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Ex-situ plasma doping of MoS_2 thin films synthesised by thermally assisted conversion process: simulations and experiment

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Abstract - Controllable doping of two-dimensional (2D) materials is one of the main research challenges associated with the practical realization of 2D semiconductors in hetero- and homo-junctions. We report that the selected-area treatment of MoS_2 films with nitrogen plasma can modify the resistivity of the film. To identify the underlying physical mechanism responsible for such observation, we systematically investigated the transport properties of cTLM-patterned contacts on ~70nm non-intentionally doped (NID), *p*- and *n*-doped MoS_2 films before and after plasma exposure. Electrical characterization demonstrates that *n*-type doping of MoS_2 is achieved by plasma-induced nitrogen doping. HR-TEM images confirm that no etching of the exposed film has occurred. Our experimental observations are supported by first principles atomic scale simulations suggesting the interaction of nitrogen with defects and vacancies in the poly-crystalline MoS_2 films as the origin of doping mechanism. The results indicate low-power nitrogen plasma is an effective approach for *ex-situ* doping of MoS_2.

Transition Metal Dichalcogenide (TMD) materials are comprised of neutral, single-atom-thick layers that are covalently or ionically bonded with their neighbors within each layer, whereas the distinct layers are held together via van der Waals bonding along the third (thickness) axis. One of the most significant groups of 2D materials is the layered TMDs, with the form MX_2 (M = Mo, Ti, Zr, Hf, V, Nb, Ta, Re; X = S, Se, Te). To date, MoS_2 has been the testing ground for many TMD based experiments. Doping semiconductors relies on the intentional introduction of impurity atoms into the semiconductor crystal lattice in order to modify properties of the material. Plasma doping of TMDs, as an *ex-situ* doping approach, has drawn significant attention in the research community [1-3]. In this study, ~70 nm non-intentionally doped (NID), *in-situ* Nb-doped (*p*-type) and Re-doped (*n*-type) MoS_2 films made by a Thermally Assisted Conversion (TAC) process [4], have been used to investigate the *ex-situ* plasma-assisted doping process. Doping type and concentration (assuming uniform distribution across the ~70 nm film) over a large area of ~1cm × ~1cm has been confirmed by Hall measurement (see Table 1) prior to plasma treatment. Fig. 1 (left) shows cTLM Ti/Au (20/200 nm) contacts formed by standard lift-off process on the three samples allowing uncovered region to be exposed to N_2 plasma in an Inductively Coupled Plasma (ICP) etching tool, where the ICP/RF powers were 100/0 W and the pressure was 30 mT with the N_2 gas flow rate of 50 sccm. Samples were exposed to a 4-minute plasma, re-measured electrically and exposed to a subsequent 4-minute plasma (identical condition).

Cross-section TEM imaging of the exposed and the metal covered MoS_2 regions acting as a mask during the plasma doping process has confirmed no physical etching of the MoS_2 films. The TEM image of the Nb-doped MoS_2 film, presented in Fig. 1(right), shows the poly-crystalline nature of the films, exhibiting grain boundaries. The resistivity of each of the three MoS_2 materials (*i.e.*, NID, Nb-doped, and Re-doped) obtained from cTLM analysis is shown in Fig. 2. As can be seen, both the NID MoS_2 film (showing *p*-type dominant carrier type - see Table 1) and the *in-situ* Nb-doped (*p*-doped) MoS_2 film, show incremental trend in resistivity as treated by N_2 plasma after each exposure step. Opposite trend in resistivity has been observed for the *in-situ* Re-doped (*n*-doped) MoS_2. This experimental finding is consistent with nitrogen acting as an effective *n*-type dopant in MoS_2. To further investigate the influence of nitrogen as an *n*-type dopant in MoS_2, we have performed atomic-scale simulations on Nb-doped (*p*-type) MoS_2. The electronic structure calculations have been performed using density functional theory (DFT) as implemented in OpenMX [5]. Fig. 3 compares the band structure of Nb-doped MoS_2 without (left) and with (right) nitrogen as dopant. As can be seen, the Fermi level of the Nb-doped MoS_2 (Nb on Mo site) is deep inside the valence band (*p*-type) while it is moved towards the edge of the valence band, *i.e.*, less *p*-doped, when molybdenum is replaced by nitrogen. This also introduces more energy states in the bandgap close to the conduction band.

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Table 1. MoS_2 film properties obtained by Hall measurements prior to plasma exposure (area ~1cm × ~1cm). Hall factor is assumed as unity.

Hall results	NID	Nb-doped	Re-doped
Carrier type	p	p	n
Mobility (cm^2/Vs)	0.62	0.4	0.14
Carrier concentration (cm^{-3})	2.39E17	2.48E17	6.19E17

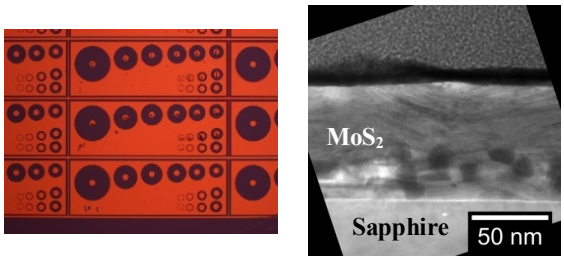

Figure 1. (left) CTLM contacts patterned on the MoS_2 films. (right) HR-TEM image of Nb-doped MoS_2 sample.

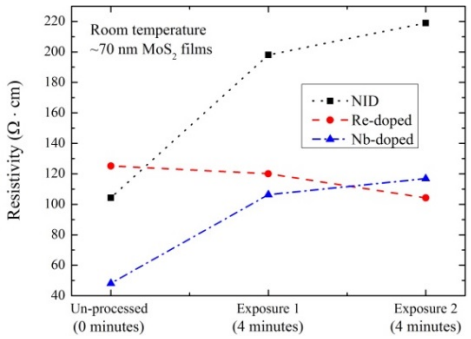

Figure 2. Resistivity of the MoS_2 films after various plasma exposure duration: zero minutes (un-processed), 4 minutes, and 8 minutes.

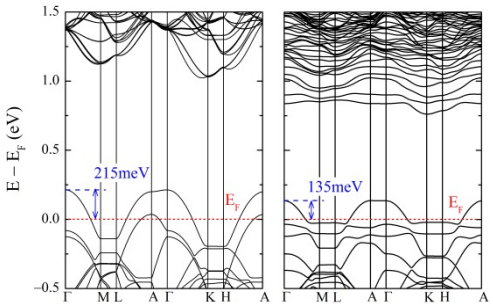

Figure 3. Band structures of Nb-doped (~3×10^{20} cm^{-3}) MoS_2 without (left) and with (right) nitrogen as dopant atom. Red dotted lines are the Fermi energy (E_F) level. As shown, nitrogen as dopant shifts E_F towards higher energies (*i.e.*, acting as *n*-dopant). Energies are referenced to E_F.