Surface-Facet-Dependent Phonon Deformation Potential in Individual Strained Topological Insulator Bi$_2$Se$_3$ Nanoribbons

Yuan Yan,*,†,‡ Xu Zhou,§,¶ Han Jin,¶ Cai-Zhen Li,§ Xiaoxing Ke,† Gustaaf Van Tendeloo,† Kaihui Liu,‡,§,¶ Dapeng Yu,‡,§ Martin Dressel,† and Zhi-Min Liao *,‡,§

†Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany, ‡State Key Laboratory for Mesoscopic Physics, Department of Physics, Peking University, 100871 Beijing, China, §Academy for Advanced Interdisciplinary Studies, Peking University, 100871 Beijing, China, ¶EMAT (Electron Microscopy for Materials Science), University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium, and †Collaborative Innovation Center of Quantum Matter, Beijing, China. *These authors contributed equally to this work.

ABSTRACT Strain is an important method to tune the properties of topological insulators. For example, compressive strain can induce superconductivity in Bi$_2$Se$_3$ bulk material. Topological insulator nanostructures are the superior candidates to utilize the unique surface states due to the large surface to volume ratio. Therefore, it is highly desirable to monitor the local strain effects in individual topological insulator nanostructures. Here, we report the systematical micro-Raman spectra of single strained Bi$_2$Se$_3$ nanoribbons with different thicknesses and different surface facets, where four optical modes are resolved in both Stokes and anti-Stokes Raman spectral lines. A striking anisotropy of the strain dependence is observed in the phonon frequency of strained Bi$_2$Se$_3$ nanoribbons grown along the (1120) direction. The frequencies of the in-plane $E_g^2$ and out-of-plane $A_1g$ modes exhibit a nearly linear blue-shift against bending strain when the nanoribbon is bent along the (1120) direction with the curved (0001) surface. In this case, the phonon deformation potential of the $E_g^2$ phonon for 100 nm-thick Bi$_2$Se$_3$ nanoribbon is up to 0.94 cm$^{-1}$%, which is twice of that in Bi$_2$Se$_3$ bulk material (0.52 cm$^{-1}$%). Our results may be valuable for the strain modulation of individual topological insulator nanostructures.

KEYWORDS: topological insulator - Bi$_2$Se$_3$ nanoribbon - Raman spectroscopy - strain - phonon confinement effect

Topological insulators (TIs) are a new class of quantum matter that possess a trivial insulating bulk phase and robust nontrivial metallic surface states. They are considered as promising candidates for novel electronic applications beyond silicon in current electronic world, attracting enormous efforts from both theoretical and experimental research. Among the TIs family, Bi$_2$Se$_3$ has been proven to be an ideal candidate for studying topological surface states due to its simple energy band structure and relatively large bulk band gap of $\sim$0.3 eV. The pressure induced phase transition from normal to superconducting phases in topological insulator Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ bulk materials have been reported; however, ultrahigh pressure is required and a full understanding of the interplay between superconductivity and topological surface states is still elusive. Compared to bulk materials, nanostructures have higher crystalline quality, surface-to-volume ratio, and elastic limit and thus are more favorable to realize topological superconductivity and to investigate the Majorana Fermions. However, to our best knowledge, the influence of size, strain and facet on the physical properties of strained Bi$_2$Se$_3$ nanoribbons has not been studied yet.

Micro-Raman spectroscopy is well established as a powerful and sensitive technique to characterize graphene-like layer materials. Substrate thickness and doping level dependent in situ and

* Address correspondence to yuan.yan@pi1.physik.uni-stuttgart.de, liaozm@pku.edu.cn.

Received for review July 2, 2015 and accepted September 12, 2015.

