

DFT Modeling of O₂-Driven Fragmentation and Islanding from MoS₂ Nanoworms

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Abstract—Oxygen (O₂) doping in sputtered MoS₂ (MoS₂:O) impacted morphology of bulk p-type film (60 nm) leading to its structural shift from nanoworm to nanoisland as O₂ was increased to 2.4 sccm. DFT simulation revealed biaxial strain (7.54 % in c axis and -1.16% in a, b) due to Mo-O in standalone MoS₂:O film, minimizing its total energy, which drove this shift

Keywords— MoS₂, Oxygen doping, Morphology, DFT simulation

I. INTRODUCTION

Molybdenum disulfide (MoS₂) is a well-known n-type transition-metal dichalcogenide (TMDC) which has attracted significant attention due to its unique electronic, optical, and structural features [1]. MoS₂ is made from ionic-covalent bonded S and Mo and S-Mo-S layers are held together by weak van der Waals force enabling the deposition of atomically thin films of MoS₂. Furthermore, monolayer (ML) of MoS₂ exhibits direct bandgap (DBG) as contrary to its bulk counterpart making realization of electronic and optoelectronic devices to be suitable [1], [2]. Electronically MoS₂ exhibits n-type character, and to further tailor its electronic nature different doping and defect-engineering strategies were explored, but non-ideal morphological characteristics of film remained a concern. For instance, substitutional nitrogen (N₂) doping at the sulfur sites through the remote N₂ plasma treatment had been demonstrated to effectively induce p-type characteristics in MoS₂, making it

suitable for CMOS where bipolarity is desirable [3], [4]. Despite altering the electrical conductivity of the film such remote N₂ plasma had been observed to induce compressive strain in the lattice leading to growth of surface cracks [3]; and deviation in the work function of the material was also observed due to the N₂ doping for a no change in morphology [4].

Beyond defect passivation and electronic tuning, more pronounced morphological changes had been observed with other dopants as well. For instance, Ag doping altered the sheet-like morphology of pristine MoS₂ into particle-like structures with increased defect density and enlarged active surface sites [5]. Furthermore cobalt (Co) incorporation converted MoS₂ nanorod arrays into three-dimensional nanoparticle aggregates with expanded interlayer spacing, indicating lattice distortion and electronic structure modification [6]. Tungsten (W) doping during the CVD growth of MoS₂ had been shown to induce lattice distortion, strain, and enhanced electron-phonon scattering [7]. In the context of morphological deformation of MoS₂, the role of the substrate effect in addition to that for the dopants had also been demonstrated for Fe-doped monolayer of MoS₂ while it was grown separately on SiO₂/Si and sapphire substrates [8]. Tunable, hexagonal, unidirectionally aligned domains and film with triangular morphology was observed for MoS₂ grown on the SiO₂ [8], since MoS₂ grown on SiO₂ typically was found to experience significantly higher tensile strain

