Complex optical conductivity of Bi$_2$Se$_3$ thin film: Approaching two-dimensional limit

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ABSTRACT

Two-dimensional Bi$_2$Se$_3$ thin films have attracted widespread attention as an ideal platform for high-performance optoelectronic applications. Understanding the intrinsic optical/electronic properties of Bi$_2$Se$_3$ thin films is vital for Bi$_2$Se$_3$-based optoelectronic applications. Here, the complex optical conductivities of a series of Bi$_2$Se$_3$ thin films with a varying number of quintuple layers are investigated by combining spectroscopic ellipsometry with the classical slab model over a broad spectral range of 0.73–6.43 eV. Results show that the zero-cross point of the imaginary complex optical conductivity exhibits a blueshift trend due to the enhanced coupling between the surface states as the thickness of Bi$_2$Se$_3$ thin film approaches the two-dimensional limit. Five feature peaks (A–E) are identified in the complex optical conductivity spectra, and their center energies exhibit interesting thickness dependencies, which are mainly attributed to the increased surface state gap due to the finite-size effects when the Bi$_2$Se$_3$ thin film gradually approaches the two-dimensional limit. Our work not only gives insights into the tunable optical properties of Bi$_2$Se$_3$ thin films but also reveals its intrinsic physical origin, which are essential and imperative for accurate modeling and design of Bi$_2$Se$_3$-based optoelectronic devices.

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Topological insulator (TI) materials, such as HgCdTe quantum wells, Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$, etc., have gained great interest in many fields, including quantum computers, condensed-matter physics, optoelectronics, and magnetism. Unlike normal insulators, the TIs not only have a narrow bulk bandgap induced by the strong spin–orbit coupling but also possess gapless and dissipationless spin-polarized edge or surface states. In three-dimensional (3D) TIs, the Dirac cones, spin-polarized surface states, and electronic band structures were observed and obtained by employing angle-resolved photoemission spectroscopy (ARPES), spin-resolved ARPES, and first principle calculations, which demonstrate the topological nature of 3D TIs. Among various 3D TIs, the Bi$_2$Se$_3$ is the most representative one, which has been extensively applied to many optoelectronic devices. Bi$_2$Se$_3$ possesses a layered structure composed of quintuple layers (QLs) with weak van der Waals-type interaction among adjacent QLs, which makes it available to obtain Bi$_2$Se$_3$ thin films. Among all the growth methods, molecular beam epitaxy (MBE) is a widely used approach to fabricate high-quality Bi$_2$Se$_3$ thin films. As the thickness of Bi$_2$Se$_3$ approaches a few QLs, the performance of Bi$_2$Se$_3$-based optoelectronic devices can be dramatically enhanced with a widely tunable surface bandgap. To provide a guidance for the design and optimization of optoelectronic devices based on Bi$_2$Se$_3$ thin films, it is critical to obtain accurate and quantitative characterization of the optical properties of Bi$_2$Se$_3$ thin films.

Generally speaking, the complex refractive index and the complex dielectric function are two basic optical functions that we regularly use to, respectively, describe the optical and dielectric properties of a material. Except for them, the complex optical conductivity, as another essential optical function, is directly relevant to the photore sistance and photocurrent, which is beneficial to the development of related optoelectronic devices, including photodetectors, photoconductors, photovoltaics, etc. Therefore, the complex optical
conductivities of Bi$_2$Se$_3$ have been extensively studied by multiple approaches, such as reflection spectrometry, UV-visible ellipsometry, terahertz spectroscopy, and first-principles calculations. Pietro et al. measured the reflectance spectrum of Bi$_2$Se$_3$ single crystal from sub-THZ to the visible region in the range of 5–300 K and calculated the real part of complex optical conductivity via the reflectivity by Kramers–Kronig transformations. Post et al. obtained the infrared complex optical conductivities of Bi$_2$Se$_3$ films with a thickness varying from 15 QLs to 99 QLs by spectroscopic ellipsometry (SE) and infrared transmission spectroscopy. By measuring the THz transmittance vs the temperature of 23-QL Bi$_2$Se$_3$ film, Kamboj et al. extracted the THz optical conductance spectra from the normalized transmission using Tinkham’s formula. However, most of the aforementioned works focus on the investigation of the complex optical conductivity of Bi$_2$Se$_3$ over a narrow band and are limited to the thick Bi$_2$Se$_3$ films or single crystal. The systematic research on the complex optical conductivity of Bi$_2$Se$_3$ at the two-dimensional limit (<6 QLs) is missing, which may hinder the performance improvement of Bi$_2$Se$_3$-based optoelectronic devices.

