Hot Carrier Filtering in Solution Processed Heterostructures: A Paradigm for Improving Thermoelectric Efficiency

Yichi Zhang  
*University of California - Santa Barbara*

Je-Hyeong Bahk  
*Purdue University, Birck Nanotechnology Center; jbahk@purdue.edu*

Joun Lee  
*University of California - Santa Barbara*

Christina S. Birkel  
*University of California - Santa Barbara*

Matthew L. Snedaker  
*University of California - Santa Barbara*

See next page for additional authors

Follow this and additional works at: [http://docs.lib.purdue.edu/nanopub](http://docs.lib.purdue.edu/nanopub)

Part of the Nanoscience and Nanotechnology Commons

Zhang, Yichi; Bahk, Je-Hyeong; Lee, Joun; Birkel, Christina S.; Snedaker, Matthew L.; Liu, Deyu; Zeng, Hongmei; Moskovits, Martin; Shakouri, Ali; and Stucky, Galen D., "Hot Carrier Filtering in Solution Processed Heterostructures: A Paradigm for Improving Thermoelectric Efficiency" (2014). *Birck and NCN Publications*. Paper 1624.  
[http://dx.doi.org/10.1002/adma.201304419](http://dx.doi.org/10.1002/adma.201304419)

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.
Hot Carrier Filtering in Solution Processed Heterostructures: A Paradigm for Improving Thermoelectric Efficiency

Yichi Zhang, Je-Hyeong Bahk, Joun Lee, Christina S. Birkel, Matthew L. Snedaker, Deyu Liu, Hongmei Zeng, Martin Moskovits, Ali Shakouri, and Galen D. Stucky*

The large-scale use of thermoelectrics for conversion of waste heat to electricity is currently limited by materials cost and efficiency. The efficiency of a thermoelectric (TE) is normally expressed through its figure of merit \(z = \frac{S^2/\sigma \tau}{\kappa}\), where \(S\) is the Seebeck coefficient, \(\sigma\) is the electrical conductivity, \(\kappa\) is the thermal conductivity, and \(T\) is the absolute temperature. A strategy that could lead to an efficient and economical thermoelectric is to fabricate nanostructured materials incorporating nanograins\(^{[1–4]}\) or pores\(^{[5,6]}\) thereby reducing the material’s thermal conductivity by disrupting the crystal’s phonon transport and consequently the lattice contribution to its thermal conductivity.\(^{[7]}\) This strategy has been shown to be effective in single-phase systems, such as p-type (Bi, Sb)\(_2\)Te\(_3\), half-Heusler and Si\(_x\)Ge\(_{1-x}\), produced by high-energy ball milling.\(^{[2–4]}\) Notably, a hierarchical PbTe material with a bulk record \(z = 2.2\) has been reported.\(^{[8]}\) However, ball milling is not scalable cost-effectively. More to the point, little room remains for further reducing \(\kappa\) by nanostructuring single-phase materials because the electronic contribution to \(\kappa\) cannot be decoupled from \(\sigma\) (Wiedemann-Franz law), while the lattice contribution cannot be reduced below the amorphous limit, which has essentially been reached, particularly for the Bi\(_2\)Te\(_3\) system whose reported lattice contribution has approached to the lower limit \(
abla 0.3\) W m\(^{-1}\)K\(^{-1}\) a-b axis at 300 K) as predicted by the Cahill model.\(^{[9]}\) Further improvements in the figure of merit must rely on new paradigms for nanostructuring multi-phase materials through which the interdependence of \(S\) and \(\sigma\) is decoupled, or better still, synergistically modified.

This article describes such a new approach based on a scalable, low-cost, solution-based synthesis that produces a stable Ag/oxide/Sb\(_2\)Te\(_3\)-Te metal-semiconductor hetero-structure that achieves a figure of merit \(z = 1.0\) at 460 K, a record for a hetero-structured material made by using wet chemistry. Moreover, by complementing our experimental data with theory, we show unequivocally that the large increase in the material’s Seebeck coefficient results from hot carrier filtering: a process that had been proposed by theory but never previously observed in poly-crystal films.

