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Zhen Lian,¹ Zeyu Jiang,² Tianmeng Wang,¹  Mark Blei,³ Ying Qin,³ Morris Washington,² Toh-Ming Lu,² Sefaattin Tongay,³ Shengbai Zhang,² and Su-Fei Shi^{1,4,a)} 

AFFILIATIONS

¹Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

²Department of Physics, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

³School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona 85287, USA

⁴Department of Electrical, Computer and Systems Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

^{a)}Author to whom correspondence should be addressed: shis2@rpi.edu

ABSTRACT

A re-discovered member of the layered material family, Titanium Trisulfide (TiS_3), has attracted intense research interest recently for the possibility of realizing an exciton insulator in the monolayer limit. However, due to their quasi-one-dimensional nature, thin TiS_3 flakes are typically in the form of nanoribbons that are challenging to characterize by optical absorption spectra, due to their small cross section. Here, we employ a sensitive photocurrent spectroscopy technique to probe the absorption of a thin TiS_3 nanoribbon in a field-effect transistor configuration. We have found a significant modification of the band structure of the thin TiS_3 nanoribbon, compared to its bulk counterpart. In addition, the polarization-dependent photocurrent spectra of thin TiS_3 nanoribbons exhibit greatly enhanced anisotropy compared to that of a thick TiS_3 device. The atomically thin TiS_3 flake, thus, not only provides an exciting platform for investigating many-body physics but also enables anisotropic quantum optoelectronics.

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Among the growing family of vast two-dimensional (2D) materials, there exists a class of layered materials with a quasi-one-dimensional (1D) structure that has attracted intense research interest recently, which includes ZrS_3 , ZrSe_3 , HfTe_3 , TiS_3 , etc.^{1–5} The 2D materials in this family naturally possess large electrical and optical anisotropy and often exhibit exotic quantum physics when thinned down to atomic thicknesses.^{1–11} For example, TiS_3 was recently predicted to be a promising candidate for hosting the long-sought exciton insulator at the monolayer limit.¹² However, limited by the quasi-1D nature, the thin flakes of such layered materials are typically in the form of nanoribbons, with the width comparable to or even much smaller than the diffraction limit of the light. As a result, optical spectroscopy, which has been a powerful tool to study the band structure of 2D materials through reflectance/absorption measurements,¹³ cannot probe the thin flake of such quasi-1D layered materials easily due to the small cross section that limits the amount of detectable optical signals. Meanwhile, photocurrent spectroscopy can reveal the absorption information by measuring the photocurrent response as a function of the excitation photon energy,^{14,15} thus providing

a sensitive probe of the band structure, especially for the semiconducting device with a low dark current. Although the anisotropic photocurrent response has been demonstrated in TiS_3 flake-based photodetectors,⁸ no absorption spectrum has been reported for quasi-1D thin flakes of TiS_3 yet, to the best of our knowledge.

In this work, by fabricating both thick (~ 200 nm thick) and thin (~ 15 nm thick) TiS_3 flakes into field-effect transistor (FET) devices, we reveal the band structure of both the thin and thick TiS_3 flakes through photocurrent spectroscopy. Our study shows that the thick TiS_3 flake possesses a bandgap around 0.90 eV and is promising for infrared optoelectronics. In contrast, the band structure of thin TiS_3 is modified by the quantum confinement, and the bandgap is increased to about 0.96 eV. Also, the absorption resonance is significantly modified as well. While the thick sample shows two major absorption resonances at 1.23 eV and 1.41 eV, the thin sample exhibits a single peak at 1.34 eV. Our work demonstrates that photocurrent spectroscopy is a powerful tool to probe the band structure and excitonic physics in quasi-1D layered materials, and TiS_3 nanoribbon is a promising candidate for anisotropic optoelectronics in the near-infrared regime.

TiS₃ crystals were synthesized via the chemical vapor transport method. One-gram stoichiometric mixture of elemental titanium and sulfur was loaded in a quartz ampule [1.5 cm outer diameter (OD) and 20 cm in length] and sealed under evacuation at 10^{-5} Torr. Crystal growth was allowed for 7 days in a two-zone furnace with precursors in the hot zone (550 °C) and crystallization in the cold zone (450 °C). We mechanically exfoliate TiS₃ flakes on the 285 nm SiO₂/Si substrate.^{7,16} Raman spectra of the flakes are in good agreement with previous reports^{5,17,18} (see the [supplementary material](#) for details). We further fabricate TiS₃ into two-terminal FET devices, with the schematic shown in [Fig. 1\(a\)](#). Metal contacts are defined by shadow masks or standard E-beam lithography process followed by E-beam evaporation of 3 nm/20 nm Ti/Au. [Figures 1\(b\)](#) and [1\(c\)](#) show the typical optical microscope image of the device made of thick and thin TiS₃ flakes, with thicknesses of ~ 200 nm and ~ 15 nm, respectively. It is worth noting that thin TiS₃ is barely visible under the optical microscope, as the width is only ~ 100 nm. The length of the nanoribbon, however, and is as long as ~ 10 μ m [[Fig. 1\(c\)](#)].

