Stable and scalable 1T MoS$_2$ with low temperature-coefficient of resistance

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Monolithic realization of metallic 1T and semiconducting 2H phases makes MoS$_2$ a potential candidate for future microelectronic circuits. A method for engineering a stable 1T phase from the 2H phase in a scalable manner and an in-depth electrical characterization of the 1T phase is wanting at large. Here we demonstrate a controllable and scalable 2H to 1T phase engineering technique for MoS$_2$ using microwave plasma. Our method allows lithographically defining 1T regions on a 2H sample. The 1T samples show excellent temporal and thermal stability making it suitable for standard device fabrication techniques. We conduct both two-probe and four-probe electrical transport measurements on devices with back-gated field effect transistor geometry in a temperature range of 4 K to 300 K. The 1T samples exhibit Ohmic current-voltage characteristics in all temperature ranges without any dependence to the gate voltage, a signature of a metallic state. The sheet resistance of our 1T MoS$_2$ sample is considerably lower and the carrier concentration is a few orders of magnitude higher than that of the 2H samples. In addition, our samples show negligible temperature dependence of resistance from 4 K to 300 K ruling out any hoping mediated or activated electrical transport.

An all two-dimensional (2D) architecture involving vertical integration of van der Waals (vW) materials has been explored as a platform for the future semiconductor technology. Hybrid devices consisting of physically stacked layers of MoS$_2$ and other vW materials has also been explored for various device applications; MoS$_2$/Graphene interfaces for improved electrical contacts, MoS$_2$/h-BN hybrid systems for mobility engineering and electrostatic confinement, MoS$_2$/WSe$_2$ PN-junction devices have been reported. Rather than stacking, a lateral monolithic integration of regions with different electrical properties while preserving the two-dimensionality is an important ingredient for future microelectronics technology. The presence of polymorphic phases with distinct electrical properties while maintaining the layered nature makes MoS$_2$ a potential system.

Among the reported structural phases, 2H, 2H', and 3R are semiconductors, 1T' and 1T'' are narrow bandgap semiconductors and 1T is metallic. The 2H is the most widely explored phase for device applications. The 1T phase has recently gained attention as an electrode for energy storage, hydrogen evolution and as a low-resistance electrical contact for 2H MoS$_2$ devices. The 2H phase belongs to the space group $P6_3/mmc$ with a trigonal prismatic coordination between Mo and S atoms and 1T belongs to $P6_3/mmc$ with an octahedral coordination between the Mo and S atoms. The 1T' and 1T'' are distorted 1T phases. The possibility of controllably and selectively engineering metallic 1T MoS$_2$ regions starting from the semiconducting 2H MoS$_2$ provides a new route for monolithic 2D circuits.

2H to 1T phase transition happens via relative gliding of the Mo and S planes. The transition has been achieved using alkali metal or hydrogen intercalation, substitutional doping by Re atom, annealing accompanied energetic electron-beam irradiation, plasmonic hot electrons and Argon plasma. Intercalation gives a mixture of 1T, 1T' and 2H phases. The 1T phase thus obtained is reported to be thermodynamically unstable and relaxes to 1T' or 2H over time or above a temperature range of 150 °C, which is in the range of standard sample processing temperatures for device applications. The recent report on the solution phase synthesis of 1T MoS$_2$ in large concentrations, from the 2H phase yielded only nanosheets and, is not suitable for scalable device fabrication schemes. The phase conversion using Argon plasma yields predominantly the 2H phase and the concentration of 1T phase is around 40%. 1T MoS$_2$ obtained by high-energy
electron bombardment in a transmission electron microscope falls short in the yield and in the adaptability required for the microelectronics industry.

