Quantum Electronic Transport of Topological Surface States in $\beta$-Ag$_2$Se Nanowire

Jihwan Kim,‡§ Ahreum Hwang,‡§ Sang-Hoon Lee,‡ Seung-Hoon Jhi,‡ Sunghun Lee,‡,¶ Yun Chang Park,§ Si-in Kim,* Hong-Seok Kim,‡† Yong-Joo Doh,‡,¶ Jinhee Kim,§,¶ and Bongsoo Kim*‡†

1Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea
2Department of Physics, Pohang University of Science and Technology, Pohang 37673, Korea
3Department of Measurement and Analysis, National Nanofab Center, Daejeon 34141, Korea
4Department of Physics and Photon Science, School of Physics and Chemistry, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Korea
5Korea Research Institute of Standards and Science, Daejeon 34113, Korea

Supporting Information

ABSTRACT: Single-crystalline $\beta$-Ag$_2$Se nanostructures, a new class of 3D topological insulators (TIs), were synthesized using the chemical vapor transport method. The topological surface states were verified by measuring electronic transport properties including the weak antilocalization effect, Aharonov–Bohm oscillations, and Shubnikov–de Haas oscillations. First-principles band calculations revealed that the band inversion in $\beta$-Ag$_2$Se is caused by strong spin–orbit coupling and Ag–Se bonding hybridization. These investigations provide evidence of nontrivial surface state about $\beta$-Ag$_2$Se TIs that have anisotropic Dirac cones.

KEYWORDS: anisotropic topological insulator, $\beta$-Ag$_2$Se nanowire, weak antilocalization, Aharonov–Bohm oscillation, Shubnikov–de Haas oscillation, band inversion

Topological insulators (TIs) are bulk insulators with metallic surface states that are topologically protected by time-reversal symmetry. The strong spin–orbit coupling (SOC) inherent to TIs causes the spin orientation of the surface electrons to be locked perpendicular to their translational momentum, resulting in the suppression of electron backscattering from nonmagnetic perturbations. The formation of spin-textured metallic edge states in TIs enables highly coherent charge and spin transport, making TIs promising for spintronics applications. Combinations of TIs with conventional superconductors can also provide useful platforms for creating and manipulating emergent particles such as Majorana fermions, which are essential for topological quantum computers. Anisotropic TIs form two-dimensional (2D) electron gases populated by massless Dirac fermions with spin-momentum locking. Photoemission spectroscopy and electrical transport measurements have been used to investigate the TSSs in 3D TIs such as Bi$_2$Se$_3$, Bi$_2$Te$_3$, and BTS$_2$, which have anisotropic Dirac cones. TSSs with highly anisotropic Dirac cones would be useful for realizing ideal quantum wires exhibiting one-directional spin and electron transport on their surfaces, which are theoretically expected in silver chalcogenides (Ag$_2$Se and Ag$_2$Te). Experimental works, however, have been reported only quite recently on the electronic transport of anisotropic Dirac fermions in silver chalcogenides TIs.

Herein, we report the observation of TI properties in nanowires and nanoribbons of $\beta$-Ag$_2$Se. We synthesized single-crystalline nanowires, nanoribbons, and nanoplates of $\beta$-Ag$_2$Se using the chemical vapor transport (CVT) method and measured quantum electrical transport properties of $\beta$-Ag$_2$Se nanowires and nanoribbons at low temperatures. Negative magnetoresistance (MR) and magnetoresistance (MC) oscillations, the so-called Shubnikov–de Haas (SdH) effect and Shubnikov–de Haas oscillations, were observed. The analysis of the SdH oscillations was applied perpendicular to the nanowire axis, implying the existence of strong SOC. When a magnetic field was applied parallel to the nanowire axis, the $\beta$-Ag$_2$Se nanowire device exhibited highly periodic MC oscillations, implying the existence of the surface electronic states. When a magnetic field was applied perpendicular to the nanowire axis, quantum magnetic oscillations, the so-called Shubnikov–de Haas (SdH) oscillations, were observed. The analysis of the SdH oscillations indicates the presence of a nonzero Berry phase due to the TSS of the $\beta$-Ag$_2$Se nanostructure. First-principles band structure calculations confirmed the existence of the TSS.