Published online September 12, 2015
10.1021/acsnano.5b04057

© 2015 American Chemical Society
EX SITU RAMAN SPECTRA OF Bi2Se3 ULTRATHIN FILM AND NANOPLATE HAVE BEEN REPORTED. IN THIS WORK, WE REPORT THE STRAIN, THICKNESS AND SURFACE FACET DEPENDENT PHONON PROPERTIES IN INDIVIDUAL Bi2Se3 NANORIBBONS. UTILIZING THE ULTRAFINE GLASS TIP OF A MICROMANIPULATOR, WE STRAINED TENS OF Bi2Se3 NANORIBBONS WITH THICKNESSES RANGING FROM 70 TO 500 NM. FOR A TYPICAL STRAIN-FREE Bi2Se3 NANORBON, ALL THE FOUR OPTICAL MODES, THE IN-PLANE E2g AND E2u MODES AND THE OUT-OF-PLANE A1g AND A1u MODES, ARE RESOLVED IN BOTH STOKES AND ANTI-STOKES RAMAN SPECTRA. AS EXPECTED, THESE MODES SOFTEN WITH DECREASING THICKNESS, WHICH IS CONSISTENT WITH THEORETICAL PREDICTIONS.25,26,28,32 IN ADDITION, A STRONG ANISOTROPIC BEHAVIOR IS OBSERVED FOR BENT Bi2Se3 NANORIBBONS, DUE TO THE TWO STRUCTURALLY DIFFERENT FACES, THE {0001} AND THE {0115} SURFACE, OF Bi2Se3 NANORIBBONS GROWN ALONG THE {1120} DIRECTION.33–36 ONLY WHEN THE NANOORBON IS BENT ALONG THE {1120} DIRECTION WITH THE CURVED {0001} SURFACE PERPENDICULAR TO THE PLANE AND WITH THE EXPOSED {0115} TOP SURFACE DO THE FREQUENCIES OF IN-PLANE E2g AND OUT-OF-PLANE A1g MODES EXHIBIT A LINEAR BLUE-SHIFT WITH INCREASING STRAIN, WHICH IS ALSO STRONGLY THICKNESS DEPENDENT. THE PHONON DEFORMATION POTENTIAL (PDP) OF THE E2g MODE IS UP TO 0.94 CM−1/% FOR 100 NM-THICK Bi2Se3 NANORIBBONS, WHILE IT IS ONLY APPROXIMATELY 0.52 CM−1/% FOR Bi2Se3 BULK MATERIAL.37 SINCE THE PHONON MODES STIFFEN LINEARLY AS THE LATTICE IS COMpressed,37,38 THE PROPERTIES OF THE Bi2Se3 NANORIBBONS ARE MORE SENSITIVE TO STRAIN THAN THAT OF BULK MATERIALS. OUR WORK INDICATES THAT THIN Bi2Se3 NANORIBBONS ARE A PROMISING CANDIDATE TO STUDY THE STRAIN MODULATED UNIQUE PROPERTIES OF THE TOPOLOGICAL SURFACE STATES.

RESULTS AND DISCUSSION

RAMAN SPECTRUM OF UNSTRAINED Bi2Se3 NANORIBBON. Bi2Se3 nanoribbons were synthesized by the Chemical Vapor Deposition (CVD) method,39 and their thickness ranges from 70 to 500 nm while the length from tens to hundreds of micrometers (Figures S1 and S2). The single crystalline nature of Bi2Se3 nanoribbons was confirmed by transmission electron microscopy (TEM) (Figure S1b), high-resolution TEM (HRTEM) (Figure S1c) and selected area electron diffraction (SAED) patterns (Figure S1d). The growth direction of the Bi2Se3 nanoribbons is always along {1120}. Figure 1a–c shows the scanning TEM (STEM) results of the cross-sectional sample of a nanoribbon, revealing the exposed facets of the as-grown nanoribbons. A TEM image of a representative cross-sectional sample is shown in Figure 1b at low magnification, and its side facet indicated by the blue box is enlarged in Figure 1a by a high resolution high-angle annular dark field (HAADF) STEM image. The Fast Fourier Transformation (FFT) pattern of Figure 1a is shown in Figure 1c, which reveals the two structurally inequivalent types of facets to be the {0001} and the {0115} surfaces.25,36 CONSEQUENTLY, THERE ARE TWO POSSIBILITIES TO POSITION THE Bi2Se3 NANORIBBONS ON THE SUBSTRATE: WITH THE {0001} SURFACE PARALLEL TO THE SUBSTRATE PLANE (Figure 1d), OR WITH THE {0115} SURFACE PARALLEL TO THE SUBSTRATE (Figure 1e). CORRESPONDINGLY, THE NANORIBBONS CAN BE BENT IN TWO DIFFERENT GEOMETRIES. LATER, WE WILL DISCUSS THE RAMAN SPECTRA OF THESE TWO KINDS OF BENT Bi2Se3 NANORIBBONS WITH DIFFERENT THICKNESSES. SURPRISINGLY THEY EXHIBIT A TOTALLY DIFFERENT STRAIN RESPONSE.

