Evidence for topological surface states in amorphous \( \text{Bi}_2\text{Se}_3 \)

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Crystalline symmetries have played a central role in the identification of topological materials. The use of symmetry indicators and band representations have enabled a classification scheme for crystalline topological materials, leading to large scale topological materials discovery. In this work we address whether amorphous topological materials, which lie beyond this classification due to the lack of long-range structural order, exist in the solid state. We study amorphous Bi$_2$Se$_3$ thin films, which show a metallic behavior and an increased bulk resistance. The observed low field magnetoresistance due to weak antilocalization demonstrates a significant number of two dimensional surface conduction channels. Our angle-resolved photoemission spectroscopy data is consistent with a dispersive two-dimensional surface state that crosses the bulk gap. Spin resolved photoemission spectroscopy shows this state has an anti-symmetric spin texture resembling that of the surface state of crystalline Bi$_2$Se$_3$. These experimental results are consistent with theoretical photoemission spectra obtained with an amorphous tight-binding model that utilizes a realistic amorphous structure. This discovery of amorphous materials with topological properties uncovers an overlooked subset of topological matter outside the current classification scheme, enabling a new route to discover materials that can enhance the development of scalable topological devices.

Introduction

Much of materials science and condensed matter physics has focused on exploiting crystal symmetries to understand physical properties, headlined by topological phases and spontaneously broken symmetries in quantum materials. The unusual properties of topological materials, such as the robustness to disorder and their quantized electromagnetic responses, have prompted ex-
tensive efforts to classify crystalline topological matter. Non-magnetic crystalline topological
insulators and metals with topological bands close to the Fermi level are relatively abundant,
representing \(\sim 30\%\) of all materials \([1, 2, 3]\), a number that may increase by including magnetic
space groups \([4]\). To identify topological crystals one asks if the band representations of a par-
ticular space group admit a trivial insulator limit compatible with the crystal symmetries; if not,
the material is labeled topological. The absence of a crystal lattice places amorphous matter
outside this classification, even though it is a subset of materials of comparable size to their
crystalline counterpart. This raises the question we have set to answer in this work: is there an
amorphous topological insulator in the solid state?

Theoretically, amorphous matter can be topological since there are non-spatial symmetries,
such as time-reversal symmetry, that protect topological phases. Topological insulator crystals
are robust against disorder; topological states do not rely on a periodic crystal lattice at all.
In the presence of time reversal invariant disorder, unless the disorder closes the bulk energy
gap, the topological states will remain robust and not be localized \([5, 6]\). Therefore, amorphous
materials, which lack translational symmetry and cannot be understood in the context of Bloch
states, can still present topological properties. Specifically, electrons in a lattice of randomly
distributed atoms with strongly disordered electron hoppings—so strong that no memory of
a lattice can be used to label the sites—can present topologically protected edge states and
quantized Hall conductivity, hallmarks of topological insulators \([7, 8, 9, 10, 11, 12, 13, 14, 15]\).
As a proof of principle, a random array of coupled gyroscopes \([10]\) was designed to act as a
mechanical analogue of an amorphous topological state with protected edge oscillating modes,
but there has so far been no experimental realization in a solid state material system.

In this work, we have grown and characterized thin films of amorphous Bi\(_2\)Se\(_3\). The tem-
perature and field dependent resistance reveals the existence of low dimensional carriers with a
reduced bulk contribution. This is supported by numerical simulations of the surface spectrum
using an amorphous topological tight-binding model. Angle-resolved photoemission (ARPES) and spin-resolved ARPES show a two dimensional surface state with strong spin-momentum locking, strongly resembling that expected for a topological Dirac cone. In its crystalline form Bi$_2$Se$_3$ is a textbook three-dimensional topological insulator \[16\]. We find that amorphous Bi$_2$Se$_3$, despite being strongly disordered and lacking translational invariance, hosts two dimensional surface states with features common to topological surface states.