There is a lack of an in-depth electrical characterization of metallic 1T MoS$_2$. Existing reports confine to two-probe (2P) transport measurements on polymorphic samples$^{11,25,34}$. A four-probe (4P) electrical characterization is essential since 2P measurements are influenced by the behaviour of contacts. A linear current-voltage ($I$-$V$) characteristics, void of gate-voltage dependence, down to the cryogenic temperatures is necessary in establishing a metallic nature. The 1T samples obtained by Argon plasma$^{34}$ treatment have shown response to gate voltages, atypical of a metallic state and, in contrast to those reported elsewhere$^{11,25}$. Temperature dependent transport measurements are reported only down to 100 K, however, the sample shows a large increase in the resistance as the temperature is lowered$^{11}$. A table summarizing the existing studies on electrical transport properties, scalability and stability on 1T MoS$_2$ is provided in Supplementary Information S1.

In this manuscript, we demonstrate a method to engineer 1T phase on 2H MoS$_2$ samples exfoliated from bulk crystals with arbitrary thickness and area, in a controllable and scalable manner. Our process involves treating mechanically exfoliated samples with high-power forming-gas microwave plasma which results in a layer-by-layer thinning accompanied by a structural phase conversion from 2H to 1T. The presence of plasma etching helps us to realize few-layer 1T MoS$_2$ samples from thicker exfoliated samples. We show that our technique can be used to selectively engineer the 1T phase on 2H MoS$_2$ samples with the help of standard lithography techniques. We perform an in-depth structural characterization using high-resolution transmission electron microscopy (HR-TEM) and Raman spectroscopy. We also examine the evolution of photoluminescence (PL) spectra as a function of plasma treatment to study the phase transition. Unlike the intercalation route, our process is faster and we do not find signatures of 1T$'$ or 1T$''$ phases. Our process yields extended 1T regions with an areal coverage in excess of 70% over the 2H phase. The 1T samples show a temporal stability in excess of a few weeks and a thermal stability up to 300 °C in ambience. We conduct 2P transport studies on lithographically defined 2H and 1T regions on the same sample for a direct comparison of electrical properties. We also perform 4P electrical transport studies on a few layer 1T MoS$_2$ sample. The contacts on the 1T phase show a clear Ohmic behaviour at all temperatures from 300 K down to 4 K and the transport show little response to the gate voltage, indicative of a metallic phase. The carrier concentration $\sim 10^{15}$ cm$^{-2}$ and sheet resistance $\sim 108 \, \Omega / \square$, suggest that the sample is in the metallic regime. In addition, our sample also qualifies the Ioffe-Regel criteria for metallic conduction. We observe negligible temperature coefficient of resistance down to 4 K for the 1T phase unlike other reports on 1T MoS$_2$,$^{11}$ ruling out hopping-mediated or activated transport in our samples.

**Results and Discussion**

The MoS$_2$ samples, exfoliated from bulk crystals are transferred on to Silicon substrates hosting a 300 nm SiO$_2$ layer. These samples are treated with forming gas (10% H$_2$ + 90% Ar) microwave plasma with 40% input power to the magnetron$^{37}$. The plasma treatment results in a layer-by-layer etching of the sample accompanied by a structural phase transformation from the 2H to the 1T phase. Lower microwave power levels result only in a layer-by-layer etching and do not yield any phase change.

**TEM analysis.** The crystallinity of the plasma treated samples is examined using HR-TEM. Figure 1(a) shows HR-TEM image of a representative plasma treated few-layer MoS$_2$ sample. The regions shaded in purple, green and brown represent the 2H, 1T and, an intermediate state between the 2H and the 1T phases respectively. Based on our TEM analysis conducted over many samples, we estimate a lateral coverage for the 1T phase in excess of 70%. We believe, this is a lower bound to the coverage since we also observe a back conversion of the 1T to the more stable 2H phase under prolonged exposure of high energy electron beam during imaging (Supplementary Information S2). We also note that the HR-TEM images do not show signatures of other distorted structural phases such as 1T$'$ or 1T$''$. The selected area electron diffraction (SAED) pattern shown in the top-right inset exhibit sharp diffraction spots, inferring good crystallinity of our samples. HR-TEM images of two more samples showing extended 1T regions are shown in Supplementary Information S3.

