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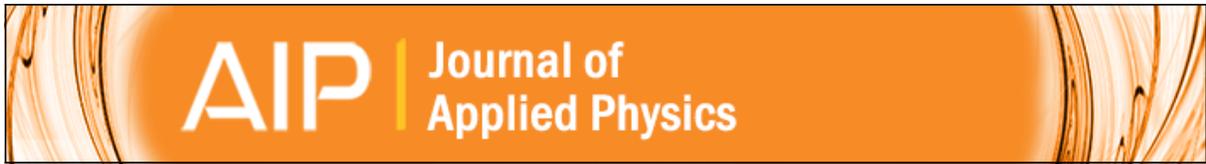
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Thermoelectric prospects of nanomaterials with spin-orbit surface bands

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Nanostructured composites and nanowire arrays of traditional thermoelectrics, like Bi, $Bi_{1-x}Sb_x$, and Bi_2Te_3, have metallic Rashba surface spin-orbit bands featuring high mobilities rivaling that of the bulk for which topological insulator behavior has been proposed. Nearly pure surface electronic transport has been observed at low temperatures in Bi nanowires, with diameter around the critical diameter, 50 nm, for the semimetal-to-semiconductor transition. The surface contributes strongly to the thermopower, actually dominating for temperatures $T < 100$ K in these nanowires. The surface thermopower was found to be -1 T $\mu V/K^2$, a value that is consistent with theory. We show that surface electronic transport together with boundary phonon scattering leads to enhanced thermoelectric performance at low temperatures of Bi nanowire arrays. We compare with bulk n-BiSb alloys, optimized $CsBi_4Te_6$, and optimized Bi_2Te_3. Surface dominated electronic transport can be expected in nanomaterials of the other traditional thermoelectrics. © *2012 American Institute of Physics*. [doi:10.1063/1.3686206]

I. INTRODUCTION

Materials of high thermoelectric (TE) figure of merit $zT = T\alpha^2\sigma/\kappa$, where T is the absolute temperature, α is the thermopower, σ is the electrical conductivity, and κ is the total thermal conductivity, are employed in solid state cooling devices and may be used in future waste heat recovery and heat energy harvesting applications.[1] Bismuth, $Bi_{(1-x)}Sb_x$ ($x \sim 0.1$) and Bi_2Te_3 are the traditional thermoelectric (TE) materials for low and room-temperature operation that have $zT \sim 1$. The material science of nanostructured TEs has advanced substantially in the past decade. Gains as high as a factor of two have been demonstrated, with nanostructured Bi_2Te_3 consisting of arrays of 1-5 nm diameter particles.[2] Such gains in zT are commonly associated with phonon and electronic phenomena in nanostructured materials. Phonon-boundary scattering decreases the phonon contribution to κ tending to increase zT.[3] The electronic properties of the bulk-like bands, α and σ, are modified also. In conduits, such as nanowires (NW) and constrictions in composites, characterized by a diameter d, electronic finite size effects[4] (arising when the electronic mean free path $mfp_e \sim d$, roughly) decrease σ without large changes in α and therefore tend to decrease zT. However, further decreases in d are considered to be beneficial, because of quantum size effects that appear when the quantum confinement energy $E_c = \hbar^2\pi^2/2m^*m_e d^2$ (where m^* is the bulk carrier effective mass and m_e is the free electron mass) is sufficiently large to allow manipulation of carrier densities and doping.[5] However, the TE effects arise in nanowires and nanostructures because surface charge conduc-tion and phonons scattering[6,7] have not been considered. Here, we show that these factors change the outlook for TEs substantially.