Received: November 23, 2015
Accepted: March 28, 2016
Published: March 28, 2016

DOI: 10.1021/acsnano.5b07368
ACS Nano 2016, 10, 3936—3943
Figure 1. SEM images of as-synthesized $\beta$-Ag$_2$Se (a) nanowire, (b) nanoribbon, and (c) nanoplate on a c-Al$_2$O$_3$ substrate. The insets in (a–c) are magnified SEM images of each of the nanostructures. (d) Cross-sectional TEM image of a $\beta$-Ag$_2$Se nanowire. (e) HRTEM image of (d). The FFT pattern (inset in (e)) is indexed to $\beta$-Ag$_2$Se with an orthorhombic lattice along the [101̅] zone axis. (f) SAED pattern of a $\beta$-Ag$_2$Se nanowire along the [101̅] zone axis.

Figure 2. (a) SEM image of the $\beta$-Ag$_2$Se nanowire device (sample D1) with a nanowire width of 102 nm. (b) Angle-dependent MC curves at $T = 2.0$ K. Magnetic field was applied at various angles $\theta$ relative to the nanowire axis. Inset: Schematic of the measurement configuration. (c) Angle-dependent differential MC, $\Delta G = G(\theta) - G(\theta = 0^\circ)$, versus perpendicular component of magnetic field, $B\sin \theta$. (d) Temperature dependence of $\Delta G(B)$ curve (symbols). Solid curves are fitting results obtained by using 1D WAL theory. (e) Characteristic lengths of $L_q$, $L_N$, and $L_{so}$ as functions of temperature. Solid lines are results of power-law fits.
Because of their anisotropic space and violation of rotational invariance, anisotropic TIs can be potentially employed for observation of exotic Fermion through its spaces.\textsuperscript{22,27} Since the in-depth studies for anisotropic TI are quite rare, detailed investigations of these TIs could provide valuable insight into their exotic electrical transport properties and may allow their possible applications for spintronics and quantum information applications.

RESULTS AND DISCUSSION

Single crystalline $\beta$-Ag$_2$Se nanostructures were synthesized on a $c$-Al$_2$O$_3$ substrate using the single-step CVT method (Figure S1, Supporting Information), which enables high-quality stoichiometry and assures clean surfaces of the nanostructures.\textsuperscript{28} The cross-section of the nanowire had a hexagonal shape, with a diameter of 100−250 nm (Figure 1). Nanoribbons and nanoplates were also synthesized on the same substrates. The widths of the nanoribbons were about 0.4−3 $\mu$m, and their lengths were 3−40 $\mu$m, while nanoplates had edge lengths of 3−10 $\mu$m.

We performed detailed structural and compositional analyses of the $\beta$-Ag$_2$Se nanowire using cross-sectional transmission electron microscopy (TEM). The high-resolution TEM (HRTEM) image and selected-area electron diffraction (SAED) pattern reveal the $[10\bar{1}]$ growth direction and the single crystalline nature of the nanowire (Figure 1e, f). Lattice spacings of 0.719 and 0.383 nm agree well to those of the (010) and (101) planes of an orthorhombic $\beta$-Ag$_2$Se crystal structure, respectively. All peaks in the X-ray diffraction (XRD) pattern of the synthesized sample are indexed to the orthorhombic $\beta$-Ag$_2$Se phase (space group $P2_12_12_1$, JCPDS card no. 01-071-2410) with a set of lattice constants of $a = 4.333$ Å, $b = 7.062$ Å, $c = 7.764$ Å (Figure S2, Supporting Information). Additional TEM analyses and TEM energy dispersive X-ray spectroscopy (EDS) measurements also confirmed that all of the synthesized nanostructures are single-crystalline with a Ag/Se atomic ratio of 2:1 (Figure S3, Supporting Information). Details of the nanowire growth, device fabrications, and the electrical measurements are described in the Experimental Methods section.

