Anomalous electron transport in back-gated field-effect transistors with TiTe$_2$ semimetal thin-film channels

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The authors report on "graphene-like" mechanical exfoliation of thin films of titanium ditelluride and investigation of their electronic properties. The exfoliated crystalline TiTe$_2$ films were used as the channel layers in the back-gated field-effect transistors fabricated with Ti/Al/Au metal contacts on SiO$_2$/Si substrates. The room-temperature current-voltage characteristics revealed strongly non-linear behavior with signatures of the source-drain threshold voltage similar to those observed in the charge-density-wave devices. The drain-current showed an unusual non-monotonic dependence on the gate bias characterized by the presence of multiple peaks. The obtained results can be potentially used for implementation of the non-Boolean logic gates. © *2012 American Institute of Physics*. [doi:10.1063/1.3679679]

Successful mechanical exfoliation of graphene[1] and investigation of its unique electrical[2,3] and thermal[4–7] properties motivated research of other quasi two-dimensional (2D) materials. We have recently exfoliated quintuples—five atomic layers—of bismuth telluride (Bi$_2$Te$_3$) and related materials, which reveal thermoelectric and topological insulator properties.[8–11] It was shown that exfoliated Bi$_2$Te$_3$ films have electrical, thermal, and optical properties substantially different from those of bulk Bi$_2$Te$_3$ crystals.[8–12] The exfoliated thin films allow one to achieve strong quantum confinement of charge carriers and acoustic phonons owing to almost infinite potential barriers for electrons and phonons in such structures.[8] The molecular-beam-epitaxial films grown on the lattice matched substrates are normally characterized by small energy-band offsets.[8,9] Even if the exfoliated films are relatively thick (no quantum confinement effects), they represent interesting objects of investigation owing to their crystallinity and possibility of tuning the charge density via electrical gating.

The essential requirement for exfoliation of quasi-2D films is a presence of the van-der-Waals gaps in the crystal structure. Here we report on the "graphene-like" exfoliation and investigation of physical properties of materials that have not been previously studied in such a context. We considered titanium dichalcogenides TiCh$_2$ (Ch = Te, Se, S), which are semimetals with the hexagonal crystal structure of the space group D$_{3d}$.[1] The TiCh$_2$ trilayers are separated by the van der Waals gaps while inside each layer, Ti is surrounded by 6 chalcogen atoms in the octahedral configuration. These types of crystals—with atomic trilayers as their structural units—differs from both graphene—a single atomic layer—and Bi$_2$Te$_3$ containing a quintuple structure. Many transition-metal dichalcogenides[13–18] show phase transitions to a modulated crystal structure, referred to as a charge-density wave (CDW).[19,20] We investigated properties of exfoliated TiTe$_2$ films with the help of the field-effect-transistor (FET) type devices. It is demonstrated that TiTe$_2$ films reveal unusual electronic properties, which can be potentially used for the information processing.

We exfoliated TiTe$_2$ films on Si/SiO$_2$ substrates following the standard "graphene-like" approach.[1,2] The thickness H of the films ranged from a few trilayers (FTL) to $H \sim 150$ nm. The thickness of the Te-Ti-Te atomic trilayer is $H = 0.271$ nm while the lattice parameters are $a = 0.377$ nm and $c = 0.6498$ nm. The FTL films are more suitable for back-gating while the thicker films can be more readily incorporated into the FET structure. The atomic force microscopy (AFM) inspection (VEECO Dimension-5000) revealed that surface roughness of the films was ~ 1 nm. We have used micro-Raman spectroscopy to verify the crystallinity and quality of the flakes with the optimum thickness. Raman spectroscopy (Renishaw InVia) was performed in a backscattering configuration under $\lambda = 488$ nm laser excitation. We used low excitation power on the sample surface (P < 0.5 mW) to avoid local heating. The details of our Raman-spectroscopy procedures are reported elsewhere in the graphene-research context.[21–23]