The reason for the new surface band in TEs is spin-orbit interaction (SOI) at the surface. Traditional TEs are formed from heavy elements that have a potential for large SOI. However, in bulk solids, time reversal symmetry combined with space inversion symmetry depresses SOI. In some cases, SOI is associated with gaps in the bulk bands. By contrast, at the crystal surface of semi-infinite surfaces of TEs, specifically bismuth, BiSb, and Bi_2Te_3, space symmetry is lost, and, at the surface, SOI effects are sufficiently strong that they give rise to a new band, which is distinct from the bulk-like band. Since this band arises because of SOI is interesting for spintronic applications. Surface state bands arising because of SOI were first observed spectroscopically with angle-resolved photoemission spectroscopy (ARPES)[8] in Bi crystals and, soon after, were identified in electronic transport of Bi nanowires.[9] Surface band conduction is relevant in nanostructures because of their high surface-to-volume ratio. Moreover, the recent discovery that selected bulk TEs, like Bi_2Te_3 and Bi_2Se_3, feature exotic three-dimensional (3D) topological insulator (TI) behavior[10] created new possibilities because, for Tis, the surface state would be protected from dissipation by time reversal symmetry and, therefore, has exotic spintronic properties and high mobility. Takahashi *et al.*[11] and Ghaemi *et al.*[12] presented models of the thermopower of surface states in interplay with bulk-like carriers in thin films and found that surface dominates at low temperatures. They were motivated by the report of Hor *et al.*[13] of enhancements in the thermopower of Bi_2Se_3; however, the surface origin of the thermopower in these experiments is uncertain. This is not surprising, since significant experimental hurdles exist (as

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well as fundamental reasons) for realizing pure surface conduction; in the field of Tis, it is observed that the most likely candidates according to theory, Bi_2Te_3 and Bi_2Se_3, are in fact not very good bulk insulators in the laboratory. Surface state band mobilities in Bi_2Te_3 are low[14] (1×10^4 cm^{2}s^{-1}V^{-1}) and unobservable in Bi_2Se_3.[15] Bi is classified as a trivial topological insulator,[16,17] which means that the surface states of Bi are not expected theoretically to be topologically protected from dissipation. Also, there is substantial bulk-surface state hybridization in Bi for some crystalline orientations[18] that may circumvent TI behavior. However, Ghaemi *et al.*[12] shows that even a strong TI-like Bi_2Se_3 that has a single massless Dirac cone hybridization between the top and bottom surfaces in a nanostructure can cause the charge carriers to be massive and the surface bands to be gapped. Bi features very low intrinsic dissipation in comparison with the strong TIs and, therefore, is a good candidate to exhibit high surface mobilities.

Bi is a semimetal where the overlap energy $E_0 \sim 37$ meV between the electron and hole band leads to a significant electron n and hole p density ($n = p = n_0 = 3 \times 10^{17}$ cm^{-3}). The TE properties of Bi are well known.[19] Also, in nanowires, when the confinement energy $E_c > E_o$ for $d \sim 50$ nm, the overlap becomes a gap and n and p can decrease critically below n_0; this phenomenon is called the semimetal-to-semiconductor (SMSC) transition.[5,20] Huber, Adeyeye, Nikolaeva, Konopko, Johnson, and Graf[21] (HANKJG) studied electronic transport, resistance, and thermopower, of 20-, 30-, 50-, and 200-nm Bi nanowire arrays—that is, nanowires that were both on the semimetal and semiconductor side of the SMSC were studied. The trends that were observed are reminiscent to those observed by Boukai, Xu, and Heath[22] and Lin, Rabin, Cronin, Ying, and Dresselhaus.[23] HANKJG also presented a Shubnikov-de Haas (SdH) study of the magnetoresistance oscillations caused by surface electrons and bulk-like holes that enable determination of their Fermi surfaces, densities, and mobilities. Surface electrons are in 3D Fermi surfaces. They showed that, for $d \sim 50$ nm, the SMSC has the effect of decreasing the bulk population several fold from n_0, the bulk value. Surface electrons are not very modified by confinement and have a density $N = -1.3 \times 10^{13}$ cm^{-2}. In these nanowires, surface high mobilities exceeding 2 m^{2}s^{-1}V^{-1} are observed and contribute strongly to the thermopower, dominating for temperatures $T < 100$ K. The surface thermopower is -1.2 T μV/K^2, a value that is consistent with theory, considering the density of surface states in Bi surfaces. For 50-nm NWs, for which the hole density is the smallest among all the NWs that were investigated, the 50 K surface charges thermopower is -60 μV/K^2. The bulk-like holes contribute $+ 35$ μV/K^2. Basing ourselves in these studies, here, we carry out an evaluation of the expected zT in NW arrays and nanostructures of Bi and BiSb and present a discussion of the prospects of Rashba surface band–dominated, nanostructured, traditional TE materials.