We measured five representative $\beta$-Ag$_2$Se nanowires and nanoribbons samples to observe quantum electronic transports. Physical parameters of the samples (D1−D5) are listed in Table S1 (Supporting Information). Figure 2a shows a SEM image of sample D1. Angle-dependent MC curves are obtained at $T = 2.0$ K (Figure 2b). Magnetic field was applied at four different angles ($\theta$). The observed MC is negative, a typical feature of WAL,\textsuperscript{29} and it becomes more negative as the perpendicular component of the magnetic field increases (with increasing $\theta$). This enhancement of negative MC indicates that the TSS is effective here instead of bulk.\textsuperscript{16,30} Since significant negative MC already exists when $\theta = 0^\circ$, which is attributable to the strong SOC in the bulk portion, we extracted the surface state contribution by subtracting the axial MC component from the total MC, \[ \Delta G(\theta, B) = G(\theta, B) - G(\theta = 0^\circ, B). \] When the $\Delta G$ curves were replotted as functions of the perpendicular magnetic field $B \sin \theta$, they mapped onto a single curve at low magnetic fields (Figure 2c). This extracted term is attributed to the surface states contribution.\textsuperscript{16,17,30}
Figure 4. (a) MR data obtained from sample D3 with a magnetic field perpendicular to the substrate. (b) Differential MR after subtracting smooth background. Solid magenta curve is a fit to LK theory (see text). Inset: FFT of ΔR with peak at Bf = 84.0 T. (c) ΔR obtained from sample D4. Solid magenta curve shows fitting result. Inset: FFT of ΔR with peak at Bf = 122 T. (d) Landau level index versus 1/B value obtained from sample D3 (black) and D4 (blue). ΔR minima (maxima) correspond to integer (half-integer) values of Landau level index. Lines are linear least-squares fits to data.

The low-field ∆G(θ = 90°, B) curve was fitted to the 2D WAL model, resulting in a phase coherence length Lφ of 270 nm at T = 2.0 K (Figure S4, Supporting Information). This estimated value of Lφ, however, is much larger than the width (w) of the nanowire, 102 nm, invalidating the 2D theoretical assumption of w ≫ Lφ. We therefore used a diffusive 1D localization model for further analysis, including the electron–electron and spin–orbit scatterings:

\[
\Delta G = \frac{\sqrt{2} e^2}{\pi \hbar} L_N \left[ \frac{3}{2} \text{Ai}' \left( \frac{2L_N}{L^2} \right) - \frac{1}{2} \text{Ai} \left( \frac{2L_N}{L^2} \right) \right]
\]

where e is the electric charge, \(\hbar\) is the reduced Planck’s constant, L is the length of the nanowire channel, L_N is the Nyquist scattering length, Ai is the Airy function, and Ai’ is its derivative. Here, \(L_1 = \left( \frac{1}{L^2} + \frac{4}{L_N^2} + \frac{1}{3} \left( \frac{\alpha B}{\hbar} \right)^2 \right)^{-1/2}\) and \(L_2 = \left( \frac{1}{L^2} + \frac{1}{3} \left( \frac{\alpha B}{\hbar} \right)^2 \right)^{-1/2}\), where L_1 is the spin–orbit scattering length. The fitting results are shown in Figure 2d, yielding \(L_\phi = 310\) nm, \(L_N = 240\) nm, and \(L_{so} = 200\) nm for the ∆G curve obtained at T = 2.0 K. L_\phi and L_N are comparable to those obtained previously from a Bi_2Se_3 nanoribbon, while L_{so} here is about five times larger than that of the Bi_2Se_3 nanoribbon. A relatively large L_{so} in the TSS of the β-Ag_2Se nanowire indicates a more reduced SOC strength than in other TI nanowires.

When the temperature increases, the ∆G curve broadens and diminishes due to increased thermal scattering (Figure 2d). The temperature dependences of the scattering lengths were obtained by fitting the ∆G(θ = 90°, B) data to eq 1, exhibiting power-law behavior (Figure 2e). It is inferred that L_\phi, L_N, and L_{so} are proportional to \(T^{-0.29}\), \(T^{-0.31}\), and \(T^{-0.22}\), respectively. Compared with the theoretical expectations, according to which L_\phi would decay with \(T^{-1/3}\) in 1D and \(T^{-1/2}\) in 2D, the exponents obtained in our experiment are significantly closer to the prediction by 1D localization theory than that by 2D localization theory.

