Electrically Driven Reversible Insulator–Metal Phase Transition in 1T-TaS₂

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ABSTRACT: In this work, we demonstrate abrupt, reversible switching of resistance in 1T-TaS₂ using dc and pulsed sources, corresponding to an insulator–metal transition between the insulating Mott and equilibrium metallic states. This transition occurs at a constant critical resistivity of 7 mohm-cm regardless of temperature or bias conditions and the transition time is significantly smaller than abrupt transitions by avalanche breakdown in other small gap Mott insulating materials. Furthermore, this critical resistivity corresponds to a carrier density of 4.5 × 10¹⁹ cm⁻³, which compares well with the critical carrier density for the commensurate to nearly commensurate charge density wave transition. These results suggest that the transition is facilitated by a carrier driven collapse of the Mott gap in 1T-TaS₂, which results in fast (3 ns) switching.

KEYWORDS: Mott insulator, resistive switching, insulator–metal-transition, charge density wave, 1T-TaS₂

The transition metal dichalcogenide 1T-TaS₂ is a two-dimensional (2D) layered material exhibiting interesting and complex behavior as a result of interplay between electron–electron and electron–lattice interactions. Below 600 K, 1T-TaS₂ is host to several distinct charge density wave (CDW) phases, which exist as a result of Fermi-surface driven instabilities (i.e., Fermi-surface nesting) that lead to a distortion of the crystal lattice and subsequent periodic charge density modulation. These charge and structural distortions eventually become fully commensurate with the lattice below a critical temperature of ~180 K, after which electron–electron interactions lead to the formation of an insulating state through a Mott–Hubbard transition.¹⁻² Recent work has explored ultrafast melting of the insulating Peierls–Mott state using pulsed optical or electronic means in order to partially collapse the Mott gap or to produce metastable states of intermediate resistivity and variable duration.³⁻⁶ In this work, we demonstrate abrupt, resistive switching between insulating and conducting states through electronic means. Both dc and pulsed voltages are used to trigger abrupt resistive switching from the insulating Mott phase to the metallic phase. After the applied electric field is removed, the 1T-TaS₂ undergoes a second abrupt transition and returns to its equilibrium insulating state. In this fashion, the material functions as an abrupt electrically driven volatile switch. Importantly, this transition is shown to occur at a resistivity of 7 mohm-cm regardless of temperature or bias conditions and the transition time of 3 ns is significantly smaller than abrupt transitions by avalanche breakdown in other small gap Mott insulating materials. Furthermore, this critical resistivity corresponds to a carrier density of 4.5 × 10¹⁹ cm⁻³, which compares well with the critical carrier density for the commensurate to nearly commensurate charge density wave transition. These results suggest that the observed transition may be caused or facilitated by a carrier driven collapse of the Mott gap, which results in a fast (3 ns) collapse of the insulating state.

Figure 1a shows the atomic structure of 1T-TaS₂ as well as the characteristic “Star-of-David” distortion of the Ta lattice. This distinctive distortion is the result of Fermi-surface nesting and is accompanied by out-of-plane distortions of the coordinating S atoms such that the sulfur lattice bulges slightly around the center of the “star.”²,⁷,⁸ As the temperature is varied from 600–0 K, three distinct phases of 1T-TaS₂ are observed. Figure 1d plots resistivity versus temperature of a 10 nm thick 1T-TaS₂ flake and captures these three equilibrium phases. The low-temperature insulating phase is structurally the most simple of the three. This phase is referred to as the commensurate CDW (CCDW) phase because in this phase, the “Star-of-

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Above this temperature, the sharp jump in resistivity and insulating behavior below the phase is referred to as the nearly commensurate CDW hexagonal domains remain commensurate with the lattice. This central Ta atom. Because of the small width of this band (12 outer atoms and other), this results in two low-lying three-band submanifolds. CCDW phase, the 12 surrounding Ta atoms contract toward that is fully commensurate with the crystal lattice. In the − structure (b). Typical current−voltage sweep showing abrupt transition to metallic phase and return to insulating phase (c). Low- and high-field resistivities extracted from current−voltage sweep at 77 K superimposed on resistivity versus temperature (d). Energy diagram showing electrically and thermally driven collapse of the Mott gap (e).

