Nature of Electrically Induced Defects in CVD-grown Monolayer MoS_2

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Supplementary Information

Supplementary note 1: <u>Electrical characterization</u>

All devices are electrically characterized inside an in-house developed vacuum probe station at 10^{-7} torr to eliminate affects of atmospheric species like moisture and oxygen on device performance. Transistors are characterized before (VD) and after (SD) electrical stress cycles for a more legitimate comparison. Low temperature measurements are also performed in the same vacuum probe station using an LN2 based open-loop cryogenic setup that reaches temperature as low as 77 K.

Supplementary note 2: <u>Raman characterization</u>

Raman spectra has been captured using a Horiba micro-Raman setup with a 532 nm laser and groove density/grating of 1800 g/mm. Raman spectra of monolayer MoS_2 of virgin and stressed devices has been obtained after calibrating the setup for a 520.7 cm^{-1} peak representing the signature Raman mode of silicon. Moreover, the Raman peak intensity values have also been normalized with respect to the silicon peak at 520.7 cm^{-1}.

Supplementary note 3: <u>Long-term electrical stress induced variation in threshold voltage</u>

Multiple field-effect transistors (device #2 to #5) in the back-gated configuration have been tested under various electrical stress conditions. This is shown in figure S1 (a-h). It is observed that all stressed devices exhibit lower threshold voltage than their virgin counterparts, irrespective of the stress condition. Moreover, shift in the threshold voltage is found to be greater when the devices are stressed closer to the subthreshold region of operation, figure S1(e-h).

Supplementary note 4: <u>Details of KPFM measurements</u>

All KPFM measurements are performed using Park system's AFM setup under ambient conditions. The Park's AFM setup comes with an in-built KPFM setup. In order to electrically ground the sample, a copper tape has been used to stick the sample on electrically conducting chuck of the AFM setup. The AFM tips used here are Pt/Ir coated Silicon probes-SCM-PIT-V2. The surface topography scan and KPFM scan happen simultaneously during which a lock-in amplifier is used to detect and amplify the error signal from the tip at 17 kHz. A DC bias is applied to the tip (3 V for these measurements) along with a small AC signal (17 kHz) while scanning along the same line with a scan rate of 0.5 Hz. The cantilever is made to oscillate close to its resonant frequency, 67 kHz in this case, to ensure maximum sensitivity. The sample substrate is highly conductive p-type Si which is grounded with respect to the conducting tip via a copper tape, as mentioned earlier.

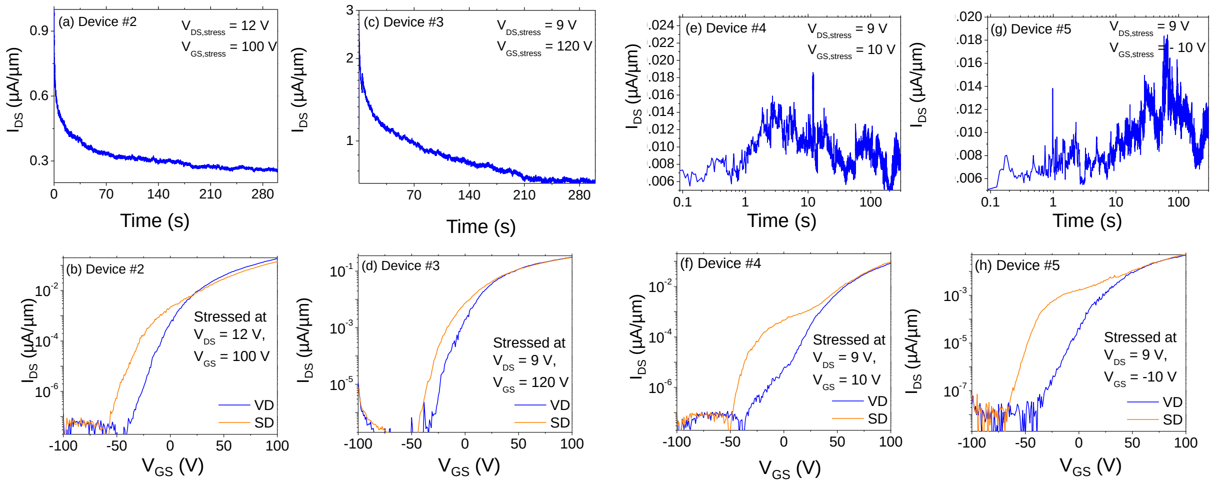

Figure S1: Multiple field-effect transistor devices electrically stressed under different conditions (a, c, e, g) and its impact on the transfer characteristics (b, d, f, h).