Two approaches have been demonstrated to increase \(S\), thereby simultaneously enhancing of \(S\) and \(S\sigma\): (a) increasing the local density of states (DOS) at the Fermi level, and (b) filtering out cold carriers \(\nu\) via band offset, which, respectively, modify the energy derivative of the number of carriers, \(d\tau(E)/dE\), and of the carrier mobility, \(d\mu(E)/dE\), terms in the Mott expression (Equation (1)).

\[
S = \frac{\pi^2 k_B^2 T}{3q} \left[ \frac{d[n(\sigma(E))]}{dE} \right]_{E=E_f} = \frac{\pi^2 k_B^2 T}{3q} \left[ \frac{dn(E)}{n dE} + \frac{d\mu(E)}{\mu dE} \right]_{E=E_f}
\]

(\(k_B\) is the Boltzmann constant, and \(q\) is electron charge.) Modification of the former term was demonstrated experimentally by Heremans and co-workers in Ti-doped PbTe with a distortion of the electronic DOS.\(^{[10]}\) In contrast, improvement based on the latter mechanism, the hot carrier filtering effect, might be obtained by synthetic structural and electronic integration of multiple phases. In this way, the interfacial potential between phases will selectively filter out the carriers with low energy thereby increasing \(d\mu(E)/dE\). In attempts to achieve this, a variety of phase combinations such as metal-semiconductor and semiconductor-semiconductor have been investigated.\(^{[11–17]}\) For example, the band bending between metals and semiconductors was shown to provide the interfacial potential necessary to selectively scatter low-energy carriers\(^{[11,12,15]}\) while a similar interfacial band offset in the semiconductor superlattice InGaAs/InGaAlAs and PbTe/PbSe core-shell structures plays the same role as a hot carrier filtering barrier.\(^{[11,17]}\)

In those experimental reports, phase-segregation from solid solutions was widely used to produce hetero-structured bulk materials. However, this top-down strategy is limited by the controllable preparation of several phase combinations defined by both the appropriate dimensions and compositions.
Alternatively, a bottom-up approach is more versatile in making it possible to build up targeted phases using molecular/nanoscaled building blocks, thereby greatly expanding the library of phase combinations. Among the bottom-up strategies, a solution process is desirable for its low cost and easy scale-up of the synthesis and for its application to a large variety of material systems. However, most of the reported solution approaches have been aimed at single-phased material rather than hetero-structures, and the $zT$ values achieved were significantly lower than those resulting from thermoelectric materials made by state-of-the-art ball milling.\cite{18,19} For example, for p-type bismuth telluride, the highest $zT$ reported by solution processing using hydrazine soluble molecular metal chalcogenide (MMC) chemistry\cite{20} is 0.6,\cite{19} $\sim$50% lower than the reported record for the same composition made using ball milling.\cite{3}

Here we report a novel hetero-structured Ag/oxide/$\text{Sb}_2\text{Te}_3$-Te, with $zT$ $\sim$1.0 at 460 K, significantly improving on previous solution-processed single-phased thermoelectric materials. More importantly, we were able to successfully stabilize a metallic silver phase in a telluride matrix by coating the silver in a thin oxide layer thereby producing a phase combination that does not form naturally because of the high solubility of silver in telluride under mild heating ($\sim$200 °C). Meanwhile, the oxide layer prevents silver atoms from alloying with telluride during annealing, thereby maintaining the carrier density in the optimal range ($5-8 \times 10^{19}$/cm$^3$). This mitigates the degradation of the Seebeck coefficient that we had previously observed.\cite{12} Theoretical modeling verifies that the high Seebeck coefficient and $zT$ of this hetero-structure are successfully explained by a hot carrier filtering model with an interfacial band offset of 0.2–0.3 eV, close to the theoretically predicted optimal value.\cite{17,21,22} To the best of our knowledge, this is the first report of this effect for a bulk, poly-crystallized material system processed in solution with both experimental observations and theoretical simulations. In addition to the advantage of preparation cost, the hetero-structure exhibits both thermal stability and enhanced TE performance. We believe that these results will enable the optimal and novel design of thermally stabilized hetero-phases in other material systems to further improve TE material conversion performance.

The hetero-structured film that we will refer to as Ag/oxide/$\text{Sb}_2\text{Te}_3$-Te was fabricated as shown in Figure 1(a). Two-dimensional (2D) array of silver NPs were first prepared by e-beam evaporating an 8-nm (mass thickness) silver film (99.999%) on a quartz substrate then, using rapid thermal annealing,
and structural layers. The layer that contains pores corresponds to the layer of solution-cast Sb$_2$Te$_3$ and Te; the sub-micron scale pores are formed by ligand decomposition during annealing.