Figure 1. Schematic representation of 1T-TaS2 structure (a) and two terminal device (b). Inset shows colorized SEM micrograph of Hall bar structure (b). Typical current−voltage sweep showing abrupt transition to metallic phase and return to insulating phase (c). Low- and high-field resistivities extracted from current−voltage sweep at 77 K superimposed on resistivity versus temperature (d). Energy diagram showing electrically and thermally driven collapse of the Mott gap (e).

David” distortions interlock to form a triangular superlattice that is fully commensurate with the crystal lattice. In the CDW phase, the 12 surrounding Ta atoms contract toward the 13th central Ta atom and become strongly bonded to each other. This results in two low-lying three-band submanifolds (B1 and B2 in Figure 1e) representing the 12 outer atoms and one narrow band at the Fermi energy, E_F, corresponding to the central Ta atom. Because of the small width of this band (~100 meV) and its half-filled nature, it has been proposed that Mott localization occurs as a result of electron−electron interactions. The opening of a Mott gap (200 meV) leads to a sharp jump in resistivity and insulating behavior below ~180 K. Above this temperature, the ”Star-of-David” distortions remain, but no longer form the interlocking triangular superlattice that is commensurate with the lattice. Instead, they form roughly hexagonal domains that are separated by small triangular regions that are incommensurate with the lattice. Here, the hexagonal domains remain commensurate with the lattice. This phase is referred to as the nearly commensurate CDW (NCCDW) phase and does not exhibit the insulating behavior of the CCDW phase. The NCCDW phase exhibits a resistivity range of approximately 5−0.5 mohm-cm, roughly 10× reduced from the CCDW phase. This resistivity range is a common feature of the 1T-TaS2 material family and is of importance in the sense that it is centered about 3 mohm-cm, which is the resistivity value if one were to assume the universal value of the maximum metallic resistivity for each 2D layer of the crystal. Above 350 K, the distortions become even incommensurate with the underlying lattice and 1T-TaS2 undergoes a 2× drop in resistivity; this is referred to as the incommensurate CDW phase (ICCDW).

Although previous works have investigated interplay between these phases by examining the collapse of the insulating Mott phase using time-resolved, angle-resolved photoelectron spectroscopy in an ultrafast pump−probe configuration, these studies focused primarily on understanding the mechanisms that govern charge and lattice reordering under nonequilibrium conditions and under the influence of electric field. Alternatively, Stojchevska et al. have recently presented work showing the presence of hidden metastable states below 50 K that are reached after a short extinction pulse (~30 fs) is applied to the CCDW phase. It is thought that these states are a result of voids due to hole recombination with the conduction electron isolated on the central Ta atom. These voids are distributed across the sample and contribute to conductivity through formation of incommensurate regions. The authors postulate that if they can be stabilized with some kind of long-range order before they can annihilate, then the material can be locked in a quasi-stable low resistivity state. After entering the hidden state, the 1T-TaS2 remains there until an erase pulse is applied to the sample for a long enough time to allow thermalization of the electron−hole variations or by heating the sample. Most recently, Vaskivskyi et al. have probed these hidden metastable states using electrical means. In their work, these states are reached after applying a short voltage pulse in order to asymmetrically introduce charge to the CCDW system. The original CCDW state cannot be recovered by increasing the applied voltage pulse magnitude or duration. Instead, application of a longer duration pulse only partially recovers the insulating behavior of the CCDW. As in previous work, these hidden states can be completely erased by heating the sample.

In this work, two-terminal dc and pulsed voltages and currents are used to demonstrate abrupt, resistive switching between the various phases of 1T-TaS2 over a range of temperatures (77−150 K). Figure 1b shows a schematic representation of a two-terminal device along with a colorized scanning electron microscopy (SEM) micrograph. 1T-TaS2 flakes on SiO2 substrates (190 nm) are prepared from bulk 1T-TaS2 crystals using an exfoliation process. The 1T-TaS2 single crystals are grown using a chemical vapor transport method to produce a TaS2 powder, that was subsequently heated in a sealed quartz tube and quenched to retain the 1T phase. Additional details are provided in the Supporting Information. Flakes are identified optically and metal contacts are patterned using electron beam photolithography (Ti/Au, 10/50 nm). A post metallization forming gas anneal at 450 °C is used to ensure that the metal leads make good contact to the 1T-TaS2. Flake thickness is measured by atomic force microscopy, with flakes ranging in thickness from 8−55 nm (14−95 atomic layers). A representative current−voltage (I−V) measurement is plotted in Figure 1c showing an abrupt
reduction in resistivity after reaching a critical field. This measurement is performed at 77 K in high vacuum for a 1T-TaS₂ flake with length 8.4 μm, width 6.6 μm, and thickness 10 nm (17 layers). Figure 1d plots the resistivity versus temperature of the same flake, which is extracted from two-terminal measurements.