In this work, high-quality and continuous Bi$_2$Se$_3$ thin films with variable thickness are prepared by MBE on sapphire substrate. We have systematically investigated the complex optical conductivities of the as-prepared Bi$_2$Se$_3$ thin films as a function of the number of QL by combining spectroscopic ellipsometry (SE) with the classical slab model. Five feature peaks (A–E) are observed in the complex optical conductivity spectra. Our studies reveal that the zero-cross point of the imaginary part of the complex optical conductivity shows a blueshift trend due to enhanced coupling between the opposite surfaces as the thickness gradually decreases. By using differential spectrum analysis method, we accurately determine the center energies of feature peaks in the optical conductivity spectra and reveal the intriguing thickness dependencies of their center energies. Results suggest that the increased surface state gap due to the finite-size effect mainly leads to the layer-dependent evolutions of these feature peaks.

High-quality and continuous Bi$_2$Se$_3$ thin films were prepared by the MBE on the sapphire (Al$_2$O$_3$) substrate. The detailed growth process was demonstrated in the supplementary material. After the growth of Bi$_2$Se$_3$ thin films, several characterization methods were applied to demonstrate the high quality of our MBE-grown Bi$_2$Se$_3$ thin film samples. The RH30OM reflection high-energy electron diffraction (RHEED) system and Raman spectrometer (inVia reflex, RENISHAW) were adopted to detect the crystal quality of Bi$_2$Se$_3$ thin films. The optical microscope (OM) measurements were conducted with a 10 times magnification to check the surface conditions of Bi$_2$Se$_3$ thin films, and the thicknesses and surface roughness of Bi$_2$Se$_3$ thin films were examined by an AFM system (Bruker Dimension Icon) and a high-resolution transmission electron microscope (HRTEM) system (FEI Titan G2–300).

The ellipsometric data were gathered using a commercial dual rotating-compensator spectroscopic ellipsometer (ME-L Muller matrix ellipsometer, Wuhan Eoptics Technology Corporation). Optical spectra of Bi$_2$Se$_3$ thin films were recorded over an ultra-broad spectral

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**FIG. 1.** (a) The schematic diagram of Bi$_2$Se$_3$: five atomic layers of Se$_1$–Bi–Se$_2$–Bi–Se$_1$ form a QL. (b) Raman spectra of 2-QL, 4-QL, 8-QL, and 10-QL Bi$_2$Se$_3$ thin films. (c) Representative OM graph of the 4-QL Bi$_2$Se$_3$ thin film. (d) Cross-sectional HRTEM image of 4-QL Bi$_2$Se$_3$ thin film. (e) and (f) The surface roughness and thickness of 8-QL Bi$_2$Se$_3$ thin film characterized by AFM.
range of 0.73–6.43 eV. A pair of focusing probes was used in the measuring process, and the diameter of the probing spot can be as small as 200 μm. The multi-incidence measurement mode was used to reduce the correlations among the variables, and the incident angles for each sample were set from 60° to 70° with a step of 5°.