Results

High resolution transmission electron microscopy (HRTEM) on amorphous Bi$_2$Se$_3$ thin films, Fig. 1(a), shows no signs of crystalline order. The diffraction pattern in the Fig. 1(a) inset shows a pattern typical of amorphous materials with well-defined coordination and inter-atomic distance. There is a diffuse but well-defined inner ring corresponding to the short-range ordering of nearest neighbors. To ensure we are not probing nanocrystalline regions and to gain insight into the medium range order, scanning nanodiffraction was performed and shown in Fig. 1(b). Four select spots each separated by 5 nm show a diffuse ring and no signs of Bragg peaks (see supplementary information for full nanodiffraction scan). The diffracted intensity versus scattering vector $k$ for eight different regions is shown in Fig. 1(c), with a single peak corresponding to the diffuse diffraction ring. The nearest neighbor spacing set by the ring is 2.39 Å, compared to 3.2 Å in crystalline Bi$_2$Se$_3$ [17]. Fig. 1(d) presents the normalized variance of the diffracted intensity for amorphous Bi$_2$Se$_3$ and nanocrystalline Bi$_2$Se$_3$ (which we grew with different growth conditions). The variance is a measure of fluctuations in diffracted intensity across the sample [18]. Bragg scattering from crystalline regions induces large variations in intensity compared to scattering from amorphous materials. The nanocrystalline sample shows a very large variance while the amorphous sample does not, providing clear evidence the amorphous samples are indeed amorphous. The electron diffraction scan shows a diffuse diffraction ring over the
entire sample; together with the HRTEM images which show no sign of nanocrystals or precursor lattice fringes, these prove the amorphous nature of the film. The Raman spectrum, Fig. 1(f), shows one broad peak between $135 \text{ cm}^{-1}$ and $174 \text{ cm}^{-1}$. As the laser power increases two peaks can be resolved, which correspond to the bulk $E^2_g$ and $A^2_{1g}$ vibrational modes, respectively. The $A^1_{1g}$ van der Waals mode at $\sim 72 \text{ cm}^{-1}$, which corresponds to the layered structure of the crystal, is absent in our samples. Instead, we observe a peak at $238 \text{ cm}^{-1}$ not present in crystalline Bi$_2$Se$_3$, which we attribute to amorphous Se-Se bonding seen in Se films [19]. The Raman peaks broaden compared to the crystalline system; the full width half maximum of the $E^2_g$ mode is $23.7 \text{ cm}^{-1}$ compared to $8.0 \text{ cm}^{-1}$ [20]. Additionally, EDS maps (presented in the supplemental information) confirm there is no clustering of Bi and Se in our films and show minimal spatial variations, further confirming that the films do not contain clusters or nanocrystals. The results in Fig. 1 show that our samples are amorphous and, while lacking a layered structure with a van der Waals gap, have a local bonding environment similar to the crystalline phase.

Figure 2 shows the temperature dependent transport data for different thicknesses in amorphous Bi$_2$Se$_3$. The resistivity, $\rho (T)$, is shown in Fig. 2(a). Quantitatively, the $\rho (T)$ values ($\sim 156-315 \text{ m}\Omega \cdot \text{cm}$) are larger than the crystalline system ($\sim 1-2 \text{ m}\Omega \cdot \text{cm}$ [21]). The amorphous system demonstrates a weakened $T$ dependence compared to the crystalline counterpart [22]. As in all amorphous metals, the carrier mean free path is determined more by disorder-driven localization than phonon interactions, leading to a largely temperature independent resistivity [23]. Moreover the high $\rho$ and the weak temperature dependence is inconsistent with either a purely metallic or purely insulating material, and suggestive of a metallic surface on an insulating bulk state with potential topological origins. Due to the potential metallic surface, we consider the resistance in Fig. 2(b), $R (T) = \rho (T) \cdot L/wt$, where $t$ is the film thickness. Again, the $R (T)$ values are greatly increased compared to the crystal ($\sim 5-250 \Omega$ for similar
thicknesses [21]). While $R(T)$ is largely temperature independent, the thicker films with more carriers show a larger activated behavior at high temperature [24], seen in the inset of Fig. 2(b). $R(T)$ for each thickness saturates at low temperature (see supplemental information); this is in contrast to crystalline Bi$_2$Se$_3$ which shows a low temperature upswing. The low temperature values range from $\sim 1h/e^2$ to $3h/e^2$, similar to other bulk insulating topological insulators when gated to bring the Fermi level into the bulk gap [25, 26, 27, 28, 29]. The low temperature $R(T)$ values lie within a factor of three, which is consistent with thickness independent two-dimensional transport channels presented in the literature [30, 31]. There are small variations in composition between sample thicknesses (< 1 at% deviation), likely leading to some variation in $R(T)$. The effect of composition needs to be explored further. Transport and ARPES results were reproducible on different samples. The $R(T)$ data was fit using a two channel conductance model [32] represented by the dashed curves in Fig. 2(b). The model includes parallel contributions from both the thermally activated bulk and metallic surface states, and provides an overall good fit to the data. Below around 150 K, $R(T)$ shows that the bulk conductance drops to near zero and the surface contribution dominates for films of all thicknesses (see supplementary information). These results indicate that the surface state contribution to conduction is metallic and dominant over a large temperature range for the amorphous samples, suggesting the existence of a topological surface state.