II. THERMOELECTRIC FIGURE OF MERIT

The diffusive thermopower (*mfp* < wirelength) is given by[24]

$$\alpha_\Sigma = \frac{(k_B^2 \pi^2 T/3e)}{E_F^\Sigma} \left[r + (d\,lnN/d\,lnE)_{E_F^\Sigma} \right]. \quad (1)$$

Here, E_F^Σ is the surface band Fermi energy, $r = (\partial \ln \tau / \partial \ln E)_{E_F^\Sigma}$, where τ is the carrier lifetime. We assume $r \sim 0$, which is appropriate in this case, as the lifetime is dominated by boundary scattering. $(\partial \ln N / \partial \ln E)_{E_F^\Sigma} = 3/2$ in 3D. From $N = -1.3 \times 10^{13}$ cm^{-2}, the Fermi energy is 18 meV, and, from Eq. (1), we find $\alpha_\Sigma = -1.2$ T μV/K^2, where the sign of the partial thermopower is related unambiguously to the sign of the charge of the carriers. In comparison, the low temperature thermopowers of electrons α_e and holes α_h in bulk Bi are found to be approximately -1 T μV/K^2 and $+3$ T μV/K^2, respectively.[19] In Bi nanowires, out-of-equilibrium effects, like the phonon-drag effect, are of negligible importance, since phonon scattering is mainly phonon-boundary rather than phonon-carrier.[25] This model for decreased phonon drag has been observed to apply in other cases of thermopower of nanowires, notably sub-100-nm-diameter Si point contacts[26] and Si and Ni nanowires, respectively.[27,28] This is relevant because Eq. (1) is not applicable in the case that there are phonon drag effects and also because such non-equilibrium effects limit zT to values that are much less than one.[1]

The normalized resistance and thermopower of the nanowires are shown in Figs. 1(a) and 2, respectively. HANKJG argued that the saturation of the resistance at low T in the normalized resistance and the trend toward negative thermopower for decreasing d can be associated with type-n surface states in Bi nanowires. The reason that surface states become dominant is that the surface-to-volume ratio increases as $1/d$ and the SMSC transition makes the bulk in the interior of the wires a semiconductor.

The data that is presented by HANKJG allows direct calculation of α and σ. The TE figure of merit zT has not been measured directly, but can be obtained from $T\alpha^2\sigma/\kappa$. However, the thermal conductivity was not measured directly. The (total) κ is $\kappa = \kappa_{electr} + \kappa_{phonon}$, where the first and second terms are the electronic and phonon conductivity, respectively. Moore, Pettes, Zhou, and Shi[28] presented a study of the κ of individual Bi nanowires with diameter in the range between 280 and 170 nm in the temperature range between 100 K and 300 K. We show Moore's data in Fig. 1(b). A trend of decreasing κ for decreasing diameter was observed; this is expected in terms of electronic and phonon size effects. Therefore, there is no reason to expect that this trend will reverse for finer nanowires and, therefore, the thermal conductivity in 30 nm and 20 nm nanowires can be expected to be even less than that for 150 nm nanowires. Measurements of κ of Bi composites by Song, Shen, Dunn, Moore, Goorsky, Radetic, Gronsky, and Chen that include fine, d down to 20 nm, nanocomposites support this expectation.[29]

Another estimate of the thermal conductivity relates to the electronic part. κ_{electr} can be estimated from the electronic conductivity σ assuming the very general Wiedeman-Franz (WF) law,