Measurement of the axial MC by applying a magnetic field \(B_{axial}\) along the nanowire axis confirmed the existence of metallic surface states in the β-Ag_2Se nanowire. After subtracting a smooth background signal from the MC curve (inset of Figure 3b), regular periodic oscillations with a differential conductance ∆G were obtained (Figure 3a). The peak position of ∆G matches well to a linear fit with the integer index n (Figure 3b), indicating that the average period of the ∆G oscillations is \(\Delta B_{axial} = 0.40\) T. Fast Fourier transform (FFT) analysis of the ∆G(B_{axial}) curve also resulted in the same oscillation period. Assuming that the nanowire has a rectangular cross-section (139 nm width and 75 nm height, Figure 3c), the cross-sectional area becomes \(1.04 \times 10^{-14}\) m^2. Thus, the oscillation period corresponds to a magnetic flux \(\Phi = 0.11\Phi_0\), where \(\Phi_0 = \hbar/e\) is the magnetic flux quantum. Similar \(\Phi_0\) periodic oscillations were obtained using sample D5 (Figure S5, Supporting Information).

Our observed MC oscillations are different from an ordinary Altshuler-Aronov-Spivak (AAS) effect exhibiting resistance oscillations with a period of \(\Phi_0/2\) and maximum resistance at \(B = 0\), which is observed in a metallic hollow cylinder. Rather the periodic MC oscillations can be attributed to the phase-coherent propagation of the surface state electrons around the
perimeter of the TI nanowire,\textsuperscript{12,25,36} which is well-known as the Aharonov–Bohm (AB) effect.\textsuperscript{7} However, there is a significant difference:\textsuperscript{36–40} Although AB theory predicts MC minima occurring at integer multiples of $\Phi_0$, TI nanowire experiments have shown MC maxima. Moreover, the periodicity can decrease to half of $\Phi_0$ depending on the gate voltage.\textsuperscript{13} A more plausible explanation than the AB effect is based on the formation of 1D subbands in the TI nanowire surface states and the nontrivial Berry phases of the surface-state electrons.\textsuperscript{13,39}

Since the 1D bandgap\textsuperscript{39} has been estimated to be $\Delta_{1D} = \hbar v_F/2(\omega + t) \approx 2.9$ meV, where $v_F$ is the Fermi velocity, $\omega$ is the width, and $t$ is the height of nanowire,\textsuperscript{24} the thermal broadening effect was neglected in our experiment (we assumed $\Delta_{1D} \gg k_0T$). In the regime of weak disorder and nonzero doping, theoretical calculations result in MC oscillations with a period of $\Phi_0$ and doping-dependent conductance maxima either at $n\Phi_0$ or at $(n + 1/2)\Phi_0$ where $n$ is an integer.\textsuperscript{39} Since the circumference of the nanowire, $2(\omega + t)$, was much larger than the mean-free path ($l_0 \approx 20$ nm) and its conductance exhibited very weak gate dependence, our $\beta$-$\text{Ag}_2\text{Se}$ nanowire was in the diffusive regime and away from the Dirac point, thus meeting the conditions assumed in the theoretical calculations.\textsuperscript{39} The absence of $\Phi_0/2$-periodic oscillations in Figure 3d indicates that the TI nanowire was weakly disordered.

In addition to the above MC oscillations, magnetic quantum oscillations such as SDH oscillations constitute the most convincing evidence of surface electronic states.\textsuperscript{41} Figure 4a shows magneto-resistance (MR) data obtained at a perpendicular magnetic field ($\theta = 90^\circ$). After subtracting the smooth background, we obtained the SDH oscillation of the differential resistance $\Delta R$ as a function of $1/B$ (Figure 4b). The FFT analysis result (Figure 4b inset) indicates an oscillation frequency $B_0$ of 84.0 T. Since the oscillation period corresponds to $\Delta(1/B) = 1/B_0 = 2\pi /\hbar n\Phi_0$ where $n\Phi_0$ is the cross-sectional Fermi surface area transverse to the applied field and $k_0$ is the Fermi wave vector, $k_0$ becomes 0.51 nm\textsuperscript{-1}. Thus, the 2D carrier concentration at the surface was $n_s = k_0^2/4\pi = 2.0 \times 10^{12}$ cm\textsuperscript{-2} for the sample D3.