Supplementary note 5: <u>Hopping transport in another device</u>

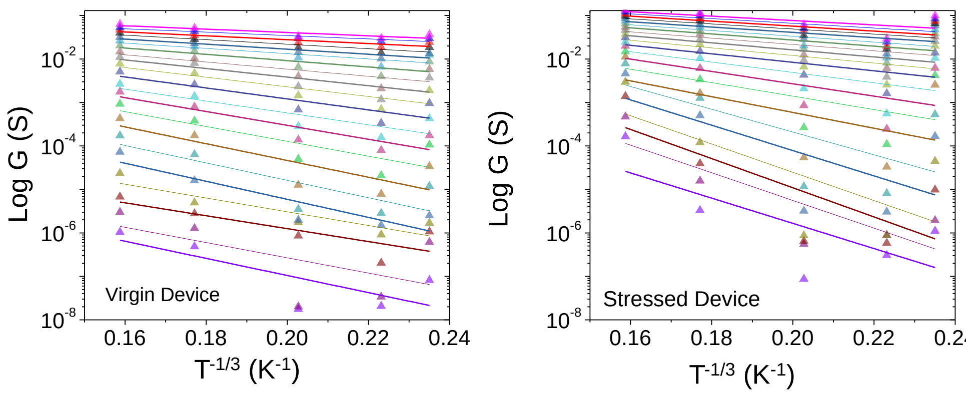

Figure S2: Temperature dependence of conductance of VD and SD for the following stress condition: V_{DS} = 9 V, V_{GS} = 10 V.

Supplementary note 6: <u>Temperature dependent Raman modes</u>

Raman spectra of virgin and stressed devices are captured at different temperatures, figure S2, to extract the evolution of E_{2g} and A_{1g} modes of MoS_2. The Raman shift values are plotted as functions of temperature and shown in figure 6. The experimental data is then used to extract temperature coefficients and Raman shift value at absolute zero temperature by fitting it to the following polynomial expression,

$$\omega (T) = \omega_0 + \chi_1 T + \chi_2 T^2 \quad \text{----------------------------} \quad (1)$$

where, ω0, χ_1 and χ_2 are Raman shift value at T = 0 K, first-order and second order temperature coefficients of both the characteristic Raman modes of MoS_2 respectively. The values are provided in table I of the main text. Reduced χ_1 for E_{2g} mode, marginally reduced χ_1 for A_{1g} mode and smaller value of ω_0 both modes imply two important facts – (i) LTES induced permanent change in the native Mo-S bonds of the 2-dimensional MoS_2 film and (ii) improved channel-substrate coupling which possibly facilitates better heat dissipation in our devices.

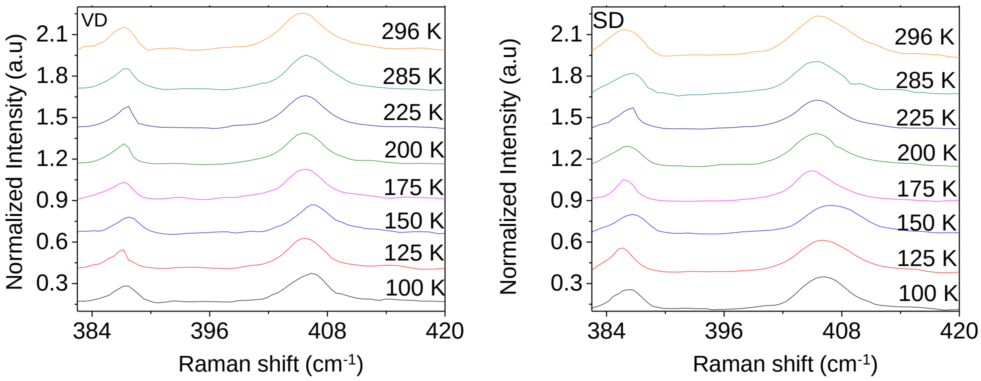

Figure S3: Raman spectra for virgin (VD) and stressed (SD) devices at various temperatures.

