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Few-layered titanium trisulfide (TiS₃) field-effect transistors[†]

Alexey Lipatov,^a Peter M. Wilson,^a Mikhail Shekhirev,^a Jacob D. Teeter,^a Ross Netusil^a and Alexander Sinitskii*^{a,b}

Titanium trisulfide (TiS₃) is a promising layered semiconductor material. Several-mm-long TiS₃ whiskers can be conveniently grown by the direct reaction of titanium and sulfur. In this study, we exfoliated these whiskers using the adhesive tape approach and fabricated few-layered TiS₃ field-effect transistors (FETs). The TiS₃ FETs showed an n-type electronic transport with room-temperature field-effect mobilities of $18-24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and ON/OFF ratios up to 300. We demonstrate that TiS₃ is compatible with the conventional atomic layer deposition (ALD) procedure for Al₂O₃. ALD of alumina on TiS₃ FETs resulted in mobility increase up to 43 cm² V⁻¹ s⁻¹, ON/OFF ratios up to 7000, and much improved subthreshold swing characteristics. This study shows that TiS₃ is a competitive electronic material in the family of two-dimensional (2D) transition metal chalcogenides and can be considered for emerging device applications.

The recently discovered remarkable properties of graphene stimulated interest in other two-dimensional (2D) atomic crystals.^{1–3} Many of the actively studied 2D materials belong to the family of transition metal chalcogenides (TMCs).^{4–6} A large number of TMCs in bulk form have a layered structure with weak interlayer van der Waals interactions.^{2–6} The layers of TMCs can be exfoliated by different approaches to produce mono- and few-layered sheets that can be used for electrical and optical measurements.^{1–7} So far, the experimental studies have been mostly focused on TMCs with MX₂ composition (M = Mo, W; X is a chalcogen), such as MoS₂, MoSe₂, WS₂ and WSe₂.^{4,5} However, the TMC family is very rich and contains many other layered materials with interesting properties that have received limited attention from the researchers.^{8,9}

One such TMC material is titanium trisulfide (TiS₃). In the bulk form, TiS_3 has been studied for several decades.^{10–23}

It was shown that millimeter-long whiskers of TiS₃ can be synthesized by a direct reaction of metallic titanium and elemental sulfur in evacuated ampules at 500–600 °C.^{11,12,15,18,22-24} These whiskers were used for physical property measurements,^{10,12,15,17,18,22,23} which revealed that bulk TiS₃ is an n-type semiconductor with an energy bandgap of about 1 eV,^{10,12,17,22,23} and a room-temperature Hall mobility of about 30 cm² V⁻¹ s^{-1,18}

While previous studies have mostly focused on the bulk properties of TiS₃, the introduction and extensive use of the micromechanical exfoliation approach¹ have opened the possibility of accessing the properties of monolayered and fewlayered TiS₃ flakes. According to a recent theoretical study,²⁵ in a certain crystallographic direction a monolayer of TiS₃ is expected to have higher electron mobility than a single layer of MoS₂. An experimental attempt to exfoliate TiS₃ whiskers into few-layered nanoribbons and study their electronic and optoelectronic properties was reported by Island et al.⁹ TiS₃ nanoribbons were shown to have high photoresponse and fast switching times, which makes nanostructured TiS₃ a promising material for applications in optoelectronics and photovoltaics.⁹ However, the room-temperature charge carrier mobilities reported for the set of field-effect transistors (FETs) based on few-layered TiS₃ nanoribbons did not exceed 2.6 cm² V⁻¹ s⁻¹,⁹ while comparable bottom-gated FETs based on trilayered and thicker MoS₂, the most studied 2D TMC material, exhibited significantly higher mobilities of 10-20 cm² V⁻¹ s^{-1} , $s^{26,27}$ and reached up to 27 cm² V⁻¹ s⁻¹ in devices with optimized contact resistances.28 Therefore, in order to demonstrate that TiS₃ is a competitive TMC material for electronic applications, it is necessary to improve its field-effect mobility by at least an order of magnitude.