According to Lifshitz–Kosevich (LK) theory,\textsuperscript{12} $\Delta R$ is given by $\Delta R = A \exp(-\pi/\mu B) \cos(2\pi(B/B_0 + 1/2 + \gamma))$, where $A$ is a temperature-dependent parameter, $\mu$ is the carrier mobility, and $2\pi\gamma$ is the Berry phase. The phase shift is expected to be $\gamma = 0$ for a conventional 2D electron gas and $\gamma = -0.5$ for 2D Dirac electrons.\textsuperscript{13} Our experimental $\Delta R$ data are well fitted by the LK theory with $\mu = 560 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\gamma = -0.43$ (see the magenta curve in Figure 4b), supporting the existence of a Berry phase of $\pi$ due to the TSS. Relatively low mobility, compared with $\beta$-$\text{Ag}_2\text{Te}$ nanostructures,\textsuperscript{25,26} is presumably due to an increased carrier density and scattering due to selenium vacancies (Figure S3, Supporting Information).\textsuperscript{44} We obtain the elastic mean-free path as $l_0 = \hbar v_F/\varepsilon_\text{phon} = 19$ nm and $k_0l_0 = 9.4$. The SDH oscillations are also observed in the sample D4 having a different geometry (Figure 4c). Sample D4 also results in similar physical parameters of $n_s$, $\mu$, and $\gamma$ (see Table 1).

The phase factor $\gamma$ was determined by analyzing the Landau levels (LLs), which are formed by the Landau quantization of the energy states in the magnetic fields. When the $\Delta R$ minima in the SDH oscillations are taken to be integer indices ($N_{LL}$) of the LLs,\textsuperscript{39} massless Dirac fermions are expected to satisfy $N_{LL} = B/B_0 - 0.5$. Landau fan diagrams are shown in Figure 4d for two different samples. Linear fitting of the fan diagrams revealed a slope $B_0$ of 84.7 T and an intercept $\gamma$ of $-0.56$ for the sample D3. Parameters for sample D4 are $B_0$ of 122.0 T and $\gamma$ of $-0.42$; these values are quite close to those estimated from the previous analyses based on the LK theory. Thus, our experimental results suggest that $\beta$-$\text{Ag}_2\text{Se}$ nanowires contain massless Dirac fermions with Berry phases of $\pi$ on their surfaces.

To clarify the nontrivial topological property of $\beta$-$\text{Ag}_2\text{Se}$, we performed the first-principles calculations based on the density functional theory.\textsuperscript{45,36} The ionic character of $\text{Ag}–\text{Se}$ bonding implies that the Ag-cation $s$ states lie higher in energy than the Se-anion $p$ states. The strong hybridization between Ag $d$ states and Se $p$ states, however, leads to the band inversion, as in Ag$_2$Te.\textsuperscript{25} The strength of the $p–d$ hybridization depends on the number of bonding neighbors of halgen atoms (seven for $\beta$-$\text{Ag}_2\text{Se}$ and eight for $\alpha$-$\text{Ag}_2\text{Te}$). Thus, the Ag $s$ states are located at about $-1.25$ eV below the Fermi level, while the Se $p$ states are above them (Figure 5b). Our band-structure calculation for a 15.53 nm-thick $\beta$-$\text{Ag}_2\text{Se}$ slab (Figure 5c) reveals that the bulk band gap is opened by the SOC, and the surface states (red lines) with a linear dispersion develop inside the gap. Without SOC, the gap is closed, and the surface states disappear. Figure 5d shows that the surface states are localized at the top and bottom surfaces of the $\beta$-$\text{Ag}_2\text{Se}$ slab. These calculation results are consistent with our experimental measurements, both providing evidence for the existence of TSSs in $\beta$-$\text{Ag}_2\text{Se}$ nanowires.

The topological nature of $\beta$-$\text{Ag}_2\text{Se}$ can be confirmed by calculating the Wannier charge centers (WCCs) on the six faces of the first Brillouin zone. Figures 5e and 5f display the evolution of WCCs for the $k_z = 0$ and $k_z = \pi$ faces, respectively, by varying the pumping parameter $k_z$. As shown, the evolution curves (red solid curves) cross an arbitrary reference line (black dashed line) odd numbers of times on the $k_x$, $k_y$, and $k_z$ faces and even numbers of times on the $k_x$, $k_y$, and $k_z$ faces. The odd numbers of crossings indicate that the Kramer pairs with time-reversal-invariant momenta exchange their partners during the pumping process, demonstrating the nontrivial topological nature of the material.\textsuperscript{47,48} Our calculation results show that the topological index of $\beta$-$\text{Ag}_2\text{Se}$ is $1/(0,0,0)$, supporting the suggestion of $\beta$-$\text{Ag}_2\text{Se}$ as a new class of 3D TI.\textsuperscript{49}