The magnetoconductance (MC) provides another mean to probe the transport and topological properties (Hall data presented in supplemental information). Fig. 2(c) shows MC data for a 120 nm film, revealing a sharp decrease in the low field $\Delta G$ (< 2 T) at low temperatures which is typical of weak anti-localization (WAL), consistent with a metallic surface state in amorphous Bi$_2$Se$_3$ [33]. This is in contrast to other amorphous systems which are topologically trivial and show an increase in the low field $\Delta G$, i.e. positive MC, due to weak localization [34]. In amorphous Bi$_2$Se$_3$, due to strong spin-orbit coupling (SOC), backscattering is
suppressed when a field is absent and time reversal symmetry is present. When time-reversal symmetry is broken with the application of a magnetic field, backscattering increases leading to a positive magnetoresistance (MR). The magnetoconductance can be fit with the standard Hikami-Larkin-Nagaoka (HLN) formula for WAL [35]:

\[
\Delta G(B) = \alpha \frac{e^2}{\pi \hbar} \left[ \Psi \left( \frac{\hbar}{4eBl_{\phi}^2} + \frac{1}{2} \right) - \ln \left( \frac{\hbar}{4eBl_{\phi}^2} \right) \right]
\]  

(1)

where \( \Psi \) is the Digamma function, \( B \) is the out-of-plane field, \( l_{\phi} \) (the phase coherence length) and \( \alpha \) are used as fitting parameters. According to this model, each conductance channel with a \( \pi \) Berry phase should contribute an \( \alpha = -1/2 \) factor to \( \Delta G \) [36]. In an ideal TI the two surfaces should each contribute an \( \alpha = -1/2 \) factor, while the bulk does not contribute, giving a total of \( \alpha = -1 \). Fitting our low field data, Fig. 2(d), at 2 K gives a value of \( \alpha = -0.81 \), suggesting we have two decoupled surface states corresponding to the top and bottom surfaces [37]. At 20 K, \( \alpha = -0.51 \) suggesting the two putative topological surface states are coupled to a bulk state, causing the entire film to act effectively as one channel, as seen in crystalline Bi\(_2\)Se\(_3\) from 2 nm to 100 nm [31, 38]. As the temperature increases the WAL contribution is diminished. The magnetoresistance becomes linear, which has been ascribed to spatially disordered current paths in disordered topological insulators [39], and then becomes quadratic in field and is dominated by the Lorentz force [40] (see supplemental information).

Based on Hall measurements presented in the supplemental information, the two-dimensional carrier density is \( n_{2d} = 2.86 \times 10^{14} \) cm\(^{-2}\) and the three-dimensional carrier density is \( n_{3d} = 2.32 \times 10^{19} \) cm\(^{-3}\), leading to a mobility of 1.72 cm\(^2\)/Vs. According to the Ioffe-Regel criterion the amorphous Bi\(_2\)Se\(_3\) samples constitute a bad metal (\( k_F l < 1 \)) [38] and are similar to values reported in the bulk insulating BiSbTeSe solid solution [41]. Additionally, the calculated mean free path at 4 K is \( \sim 2 \) \( \AA \), similar to the observed interatomic spacing. This \( n_{3d} \) likely places \( E_F \) into the conduction band (seen in ARPES presented below), although the depth depends on the
effective mass [38]. Regardless, since our system is amorphous the bulk carriers are expected to be localized and provide little contribution to the transport, leading to the observed high \( \rho \). The observed behavior in the sheet resistance and MR is consistent with a metallic topological surface state that dominates over a wide range of temperatures.

If amorphous Bi\(_2\)Se\(_3\) is a time-reversal invariant three-dimensional topological state, it should present topologically protected Dirac surface states. It is important to note that an amorphous system lacks translational symmetry; unlike crystalline systems, none of the momentum components, \( k_x \), \( k_y \), and \( k_z \), are good quantum numbers. However, since the nearest neighbor distance is still well defined (inset Fig. 1(a)), there exists a good reciprocal length scale. The spherical coordinate \(|k|\) is still a good quantum number due to its relationship to energy \( (E \propto k^2)\). Furthermore, the lack of a preferential direction in the bulk of an amorphous system implies spherical symmetry in momentum space. This allows for a spherically symmetric bulk band structure and the existence of topologically protected surface states. The amorphous wavefunctions can be parameterized in spherical coordinates \((k^2, \theta, \phi)\), where \( \theta \) is the azimuthal angle and \( \phi \) is the polar angle. The spherical coordinates \( \theta \) and \( \phi \) are experimentally measured and refer to the respective angles of photoemission from the sample surface (see supplementary information for details).