Bi2Se3 has a layered rhombohedral structure, which belongs to the space group D3d (R3m) as shown in Figure 2a. Each unit cell includes five atomic layers in the sequence of Se II—Bi—I Se—I Se—Bi—I Se, WHICH IS OFTEN REFERRED AS Quintuple layer (QL) WITH A DIMENSION OF ~1 NM ALONG C AXIS. STACKS OF QLS ARE LINKED BY WEAK VAN DER WAALS FORCES WITH A Slightly COVARIANT NATURE, WHILE INTRA QL POSSESS STRONG COVARIANT BONDS. CONSIDERING THE SYMMETRY OF THE SPACE GROUP D3d, THE PRIMARY UNIT CELL CONTAINS FIVE ATOMS CORRESPONDING TO THE CHEMICAL FORMULA OF Bi2Se3. ACCORDINGLY, THERE ARE 15 LATTICE DYNAMICAL MODES AT THE CENTER OF ITS BRILLIION ZONE (q = 0), THREE OF WHICH ARE ACOUTIC AND 12 ARE OPTICAL MODES. THESE 12 OPTICAL MODES CAN BE CLASSIFIED BY THE IRREDUCIBLE REPRESENTATIONS $\chi = 2E_g + 2A_{1g} + 2E_u + 2A_{1u}$.32 ACCORDING TO THE SELECTION RULES, 2A1u AND 2Eu ARE INFRARED-ACTIVE, WHILE 2A1g AND 2Eg ARE RAMAN-ACTIVE MODES.31 THE RAMAN TENSORS OF THE LATTER ONE ARE

$$A_{1g} : \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

$$E_g : \begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}$$

THE INTENSITY OF RAMAN SCATTERING $I \sim |e_r \cdot R \cdot e_s|^2$ MAY BE DIFFERENT FOR THE {0115} OR THE {0001} SURFACE PERPENDICULAR TO THE DIRECTION OF INCIDENT LIGHT, WHERE $e_r$ AND $e_s$ REPRESENT THE UNIT POLARIZATION VECTORS OF SCATTERED AND INCIDENT LIGHT, RESPECTIVELY, AND ARE RELATED TO THE ORIENTATION OF THE SAMPLE.