**CONCLUSIONS**

We synthesized single-crystalline $\beta$-$\text{Ag}_2\text{Se}$ nanostructures and studied their electrical transport properties. We observed the WAL effect, AB oscillations, and SDH oscillations, all of which support the existence of the conducting surface states. Furthermore, our analysis indicated that the $\beta$-$\text{Ag}_2\text{Se}$ nanowires had a nonzero Berry phase as a characteristic property of massless Dirac fermions. First-principles calculations confirmed the existence of TSSs in this material. $\beta$-$\text{Ag}_2\text{Se}$ has been predicted to be a TI with anisotropic Dirac cone. To investigate the unique characteristic of anisotropy, further experimental

---

**Table 1. Physical Parameters of the Surface States Obtained From the LK Analysis of SDH Oscillations**

| sample | $B_0$ (T) | $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) | $\gamma$ | $n_s$ (cm$^{-2}$) | $k_0$ (nm$^{-1}$) | $l_0$ (nm) |
|--------|-----------|-------------------------------|---------|-----------------|----------------|-------------|
| D3     | 84.0      | 560                           | -0.43   | $2.0 \times 10^{12}$ | 0.51           | 19          |
| D4     | 122       | 580                           | -0.55   | $3.0 \times 10^{12}$ | 0.61           | 23          |

---

ACS Nano 2016, 10, 3936–3943
studies are needed, such as angle-dependent MC or gate-dependent MC. As a new TI, $\beta$-Ag$_2$Se could provide a useful platform for studying the exotic electronic transport due to the anisotropic Dirac cone and for developing novel spintronic devices.

**EXPERIMENTAL METHODS**

**Synthesis.** Single crystalline $\beta$-Ag$_2$Se nanowires, nanoribbons, and nanoplates were synthesized in a horizontal hot-wall two-zone furnace with a 1 in. diameter inner quartz tube, as shown in Figure S1. Ag$_2$Se powder of 0.02 g (Sigma-Aldrich) in a alumina boat was placed at the center of the upstream (US) zone, and sapphire ($\beta$-Al$_2$O$_3$) substrates were placed at $\sim$30 cm downstream (DS) from the boat. The carrier Ar gas was supplied through a mass-flow controller at a rate of 30 sccm. The temperatures of the US zone and DS zone were maintained at 900 and 950 °C, respectively. The reaction time was 40 min, while the pressure was maintained at 3.6 Torr during the reaction.

**Characterization.** SEM images of $\beta$-Ag$_2$Se nanostructures were taken on a Nova 230 (FEI Co.). The XRD pattern of the as-grown nanostructures was recorded on a RIGAKU D/MAX-RC (12 kW) diffractometer operated at 30 kV and 60 mA with filtered CuK$\alpha$ radiation. TEM and HRTEM images, SAED patterns, and EDS spectra were taken by a JEO L JEM-2100F TEM (200 kV operation) and a FEI Tecnai G2 F30 (300 kV).

**Device Fabrication and Transport Measurement.** A single $\beta$-Ag$_2$Se nanowire was transferred from a sapphire substrate to a SiO$_2$-coated Si substrate with prepatterned Ti/Au pad. Conventional electron-beam lithography and RF sputtering were used to form Ti (15 nm)/Au (150 nm) electrodes. The e-beam resist, poly(methyl methacrylate) (PMMA 4% 950 K) was baked at 170 °C for 2 min. The MR was measured using a Physical Properties Measurement System (PPMS, Quantum Design Inc.) equipped with a rotating probe. We used a conventional four-probe measurement configuration combined with AC lock-in technique.

**Computational Methods.** All calculations were performed using the first-principles methods based on the density functional theory as implemented in the Vienna ab initio simulation package (VASP) (for $\beta$-Ag$_2$Se bulk) and the OpenMX codes (for $\beta$-Ag$_2$Se slab). The exchange–correlation energy functional was treated with the generalized gradient approximation parametrized by Perdew, Burke, and Enzerhof. For bulk calculations, we used the projector augmented wave pseudopotentials provided by VASP. We selected 400 eV as the energy cutoff for the plane-wave basis set. For slab calculations, we used the norm conserving pseudopotentials proposed by Morrison, Bylander, and Kleinman. The pseudoatomic basis orbitals are chosen as Ag 7.0-s2p2d1 and Se 7.0-s2p2d1. The lattice parameters of $\beta$-Ag$_2$Se were determined experimentally ($a = 4.333$ Å, $b = 7.062$ Å, and $c = 7.764$ Å), and the first Brillouin zone was integrated using Γ-centered 16 × 10 × 9 k-point samplings for bulk and 9 × 6 × 1 for slab.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.5b07368.