The inset image highlights the hemi-spherical shaped thin oxide layer, and further confirms the existence of thin oxide coated silver NPs on the film. X-ray diffraction (Figure 1(d)) confirmed the existence of two main phases, rhombohedral Sb$_2$Te$_3$ and hexagonal Te, in the three samples (Sb$_2$Te$_3$-Te, Ag/oxide/Sb$_2$Te$_3$-Te, Ag/Sb$_2$Te$_3$-Te). The high doping level and inter-metallic impurities in the Ag/Sb$_2$Te$_3$-Te sample were not taken into account in the Rietveld refinement, which resulted in larger error than for the other samples in the fitting of the experimental X-ray diffraction patterns.

The composition and thickness of the oxide layer that covers the silver particles in Ag/oxide/Sb$_2$Te$_3$-Te are critical in defining the overall TE properties. Trimethylaluminum and vaporized water were chosen to grow amorphous Al$_2$O$_3$ with a thickness from 1 to 2 nm during ALD coatings. This avoids the silver oxidation that results if oxygen plasma is used. The inset image highlights the semi-spherical shaped thin oxide layer, and further confirms the existence of thin oxide coated silver NPs on the bottom of the film. X-ray diffraction (Figure 1(d)) confirmed the existence of two main phases, rhombohedral Sb$_2$Te$_3$ and hexagonal Te, in the three samples (Sb$_2$Te$_3$-Te, Ag/oxide/Sb$_2$Te$_3$-Te, Ag/Sb$_2$Te$_3$-Te). The high doping level and inter-metallic impurities in the Ag/Sb$_2$Te$_3$-Te sample were not taken into account in the Rietveld refinement, which resulted in larger error than for the other samples in the fitting of the experimental X-ray diffraction patterns.

Secondary ion mass spectroscopy (SIMS) (Figure 1(b)) combined with cross-sectional SEM imaging (Figure 1(c)) confirmed the layered structures of the film. Specifically, a depth profile comparison between Ag/oxide/Sb$_2$Te$_3$-Te film and a homogeneous film, Ag$_2$SbTe$_3$, which was prepared by casting a similar precursor containing cubic Ag$_2$SbTe$_3$ compound and Te, shows that the relative $^{107}$Ag signal increases significantly on the bottom for Ag/oxide/Sb$_2$Te$_3$-Te. This confirms that the silver atoms primarily accumulated on the bottom of the film for the hetero-structure. It is worth noting that the distribution profiles shown in this figure are broadened by the roughness of the film. SEM (Figure 1(c)) further confirms these morphologies and structural layers. The layer that contains pores corresponds to the layer of solution-cast Sb$_2$Te$_3$ and Te; the sub-micron scale pores are formed by ligand decomposition during annealing. The inset image highlights the hemi-spherical shaped thin oxide layer, and further confirms the existence of thin oxide coated silver NPs on the bottom of the film. X-ray diffraction (Figure 1(d)) confirmed the existence of two main phases, rhombohedral Sb$_2$Te$_3$ and hexagonal Te, in the three samples (Sb$_2$Te$_3$-Te, Ag/oxide/Sb$_2$Te$_3$-Te, Ag/Sb$_2$Te$_3$-Te). The high doping level and inter-metallic impurities in the Ag/Sb$_2$Te$_3$-Te sample were not taken into account in the Rietveld refinement, which resulted in larger error than for the other samples in the fitting of the experimental X-ray diffraction patterns.

The composition and thickness of the oxide layer that covers the silver particles in Ag/oxide/Sb$_2$Te$_3$-Te are critical in defining the TE properties. Trimethylaluminum and vaporized water were chosen to grow amorphous Al$_2$O$_3$ with a thickness from 1 to 2 nm during ALD coatings. This avoids the silver oxidation that results if oxygen plasma is used. The main function of the Al$_2$O$_3$ layer is to protect the silver NPs and prevent the diffusion of silver. The surface of Al$_2$O$_3$, a second layer of oxide, HfO$_2$ (~1 nm) was deposited to prevent the etching of Al$_2$O$_3$ by the basic (pH = 9) hydrazine solutions that were used to cast the metal chalcogenide in the following step. The total converting the silver film to a 2D array of NPs with a diameter of 40 ± 10 nm (s.d.). Two oxide layers: aluminum oxide (~1–2 nm) and hafnium oxide (~1 nm) were sequentially deposited using atomic layer deposition (ALD) on the exposed surface of the silver. In the final step, we used the hydrazine chemistry that has been developed previously.[19,20] Specifically, a solution containing Sb$_2$Te$_3$ with excess Te was cast on the substrates to cover the silver particles, following an annealing process at 200 °C. Control samples, referred to as Ag/Sb$_2$Te$_3$-Te and Sb$_2$Te$_3$-Te, (e.g. in Figure 2), were synthesized by skipping step 2 (thin oxide coating); or, both step 1 (forming of silver NPs) and step 2, while retaining all other step(s).