THE CORRESPONDING ATOMIC DISPLACEMENTS OF THE RAMAN-ACTIVE MODES ARE DEPICTED IN Figure 2b, WHERE THE $E_g$ MODES ARE 2-FOLD IN-PLANE VIBRATIONAL MODES AND THE $A_{1g}$ MODES VIBRATING ALONG THE {0001} DIRECTION ARE OUT-OF-PLANE MODES. THESE TWO TYPES OF RAMAN-ACTIVE MODES CAN BE DISTINGUISHED BY THE NONZERO OFF-DIAGONAL COMPONENTS IN THE $E_g$ RAMAN TENSOR. IN Figure 2c, A TYPICAL UNPOLARIZED RAMAN SPECTRUM OF AN UNSTRAINED Bi2Se3 NANORIBBON IS PLOTTED CONSISTING OF BOTH STOKES AND ANTI-STOKES CONTRIBUTIONS. ALL FOUR BULK VIBRATIONAL MODES $E_{1g}$, $A_{1g}$, $E_{2g}$, AND $A_{1g}$ ARE OBSERVED, WITH THE CORRESPONDING PEAK POSITIONS AT 37.3, 70.4, 131.9, AND 171.2 CM−1. TO DETERMINE THE RAMAN PEAK POSITION AND THE LINE WIDTH, ALL THE RAMAN SPECTRA ARE FITTED BY LORENTZIAN LINE SHAPE.
Strain Dependent Raman Spectra of Bi$_2$Se$_3$ Nanoribbons with the \{0001\} Surface Parallel to the Substrate Plane. To investigate the influence of strain on the physical properties of topological insulator Bi$_2$Se$_3$ nanoribbons, a series of samples with various thickness and width are bent and measured. Figure 3a shows the scanning electron microscopy (SEM) image and scheme of a typical bent Bi$_2$Se$_3$ nanoribbon. To distinguish whether a given nanoribbon was lying either with its \{0001\} facets facing up and down on the substrate or the facets on the other long edge of the nanoribbon (\{0115\}) facing up and down, the sample was characterized by atomic force microscopy (AFM) to get the thickness and width. The width of this nanoribbon is 300 nm and the thickness is 180 nm. According to the STEM results, tens more cross-sectional Bi$_2$Se$_3$ nanoribbon samples with different sizes had been prepared, and we found, without an exception, the width of the samples is always larger than the thickness, which implies that the \{0001\} facets are bigger than the \{0115\} facets. This can be easily understood by the growth mechanism. Because Bi$_2$Se$_3$ is a layered material, the in-plane growth is much easier than the growth along [0001] direction. For this sample shown in Figure 3a, the Bi$_2$Se$_3$ nanoribbon should be with the \{0001\} surface parallel to the substrate plane. Raman spectra collected from three different positions along the Bi$_2$Se$_3$ nanoribbon, marked by red, green, and blue color in Figure 3a, are shown in Figure 3b plotted with respective color. The frequencies of all four vibrational peaks $E_g$, $A_{1g}$, $E_g$, and $A_{2g}$ are denoted by the dashed lines.

Quantitatively, the maximum tensile and compressive strain $\varepsilon_{ab}^{\text{max}}$ at the outer and inner side of the bent Bi$_2$Se$_3$ nanoribbon can be calculated by

$$\varepsilon_{ab}^{\text{max}} = \frac{d - a_0}{a_0} = \pm \frac{d}{2R_{ab}}$$

(2)
where \( a \) and \( a_0 \) are the lattice constants of the strained and unstrained case, \( d \) is the width of the Bi\(_2\)Se\(_3\) nanoribbon here, and \( R_{ab} \) is the radius of curvature with \( R = \frac{1}{2} \left( 1 + \left( \frac{y}{y_f} \right)^2 \right)^{3/2} \), where \( y = f(x) \) is the curve function of bent Bi\(_2\)Se\(_3\) nanoribbon. When the bending strain increases from 0 to 2.4%, the frequencies of all four vibrational modes \( E_g^1, A_1g, E_g^2 \) and \( A_2g \) remain constant (Figure 3c). The full width at half-maximum (FWHM) of the in-plane \( E_g^2 \) peak exhibits a negligible increase from 6 to 8 cm\(^{-1}\) with increasing strain, while the ratio of Raman intensities \( I_{A_1g}/I_{A_2g} \) does not change (Figure 3d). Considering the much larger spot size (\( \sim 1 \) \( \mu \)m) of incident laser compared to the width of the nanoribbon, the contributions from the tensile outer side and the compressive inner side of the narrow nanoribbon will add up and cancel the frequency shift, as well as induce the broadening of the FWHM of the \( E_g^2 \) mode. As there is no strain along the [0001] direction in this case, the Raman intensity of the out-of-plane modes does not change with the bending strain \( \varepsilon_{ab} \). Similar results of three more samples are shown in Figures S3–S5 in the Supporting Information.