Figure 1(b) shows a magnified image of the 2H region while Fig. 1(c) shows that of the 1T region obtained from the same sample as in Fig. 1(a). The lower panels in Fig. 1(b,c) shows the intensity line-profiles obtained along the directions indicated by the dashed-lines in the respective panels. The arrangements of Mo and S atoms for the 2H and 1T phases are shown in the overlaid diagrams in Fig. 1(b,c) respectively. In the 2H phase the S-Mo-S atoms are arranged in an A-B-A stacking fashion along the c-axis. Mo atoms appear brighter in intensity compared to the S atoms in the TEM images owing to its higher atomic number$^{38}$. Due to this reason, the intensity for the S-peaks is very weak for monolayer MoS$_2$. For a few-layer 2H MoS$_2$, the position of S atoms in one layer coincides with that of the Mo atoms in the adjacent layer. This gives an appreciable intensity for the peaks corresponding to the S sites$^{38}$, as evident from the intensity profile shown in the bottom panel of Fig. 1(b). We extract a nearest Mo-Mo separation of 3.19 (+/- 0.08) Å from the HR-TEM images.

In the 1T phase, the Mo atom is octahedrally coordinated with six S atoms with the S-Mo-S in an ABC stacking fashion. In this case, atoms in one layer align with the corresponding atoms in the adjacent layer. This arrangement makes the intensity of the peaks corresponding to the S atoms in 1T phase much weaker compared to that of the 2H phase in the TEM images. As seen in the bottom panel of Fig. 1(c) there are two small peaks corresponding to the Sulphur atoms in the top and bottom plane (S and S$'$) while the peaks for Mo atoms are clearly visible. For the 1T phase the Mo atoms form a hexagonal lattice as shown in Fig. 1(c). We obtain a mean nearest Mo-Mo separation of 3.19 (+/- 0.04) Å from line-profiles taken along different directions in the (001) plane [Supplementary Information S4]. These values are in good agreement with the reported ones$^{40}$. We rule out the presence of any 1T$'$ or 1T$''$ phases where Mo-Mo separations are unequal in different directions, as observed elsewhere$^{40}$.
Figure 1(d) shows a magnified HR-TEM image of a region where the 2H and 1T phases intersect. The lower panel shows intensity profile taken along the direction represented by the dashed-line in the corresponding TEM image. We also note that the relative intensity of the Mo peaks in the 1T region is higher than that of the 2H region; possibly due to the difference in the alignment of Mo atoms, corresponding to different layers, along the c-axis.

The transformation between the 2H and the 1T phases involves an intra-layer S plane gliding. For a few layer MoS2 sample, transition between the 2H and 1T phases also require an Mo-plane gliding. In support of this we observe in a few of our HR-TEM images, an intermediate atomic arrangement between the 2H and the 1T phases, as shown in Fig. 1(e). The visible stripe-like patterns in Fig. 1(e) is due to the rearrangement of Mo and S atoms during the transformation. A possible atomic arrangement is shown in the inset to Fig. 1(e). We note here that this transformation can also happen to regions subject to repetitive TEM imaging as a result of prolonged exposure to high energy electrons [Supplementary Information S2].

We also examine HR-TEM image of a pristine 2H MoS2 sample taken with the same exposure parameters as those for the 1T samples. Figure 1(f) shows the HR-TEM image and the inset shows a magnified view, 3 x 3 nm in area.

**Raman and PL studies.** We perform Raman scattering and PL studies on plasma treated samples. These samples consist of regions with different thickness starting from a few nanometres to a few tens of nanometres prior to the plasma treatment. Figure 2(a) shows optical images of a representative sample where the top panel
shows the pristine exfoliated sample while the bottom panel shows the image after a 7.5 minutes of plasma treatment. We have conducted Raman scattering studies on all the regions. Here we focus on regions labelled I and II. Figure 2(b,c) shows the Raman spectra from region I (region II). The black(red) traces in both Fig. 2(b,c) represent Raman spectra taken before (after) the plasma treatment. Samples post-plasma treatment (red traces) show clear J1 and J2 vibrational modes corresponding to the 1T phase (The Raman scattering studies conducted on other regions are shown in Supplementary Information S5).