For this voltage-mode measurement (V-mode, Figure 1c), the voltage across the device is swept from 0 to 20 V and back to 0 V while measuring the current through the device. In the low field regime, the flake exhibits a linear $I-V$ response with a resistivity of approximately 9 mohm-cm. We find that the resistivity of the flake in this regime remains constant over a broad range and matches closely with the resistivity of the CSDW phase (which is the equilibrium phase at this temperature). Figure 1d superimposes the extracted low-field resistivity from the 2-terminal $I-V$ characteristics (black dashed line) on the resistivity versus temperature plot. After reaching a critical threshold electric field and threshold current (18 kV/cm, 1.5 mA), the current through the flake increases abruptly. After this abrupt transition, the $I-V$ response remains linear in nature, but indicates a resistivity roughly 10X lower than the initial insulating CSDW phase. This reduced resistivity (blue dashed line) matches with the resistivity of the NCCDW or ICCDW phases (Figure 1d), suggesting that the flake has undergone an abrupt transition from the insulating to metallic phase. On the return sweep back to zero bias, the flake undergoes another abrupt transition after reaching another critical point (12 kV/cm, 1 mA). In this transition, the flake switches from the metallic state back to its original insulating state.

The abrupt and reversible change in resistivity observed in this work may be a result of one of several mechanisms. An insulator-to-metal transition (IMT) can occur in conventional insulating materials by mechanisms such as avalanche or Zener breakdown where application of large electrical field leads to impact ionization or direct tunneling of the carrier across the band gap, respectively. For Mott insulators, an IMT can occur through an additional mechanism: the collapse of the Mott gap. This can be realized by surpassing a critical carrier concentration such that the electron-electron interactions that lead to Mott–Hubbard localization can be screened out. The critical carrier concentration at which the Mott gap collapses is defined according to the Mott criterion: $n_c = \frac{\alpha_1}{a_{1d}} \approx 0.25$. Here, $a_{1d}$ is the effective Bohr radius and $\alpha_1$ is the critical carrier density to initiate the insulator-to-metal transition from the insulating state. The effective Bohr radius can be calculated according to $a_{1d} = \frac{\left(e\hbar^2}{4\pi\varepsilon m^*e^2}$, where $\varepsilon$ is the permittivity of the material and $m^*$ represents the effective mass of the charge carrier. Alternatively, $n_c$ can be approximated by determining $n_d$, the equilibrium carrier density in the insulating state as the insulator-to-metal transition threshold is approached. In other Mott insulators, the value of $n_c$ has been found to be of the order of $n_d$.\textsuperscript{11}

In the case of bulk 1T-TaS₂, Hall effect measurements can be utilized to determine $n_d$ and, subsequently, $n_c$. Hall effect measurements on bulk 1T-TaS₂ used in this work indicate a carrier density of approximately $2.5 \times 10^{19}$ cm$^{-3}$ and a carrier mobility of approximately 20–15 cm$^2$/V-sec at a temperature of 150 K. Inada et al. show a monotonic increase in carrier density from roughly $5 \times 10^{18}$ to $5 \times 10^{19}$ cm$^{-3}$ as temperature is increased from 50 to 200 K.\textsuperscript{12} Within this temperature range, the Hall effect data is consistent with a single carrier model and the carriers are found to be hole like (p-type). As the temperature is increased further toward the CSDW to NCCDW transition point, the carrier concentration within the 1T-TaS₂ saturates at a value of approximately $5 \times 10^{19}$ cm$^{-3}$. At the transition point, it exhibits a sudden increase in carrier density to approximately $5 \times 10^{21}$ cm$^{-3}$, which subsequently increases with increasing temperature to values as high as $2 \times 10^{22}$ cm$^{-3}$ at temperatures above 350 K (i.e., the ICCDW phase).\textsuperscript{22} These data compare well with the measured carrier density and mobility in this work, indicating an $n_c$ of $\sim 5 \times 10^{19}$ cm$^{-3}$.