We then measure the photocurrent spectra of the two different devices, recording the photocurrent response as a function of the excitation photon energy. For such measurements, we use a super-continuum white laser source (Fianium or YSL Photonics) combined with a monochromator (with a grating of groove density 600 g/mm) and optical filters (550 nm longpass filter for visible spectra and 850 nm longpass filter for infrared spectra) to generate monochromatic excitation light (bandwidth ~ 1.0 nm). The sample is mounted in an optical cryostat, cooled with liquid nitrogen. A polarizer and a $\lambda/2$ Fresnel rhomb are used to convert the excitation laser into polarized light with the polarization aligned along either the a or b direction of the nanoribbon [directions perpendicular or parallel to the 1D chain, shown in [Figs. 1\(d\)](#) and [1\(e\)](#)], which can be determined under the confocal optical microscope. The excitation laser is then focused with an objective to a relatively large spot (typically 10–40 μ m) that uniformly illuminates the whole conducting channel of the sample, and a low excitation intensity (0.2–1 mW/cm²) is used to ensure a linear response from the sample (see the [supplementary material](#) for details). The laser excitation is modulated with a mechanical chopper operating

at 636 Hz. A DC bias of 1 V is applied to the TiS₃ device, and the resulting photocurrent signal is collected with a current amplifier and a lock-in amplifier. After we measure the photocurrent spectra of the TiS₃ device, the sample is immediately replaced with a commercially available Si or InGaAs detector to measure the power spectrum of the laser spot, which is then used to normalize the photocurrent response as $I_{pc}(h\nu)$. The ultra-high sensitivity of this setup is evident from the photocurrent spectra shown in [Figs. 2\(a\)](#) and [2\(b\)](#), with the signal to noise ratio as high as more than three orders of magnitude.

The normalized photocurrent response from the two different devices exhibits distinctively different behaviors, as shown in [Figs. 2\(a\)](#) and [2\(c\)](#). First, for the optical field aligned along the b axis, there are two pronounced peaks for the thick flake device [[Fig. 2\(a\)](#)] located at ~ 1.23 eV and ~ 1.41 eV (the dip at ~ 1.17 eV is an artifact due to the laser spectrum, see the [supplementary material](#) for details). In contrast, the photocurrent spectrum of the thin flake device [[Fig. 2\(b\)](#)] with the optical field aligned along the b axis only shows one peak at ~ 1.34 eV. Second, the photocurrent spectra for the polarization along the b axis and the a axis can be used to define the anisotropy as $A = \frac{I_{pc}(b) - I_{pc}(a)}{I_{pc}(b) + I_{pc}(a)}$. For the thick flake device [[Fig. 2\(a\)](#)], Anisotropy A can be as large as 0.71 and 0.43 at the resonance at ~ 1.23 eV and ~ 1.41 eV, respectively. However, this anisotropy quickly diminishes as the excitation photon energy increases, approaching zero at the excitation photon energy of 1.8 eV. In contrast, the anisotropy of the thin flake device [[Fig. 3\(c\)](#)] not only exhibits enhanced anisotropy (0.86) at the resonance excitation of ~ 1.34 eV but also retains the anisotropy for high excitation photon energy, ~ 0.46 , for the excitation photon energy of 1.8 eV.

As the photocurrent is proportional to the absorption,^{15,19} we speculate that the distinct photocurrent spectra of the thick and thin TiS₃ devices originate from the quantum confinement-modified band structure. We first investigate the rising of the photocurrent spectra, as shown in [Figs. 2\(b\)](#) and [2\(d\)](#). In the linear absorption regime, the normalized photocurrent $I_{pc}(h\nu)$ is linked to the absorption coefficient $\alpha(h\nu)$ by the expression:¹⁵