The interpretation of a topological surface state in our amorphous Bi\(_2\)Se\(_3\) films is further supported by our numerical model that realizes a Dirac-like state regardless of the absence of crystalline symmetry (see supplementary information for details). Motivated by the similarity of local environments between the crystalline and amorphous Bi\(_2\)Se\(_3\) found in Fig. 1, we use an amorphous variant of the three-dimensional four-band (spin-1/2 x 2-orbital) BHZ model [16, 7]. From the model we numerically obtain a spin resolved spectral function, shown in Fig. 3(a), for both the trivial and topological phase of amorphous Bi\(_2\)Se\(_3\). While inversion is expected to be an average bulk symmetry in amorphous solids, it will be broken by the surface, allowing
us to include a surface onsite surface potential that breaks this symmetry. As for the crystal surface states, this term spin-splits trivial surface states at $E_F$. This surface potential depends on the details of the surface termination (such as dangling bonds, Se vacancies, or surface reconstruction [42, 43]) and can tune the Dirac point to arbitrary binding energies [44, 45, 46]. However, it does not affect the bulk topological properties, and preserves the Dirac cone pinned to $\phi = 0$, guaranteed by time-reversal symmetry, spanning the bulk gap (see Fig. 3(a)).

Fig. 3(b) displays the raw ARPES spectrum as a function of energy and emission angle $\phi$ at a specific $\theta$, a momentum space slice that intersects $\Gamma$ ($\phi = 0^\circ$). The spectrum shows two vertical features at the Fermi level crossing the bulk gap which we attribute to the putative topological surface state. The raw spectrum reveals an intensity peak near $E_F$ starting at $-0.2\, eV$ and a sharp rise in intensity below $-0.5\, eV$. The increased intensity of the surface states near $E_F$ may be due to photoemission enhancement from the less-visible bulk conduction band (see supplementary information for details). The increased intensity below $-0.5\, eV$ coincides with a less-dispersive band which is most likely the bulk valence band. The exact bottom of the conduction band and top of the valence band is obscured in the ARPES spectra due to intrinsic broadening. However, using angle-integrated photoemission, we can roughly estimate the band gap to be $\sim 350\, meV$ (see discussion in supplementary information), consistent with the calculated DOS from amorphous structures using ab-initio molecular dynamics ($299\, meV$). Fig. 3(c) shows a cartoon of the electronic structure in amorphous Bi$_2$Se$_3$ drawn from our experimental data and numerical calculations. The topological surface states cross the bulk gap, forming a Dirac point at the top of the valence band, similar to the surface states observed in related topological insulator crystals [47]. However, the amorphous spectrum is not a result of averaging over nanocrystallite domains (see supplementary information). It is also distinct from the crystalline spectrum [48], the amorphous Bi$_2$Se$_3$ spectral features extend further in $\phi$ than the crystalline case. As discussed above, although a Dirac node crossing is a protected feature of
topological insulators, the binding energy of the node is not. From our tight binding model, we expect trivial spin-split states of Rashba-type to develop at the Fermi level, with opposite polarization from the topological surface state, due to broken inversion symmetry at the surface, as observed in Ref. [48]; this will be discussed below and shown to be consistent with our spin-ARPES data.

Fig. 3(d) presents the experimental in-plane Fermi surface in amorphous Bi$_2$Se$_3$. The annular Fermi surface is consistent with crystalline Bi$_2$Se$_3$, where the conical dispersion associated with the topological surface state produces a ring at the Fermi surface. To confirm that these states are localized to the surface, in Fig. 3(e) we show the photon energy plotted versus emission angle $\phi$. Due to conservation of energy, photon energy ($h\nu$) and $k^2$ of the photoemitted electron are nearly-proportional for large $h\nu$, and related by $\hbar^2 k^2 / 2m = h\nu - W - E_b$ where $W$ is the work function of the material and $E_b$ is the binding energy. In the plane ($k^2, \phi$) the states are near vertical features (red lines in Fig. 3(e)). For a 3D amorphous system (or even a 3D polycrystalline system), bulk states must be spherically symmetric and independent of $\phi$ due to the absence of an average preferred direction. Therefore the strong phi-dependence suggests the electrons are not from the bulk and instead originate from surface states. These observations motivate us to interpret these states as two-dimensional topological surface states. It is important to note that there exist significant density of states at the Fermi energy associated with the 2D surface states, confirming a two-dimensional transport channel as determined by our magnetoresistance measurements.

