Electrical Transport Properties of Polymorphic MoS$_2$

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ABSTRACT: The engineering of polymorphs in two-dimensional layered materials has recently attracted significant interest. Although the semiconducting (2H) and metallic (1T) phases are known to be stable in thin-film MoTe$_2$, semiconducting 2H-MoS$_2$ is locally converted into metallic 1T-MoS$_2$ through chemical lithiation. In this paper, we describe the observation of the 2H, 1T, and 1T$'$ phases coexisting in Li-treated MoS$_2$, which result in unusual transport phenomena. Although multiphase MoS$_2$ shows no transistor-gating response, the channel resistance decreases in proportion to the temperature, similar to the behavior of a typical semiconductor. Transmission electron microscopy images clearly show that the 1T and 1T$'$ phases are randomly distributed and intervened with 2H-MoS$_2$, which is referred to as the 1T and 1T$'$ puddling phenomenon. The resistance curve fits well with 2D-variable range-hopping transport behavior, where electrons hop over 1T domains that are bounded by semiconducting 2H phases. However, near 30 K, electrons hop over charge puddles. The large temperature coefficient of resistance (TCR) of multiphase MoS$_2$, $-2.0 \times 10^{-2} \text{K}^{-1}$ at 300 K, allows for efficient IR detection at room temperature by means of the photothermal effect.

KEYWORDS: molybdenum disulfide, phase transition, Li intercalation, variable range-hopping transport, IR detection

Transition metal dichalcogenides (TMDs) composed of MX$_2$, where M is a metal, such as Mo, W, and Ti, and X is a chalcogenide, such as S, Se, and Te, can be synthesized with a wide variety of electrical properties ranging from those of semiconductors and metals to those of superconductors. MoS$_2$ specifically has been intensively investigated due to the presence of its direct bandgap and high electron mobility. These are promising features for various types of van der Waals materials; such materials hold specific advantages over graphene, including the presence of a bandgap that is critical for electronic and optoelectronic devices.

MoS$_2$-based field-effect transistors (FETs) exhibit n-type behavior with a large contact resistance. For this reason, various metal electrodes have been studied in an effort to reduce contact resistance and to establish ambipolar MoS$_2$ FETs, which are crucial for complementary metal–oxide–semiconductor (CMOS) technologies. However, the contact between metal and MoS$_2$ does not follow Schottky-type behavior; instead, it displays a Fermi-level pinning effect. Metallic MoS$_2$ with a lithium-solution treatment has recently been introduced for the reduction of contact resistance, which is dissimilar to the conventional methods, such as chemical doping and ion implantation, used for the reduction of contact resistance in other devices. The phase engineering technique used to fabricate TMDs materials demonstrates new pathways for controlling the junction barrier. Li-treatment of MoS$_2$ results in the coexistence of various MoS$_2$ phases and consequently develops significantly different electronic and magnetic properties. Therefore, studying the transport properties of polymorphic MoS$_2$ is a key factor for understanding metallicity in two-dimensional materials, although such metallic properties have not yet been thoroughly explored.

In this study, Li-treated MoS$_2$ showed various phases, including 2H, 1T, and 1T$'$, which were confirmed by high-resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS). Furthermore, characteristic vibrational modes of zigzag-Mo atoms, indicating the presence of 1T and 1T$'$-MoS$_2$, were probed using Raman spectroscopy. In multiphase MoS$_2$, electron transport is governed by hopping among localized metallic domains of 1T phases that are separated by 2H phases. Therefore, no gating effect was observed due to metallic 1T phases. However, the resistance of multiphase MoS$_2$ decreases with temperature, which results from the increased hopping transport of electrons.
among metallic phases. Near 300 K, variable range-hopping (VRH) transport of multiphase MoS2 showed a large temperature coefficient of resistance (TCR) of \((-2.0 \rightarrow -4) \times 10^{-3} \text{K}^{-1}\). Such a large TCR of Li-treated MoS2 was adopted to demonstrate the detection of IR ranging from 2–14 μm, which was not feasible with pristine 2H-MoS2.

