Growth of highly conducting MoS$_{2-x}$N$_x$ thin films with enhanced 1T’ phase by pulsed laser deposition and exploration of their nanogenerator application

Swati Parmar, Neetu Prajesh, Minal Wable, Ram Janay Choudhary, Suresh Gosavi, Ramamoorthy Boomishankar, Satishchandra Ogale

Highlights
MoS$_{2-x}$N$_x$ films grown on c-Al$_2$O$_3$ and ITO/PET by pulsed laser deposition in NH$_3$

- Increased work-function of MoS$_{2-x}$N$_x$ films over pristine MoS$_2$ is realized
- p-type doping with high conductivity and 1T’+2H dual polymorph state is realized
- Impressive Triboelectric Nanogenerator application is demonstrated with MoS$_{2-x}$N$_x$

Parmar et al., iScience 25, 103898
March 18, 2022 © 2022 The Author(s).
https://doi.org/10.1016/j.isci.2022.103898
Growth of highly conducting MoS$_2$-$x$N$_x$ thin films with enhanced 1T’ phase by pulsed laser deposition and exploration of their nanogenerator application

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SUMMARY
High-quality growth of MoS$_2$-$x$N$_x$ films is realized on single-crystal c-Al$_2$O$_3$ substrates by the pulsed laser deposition (PLD) in ammonia rendering highly stable and tunable 1T’/2H biphasic constitution. Raman spectroscopy reveals systematic enhancement of 1T’ phase component due to the incorporation of covalently bonded N-doping in MoS$_2$ lattice, inducing compressive strain. Interestingly, the film deposited at 300 mTorr NH$_3$ shows ~80% 1T’ phase. The transport measurements performed on MoS$_2$-$x$N$_x$ films deposited at 300 mTorr NH$_3$ display very low room temperature resistivity of 0.03 m$\Omega$-cm which is 100 times enhanced over the undoped MoS$_2$ grown under comparable conditions. A triboelectric nanogenerator (TENG) device containing biphasic MoS$_2$-$x$N$_x$ film as an electron acceptor exhibits a clear enhancement in the output voltage as compared to the pristine MoS$_2$. Device architecture, p-type N doping in MoS$_2$ lattice, favorably increased work-function, multiphasic component of MoS$_2$, and increased surface roughness synergistically contribute to superior TENG performance.

INTRODUCTION
Transition metal chalcogenides (TMCs) have rapidly acquired the status of technology materials of interest during the past decade because of their immensely interesting application-worthy physical properties (Jarriwa et al., 2014)(Sebastian et al., 2021) (Barani et al., 2021) (Zhang et al., 2019) (Lee et al., 2017) (Briggs et al., 2019) (Mak et al., 2019), (Shin et al., 2012). Amongst the various materials belonging to this class, MoS$_2$ has perhaps been the most investigated one in recent years, a remarkable feature of MoS$_2$ being its intrinsic ability to support multiple polymorphs (Acerce et al., 2017). The polymorphs of MoS$_2$ afford wide bandgap tunability, with 1T’ phase being metallic and its polymorphs being metastable semiconductors with bandgap from <0.8 meV to 1.9 eV (Zhao et al., 2018). This aspect has brought MoS$_2$ to the center stage along with graphene and other 2D carbides and nitrides from the standpoint of both fundamental research and technological applicability.

Structurally, a monolayer of MoS$_2$ consists of a layer of three atoms in zigzag configuration, where one Mo atom is sandwiched between the two S atoms and the layers are stacked with very weak van der Waals forces. The primary polymorphs of MoS$_2$ are 1T (trigonal phase), 1H and 2H (hexagonal phase), and 3R (rhombohedral phase). Amongst these phases, the 1T phase is the least stable because of its thermodynamically metastable nature and tends to form the more stable 2H phase by reorganizing its stacking layers and geometry. The metastable 1T phase can also transform to other polymorph intermediates such as 1T’, 1T”, and 1T’’ via Jahn-Teller distortions (Zhao et al., 2018). Indeed, doping of octahedral and tetrahedral geometry in VDW in TMDCs drives several factors such as registry of interlayer stacked atoms, tilting of octahedrons, bond length, and bond angle, which cause structural distortions leading to the superlattices of a$_2$ × 2a$_2$ dimer chain (1T’), 2a$_2$ × 2a$_2$ diamond shape (1T”) and 3a$_2$ × 3a$_2$ trimerized clustering (1T’’’) (Zhao et al., 2018). A well-established method of formation of 1T phase from 2H phase of MoS$_2$ is the alkali ion (Li”, Na” and K”) intercalation route.