Secondary ion mass spectroscopy (SIMS) (Figure 1(b)) combined with cross-sectional SEM imaging (Figure 1(c)) confirmed the layered structures of the film. Specifically, a depth profile comparison between Ag/oxide/Sb$_2$Te$_3$-Te film and a homogeneous film, Ag$_2$SbTe$_3$, which was prepared by casting a similar precursor containing cubic Ag$_2$SbTe$_3$ compound and Te, shows that the relative $^{107}$Ag signal increases significantly on the bottom for Ag/oxide/Sb$_2$Te$_3$-Te. This confirms that the silver atoms primarily accumulated on the bottom of the film for the hetero-structure. It is worth noting that the distribution profiles shown in this figure are broadened by the roughness of the film. SEM (Figure 1(c)) further confirms these morphologies and structural layers. The layer that contains pores corresponds to the layer of solution-cast Sb$_2$Te$_3$ and Te; the sub-micron scale pores are formed by ligand decomposition during annealing. The inset image highlights the hemi-spherical shaped thin oxide layer, and further confirms the existence of thin oxide coated silver NPs on the bottom of the film. X-ray diffraction (Figure 1(d)) confirmed the existence of two main phases, rhombohedral Sb$_2$Te$_3$ and hexagonal Te, in the three samples (Sb$_2$Te$_3$-Te, Ag/oxide/Sb$_2$Te$_3$-Te, Ag/Sb$_2$Te$_3$-Te). The high doping level and inter-metallic impurities in the Ag/Sb$_2$Te$_3$-Te sample were not taken into account in the Rietveld refinement, which resulted in larger error than for the other samples in the fitting of the experimental X-ray diffraction patterns.

Figure 2. (a) The temperature dependence of electrical conductivities and Seebeck coefficients of Ag/oxide/ Sb$_2$Te$_3$-Te samples with 2-nm oxide layer in total (squares □) and 3-nm oxide layer in total (circles ○); (b)-(d) The temperature dependence of electrical conductivities (b), Seebeck coefficients (c) and power factors (d) of sample Sb$_2$Te$_3$-Te (squares □), Ag/oxide/Sb$_2$Te$_3$-Te (circles ○) and Ag/Sb$_2$Te$_3$-Te (triangles △). The error bars of Seebeck coefficients in (a) and (c) include the variation from batch to batch and the measurement error from cycle to cycle. Compared to the Seebeck coefficient errors, the test errors in the measurement of the electrical conductivities (b) are negligible. In addition, no significant trend of variation can be observed from the first cycle to the last.

thickness of the dielectric layer was minimized in order to facilitate carrier tunneling and maintain the high electrical conductivity. The optimum thickness of the oxide layer in terms of the TE performance was determined by investigating the electronic properties of several Ag/oxide/Sb₂Te₃ samples with different oxide thicknesses. As shown in Figure 2(a), the one with 1 nm Al₂O₃ and 1 nm HfO₂ in total, is more electrically conductive than the one with 2 nm Al₂O₃ as well as 1 nm HfO₂, 3 nm in total. However, the Seebeck coefficient of the 2-nm sample is lower than that of the one with a 3-nm oxide layer since the thin oxide layer of 2 nm in total is not thick enough to form a pinhole-free layer that effectively limits the diffusion of silver atoms. With the 2-nm oxide coating, the silver atoms can still pinhole-free layer that effectively limits the diffusion of silver atoms. With the 2-nm oxide coating, the silver atoms can still.

In summary, 2 nm Al₂O₃ plus 1 nm HfO₂ is the optimal thickness for the purpose of protecting silver NPs. A thinner layer than the optimum does not provide the required chemical confinement for the silver NPs and enhancement of the Seebeck coefficient. A thicker layer than the optimum jeopardizes the transport of carriers from Ag to Sb₂Te₃ and Te, and thereby leads to the degradation of conductivity. Accordingly, in the discussion of this paper, Ag/oxide/Sb₂Te₃ refers to the sample with optimum thickness and composition (2 nm Al₂O₃ plus 1 nm HfO₂) unless otherwise specified.