In this study, we report bottom-gated FETs based on fewlayered TiS₃ nanoribbons that have room-temperature fieldeffect mobilities of 18–24 cm² V⁻¹ s⁻¹. Furthermore, according to theoretical predictions, charge carrier mobilities of 2D semiconductor nanostructures can be significantly improved by modifying their dielectric environment.^{29,30} Previously, the dielectric screening approach has been successfully applied to

^aDepartment of Chemistry, University of Nebraska – Lincoln, Lincoln, NE 68588, USA. E-mail: sinitskii@unl.edu

^bNebraska Center for Materials and Nanoscience, University of Nebraska – Lincoln, Lincoln, NE 68588, USA

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graphene^{30,31} and MoS₂.^{32–35} Here we demonstrate the validity of this approach for mobility improvement in few-layered TiS₃ FETs by coating the devices with a thin layer of a high- κ dielectric, Al₂O₃, which results in measured field-effect mobilities up to 43 cm² V⁻¹ s⁻¹ as well as much improved subthreshold swing (*S*) characteristics. These results demonstrate that TiS₃ is a competitive electronic material in the 2D TMC family and can be considered for emerging device applications.^{3,4,6}

Following previous studies, we have grown TiS₃ whiskers via the direct reaction of titanium and sulfur.^{11,12,15,18,24} In a typical synthesis, ~0.1 g piece of a 0.25 mm thick Ti foil and ~0.2 g of S are sealed in an evacuated ($p \sim 200$ mTorr) quartz ampule. The ampule is placed in a tube furnace, where it is heated up to 500 °C and annealed for 3 days. During the reaction sulfur exists in a gaseous phase, as can be seen by the orange-brown vapor inside the ampule (Fig. 1a); three pieces of Ti foil are indicated by the blue arrow. Fig. 1b demonstrates the optical photograph of the reaction ampule after the synthesis. The arrow (1) shows one of the pieces of Ti foil; it is covered by dense forest of TiS3 whiskers that are typically 100-200 µm long. Interestingly, the whiskers grow not only on Ti foil, but also on the surface of the quartz ampule, as shown by the arrow (2) in Fig. 1b. These whiskers generally grow longer than the whiskers on Ti foil and often exceed 5 mm in length after 3 days of growth. At the end of the synthesis the ampule is moved away from the center of the furnace to create an ~100 °C temperature gradient, such that the end of the ampule containing the pieces of Ti foil remains at ~500 °C while the opposite end of the ampule is cooled below the

boiling point of sulfur (444.7 °C). As a result, TiS_3 whiskers are cleaned from unreacted sulfur, which condenses in the cold end of the ampule. One hour later the ampule is cooled down to room temperature and TiS_3 whiskers are collected for materials characterization and electrical measurements.

Fig. 1c shows scanning electron microscopy (SEM) images at different magnifications of the TiS₃ whiskers grown on a Ti substrate. These whiskers have a shape of thin ribbons that are typically over 100 µm long, a few µm wide and less than half a micrometer thick; these dimensions are in accord with previously reported observations for similarly prepared samples.^{9,22} The ribbon shape of TiS₃ whiskers is illustrated in the second panel of Fig. 1c, which shows several bent whiskers (two of them are indicated by the blue arrows). Additional SEM data for TiS₃ whiskers grown on a Ti substrate is provided in Fig. S1.† Based on the data presented in Fig. 1c, S1a† and similar SEM images we prepared a width distribution of TiS₃ whiskers, which is shown in Fig. S1b.† The size distribution is quite broad with a maximum at $w \sim 7 \mu m$; a substantial number of whiskers are wider than 20 µm. TiS₃ whiskers were also characterized by Raman spectroscopy; the results presented in Fig. S2[†] are in agreement with the previously reported data.36

For the device fabrication and electrical measurements we used TiS_3 whiskers grown on quartz (see the arrow (2) in Fig. 1b), which were easier to handle because of their larger size. The inset in Fig. 1d shows the optical microscopy image of one of these larger TiS_3 whiskers, which had a length of about 0.6 mm and a width of about 8 µm. This whisker was



Fig. 1 Synthesis and characterization of TiS_3 whiskers. (a) Optical photograph of the reaction ampule during the synthesis. The ampule is filled with orange-brown sulphur vapour. The arrow shows three pieces of Ti foil. (b) Optical photograph of the reaction ampule after the synthesis. Arrows show (1) a piece of Ti foil covered with a forest of TiS_3 whiskers and (2) larger TiS_3 whiskers that have grown on the surface of quartz. (c) SEM images of TiS_3 whiskers grown on Ti foil, see (1) in panel (b), at different magnifications. The arrows in the second panel show bent TiS_3 whiskers. (d) Crystal structure of TiS_3 with the lattice parameters. Inset: optical photograph of one of the TiS_3 whiskers shown by the arrow (2) in panel (b).

