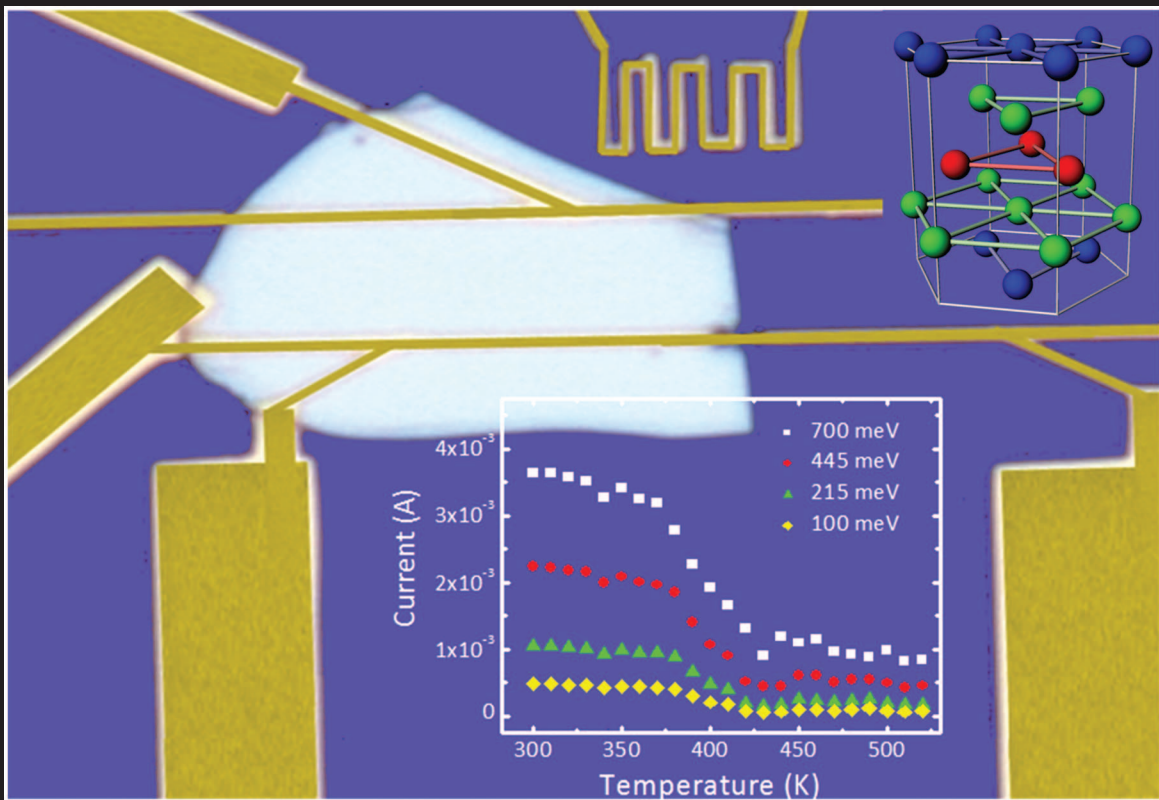


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AIP

Atomically-thin crystalline films and ribbons of bismuth telluride

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The authors report on “graphene-like” exfoliation of the large-area crystalline films and ribbons of bismuth telluride with the thicknesses of a few atoms. It is demonstrated that Bi_2Te_3 crystal can be mechanically separated into its building blocks— $\text{Te}-\text{Bi}-\text{Te}-\text{Bi}-\text{Te}$ atomic fivefolds—with the thickness of ~ 1 nm and even further—to subunits with smaller thicknesses. The atomically-thin films can be structured into suspended crystalline ribbons providing quantum confinement in two dimensions. The quasi two-dimensional crystals of bismuth telluride revealed high electrical conductivity and low thermal conductivity. The proposed *atomic-layer engineering* of bismuth telluride opens up a principally new route for drastic enhancement of the thermoelectric figure of merit. © 2010 American Institute of Physics. [doi:10.1063/1.3280078]