In Figure 2(b)-(d), two control samples, Sb₂Te₃ (squares) and Ag/Sb₂Te₃ (triangles) are compared with Ag/oxide/Sb₂Te₃ (circles). The errors include the variation from batch to batch and the measurement error from cycle to cycle. Compared to the Seebeck-coefficient errors, the test errors in the measurement of electrical conductivity are negligible. In addition, no significant trend of variation can be observed from the first cycle to the last. The oxide-coated sample exhibits the highest power factor $S^2\sigma$ (~10 $\mu$W/(cm·K²) at ~300 K); this is the result of a significantly higher Seebeck coefficient than that of Ag/Sb₂Te₃ and a respectable electrical conductivity that is between those of Ag/Sb₂Te₃ and Sb₂Te₃. The behaviors of these three samples can be well explained by the carrier densities at room temperature. Although the thin (3-nm) oxide layer in Ag/oxide/Sb₂Te₃ prevents most of the silver atoms from alloying with telluride, a small number of silver atoms still dope into the telluride to slightly increase the hole density from $3 \times 10^{19}$ to $6 \times 10^{19}$/cm³ (inset of Figure 3). According to the literature on silver doped Sb₂Te₃, (22) one silver atom in Sb₂Te₃ acts as an acceptor to produce two holes, so that the doped concentration of a silver impurity in Sb₂Te₃ matrix of Ag/oxide/ Sb₂Te₃ is estimated to be $1.5 \times 10^{19}$/cm³. This is an order of magnitude lower than that of Ag/Sb₂Te₃ since the hole density in Ag/Sb₂Te₃ (1.6 $\times 10^{20}$/cm³) is substantially higher than that in Ag/oxide/ Sb₂Te₃ (5.7 $\times 10^{19}$/cm³). This suggests that the oxide coating layer is responsible for the overall hole density in a moderate range (5–8 $\times 10^{19}$/cm³). Figure S1(c) in the supporting information is the top view of the sample after thermal treatment at 400 °C over one hour. At this extreme temperature, the cast Sb₂Te₃ layer mostly sublimed and the particles underneath could be observed. The average size and distribution of the oxide-coated silver NPs were the same as they were before the heating was experimentally initiated (Figure S1(a)). This result suggests that the oxide-coated silver NPs are inherently thermally stable to 400 °C, which is well above the entire application temperature range from room temperature to 200 °C.

In Figure 3, we show the room-temperature Pisarenko plot along with results of theoretical calculation in order to highlight the enhancement of the Seebeck coefficient for Ag/oxide/
Sb$_2$Te$_3$-Te hetero-structures. Figure 3 and Table S2 include the results of all the test samples with similar thickness (~1 µm). More specifically, the circles in carrier range 1 (R1) show Sb$_2$Te$_3$-Te data; the R2 and R3 circles, data for Ag/oxide/Sb$_2$Te$_3$-Te with an optimum oxide thickness (~3 nm in total) and the minimum oxide thickness (~2 nm in total) respectively; and the R4 circles, Ag/Sb$_2$Te$_3$-Te without oxide layer. As shown in this plot, Ag/oxide/Sb$_2$Te$_3$-Te samples possess moderate hole density in the range 5–8 × 10$^{19}$/cm$^3$. Moreover, the electronic properties of the samples (green circles) with 2-nm oxide layer (which results in only partial confinement of the silver atoms) are more like those of Ag/Sb$_2$Te$_3$-Te with a high carrier density (>10$^{20}$/cm$^3$). In order to further compare the Seebeck coefficient enhancement quantitatively, as shown in the inset table, several typical results in Figure 3 were selected and labeled: “Control 1” for Sb$_2$Te$_3$-Te, “Control 3” for Ag/Sb$_2$Te$_3$-Te, and “Sample” for Ag/oxide/Sb$_2$Te$_3$-Te. In addition, a Sb$_2$Te$_3$-Te sample with conventional silver doping was prepared by Arc melting, followed by the same solution casting route as presented in this paper (“Control 2”). During the synthesis of this control sample, the amount of silver used was chosen on the basis of a previous report to increase the hole density of Sb$_2$Te$_3$-Te slightly to a conventional silver doping was prepared by Arc melting, followed by the same solution casting route as presented in this paper (“Control 2”). During the synthesis of this control sample, the amount of silver used was chosen on the basis of a previous report.[23] to increase the hole density of Sb$_2$Te$_3$-Te slightly to a level equivalent to that of Ag/oxide/Sb$_2$Te$_3$-Te. With similar hole densities, 4.0 × 10$^{19}$/cm$^3$ for Control 2 and 5.7 × 10$^{19}$/cm$^3$ for Sample, the Seebeck coefficient of Ag/oxide/Sb$_2$Te$_3$-Te (Sample) is more than 30% higher than that of silver doped Sb$_2$Te$_3$-Te (Control 2). We believe this enhancement to be the result of oxide-maintained metal-semiconductor hetero-structures rather than the oxide itself since the oxide itself in this work is barely a dielectric layer with no free carriers, as supported by the evidence in supporting information (Table S1). This enhancement indicates that the efficiency for this materials system as given by $\sigma T$ was further improved by the hetero-structure design in a manner that has not been reported previously.

