ADVANCED ELECTRONIC MATERIALS

Supporting Information

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Hole Injection and Rectifying Heterojunction Photodiodes through Vacancy Engineering in MoS_2

Shubhadeep Bhattacharjee, Ritwik Vatsyayan, Kolla Lakshmi Ganapathi, Pramod Ravindra, Sangeneni Mohan, and Navakanta Bhat**

Supplementary Information:

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Shubhadeep Bhattacharjee[1], Ritwik Vatsyayan[2], Kolla Lakshmi Ganapathi[3], Pramod, Ravindra[1], Sangeneni Mohan[1], Navakanta Bhat[1].

[1] Centre for Nano Science and Engineering, Indian Institute of Science, Bangalore

[2]Electrical Engineering, Indian Institute of Technology, Guwahati

[3]Dept. of Physics, Indian Institute of Technology, Madras

S1 Ultra-violet photoeletron spectroscopy measurements

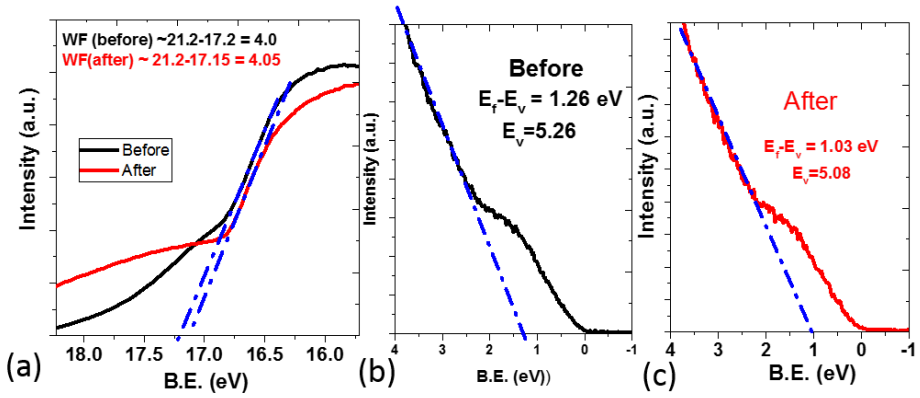

Fig. S1: UPS measurements on MoS_2 before and after vacancy engineering.

To understand the change in valence band position, UPS measurements before and after vacancy engineering were performed on the MoS_2 samples. We make two primary observations. First we observe that there is not much change in the Work function of the MoS_2 (Fig. S1 (a)). However, the difference between the fermi level and valence band maxima [E_f-E_v] has reduced significantly (Fig. S1(b,c) below) indicating a shift towards more p-type doping. Therefore there is an upward movement of valence band maxima of 0.18eV which closely matches the DFT calculations (~0.21 eV) for 7.4 % vacancy engineering. Furthermore it is important to note that this value is close to the activation energy of 0.17 eV (value of acceptor level above the valence band maximum) obtained using temperature dependent measurements. Hence the reduction in the VBM due to new oxygen acceptor levels along with use of high work function metal is responsible for effective p-type conduction.

S2 DFT Calculations.

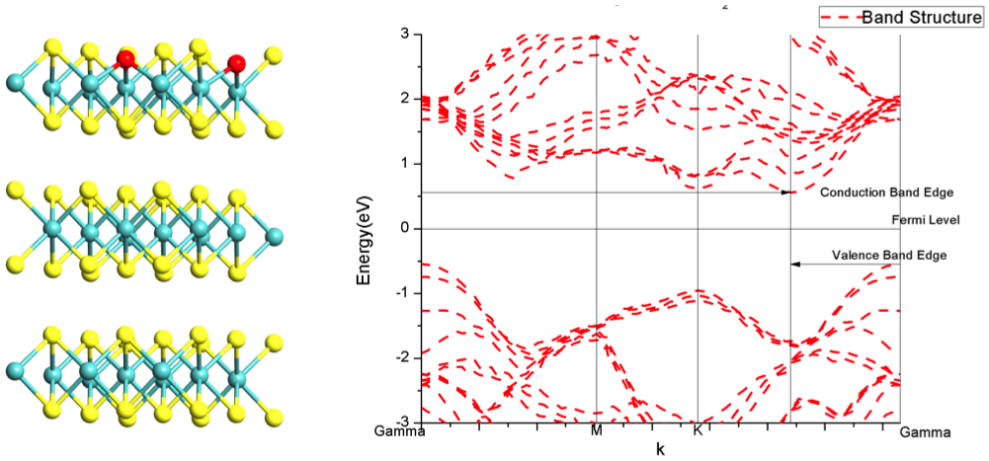

Figure S2: MoS_2 doped with 3.3% oxygen in the top layer and the change in bandstructure.