The mechanical exfoliation of graphene by the Manchester, U.K.—Chernogolovka, Russia team¹ and discovery of its unique electrical,^{2,3} thermal,^{4,5} and optical⁶ properties stimulated major interest to the atomically-thin films. In this letter we show that bismuth-telluride (Bi_2Te_3), a vital material for thermoelectric industry, can also be subjected to mechanical exfoliation resulting in the atomically-thin crystalline films, i.e., quasi two-dimensional (2D) crystals. The successful exfoliation of the quasi 2D crystals of bismuth telluride opens up tremendous opportunities for re-engineering its thermoelectric properties and enhancing the thermoelectric figure of merit $ZT=S^2\sigma T/K$ (here $S=-\Delta V/\Delta T$ is the Seebeck coefficient, ΔV is the voltage difference corresponding to a given temperature difference ΔT , σ is the electrical conductivity, and K is the thermal conductivity). It has been predicted theoretically that ZT can be drastically increased in crystalline Bi_2Te_3 quantum wells with the thickness of just few atomic layers (~ 1 nm) owing to either charge carrier confinement⁷⁻⁹ or acoustic phonon confinement.^{10,11} Conventional chemical vapor deposition, electrochemical, or other means are not suitable for fabrication of crystalline structures with such a thickness. Most of the thermoelectric thin films or superlattices on the basis of Bi_2Te_3 investigated so far were either polycrystalline or alloyed, or had the thicknesses far greater and the potential barrier height far less than those required for strong spatial confinement of electrons and phonons.

In this letter, we show that quasi 2D crystals of bismuth telluride can be mechanically exfoliated following a “graphene-like” procedure. The presence of the *van der Waals gap* allows one to disassemble Bi_2Te_3 crystal into its building blocks—five monatomic sheets of $\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}$, which have the thickness of ~ 1 nm. In some cases, the *atomic fivefolds* can be broken further leading to $\text{Bi}-\text{Te}$ atomic bilayers and $\text{Bi}-\text{Te}-\text{Bi}$ atomic trilayers. The resulting quasi 2D crystals retain their good electrical conductivity and low thermal conductivity important for thermoelectric applications.

The crystal structure of Bi_2Te_3 is rhombohedral with five atoms in one unit cell.¹² The lattice parameters of the hexagonal cells of Bi_2Te_3 are $a_H=0.4384$ nm and $c_H=3.045$ nm. Its atomic arrangement can be visualized in terms of the layered sandwich structure (see Fig. 1). Each sandwich is built up by five monatomic sheets $\{-\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}-\}$, referred to as atomic fivefolds, along the c_H axis. The superscripts (1) and (2) denote two different chemical states for the anions. The outmost atoms $\text{Te}^{(1)}$ are strongly bound to three planar $\text{Te}^{(1)}$ and three Bi metal atoms of the same fivefold (also referred to as *quintuple*) layers, and weakly bound to three $\text{Te}^{(1)}$ atoms of the next fivefold. The van der Waals bonds between the fivefolds can be broken leading to exfoliation of the five-atomic-units relatively easily. The bond strength within the fivefold is not the same. The $\text{Bi}-\text{Te}^{(2)}$ bond is the second weakest points within the crystal structure. The latter creates a possibility for producing quasi 2D atomic trilayers and bilayers.

In order to isolate Bi_2Te_3 fivefolds and break them into atomic planes we employed a method similar to the one used for exfoliation of single-layer graphene.¹⁻³ We previously

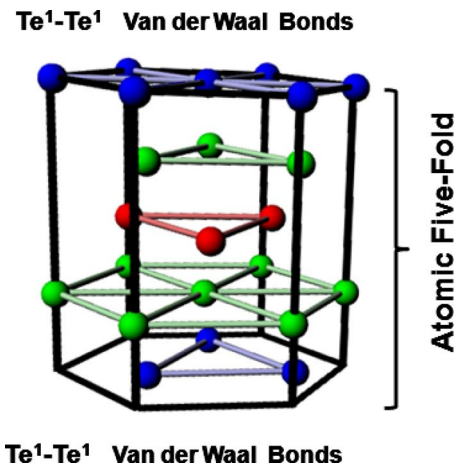


FIG. 1. (Color online) Schematic of $\{-\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}-\}$ atomic fivefolds, referred to as quintuples, which are building blocks of Bi_2Te_3 crystal. The fivefolds are bound to each other via weak van der Waals forces, which allow for their mechanical exfoliation.