Controllable in-situ doping of 2D materials is highly desirable for high-performing heterojunction devices to control the electronic structure, device parameters, and overall device functionality. In this regard, many strategies have been developed to enhance the MoS$_2$ electronic properties such as molecular doping of 2D materials is highly desirable for high-performing heterojunction devices to control the electronic structure, device parameters, and overall device functionality. In this regard, many strategies have been developed to enhance the MoS$_2$ electronic properties such as molecular...
surface doping by oleylamine (Rosa et al., 2016), polyethyleneimine (Du et al., 2013), and benzyl viologen (Kirya et al., 2014) for effective electronic charge transfer (Tang and Jiang, 2015). Nevertheless, the non-covalent bonding behavior of these doped molecules is volatile, which makes it difficult to control the doping concentration over time and stabilize the desired phase(s). Doping of transition elements (Re, W, Pd, Cu, Co, Ni, Fe, Nb etc.) (Gao et al., 2020) (Fu et al., 2020) (Martinez et al., 2018), noble metal el-
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The growth of MoS$_2$-N$_x$ (anionic doping) thin films examined in this study was accomplished by employing NH$_3$-assisted PLD for in-situ N doping in MoS$_2$ lattice via laser-generated plasma. A comprehensive and rigorous analysis of Raman, XPS, VBS, and XANES spectra for the MoS$_{2-x}$N$_x$ deposited under 10, 100 and 300 mTorr NH$_3$ pressure reveals that substantial enhancement in the 1T'-phase component results for films grown at 300 mTorr NH$_3$ pressure. It can be attributed to the substitution of S with N forming its covalent bonding with the Mo atom. While the possibility of incorporation of some hydrogen cannot be ruled out, we did not find evidence of the same in the set of characterizations employed. The growth pressure also plays a key role in the tunability and stabilization of the 1T' phase. Interestingly, the carrier transport properties also evolve rapidly as a function of doping rendering very high electrical conductivity in films grown at high (300 mTorr) ammonia pressure. We also examined the applicability of such highly doped films for the triboelectric nanogenerator (TENG) device by growing them on flexible conducting ITO/PET substrate at 100 °C. Notably such films can be expected to be poly or micro-crystalline, yet the grains could be expected to preserve the virtues of the doping effects. Indeed, the device based on this material demonstrated impressive voltage/current output with the p-type property of the material getting reflected therein. It is important to note that the N doped MoS$_2$ material is in itself very interesting and is an important object of this study. Dry processing routes such as PLD are compatible with clean deposition environments and as such once proper growth parameters are identified, multilayer structures involving other metal oxides, sulfides and nitrides would be feasible. TENG application is used as a proof of concept to elucidate how the nitrogen doping could affect the involvement of such doped 2D material in a device configuration.

**RESULTS AND DISCUSSIONS**

**Structural and surface characterization**

The Raman spectra for N doped MoS$_2$ grown on single crystal c-Al$_2$O$_3$ (0001) substrate by using PLD in ammonia at pressures of 10, 100, and 300 mTorr are shown in Figure S1. All the spectra were normalized vis-à-vis the high-intensity A$_{1g}$ phonon mode for better comparison, as this mode is present in all cases and is common for both the 1T' and 2H phases of MoS$_2$. It is observed that the 300 mTorr film shows remarkably strong intensity for J$_2$, J$_3$ and E$_{2g}$ phonon modes over the 10 and 100 mTorr cases; and the J$_2$ mode contribution gets smaller in the order of 300 mTorr > 100 mTorr>10 mTorr. All the observed Raman modes are tabulated in Table 1. Two distinct zone center first order sharp peaks at ~406 cm$^{-1}$ and ~382 cm$^{-1}$ corresponds to A$_{1g}$ (out of plane) and E$_{2g}$ (in-plane) modes, respectively, in the case of pristine MoS$_2$ and 300 mTorr grown MoS$_2$-N$_x$ represent the 2H phase component (Figure 1A). The red-shift in the vibrational frequency in the doped film (Figure 1A, inset) can be attributed to the change in intra and intermolecular force constants of VDW MoS$_2$. The packing of MoS$_2$ lattice is affected by the external defects and dopants that change the intermolecular distances and hence the intermolecular force constants, resulting in the red shift of the A$_{1g}$ phonon mode. Interestingly, the peak splitting of E$_{2g}$ mode into and is significantly high in the 300 mTorr grown MoS$_2$ case, which corresponds to the symmetry breaking of the E$_{2g}$ phonon mode because of N doping (Parmar et al., 2019). Further, a slight increase in FWHM in the doped system is due to the defect states reflecting the structural distortion(s). Interestingly, the disappearance of peak at ~287 cm$^{-1}$ (resemble E$_{1g}$ in-plane mode of 2H MoS$_2$) in 300 and 100 mTorr NH$_3$ case depicts the enhancement of 1T' phase MoS$_2$ in the doped films. This implied that because of N doping in MoS$_2$ lattice, the structural distortion occurs that modifies the bond length and angle; and the structure of the 2H MoS$_2$ transforms from 2H to 1T' phase, which modifies the electronic properties of the MoS$_{2-x}$N$_x$ film, as discussed in the later section.