**Strain Dependent Raman Spectra of Bi\(_2\)Se\(_3\) Nanoribbons with the Exposed \{01T\} Top Surface on the Substrate.** A typical SEM image and scheme of a bent 100 nm-thick Bi\(_2\)Se\(_3\) nanoribbon are produced in Figure 4a, where the \{0001\} surface is perpendicular to the substrate plane and the exposed top surface is the \{01T\} surface. The nanoribbon is bent along the \{11\} direction with the curved \{0001\} surface. The Raman spectra are fitted by Lorentzian line shape and plotted in Figure 4b. Five curves with different colors correspond to the five positions on the Bi\(_2\)Se\(_3\) nanoribbon marked by the same colors in Figure 4a. With increasing strain, the Raman frequencies of the \( A_1g \) and \( E_g^2 \) features rise linearly, similar to the typical pressure-induced phonon stiffening.\(^{37}\) The shear stress along \( c \) direction enhances the bond interaction by decreasing the bond length of Bi—Se and Se—Se, resulting in the blue shift of the vibrational frequencies of the \( A_1g \) and \( E_g \) modes. The corresponding PDP of these two modes are about 0.66 and 0.94 cm\(^{-1}\)/%, respectively (Figure 4c).

For a comparison, the reported PDP of the \( E_g^2 \) mode in bulk Bi\(_2\)Se\(_3\) material under pressure (3.13 cm\(^{-1}\)/GPa)\(^{37}\) can be converted to a strain value (%) by

\[
\frac{\partial \Delta \omega}{\partial \varepsilon} = (1 - 2\nu) E_{ab} \frac{\partial \Delta \omega}{\partial \sigma_{ab}} \tag{3}
\]

The Poisson’s ratio \( \nu \) used here is 0.27, and the value of Young’s modulus of Bi\(_2\)Se\(_3\) bulk material along the \{11\} direction \( E_{ab} \) is 35.9 GPa;\(^ {31}\) thus, the PDP of bulk material is 0.52 cm\(^{-1}\)/%. It is worth noting that the frequency shift of the \( E_g^2 \) mode induced by the same strain in the Bi\(_2\)Se\(_3\) nanoribbon is nearly twice of what is observed in bulk. In contrast to the blue-shift of the \( A_1g \) and \( E_g^2 \) modes, the Raman frequencies of the \( A_2g \) peak exhibit a red-shift with the PDP value about \(-1.78 \) cm\(^{-1}\)/%. The red-shift of the out-of-plane...
A mode may be caused by the strain modulation of the opposite vibrations of the Bi and SeII atoms. The FWHM of both $A_{1g}$ and $E_g$ modes remains almost unchanged, implying that the phonon–phonon scattering stays the same (Figure 4d). Usually, the vibrational peaks broaden when contributions from tensile strain at outer surface and compressive strain at inner surface add up. On the other hand, the FWHM decreases when the strain-induced carrier concentration rises. It has been reported that the carrier concentration of Bi$_2$Se$_3$ bulk materials is enhanced more than 10 times when the pressure increases from 0 to 10 GPa, even without a structural phase transition. We conclude that the FWHM of both $A_{1g}$ and $E_g$ modes is unaltered as these two opposite effects cancel each other.

A series of bent Bi$_2$Se$_3$ nanoribbons with different thicknesses have been measured (Figures S6 and S7). As shown in Figure 5a, the Raman shift of the $E_g$ modes in 100, 120, 190, 220, and 260 nm-thick Bi$_2$Se$_3$ nanoribbons all exhibit a blue-shift with increasing strain. Some deviations from the linear relationship may be caused by the nonuniform interaction between Bi$_2$Se$_3$ nanoribbons and the substrate. The most interesting discovery is that the PDP of the $E_g$ feature increases with reducing the sample thickness (Figure 5b), which may arise from the surface effect. Therefore, the strain modification on the phonon properties depends on the thickness of the Bi$_2$Se$_3$ nanoribbons strongly.