To demonstrate the controllability and scalability of the process we use the Aluminium masking technique to selectively phase engineer the sample. Figure 2(d) shows optical images of the sample before (top) and after (bottom) the plasma treatment. The centre region (labelled I) on the bottom panel of Fig. 2(d) is masked and the remaining area is treated with the plasma and etched down to a thickness of ~6 layers of MoS2. Figure 2(e) shows the PL spectra of the sample before (black) and PL spectra from region II after (red) the plasma treatment. The sample is in excess of ~50 nm in thickness prior to plasma treatment and exhibits only a weak excitonic peak (black trace). The plasma treated region (II), reduced to 6 layers in thickness, does not exhibit any PL (red trace) in contrast to a pristine six-layer 2H MoS2, shown in blue-trace. Raman spectra of the sample before and after the plasma treatment are shown in the inset. Only region II, exposed to the plasma, develops the J1 and J2 peaks (red trace) while the Raman spectra of region I post plasma treatment (purple trace) is akin to that of the sample prior to the plasma treatment. The quenching of the PL spectra, post plasma treatment, as a result of a semiconducting to metallic phase transition is shown in Fig. 2(f). The optical images of the sample before and after plasma treatment is shown in the insets. The black-trace shows the PL spectra obtained from region I (~6 layers) and the red trace shows the PL spectra from the same region after the plasma treatment (~4 layers). While the PL spectra undergo a substantial quenching, the Raman spectra, shown in the inset, develop the characteristics J1 and J2 peaks as a result of the plasma treatment.
Post plasma treatment, our samples exhibit clear J₁ and J₂ peaks while the J₃ peak is very weak in intensity. In addition, we observe emergence of a peak at 180 cm⁻¹ which was not reported in the past. The J₁ and the J₃ peaks are predicted to be much lower in intensity compared to the J₂ peak. The relative intensities and the peak positions vary from sample to sample and process to process. 1T MoS₂ prepared by chemical routes exhibit a weaker J₁, J₂, and J₃ MoS₂ prepared by physical routes exhibit strong J₃ while the J₁ is very weak. Both the J₁ and J₃ peaks are clearly visible on electron-beam irradiated and Argon RF plasma treated samples while J₃ is not well formed.

Now we discuss the stability of the phase engineered 1T samples. Figure 3(a) shows the optical images of the sample before and after plasma treatment. Raman spectra from the region I of the sample before (black-trace) and after (red-trace) the plasma treatment is shown in Fig. 3(b). The green-trace shows Raman spectra obtained from the same region after keeping the sample for 27 days at ambient temperature and pressure. Both the red-trace and the green-trace show J₁, J₂, and J₃ peaks with similar shape and intensity suggesting good temporal stability of our samples. We also note here that the HR-TEM images taken after 30 days of plasma treatment also show rich concentration of the 1T phase suggesting good temporal stability of our samples.

Now we explore the stability of the 1T samples as a function of the annealing temperature. Figure 3(c) shows the PL spectra taken from the region labelled I of the sample shown in Fig. 2(f) post plasma treatment with positions of the J₁, J₂, and J₃ peaks marked. The green trace in (b) shows the Raman spectra taken after 27 days from plasma treatment. (c) PL spectra from region I of the sample shown in Fig. 2(f) before (black), after (red) plasma treatment and, subsequently annealing the sample at 300 °C for 5 minutes (cyan) and 15 minutes (magenta). The inset shows the Raman spectra for the same with corresponding colours.

Transport studies. Electrical transport studies are conducted on two kinds of devices. (1) On a device where a 1T region is lithographically defined on a pristine 2H MoS₂, for a direct comparison of electrical properties of both phases on the same sample. (2) On a fully phase engineered 1T MoS₂ device.