| Phonon Mode | 300 mTorr (cm$^{-1}$) | 100 mTorr (cm$^{-1}$) | 10 mTorr (cm$^{-1}$) | MoS$_2$ (cm$^{-1}$) |
|-------------|----------------------|----------------------|---------------------|-------------------|
| A$_{1g}$    | ~405.6               | ~406.2               | ~407.2              | ~407.5            |
| E$_{2g}$    | ~376.1               | ~381.8               | ~381.4              | ~381.5            |
| E$_{1g}$    | ~285.4               | ~287.1               | ~287.6              | ~288.2            |
| J$_1$       | ~148.8               | ~151                 | ~151                | ~151              |
| J$_2$       | ~197, and ~222       | ~227                 | ~225.4              | ~225.1            |
| J$_3$       | ~333                 | ~332                 | ~332                | ~332              |

Here the intensities of the most intense (A$_{1g}$) peak are normalized.
Ubiquitously, the key spectral signatures noted at 151 cm\(^{-1}\), 196 cm\(^{-1}\), 226 cm\(^{-1}\), and 321 cm\(^{-1}\) correspond to the \(J_1, J_2,\) and \(J_3\) modes for the 1T\(^\prime\) phase, respectively (Guardia et al., 2014). Here the atomic vibrations of Mo zig-zag chain correspond to \(J_1\) and \(J_3\) modes and the vibration of S atoms corresponds to the \(J_2\) mode. The peak intensity for these modes can be seen to increase with the increase of NH\(_3\) pressure and is exceptionally high for the film grown at 300 mTorr ammonia. The high-intensity peak at 196 cm\(^{-1}\) (\(J_2\)) with the broad full-width half maximum (FWHM) represents the defect generated low frequency mode leading to the shortening of the distance between Mo-Mo zig-zag chains (Mignuzzi et al., 2015). Further, the splitting of \(J_2\) phonon at \(\sim 197\) and \(\sim 222\) cm\(^{-1}\) can be understood in terms of the accommodation of compressive strain generated into the film due to N doping, leading to the formation of the distorted octahedron. The peaks at 125 and 150 cm\(^{-1}\) correspond to the combinatorial mode that arises because of the difference of \(A_{1g}\) and \(E_{2g}\) mode from the frequency range 350–435 cm\(^{-1}\). A significant enhancement of polymorphic \(J_2\) mode and \(E_{2g}\) mode splitting corresponds to the co-existence of polymorph and enhanced doping concentration of N in MoS\(_2\) lattice.

The chemical structure and chemical components of pristine and doped MoS\(_2\) were further studied by the XPS technique. Figures 1B1, B2 and 1C1, C2 display the XPS spectra of pristine MoS\(_2\) and MoS\(_2\)-N\(_x\) (grown at 300 mTorr ammonia pressures) films. Based on previous reports (Yang et al., 2019), (Hu et al., 2018) N doped
MoS$_2$ (397-399 eV), MoN (395 eV), and Mo$_2$N (397 eV) related signatures correspond to specific Mo-N bonding/coordination. Therefore, the broad peak at around 397.3 eV observed in Figure 1C$_2$ can be assigned to Mo-N non-specific bonding. Further, the systematic shift toward the lower binding energy is found to be related to the increased doping concentration due to the increase in the NH$_3$ pressure from 10, 100, to 300 mTorr (Figures S2, S3, and S4). Therefore, it is important to calculate the concentration of N (N$_c$) in MoS$_2$-N$_x$ lattice. We quantitatively calculated the N$_c$ of the doped films grown at NH$_3$ pressures of 100 and 300 mTorr, and the corresponding values were found to be 18.5%, and 25%, respectively. This represents significant degree of nitrogen incorporation, more of an anionic alloy. The percentage was obtained by the ratio of integrated intensities of N 1s core to Mo 3d$_{5/2}$ (Azcatl et al., 2016).

The doublet structure of the Mo 3d and S 2p spectra illustrated in Figures 1B$_1$, B$_2$ and 1C$_1$, C$_2$ reflect the characteristic spin-orbit splitting between Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ states at 232.6 and 229.5 eV respectively (Li et al., 2017), and for S 2p$_{1/2}$ and S 2p$_{3/2}$, states at 163.7 and 162.5 eV, respectively. The sharp peaks of Mo 3d core for pristine MoS$_2$ are indicative of the good local crystallinity of the samples. The shift of ~0.5 eV toward the lower binding energy of the doped system reflects the presence of polymorphism due to N doping and consequent possible decrease in the effective charge state of Mo. The defective structure with non-metal dopants causes displacement of the Mo$^{4+}$ 3d peaks toward the lower binding energies in the Mo 3d spectra (Pal et al., 2017). The percentage of 1T’ and 2H was also been calculated by assigning the peak in regions 229 and 232 eV, as shown in Figure 1B$_1$, B$_2$. The 300 mTorr case shows significantly higher fraction of (~80%) 1T’ phase of MoS$_2$, which is the metallic phase. Notably, the peak at 229.5 eV also corresponds to the Mo-N bonding which is at about the same location as that of Mo-S bonds of 2H phase MoS$_2$ (Azcatl et al., 2016). Therefore, this XPS signature will also have the corresponding Mo-N contribution in 100 and 300 mTorr cases that cannot be neglected. Similarly, in Figure 1C$_2$ the consecutive shift toward the lower binding energy in S 2p$_{1/2}$ and 2p$_{3/2}$ spin-orbit splitting for 100 and 300 mTorr MoS$_2$ films again reflects the enhancement of 1T’ phase with the increase of dopant concentration. All the peaks were corrected with the reference binding energy of C (Figure S5). All these results indicate that the doping of non-metals brings about dramatic microstructural changes and the modification of strain state by altering the bond lengths and bond angles.