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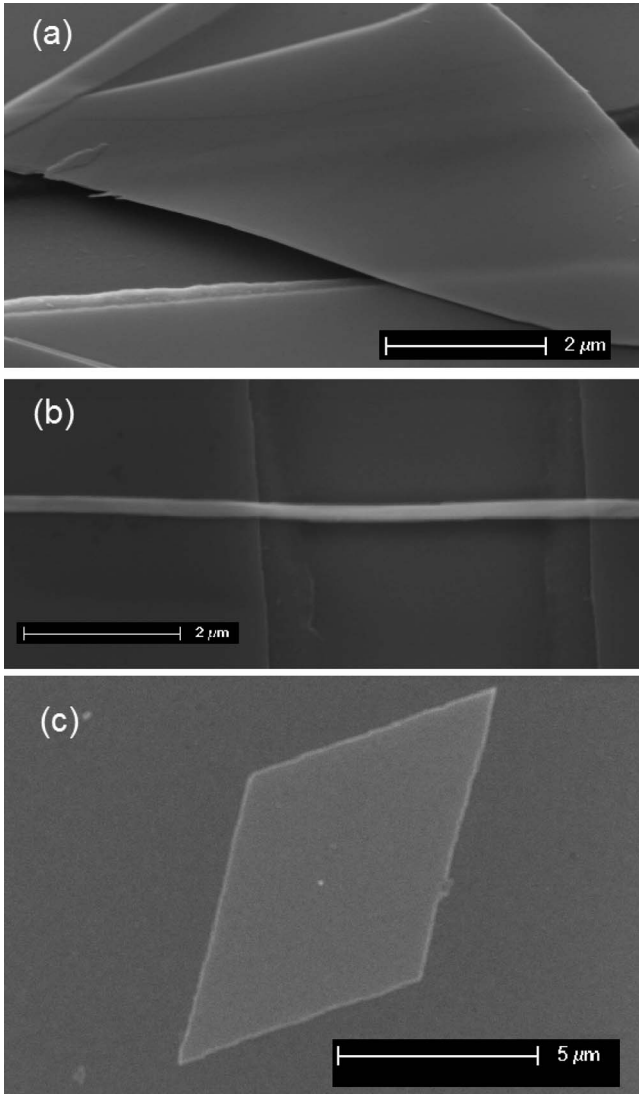


FIG. 2. SEM images of quasi 2D bismuth telluride crystals demonstrating the possibilities of the exfoliation technique. (a) Few-atomic-layer Bi-Te crystals suspended across a trench in Si/SiO₂ wafer. Note that the sides of the trench are clearly seen through the film owing to its few-atomic thickness. (b) Long (>6 μm) suspended ribbon made of quasi 2D bismuth telluride crystal. (c) Large-area uniform atomic fivefold of rhombic shape.

had extensive experience with mechanical exfoliation of graphene from various bulk graphite sources¹³ and determining the number of layers through Raman spectroscopy on different substrates.¹⁴ In the present case of bismuth telluride, the number of atomic planes was verified through a combination of the optical inspection, atomic force microscopy (AFM) and the scanning electron microscopy (SEM). The thickness of the atomic fivefold is ~1 nm. We scanned the steplike edges of the flakes with an advanced AFM (Veeco Dimension ICON) capable of ~0.1 nm vertical resolution. Some of the obtained few-atomic layer flakes were transferred to the Si/SiO₂ wafers with prefabricated trenches for better visualization [see SEM images in Fig. 2(a)]. We found that the Bi-Te atomic planes can also be broken into long ribbons as the one shown in Fig. 2(b). The latter can potentially lead to the electron (hole) quantum confinement in two lateral dimensions owing to the very small effective masses of the charge carriers. The rectangular and rhomb-shaped films were present among the exfoliated flakes, which facilitated the device fabrication. Based on AFM and SEM

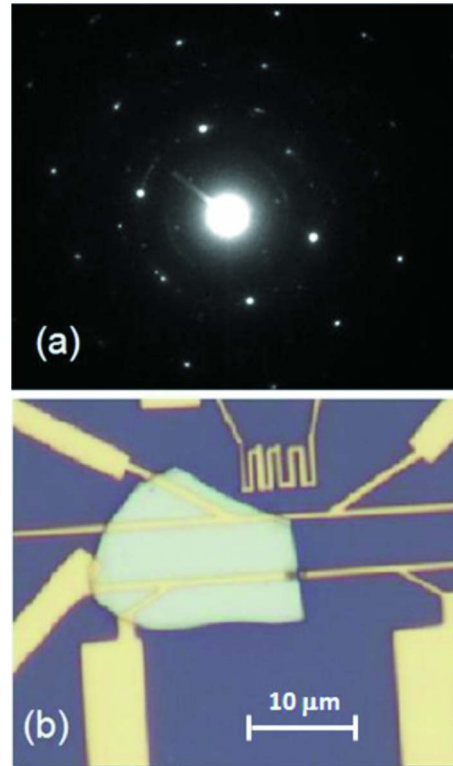


FIG. 3. (Color online) (a) SAED pattern indicating that the atomically-thin films of bismuth telluride are crystalline. (b) Fabricated device structure to test the electrical properties of the quasi 2D bismuth telluride crystals.

inspection the rhomb-shaped crystalline film shown in Fig. 2(c) is an atomic $\{-\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}-\}$ quintuple or fivefold. It is interesting to note that its thickness of ~1 nm should be sufficient for a drastic enhancement of ZT in the bismuth telluride quantum well according to the predictions of Dresselhaus *et al.*⁷ Note that in our mechanically exfoliated Bi-Te quasi 2D crystals the potential barrier height is essentially infinite unlike in the Bi₂Te₃-based superlattices. The latter creates interesting possibilities for the electron and phonon band-structure engineering, which were not available previously.