studied by the single-crystal X-ray diffraction (XRD). A single crystal had a monoclinic symmetry with the space group $P2_1/m$ and lattice parameters a = 0.4948(7), b = 0.3379(5), c = 0.8748(12) nm, and $\beta = 97.62(2)^{\circ}$. Direct methods yielded a completely ordered atom arrangement isotypic with the structure type of ZrSe₃;³⁷ the results of XRD measurements are summarized in Tables S1 and S2 in the ESI.† The crystal structure of TiS₃ can be described as a stack of 2D layers formed by one-dimensional (1D) chains of TiS₃ prisms, see Fig. 1d. TiS₃ can be viewed as Ti⁴⁺S^{2–}S₂^{2–}, containing both sulfide and disulfide units; these units form trigonal prisms with Ti⁴⁺ centers.

For the device fabrication, one of the TiS₃ whiskers grown on a quartz surface was mechanically exfoliated using an adhesive tape¹ and transferred to a p-type silicon substrate covered with a 300 nm thick layer of SiO_2 (SQI). Because of the quasi-1D structure of TiS₃, the whiskers not only exfoliate into 2D sheets but also break longitudinally along the *b*-axis, resulting in thin TiS₃ nanoribbons that are much narrower than the original whiskers. Few-layered TiS₃ nanoribbons with thicknesses of 9-11 nm were found on the surface of a Si/SiO₂ substrate by optical microscopy. Electronic devices with fewlayered TiS₃ nanoribbons bridging Cr/Au (3 nm/20 nm) electrodes were fabricated by standard electron-beam lithography followed by electron-beam evaporation; the details of the device fabrication and materials characterization can be found in the ESI.[†] The schematic of a typical TiS₃-based device with Cr/Au source (S) and drain (D) electrodes on a p^{++} -Si/SiO₂ substrate (the heavily doped p-type silicon was used as the back gate electrode, G) is shown in Fig. 2a.

Fig. 2b shows the SEM image of one of the four TiS_3 FETs that were fabricated and tested in this study; SEM and AFM images of other devices are shown in Fig. S3 in the ESI.[†] Fig. 2c shows the AFM image of the central portion of the TiS_3 nanoribbon channel of the device. The height profile measured across this TiS_3 nanoribbon shows a step of ~9.5 nm; see the black line in Fig. 2d. For comparison, we also show the height profiles measured for the other three devices (Fig. 2d) to demonstrate that all TiS_3 nanoribbons measured in this work had comparable thicknesses.

Electrical measurements of TiS₃ FETs were performed under vacuum ($p \sim 1 \times 10^{-6}$ Torr). Prior to the measurements the devices were evacuated for ~24 h to minimize the effect of surface adsorbates.³⁸ Fig. 2e shows that all four TiS₃ devices exhibited very similar electronic behavior. For all devices the drain-source current (I_{DS}) -drain-source voltage (V_{DS}) dependencies at different gate voltages (V_G) were linear, indicating Ohmic contacts between TiS₃ nanoribbons and Cr/Au electrodes; a representative set of data for one of the TiS₃ FETs is shown in the inset in Fig. 2e. This figure also shows conductivity (σ)-gate voltage ($V_{\rm G}$) dependencies for all devices, demonstrating the electronic behavior typical for FETs with n-type channels. These dependencies are also hysteretic, which is likely caused by the charge traps at the SiO₂/TiS₃ interface similar to SiO₂/MoS₂.²⁷ From the linear regions in the σ -V_G dependencies we estimate that the few-layered TiS₃ FETs have field-effect mobilities of 18-23 cm² V⁻¹ s⁻¹, which is compar-