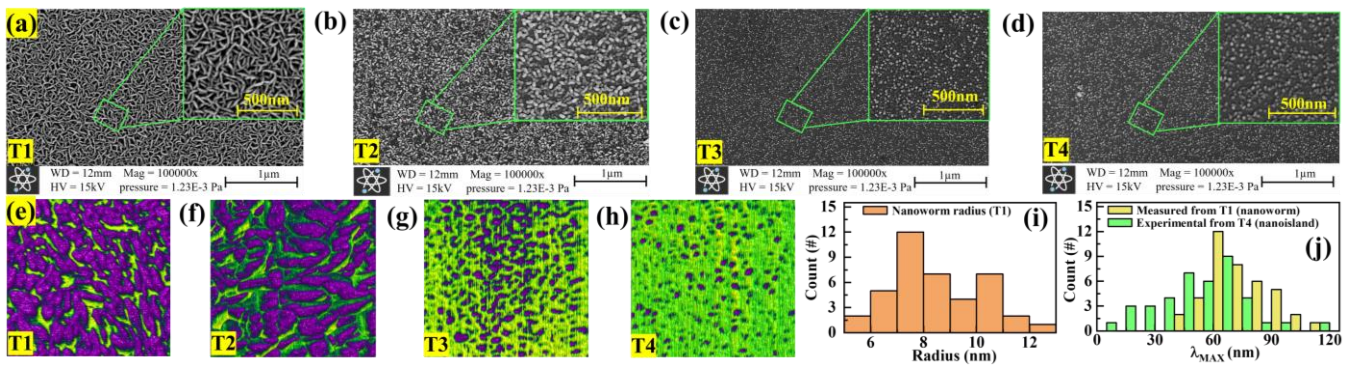


Fig.1. Field-emission scanning electron microscopy (FE-SEM) images of (a) MoS₂ and (b)-(d) MoS₂:O films - based on Ar:O₂ sccm in MoS₂ (a) T1 (20:0), (b) T2 (20:0.8), (c) T3 (20:1.6) and (d) T4 (20:2.4); (e)-(h) related AFM scans [300×300 (nm×nm)]; distributions of (i) measured radii (r) of nanoworms (T1) and (j) theoretical (T1) and experimentally obtained [measured island separation from T4 (ImageJ)] maximum perturbation length (λ_{MAX}) for the Rayleigh instability

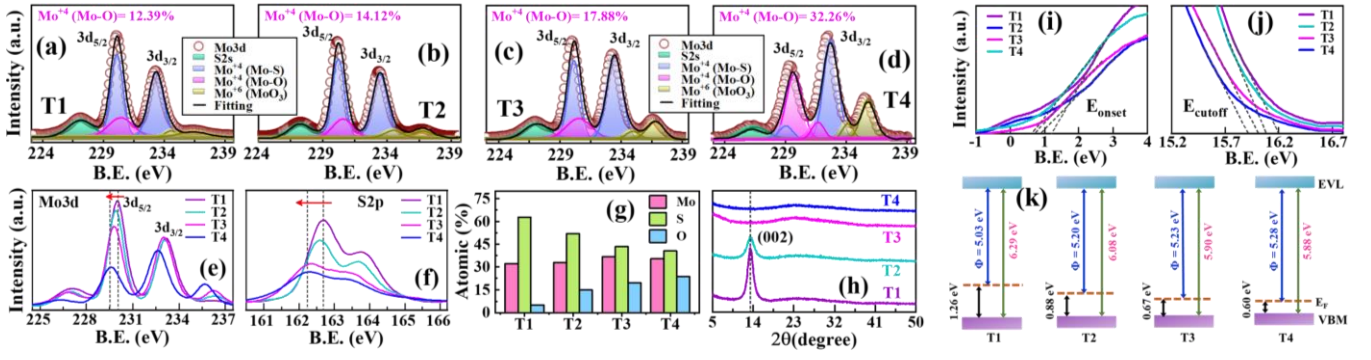


Fig. 2. (a-d) shows XPS characterized and deconvolved Mo3d [deconvolved into Mo^{4+} (Mo-S; $\sim 229.97\text{eV}$, 232.98eV), Mo^{4+} (Mo-O; $\sim 230.48\text{eV}$), Mo^{6+} (MoO_3 ; $\sim 234.36\text{eV}$, 236.22eV), and S2s ($\sim 227.02\text{eV}$)] for as-deposited MoS_2 and $\text{MoS}_2\text{:O}$ films corresponding to (a) T1, (b) T2, (c) T3, and (d) T4; (e-f) shows XPS measured binding energy (B.E.) shift for (e) Mo3d, and (f) S2p; (g) XPS measured atomic % in films; (h) characterized XRD and (i) photoemission onset (E_{onset}), and (j) secondary electron cutoff region (E_{cutoff}) through UV-photoemission spectroscopy (T1 – T4). Work function (Φ) and valance band maximum (VBM) [EVL – vacuum level] were determined by $\Phi = h\nu - E_{\text{cutoff}}$ and $\text{VBM} = h\nu - E_{\text{cutoff}} + E_{\text{onset}}$. Photon energy ($h\nu$) was 21.22eV [He-I source].

than it could have been on sapphire due to thermal expansion mismatch, leading to pronounced spectral redshifts and modified structural properties [9].

Environmental exposure had further been shown to significantly impact the structural and electronic characteristics of MoS_2 . However, O_2 had been recently shown to be a p-type dopant for the MoS_2 due to spontaneous substitution of the sulfur atoms by O_2 in the monolayer MoS_2 leading to the formation of the $\text{MoS}_{2-x}\text{O}_x$ phase [10]. In contrast, harsh oxidation could typically promote MoO_3 formation, resulting in lattice disorder, structural fragmentation, and eventual etching of the MoS_2 crystal [10]. Subsequently, etching caused to the basal plane by excessive O_2 ($>20\text{ sccm}$) was shown to deteriorate the film quality of MoS_2 [11]. Likewise, incorporation of O_2 plasma at the time of CVD of MoS_2 was shown to degrade FET characteristics [12]. In the recent past, we have shown O_2 doped MoS_2 in the Ru/ $\text{MoS}_2\text{:O}$ /Pt RRAM could improve its temporal retention characteristics due to slow oxidation of the basal plane [13]. Accordingly, to better tailor the retention characteristics optimization of the bulk MoS_2 film (which is less susceptible to switching variability than monolayer) through the control of O_2 became more relevant. In fact, we have observed significant nano structural-morphology changes in the $\text{MoS}_2\text{:O}$ film (nano-worm to the nano-island), while the root cause of it had not been discussed previously, and by far our knowledge, neither such morphological distinction was previously observed in O_2 incorporated MoS_2 film.