$$\kappa_{electr} = L_0 \sigma(T)T, \quad (2)$$

where $L_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.4 \times 10^{-8}$ (Volt)^2/K^2 is the usual Lorenz number. We are assuming that the electron gas is degenerate, a simplifying approximation.[1,30] Since the normalized resistance is known, a close (better than order of magnitude) estimate of the absolute conductivity can be obtained by considering that the room temperature resistance R (300 K) is more than $\rho_0 L/(\pi/4)d^2$, where ρ_0 is the 300 K resistivity, due to finite size effects.[4,31] The ratio ρ/ρ_{bulk} is proportional to mfp/d, where mfp, the mean free path, is the distance over which the carriers travel before being scattered. The mfp is of the order of the mm at low temperatures and a few microns at room temperature. Therefore, ρ/ρ_{bulk} is larger than one, and a close inequality at 300 K. The weakness of finite size effects at room temperatures is observed in four-point measurements of isolated individual Bi nanowires.[32] Here, we show our estimate of κ_{electr} in the case of our nanowires in Fig. 1(b). We find an inconsistency; the expected electronic term from Eq. (2) is larger than the measured total thermal conductivity from Moore *et al.*[28] However, in these experiments, electrical contact was not made to the nanowires and, therefore, electrical conductivity was not measured. The κ_{electr} term depends upon σ that, in turn, exhibits great variability, depending upon fabrication and prepara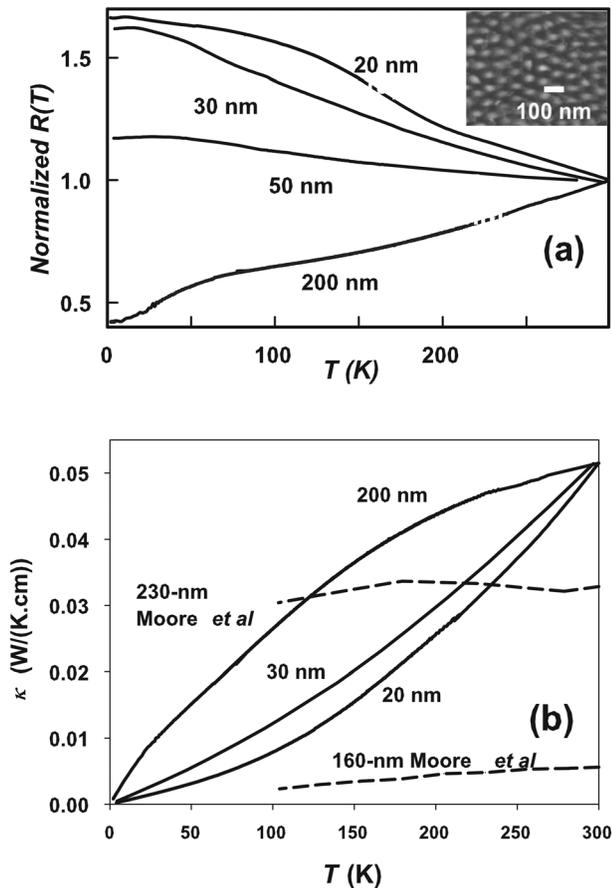tion. One way to reconcile the two measurements is to assume that the actual electrical conductivity in the Moore case was much smaller than in the HANKJG case and the phonon thermal conductivity is much smaller than the electrical thermal conductivity.

If $\kappa_{electr} \gg \kappa_{phonon}$, that is, for composites where the phonon conductivity is completely quenched, we have

$$zT = \frac{\alpha^2}{(\kappa/\sigma)}T = \frac{\alpha^2}{L_0}. \tag{3}$$

In their analysis of bulk Bi thermoelectricity, Gallo *et al.* remarked that, since the macroscopic parameter Z is a sensitive function of the carrier concentrations, it is convenient to speak of a "hypothetical optimum index of efficiency," z_oT. z_o occurs only when electronic transport involves only one type of carrier (electrons), ensuring (a) that the Seebeck coefficient is a maximum because holes do not participate and (b) that thermal conduction by bipolar diffusion is essentially zero. The hypothetical optimum applies to the case of a hypothetical Bi alloy, whereby the electrons dominate absolutely (we do not know that such an alloy exists). We introduce the same concept for Bi nanostructures. We use Eq. (3) to arrive at the hypothetical optimum values for nanostructures where only surface states contribute, shown in Fig. 3. Inspection of Fig. 2 shows that the most favorable case is the one of 50-nm Bi nanowires[19] that exhibits pure surface conduction for $T < \sim 50$ K. For higher temperatures, holes contribute to electronic transport and decrease α and zT. In this regard, the study by Lin *et al.* of 45-nm BiSb nanowires is interesting in that their thermopower is linear for temperatures as high as 100 K.[23] We have compared nanowire arrays to the select number of materials that are known to have large zT at low temperature. These results are shown in Fig. 3 also. Most successful are the Bi$_{1-x}$Sb$_x$ alloys. We show representative data