Fig. 2 Few-layered TiS₃ FETs. (a) Scheme of a TiS₃-based device on a Si/SiO₂ substrate; see text for details. (b) SEM image of a typical TiS₃ FET. Dark strip in the image is a TiS₃ nanoribbon that connects two Cr/Au electrodes. (c) Atomic force microscopy (AFM) image of the fragment of the TiS₃ nanoribbon shown in (b). (d) Representative height profiles measured across the TiS₃ nanoribbon shown in (c), see device #1, and three other TiS₃ nanoribbons used in this study; see text for details. (e) Conductivity (σ)-gate voltage (V_{G}) dependencies for all four TiS₃ FETs measured in this study. $V_{DS} = 0.1$ V. The mobility (μ) values are extracted from the linear regions (solid lines) in these dependencies. The inset shows drain–source current (I_{DS})-drain–source voltage (V_{DS}) dependencies for the device shown in panel (b) (device #1) measured at different V_G ranging from –40 to 40 V with a 10 V step.

able with the mobilities reported for few-layered MoS_2 devices.^{26–28} The ON/OFF ratios defined as the ratios of the largest and smallest I_{DS} values in V_G dependencies were in the range of 30–300.

The conductivities presented in Fig. 2e were measured using a two-contact method and therefore include a contribution from the contact resistances. In order to evaluate the intrinsic electronic properties of exfoliated TiS_3 whiskers we fabricated and tested two multiterminal devices and used

them for four-point probe conductivity measurements, see Fig. S4 and S5[†] and associated comments in the ESI.[†] The field-effect mobilities measured for multiterminal TiS₃ devices using a four-point probe method to exclude the contact resistance contribution were 21.1 and 24.2 cm² V⁻¹ s⁻¹. These values are in a great agreement with the mobilities measured for two-terminal devices (Fig. 2e). While a more detailed investigation of contact resistance effects could be the subject of a separate study,³⁹ our results show that contact resistances appear not to have a dominant effect on the electronic characteristics of TiS₃ FETs.

As we indicated earlier, dielectric screening is a very effective approach to improve charge carrier mobilities of 2D semiconductor nanostructures.²⁹⁻³⁵ In order to demonstrate the effectiveness of this approach for the mobility enhancement in few-layered TiS₃ FETs, we used atomic layer deposition (ALD) to coat the devices with a 30 nm layer of Al₂O₃. Trimethylaluminum and water were used as Al₂O₃ precursors; additional details on ALD are given in the ESI.[†] Since TiS₃ has not been long considered as a material for electronics, nothing has been reported so far about its compatibility with conventional ALD procedures. For example, preparation of uniform dielectric layers on graphene has proved to be a challenge,^{40–42} as graphene has no functional groups, which hinders the surface modification with common ALD precursors (the direct ALD of Al2O3 using the same precursors results in oxide nucleation only at the edges of graphene).⁴⁰ In contrast, the standard ALD procedure for Al₂O₃ growth worked well for TiS₃. Fig. 3a and b shows the same area of a TiS₃ nanoribbon channel of one of the devices before and after ALD of Al₂O₃, respectively. In the process, the color of the Si/SiO₂ substrate changed from purple to green. However, on the nanoscale the morphology of the TiS₃ nanoribbon and the substrate barely changed, suggesting a very uniform growth of Al₂O₃ by ALD (Fig. 3a and b). This conclusion is further confirmed by the representative height profiles shown in Fig. 3c. Before ALD of Al₂O₃ the height profile measured across the TiS₃ nanoribbon along the yellow line in Fig. 3a showed a step height of about 10 nm. After the growth of 30 nm of Al₂O₃ the height profile measured in the same place is nearly the same, suggesting that alumina layers of comparable thicknesses have grown on the TiS₃ and Si/SiO₂ substrate. Thus, this work demonstrates the compatibility of TiS₃ with conventional ALD procedures, which is important for the future studies of TiS₃ electronic devices.