In this work, morphology evolution from pristine bulk MoS_2 (nano-worms) to bulk $\text{MoS}_2\text{:O}$ (nano-islands) has been investigated through experiments and DFT simulation, so that impact of deposition process on the morphology of film could be comprehended for further successful integration of this process with the $\text{MoS}_2\text{:O}$ -based devices.

II. PROCESS RECIPES OF FILM DEPOSITION

MoS_2 (undoped) and O_2 doped MoS_2 films ($\text{MoS}_2\text{:O}$) were deposited on RCA cleaned p-Si ($<100>$) substrate using DC sputtering using target power of 60W [MoS_2 (99.99% pure) target] and deposition pressure of 5 mTorr . Depositions were conducted at 300°C with Ar to O_2 sccm ratio (Ar: O_2) of 20:0 (T1), 20:0.8 (T2), 20:1.6 (T3), and 20:2.4 (T4), resulting in a thickness of 60 nm , assessed by a surface profilometer (Model: Bruker). The crystal structures of the MoS_2 and $\text{MoS}_2\text{:O}$ films were analyzed using X-ray diffraction (XRD;

Rigaku Smart Lab) method. Surface morphologies of the films were characterized by field emission scanning electron micrograph (FESEM) and atomic force microscopy (AFM, Bruker). Chemical compositions and elemental states of the films were investigated using X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe III) equipped with an Al K α radiation source (1.48 keV).

III. CHARACTERIZATION AND DFT SIMULATION

Fig. 1(a)–(d) shows the surface morphologies of MoS_2 and $\text{MoS}_2\text{:O}$ films for varied O_2 characterized via FESEM (Apreo S LoVac) at $\times 100\text{k}$ magnification (insets at $\times 150\text{k}$). MoS_2 film exhibited nanoworm like structure with their diameter of $\sim 12 - 24\text{ nm}$ (Fig. 1(a)), whereas O_2 incorporation induced a distinct morphological transition from quasi-continuous nanoworm (Fig. 1(b)) to discrete nanoislands (Fig. 1(c)–(d)) via structural fragmentation and islanding - also validated by AFM measurement [Fig. 1(e) – (h)]. At the molecular level, O_2 preferentially was incorporated at the basal-plane sulfur vacant sites forming Mo–O, which locally perturbed the lattice. XPS analysis [Fig. 2(a)–(d)] further corroborates it, and deconvolution of the Mo 3d spectra revealed a dominant Mo^{4+} (MoO_2) contribution over the Mo^{6+} (MoO_3) indicating that oxidation in MoS_2 predominantly occurred within its basal plane during O_2 incorporation. Further, with increasing the O_2 , Mo 3d and S 2p peaks were shifted towards lower binding energies (BE) [Fig. 2(e) – (f)], which could be attributed to dominant tensile strain in the bulk film as might be resulting from the substitution of smaller and more electronegative oxygen (ionic radius $\sim 1.32\text{ \AA}$) in the place of sulfur ($\sim 1.82\text{ \AA}$). Lower O_2 atomic % (Fig. 2(g)) could lead to inhomogeneous strain distribution, which broadened XRD peak for the (002) plane [Fig. 2(h)]. To further quantify, density functional theory (DFT) simulations were performed using Synopsys QuantumATK® [14]. Pristine and oxygen-substituted MoS_2 hexagonal structures were modelled using $2\times 2\times 1$ supercells. The structure was surface cleaved along the (002) plane for the bulk condition (stacking in z direction – Fig. 3). Structural optimization was carried out via linear combination of atomic orbitals (LCAO) approximation and using the generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional. For the LCAO method, a medium basis set was utilized with norm-conserving pseudopotential (NCP) obtained from the PseudoDojo library. Density mesh cut-off of 55 Hartree , $7\times 7\times 7\text{ k-point}$ grid, and 298 K broadening were considered. Force tolerance of $0.05\text{ eV/\AA}$, $0.2\text{ \AA}$ step size, and