Experimental details and data (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: bongsoo@kaist.ac.kr.*
*E-mail: jinhee@kriss.re.kr.*
*E-mail: yjdoh@gist.ac.kr.*

**Present Address**
*#(S.L.) School of Chemistry and Centre for Research on Adaptive Nanostructures and Nanodevices, Trinity College, Dublin 2, Ireland*

**Author Contributions**
¶These authors contributed equally.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

B.K. acknowledges support of this work from National Research Foundation of Korea grant (NRF-2013R1A2A2A01069073, NRF-2012M3A2A1051686). Y.-J.D. acknowledges support of this work from National Research Foundation of Korea through the Basic Science Research Program (grant no. 2015R1A2A1A01006833). We are grateful to Kicheon Kang for useful discussions.
REFERENCES

(1) Hasan, M. Z.; Kane, C. L. Colloquium: Topological Insulators. Rev. Mod. Phys. 2010, 82, 3045–3067.
(2) Moore, J. E. The Birth of Topological Insulators. Nature 2010, 464, 194–198.
(3) Li, C. H.; van ’t Erve, O. M.; Robinson, J. T.; Liu, Y.; Li, L.; Jonker, B. T. Electrical Detection of Charge-Current-Induced Spin Polarization due to Spin-Momentum Locking in Bi2Se3. Nat. Nanotechnol. 2014, 9, 218–224.
(4) Qi, X. L.; Zhang, S. C. Topological Insulators and Superconductors. Rev. Mod. Phys. 2011, 83, 1057–1110.
(5) Beenakker, C. W. J. Search for Majorana Fermions in Superconductors. Annu. Rev. Condens. Matter Phys. 2013, 4, 113–136.
(6) Alescia, J.; Oreg, Y.; Refael, G.; von Oppen, F.; Fisher, M. P. Non-Abelian Statistics and Topological Quantum Information Processing in 1D Wire Networks. Nat. Phys. 2011, 7, 412–417.
(7) Fu, L.; Kane, C. L.; Mele, E. J. Topological Insulators in Three Dimensions. Phys. Rev. Lett. 2007, 98, 106803.
(8) Hsieh, D.; Qian, D.; Wray, L.; Xia, Y.; Hor, Y. S.; Cava, R.; Hasan, M. Z. A Topological Dirac Insulator in a Quantum Spin Hall Phase. Nature 2008, 452, 970–974.
(9) Xia, Y.; Qian, D.; Hsieh, D.; Wray, L.; Pal, A.; Lin, H.; Bansil, A.; Grauer, D.; Hor, Y.; Cava, R. Observation of a Large-Gap Topological-Insulator Class with a Single Dirac Cone on the Surface. Nat. Phys. 2009, 5, 398–402.
(10) Chen, Y.; Analytis, J.; Chu, J.-H.; Liu, Z.; Mo, S.-K.; Qi, X.-L.; Zhang, H.; Lu, D.; Dai, X.; Fang, Z.; et al. Experimental Realization of a Three-Dimensional Topological Insulator, Bi2Te3. Science 2009, 325, 178–181.
(11) Hsieh, D.; Xia, Y.; Qian, D.; Wray, L.; Dill, J.; Meier, F.; Osterwalder, J.; Patthey, L.; Checkelsky, J.; Ong, N. A Tunable Topological Insulator in the Spin Helical Dirac Transport Regime. Nature 2009, 460, 1101–1105.
(12) Peng, H.; Lai, K.; Kong, D.; Meister, S.; Chen, Y.; Qi, X.-L.; Zhang, S.-C.; Shen, Z.-X.; Cui, Y. Aharonov–Bohm Interference in Topological Insulator Nanoribbons. Nat. Mater. 2010, 9, 225–229.
(13) Hong, S. S.; Zhang, Y.; Cha, J. J.; Qi, X.-L.; Cui, Y. One-Dimensional Helical Transport in Topological Insulator Nanowire Interferometers. Nano Lett. 2014, 14, 2815–2821.
(14) Qiu, D. X.; Hor, Y. S.; Xiong, J.; Cava, R. J.; Ong, N. P. Quantum Oscillations and Hall Anomaly of Surface States in the Topological Insulator Bi2Te3, Science 2010, 329, 821–824.
(15) Tang, H.; Liang, D.; Qiu, R. L.; Gao, X. P. A Two-Dimensional Transport-Induced Linear Magnetosensitivity in Topological Insulator Bi2Se3 Nanoribbons. ACS Nano 2011, 5, 7510–7516.