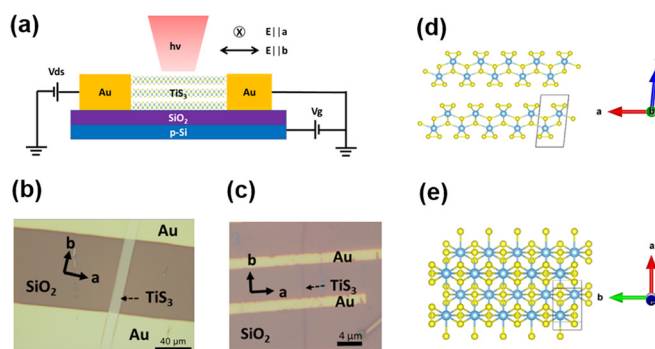


FIG. 1. Two-terminal TiS₃ FET devices on the SiO₂/Si substrate. (a) The schematic of the two-terminal TiS₃ FET device and the configuration of polarization-dependent photocurrent spectroscopy. (b) and (c) show optical microscope images of the two devices based on the thick (b) and thin (c) TiS₃ flakes. (d) and (e) display the out-of-plane and in-plane atomic structures of the TiS₃ crystal produced using VESTA.³⁴ Yellow spheres: S atoms. Blue spheres: Ti atoms.

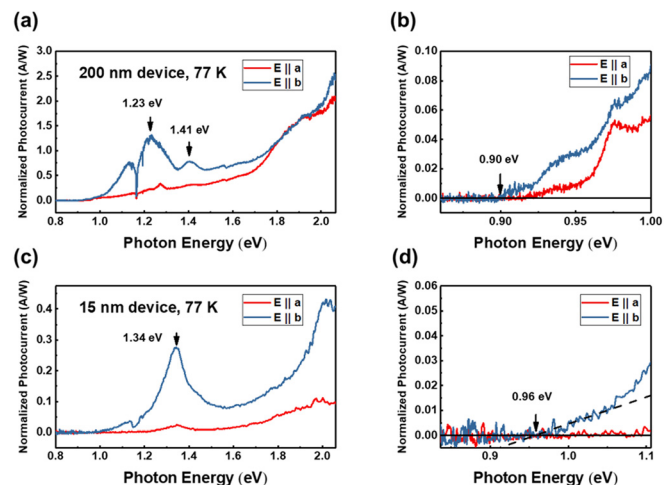


FIG. 2. Photocurrent spectra of TiS₃ FET devices. (a) and (c) show polarized photocurrent spectra of the thick and thin TiS₃ flake devices measured at 77 K. (b) and (d) show corresponding zoom-in spectra near the absorption cutoffs.

