related SrNb$_{0.2}$Ti$_{0.8}$O$_3$, the enhanced Seebeck coefficient for SrNb$_{0.2}$Ti$_{0.8}$O$_3$/SrTiO$_3$(001) in this work is not strongly related to spatial confinements. The present achieved performance is comparable with the one for oxygen-annealed LaAlO$_3$/SrTiO$_3$, in which case similar magnitudes of $S$ (~600 μV K$^{-1}$) at large $\eta_{2D}$ (an order of high 10$^{13}$ up to 10$^{14}$ cm$^{-2}$) were achieved by interfacial polarization-induced EPC. The high relative permittivity ($\varepsilon_r$ > 10$^6$) and ferroelectric nature of strain-distorted SrTiO$_3$ make an electronic 2D confinement of carriers by the aligned
domains of lattice polarons be practicable (see more detailed discussions in the SI, Figure S9).

Following this understanding, an increasing deposition thickness weakens the strain-induced lattice polarization and/or reduces their ordering in alignment, as previously demonstrated in Figure 3d,e, respectively. As a result, the 2D confinements of carriers by lattice polarization are expected to be reduced. This is in agreement with the reducing trend in the Seebeck coefficient with an increasing film thickness.

The relevance to lattice/interfacial polarization is also demonstrated by the anisotropy observed in the Seebeck coefficient when growing SrNb0.2Ti0.8O3 on a SrTiO3 substrate with other orientations from tilting the direction of lattice polarization. For example, as compared to SrNb0.2Ti0.8O3/SrTiO3(001) with the same thickness, SrNb0.2Ti0.8O3/SrTiO3(110) exhibits similar electrical conductance and interfacial strains but shows a significantly reduced Seebeck coefficient (see detailed results in Figure S10a). This observation is consistent with the previous reports that the [001] direction exhibits optimal ferroelectric behaviors for perovskite oxides with charge-center asymmetry.33,34 Following our previous understanding, a more effective well-like confinement of the carrier is expected for SrNb0.2Ti0.8O3/SrTiO3(001) because the alignment of [001] lattice polarization is parallel to the interfacial polarization and perpendicular to the transportation plane of the carriers. In contrast, the 2D confinement of carriers is indirect for SrNb0.2Ti0.8O3/SrTiO3 because the [001] lattice polarization is offset by ~45° with respect to both the interfacial polarization and also to the electron transportation plane. Apart from the lattice polarization and its alignment, we also emphasize the relevance of the ultrahigh TE performance to the interfacial polarization, which is assumed to be coupled with the strain-induced lattice polarizations. This is further demonstrated for compressive-strained SrNb0.2Ti0.8O3 grown on DyScO3(001) substrates, which shows similar TE performance to that of the bulk material (see Figure S10).

In summary, ultrahigh TE performance of the 2DEG-related material has been achieved in SrNb0.2Ti0.8O3 oxide films at a submicrometer-scale thickness by regulating strain-induced lattice polarizations and interfacial polarizations. As compared to the reported 2D SrNb0.2Ti0.8O3, the critical film thickness to preserve a large Seebeck coefficient at a high carrier concentration is significantly improved from the previous subnanometer scale to a submicrometer scale. A large ZT up to 1.6 and ultrahigh PF of ∼103 μW cm−1 K−2 were achieved at room temperature. These performances exceed those of all existing n-type TE materials and the best TE oxide materials beyond a subnanometer scale for room-temperature use. The strain-induced lattice polarization and its relative alignment with the interfacial polarization are demonstrated to strongly affect the TE properties. These observations shed light on the possible mechanisms that are relevant to polarization and polar discontinuity-induced 2D carrier confinements. Beyond the ultrahigh TE performance, the present oxide films are less toxic and not largely dependent on heavy elements, such as Bi, Sb, or Te. This favors potential applications in microscale energy harvesters, on-chip coolings, and thermal sensors used at room temperature or below.

■ ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.7b00197.

Experimental details, additional structural results from XRD and RSM, detailed derivations to separate the contribution of the film and substrate to the TE performance, more results to confirm the observed high TE performance in this work, additional calculated and experimental results to demonstrate the relevance of the present high TE performance to alignment of lattice polarizations, and the contributions of each author (PDF)

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**Author Contributions**

J.C. and H.C. contributed equally to this work. J.C. proposed the idea, planned for the experiments, developed the film deposition strategy, performed film growth, and wrote the manuscript, assisted by L.C.; H.C. and F.H. performed the verification experiments, advised by L.C., J.C., X.S., and H.Z.; H.C., F.H., K.Z., and T.Z. characterized the transportation performances; J.C., X.K., and W.W. contributed to the RSM measurement and analysis; B.G., F.H., and H.D. contributed to the TEM measurement; M.D. performed the RBS measurement; and Y.T., N.C., and Y.J. provided experimental support and useful discussions.

**Notes**

The authors declare no competing financial interest.

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