RESULTS AND DISCUSSION

All devices were fabricated using several layers of MoS2 flakes (3–7 layers) obtained through mechanical exfoliation onto SiO2 (300 nm)/Si (500 μm) substrates. The device electrode was then patterned by e-beam lithography, Cr (5 nm)/Au (50 nm) was deposited using thermal e-beam evaporation at a pressure of 1 × 10\(^{-6}\) Torr. The channel length of exfoliated MoS2 was approximately 3 μm. The 2H-MoS2 device was then annealed in vacuum chamber at 200 °C for 2 h to improve adhesion between metal electrode and MoS2.

The electrical properties of MoS2 before the phase transition were investigated inside a closed-cycle refrigerator (CCR) at a base pressure of 2 × 10\(^{-6}\) Torr. The temperature was lowered from 300 to 100 K. The 2H-MoS2 FET showed a large on-current at a positive gate bias in Figure 1a, indicating that electrons were the majority carrier. This was further proven by observing \(I_{DS}-V_{GS}\) as a function of gate bias, as shown in Figure 1b. Figure 1c shows that the Schottky-barrier height (E_{SBH}) at the junction between 2H-MoS2 and metal electrode (Cr/Au) as a function of the gate voltage.

In order to study the transport properties of Li-treated MoS2, the 2H-MoS2 device was treated with lithium solution under inert atmosphere. (See Materials and Methods.) During the lithium treatment, the Li-ions diffused between layers, inflating the interlayer space (see Supporting Information, Section 1), transferring charges, and leading to a phase transition of MoS2 from the 2H phase to the 1T phase.\(^{22,23}\) Then the sample was washed several times with hexane to remove residual organic molecules and unreacted lithium ions; it subsequently was cleaned again with deionized water and isopropyl alcohol (IPA) to remove the remaining lithium ions. Then the sample was dried at room temperature in a vacuum for 12 h.

After the Li treatment, a no-gate dependence of \(I_{DS}\) was observed, as shown in Figure 2a, which shows a stark difference compared to the \(I-V\) curve in Figure 1a. The absence of a gating effect after the Li treatment may imply an evolution of a different phase of MoS2. In Figure 2b, all the \(I_{DS}-V_{DS}\) curves are linear, regardless of gate bias. The existence of different phases of MoS2 has been identified using HR-TEM, which is presented in Figure 2c,d. For the microscopy, a chemically exfoliated MoS2 monolayer was used, which was reconstituted using chemical processes adopted for metallic MoS2 FET. The areas colored in blue in Figure 2c indicate the 1T phases after the Li treatment. (See Supporting Information, Sections 2–3 for more detailed TEM characterizations.) The 1T-MoS2 phases are randomly distributed and intervened with 2H-MoS2 phases. On the micrograph, the physical separation among 1T islands was approximately a few to several nanometers. A newly emerged 1T phase after Li treatment goes through another transition into a semimetallic 1T\(^{′}\) phase, which is marked by yellow in Figure 2d. Thus, Li-treated MoS2 resembles to the metallic granular electrically insulated by oxide or semiconductor materials.\(^{26}\) After the removal of the lithium ions, Li-treated MoS2 layers restack and undergo an additional phase transition from the 1T phase to the 1T\(^{′}\) phase.\(^{27,28}\) The second transition from the 1T phase to the 1T\(^{′}\) phase is considered to be initiated by restacking; the 1T\(^{′}\) phase can be stabilized by the negative chemical species that are introduced during the rinsing process. In addition, it is known that the 1T\(^{′}\) phase is energetically more stable than the 1T phase.\(^{29,30}\)
Figure 3. (a) $I_{ds}-V_{gs}$ characteristics of the multiphase MoS$_2$ device at $V_{dd}=0.1$ V from temperatures between 100 and 300 K. (b) Plots of resistance ($Y_1$) and TCR ($Y_2$) vs temperature characteristics of a multiphase MoS$_2$ device. (c) Ln($G$) vs $T^{-1/3}$ of a multiphase MoS$_2$ device at $V_{dd}=0.1$ V. The inset shows ln($G$) vs $T^{-1/2}$ at $V_{dd}=0.1$ V. (d) ln($W$) vs ln($T$) plot of multiphase MoS$_2$. (e) Schematics of variable range-hopping transport in polymorphic MoS$_2$.