In order to better understand this enhancement of $S$ and $S\sigma T$, simulations were carried out based on various models. To simplify the calculation for Sb$_2$Te$_3$-Te (R1 circles), we assumed a single-phase p-type Sb$_2$Te$_3$ with multiple non-parabolic bands, ignoring the existence of excess Te.[24–26] The calculated Seebeck coefficients for bulk p-type Sb$_2$Te$_3$ (M1, light grey curve) steadily decrease with increasing carrier density. Since we applied additional ionized impurity scattering (IIS) to the bulk scattering time to fit the reduced electrical conductivities of the samples, the Seebeck coefficient also shifted up in magnitude by 10–12% at a given carrier density (M2, dark grey curve in Figure 3). The Seebeck coefficients of the control samples that have no silver NPs (Sb$_2$Te$_3$-Te, R1 circles) all fall between these two theoretical curves, showing a good agreement with the theory. However, the samples with oxide-coated Ag NPs (Ag/oxide/Sb$_2$Te$_3$-Te, R2 circles) show much higher Seebeck coefficients than the predicted values by theory at the equivalent carrier densities. Our hypothesis is that this enhancement is due to the carrier energy filtering by the band offset at the interface between the NPs and the matrix. Indeed, theoretical calculations show that this degree of Seebeck enhancement is possible when there is a carrier energy filtering with a cut-off energy ranging from 0.1 to 0.3 eV (M3, 0.1–0.3 eV curves) in the material, as shown in Figure 3 and supporting information (Figure S2 and Figure S3).[27] The cut-off energy is due to the interfacial band offset between the metallic Ag and the semiconducting matrix including both p-type Te and Sb$_2$Te$_3$, and assumes that the dielectric oxide layer is thin enough to not interfere with the band alignment as indicated in Figure S4. We propose that this present experimental study is an important evidence for the carrier energy filtering effect occurring in this kind of metal-semiconductor hetero-structures.

It is important to note that the total thickness of the hetero-structure is crucial to the performance as well. The dependence of carrier density and Seebeck coefficient on sample thickness is shown in Figure S5. We attribute this dependence to the constant number of activated dopants in telluride after the thin oxide coating, which are concentrated near the bottom of the sample. As the thickness of telluride decreases, total volume decreases but the number of silver dopants remains almost the same, resulting in a higher hole concentration and hence a lower Seebeck coefficient. This behavior of the samples with thicknesses less than 1 µm is similar to what was observed for samples without oxide layers on the silver particles (Ag/Sb$_2$Te$_3$-Te), since in both sets of samples, the concentration of silver dopants is high (>10$^{20}$/cm$^3$).

The thermal conductivities were measured by the 3ω method as shown in Figure 4(a) and described in the supporting information (Figure S6).[28] Compared to the other two control samples, Ag/oxide/Sb$_2$Te$_3$-Te has the lowest thermal conductivity. According to the carrier energy filtering theory,[27] the Lorenz number is reduced due to inclusion of the transport energy cutoff. We calculate the Lorenz number to be 1.7 × 10$^{-8}$ W·Ω$^{-1}$K$^{-2}$ for the Ag/oxide/Sb$_2$Te$_3$-Te sample with a 0.2 eV cut-off energy over the temperature range, while the other two samples have the conventional Lorenz number, $L = 2.45 \times 10^{-8}$ W·Ω$^{-1}$K$^{-2}$, as they are highly degenerate with high doping densities. From the Wiedemann-Franz law, $\kappa_e = L \sigma T$, we obtain electronic
thermal conductivity values of 0.18, 0.37, and 0.22 W·m⁻¹·K⁻¹ for Sb₂Te₃−Te, Ag/Sb₂Te₃−Te, and Ag/oxide/Sb₂Te₃−Te samples at room temperature, respectively. The lattice thermal conductivities are 0.84, 1.05, and 0.65 W·m⁻¹·K⁻¹, for Sb₂Te₃−Te, Ag/Sb₂Te₃−Te, and Ag/oxide/Sb₂Te₃−Te samples at room temperature, respectively. This indicates that the oxide-coated Ag NPs scatter phonons effectively to reduce the lattice thermal conductivity as shown in Figure 4(a) inset.