Temperature dependent Raman measurements are carried out inside a Montana Cryostat (at 10^{-6} torr chamber vacuum) equipped with a closed loop He-based cryogenic setup.

Supplementary note 7: Bandstructure of MoS_2 with weaker Mo-S bonds

(a) Details of simulation: We used Quantum ATK computational package the DFT simulations. A 7x7 supercell of monolayer MoS_2 with periodic boundary conditions was used for electronic band structure calculation. The simulating supercells were optimized with 0.01 eV/Å and 0.001 eV/Å3 force and energy cutoffs. The simulating setup consists of Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) functional, with 5x5x1 k point sampling. Grimme DFT-D2 Van der Walls (vdW) correction was incorporated to capture long-range force during the bond stretch. Periodic boundary condition was applied to replicate bulk MoS_2 planes. Vacuum space of ~15 Å was added on both sides of the MoS_2 plane to avoid interlayer interactions during the parodic boundary condition. Phonon band structure was calculated using the semiempirical forcefield method over a 1x1 MoS_2 monolayer supercell.

(b) It is observed that MoS_2 with stretched Mo-S bonds exhibits non-zero DOS of midgap states closer to CBM as compared to defect-less MoS_2, unlike defect-less MoS_2 for which the bandstructure and density of states are shown in figure S5. This is shown in figure S4 for MoS_2 with Mo-S bond stretched by 40 Å in the out-of-plane direction. These states are expected to pin the Fermi-level at lower energy. As a result, the critical charge concentration for the device to turn on is achieved at a lower voltage which manifests as lower threshold voltage in stressed devices. This is a possible explanation for the observed shift in the threshold voltage, however further studies must be performed to validate any change induced by electrical stress at the contact.

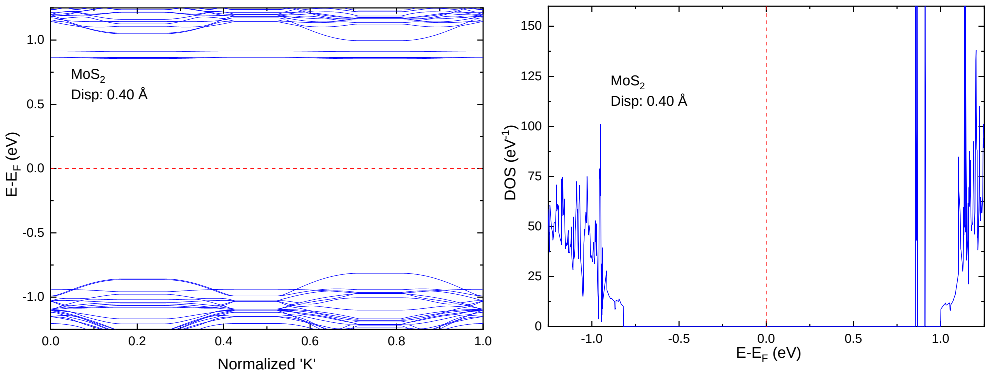

Figure S4: Bandstructure and DOS of MoS_2 with Mo-S out-of-plane bonds stretched by 40 Å.

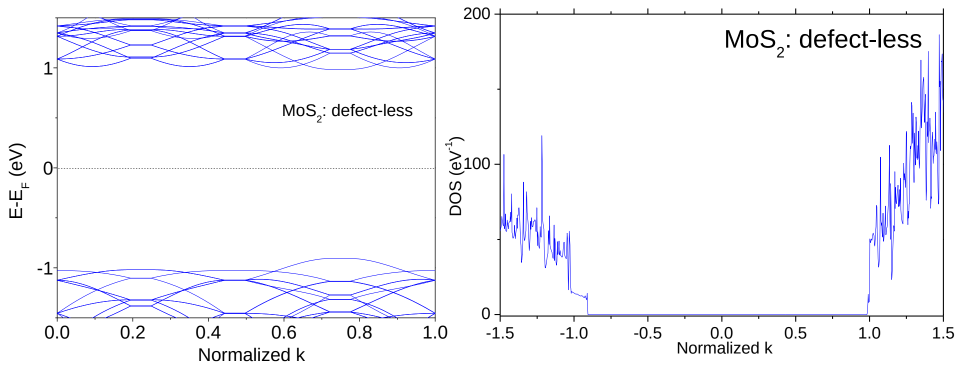

Figure S5: Bandstructure and DOS of defect-less MoS_2.