**AFM and HRTEM characterisation**

The atomic force microscopic (AFM) topography in Figures S6A and S6B shows the increase in mean roughness from 2.78 nm to 5.2 nm in MoS$_2$-N$_x$ over pristine MoS$_2$. In order to get an idea about the local structure development during initial film growth, we recorded High-resolution transmission electron microscopy (HRTEM) images on ultrathin films of MoS$_2$ and MoS$_2$-N$_x$ deposited directly on carbon-coated holy grids by giving only 30 shots at room temperature. It may be noted that these data do not correspond to the films grown at higher temperature which are expected to be structurally far superior on larger length scales. The pristine MoS$_2$ film was prepared under Ar atmosphere, whereas the MoS$_2$-N$_x$ film was deposited under 300 mTorr NH$_3$ atmosphere. It is very clear from the obtained FFT image (Figures S7A and S7B) that the pristine MoS$_2$ has common honeycomb lattice corresponding to the 2H phase, whereas the co-existence of 1T’ and 2H phases is evident in the case of the MoS$_2$-N$_x$ film, with trigonal lattice reflecting the 1T’ phase.

**XANES characterization**

The X-ray absorption near edge spectra (XANES) is a powerful tool to reveal microstructural details and electronic information on metal coordination sites. The formation of MoS$_2$-N$_x$ species under NH$_3$ pressure was therefore confirmed by synchrotron-based XANES. We have analyzed the N K-edge, Mo M-edge, and S L-edge of MoS$_2$-N$_x$ films and the Mo and S edges for the pristine MoS$_2$ films grown on c-Al$_2$O$_3$. The Nitrogen K-edge X-ray absorption energy is about 400 eV (Figure 2A), and the main absorption edge is observed at ~405 eV (Reinholdt et al., 2021). Importantly, the Mo M$_3$-edge also occur at ~400 eV that arises from 3p $\rightarrow$ 4d transition (George et al., 2009), (Lajaunie et al., 2015) The substantially enhanced intensity of the near 400 eV signature in the case of MoS$_2$-N$_x$ as compared to pristine MoS$_2$ suggests addition of the Mo N and N K edge contributions. Further, in S L$_{2,3}$-edge the spin orbit splitting occur in the range of 164–168 eV, as shown in Figure 2B (George et al., 2009). In addition, a comparative analysis based on the observed shape, peak area, and intensities provides information on the local bonding environment responsible for M edge, N edge, and L edge positions (Cai et al., 2015). The shoulder peak in N K-edge indicates that there is substantially extended energy states distribution which corresponds to Mo 4d electrons in the MoS$_2$-N$_x$ case, further indicating the incorporation of the 1T’ phase in MoS$_2$-N$_x$ (Cai et al., 2015; Lajaunie et al., 2015). According to the crystal field theory (CFT), the 2H semiconductor MoS$_2$ is
due to the symmetry-induced splitting of Mo 4d orbitals of MoS6 D3h group into fully occupied Mo 4dz2, Mo 4dxy, Mo 4dxz, and unoccupied Mo 4dxy, Mo 4dx2−y2 (Zhao et al., 2018). On the other hand, in the case of 1T MoS2 semi-metallic character stems from the octahedral splitting of 4d orbital into triple-degenerate t2g (dxy, dxz, dyz) and double-degenerate eg sets, with the t2g orbitals partly occupied by the two 4d electrons. The N K-edges also reflects the high content of N in the MoS2-xNx case. From the S L-edge, it is divulged that in the MoS2-xNx case, the feature at 166.5 eV arising because of the transition between S 2p to S 4d hybridized with Mo 5p states, is broadened and comprises two features. The additional feature compared to undoped MoS2 indicates the mixing of S 4d and N 2p states via Mo 5p states. The lower content of Si in the MoS2-xNx case due to N substitution over pristine MoS2 is clearly seen from the drop in intensity of the S L2,3-edge (Figure 2B). (Cai et al., 2015) The above observations corroborate well with the noticeable changes in the electronic band structure due to the formation of 1T phase upon N doping in MoS2 lattice.