Abrupt changes in resistivity can be realized through additional mechanisms as well. In the case of CDW materials, sliding CDW conduction is one such mechanism, where CDWs that are initially pinned at a defect site can be triggered by application of an external field.\textsuperscript{13,14} Although sliding CDW conduction leads to an abrupt increase in conduction through the material, it typically does not lead to a sharp jump to higher currents, but instead exhibits a kink or elbow in the $I-V$ relationship.\textsuperscript{15–17} Furthermore, the critical fields at which CDW sliding occurs are typically below 1 kV/cm, which is over an order of magnitude lower than the critical field observed in this work.\textsuperscript{16} Additionally, Hall et al. utilized a temperature-dependent investigation into CDW depinning in NbSe₃ in order to distinguish between “CDW sliding” and “CDW switching”. CDW sliding was shown to result in a kink type transition in the $I-V$ response while CDW switching was shown to result in an abrupt change in resistivity.\textsuperscript{17} Although they were unable to pinpoint the exact mechanism by which CDW switching occurred, Hall et al. were able to show that these were two distinct phenomenon, which can be triggered separately at two distinct critical fields.\textsuperscript{17} IMTs may also occur without field assistance (i.e., avalanche and Zener breakdown) or carrier assistance (i.e., satisfying the Mott criterion). Many IMTs are thermally driven, such as the case for perovskite rare-earth nickelates, or may be driven by local Joule heating as current flows through the material.

Figure 2a plots the critical fields for avalanche and Zener breakdown as a function of bandgap and the typical range of critical fields observed in this work for the IMT in 1T-TaS₂ (marked with red line). Although dielectric breakdown in Mott insulators has been investigated theoretically in various studies, few experimental reports exist detailing the phenomenon. Recently, Guiot et al. studied resistive switching of several small gap Mott insulators in the GaTa₅Se₆–Teₓ family induced by electronic breakdown of the Mott insulating state.\textsuperscript{18} In their work, a dependency on the critical threshold field for the IMT was found according to the universal law of $E_{th} \propto E_{th}^{2.5}$ for avalanche breakdown. According to their results, this dependency predicts a critical threshold field of roughly 3 kV/cm for 1T-TaS₂ in the Mott insulating state ($E_{th} = 200$ meV). In this work, the observed threshold fields for 1T-TaS₂ range from 10 to 20 kV/cm. Although the observed $E_{th}$ is substantially larger than that predicted for avalanche breakdown, they are significantly lower than that predicted for Zener breakdown by tunneling across the Mott gap.\textsuperscript{19}

In order to probe the field, temperature, and carrier dependency of the IMT in 1T-TaS₂, voltage and current mode measurements were performed as a function of temperature. Figure 2b plots V-mode measurements as a function of temperature from 77 to 150 K. Above $\sim$150 K, 1T-TaS₂ exists in the metallic NCCDW phase as its equilibrium state. Again, the voltage across the device is swept from 0–20 V and back to 0 V while measuring the current through the
device. Current mode (I-mode) measurements are also performed (Figure 2c), wherein the current sourced through the flake is swept from 0 to 3 mA and back to 0. For both measurement techniques, an abrupt transition from CCDW to metallic phase is observed. The absolute field and current at the IMT and metal-to-insulator transition (MIT) points are plotted as a function of temperature for the V- and I-mode measurements in Figure 2d,e. The threshold field ($E_{th}$) and threshold current ($I_{th}$) appear to be independent of measurement mode. Both V- and I-mode measurements show $E_{th}$ and $I_{th}$ that monotonically decrease with increasing temperature. Although the low-field (low-current) $I$-$V$ response exhibits linear behavior, we note that as the transition point is approached the $I$-$V$ response begins to show a superlinear behavior while others have reported exponential behavior. Exponential dependency of current density on voltage may be indicative of an increase in carrier density due to impact ionization, which can be thought of as a doping process, which introduces additional carriers to the system. Another possible source for the superlinear behavior is the conduction due to sliding CDWs after reaching a critical pinning threshold field.