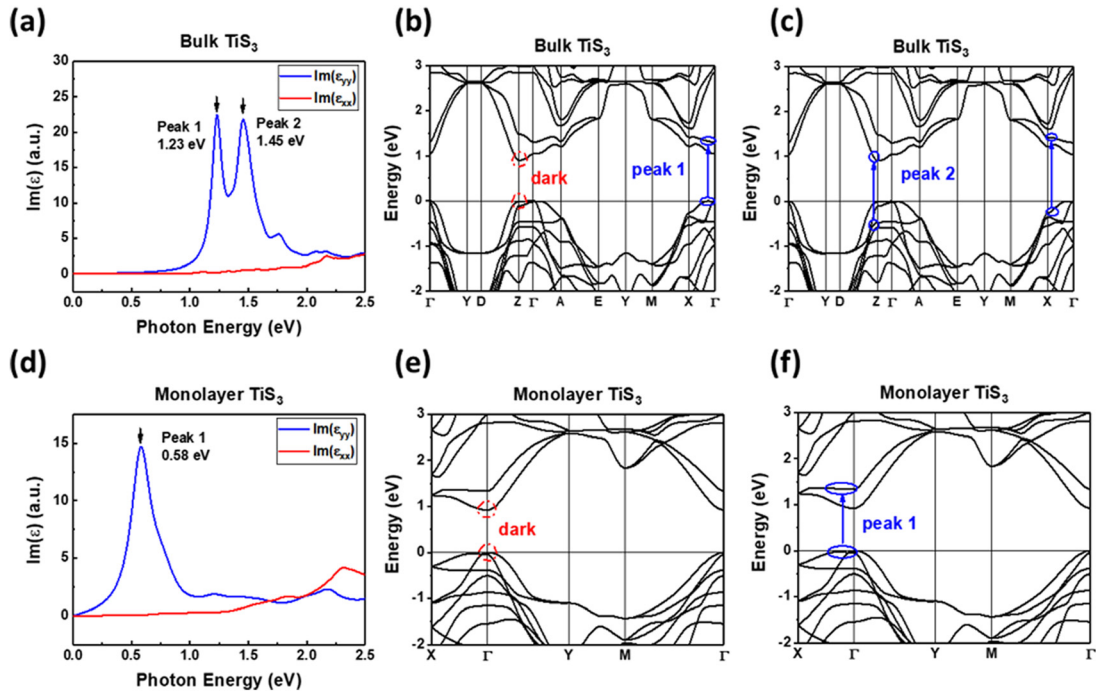


FIG. 3. Calculated band structure and imaginary part of the dielectric constant of bulk and monolayer TiS_3 . (a) and (d) show imaginary part of the dielectric constant along b and a directions in (a) bulk and (d) monolayer TiS_3 . (b) and (c) show the same calculation of the bulk TiS_3 band structure with the different transitions labeled, corresponding to the peaks in (a). (e) and (f) show the same calculation of monolayer TiS_3 , labeled with the dark ground state and the peak 1 transition in (d). High symmetry points: Γ (0, 0, 0), Y (0, 0.5, 0), D (0, 0.5, 0.5), Z (0, 0, 0.5), A (0.5, 0, 0.5), E (0.5, 0.5, 0.5), M (0.5, 0.5, 0), X (0.5, 0, 0).

$$I_{pc}(h\nu) = \frac{\eta e}{h\nu} \alpha(h\nu),$$

where e is the electron charge, $h\nu$ is the photon energy, and η is the photogain and is independent of $h\nu$. The corresponding bandgap E_g can be determined by reading the photon energy corresponding to the photocurrent cutoff since the value of kT is significantly smaller than the bandgap of TiS_3 . Figure 2(b) shows that, for the thick TiS_3 , the bandgap $E_g = 0.90$ eV. This result is consistent with the value (0.97–1.10 eV)^{20–25} reported previously for the bulk TiS_3 . For the thin TiS_3 device, Fig. 2(d) shows a bandgap of 0.96 eV, which indicates a modification of the bandgap owing to quantum confinement.

We further perform first-principles calculations to understand the different normalized photocurrent spectra shown in Figs. 2(a) and 2(c). The calculated band structure for the bulk and monolayer TiS_3 is shown in Figs. 3(b), 3(c) and 3(e), 3(f), respectively [Figs. 3(b) and 3(c) show the same calculation results with different transitions labeled, the same for Figs. 3(e) and 3(f)]. As shown in Fig. 3(b), bulk TiS_3 possesses an indirect bandgap, and its conduction band minimum (CBM) and valence band maximum (VBM) are located at Z and Γ points, respectively, consistent with the previous theoretical study.^{26,27} The calculated value of the bandgap is corrected by the experimental value of 0.90 eV with a scissor operator. The imaginary part of dielectric constant $\text{Im}(\epsilon)$, which is proportional to the absorption, is further calculated as a function of excitation photon energy by solving the Bethe–Salpeter equation (BSE) [Fig. 3(a)]. We denote the dielectric function along the b axis and a axis by ϵ_{yy} and ϵ_{xx} , respectively. It is evident from Fig. 3(a) that $\text{Im}(\epsilon_{yy})$ shows two pronounced peaks at

1.23 eV and 1.45 eV, which are in excellent agreement with our experimental values of 1.23 eV and 1.41 eV. In contrast, these peaks do not appear in the spectrum of $\text{Im}(\epsilon_{xx})$, also consistent with our experimental observation [Fig. 2(a)]. The optical transitions corresponding to each peak are labeled with arrows in Figs. 3(b) and 3(c). The lowest direct transition at the Z point [marked as the red dashed circle in Fig. 3(b)] is forbidden for the in-plane polarizations due to the inversion symmetry of the wave function near the band edge, similar to the case of Γ excitons in the monolayer¹¹ [shown in Fig. 3(e)]. The first peak at 1.23 eV in Fig. 2(a) is a result of the transition shown in Fig. 3(b), with the energy difference between the corresponding conduction band and valence band being ~ 1.30 eV. As a result, the exciton binding energy is ~ 70 meV for the observed peak of 1.23 eV in Fig. 2(a). The second peak at 1.41 eV in Fig. 2(a) has two major contributions, which, as shown in Fig. 3(c), originate from the bands near X and Z points and correspond to the calculated 1.45 eV peak in Fig. 3(a). These transitions correspond to the energy difference around 1.51 eV, indicating an exciton binding energy around 60 meV.