Work-function and valance band maxima (UPS and VBS)
The work function values of MoS2-xNx and pristine MoS2 films were measured by UV photoelectron spectroscopy. The work function (Φ) of the heterostructures is calculated by:

\[ \Phi = h\nu - E_{\text{onset}} \]  

where \( h\nu = 21.22 \text{ eV} \) is the incident photon energy and \( E_{\text{onset}} \) is the onset energy of the secondary electrons obtained from the extrapolation of the slope drawn at the leading edge of the spectra to the baseline as shown in Figure 3A. From the equation, the work functions were estimated to be 4.67 and 4.85 eV for MoS2/c-\( \text{Al}_2\text{O}_3 \) and MoS2-xNx/c-\( \text{Al}_2\text{O}_3 \) respectively. (Tao et al., 2014) The covalent N doping in MoS2 lattice effectively engineers the work-function. The n-type behavior of pristine MoS2 is attributed to sulfur vacancies and its significant depletion by N doping in the case of MoS2-xNx films can cause the enhancement of the work function.

The hybridization of Mo 4d and S 3p orbitals leads to the formation of valance band states. In 2H MoS2, the conduction band and valance band are mainly composed of Mo 4d orbitals. The noticeable Mo 4d states across the Fermi energy in MoS2-xNx suggests the formation of 1T’ MoS2 and hence with more conducting nature. Figure 3B compares the VBS spectra of MoS2-xNx/c-\( \text{Al}_2\text{O}_3 \) grown at 300 mTorr and pristine MoS2-xNx/c-\( \text{Al}_2\text{O}_3 \) case. Figure S8 compares the same for different pressures. The extraction of the Valance band maxima (VBM) positions was done by taking the intersection of the linear extrapolation of the prominent edge in VBS spectra. The electronic states at ~1.8 eV belong to the Mo 4d\( _{\text{dxz}} \) band of 2H MoS2 which is below the Fermi energy, implying the intrinsic n-type doping. The well-established hybridization of Mo 4d and S 3p suggests the long-range in-plane ordering of MoS2. (Tao et al., 2015) The progressive shift in the valance band edge toward the Fermi energy with increase of NH3 growth pressure suggests the change in the electronic structure. For MoS2-xNx/c-\( \text{Al}_2\text{O}_3 \) grown at 300 mTorr the observed VBM position is located at ~0.1 eV with reference to the Fermi energy rendering finite density of states at \( E_F \) and hence higher conductivity. This comes about by the increased 1T’ component with the nitrogen doping concentration. The
binding energy of S 2p, Mo 3d and N 1s core (primary peaks), along with work-function and VBM of MoS2/c-Al2O3 and MoS2-xNx/c-Al2O3 films are tabulated for comparison in Table 2.

Electronic transport properties (resistivity and I-V characteristics)
Doping of 2D materials often leads to new phenomena and is often considered as a proposition to enhance the electronic transport properties. Specifically, enhancing the electrical conductivity of MoS2 films by doping is always interesting for enhancing its potential application-worthiness. Heavy doping can even cause significant changes to the band edges and work function, thereby boosting the functionality. Because our doped film consist of a high content of 1T phase rendered by N substitution at the sulfur site, the investigation of electrical transport is very interesting in this case. Indeed, the temperature-dependent in-plane four-probe resistivity measurement on 300 mTorr grown MoS2-xNx thin-film shows an extremely (by a factor of about 500) low room temperature resistivity as compared to that of pristine (undoped) MoS2 film. Because we used different NH3 pressures to grow the films leading to differing N doping concentrations, the intra-atomic interaction and the degree of covalent bonding between N and Mo should differ, leading to distinct differences in the d-electron hopping (Parmar et al., 2019), (Park et al., 2015). We measured the electrical resistivity of MoS2-xN thin films comprising >80% 1T+20% 2H phase and pure 2H MoS2 phase film on c-Al2O3. The data over the 200–300 K regime are plotted and compared in Figure 3C. Indeed, the room temperature resistivity (ρ) shows much-enhanced conductivity for the MoS2-xN/c-Al2O3 (0001) thin films (~0.036 mΩ-cm) with respect to the pristine 2H phase MoS2/c-Al2O3 (0001) thin films (~16.8 mΩ-cm). Further, the pressure dependent comparison of T-dependent carrier transport of pristine MoS2/c-Al2O3 (0001) and MoS2-N/c-Al2O3 (0001) deposited under different NH3 pressure (10, 100, and, 300 mTorr) depicts the lowest resistivity in the 300 mTorr case (Figure S9). It is quite interesting that although the mixed-phase film shows >80% 1T+ phase (which is much above the percolation threshold), it does not show a fully metallic (i.e., decrease in resistivity while lowering the temperature) feature. Because it contains <20% 2H phase (dielectric proximity), electron localization in the semiconducting regions (along with grain boundary scattering effects) may be the contributing factor for this observation.