In contrast to the typical trend for degenerate semiconductors, the three samples do not show an obvious decrease in thermal conductivity as temperature increases. Note that for Ag/Sb₂Te₃−Te, the thermal conductivity increases as temperature increases, consistent with the behavior of metals. This suggests that the silver doping levels of the samples, especially for Ag/Sb₂Te₃−Te, are so high that the electronic contribution to the thermal conductivity is significant. This phenomenon has been observed also in the film system previously assembled by nanoparticles.[19] Using the power factors shown in Figure 2(d), the estimated zT values are shown in Figure 4(b). The maximum zT for Ag/oxide/Sb₂Te₃−Te is ∼1.0 at 460 K, more than two times higher than the zT values obtained for the control samples. Note that the zT values are calculated from the in-plane electronic properties (σ and S), and the cross-plane thermal conductivity κ. In this work, according to the calculated in-plane electronic contribution of thermal conductivity (κe), the heterostructure, Ag/oxide/Sb₂Te₃−Te, exhibits a lower value for κe than the semiconducting reference, Sb₂Te₃−Te (Figure S3), so that as expected, as the dielectric nano-structures are incorporated into the matrix, the overall in-plane lattice thermal conductivity for the heterostructure is estimated to be smaller than the thermal conductivity for the semiconducting matrix, Sb₂Te₃−Te. X-ray diffraction patterns are consistent with (see page S-8 in supporting information) the grains of Sb₂Te₃−Te being isotropic, so that one would expect their contribution to the phonon scattering to be similar to the in-plane and cross-plane thermal conductivity of Sb₂Te₃−Te. Based on this, the cross-plane thermal conductivity of sample Sb₂Te₃−Te gives an upper limit value of the in-plane thermal conductivity sample Ag/oxide/Sb₂Te₃−Te which is about 10%-20% higher than the measured cross-plane thermal conductivity. This variation is included in the zT values by using the above and the measured cross-plane thermal conductivity to give a possible deviation of 10%-20% in the error bars as shown in Figure 4. The details of this analysis are presented in the supporting information (Figure S7).

In conclusion, a thin oxide layer coating is shown to confine and protect silver NPs, thereby significantly reducing diffusion of silver atoms into the telluride with consequential improved stability of the silver NPs up to 400 °C; while at the same time, the 3-nm oxide layer helps retain the carrier density at S × 10¹⁷/cm³, resulting in an enhancement of the Seebeck coefficient by ∼30% over what was observed for control sample at an equivalent carrier density. This enhancement is accounted for with a simulation that includes an extensive IIS mechanism as well as a cut-off potential of 0.2 eV for hot carrier filtering. The cut-off is the interfacial band offset between the metallic Ag and the semiconducting matrix and we assume that the dielectric oxide coating is thin enough to not interfere with the band alignment, as indicated in Figure S4. The resulting power factor combined with the low thermal conductivity gives a zT of 1.0 at 460 K, significantly higher than reported for materials chemically synthesized previously.[11,19] To the best of our knowledge, this is the first successful experimental and theoretical demonstration of a hot carrier filtering effect in a thermally stable metal-semiconductor hetero-structure processed in solution, which opens up a new route for producing TE materials with high efficiencies due to the synergistic increase in both S and σ, with decreasing κ.

Experimental Section

All reagents were used directly from commercial suppliers without any purification except anhydrous hydrazine. Hydrazine (anhydrous, 98%, Sigma-Aldrich) was distilled firstly and stored in glove box for further use.

Film Preparation:

Step 1: Deposition of a two-dimensional (2D) array of silver NPs. The silver NPs were firstly prepared by e-beam evaporating an 8-nm (mass thickness) silver film (99.999%) on a cleaned quartz substrate then, using rapid thermal annealing to 850 °C for 1 minute, converting the silver film to a 2D array of NPs.

Step 2: Atomic layer deposition (ALD) of dielectric thin layer. Using an atomic layer deposition (ALD) process (Oxford FlexAL), two layers of oxide, aluminum oxide (~1–2 nm) and hafnium oxide (~1 nm) were deposited sequentially on the exposed surface of the silver NPs to form the corresponding thin oxide layers. The growth temperatures were 300 and 100 °C for aluminum oxide and hafnium oxide, respectively. Trimethylaluminum (TMA) and vaporized water, tetraethyl(hydrazinium) hafnium (TEMAH) and oxygen plasma were the precursors for the growth of Al₂O₃ and HfO₂, respectively. The growth rates and cycles numbers are shown in Table S1.