The Bi2Se3 thin film possesses a rhombohedral crystal structure, and it belongs to the space group R3m.29 As denoted in Fig. 1(a), from the top to the bottom atomic layers in a QL, the Se and Bi atoms are stacked on the order of Se1–Bi–Se2–Bi–Se1. The purity and crystal quality of Bi2Se3 thin films are checked by Raman spectra, as presented in Fig. 1(b). The Raman spectra show that the Bi2Se3 thin films possess three characteristic intensity peaks (A1g, E2g, and A2g) around 73.4, 131.5, and 174.5 cm⁻¹, respectively, suggesting the high purity and crystal quality of our Bi2Se3 thin film samples.28,30 The typical RHEED pattern of Bi2Se3 is presented in Ref. 31, indicating the lattice constant of Bi2Se3 is 4.194 Å. The smooth surface shown in the OM image in Fig. 1(c) indicates that our Bi2Se3 samples are flat and continuous. Besides, as shown in Fig. 1(d), the thickness of the 4-QL Bi2Se3 thin film is determined by the HRTEM, and it is 3.83 nm. The clear layered structures shown in the HRTEM image indicate the high crystalline quality of the Bi2Se3 thin film. Figures 1(e) and 1(f) present the surface condition and thickness of 8-QL Bi2Se3 thin film detected by AFM. It is clear that the roughness values (Rq) of film are extremely low, demonstrating the Bi2Se3 thin film has great flatness. The AFM image also shows that the thickness of 8-QL Bi2Se3 thin film is 7.82 nm. All these characterizations show that the Bi2Se3 thin films in our study are high quality and continuous.

Figures 2(a) and 2(b) show the complex refractive indices N = n − iκ extracted from ellipsometric analysis processes (detailed analysis processes are demonstrated in the supplementary material), where n and κ represent the refractive index and the extinction coefficient, respectively. Up to five absorption peaks (A–E) can be observed in the complex refractive index spectra of 2–10 QL Bi2Se3 thin films. As the thickness of Bi2Se3 thin films decreases from 10 QLS to six QLS, both the magnitudes of n and κ remain nearly unchanged. While the thickness becomes thinner than six QLS, the evolution trends of the magnitudes are different for n and κ. Figure 2(a) shows that with the thickness decreasing, the magnitude of n gradually decreases in the energy range from 0.73 to 2.2 eV, but it turns to gradually increases when the photon energy is greater than 2.2 eV. Different from n, Fig. 2(b) shows that with the thickness decreasing, the magnitude of κ gradually decreases in the energy range from 0.73 to 4.5 eV. Additionally, the energy positions of these five absorption peaks (A–E) present blueshift trends as the thickness approaches the two-dimensional limit. The spectral shape of Bi2Se3 thin films in Figs. 2(a) and 2(b) is similar to that of few-layer black phosphorus and tellurium, and their optical respond is sensitive to thickness.32,33 Previous studies32,33 on few-layer black phosphorus and tellurium are focused on infrared range and anisotropy, while our study on Bi2Se3 thin films is on a wide range and isotropic, similar to normal 2D transition metal dichalcogenides (TMDCs).34

Base on the complex refractive index, the complex optical conductivities σ = σr + iσi of Bi2Se3 thin films can be evaluated by the classical slab model. In the classical slab model, the thin film is
considered as a slab with a finite thickness \(d\), and the complex optical conductivities can be calculated by \(^{17}\)

\[
\sigma = \sigma_r + i\sigma_i = id\epsilon_0\omega(N^2 - 1),
\]

(1)

where \(d\) is the thickness of the Bi\(_2\)Se\(_3\) thin film determined by SE (Table S1), \(N\) is the complex refractive index shown in Figs. 2(a) and 2(b), \(\epsilon_0\) and \(\omega\) refer to the free-space permittivity and the angular frequency of light, respectively. Figures 2(c) and 2(d) present the complex optical conductivities of 2–10 QL Bi\(_2\)Se\(_3\) thin films evaluated by the classical slab model, which have been normalized by \(2e^2/h\) (\(e\) and \(h\) represent the electronic charge and Plank constant). Similar to the complex refractive index, five feature peaks are also observed in the complex optical conductivity spectra. In the real complex optical conductivity \((\sigma_r)\), it is obvious that \(\sigma_r\) monotonically decreases as the thickness of Bi\(_2\)Se\(_3\) thin film approaches the two-dimensional limit, and in the imaginary complex optical conductivity \((\sigma_i)\), the absolute value of \(\sigma_i\) also shows a decrease trend as the thickness of Bi\(_2\)Se\(_3\) thin film gradually decreases. These decrease trends in the real and imaginary parts of complex optical conductivity can be attributed to the gradually attenuated light absorption and propagation effects with the thickness decreasing. In addition, it can be observed that there exists a region highlighted by the blue area in Fig. 2(d), where the \(\sigma_i\) becomes negative. This negative phenomenon is related to the surface plasma and expected to present some novel insights for the design of Bi\(_2\)Se\(_3\) based devices, such as plasmon-based radiation generation, sensing, and waveguides.\(^{15,21,35,36}\) Specifically, as the thickness of Bi\(_2\)Se\(_3\) thin film approaches the two-dimensional limit, the zero-cross point \((E_{zc})\) shows a blueshift trend, and the area where \(\sigma_i\) is negative gradually becomes smaller in Fig. 2(d). We propose that when the Bi\(_2\)Se\(_3\) thin film is getting thinner, the enhanced coupling between the opposite surface states causes an increase in surface state gap,\(^{26,27}\) and then makes the resonance frequencies of surface plasma increase, which finally lead to the blueshifted \(E_{zc}\) and the shrunken negative \(\sigma_i\) area.