The Density Functional Theory calculations were performed using the open source SIESTA simulation package [1]–[2]. The electron-electron interaction energies are estimated within Generalized Gradient Approximation (GGA) with Perdew, Burke, and Ernzerhof (PBE) as exchange and correlation functional [3]. The Troullier-Martins pseudopotential is used to calculate interaction energies between ions and electrons [4]. Atomic orbitals are realized with Double Zeta basis plus the polarization orbital (DZP) basis set. The optimized Mesh Cutoff and the k-point grid is found to be 360 Rydberg and 6x6x1 respectively. For the modeling of oxygen doping within the MoS_2 crystal, we considered a 3× trilayer 2H-MoS2 supercells. The concentration of oxygen was varied in the top layer from 0% to 11%. Before performing the energy calculations and atomic structure calculation the structures was relaxed using Conjugate Gradients (CG) algorithm with the force tolerance per atom to be less than 0.01 eV/Ang. The bandstructures calculated from the SIESTA code are folded onto each other. An approximate unfolding was performed by comparing the bandstructure for a 3x3 supercell with the unit cell of pristine MoS_2. This was extended to the other cases with oxygen incorporation.

S3 Ambipolar behavior

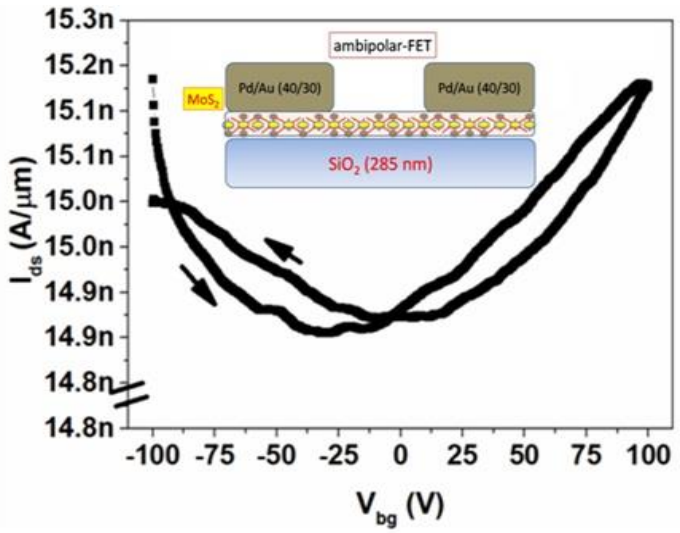

Figure S3: Ambipolar behavior is observed in very thin flakes after the vacancy engineering.

S4 ON current and On/Off ratio with time of argon ion exposure

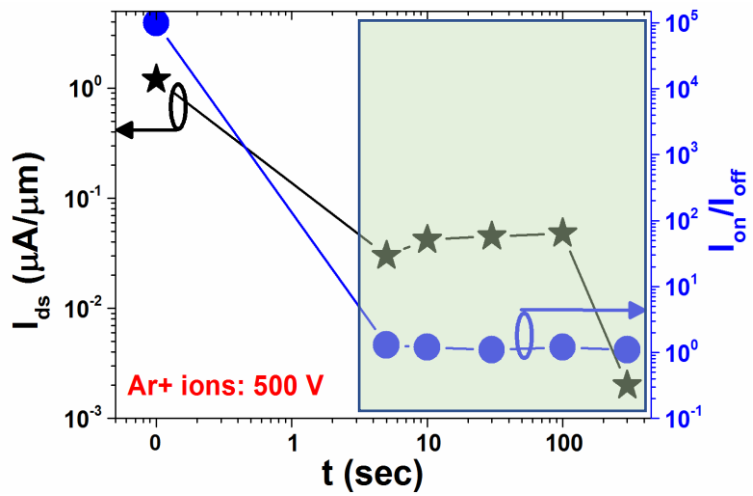

Figure S4: The On currents start increasing with time of exposure due to increased doping density, followed by a drop after 100 sec because of increased damage to the lattice structure.