Another important feature of our quasi 2D bismuth telluride atomic films is their perfect crystalline nature, which was verified by the selected area electron diffraction (SAED). We used SAED crystallographic technique because it is more sensitive to the in-plane atomic arrangement as compared to other techniques such as x-ray diffraction. Many spots in the atomic films have been examined with this technique. The pattern shown in Fig. 3(a) is characteristic for the hexagonally structured sublattices of the rhombohedral crystal lattice of Bi₂Te₃. In order to test the electrical properties of the obtained atomically-thin films we fabricated device structures with Ti/Au contacts on the top surface. The thickness of the SiO₂ layer was chosen to be ~300 nm (i.e., the same as in graphene devices) for better optical identification. A representative device is shown in Fig. 3(b). The contacts seen on the image are to provide source-drain (SD) voltage. The gate bias was supplied from the back through the heavily doped Si wafer.

The room-temperature (RT) SD current-voltage characteristics of the devices made from the bismuth telluride flakes with the uniform thickness (number of atomic planes) revealed linear dependence (see inset to Fig. 4) and a rather

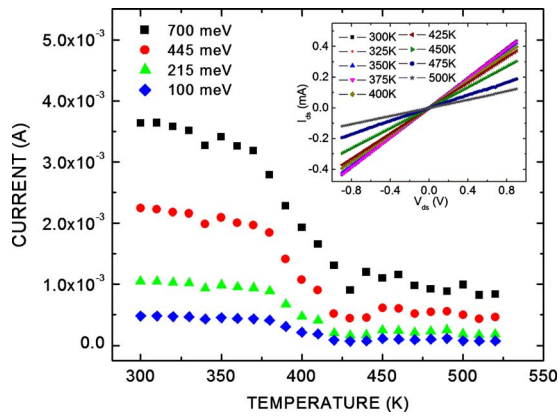


FIG. 4. (Color online) Current as a function of temperature in Bi-Te atomic crystals shown for different source—drain voltages. Inset shows current—voltage characteristics of a device in the low-bias region for different temperature.

low electrical resistivity on the order of $\sim 10^{-4} \Omega\text{m}$. The measured RT resistivity is comparable to the values reported for thick Bi_2Te_3 films used in thermoelectric devices.^{15–19} The resistivity of $\sim 10^{-5} \Omega\text{m}$ is considered to be optimal in conventional Bi_2Te_3 films because its further reduction leads to decreasing Seebeck coefficient. A weak nonlinearity was observed for higher SD voltage and higher temperature T . Figure 4 shows I_{SD} current in the atomically-thin crystalline bismuth telluride films as the function of temperature for several different voltages. One can see that the current is nearly constant for T below ~ 375 – 400 K but then starts to decrease rapidly before it saturates at $T \sim 450$ K. Such temperature dependence was reproducible for several tested devices and observed before and after annealing. The data shown in the inset for a different device revealed a similar trend. In general, the increase in the resistance with increasing temperature is more typical of metals rather than semiconductors. But it is rather common for Bi_2Te_3 films and was observed for materials produced by a range of different techniques.^{15–19} It is explained by the specifics of the electron scattering on acoustic phonons and defects in Bi_2Te_3 (Ref. 20) although few exceptions from this dependence were also reported.²¹ In our case, the dependence is not monotonic with the bending point ~ 400 K. In the thin films with the thickness of just few atomic layers the electron transport may strongly depend on the coupling to the substrate and remote impurity scattering.

Our technique for preparation of quasi 2D thermoelectric crystals and ribbons open up an entirely different route for re-engineering properties of thermoelectric materials via the electron and phonon confinement. It also allows for creation of the “designer” nonstoichiometric atomic crystals with both types of conductivity (n and p) defined by the number of atomic planes. The mechanically exfoliated quasi 2D bismuth telluride crystals are suitable for the experimental verification of recent ideas for increasing ZT via perpendicularly applied electric field.²² Thermoelectric applications require low values of K . Although we have not conducted detail study of heat conduction in these films, preliminary observations suggest that the atomic fivefolds on Si/SiO₂ substrates have small K . This conclusion is based on strong local heating induced by very weak laser powers focused on the films. The bulk quantity of material for practical thermoelectric ap-

plications can be obtained by preparing thick films consisting of overlapping atomic crystals. The proposed approach can be extended to other thermoelectric materials.²³