As presented in Fig. 2, except for that the magnitudes of feature peaks (A–E) in complex optical conductivity spectra demonstrate layer-dependencies; the center energies of these peaks also exhibit interesting layer-dependent shifts. In order to accurately determine the center energies of these peaks and further reveal the underlying physical essence, we calculate the first-order and second-order differential spectra of the complex optical conductivities of Bi\(_2\)Se\(_3\) thin films, as shown in Fig. 3. The feature peaks of complex optical conductivity

![Differential spectra](https://example.com/differential_spectra.png)

**FIG. 3.** Differential spectra of the complex optical conductivities of 2–10 QL Bi\(_2\)Se\(_3\) thin films. (a)–(e) First-order differential spectra over the region of 1.5–5.5 eV. (f)–(j) Second-order differential spectra over the region of 1.0–4.5 eV. Five feature peaks are labeled with A–E.
spectra in Fig. 2 can be classified into extreme peaks and shoulder peaks. The center energies of extreme peaks are identical to the positive-to-negative zero-cross points in first-order differential spectra, and the center energies of shoulder peaks are equivalent to the local minima of the second-order differential spectra. The red (blue) solid lines in Figs. 3(a)–3(e) show the first-order differential spectra of the real (imaginary) parts of the complex optical conductivities of 2–10 QL Bi$_2$Se$_3$ thin films. The extreme peak D in $\sigma_r$ and extreme peak C in $\sigma_i$ are accurately identified at the positive-to-negative zero-cross point in Figs. 3(a)–3(e). Apart from extreme peak D in $\sigma_r$ and extreme peak C in $\sigma_i$, other feature peaks are shoulder peaks and can be identified at the local minima in the second-order differential spectra of $\sigma$, as shown in Figs. 3(f)–3(j). The center energies of the feature peaks (A–E) in the real and imaginary part of complex optical conductivity spectra are listed in Tables S2 and S3.

Figures 4(a) and 4(b) present the layer-dependent evolutions of the center energies of the feature peaks A–E in the complex optical conductivity spectra. The $E^0_{Re}$ in Fig. 4(a) and the $E^0_{Im}$ in Fig. 4(b) illustrate the center energies of feature peaks A–E in the real and imaginary part of the complex optical conductivity spectra, respectively. In the real complex optical conductivity spectra $E^0_{Re}$, when the QL number of Bi$_2$Se$_3$ thin film decreases from 10 to 6, the center energies of feature peaks A–E remain nearly unchanged. As the QL number of Bi$_2$Se$_3$ thin film continues to decrease, the center energies of feature peak A–E show a blueshift trend. Among these five feature peaks, the feature peak D shows a maximum blue shift of 0.64 eV, while the feature peak C shows a minimum blue shift of 0.13 eV. Previous work shows that electron energy-loss spectroscopy (EELS) spectrum of Bi$_2$Se$_3$ bulk system has two main spectral features near 7 and 17 eV, and the spectral feature near 7 eV is related to $\pi$ plasmon resonances, similar to the $\pi$ plasmon in carbon nanotubes. So, feature peaks A–E in Fig. 4(a) should be normal absorption peaks. In the imaginary optical conductivity spectra $E^0_{Im}$, as the thickness of Bi$_2$Se$_3$ thin film decreases from 10 QLs to six QLs, the center energy of feature peak C has some fluctuations, while the center energies of other feature peaks remain nearly the same. When the QL number of Bi$_2$Se$_3$ thin film is less than six QL, the center energies of all these five feature peaks A–E also present a blueshift trend. In addition, as the thickness of Bi$_2$Se$_3$ thin films

![Fig. 4](image_url)
approaches two-dimensional limit, the feature peaks C and D gradually move away from each other in $E_{\text{Re}}^0$, but the feature peaks C and D are gradually approaching each other in $E_{\text{Im}}^0$.