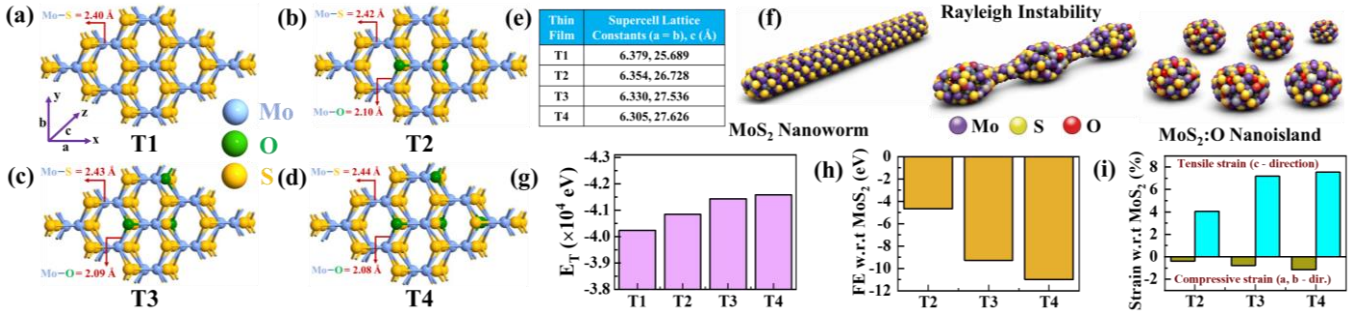


Fig. 3. Optimized geometric crystal structures with GGA for $2 \times 2 \times 1$ supercells [surface cleavage (002) and applying bulk-like condition (stacking in z)] (a) MoS₂ (T1) and (b)-(d) MoS₂:O [T2-T4]; (e) their in-plane (a=b) and out-of-plane (c) supercell lattice constants; (f) schematic illustrating Rayleigh instability that governed the morphology change (nanoworm to nanoislands); DFT calculated (g) total energy (E_T) [T1 – T4], (h) formation energy (FE) [$FE = E_{\text{MoS}_2\text{:O}} - E_{\text{MoS}_2} - nE_{\text{O}} + nE_{\text{S}}$] of MoS₂:O [T2-T4] w.r.t MoS₂ (n: number of atoms added/removed as per XPS at. %) and (i) % of biaxial strain in MoS₂:O w.r.t MoS₂

0.1 GPa stress error tolerance were used. The optimized structures revealed a systematic reduction in the bond length (Mo-O) [13.33% smaller than Mo-S] upon O₂ incorporation [Fig. 3 (a)-(d)]. Induced strain (%) in free standing films was calculated using $(a_d - a_p)/a_p \times 100$, both for in-plane (a = b) and out-of-plane (c) deformations of supercell lattice constants (Fig. 3(e)), where a_d and a_p are doped and pristine lattice constants of MoS₂, respectively; biaxial strain with O₂ was obtained for the highest 7.54% tensile in c and -1.16% compressive in a=b [Fig. 3 (i)]. From the electronic point of view, simulated total density of states (TDOS) [Fig. 4(a) – (d)] show a decrement of electron TDOS near the conduction band minimum (CBM) and corresponding increase of hole TDOS near the valance band maximum (VBM) showing p-type character of the MoS₂:O as O₂ increases, which was further corroborated through UV-photoemission spectroscopy (UPS) - used to determine VBM and E_F offsets [Fig. 2(k)]. In fact, simulated projected density of states (PDOS) of MoS₂ and MoS₂:O in Fig. 4(e) – (h) show CBM and VBM to be contributed by hybridized Mo d and S p orbitals, and their observed higher hybridization for the VBM (area-wise) is expected to localize the centroid (ε) of Mo d within the VBM. ε was calculated ([15]; Fig. 4(e)-(h)) and found to be displaced