If the structure in Fig. 3 is truly a topological surface state, then the contributing states will be spin-polarized as seen in our calculations in Fig. 3(a). Fig. 4 shows spin-resolved angle-resolved photoemission spectroscopy taken with 11 eV photons. Fig. 4(a) illustrates the experimental geometry where the measured spin polarization is $P_y$ in which $y$ points along the axis of rotation used in the experiment, parallel to the sample surface.
The spin-polarized energy distribution curves (EDCs) with $p$-polarized light are shown in Fig. 4(b) at $\phi = -6^\circ$, $0^\circ$ and $6^\circ$. The spin-polarization is measured by the relative difference between spin-up and spin-down photoelectrons weighted by the Sherman function ($S$) of the detector in the form $P_y = S \times (I_\uparrow - I_\downarrow) / (I_\uparrow + I_\downarrow)$. The most evident feature from the three spin-polarized EDCs is the large positive polarization between $-0.6$ and $0.0$ eV that reaches a maximum of $\sim 50\%$. This large polarization offset is due to spin-dependent photoemission matrix elements (SMEs) in which SOC leads to selective emission of electrons with a particular spin-state. This is observed in crystalline Bi$_2$Se$_3$ near the upper Dirac cone with similar intensity [49].

In order to uncover the intrinsic spin texture (i.e. the sign of the polarization) within the SME background we follow a similar background subtraction to Ref. [49] (see supplementary information). Fig. 4(c) presents the spin polarization as a function of binding energy and $\phi$ after performing the background subtraction. From this spin polarized map, three ranges of binding energy demonstrate distinct anti-symmetric spin polarizations with respect to $\phi$: $E_F$ to $-0.20$ eV (region I), $-0.20$ eV to $-0.55$ eV (region II), and $-0.55$ eV to $-0.75$ eV (region III). The spin polarization has a magnitude of $\pm 15\%$ and changes sign between these ranges as a function of binding energy. By comparing Fig. 4(c) with the spin-integrated spectrum in Fig. 3(b) we see that region I corresponds to the conduction band, region III corresponds to the valence band, and region II corresponds to the in-gap states. The in-gap states of region II have opposite spin-polarization to both the conduction band and valence band, suggesting that these states are indeed separate features from region I and III and not a consequence of inelastic scattering from region I states or from local variations in composition. The measured spin-polarization matches the expected spin-polarization from our tight-binding model shown in Fig. 3(a) for the topological case with region I representing the spin texture of the trivial Rashba split bulk states near the Fermi level, region II representing the spin texture of the upper
Dirac cone of the topological surface state in the bulk band-gap, and region III representing the spin texture of the lower Dirac cone within the bulk valence band. Given this interpretation, we conclude that the topological surface state forms a node around $-0.55\, \text{eV}$, and the anti-symmetric spin-resolved spectrum around $\Gamma$ at $E_F$ is associated with trivial states with a large component at the surface stemming from Rashba-type spin-splitting in our system, as seen also in crystalline Bi$_2$Se$_3$ [48].

Our data is consistent with a spin-polarized two-dimensional surface state resulting from a topological bulk state in amorphous Bi$_2$Se$_3$ and poses a rich set of questions for further investigation. These findings suggest that amorphous phases of known crystalline topological insulators can be topological as well, greatly expanding the pool of potential topological materials for applications. Our work therefore motivates the search to find a systematic way to identify amorphous topological materials, including amorphous topological materials without crystalline counterparts.

Spin resolved ARPES shows an anti-symmetric spin-polarization on either side of the nodal region observed at $-0.55\, \text{eV}$, that we attribute to a spin-polarized two-dimensional topological surface state. The spectra are broadened by the atomic disorder as well as the presence of vacancies and dangling bonds at the surface, which are a significant source of final state scattering. While the lack of inversion symmetry at the surface gives rise to trivial Rashba states and a spin-polarization in the bulk conduction band and possibly the bulk valence band, it cannot provide a complete description for the observed spin texture. The presence of two independent gap crossing features (Fig. 3(c)), each with opposite spin polarization (see region II), suggests a singular helical spin texture in the gap which would not be possible if the origin of the spin texture was due to trivial Rashba bands. Moreover, all three spin-polarized regions are predicted by our theoretical calculations which show the in-gap spin texture originates from a nontrivial topological state not trivial Rashba states. The non-trivial argument is further supported by our
WAL analysis. Each trivial surface state can contribute a value of $-1/2 \leq \alpha \leq 1$ to the HLN fit depending on if the states are weakly antilocalized or weakly localized, with weakly localized states tending towards more positive $\alpha$ values. Trivial states that originate from the bulk bands, such as the trivial states in region I, have been shown to reside in the weak localization or unitary regime [50]. The observed values of $\alpha \approx -1$ at 2 K and $\alpha = -1/2$ at 20 K (Fig. 2(d)) suggest that the weak antilocalization originates from topological surface states rather than trivial Rashba states since the weakly localized Rashba states would contribute $\alpha$ values greater than $-1/2$ or $-1$ depending on if there are one or two channels, respectively.