Figure 4(a) shows the optical image of the sample on which the central region enclosed between the dashed-lines (labelled 2H) is covered using a lithographically defined Al mask, and the flanked regions labelled 1T are exposed to the plasma and converted to the 1T phase. Post plasma treatment the mask is removed using NaOH (0.1 N) and Cr/Au source and drain contacts are fabricated onto both the 1T and the 2H regions. The Raman spectra of the 1T region shown in the Supplementary Information 56 exhibit the signature peaks, the J₁, J₂, and J₃ of the 1T phase. Figure 4(b) shows the 2P I-V characteristics of the 2H region at 300 K (red trace), 77 K (green trace) and 4 K (blue trace). The I-V characteristics of the 2H-region exhibit a Schottky behaviour at all temperatures and the span of the non-linearity increases as the temperature is lowered down to 4 K. We note that Cr/Au contacted MoS₂ generally exhibit non-linear I-V characteristics, which has also been verified by us independently. The inset to Fig. 4(b) shows the 2P conductance of the 2H region as a function of the back-gate voltage, Vbg at 300 K (red trace) and 4 K (blue trace). The device exhibits clear n-type behaviour with a field effect mobility of 16.4 cm²/V-s at 300 K and 84 cm²/V-s at 4 K, which are in the range of typically observed mobility values for an uncapped, back-gated 2H MoS₂, FET. In contrast, the I-V characteristics of the plasma treated region, 1T, shown in Fig. 2(c), exhibits excellent Ohmic behaviour at all temperatures down to 4 K. The inset shows the conductance of the 1T region as a function of Vbg. The device shows little change in conductance as Vbg is varied in a large voltage range of −20 to 40 V at 300 K (red trace) and −10 to 20 V at 4 K (blue trace). We also note that the 2P resistance of the 1T region shows only a small change (~12 Ohms) as the sample was cooled down to 4 K from 300 K while that of the 2H region shows a large variation in excess of three orders in magnitude.

Figure 3. (a) Optical images of the sample before (top) and after (bottom) plasma treatment, scale bar is 20μm. (b) Raman spectra of the sample, shown in (a), before (black) and after (red) plasma treatment with positions of the J₁, J₂, and J₃ peaks marked. The green trace in (b) shows the Raman spectra taken after 27 days from plasma treatment. (c) PL spectra from region I of the sample shown in Fig. 2(f) before (black), after (red) plasma treatment and, subsequently annealing the sample at 300 °C for 5 minutes (cyan) and 15 minutes (magenta). The inset shows the Raman spectra for the same with corresponding colours.
Electrical transport data at 4 K from a similar sample consisting of lithographically defined 1T and 2H regions is shown in the Supplementary Information S7. The 1T (2H) region shows linear (non-linear) I-V characteristics without (with) gate voltage dependence. Also, we have conducted 2P transport measurements on a monolayer phase engineered 1T MoS2 sample and verified the linear I-V characteristics and the absence of back-gate voltage dependence on conductance independently [Supplementary Information S8].

To exclude any contribution from the contact resistance to the electrical characteristics we conduct 4P transport measurements on an ~8 nm thick 1T phase engineered sample. The optical image of the device is shown in Fig. 4(d). The 4P I-V characteristics of the sample at 300 K (red) and 4 K (blue), shown in (d), probes labelled 8 & 9 are used for current sourcing and probes labelled 7 & 13 are used for voltage sensing. The inset shows the resistance vs $V_{bg}$ at 300 K (red) and 4 K (blue). (f) 2P I-V characteristics of the sample, shown in (d), taken across the probes 8 & 9 (blue) and 7 & 13 (cyan) at 4 K, showing a clear Ohmic behaviour. The inset shows Hall resistance of the sample at 4 K.