by 218 meV (max.) with respect to MoS₂, increasing overlap with S p near the E_F [Fig. 4(i) – (l)], which justifies up-side shift of the VBM edge and reduction of BE agreeing with XPS (Fig. 2(e) – (f)), and UPS (Fig. 2 (i) – (k)). Furthermore, O₂ doping was found to stabilize MoS₂:O since it reduced the total energy of the system (E_T) [Fig. 3(g)], as well as the formation energy (FE) with respect to the undoped MoS₂ [Fig. 3(h)]. Thus, fragmentation and islanding from MoS₂ nanoworms due to O₂ doping (Fig. 3(f)) can be explained jointly by minimization of E_T and increase of biaxial strain (7.54 % stays higher than the onset of plastic deformation), as similarly in the light of Rayleigh instability (RI) [16]. RI predicts conversion of column (nanoworm) into droplets (nanoislands) by the action of strain field that could minimize the surface energy. For nanoworm radii distribution [Fig. 1(i)] the critical wavelength for RI considering isotropic surface energy was calculated as, $\lambda_{MAX} = \sqrt{2} \cdot (2\pi r)$, which closely correlated with the distribution of metric separation between nanoislands [Fig. 1(j)] in Fig. 1(d). Interestingly, film growth temperature was kept constant everywhere (300°C). Hence, unlike higher anneal induced fragmentation (largely by misfit strain), it was primarily driven by O₂, remarkably which minimized E_T for higher % change of biaxial strain; and it

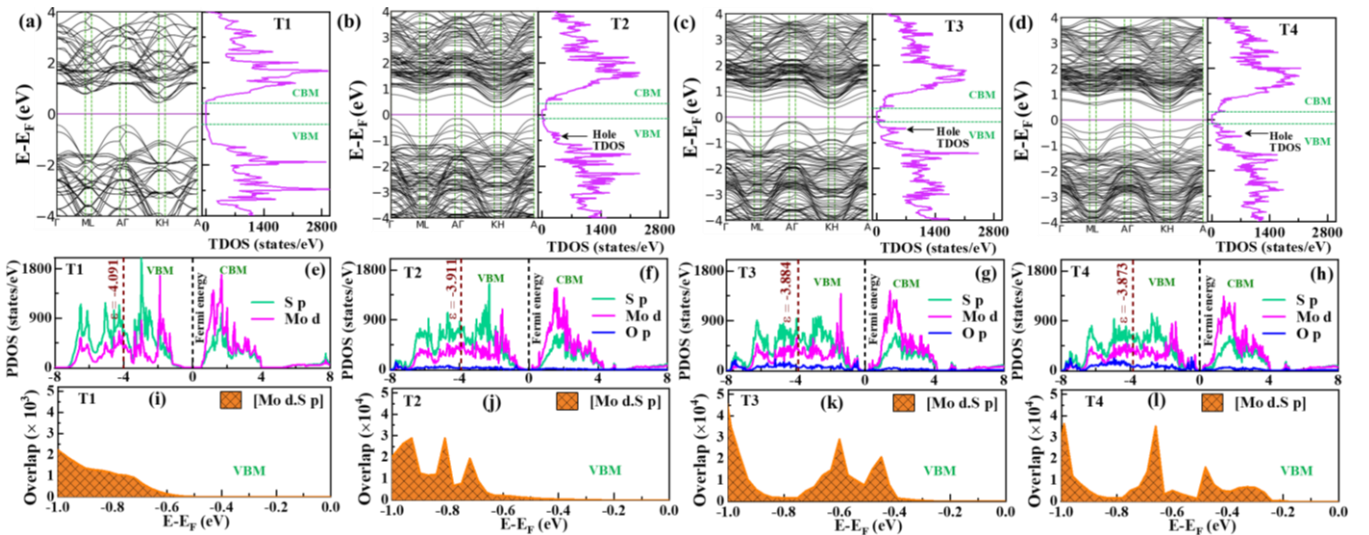


Fig. 4. DFT calculated band structure and total density of states (TDOS) for (a) T1, (b) T2, (c) T3, and (d) T4; calculated projected density of states (PDOS) due to Mo d, S p, and O p orbitals (e) T1, (f) T2, (g) T3 and (h) T4. Shifting of d-band centroid (ε) in VBM from the Fermi energy level (E_F) was calculated by taking the weighted average, $\varepsilon = \frac{\int_{E_F}^{E_F} E \cdot PDOS(E) dE}{\int_{E_F}^{E_F} PDOS(E) dE}$, where, $PDOS(E)$ is the PDOS of Mo d as a function of energy (E); (i) – (l) orbital overlap (in valance band) as the scalar product of PDOS of Mo d and S p (Mo d. S p) versus $E - E_F$

aptly explains the observed morphology shift from MoS₂ nanoworms to thermodynamically stable MoS₂:O nanoislands.

IV. CONCLUSION

Detail DFT simulation showed that, O₂ incorporation significantly impacted morphology of the bulk MoS₂:O film, which was credited to O₂ induced biaxial strain and minimization of the total energy in the standalone MoS₂:O that favored islanding from the nano-worms. The framework should be helpful for the optimization of p-MoS₂:O recipes for better film uniformity and related process control.

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