TEM and Raman data suggests that the typical local structure of the amorphous system are comparable to the crystalline case, indicating that a possible condition to preserve the topological nature of the bulk in the amorphous state is to retain a local ordering similar to that of the crystal [14]. However, it should be noted that there is no continuous pathway from the crystalline phase to amorphous phase. There is a discontinuous phase transformation associated with the nucleation of crystalline domains [51]. This explains why nanocrystalline Bi$_2$Se$_3$ has been shown to be topologically trivial due to the presence of grain boundaries and other structural defects [52] (see also supplemental information for our data on this topic). The impact of coupling strengths and local field environments can be assessed theoretically via ab-initio calculations to refine the Hamiltonian modeling of amorphous topological materials [16]. This approach can be extended to amorphous material systems without topological crystalline counterparts, where local ordering coupled with disorder and strong SOC can mix energy levels to produce a topologically nontrivial electronic structure.

**Conclusion**

In conclusion, we have found that amorphous Bi$_2$Se$_3$ hosts a two-dimensional metallic surface state with a spin texture consistent with helical spin-polarization, indicating that the bulk is a
three-dimensional amorphous topological insulator. This first experimental evidence consistent with topological states in an amorphous solid state system highlights that topological physics is not restricted to crystalline systems. Our work provides a study of topology in an amorphous solid state system with chemical specificity and local bonding environments, a system which can be implemented into devices. To the best of our knowledge there have been no previous reports of ARPES/SARPES on an amorphous solid. Our results represent the first step towards realizing, in real materials, recently proposed non-crystalline topological phases \[53, 14\] that lie outside the known classification schemes for topological crystalline matter \[54, 2, 3, 4, 55\]. Amorphous materials could also host topological phases more robust than their crystalline counterparts \[15\]. We expect our work to motivate an effort to understand topological amorphous matter, enabling materials discovery that can provide a path towards cheaper and better implementation into modern thin film processes.

**Methods**

Amorphous Bi$_2$Se$_3$ thin films were thermally evaporated in a UHV chamber with base pressure of $10^{-9}$ Torr. The films were grown at room temperature from high purity (99.999\%) elemental Bi and Se single sources (for further growth and composition details see the supplementary information). Stoichiometry of the films was confirmed using XPS (X-ray photoelectron spectroscopy), EDS (Energy dispersive X-ray spectroscopy), and RBS (Rutherford backscattering spectroscopy). High resolution TEM and Fluctuation electron microscopy (FEM) were performed on 10 nm thick Bi$_2$Se$_3$ films deposited on a 10 nm thick SiN window. FEM experiments were performed using an FEI TitanX operated at an acceleration voltage of 200 kV. Diffraction images were collected on an Orius CCD system with an exposure time of 0.3 seconds and a camera length of 300 mm. The probe convergence angle was set to 0.51 mrad by adjusting the third condenser lens current, resulting in a probe diameter of 2.2 nm and a probe current of 15.5
Nanodiffraction data were collected as 15-by-15 image stacks (225 total images). Multiple 225-image datasets were collected for both the amorphous and polycrystalline Bi$_2$Se$_3$ for statistical averaging. Each data set covered an area on the film of approximately 77-by-77 nm. The first image from each dataset was excluded to avoid including any potential sample damage or contamination in the data resulting from the parked beam. The central beam was covered using a beam stop and the beam position remained constant across all FEM images for each sample. Variation in peak positions and intensities were negligible across data from different locations on a single film. Imaging conditions were held constant for all data collection to prevent variations in microscope alignment. The amorphous structure of the film was confirmed with XRD, Raman spectroscopy, and TEM.

The amorphous Bi$_2$Se$_3$ samples $\rho (T)$ was measured using a four point probe. The samples were grown as a bar using a metal mask onto pre-deposited Au(5 nm)/Cr(2 nm) contacts to ensure ohmic contact (shown in Fig. 2(a) inset). Magnetotransport was measured in the Van der Pauw configuration with samples grown onto pre-deposited Au(5 nm)/Cr(2 nm) contacts.