S5 Calculation of doping density and depletion width

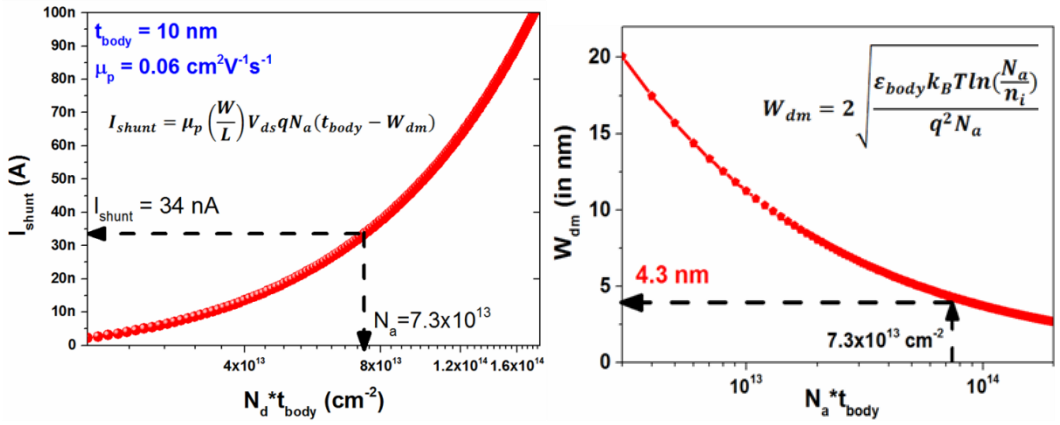

Figure S5: The doping density of 7.3 x10^{13} cm^{-2} is extracted for the devices with vacancy engineering for t=100 sec of exposure using the model described in [1]

S6 Raman map on p/n heterojunction

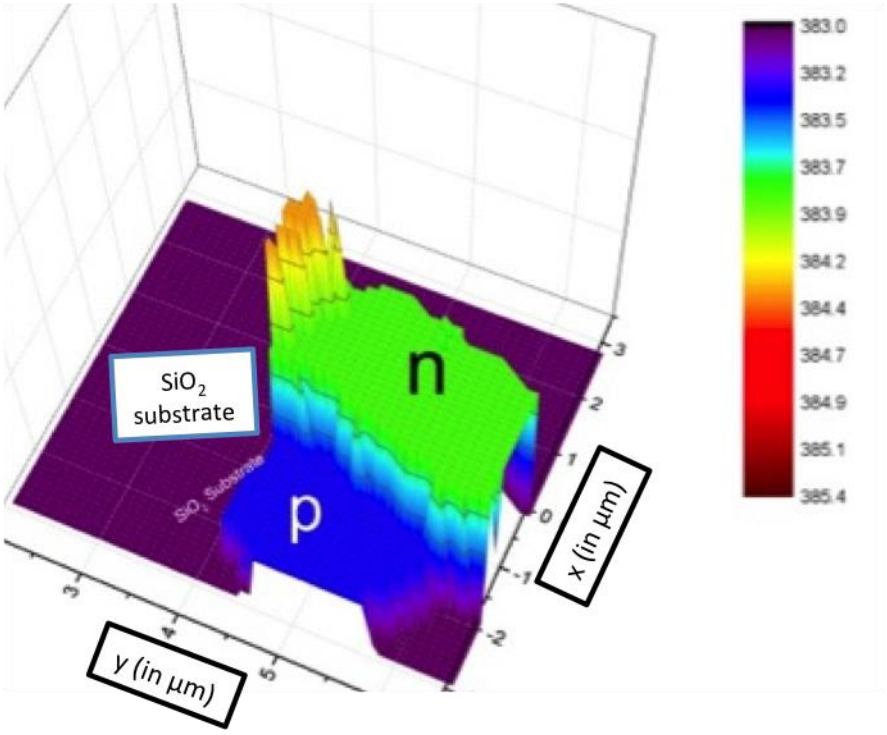

Figure S6: The spatial E^1_{2g} peak position reveals abrupt p/n junction

References:

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