Figure 3. Electronic property exploration by UV photoelectron spectroscopy, valance band maxima, temperature dependent resistivity and I-V characteristics of pristine MoS2 and MoS2-xNx films grown on c-Al2O3
(A) Secondary electron cutoff vs kinetic energy plot for work function calculation.
(B) Valance band spectra of pristine MoS2 and MoS2-xNx films grown on c-Al2O3, representing the Fermi-level overlapping for MoS2-xNx (300 mTorr NH3 pressure).
(C) Temperature-dependent carrier transport of 20 nm MoS2 and MoS2-xNx films grown on c-Al2O3 (0001) substrate, resistivity shows a highly conducting nature of MoS2-xN at room temperature.
(D) I-V characteristics of Au/MoS2/c-Al2O3 and Au/MoS2-xNx/c-Al2O3 heterostructure.
transport across the electrode. However, the highly doped system provides a uniform 1T pristine MoS2 films as an active material electrode in a vertical contact separation mode TENG design. This can be attributed to the fact that the enhancement in the 1T/2H phase via covalent doping provides a smooth electronic transport through the grain boundaries. Generally, the transport in the polymorphic MoS2 is driven by the tunneling of electrons and percolation from the metal-semiconductor grain boundaries of the 1T phase. In addition, much lower activation energy of MoS2-Nx (~0.6 meV) is observed over that of pristine MoS2 (~91.3 meV) which also indicates the modification in the electronic correlation and consequent enhancement in electrical conductivity (Mitterreiter et al., 2021). Moreover, reported theoretical calculations reveal that the structural distortion-induced changes in crystal field splitting opens up a gap of ~100 meV for the semiconducting 1T phase (Pal et al., 2017).

In addition, we have also examined the I-V characteristics of heavily doped MoS2-Nx thin films and compared the current with respect to pure 2H MoS2 film. The in-plane current was measured across Au/MoS2 and Au/MoS2 interfaces on the application of ±15 V sweep voltage (Figure 3D). The channel length was kept ~0.6 μm between the two Au contacts. It is important to note here that the doped films show three order enhancement in the current as compared with pristine 2H MoS2. This can be attributed to the fact that the enhancement in the 1T phase via covalent doping provides a smooth electronic transport through the grain boundaries. Generally, the transport in the polymorphic MoS2 is driven by the tunneling of electrons and percolation from the metal-semiconductor grain boundaries of the 1T phase and 2H phase. However, the highly doped system provides a uniform 1T channel with pertinent electronic transport across the electrode.

### Table 2. Obtained binding energies for MoS2 and MoS2-Nx films grown on c-Al2O3 substrate

|                | MoS2/c-Al2O3 | MoS2-Nx/c-Al2O3 |
|----------------|-------------|-----------------|
| S 2p3/2        | ~162.5 eV   | ~162.1 eV       |
| Mo 3d5/2       | ~229.5 eV   | ~228.7 eV       |
| N 1s           | ~397 eV     | ~397 eV         |
| Work-function  | ~4.67 eV    | ~4.85 eV        |
| Valance band maxima | ~1.8 eV | ~0.13 eV       |

The low-temperature resistivity data can be best fitted with the Mott-variable range hopping (Mott-VRH) model (i.e. \( \sigma = \frac{1}{2} \left( \frac{d}{2} \right)^{1/12} \)) where \( \sigma \) is the conductivity and \( d \) the dimension, signifying the important role of Anderson localization due to intrinsic disorder effect (possible structural defects, vacancies, and dislocations to lower the strain energy) for this insulating-like behavior (Figure S10) (Cho et al., 2021), (Zhou et al., 2016). In addition, much lower activation energy of MoS2-Nx (~0.6 meV) is observed over that of pristine MoS2 (~91.3 meV) (Figure S11) which also indicates the modification in the electronic correlation and consequent enhancement in electrical conductivity (Mitterreiter et al., 2021). Moreover, reported theoretical calculations reveal that the structural distortion-induced changes in crystal field splitting opens up a gap of ~100 meV for the semiconducting 1T phase (Pal et al., 2017).

In addition, we have also examined the I-V characteristics of heavily doped MoS2-Nx thin films and compared the current with respect to pure 2H MoS2 film. The in-plane current was measured across Au/MoS2 and Au/MoS2 interfaces on the application of ±15 V sweep voltage (Figure 3D). The channel length was kept ~0.6 μm between the two Au contacts. It is important to note here that the doped films show three order enhancement in the current as compared with pristine 2H MoS2. This can be attributed to the fact that the enhancement in the 1T phase via covalent doping provides a smooth electronic transport through the grain boundaries. Generally, the transport in the polymorphic MoS2 is driven by the tunneling of electrons and percolation from the metal-semiconductor grain boundaries of the 1T phase and 2H phase. However, the highly doped system provides a uniform 1T channel with pertinent electronic transport across the electrode.