The Hamiltonian used to describe amorphous Bi$_2$Se$_3$ features direction-dependent spin-orbit hoppings set by the normalized hopping vector $\hat{d}$ and is the sum of onsite and hopping terms

$$H_{\text{onsite}} = m \sigma_0 \tau_z,$$

$$H_{\text{hop}}(\hat{d}) = it_1 (\hat{d} \cdot \sigma) \tau_x + t_2 \sigma_0 \tau_z$$

where $\sigma_i$ and $\tau_i$ are the spin and orbital Pauli matrices respectively, $m$ sets the splitting between the local $s$ and $p$-like orbitals, $t_1$ is the spin-orbit hopping, and $t_2$ is the normal hopping amplitude. In the crystalline case this Hamiltonian correctly reproduces key features of the topologically nontrivial bands closest to the Fermi level [16]. We implement this tight-binding model on large systems of short-range correlated amorphous structures (see supplementary information) and investigate the topological surface states by calculating spectral functions using
the Kernel Polynomial Method [56, 57].

We performed ARPES at the Advanced Light Source MAESTRO (7.0.2) and MERLIN (4.0.3) beamlines with photon energies in the range of 65 - 125 eV. ARPES results taken on different samples and at different beamlines produce the same results. The spin-resolved spectra were acquired from a high-efficiency and high-resolution spin-resolved time-of-flight (TOF) spectrometer that utilizes the spin-dependent reflection from a magnetic thin-film due to the exchange interaction [58]. The light source for the spin measurements was a Lumeras 11eV Xenon gas-cell laser with 1MHz repetition rate [59]. Synchrotron ARPES measurements and spin-resolved measurements were taken at 20K and 75K, respectively. ARPES was analyzed using the PyARPES software package [60].

Density functional theory (DFT) calculations were performed using the projector augmented wave (PAW) formalism in the Vienna ab initio Simulation Package (VASP) [61, 62]. The exchange-correlation potentials were treated in the framework of generalized gradient approximation (GGA) of Perdew-Burke-Ernzerbof (PBE) [63]. Bi (6s, 6p) and Se(4s, 4p) electrons were treated as valence, and their wavefunctions expanded in plane waves to an energy cut-off of 500 eV. A k-point grid of 3x3x1 with Gamma sampling was used. Spin-orbit coupling was added self-consistently for all density of states calculations. Amorphous structures were generated with ab initio molecular dynamics using VASP.

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Acknowledgments

P. C. and S. C. would like to thank E. Parsonnet and D. Rees for their discussions. A. G. G. is grateful to J. H. Bardarson, S. Ciuchi, S. Fratini, and Q. Marsal for discussions. D. V.
thanks A. Akhmerov, A. Lau and P. Perez Piskunow for discussions. The growth and transport work was primarily funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the Nonequilibrium Magnetic Materials Program (MSMAG). The ARPES and SARPES work was supported by Berkeley lab’s program on ultrafast materials sciences, funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 and the Quantum Materials Program at Lawrence Berkeley National Laboratory, funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, under contract DE-AC02-05CH11231. TEM at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Computational resources were provided by the National Energy Research Scientific Computing Center and the Molecular Foundry, DoE Office of Science User Facilities supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The work performed at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under the same contract. P. C. is supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1752814. S.C. was supported by the National Science Foundation Graduate Research Fellowship under Grant No. DGE1852814 and DGE1106400. A. G. G. is supported by the ANR under the grant ANR-18-CE30-0001-01 and the European Union Horizon 2020 research and innovation programme under grant agreement No. 829044. D. V. is supported by NWO VIDI grant 680-47-53. S. E. Z. was supported by the National Science Foundation under STROBE Grant No. DMR 1548924.
Author contributions

P. C. and S. C. contributed equally to this work. The project was initiated and oversaw by P.C., S.C., A. G. G., A.L., and F. H.. P. C. grew the films. S.C. performed synchrotron ARPES, S. C. and P. C. performed SARPES measurements, and S.C. performed the data analysis. P. C. performed transport measurements. S. Z., E.K., S. C., and P. C. performed TEM. M. M. R. and P. C. performed Raman measurements. Z.C. performed the molecular dynamics and S.G. performed the DOS calculations. A. G. G. and D. V. constructed the tight-binding model, and D. V. performed numerical calculations. P. C., S. C., A. G. G. and D. V. took part in interpreting the results. All authors contributed to writing the manuscript.

Competing interests:

The authors declare no competing financial interests.