In conclusion, we succeeded in the graphene-like exfoliation of the crystalline films of bismuth telluride films with the thicknesses of few atoms. It was established from the comprehensive microscopic study that Bi_2Te_3 crystal most readily cleaves into its building blocks, $\{-\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}-\}$ atomic fivefolds also referred to as quintuples. The atomic films of bismuth telluride reveal high electrical conductivity with unusual temperature dependence. The obtained results open up a possibility of the atomic-layer engineering of bismuth telluride properties, and may lead to a drastic enhancement of the thermoelectric figure of merit.

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- ¹K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666 (2004).
- ²K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Nature (London)* **438**, 197 (2005).
- ³Y. Zhang, J. W. Tan, H. L. Stormer, and P. Kim, *Nature (London)* **438**, 201 (2005).
- ⁴A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, *Nano Lett.* **8**, 902 (2008); S. Ghosh, I. Calizo, D. Teweldebrhan, E. P. Pokatilov, D. L. Nika, A. A. Balandin, W. Bao, F. Miao, and C. N. Lau, *Appl. Phys. Lett.* **92**, 151911 (2008).
- ⁵D. L. Nika, S. Ghosh, E. P. Pokatilov, and A. A. Balandin, *Appl. Phys. Lett.* **94**, 203103 (2009); D. L. Nika, E. P. Pokatilov, A. S. Askerov, and A. A. Balandin, *Phys. Rev. B* **79**, 155413 (2009).
- ⁶R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, *Science* **320**, 1308 (2008).
- ⁷M. Dresselhaus, G. Dresselhaus, X. Sun, Z. Zhang, S. Cronin, and T. Koga, *Phys. Solid State* **41**, 679 (1999).
- ⁸L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B* **47**, 12727 (1993).
- ⁹F. J. DiSalvo, *Science* **285**, 703 (1999).
- ¹⁰A. Balandin and K. L. Wang, *Phys. Rev. B* **58**, 1544 (1998).
- ¹¹A. Balandin and K. L. Wang, *J. Appl. Phys.* **84**, 6149 (1998).
- ¹²W. Richter, H. Kohler, and C. R. Becker, *Phys. Status Solidi B* **84**, 619 (1977).
- ¹³I. Calizo, A. A. Balandin, W. Bao, F. Miao, and C. N. Lau, *Nano Lett.* **7**, 2645 (2007); I. Calizo, F. Miao, W. Bao, C. N. Lau, and A. A. Balandin, *Appl. Phys. Lett.* **91**, 071913 (2007).
- ¹⁴I. Calizo, W. Bao, F. Miao, C. N. Lau, and A. A. Balandin, *Appl. Phys. Lett.* **91**, 201904 (2007); I. Calizo, I. Bejenari, M. Rahman, G. Liu, and A. A. Balandin, *J. Appl. Phys.* **106**, 043509 (2009).
- ¹⁵X. H. Ji, X. B. Zhao, Y. H. Zhang, B. H. Lu, and H. L. Ni, *Mater. Lett.* **59**, 682 (2005).
- ¹⁶O. Yamashita and S. Tomiyoshi, *Jpn. J. Appl. Phys., Part 1* **42**, 492 (2003).
- ¹⁷W. Xie, X. Tang, Y. Yan, Q. Zhang, and T. M. Tritt, *J. Appl. Phys.* **105**, 113713 (2009).
- ¹⁸J. P. Fleurial, L. Gaillard, and R. Triboulet, *J. Phys. Chem. Solids* **49**, 1237 (1988).
- ¹⁹V. A. Kulbachinskii, M. Inoue, M. Sasaki, H. Negishi, W. X. Gao, K. Takase, Y. Gimman, P. Lostak, and J. Horak, *Phys. Rev. B* **50**, 16921 (1994).
- ²⁰T. A. Christakudi, S. K. Plachkova, and G. C. Christakudis, *Phys. Status Solidi B* **195**, 217 (1996).
- ²¹V. Damodara Das and N. Soundararajan, *Phys. Rev. B* **37**, 4552 (1998).
- ²²I. Bejenari, V. Kantser, and A. A. Balandin, arXiv:0908.0624v2 (unpublished); I. Bejenari and V. Kantser, *Phys. Rev. B* **78**, 115322 (2008).
- ²³A. Casian, I. Sur, H. Scherrer, and Z. Dashevsky, *Phys. Rev. B* **61**, 15965 (2000).