FIG. 1. (a) Inset. SEM image of the top of a 50-nm Bi nanowire array. Light spots represent nanowires. Electron energy is 10 keV. Normalized resistance of arrays of 200-, 50-, 30-, and 20-nm Bi nanowires as indicated. (b) Thermal conductivity from various sources as indicated. Solid line: κ_{electr} evaluated using Eq. (2). Dashed lines: κ_{phonon} from Moore, Pettes, Zhou, and Shi (Ref. 28); diameters are indicated.
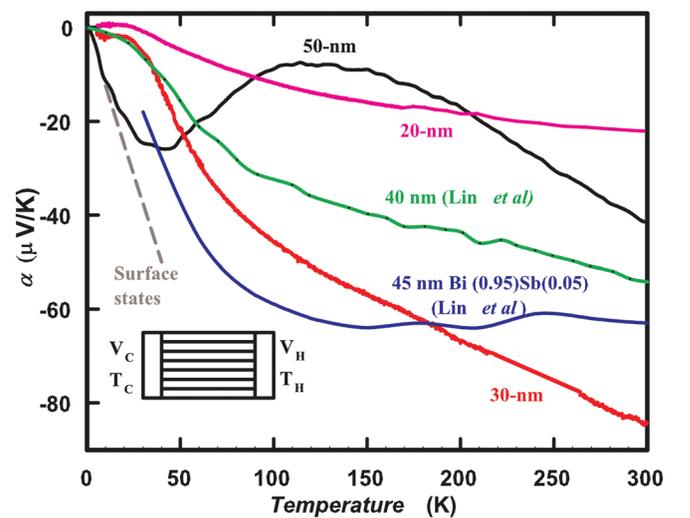

FIG. 2. (Color) Inset: Anvil-type experimental set-up for thermopower α of massive nanowire arrays. The set-up assumes that there is a heater that maintains heat current from the hot (H) to the cold (C) side. Then, $\alpha = (V_H - V_C/(T_H - T_C)$, where V_H and V_C are the electrochemical potentials, T_H T_C. Main panel: Thermopower of 200-, 50-, 30-, and 20-nm Bi nanowires as indicated. Forty-nm data from Lin, Rabin, Cronin, Ying, and Dresselhaus (Ref. 23) is also shown. The dashed line on the 50-nm data is a linear fit.
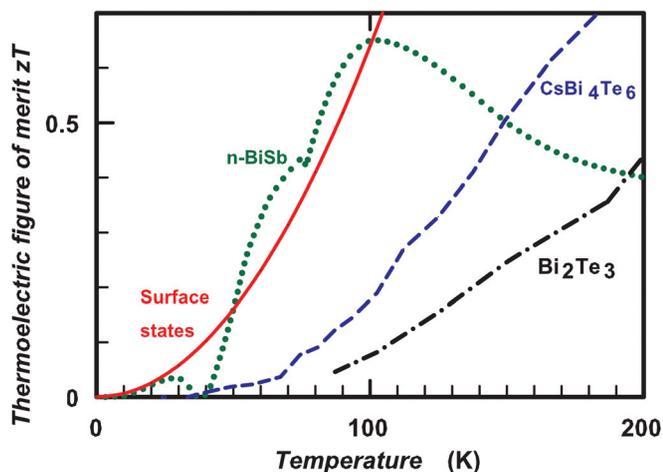
FIG. 3. (Color) Thermoelectric figure of merit zT. Hypothetical optimum zT of arrays of nanowires featuring surface state bands in comparison to that of bulk n-BiSb (Ref. 33), optimized $CsBi_4Te_6$ (Ref. 34), and optimized Bi_2Te_3 (Ref. 1).