Supporting Information, Sections 2–5 for in-depth characterizations of TEM, XPS, and Raman spectroscopy. Although Li treatment of 2H-MoS$_2$ leaves metallic 1T and semimetallic 1T’ puddles that are connected by 2H phases, $I_{ds}-V_{gs}$ curves in Figure 2a indicate the dominant role of metallic phases of 1T and 1T’ in device transport. No gating behaviors are observed consistently at low temperatures, as shown in Figure 3a. The transport properties are measured down to 100 K because the feasibility of Li-treated MoS$_2$ is tested for Ir detection in the later part of present manuscript. The operational temperature of most IR detectors is above 100 K. No gating effect implies that the population of the metallic phase may exceed for the threshold for a percolation transport that will be discussed further later. However, unlike the metallic characteristics seen in Figure 2a, the current-temperature ($I_{ds}-T$) curves measured from 100 to 300 K in increments of 20 K, presented in Figure 3a, exhibit increasing $I_{ds}$ in proportion to temperature, indicating semiconducting behavior. Such a temperature dependence of resistance of our sample shows a similar behavior to that of inhomogeneous mixture of metal and nonmetals. The current increases over 2 orders of magnitude in this temperature range, whereas no gate modulation of $I_{ds}$ occurs at each temperature step in Figure 3a. It is possible that the patches of 2H-MoS$_2$ are responsible for the resistance lowering through the thermal excitation of valence electrons over the bandgap, because 2H-MoS$_2$ still occupies a large portion in Li-treated MoS$_2$ flakes, which is determined by TEM and XPS investigations. We rule out this possibility because the bandgap energy of 2H-MoS$_2$ approximately 1.8 eV is too large to explain the corresponding increase of $I_{ds}$ with temperature.

The resistance of multiphase MoS$_2$, obtained as a function of temperature, decreases from 57 to 0.3 MΩ when the temperature changes from 100 to 300 K, with a negative TCR ranging from $-0.08$ K$^{-1}$ at 100 K to $-0.016$ K$^{-1}$ at 300 K, as shown in Figure 3b. This value is quite large compared to the TCR of typical metals, such as Au, Fe, Mo, and Al. The variation in the TCR indicates that different energy levels are involved with electron conduction in a response to temperature change, and a fit of ln($G$) to $T^{-1/3}$ demonstrates a clear linear relationship as shown in Figure 3c. This strongly supports that electron conduction occurs through the hopping process on a two-dimensional plane through localized metallic states, whose temperature dependence of conductance $G$ is described as