### Triboelectric nanogenerator performance

VDW-based TENGs represent an interesting mechano-electronic device (Lim et al., 2019). Herein, each VDW layer acts as an active electrode layer toward inter- and intra-layer charge generation and transfer. The strong interlayer coupling in VDW plays an important role in the charge generation/transfer. With the incorporation of defects, dopants, and charge distributions, this device functionality can be interesting and could generate superior performance. We therefore fabricated a TENG device using MoS2-Nx and pristine MoS2 films as an active material electrode in a vertical contact separation mode TENG design. A 20 nm film was coated on ~1.3 × 1.3 cm² area ITO/PET for this purpose. A 1-mm thick 3M double-sided tape boundary was used to maintain a distance between the top and bottom layers as depicted in Figure 4A. The MoS2 or MoS2-Nx film on ITO coated PET and microfiber separator in the middle were assembled with the aluminum tape upside down as top contact (Figure 4A) where the microfiber is composed of cellulose, a commercially available microfiber paper (α-cellulose content ≥98%) which is an environmentally friendly material. The device was laminated with a Kapton tape allowing some space for electrode connections to prevent damage to the device from the external environment. Then the Cu wires were soldered to the conducting sides of the top and bottom electrodes. A mechanical input of 10 N (measured by PASCO force sensor) was applied at 21 Hz frequency. During measurement, the Cu wires were connected to the oscilloscope to record the open-circuit voltage. A remarkably enhanced open-circuit value obtained for the pristine MoS2 and MoS2-Nx, is in the ratio of ~1.3. The obtained peak to peak voltages were ~0.8 and ~2.7 V for pristine MoS2 and MoS2-Nx, respectively (Figure 4B). The enhanced \( V_{oc} \) in doped films can result from polymorphism with high 1T component and very high electrical conductivity. The peak-to-peak voltage and current density were also calculated to obtain the overall MoS2-Nx TENG efficacy under application of different external loads of 0.1, 0.4, 0.8, 1, 10, 20, 30, and 40 MΩ resistance (Figure S12) and the corresponding signal is shown in Figure S13. It is to be noted here that the asymmetric behavior in alternating output voltage in the vertical contact-separation mode can be observed because of the lower charge pushing from one to another electrode (Chen et al., 2020). In this mode when the upper electrode separates, the voltage is mainly associated with the dielectric film. Thus, the output voltage is much higher.
in the upper electrode than the former electrode. The power density was also obtained to realize the net output powering capability of TENG for the different sets of loads (Figure S14). Figure S15 shows the cross-section FESEM image of MoS$_2$-$x$N$_x$ film grown on a flexible ITO-coated PET substrate.

Cellulose fibers are bio-degradable, lightweight, and high strength materials and have a high propensity to lose an electron because of the presence of abundant oxygen atoms, making it a prominent material for a tribo-positive layer (Chen et al., 2020). Here, the effective work-function of the MoS$_2$ and MoS$_2$-$x$N$_x$ films was calculated via UV photoelectron microscopy, which was the main factor for deciding upon its use in the triboelectric charging behavior. It is observed that the MoS$_2$-$x$N$_x$ films exhibit higher effective work function as compared to pristine MoS$_2$ film. Thus, the p-type Nitrogen doping in MoS$_2$ leads to the enhancement of work-function making it more negative in the triboelectric series. Thus, the triboelectric charging features are successfully modified by N doping in the MoS$_2$ lattice that change the effective work-function.

Under the application of external impulse-force, the physical contact between MoS$_2$-$x$N$_x$/microfiber/Al is instantly established and contact charging occurs. While triboelectricity basically embodies the contact charging process, the charge transfer has to take place between the two interfacing materials to generate a voltage across and drive currents across. This intrinsically involves their propensity to give and accept the charge; a consideration that lays the foundation for the existence of the triboelectric series. Moreover, because the currents have to flow through the bulk for compensating the charge imbalances resulting from the contact charging, the electronic band structures of the participating materials also come into play. There are situations where the electronic character of the two materials differs by way of being a metal, semiconductor, or insulator and this causes further complications of electronic currents and depolarization currents. Thus, the whole process is rather complex to elucidate in simple terms. In our case, the microfiber and Al hold different triboelectric polarity. When both the layers brought into contact, the electrons are exchanged the effective differential work function. Thus, the MoS$_2$-$x$N$_x$ TENG performance
enhancement over pristine MoS$_2$ TENG can be attributed to the synergy of the device architecture, p-type N doping in MoS$_2$ lattice, favorably increased work-function, multiphasic component of MoS$_2$ with enhanced conducting component 1T$'$ and increased surface roughness enhancing the trapped charge kinetics via locally enhanced field.