Figure 1 shows Raman spectra from TiTe$_2$ FTL film for the temperature T varying from ~ 165 K to ~ 425 K. One can clearly see two main peaks at ~ 120 to 124 cm^{-1} and ~ 141 to 145 cm^{-1}. These peaks can be associated with the E_g and A_{1g} modes reported for bulk TiTe$_2$ and related materials.[24] It is interesting to note that we have not observed distinctive shoulders near ~ 160 cm^{-1}, which were previously attributed in TiCh$_2$ materials to poorly defined stoichiometry and defects.[24] The latter indicates the high purity of our samples. The crystallinity and elementary composition of the films were further confirmed by the energy dispersive spectroscopy (EDS) and the high-resolution scanning electron microscopy (SEM). The inset to Fig. 1 is a representative SEM image (XL-30 FEG) of a TiTe$_2$ flake.

The back-gated FET with TiTe$_2$-film channels were prepared by depositing the source, drain, and back-gate metal

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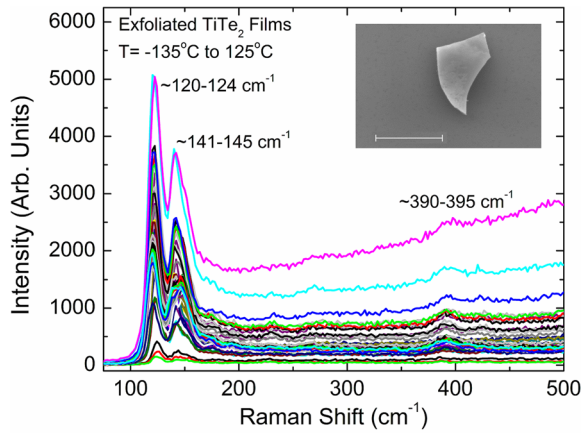
FIG. 1. (Color online) Raman spectra of the mechanically exfoliated $TiTe_2$ films at different temperatures. One can see two main E_g and A_{1g} phonon modes. The absence of the shoulder near $\sim 160\,cm^{-1}$ suggests the high quality, stoichiometry, and low defect concentration in the examined $TiTe_2$ films. The inset shows the SEM image of the "graphene-like" exfoliated $TiTe_2$ film.

FIG. 3. (Color online) Drain current as the function of the source-drain voltage for the $TiTe_2$ FETs in the dark and under light illumination. The inset shows a SEM image of the tested device with Al/Ti/Au contacts and metal electrodes.

contacts. The degenerately doped Si substrate acted as a back gate separated from the channel by the 300-nm-thick SiO_2 layer. The substrate was spin-coated (Headway SCE) with the copolymer (MMA) and polymethyl methacrylate (PMMA) for the top contact fabrication. The source and drain of the FET structure were defined by the electron beam lithography (Leo 1150). The metal layers Al/Ti/Au (8 nm/10 nm/100 nm) were sequentially deposited on the $TiTe_2$ in the defined contact patterns.