Fig. 3d–g shows $I_{DS}-V_G$ dependencies in linear and semilogarithmic coordinates for two TiS₃ FETs before and after ALD of Al₂O₃; other devices showed similar behavior. These $I_{DS}-V_G$ plots show that Al₂O₃ deposition may have different effects on the hysteresis of electronic transport observed in alumina-coated TiS₃ FETs. The Al₂O₃-coated device shown in Fig. 3d and e exhibits a considerable hysteresis, while in the other Al₂O₃-coated FET (Fig. 3f and g) the hysteresis visibly shrinks compared to the as-made TiS₃ FET before Al₂O₃ ALD. As in the case of as-made TiS₃ FETs we attribute this hysteretic behavior to interfacial charge trapping.²⁷ While we did not



Fig. 3 ALD of Al₂O₃ on TiS₃ FETs. (a) AFM image of a fragment of TiS₃ nanoribbon channel of a device. (b) AFM image of the same area as in (a) after ALD of 30 nm of Al₂O₃. Scale bars in (a,b) are 100 nm. (c) Height profiles measured across the TiS₃ nanoribbon along the yellow lines in (a) and (b). (d, e) Comparison of the drain–source current (I_{DS})–gate voltage (V_G) dependencies for the same device (# 4) before and after ALD of Al₂O₃ shown in (d) linear and (e) semi-logarithmic coordinates. $V_{DS} = 0.1 \text{ V}$. (f, g) Comparison of the drain–source current (I_{DS})–gate voltage (V_G) dependencies for another device (# 1) before and after ALD of Al₂O₃ shown in (f) linear and (g) semi-logarithmic coordinates. $V_{DS} = 0.1 \text{ V}$.

investigate this effect in detail, it is interesting to note that the alumina or another high- κ dielectric layer on top of TiS₃ may provide another interface for charge-trap engineering. The data presented in Fig. 3d–g suggest that with a proper optimization of the deposition procedure it may be possible to either minimize the hysteretic behavior of TiS₃ FETs or create devices with large σ - V_G hysteresis loops, which may be of interest, for example, for memory applications.⁴³ The optimization of the ALD procedure using high- κ dielectrics, not limited to Al₂O₃, will be the subject of our future studies.

Other than the different features in the shape of $I_{\rm DS}$ - $V_{\rm G}$ hysteresis loops, the effect of Al₂O₃ deposition on the electronic properties of TiS₃ devices was quite consistent. Fig. 3d–g shows that the Al₂O₃ deposition has an overall positive effect

on the electronic properties of TiS₃ FETs. For the TiS₃ FET shown in Fig. 3d the dielectric screening resulted in the fieldeffect mobility improvement from 20.3 to 36.8 cm² V⁻¹ s⁻¹, and for the other device the mobility improved from 20.1 to 42.6 cm² V⁻¹ s⁻¹ (Fig. 3f). Interestingly, the Al_2O_3 ALD also improved the ON/OFF ratios of TiS₃ FETs, which can be seen in logarithmic I_{DS} coordinates (Fig. 3e and g). For the device shown in Fig. 3e, the ON/OFF ratio improved from 300 to 7100, and for the other device (Fig. 3g) it improved from 40 to 170. The other two Al₂O₃-coated TiS₃ FETs exhibited ON/OFF ratios of 155 and 180. The positive effect of alumina ALD on the device characteristics of TiS₃ FETs can be further illustrated by the subthreshold swing (S) change. As can be seen in Fig. 3e and g and S6,[†] the as-prepared TiS_3 FETs had S values ranging from 19.1 to 44.3 V dec⁻¹. After Al_2O_3 ALD the S values decreased to $3.4-4.8 \text{ V dec}^{-1}$; the S values for all four devices before and after alumina ALD are summarized in Fig. S6c.† With these device properties TiS₃ appears to be a promising electronic material that can be positively compared with other more intensively studied members of the 2D TMC family.⁴

In summary, we have fabricated few-layered TiS_3 FETs and tested their electronic properties. The TiS_3 FETs showed an ntype electronic transport with room-temperature field-effect mobilities of 18–24 cm² V⁻¹ s⁻¹ and ON/OFF ratios up to 300. We also demonstrate that TiS_3 is compatible with the conventional ALD procedure for Al_2O_3 . ALD of alumina on TiS_3 FETs resulted in mobility improvement up to 43 cm² V⁻¹ s⁻¹ and ON/OFF ratios of up to ~7000; *S* values after Al_2O_3 ALD decreased from 19.1–44.3 to 3.4–4.8 V dec⁻¹. This study shows that TiS_3 is a promising 2D TMC material that can be further explored in the future device studies.

Note added in proof: After the submission of this paper we became aware of the recently published study, which shows that the TiS_3 growth temperature could be a promising tool to tune the material's morphology and electronic properties, possibly through the change in the concentration of sulfur vacancies.⁴⁴

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