from Redko.[33] This data shares many commonalities with the data presented by Lenoir *et al.*[34] The data labeled with Bi_2Te_3 is representative of the $(Bi-Sb)_2(Te-Se)_3$ alloys.[1] We also show data for $CsBi_4Te_6$.[35] The values of optimal hypothetical zT of surface states and of 50-nm Bi and of 45-nm Bi(0.95)Sb(0.05) exceed that of the other materials that are known to display excellent TE properties at low temperatures. This capability can be employed directly in thermoelectric coolers, where the fractional temperature decrease $(T_H - T_C)/T_C$ per stage is $(1/2)zT_C$.[1]

In practice, nanowire arrays are embedded in an alumina matrix that is amorphous. The κ of the alumina at room temperature has been estimated[35] to be 1.4 W/(m K), which represents a small fraction of the κ_{electr}. Therefore, we expect that the contribution of the matrix can be neglected in nanowire arrays.

III. CONCLUSION: PROSPECT OF NANOSTRUCTURED TRADITIONAL THERMOELECTRICS

The theory of topological insulators predicts many interesting properties; however, substantial hurdles exist for realizing these predictions, since the candidate materials are, in fact, poor bulk insulators. Our proposal for aiding bulk insulator behavior in semimetal, like Bi, Sb, and BiSb, is to shape these TEs into nanowires that become semiconductors as a result of bulk quantum confinement. We tested Bi nanowires that show strong quantum confinement effects for large diameters (comparatively to most of the other thermoelectrics) due to small bulk effective mass. Fifty-nm wires feature almost pure surface conduction. Bi is not a true topological insulator. Still, nanowires of Bi are exceptional materials that exhibit carrier mobilities of over 2 $m^2 s^{-1} V^{-1}$ with a density of 2.2×10^{12} cm^{-2}. This mobility is large, 2/3 of the values that are found for unsuspended graphene,[36] with significantly lower charge densities. Mobility values are twice those found by Qu *et al.*[14] for Bi_2Te_3 surface bands. The high value of surface mobility appears to be related to the special conditions in 50-nm wires, since it is significantly

less for 30- and 20-nm wires. Fifty-nm Bi nanowires are the most compelling case of pure surface conduction for $T < \sim 50$ K. As put forth by Lin *et al.*[23] in their study of 45-nm BiSb nanowires, maybe the advantages of alloying and quantum confinement can be advantageously combined in future experiments with BiSb nanostructures.

Our estimate of the TE figure of merit is shown in Fig. 3. The values of optimal hypothetical zT of surface states and of 50-nm Bi and of 45-nm Bi (0.95)Sb(0.05) exceed that of the other materials that are known to display excellent TE properties at low temperatures. From this study, it appears that nanowire arrays and composites based on nanowires of traditional TEs Bi, BiSb, and also of other TEs that exhibit topological insulator behavior will be of practical interest for cooling and energy sensing. Since the surface bands arise because of spin-orbit interactions, spin-dependent transport devices can probably be engineered using these materials, and, therefore, spintronic applications may be realized in the future.

Many experimental studies of fine nanowires and composites point out the relevance of phonon boundary scattering that results in a decreased phonon thermal conductivity.[6,7,28,29] Unfortunately, experiments have not measured all the properties of Bi (or other TIs) in the same system. HANKJG measured thermopower and electrical conductivity only, and not κ. Others, notably Moore *et al.*[28] and Song *et al.*[29] measured κ, but did not measure σ or α. Integrated experiments with state-of-the-art materials are necessary to fully understand the new TE nanomaterials.

[1]H. J. Goldsmid, in *Electronic Refrigeration* (Pion Limited, London, 1986).
[2]R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, Nature **413**, 597 (2001).
[3]D. G. Cahill, W. K. Ford, K. E. Goodson, G. D. Mahan, H. J. Maris, A. Majumdar, R. Merlin, and S. R. Phillpot, J. Appl. Phys. **93**, 793 (2003).
[4]E. H. Sondheimer, Adv. Phys. **1**, 1 (1952).
[5]L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B **47**, 16631 (1993).
[6]A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. Yang, Nature **451**, 163 (2008).
[7]A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J.-K. Yu, W. A. Goddard III, and J. R. Heath, Nature **451**, 168 (2008).
[8] Ph. Hofmann, Prog. Surf. Sci. **81**, 191 (2006).
[9]T. E. Huber, A. Nikolaeva, D. Gitsu, L. Konopko, C. A. Foss, Jr., and M. J. Graf, Appl. Phys. Lett. **84**, 1326 (2004).
[10]M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. **82**, 3045 (2010).
[11]R. Takahashi and S. Murakami, Phys. Rev. B **81**, 161302 (2010).
[12]P. Ghaemi, R. S. K. Mong, and J. E. Moore, Phys. Rev. Lett. **105**, 166603 (2010).
[13]Y. S. Hor, A. Richardella, P. Roushan, Y. Xia, J. G. Checkelsky, A. Yazdani, M. Z. Hasan, N. P. Ong, and R. J. Cava, Phys. Rev. B **79**, 195208 (2009).
[14]D.-X. Qu, Y. S. Hor, J. Xiong, R. J. Cava, and N. P. Ong, Science **329**, 821 (2010).