Step 3: Solution cast of metal chalcogenide. In the final step, the molecular metal chalcogenide (MMC) were prepared following the same procedure previously reported.[12] The overall concentrations of elemental Te and Sb are about 0.24 M and 0.08 M, respectively. About 5 drops of the as-prepared solution containing Sb and Te were drop-casted to cover the oxide-coated silver nanoparticles. This sample was naturally dried in glove box following annealing at 200 °C for 1 hour under an inert atmosphere. As for the synthesis of sample “Control2” as shown in Figure 3, Ag-doped Sb₂Te₃ and Te was firstly prepared by Arc melting a cold-pressed pellet containing 3.25 g Sb₂Te₃ and 1.8 × 10⁻³ g Ag powders. The Arc melted product was then ground into fine powders by regular ball milling and then following the same procedures as other samples for the preparation of the corresponding MMC.

Materials Characterization: Wide-angle XRD (WAXRD) data were obtained on a Philips X’Pert with Cu Kα radiation and Rietveld-refined using REX software (http://www.rexpd.com/rex/). The powder patterns of all crystalline phases were refined using fits with lattice cell parameters of Sb₂Te₃ (JCPDS 015–0874) and Te (JCPDS 089–4899). Scanning electron microscopy (SEM) images were taken on a Philips XL40 electron microscope after low angle ion milling in the FEI DB235 dual-beam FIB system. A Physical Electronics 6650 Dynamic Secondary Ion Mass Spectroscopy (SIMS) system was used to measure the [¹²⁸Ag to ¹²⁹Ag] ratio. A Dektak VI Profilometer tested the average thickness of each sample.

Measurements of Electronic Properties: 150-nm-thick Au contacts were thermally deposited on the film following van der Pauw pattern. A detailed description of the Hall and Seebeck measurements can be found in the literature.[12]

Measurements of Thermal Conductivities: For the thermal conductivity measurement, the film was deposited on a Si wafer with ~200 nm thermally grown oxide instead of using quartz. The plasma enhanced chemical vapor deposition (PECVD) was applied to grow a silica layer (~500 nm) on top of the film. A wire made of 4000 Å of Au on top of 200 Å of Ti, which functioned as both heater and thermometer, was patterned on each sample surface and fabricated by photolithography.
e-beam evaporation, and finally lift-off. These processing procedures were kept consistent in the preparation of both bare reference without telluride film and the real sample. The electrical resistance and the coefficient \( dR/dT \) of the metal wire were determined by measuring the electrical resistance at different temperatures between 20 and 200 °C. The third-harmonic voltage drop across the metal wire was measured at five different frequencies between 500 and 2 kHz.

Simulations: We modeled the carrier transport in bulk Sb\(_2\)Te\(_3\) based on the Boltzmann transport under the relaxation time approximation.\(^{[24]}\) Multiple non-parabolic bands were considered in the model with anisotropic effective masses. Antimony telluride has a rhombohedral crystal structure with a small direct band gap of ∼100 meV at the center of the Brillouin zone (BZ), T\(_\Gamma\) valley.\(^{[25]}\) Two other valence bands on the lines T–U and Z–F in the BZ have their band maxima close to that of the primary valence band.\(^{[25,26]}\) The acoustic phonon deformation potential scattering, polar optical phonon scattering, and the screened ionized impurity scattering were included in the bulk transport model. The charge carrier energy filtering scheme was then applied to the bulk model by introducing a cut-off energy level \( E_C \) in the transport integrals. It is assumed in the calculations that below the cut-off energy, all the carriers are prevented from participating in the conduction. Details of the carrier energy filtering theory are described elsewhere.\(^{[27]}\)

Supporting Information

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

Acknowledgments

Y.Z. and J.H.B. sincerely thank A. Gossard and P. Burke for helpful discussions and A. Sztein, P. Burke, B. Curin, and H. Lu for assistance with instrument use. This work was primarily supported as part of the Center for Energy Efficient Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0001009. The characterizations used the MRL Central Facilities, supported by the MRSEC Program of the NSF under Award No. DMR 1121053; a member of the NSF-funded Materials Research Facilities Network (www.mrfn.org). C.S.B. acknowledges the Feodor Lynen Research Fellowship supported by the Alexander von Humboldt Foundation.

Received: September 2, 2013
Revised: November 20, 2013
Published online: January 28, 2014

References