Figure 4. (a) Optical image of a selectively phase engineered sample. The region labelled 2H is masked and the regions labelled 1T are exposed during plasma treatment. (b,c) I-V curves from 2H & 1T regions respectively; 4 K (blue), 77 K (green) and 300 K (red). Insets show conductance of the corresponding regions as a function of $V_{bg}$ at 4 K (blue) and 300 K (red). (d) Optical image of a ~8 nm thick phase engineered 1T MoS2 sample with photo-lithographed electrical contacts, scale bar is 20 µm. (e) 4P I-V characteristics of the sample at 300 K (red) and 4 K (blue), shown in (d); probes labelled 8 & 9 are used for current sourcing and probes labelled 7 & 13 are used for voltage sensing. The inset shows the resistance vs $V_{bg}$ at 300 K (red) and 4 K (blue). (f) 2P I-V characteristics of the sample, shown in (d), taken across the probes 8 & 9 (blue) and 7 & 13 (cyan) at 4 K, showing a clear Ohmic behaviour. The inset shows Hall resistance of the sample at 4 K.

Conclusions

In this manuscript, we demonstrated a controllable and scalable 2H to 1T phase conversion technique for MoS2. The process involves treating exfoliated 2H MoS2 of arbitrary thickness with forming-gas microwave plasma. We performed an in-depth structural analysis using HR-TEM and Raman microscopy. Our processed samples consist mostly 1T phase. We did not find presence of other commonly observed phases such as 1T' or 1T". We
observed the evolution of the signature Raman peaks of 1T MoS$_2$ accompanied by quenching of the PL on plasma treatment, indicative of a metallic phase formation. We believe that the phase transition happens by the gliding of the S and Mo planes; HR-TEM images also show signatures of plane gliding in support of this. The momentum transfer from the ions in the plasma could be twisting the Mo-S bonds. Similar phase transition mechanism caused by momentum transfer induced plane gliding under the exposure of energetic ions and electrons are reported elsewhere\textsuperscript{12,34}. Those processes yielded nanoscale patches as opposed to extended 1T regions and also are prone to defects and disorder. The reducing atmosphere provided by the H$_2$ and the microwave heating could be annealing the defects, if any, resulting in extended low-disordered 1T regions in this case. In support of this, we note that the samples treated with plasma in the absence of H$_2$ did not show the J$_1$, J$_2$ and the J$_3$ peaks [Supplementary Information S10] and, these samples are found to be highly resistive. Our 1T samples withstood aging for more than a month and also showed a thermal stability up to 300 °C, making it suitable for standard device fabrication techniques. The transport measurements conducted on the same sample over various durations show negligible change in resistance. We demonstrated lateral monolithic integration of metallic 1T and semiconducting 2H phases with the help of standard lithography techniques. We have conducted extensive transport characterization of our 1T samples from 300 K down to 4 K. Both the 2P and the 4P I-V characteristics showed conducting 2H phases with the help of standard lithography techniques. We have conducted extensive transport characterization of our 1T samples from 300 K down to 4 K. Both the 2P and the 4P I-V characteristics showed negligible change in resistance. We demonstrated lateral monolithic integration of metallic 1T and semiconducting 2H phases with the help of standard lithography techniques. We have conducted extensive transport characterization of our 1T samples from 300 K down to 4 K. Both the 2P and the 4P I-V characteristics showed negligible change in resistance. We demonstrated lateral monolithic integration of metallic 1T and semiconducting 2H phases with the help of standard lithography techniques. We have conducted extensive transport characterization of our 1T samples from 300 K down to 4 K. Both the 2P and the 4P I-V characteristics showed negligible change in resistance. We demonstrated lateral monolithic integration of metallic 1T and semiconducting 2H phases with the help of standard lithography techniques.
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Author Contributions
M.T. conceived the problem. A.V. optimized the microwave plasma system. A.P.S. prepared the samples and performed the structural characterizations. A.P.S. and C.H.S. analyzed the Raman, PL. and T.E.M. data. C.H.S. and A.P.S. fabricated devices for the transport measurements, C.H.S. performed the transport measurements and analyzed the data. C.H.S. and M.T. co-wrote the manuscript.
Additional Information

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