Since SiO_2 oxide and $TiTe_2$ channels were relatively thick we had to apply large gate biases. The room-temperature (RT) electrical resistance of the exfoliated films was $\sim 10^{-4}\,\Omega\,cm$. The device structure is shown in the inset of Fig. 2. In such a design the gate is global and affects not only the channel but also the Al/Ti/Au–$TiTe_2$ contact. The current-voltage (I-V) characteristics of $TiTe_2$ devices are presented in Fig. 2. The curves marked A and B correspond to two different positions of the probe-station contacts on the
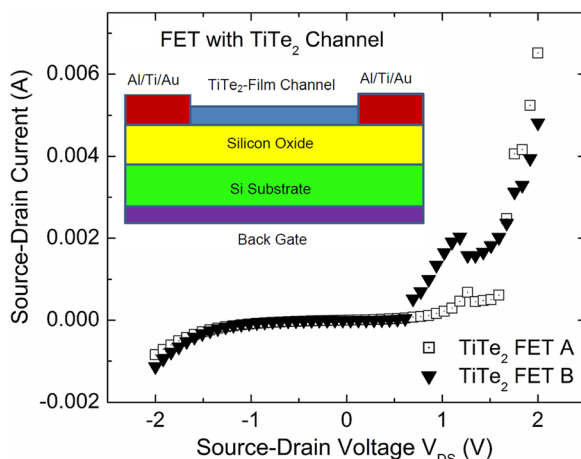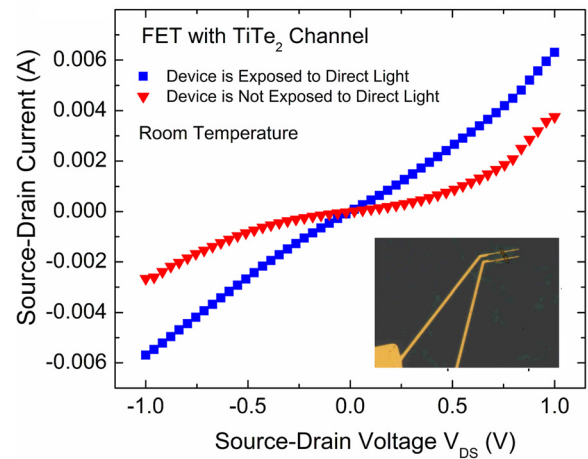
source and drain electrodes. One can see that I-Vs are asymmetric and reveal a threshold voltage $V_{DS} \sim 1.5$ V, where the conductance increases strongly. The measured I-Vs are reminiscent of those observed in CDW materials.[19,20] In CDW conductors, the threshold V_{DS} indicates the electrical field E_T at which the CDW depins and slides relative to the lattice.[19] The I-Vs are also similar to those resulting from tunneling contacts.[25] In this case, the Al/Ti/Au–$TiTe_2$ contact effects can be responsible for the observed threshold-type characteristics. It has been reported that oxidation of Ti layers used in the electrodes to CDW materials such as TaS_3 can lead to formation of a tunnel barrier resulting in non-linear I-Vs.[25]

The existence of the tunnel barrier contacts is consistent with the sensitivity of the I-Vs to light exposure. Figure 3 presents the source-drain current as a function of V_{DS} at RT. One can see that the exposure of the device to the direct light increases the low-bias current and reduces the non-linearity. The light is exciting carriers that can then either go over the tunnel barrier or more easily tunnel through the tunnel barrier with the net result being increased current and less non-linearity in the I-Vs.

The back-gate V_{GS} dependence of the drain-current I_{DS} reveals unusual non-monotonic features—multiple and almost equidistant peaks (see Fig. 4). Both the sensitivity of the channel current to V_{GS} and the multiple, almost periodic peaks in the channel current as a function of V_{GS} are difficult to explain. The periodicity suggests possible CDW effects, since a gate voltage can periodically modulate the phase of the CDW. We note that CDW effects in $TiTe_2$ are still the subject of debate.[13,15] At $T_P = 150$ K a phase transition was detected in the magnetic susceptibility measurements of the bulk $TiTe_2$, which was attributed to CDW.[13] It is not known how the Peierls transition temperature T_P would depend on the thickness of $TiTe_2$ films when H is in nanometer scale. It was shown that T_P can increase in thin films owing to the formation of a single-domain CDW. The anomalous CDW depinning above T_P was observed in thin crystals of $NbSe_3$.[26]

In a simple one-dimensional model, the wavevector of the CDW is $Q = 2k_F$, where k_F is the Fermi wavevector. If periodic features in the I-V_{GS} curve are related to the periodic