$$G \cong \exp \left( -\frac{T}{T_1} \right)^{1/3}$$

where $T_1$ is characteristic temperature. Although a similar transport, nearest-neighbor hopping (NNH), has been observed in pristine MoS$_2$ through defect states of S vacancy even near room temperature. In this transport regime, the conductance shows a stronger temperature dependence, ln($G$) $\cong T^{-1}$. However, Li-treated MoS$_2$ shows VRH, which has not yet been reported from Li-treated MoS$_2$. Because the fit of ln($G$) to $T^{-1/4}$, where $d$ is dimensionality, does not clearly differentiate the dimensional dependence. For example, a fit of ln($G$) to $T^{-1/2}$, corresponding for Efros–Shklovskii (ES) hopping transport, still looks linear, as shown in the inset of Figure 3c. Therefore, we introduce, in order to confirm 2D Mott VRH, a parameter $W = \frac{d\langle\ln(e)\rangle}{d\langle\ln(T)\rangle}$. Electrical conductivity, $\sigma$, can be expressed as $\sigma = \sigma_0 e^{-\langle T_e/T \rangle^{(1/4)}}$, where $\sigma_0$ is electrical conductivity at $T_0$ a reference temperature. Therefore, a more precise determination of the temperature dependence of electrical conductivity can be made by extracting the slope from a plot of ln($W$) vs ln($T$) as shown in Figure 3d. The slope of the curve in Figure 3d is approximately $-0.37$. The negative value explains the semiconducting behavior, as electrical resistance decreases with temperature, and 0.37 signifies 2D Mott-type electron hopping, whose theoretical value is 0.33. Therefore, although multiphase MoS$_2$ exhibits metallic properties without any gate modulation, the resistance–temperature ($R-T$) behavior is semiconductor-like due to electron hopping through semiconducting 2H-MoS$_2$ puddled to the metallic 1T-MoS$_2$, as schematically shown in Figure 3e. The transport behavior of Li-treated MoS$_2$ has a similarity to a metal alloyed
with a semiconductor in which metal grains are surrounded by thin insulating layers. The alloy shows metal–insulator transitions depending on their relative composition ratio.\textsuperscript{39} Our TEM observation in Figure 2c,d reveals a similar compositional structure to a semiconductor-alloyed metal. The randomly scattered metallic puddles in a few layers of Li-treated MoS\textsubscript{2} are expected to screen the gate electric field, which contributes no gating effect. The electrical resistance decreases as the temperature increases due to the enhanced hopping among the metallic grains bounded by the thin semiconducting layers. Another possible electron conduction for \( \ln(G) \) to \( T^{−1/3} \) relation is the transport through inhomogeneities in Li-treated MoS\textsubscript{2} including charge puddles, S vacancies, and defects. In order to examine the influence of them on the transport, \( I_{\text{th}} \sim V_{\text{th}}^{1.5} \) characteristics of Li-treated MoS\textsubscript{2} are plotted in log–log scale as a function of temperature because the value of \( \alpha \) changes with the types of inhomogeneities associated with the transport. For instance, \( \alpha = 1.0 \) indicates an ohmic conduction, but \( \alpha = 1.3 \) and \( \alpha = 2.0 \) means the conduction of charged puddles and trap-free space charge limited current, respectively. Within the temperature range from 100 to 300 K, \( \alpha \) remains a unity, indicating no contribution from those disorders \cite{Supporting Information, Section 6}. The results clearly concord with a linearity of \( \ln(G) \sim T^{−1/3} \) in Figure 3c that indicates a single transport mechanism, Mott VRH. This is different from the previous study that showed additional transport mechanisms as the temperature becomes low.\textsuperscript{40,41} This strongly supports the VRH among metallic 1T-MoS\textsubscript{2} near the room temperature. However, when the temperature drops near 30 K, a nonlinear behavior in \( I_{\text{th}} \sim V_{\text{th}}^{1.5} \) with \( \alpha = 1.3 \) appears in the plot, \( \log(I_{\text{th}}) \sim \log(V_{\text{th}}) \) \cite{Supporting Information, Section 7}, a sign of contribution of disorders.\textsuperscript{42}

We performed density-functional theory (DFT) calculations using the generalized-gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE96) functional\textsuperscript{43,44} and the projector-augmented wave (PAW) method, as implemented in VASP.\textsuperscript{45} Monolayers of MoS\textsubscript{2} were built in a unit cell of each phase of 2H, 1T, and 1T', with a vacuum distance of 1.6 nm along the c axis and a cutoff energy for the plane-wave basis set to 350 eV. In most calculations, 25 \( \times \) 25 \( \times \) 5 sampling of the Brillouin zone was used. All calculations were spin-polarized; both the positions of atoms and the shape of the unit cell were fully relaxed to obtain the optimized lattice structure.

Our calculations show the number of energy states at \( E_{\text{F}} \) of the 1T and 1T' phases of MoS\textsubscript{2} whereas a narrow energy gap \((E_{\text{g}} < 30 \text{ meV})\) at \( E_{\text{F}} \) is found from 1T' phase one, as shown in Figure 4a,b. In addition, the density of states at \( E_{\text{F}} \) in the 1T phase, approximately \( 1 \times 10^{15} \text{ eV}^{-1} \cdot \text{cm}^{-2} \), is almost 2 orders of magnitude larger than that of the 1T' phase. These results lead us to postulate that although Li treatment of MoS\textsubscript{2} contributes to the existence of polymorphic phases, electron conduction by hopping mostly occurs through metallic 1T, rather than through 1T' phases. Furthermore, the previous reports on 2H-MoS\textsubscript{2} have shown VRH transport, which is mediated by S vacancy.\textsuperscript{46} However, the absence of any gating effect of Li-treated MoS\textsubscript{2} indicates negligible contributions of 2H-MoS\textsubscript{2} to the transport shown in Figure 3a.

Here, 2H-MoS\textsubscript{2} is expected to operate as a thin insulating layer between 1T phases. In order to extract hopping parameters among 1T metallic puddles, a slope \( S \) of the plot in Figure 3c is estimated. The slope \( S \) is equivalent to \( T_{1/3} \), which is further described as \( T_{\text{j}} = \frac{3}{k_{\text{B}}N(E_{\text{F}})} \), where \( k_{\text{B}} \) is the Boltzmann constant, \( N(E_{\text{F}}) \) is the number of states near \( E_{\text{F}} \) and \( L_{\text{f}} \) is the localization length.\textsuperscript{47} The localization length of the electronic wave function in our polymorph MoS\textsubscript{2} becomes \( L_{\text{f}} = 7.75 \text{ Å} \). The hopping distance of electrons depends on the temperature because the tunneling of electrons among 1T puddles is promoted by lattice vibrations that allow for hopping between the states in the 1T' phase. At a given temperature \( T \), the optimal hopping distance \( R_{\text{0}} \) is expressed as \( R_{\text{0}} = \frac{L_{\text{f}}}{3} \left( \frac{3}{T} \right)^{1/3} \).

Within the temperature range between 300 and 100 K, \( R_{\text{0}} \) is estimated between 3.19 and 4.60 nm. The distribution of 1T islands in the TEM images shown in Figure 2c reveals that the average separation among them varies approximately from a few to several nanometers. Our \( R_{\text{0}} \) is consistent with the TEM observations. The transport nature of Li-treated MoS\textsubscript{2} is driven by the tunneling of electrons among 1T puddles with nearly the same \( E_{\text{F}} \) level. At low temperatures, hopping to higher energy states is not feasible because of low thermal energy; electron hopping is allowed through mostly similar energy levels. Thus, hopping distance at a certain 1T puddle depends on the location of the next 1T puddle that has similar \( E_{\text{F}} \) levels. Because different energy states are distributed at each 1T site, the hopping distance is supposed to change. The activation energy for the tunneling increases at high temperatures. Tunneling occurs through 1T puddles with a wide energy window, which can decrease the hopping distance, as shown in Figure 4c.

In addition to the localization distance \( L_{\text{f}} \), the Coulomb gap \( \Delta \) that forms at \( E_{\text{F}} \) due to Coulomb interaction between electrons is estimated because it characterizes ES hopping mechanism. No Coulomb gap exists in Mott VRH, unlike ES hopping. Because the Coulomb gap in 2D space can be expressed \( \Delta \approx e^2N(E_{\text{F}}) \), the Coulomb gap of Li-treated MoS\textsubscript{2} is negligibly small, \( \Delta_{\text{MoS}_2} < 1 \text{ mK} \). Therefore, the Mott VRH...
hopping transport is dominant at room temperature, as seen in Figure 3c. In addition, the conductance-temperature dependence in Mott VRH is also subject to change upon the average diameter of metallic 1T-MoS$_2$, density of states at $E_F$, and temperature.$^{48,49}$

The large TCR found in multiphase MoS$_2$ can be advantageous for IR detection by converting the incident light into heat, resulting in a significant decrease in resistance. For the detection of midrange IR, the change in current flow observed in multiphase MoS$_2$ is monitored at a given voltage during the IR exposure. In Figure 5, the responsivity surfaced in our samples at the temperature far below 100 K. Therefore, VRH at 300 K observed from Li-treated MoS$_2$ is attributed to the hopping of electrons via metallic 1T phases. A large TCR of $-0.08$ to $-0.016$ K$^{-1}$ is obtained from polymorphic MoS$_2$. We demonstrated that, at room temperature, an IR bolometer, using Li-treated MoS$_2$, showed resistance changes sharply based on temperature variations.

**MATERIALS AND METHODS**

**Fabrication Procedure for a Multiphase MoS$_2$ Device.** A 1.6 M n-butyl lithium solution (Sigma-Aldrich) was used to induce a phase transition of MoS$_2$. The 2H-MoS$_2$ devices were immersed in 10 mL of 1.6 M n-butyl lithium in a sealed flask at room temperature under argon (99.999%). In particular, the flake sizes less than $\sim$5 $\mu$m were selectively used for the uniform distribution of Li-ions inside the MoS$_2$ flakes. After 12 h, the sample was washed with n-hexane (anhydrous) several times to remove the residual organic molecules and the unreacted lithium ions. Then, the device was rinsed further with deionized water in order to remove the remaining lithium ions. Finally, the device was cleaned with isopropl alcohol (IPA), which was followed by drying at room temperature under vacuum conditions for 12 h.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b02267.

More information on the interlayer spacing of multiphase MoS$_2$, structural characterizations using TEM and XPS, temperature dependence measurement, low temperature measurement, IR source and additional references (PDF)

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**Notes**

The authors declare no competing financial interest.

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