As reported, the relationship between the FWHM and thickness had been explained using exponential format. Similarly, here we also use the exponential fit to thickness dependence of the PDP of $E_g$ mode in Figure 5b.

**Thickness Dependent Raman Spectra of Strain-Free Bi$_2$Se$_3$ Nanoribbons.** To explore the size effect in topological insulators, Raman spectra of three-dimensional (3D) bulk materials and 2D thin films have been collected, where infrared features were observed due to the symmetry breaking in 2D thin film samples. Here, quasi 1D Bi$_2$Se$_3$ nanoribbons with various thicknesses are measured to further investigate the size effect.

In Figure 6a, the Raman peak positions of individual Bi$_2$Se$_3$ nanoribbons are plotted as a function of the sample thickness. When the thicknesses $d$ of unstrained Bi$_2$Se$_3$ nanoribbons decreases from 500 to 70 nm, the frequencies of both $A_{1g}$ and $E_g$ modes exhibit a red-shift about 4 cm$^{-1}$, which is consistent with previous results of thin film materials. Considering the phonon confinement effects, the red-shift would relate to the surface-to-volume ratio, or $1/d$. Then, the relationship of the frequency and $d$ can be fitted by

$$\omega(d) = \omega(0) - A/d$$

where $\omega(0)$ is the phonon frequency in the bulk (Figure 6a). Meanwhile, the surface relaxation and
structural defects should also be considered to explain the red-shift.

The ratio of the Raman intensities $I_{A1g1}/I_{A1g2}$ increases as the thickness is reduced, in contrast to the results reported for thin films.$^{32}$ Considering the surface tension in the nanostructure with large surface-to-volume ratio, the strength of the out-of-plane vibration $A1g1$ mode should be enhanced by decreasing thickness, as shown in Figure 6b.

**DISCUSSION**

Our systematic investigations of the strain, thickness and surface facet dependent Raman spectra of Bi$_2$Se$_3$ nanoribbons yield the basis for some important points. For strain-free samples, all the optical phonon frequencies become red-shifted as the sample thickness is reduced, due to the increased phonon confinement effect and surface tension, which is insensitive to the way the nanoribbons are placed on the substrate, while for strained samples with the $\{0001\}$ or the $\{01\bar{T}S\}$ surface parallel to the substrate plane, strong anisotropies are observed, caused by the different bending loading method on the nanoribbon.

The strain induced anisotropy demonstrates that Raman spectra of Bi$_2$Se$_3$ nanoribbon are more sensitive to the stress along $c$ direction. Furthermore, the PDP of the $E2$ mode of Bi$_2$Se$_3$ nanoribbon was found to increase with decreasing the nanoribbon thickness. Therefore, a much lower critical pressure (stress) is expected to be sufficient to induce a superconducting phase transition in thin Bi$_2$Se$_3$ nanoribbons compared to the bulk counterpart. With the use of this great advantage of nanostructures, a superconducting dome was observed recently in WTe$_2$ nanoflakes with a pressure even smaller than 5 GPa.$^{46}$

**CONCLUSIONS**

In conclusion, the influence of size and strain on the Raman spectra of topological insulator Bi$_2$Se$_3$ nanoribbons is investigated systematically. All four optical modes, the in-plane $E1$ and $E2$, and out-of-plane $A1g1$ and $A1g2$ modes, are resolved in both Stokes and anti-Stokes Raman spectra, and they all soften as the thickness of unstrained Bi$_2$Se$_3$ nanoribbons reduces, while for bent Bi$_2$Se$_3$ nanoribbons, a strong anisotropy is observed, due to the differences in the exposed top
facets on the substrate: the \{0001\} and the \{01\overline{1}T\} surfaces. Only when the \{0001\} surface is perpendicular to the substrate plane and the exposed top surface is the \{01\overline{1}T\} surface, that is, the nanoribbon is bent along the (11\overline{2}0) direction with the curved \{0001\} surface, the \E_2^0 and \A_{1g}(\overline{A}_{1g}) modes of the Bi$_2$Se$_3$ nanoribbon show a blue-shift (red-shift) with strain, and the phonon deformation potential of the \E_2^0 mode rises nonlinearly with decreasing sample thickness. The results are helpful for further investigations on the quantum transport of strained Bi$_2$Se$_3$ nanoribbons.