Extracting the resistivity at the transition point, we find a constant critical resistivity, $\rho_{th}$, of 7 mohm-cm that is independent of both temperature and measurement mode. Similar behavior for a metal-to-insulator transition has also been reported for the case of VO$_2$, where it has been suggested that a critical threshold resistivity is indicative of a critical carrier density that triggers the phase transition. Considering the measured $\rho_{th}$ and assuming a carrier mobility of 20 cm$^2$/V$\cdot$s, the critical resistivity of 7 mohm-cm corresponds to a critical carrier density, $n_{th}$, of $\sim$4.5 x 10$^{19}$ cm$^{-3}$ which compares well with the measured $n_{th}$ at the insulator-to-metal transition in 1T-TaS$_2$. This mobility was selected based on experimental results in the literature. Furthermore, this critical carrier density can be used to calculate an effective Bohr radius according to the Mott criterion. Using the $n_{th}$ calculated from the constant critical resistivity, an effective Bohr radius of 6.9 Å is found.

In order to probe the IMT further, a V-mode measurement was performed with varying resistances in series with the 1T-TaS$_2$ flake. Figure 3a shows a schematic representation of the measurement setup while Figure 3b plots the measured results for different series resistances at 110 K. Here, the current through the device is calculated by considering the bias conditions and series resistor. An I-mode measurement is plotted for comparison. Viewing the ideal current source as an open circuit, one may consider the I-mode measurement equivalent to a V-mode measurement with series resistance that is effectively infinite. Use of a resistor in series with the flake produces a negative differential resistance across the IMT as well as the MIT, where the slope of the negative differential resistance can be related to the series resistance ($R_{load}$) Figure 3b). Here, the “s”-shaped character of the $I$-$V$ sweep and the negative differential resistance point to a carrier (current) driven process. Negative differential resistance is also observed for avalanche breakdown, which can be viewed as, effectively, a carrier driven process.

The time scale of the IMT was investigated using pulsed V-mode measurements. In order to capture the voltage across the 1T-TaS$_2$ flake while pulsing, a load resistor ($R_L$) was placed in series with a flake and the output waveform was captured as the voltage measured across $R_L$. In this experiment, the flake used was 4 $\mu$m long, 13 $\mu$m wide, and roughly 20 nm thick. All pulse measurements were made at a temperature of 150 K. Figure 4a shows a schematic representation of the setup while Figure 4b shows the input voltage waveform. A triangular pulse was used so that the MIT could be captured in the output waveform and the critical fields, currents, and resistivities could be extracted for each pulsed measurement. The pulse width was varied from 3 s to 30 $\mu$s. Figure 4c shows a pair of representative input and output waveforms ($I_{pulse} = 300$ $\mu$s). Within the measured output waveform, an abrupt transition from lower voltage to higher voltage is observed. This behavior indicates an IMT within the...
from the pulsed $I−V$ and plotted as a function of pulse width in Figure 4e. A value of $\sim 7.5$ mohm-cm is extracted for pulse widths ranging from 3 s to 300 $\mu$s. The critical resistivity extracted from the longer pulse widths matches with the dc data and further supports the idea that the abrupt switching behavior is the result of a carrier driven collapse of the Mott insulating state. For the pulsed $I−V$ with pulse width below 300 $\mu$s, RC time delay from parasitic capacitances in the cabling and measurement setup begin to dominate, which result in artificially high critical resistivities.

1T-TaS$_2$ represents an interesting material for study of correlated phases in low-dimensionality materials with several competing equilibrium states and a Mott insulating phase. Recent work has explored ultrafast melting of 1T-TaS$_2$’s insulating Mott state using pulsed optical or electronic means to produce metastable states of intermediate resistivity and variable duration. In this work, we have probed the abrupt, resistive switching between equilibrium states using dc and pulsed voltages as well as dc current sourcing. An abrupt reduction in resistivity corresponding to a phase transition from the Mott state to the metallic phase is observed for both pulsed voltages as well as dc current sourcing. An abrupt transition to produce metastable states of intermediate resistivity and variable duration. Importantly, this phase transition is shown to occur at a constant critical resistivity of 7 mohm-cm regardless of temperature or bias conditions and the transition time is significantly smaller than abrupt transitions by avalanche breakdown in other small gap Mott insulating materials that occur in a time range of 10 $\mu$s to 1 ms. Furthermore, the measured critical resistivity is shown to correspond to a carrier density of $4.5 \times 10^{19}$ cm$^{-3}$, which compares well with the observed critical carrier density for the CCDW to NCCDW transition. These results suggest that the transition is facilitated by a carrier driven collapse of the Mott gap in 1T-TaS$_2$ insulating state, which results in fast (3 ns) switching.

**ASSOCIATED CONTENT**

**Supporting Information**

Synthesis and fabrication details. Additional resistivity versus temperature plots are included for flakes of varying thicknesses. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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