FIG. 2. (Color online) Drain current as the function of the source-drain voltage in back-gated FETs with $TiTe_2$ channel and Al/Ti/Au source and drain contacts. The measured I-V characteristics are strongly non-linear with a clear threshold voltage at $V_{DS} = 1.5$ V ($V_{GS} = 50$ V). The source-drain distance is 8 μm. The inset shows a schematic of the FET device with the $TiTe_2$ channel.
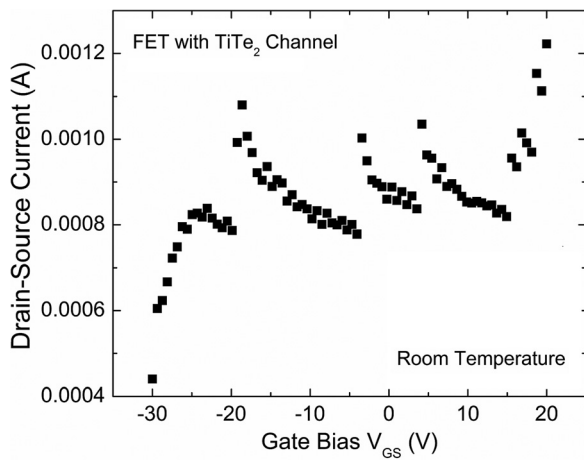
FIG. 4. Drain current as the function of the back-gate voltage at $V_{DS} = 100$ mV. Note a number of nearly equidistant peaks in I-V characteristics of the TiTe$_2$ FET at room temperature.

modulation of a CDW phase, it is interesting to determine whether the change in the accumulated phase between the two contacts is approximately 2π, i.e., is $\delta QL \approx 2\pi$? To estimate δQ, we must find k_F in the k_x–k_y plane. The electron density of 1.12×10^{21} cm^{-3} gives a sheet density per trilayer of $n_L = 7.28 \times 10^{13}$ cm^{-2}. The Fermi surface of TiTe$_2$ is complex with multiply disconnected parts in the k_x–k_y plane. It has small dependence on k_z. An order of magnitude estimate of k_F in the k_x–k_y plane is $k_F^2 = 2\pi n_L$, and the change in k_F is $\delta k_F = \pi \delta n_L / k_F$. The change in charge is $\delta n_L = \frac{C \delta V_{GS}}{qN}$ where $N = 154$ is the number of trilayers in a 100 nm thick film and $C \approx 1.15 \times 10^{-8}$ F/cm^2 is the 300-nm back-gate oxide capacitance. Using $\delta V_{GS} = 10$ V and $L = 8\ \mu$m, $\delta QL = 2\delta k_F L = 1.1$ which is the same order of magnitude as 2π.

The high sensitivity of the channel current to the gate voltage is difficult to explain considering that the screening length $\lambda_D = (\varepsilon k_B T / nq^2)^{1/2} = 0.36$ Å using $\varepsilon = \varepsilon_0$ and $T = 300$ K. A back-gate voltage should not be able to modulate the charge in a 100-nm thick sample. However, this same contradiction was apparent in the first demonstration of a CDW FET.[27] The screening length was one to two orders of magnitude smaller than the channel thickness, yet the channel current was still highly sensitive to the back-gate voltage. A number of different modulation mechanisms were considered, however, it was concluded that none of the mechanisms could easily account for the high sensitivity of the current to the back-gate voltage.[27] Prior studies of photoconduction in CDW materials[28–31] also revealed varying results: from to an order of magnitude increase in the linear current under the light illumination[28] to the absence of photoconduction.[29,30]

While the exact physical mechanism of the observed multiple peaks in the drain current is not known one can envision a possible use of such I-Vs for information processing. Currently, there is a strong interest to alternative state variables—other than charges or electric currents—which can be used for information processing.[32–35] The abundance of non-linear physical phenomena observed in our devices provides possibilities for information processing. The intriguing I-V features, possibly related to the pinning-depinning CDW transitions, can be used in FET-type devices for implementing Boolean or non-Boolean logic gates. The design of such metal-semimetal logic gates can utilize the principles similar to those envisioned for the spin-wave devices.[36–38] The use of phases in CDW devices in addition to amplitudes is a powerful tool, which allows one to construct logic circuits with a fewer number of elements than required for CMOS technology.

In conclusion, we used the "graphene-like" exfoliation to prepare thin films of TiTe$_2$. The films were utilized as the channel layers in FET-type devices with Ti/Al/Au-metal contacts. Our measurements demonstrated intriguing non-linear I-Vs of the TiTe$_2$ FETs, which resemble those of CDW materials. Although no accurate explanation of the observed phenomena can be given at the present moment, we argue that the measured non-monotonic multi-peak characteristics can be potentially useful for the low-power information processing.

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