**MATERIALS AND METHODS**

**Synthesis of Bi$_2$Se$_3$ Nanoribbons.** Bi$_2$Se$_3$ nanoribbons were synthesized by CVD method. Bi$_2$Se$_3$ powder (Alfa Aesar) with high purity (>99.99%) was put in the center of a horizontal tube furnace (Lindberg/Blue M) as the source, while several undoped silicon pieces with 5 nm gold film deposited by electron beam evaporation were placed downstream approximately 9 cm away from the source as the collecting substrates. High purity Ar gas was used to pump and flush the tube, maintain the inside pressure and carry the source vapor from central hot zone (700 °C) to the cold edge (about 300 °C). After the growth, desirable Bi$_2$Se$_3$ nanoribbons were chose from the as-grown products, transferred onto the Si/SiO$_2$ substrate with marks, and then manipulated to be curved under an optical microscope with micromanipulator by using two needle-shaped glass tips.

**Characterization of Bi$_2$Se$_3$ Nanoribbons.** The as-synthesized Bi$_2$Se$_3$ nanoribbons were characterized by the field-emission SEM (FEI NanoSEM 430) with the accelerating voltage 10 kV. The Bi$_2$Se$_3$ nanoribbons were transferred onto a copper grid by gently rubbing it on an as-grown substrate and then characterized by 200 kV field-emission TEM (Tecnai G2 F20). To prepare the cross-sectional TEM sample, 10 more Bi$_2$Se$_3$ nanoribbons were transferred onto Si/SiO$_2$ substrate. The nanoribbons were randomly chosen using focused ion beam (FIB, FEI Helios NanoLab DualBeam system). Amorphous carbon/ Pt protection layer was deposited to protect the Bi$_2$Se$_3$ nanoribbon surface by electron beam induced deposition method in the FIB system. Then, the Bi$_2$Se$_3$ nanoribbon was cut along the cross-section by the FIB and then transferred onto a TEM grid by a nano-manipulator in the FIB system. HAADF-STEM was performed using an FEI Titan Cube 60-300 microscope fitted with an aberration corrector for the probe forming lens operated at 200 kV.

**Raman Spectral Measurement.** Unpolarized Raman spectra of the Bi$_2$Se$_3$ nanoribbons were measured by a home-built confocal micro-Raman microscopy system (Princeton Instruments Acton SP 2500i) in the backscattering configuration at room temperature. The Raman spectra are excited by a 532 nm laser and the lowest available frequency is better than 20 cm$^{-1}$ by a set of 532 nm BraggGrate Notch Filter (532 BNF). The incident laser power after B0 was used to pump and flush the tube, maintain the inside pressure and carry the source vapor from central hot zone (700 °C) to the cold edge (about 300 °C). After the growth, desirable Bi$_2$Se$_3$ nanoribbons were chose from the as-grown products, transferred onto the Si/SiO$_2$ substrate with marks, and then manipulated to be curved under an optical microscope with micromanipulator by using two needle-shaped glass tips.

**Conflict of Interest:** The authors declare no competing financial interest.

**Supporting Information Available:** The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b04057.

SEM picture of as-synthesized Bi$_2$Se$_3$ nanoribbons. Typical TEM, HRTEM images and SAED patterns of a strain-free Bi$_2$Se$_3$ nanoribbon. Typical AFM image of a strained Bi$_2$Se$_3$ nanoribbon. Raman spectra of strained Bi$_2$Se$_3$ nanoribbons with different thicknesses in two cases (PDF)

**Acknowledgment.** Y.Y. would like to thank Xuewen Fu for helpful discussions. This work was supported by MOST (Nos. 2013CB934600, 2013CB932602) and NSFC (Nos. 11274014, 11234001).

**REFERENCES AND NOTES**