[15]N. P. Butch, K. Kirshenbaum, P. Syers, A. B. Shuskov, G. S. Jenkins, H. D. Drew, and J. Paglione, Phys. Rev. B **81**, 241301 (2010).

[16]Y. Liu and R. E. Allen, Phys. Rev. B **52**, 1566 (1995).

[17]L. Fu and C. L. Kane, Phys. Rev. B **76**, 045302 (2007).

[18]T. Hirahara, T. Nagao, I. Matsuda, G. Bihlmayer, E. V. Chulkov, Yu. M. Korotev, P. M. Echenique, M. Saito, and S. Hasegawa, Phys. Rev. Lett. **97**, 146803 (2006).

[19]C. F. Gallo, B. S. Chandrasekhar, and P. H. Sutter, J. Appl. Phys. **34**, 144 (1963).

[20]T. E. Huber, A. Nikolaeva, L. Konopko, and M. J. Graf, Phys. Rev. B **79**, 201304 (2009).

[21]T. E. Huber, A. Adeyeye, A. Nikolaeva, L. Konopko, R. C. Johnson, and M. J. Graf, Phys. Rev. B **83**, 235414 (2011).

[22]A. Boukai, K. Xu, and J. R. Heath, Adv. Mater. **18**, 864 (2006).

[23]Y.-M. Lin, D. Rabin, S. B. Cronin, J. Y. Ying, and M. S. Dresselhaus, Appl. Phys. Lett. **81**, 2403 (2002).

[24]R. Fletcher, Semicond. Sci. Technol. **14**, R1 (1999).

[25]D. Gitsu, T. Huber, L. Konopko, and A. Nikolaeva, Phys. Status Solidi B **242**, 2497 (2005).

[26]R. Trzcinski, E. Gmelin, and H. J. Queisser, Phys. Rev. Lett. **56**, 1086 (1986).

[27]A. Soni and G. S. Okram, Appl. Phys. Lett. **95**, 013101 (2009).

[28]A. L. Moore, M. T. Pettes, F. Zhou, and L. Shi, J. Appl. Phys. **106**, 034310 (2009).

[29]D. W. Song, W. N. Shen, B. Dunn, C. D. Moore, M. S. Goorsky, T. Radetic, R. Gronsky, and G. Chen, Appl. Phys. Lett. **84**, 1883 (2003).

[30]N. W. Ashcroft and N. D. Mermin, in *Solid State Physics* (Saunders College Publishing, Fort Worth, 1976), p. 258.

[31]R. Hartman, Phys. Rev. **181**, 1070 (1969).

[32]A. Nikolaeva, T. E. Huber, D. Gitsu, and L. Konopko, Phys. Rev. B **77**, 035422 (2008).

[33]N. A. Redko, *Proceedings of the 14th International Conference on Thermoelectrics* (IEEE, Piscataway, NJ, 1995).

[34]B. Lenoir, M. Cassart, J.-P. Michenaud, H. Scherrer, and S. Scherrer, J. Phys. Chem. Solids **57**, 89 (1996).

[35]D. Chung, T. Hogan, P. Bazis, M. Tocci-Lane, C. Kannenwurf, M. Bastea, C. Uher, and M. Kanatzidis, Science **287**, 1024 (2000).

[36]K. I. Bolodin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer, Solid State Commun. **146**, 351 (2008).