Generally speaking, the real part of complex optical conductivity ($\sigma_r$) shows the energy loss component caused by the light-induced conduction current, while the imaginary part of complex optical conductivity ($\sigma_i$) reflects the energy storage capacity of Bi$_2$Se$_3$ thin films. So, the feature peaks A–E in $E_{\text{Re}}^0$ actually reflect energy loss in the light propagation process and should be related to different optical transitions. First-principles study in Ref. 24 demonstrates that weak excitonic effects exist in optical properties of Bi$_2$Se$_3$, indicating the feature peaks A–E in $E_{\text{Re}}^0$ have excitonic character. Besides, the feature peaks A–E are relevant to different direct transitions from valence bands to conduction bands along the $\Gamma$–M–K branch in the band structures of the Bi$_2$Se$_3$ thin films, as discussed in detail in previous work. In 2D MoS$_2$ and 2D WSe$_2$, as the thickness decreases from multilayers to monolayer, most of the energy shift values of feature peaks are below 0.2 eV, and high-energy feature peaks have a different trend from low-energy feature peaks. The underlying physical cause is explained as the alternate domination of the layer-dependent increasing exciton binding energy and the band renormalization.

Compared with 2D MoS$_2$ and 2D WSe$_2$, we elucidate that the excitonic effect is weak in Bi$_2$Se$_3$ thin films, and there are two factors that mainly affect the distinctive QL–dependent shifts in $E_{\text{Im}}^0$: one factor is the band shape evolution and the other is the increasing surface bandgap when the Bi$_2$Se$_3$ thin film varies from six QLs to two QLs. As shown in Fig. 4(c), the Bi$_2$Se$_3$ thin film experiences a dimensional crossover from 3D topological insulator to trivial insulator at six QLs, which means as the QL number of Bi$_2$Se$_3$ thin film is less than six QLs, a finite bandgap opens in the surface states of the Bi$_2$Se$_3$ thin film due to the finite-size effects. We think that the fluctuations of A–E from 10 QLs to six QLs and the different blueshift values (0.13 eV–0.64 eV) of A–E below six QL could be attributed to band shape evolution as the thickness of Bi$_2$Se$_3$ thin film approaches two-dimensional limits, and the overall blueshift tendency is mainly caused by the increased surface state gap due to the finite-size effects when the QL decreases from 6 to 2.

In summary, we have provided systematic investigation of the QL–dependent optical conductivities of Bi$_2$Se$_3$ thin films by combining SE with the classical slab model. Five feature peaks (A–E) can be identified in the complex optical conductivity spectra, and the zero-cross point of the imaginary complex optical conductivity shows a blueshift trend due to enhanced coupling between the opposite surfaces as the thickness of Bi$_2$Se$_3$ thin film approaches the two-dimensional limit. With the help of differential spectrum analysis method, we determined the center energies of A–E in the optical conductivity spectra, whose center energies exhibit intriguing thickness dependencies. While the QL number of Bi$_2$Se$_3$ thin film decreases from ten to six, the center energies of A–E remain almost unchanged. While the QL number continues to decrease, the center energies of A–E present a blue-shift trend as the QL number decreases. We attribute this evolution mainly to the increased surface state gap caused by the finite-size effects as the thickness gradually decreases. We anticipate that the determined complex optical conductivity of Bi$_2$Se$_3$ alongside their layer-dependent properties may pave the route to the design and performance improvement of photodetectors, photoconductors, and photovoltaics.

See the supplementary material for the detailed MBE growth process and ellipsometric analysis, and the center energies of the feature peaks (A–E) in the real and imaginary part of complex optical conductivity spectra from differential spectrum analysis.

AUTHORS’ CONTRIBUTIONS

M.F. and Z.W. contributed equally to this work.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES


