Self-Terminated Surface Monolayer Oxidation Induced Robust Degenerate Doping in MoTe₂ for Low Contact Resistance

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ABSTRACT: We introduce an effective method to degenerately dope MoTe₂ by oxidizing its surface into the p-dopant MoOₓ in oxygen plasma. As a self-terminated process, the oxidation is restricted only in the very top layer, therefore offering us an easy and efficient control. The degenerate p-doping with the hole concentration of 2.5 × 10¹³ cm⁻² can be obtained by applying a ~300 s O₂ plasma treatment. Using the degenerately doped MoTe₂, we demonstrate a record low contact resistance of 0.6 kΩ μm for MoTe₂. Our measurement highlights an excellent stability for the plasma-doped MoTe₂. The doped characteristics are robust with no significant degradation even after a one-year exposure to the air. The oxygen plasma doping technique is compatible with the conventional semiconductor processes, which can be utilized to realize high-performance MoTe₂ field-effect transistors (FETs) or tunnel FETs in the future.

KEYWORDS: molybdenum ditelluride, oxygen plasma, surface oxidation, self-terminated oxidation, degenerate doping, contact resistance

1. INTRODUCTION

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) are promising material platforms for realizing high-performance field-effect transistors (FETs) with high on–off ratio, excellent electrostatic gate controllability, and large carrier mobility because of their sizeable energy band gap, atomic thickness, and high quality crystal lattice.¹,² Among the 2D TMD family, few-layer semiconducting MoTe₂ have recently attracted particular attention owing to its relatively small band gap of ~0.9 eV, which makes MoTe₂ promising for the applications such as tunnel FETs and near-infrared photodetectors.³–⁵ Despite these merits, the large contact resistance (R_c) at the metal 2D TMD interface and their air-sensitive surfaces hinder the practical applications of 2D TMDs.⁶,⁷

Normally, the large R_c originates from the Schottky barrier (SB) formed at the metal 2D TMD interface as a result of poor band alignment or Fermi-level pinning because of the massive disorders induced in TMDs during metal deposition. Hence, the charge carriers can only be injected into the semiconductor channel either by tunneling through a thin SB or by thermionic emission at a considerable temperature, therefore resulting in a low current density.⁸ A lot of efforts have been carried out to reduce R_c by lowering the SB.⁹–¹¹ Recently, Liu et al. demonstrated the Fermi-level pinning free metal contacts to TMDs using the transferred van der Waals metal layers.¹² Additionally, phase engineering also offers the potential to reduce contact resistance. As a material possessing easy phase transition, the 1T’ metallic phase of MoTe₂ has been employed as the contact to the n-type 2H semiconducting MoTe₂ FETs.¹³ However, the current was still maintained at a relatively low level in the reported devices. Moreover, such a device may suffer from insufficient thermal stability.

Another strategy of reducing contact resistance is to use degenerate doped materials as electric contacts which is widely employed in the complementary metal-oxide semiconductor (CMOS) technology. The extremely low R_c = 0.3 kΩ μm was demonstrated in a p-type WSe₂ transistor using the synthesized Nb₀.₀₀₅W₀.₉₉₅Se₂ as van der Waals contacts.¹⁴ However, to induce degenerate doping in situ to the 2D TMDs is still technically challenging. The long ozone treatments at a high temperature of >100 °C have been applied to both WSe₂ and MoTe₂ to oxidize the top few layers into the large electron affinity WOₓ and MoOₓ (x < 3) as a self-limiting layer-by-layer process.¹⁵–¹⁶ As a result, the materials are degenerately hole-doped because of the severe charge transfer from the surface oxide. In addition, the surface oxidation provides a good passivation to prevent the materials from further degradation.

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in the air. Nevertheless, the required high temperature conditions and the poor time stability limit the application of ozone treatment in practice. Moreover, a low contact resistance of $< 1 \ \text{k}\Omega \ \mu\text{m}$ with degenerately doped MoTe$_2$ or WSe$_2$ has not been demonstrated yet.

In this work, we demonstrate the degenerate hole doping to MoTe$_2$ by using room-temperature oxygen (O$_2$) plasma treatment. This treatment leads to the self-terminated surface oxidation only on the very top layer of MoTe$_2$, while keeping the underlying layers untouched. We found that doping concentration can still be controlled before the top layer is fully oxidized by the treatment duration. The hole concentration of the MoTe$_2$ reaches $2 \times 10^{13} \ \text{cm}^{-2}$ without additional gate modulation, that is, degenerate doping. Subsequently, using it as the contacts, a low contact resistance $R_c$ of 0.6 k$\Omega$ $\mu$m is measured with the transmission line model, which is, to the best of our knowledge, the record low value ever obtained for the p-type MoTe$_2$ FETs. Moreover, the plasma-treated MoTe$_2$ exhibits robust p-doping characteristics even after long storage in air or soaking in organic solutions. This technique potentially can be applied to other TMDs. The good compatibility to conventional CMOS technology makes it promising for future applications in the next-generation electronics.

2. EXPERIMENTAL SECTION

Few-layer MoTe$_2$ flakes are mechanically exfoliated from a single-crystalline bulk material onto a heavily doped silicon substrate capped with 285 nm-thick thermal SiO$_2$. The metal electrodes of chrome/gold (5 nm/50 nm) are deposited on MoTe$_2$ flakes with both monolayer and bilayer parts before and after O$_2$ plasma treatment of varied durations. After device fabrication, the plasma treatment was carried out at room temperature in an inductively coupled plasma system equipped with a 13.56 MHz microwave source (miniplasma-station, Plasmart) at a pressure of 20 Pa, $\text{O}_2$ system equipped with a 13.56 MHz microwave source (miniplasma-station, Plasmart) at a pressure of 20 Pa and an O$_2$ flow rate of 30 sccm. A power of 20 W, which is the lowest to introduce plasma in this system, was applied. The electrical properties of all devices are measured in a vacuum probe station at 0.1 Pa using the SiO$_2$ layer as the dielectric and highly doped silicon substrate as the gate.

X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific ESCALAB 250 Xi X-ray photoelectron spectrometer with a monochromatic KR Al X-ray line. Core-level spectra were collected with a pass energy of 30 eV and a dwell time of 50 ms. All spectra are calibrated using the 1s peak at 284.6 eV as a reference. The surface morphologies of the samples were measured using tapping mode atomic force microscopy (AFM) (Veeco Icon). Raman spectra were measured with a laser micro-Raman spectrometer (RAMANRXN1, Kaiser Optical Systems) with a laser wavelength of 532 nm and at a low power of 0.1 W.

3. RESULTS AND DISCUSSION

First, we show that the surface oxidation on the surface of MoTe$_2$ induced by the oxygen plasma is a self-terminated process. An exfoliated flake with both monolayer and bilayer MoTe$_2$ is subjected to plasma treatment with varied durations. The color contrast of the monolayer and bilayer MoTe$_2$ and their thicknesses are measured using optical microscopy and AFM, respectively (Figure 1). Compared to the pristine state, both monolayer and bilayer flakes present a lower color contrast after 10 s of plasma treatment (Figure 1a). The monolayer flake is almost transparent, while the bilayer flake changes to the color similar to that of the monolayer at the pristine state. Interestingly, the contrasts of both mostly stay unchanged after further treatments. Usually, the weakened color contrast indicates the thinning of the flake. However, we find that both flakes actually become thicker after the treatment. The AFM measurement shows the pristine monolayer flake thickness as 1.09 nm, which agrees with the previously reported value of 1.2 nm. The incremental thickness between the monolayer and bilayer flake is around 0.85 nm, corresponding to a single layer of MoTe$_2$. After a short plasma treatment of 10 s, surprisingly, the monolayer flake thickness increases to $\sim 2.12$ nm, while the thickness difference between the monolayer and bilayer MoTe$_2$ is maintained at $\sim 0.85$ nm. It is known that the oxide of MoTe$_2$, MoO$_x$ ($x < 3$), is transparent and has the thickness of $\sim 2$ nm in its amorphous form. The increased surface roughness measured on the MoTe$_2$ surface by AFM along with plasma treatments actually suggests the eventual transition from the crystalline MoTe$_2$ to the amorphous MoO$_x$. The AFM measurements manifest that the very top layer of the MoTe$_2$ flake is oxidized into MoO$_x$ in the oxygen plasma, while the underlying layer is not affected.

To confirm the formation of MoO$_x$, we investigate the surface composition of the plasma-treated MoTe$_2$ by using XPS. Because the X-ray has a large spot size of $\sim 0.2$ mm, a large bulk MoTe$_2$ is measured. Nevertheless, XPS, as a surface analysis tool, only penetrates into the material by a certain depth of a few nanometers and gathers information within this range. Using a bulk sample still gives us the information of MoTe$_2$ within a few layers near its surface. Figure 2 presents the XPS core-level spectra of Mo3d of MoTe$_2$ flakes after varied O$_2$ plasma treatment durations. In the pristine MoTe$_2$, typical binding energies of the Mo3d$_{5/2}$ mode at 231.5 eV and Mo3d$_{3/2}$ mode at 228.4 eV are obtained. After an O$_2$ plasma of 100 s, the formation of MoO$_x$ on MoTe$_2$ surface is clearly noticed by the appearance of two additional Mo3d peaks at 235.5 and 232.4 eV. Their locations mostly resemble...
these of the Mo3d peaks in MoOx, therefore strongly revealing MoO3 as the major component in MoOx.20,21 The intensities of the MoOx-related peaks grow with longer plasma treatment, indicating the growth of surface oxide MoOx. Additionally, the areas under the Mo3d peaks of MoOx and MoTe2 carry the information of the quantity ratio between these two molybdenum-containing materials. Using Mo3d5/2 peaks, we extract the ratio between the molybdenum in MoOx and MoTe2 as 0.9, 1.02, and 1.05 after the treatment of 100, 300, and 600 s, respectively. The ratio between the molybdenum in MoOx and MoTe2 does not change after the treatment longer than 300 s, offering another evidence to support the self-terminated oxidation besides AFM measurements. In addition, the 1:1 ratio suggests a penetration depth of XPS in MoTe2 as about two layers. The oxidation also results in the nonvolatile tellurium dioxide left on the surface which is noted by the Te3d peaks of TeO2 observed in the XPS measurement (Supporting Information, Figure S1).18

It is known that the phase transition is very likely to occur in MoTe2 when being subjected to high temperature, plasma, or energy irradiation.13,24,25 To verify no phase transition led by the plasma process, we measure the Raman spectra before and after plasma treatment. A low laser power of 0.1 W is used to avoid impact to the MoTe2. Figure 3 plots the Raman spectra of monolayer and bilayer MoTe2 before and after O2 plasma of varied lengths. The pristine bilayer flakes exhibit the typical A1g, E2g1, and B2g1 Raman modes of the semiconducting 2H phase MoTe2 at 174, 236, and 290 cm−1, respectively. The bulk-inactive B2g1 mode at 290 cm−1 is absent in the monolayer MoTe2. After a treatment of 10 s, all Raman modes disappear in the monolayer MoTe2, as the single-crystalline lattice of monolayer MoTe2 is destructed. In contrast, in the case of a bilayer MoTe2, clear Raman modes at 174 and 236 cm−1 as strong evidence indicating a 2H crystalline MoTe2 are observed after the plasma treatment. Moreover, no evidence of the 1T′ phase, such as the modes at 165 cm−1, is identified.26 The vanishing B1g mode of the bilayer MoTe2, in 10 s manifests a transition from a bilayer MoTe2 into a single layer of crystalline MoTe2. This is to say the crystalline structure of the topmost MoTe2 layer is very rapidly destructed in the plasma. The Raman spectrum of the bilayer MoTe2 barely changes after further plasma treatment, indicating the preservation of the 2H phase crystalline in the bottom layer. This is consistent with what is suggested by the AFM and XPS
data that self-terminated oxidation in plasma only happens on the top layer of the bilayer MoTe2. A small decrease of Raman intensity is noted, which possibly shows weak degradation induced in the underlying MoTe2 by the plasma treatment (Supporting Information, Figure S2). In addition, we observe a slight blueshift in the $E_{1g}$ peak with increased treatment duration at the beginning of the oxidation process (see the details in the Supporting Information, Figure S2). This suggests that weak compressive strain is likely built up in the underlying MoTe2 by the interaction with the nonuniform surface. When the surface is fully oxidized, for instance, after the treatment of 270 s, strain is weakened, and therefore, the $E_{1g}$ peak is red-shifted. The Raman mappings shown in Figure 3b suggest that the oxidation process occurs uniformly on the surface. At a pressure of 20 Pa, the lateral effect of the plasma is non-negligible. Subsequently, the underlying layers can also be oxidized slowly from the edges, which is indeed noted from the dark and blurry edges of the $E_{1g}$ mode mapping of the treated bilayer MoTe2.

Now, we are able to conclude the possible scenario of plasma-induced surface oxidation on MoTe2. Initially, the gentle physical bombardment of the low-power plasma creates massive defects instantaneously on the very top surface of MoTe2. Subsequently, the oxidation of MoTe2 into MoOx is possible at the defect sites with the reaction with oxygen radicals. We should note that the low-power plasma does not have enough energy to penetrate through the top layer of MoTe2 as well as the resulted MoOx. Therefore, the underlying MoTe2 layers are protected from O2 plasma, and the oxidation of MoTe2 is restricted on the very top layer of MoTe2. Then, the nuclei of MoOx expand laterally until they coalesce. This scenario is consistent with the increased surface roughness observed in the AFM measurements. Finally, a continuous amorphous MoOx is attained on the top surface of MoTe2 and the surface oxidation is terminated even with further treatment. The evolution process of the O2 plasma-treated MoTe2 surface is shown in Figure 4.

![Figure 4. Evolution process of the O2 plasma-treated MoTe2 surface.](image)

Next, we investigate the transport characteristics of the plasma-treated MoTe2 with the FET devices. The pristine MoTe2 transistor exhibits n-dominated ambipolar characteristics, as shown in Figure 5a. After a 10 s plasma, it changes into a heavily p-doped characteristic with its charge neutral point out of the measurable gate voltage range. The current density increases monotonically with the extended plasma treatment. It is known that the surface oxide, that is, the amorphous MoOx and TeOx, is basically insulating with a much higher resistivity than MoTe2.27 These measured characteristics stems from the transport in the underlying MoTe2 channel. With the treatment longer than 300 s, the transfer characteristics are highly degenerate with negligible gate dependence. It reveals that the top layer of MoTe2, mostly oxidized into MoOx after 300 s. Finally, the treated MoTe2 transistor exhibits a high current density of 60 $\mu$A/μm and on-off ratio less than two, indicating a highly degenerate hole doping achieved in MoTe2.

The hole sheet density $n_h$ of MoTe2 can be calculated from its transfer curve by using the equation $n_h = \frac{k_f L}{q W V_D}$, where $L$ and $W$ are the channel length and width, respectively.28 Field effect mobility $\mu$ is expressed as $\mu = \frac{L}{V_{GS} C_{ox} W}$, where $C_{ox} = 1.2 \times 10^5$ F/cm² is the gate oxide capacitance of the 285 nm-thick SiO2 wafer and $g_m = \frac{dI_D}{dV_G}$ is the transconductance. The hole mobility is plotted with respect to plasma treatment durations (Supporting Information, Figure S3). The trend resembles mobility-carrier concentration correlation, which is governed by different dominant scattering mechanisms at the MoTe2-substrate interface associated with the varied carrier concentrations.29 The calculated values of $n_h$ at $V_D = 0$ V are shown in Figure 5b; the maximum $n_h$ is found to be $2.0 \times 10^{13}$ cm², exceeding the limit of degenerate doping for 2D TMDs.30

Such degenerately doped MoTe2 can be utilized to improve the metal-MoTe2 contact. We evaluate the contact resistance from metal to degenerately doped MoTe2 by using the transmission line method. The inset of Figure 5c shows the optical images of the MoTe2 junctions with varied channel lengths, which is treated in the plasma for 400 s. The relatively high pressure applied during the plasma process guarantees the considerable lateral effect, which induces the growth of oxidation under the metal contacts as illustrated in the inset of Figure 5b. Subsequently, the metal can be directly contacted to the plasma-treated MoTe2 near its edges. The degenerate doping induced by the thin surface oxide highly suppresses the SB at the contact interface, facilitating significant hole tunneling via the surface oxide and SB into the MoTe2 channel near the edges of the contacts (inset of Figure 5b). Considering the low thickness of the channel, the nearly uniform doping leads to the homogeneous current distribution in vertical. The application of gate voltage electrostatically increases the hole concentration in the channel, which can further reduce the contact resistance. The value of $R_c$ between metal and plasma-treated MoTe2 is extracted from a linear fit of the total resistance versus channel length under varied gate voltages. $R_c$ of the plasma-treated MoTe2 is shown in Figure 5c. The relatively low $R_c$ of 1.3 kΩ is noted with no gate, and it is tuned from 4 to 0.6 kΩ μm when scanning $V_G$ from 60 to −60 V. The reduction of effective SB and contact resistance can be further verified by the linear and symmetric output curves of the device after plasma treatments (Supporting Information, Figure S4). To the best of our knowledge, an $R_c$ of 0.6 kΩ μm is the lowest value ever achieved for the p-type MoTe2 FETs. This extremely low $R_c$ highlights the importance of the self-terminated oxidation process, which results in the thinnest oxide and therefore a transparent tunnel barrier as a key factor for the excellent device performance.

Previous works report that ozone-treated MoTe2 and WSe2 suffer from the poor stability issue. The degenerate doping
rapidly degrades in a few minutes when exposing the materials to the air.\textsuperscript{18} We degenerately dope MoTe\textsubscript{2} with a 400 s plasma treatment and monitor the evolution of its characteristics in varied storage conditions. The results are plotted in Figure 6a, and the corresponding hole concentrations \( n_h \) are extracted and shown in Figure 6b. To further process the plasma treatment of MoTe\textsubscript{2} into electronic devices, the material should be chemically compatible. We first soak it in the frequently used organic solutions, that is, isopropanol (IPA) and acetone, for 5 min each in sequence after the plasma treatment. Both IPA and acetone show no significant impact on MoTe\textsubscript{2}’s doping condition. \( n_h \) is reduced from 2.5 \( \times \) 10\textsuperscript{13} cm\textsuperscript{-2} as treated to 2.0 \( \times \) 10\textsuperscript{13} and 1.3 \( \times \) 10\textsuperscript{13} cm\textsuperscript{-2}, respectively, making the treated MoTe\textsubscript{2} compatible with the organic solvent process. A subsequent 7-day storage in the air only further reduces \( n_h \) to 1.1 \( \times \) 10\textsuperscript{13} cm\textsuperscript{-2}. Finally, after a one-year long exposure to the air, \( n_h \) decreases to 0.7 \( \times \) 10\textsuperscript{13} cm\textsuperscript{-2}, which is still higher than the carrier density which can be reached by the degenerately doped MoTe\textsubscript{2} by plasma treatment. During plasma treatment, the oxygen radicals are unlikely to adsorb on the MoTe\textsubscript{2} surface because of the physical bombardment. In contrast, there may be a lot of ozone molecules adsorbed on the ozone-treated MoTe\textsubscript{2} and they desorb quickly in the air, leading to the massively reduced doping characteristics. Hence, the degenerate doping induced by the oxygen plasma treatment is much more robust compared to the ozone-treated one.

4. CONCLUSIONS

In conclusion, we have developed a simple and effective method to induce degenerate hole doping to MoTe\textsubscript{2} by applying O\textsubscript{2} plasma. The O\textsubscript{2} plasma oxidizes the very top layer of MoTe\textsubscript{2} into MoO\textsubscript{3}, which is a strong p-dopant to the underlying MoTe\textsubscript{2}. The process is terminated by itself, providing us an easy and good control of the process. A > 300 s O\textsubscript{2} plasma treatment lead to a high hole concentration of 2.5 \( \times \) 10\textsuperscript{13} cm\textsuperscript{-2}. Excellent stability of the plasma-doped MoTe\textsubscript{2} is found in the air, while it can also survive from gentle chemical treatments. More importantly, with the degenerately doped MoTe\textsubscript{2}, we demonstrate a record low contact resistance of 0.6 kΩ \( \mu \text{m} \) for MoTe\textsubscript{2}. In the future, this method can be utilized to make high-performance MoTe\textsubscript{2} FETs or tunnel FETs, where the degenerately doped MoTe\textsubscript{2} contacts can be spatially selected by using the h-BN masking technique.\textsuperscript{19}

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c03762.

XPS spectra before and after O\textsubscript{2} plasma treatment with varied durations, evolutions of the wave number and intensity of Raman E\textsubscript{2g}\textsuperscript{1} peak with respect to plasma treatment durations, evolution of field-effect hole mobility with respect to plasma treatment durations, and output curves of a pristine transistor and a p-type MoTe\textsubscript{2} transistor (PDF)

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