(16) Cha, J. J.; Kong, D.; Hong, S.-S.; Analytis, J. G.; Lai, K.; Cui, Y. Weak Antilocalization in Bi2Se3 Nanoribbons. Nano Lett. 2012, 12, 4355–4359.
(17) Analytis, J. G.; McDonald, R. D.; Riggs, S. C.; Chu, J. H.; Boebinger, G. S.; Fisher, I. R. Two-Dimensional Surface State in the Quantum Limit of a Topological Insulator. Nat. Phys. 2010, 6, 960–964.
(18) Sacapé, B.; Oostinga, J. B.; Li, J.; Ubaldi, A.; Couto, N. J.; Giannini, E.; Morpurgo, A. F. Gate-Tuned Normal and Superconducting Transport at the Surface of a Topological Insulator. Nat. Commun. 2011, 2, 575.
(19) Kim, H.-S.; Shin, H. S.; Lee, J. S.; Ahn, C. W.; Song, J. Y.; Doh, Y.-J. Quantum Electrical Transport Properties of Topological Insulator Bi2Te3 nanowires.Curr. Appl. Phys.2016,16,51–56.
(20) Wang, J.; Cui, A. M.; Chang, C. Z.; He, K.; Jain, J. K.; Samarth, N.; Ma, X. C.; Xue, Q. K.; Chan, H. W. M. Evidence for Electron-Electron Interaction in Topological Insulator Thin Films. Phys. Rev. B: Condens. Matter Mater. Phys. 2011, 83, 245438.
(21) Tang, S.; Dresselhaus, M. S. Constructing Anisotropic Single-Dirac-Cones in Bi2–Sb Thin Films. Nano Lett. 2012, 12, 2021–2026.
(45) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. Phys. Rev. 1964, 136, B864–B871.
(46) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. 1965, 140, A1133–A1138.
(47) Soluyanov, A. A.; Vanderbilt, D. Computing Topological Invariants without Inversion Symmetry. Phys. Rev. B: Condens. Matter Mater. Phys. 2011, 83, 235401.
(48) Fu, L.; Kane, C. L. Time Reversal Polarization and a $Z_3$ Adiabatic Spin Pump. Phys. Rev. B: Condens. Matter Mater. Phys. 2006, 74, 195312.
(49) Zhao, Z.; Wang, S.; Oganov, A. R.; Chen, P.; Liu, Z.; Mao, W. L. Tuning the Crystal Structure and Electronic States of Ag$_2$Se: Structural Transitions and Metallization under Pressure. Phys. Rev. B: Condens. Matter Mater. Phys. 2014, 89, 180102.
(50) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors using a Plane-Wave Basis Set. Comput. Mater. Sci. 1996, 6, 15–50.
(51) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations using a Plane-Wave Basis Set. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169–11186.
(52) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. Phys. Rev. B: Condens. Matter Mater. Phys. 1993, 47, 558–561.
(53) Ozaki, T. Variationally Optimized Atomic Orbitals for Large-Scale Electronic Structures. Phys. Rev. B: Condens. Matter Mater. Phys. 2003, 67, 155108.
(54) Ozaki, T.; Kino, H. Numerical Atomic Basis Orbitals from H to Kr. Phys. Rev. B: Condens. Matter Mater. Phys. 2004, 69, 195113.
(55) Ozaki, T.; Kino, H. Efficient Projector Expansion for the Ab Initio LCAO Method. Phys. Rev. B: Condens. Matter Mater. Phys. 2005, 72, 045121.
(56) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
(57) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 1758–1775.
(58) Morrison, I.; Bylander, D.; Kleinman, L. Nonlocal Hermitian Norm-Conserving Vanderbilt Pseudopotential. Phys. Rev. B: Condens. Matter Mater. Phys. 1993, 47, 6728–6731.
(59) Shimojo, F.; Okazaki, H. Phase Transition in Superionic Conductor Ag$_2$Se: A Molecular Dynamics Study. J. Phys. Soc. Jpn. 1991, 60, 3745–3753.