Additional Information

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Information. Additional data related to this paper may be requested from the authors.
Fig. 1. Structural and spectral evidence for the amorphous atomic structure of Bi$_2$Se$_3$ (a) A HRTEM image. Inset: Diffraction pattern for the amorphous Bi$_2$Se$_3$ films. At $\sim 2.4$ Å we observe a diffuse ring due to the amorphous nature of the film. (b) Scanning nanodiffraction patterns taken with a beam spot of 2 nm separated by 5 nm. Each spot shows a diffuse ring and no signs of crystallinity. (c) A 1D intensity cut, as a function of scattering vector $k$, for 8 different regions as well as the average intensity. A peak is observed $\sim 3.2$ nm$^{-1}$. (d) FEM variance, $V(k)$, as a function of scattering vector $k$ for amorphous and nanocrystalline Bi$_2$Se$_3$. The nanocrystalline sample exhibits Bragg diffraction peaks leading to large variations in the intensity, while the amorphous sample does not. (e) A XRD 2θ scan for amorphous Bi$_2$Se$_3$ after the Se decap showing no signs of incipient crystallization. XRD provides a macroscopic probe of the films structure. The substrate peak is labeled. (f) Raman spectra for 50 nm amorphous
$\text{Bi}_2\text{Se}_3$ films using a 488 nm laser. The peaks are labeled with their respective Raman mode. Different curves (blue and purple) correspond to different laser powers, indicating bulk Raman modes become more well-defined and do not shift as the films become more ordered. All samples presented in this work show similar spectra to the lower power spectra shown in this figure. Crystalline data [64] (green curve) is overlayed to show the lack of a Van der Waal mode at $\sim 72 \text{ cm}^{-1}$ in the amorphous films.
Fig. 2. Transport signatures of putative topological electronic states in amorphous Bi$_2$Se$_3$

(a) $\rho (T)$ for 76 nm, 96 nm and 129 nm films. All films show a high resistivity with little temperature dependence. Inset: Schematic of the structure used to measure resistivity. (b) The resistance for 76 nm, 96 nm and 129 nm films. All films show high temperature activated behavior (inset) and low temperature metallic behavior in $R$ with a low temperature saturation. Two-channel conductance fits the data reasonably well indicating a metallic surface and insulating bulk behavior. (c) Conductance change as a function of the magnetic field for a 120 nm film, measured at 2 K, 4 K, 10 K, 20 K, 40 K and 80 K, where $\Delta G_{xx} = G(B) - G(0)$. The deep cusp in the low field regime is characteristic of the WAL effect. (d) Magnetoconductance HLN
fits showing $\alpha$ values indicating decoupled surface surface states at 2 K and a single conduction channel at 20 K. The dephasing length $l_\phi$ decreases with increasing temperature.
Fig. 3. ARPES spectra of putative topological electronic states in amorphous Bi$_2$Se$_3$ (a)
A calculated spin-resolved surface spectral function as a function of \( \phi \) for the trivial and topological phase. In the topological phase the Dirac point is low in binding energies and Rashba spin-split states develop near the Fermi level. (b) ARPES spectrum \( E \) vs. \( \phi \) taken at normal emission at \( h\nu = 117.5 \text{ eV} \). The spectrum reveals vertical states that cross the bulk gap and meet at \(-0.6 \text{ eV}\) near the bulk valence states. (c) Proposed spin-resolved electronic structure in amorphous \( \text{Bi}_2\text{Se}_3 \) corresponding to the ARPES in (b). The topological surface state traverses the electronic gap and meets near the bulk valence states, while trivial Rashba states develop near the bulk conduction states. (d) The ring-like in-plane Fermi surface. \( \phi \) are the angles simultaneously collected by the detector referenced to normal incidence at a given sample tilt \( \phi' \). (e) \( h\nu \) vs. \( \phi \) with binding energy integrated from \(-0.6 \text{ eV}\) to the Fermi level and normalized by photon energy. The \( h\nu \) vs. \( \phi \) plot displays no photon energy dependence of the photoemission angle. Red dotted lines are fit to intensity peaks in the \( h\nu \) vs. \( \phi \) spectrum.
Fig. 4. Spin-resolved ARPES spectra of electronic states in amorphous Bi$_2$Se$_3$. (a) S-ARPES experimental geometry. (b) Spin-resolved EDC’s taken at $\phi = -6^\circ$, $\Gamma$, and $\phi = 6^\circ$, respectively. The spin contributions at each binding energy vary with respect to $\phi = 0^\circ$. (c) Spin-resolved EDC map of $E$ vs $\phi$ with SME background subtraction taken from $\phi = -9^\circ$ to $\phi = 9^\circ$. The spin polarization switches from red to blue (or vice versa on the other side of $\Gamma$) at $-0.2$ eV and from blue to red at $-0.55$ eV.