We also perform first-principles calculations for the TiS_3 monolayer. The obtained band structure and dielectric function are consistent with the results of previous theoretical studies.^{11,27} As shown in Fig. 3(e), due to the absence of the Z point in the 2D Brillouin zone, monolayer TiS_3 possesses a direct bandgap of 0.92 eV at the Γ point. It is worth noting that the energies of the bands near the Γ point only show minor changes compared to the bulk TiS_3 . This unusual thickness dependence behavior is due to the orbital components of the CBM and the VBM, which originate from the center atoms in the unit

cell and are not sensitive to interlayer interaction.²⁷ Therefore, there is a transition [peak 1 in Fig. 3(f)] similar to that associated with peak 1 in bulk TiS_3 . However, the band structure near the X point is drastically different, and the Z point disappears with the out-of-plane dispersion of the band structure. As a result, the transition corresponding to peak 2 in bulk TiS_3 cannot find its counterpart in the monolayer limit. These results are clearly shown in the spectrum of $\text{Im}(\epsilon_{yy})$, which is significantly different from that of bulk TiS_3 and has only one resonance peak at 0.58 eV, which is a result of the exciton originating from the valence band near -0.03 eV along the Γ -X direction to the conduction band at around 1.35 eV.¹¹

Our experimental data of the thin TiS_3 device are more like the monolayer TiS_3 , and we further analyze the theoretical calculations to compare with our data quantitatively. First, we believe that our observed peak at 1.34 eV corresponds to the optical transition shown as peak 1 in Fig. 3(e). First, according to our previous discussion, the energies of the bands involved in this transition are not a sensitive function of the thickness. Second, the resonance at 0.58 eV shown in Fig. 3(d) is a result of large exciton binding energy of ~ 800 meV for monolayer TiS_3 . Considering that the thickness of 15 nm is likely much larger than the exciton radius, we expect a similar exciton binding energy in the thin TiS_3 flake compared to the thick TiS_3 (~ 200 nm thick),^{28–33} which is 70 meV. As a result, the exciton absorption resonance for 15 nm TiS_3 is expected at ~ 1.31 eV. Finally, we have to consider the experimentally extracted bandgap for the thin TiS_3 flake, 0.96 eV, which is slightly larger than the calculated bandgap of 0.92 eV for monolayer TiS_3 that is obtained by adopting the same shift to the bandgap correction as the bulk TiS_3 . Therefore, the expected exciton resonance for the thin TiS_3 flake should be at 1.35 eV. This expectation is in excellent agreement with our observed resonance at 1.34 eV [Fig. 2(c)].

Finally, we discuss the different anisotropy observed in thick and thin TiS_3 flakes experimentally. The theoretical calculations show similar anisotropy behaviors for bulk and monolayer TiS_3 : large anisotropy in absorption at resonance and negligible anisotropy at high excitation photon energy. Our photocurrent spectra of the thick TiS_3 device are consistent with this picture. In contrast to the experimental observation in the thick TiS_3 device, the thin TiS_3 device retains a reasonably large anisotropy in the photocurrent response at high excitation photon energy, besides a large anisotropy at resonance excitation. This is because the thin TiS_3 flake is in the form of nanoribbons, which has a width of ~ 100 nm, smaller than the wavelength. As a result, the geometry anisotropy contributes to the absorption process and results in the additional photocurrent anisotropy observed experimentally. The thick TiS_3 flake has a width of $\sim 11 \mu\text{m}$ and does not have a contribution from geometry anisotropy. We note here that, due to the monoclinic structure of TiS_3 , the off diagonal components of the imaginary dielectric tensor might not be zero and might affect the experimentally measured anisotropy. However, our calculations show that such contributions are not significant in our measurements (see the [supplementary material](#)).

In summary, by exploiting polarization-dependent photocurrent spectroscopy, we have measured the absorption spectra of the quasi-1D thin flake of TiS_3 , which is hard to obtain using other convention optical spectroscopy methods. The photocurrent spectra of thin TiS_3 are significantly different from those of the thick TiS_3 flake (bulk). Our results are in excellent agreement with the first-principles calculations,

showing that the TiS_3 thin flake possesses a band structure that is close to the monolayer TiS_3 flake, but significantly different from the bulk TiS_3 . Therefore, the thin TiS_3 flake provides a platform to investigate intriguing quantum physics in the quantum confined TiS_3 . In addition, the greatly enhanced anisotropy of the quasi-1D thin flake of TiS_3 promises future applications of polarized optoelectronics.

See the [supplementary material](#) for Raman and AFM characterization of TiS_3 flakes, power dependence of the photocurrent spectra, calculated off diagonal components of the imaginary dielectric tensor, and the method of density functional theory (DFT) calculations.

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DATA AVAILABILITY

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

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