Conclusion
In summary, we report on the growth, properties, and applicability of high-quality thin films of MoS$_2$-$x$N$_x$ on single-crystal c-Al$_2$O$_3$ substrates under ammonia ambient by the pulsed laser deposition (PLD) technique. We find that the films exhibit 1T$'$/2H biphasic constitution, with the 1T$'$ component increasing dramatically with enhanced growth pressure of ammonia (~80% 1T$'$ phase @ 300 mTorr growth pressure). Raman characterization reveals that the enhancement of the 1T$'$ phase component can be attributed to the incorporation of covalently bonded N in the MoS$_2$ lattice inducing compressive strain. Transport measurements show progressive drop in resistivity with enhanced ammonia growth pressure and the MoS$_2$-$x$N$_x$ films grown at 300 mTorr NH$_3$ show extremely low room temperature resistivity of 0.03 m$\Omega$-cm which is two orders of magnitude lower than the undoped MoS$_2$. In a triboelectric nanogenerator (TENG) device the biphasic MoS$_2$-$x$N$_x$ film grown at 300 mTorr NH$_3$ pressure serves as an electron acceptor and exhibits a 3-fold enhancement in the output voltage as compared to the pristine MoS$_2$. Increased work-function due to highly conducting covalent p-type N doping in multiphasic MoS$_2$ with increased roughness and device assembly synergistically contributes to this superior TENG performance.

Limitations of the study
In this study, we have fabricated, optimized, and characterized MoS$_2$-$x$N$_x$ films using pulsed laser deposition (PLD) in NH$_3$ ambient. In addition, we have elucidated the role of N in the MoS$_2$ lattice, which is responsible for enhancing its electronic properties via modulating the chemical and structural properties. While the possibility of incorporation of some hydrogen cannot be ruled out during the deposition in NH$_3$-assisted PLD, we did not find evidence of the same in the set of characterizations employed. However, a solid-state Nuclear Magnetic Resonance (NMR) can possibly bring out the role of Hydrogen in the MoS$_2$-$x$N$_x$ lattice, as H bonding can contribute to the changes of the electronic bands. Also, PLD is difficult to scale up; therefore, after the basic results are established by PLD studies, one could perform a follow-up with scalable sputtering or PVD techniques.

STAR+METHODS
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Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.103898.

ACKNOWLEDGMENT
Swati Parmar would like to thank CSIR for SRF fellowship. Satish Ogale and R. Boomishankar would like to thank DST Nanomission Thematic unit project (SR/NM/TP/13/2016) for funding support. We would like to thank Prof. Surjeet Singh and Ms. Dibyata Rout for providing the facility for the R-T measurement.
AUTHOR CONTRIBUTIONS

S.P. and S.O. developed the idea and design the experiments, S.P. performed and analyzed the thin film growth, characterization, and device fabrication. N.P. carried out the TENG device testing and B.R. helped with the analysis. M.W. helped in the FESEM characterization. R.C. helped in providing the XANES experiment and analysis. S.P. and S.O. co-wrote the paper. All the authors contributed to the discussion and analysis.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: October 6, 2021
Revised: January 15, 2022
Accepted: February 5, 2022
Published: March 18, 2022

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | Sigma-Aldrich | CAS# 1317-33-5 |
| Molybdenum di sulfide (99.9%) | Sigma-Aldrich | CAS# 67-64-1 |
| Aceton, 99.9% | Sigma Aldrich | |
| c-Al2O3 Substrate (99.99%) | MTI | Product# ALC25D05C1 |
| ITO PET sheets | Sigma Aldrich | Product# 639303-1EA |
| Aluminum Foil Tape | 3M | Product# 3363 |
| Copper Foil Tape | 3M | Product# 1182 |
| Microfiber paper | Sigma Aldrich | Product# WHA2200070 |
| Double sided tape | 3M | Product# GPH-110GF |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Satishchandra Ogale (satishogale@iiserpune.ac.in).

Materials availability
This work is an experimental study of thin-film growth and nanogenerators and there is no new code generated.

Data and code availability
- All data reported in this paper will be shared by the lead contact upon request.
- No new code was generated during the course of the study.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

EXPERIMENTAL MODEL AND SUBJECT DETAILS

Molybdenum di-sulfide (MoS2, 99.9%) was purchased from Sigma-Aldrich. The chemical was used without further purification. Ammonia-Argon gas cylinder (30% Ammonia Bal Argon Pressure 20 Bar/cm² Purity-99.9%) was used for the deposition of MoS2-Nx thin films. The c-Al2O3 substrates were cut into 5x5 mm² area using diamond cutter and sintered at 1000°C to obtain atomically flat substrate followed by washing away residual dust/particle with sonicating under acetone and deionized water at room temperature for 15 min each. They were then blow dried in Ar air before loading into the PLD chamber. The ITO coated PET was directly used for deposition without any treatment.

METHOD DETAILS

MoS2-Nx thin-film growth
In this work, we have grown 50 nm thin-films of MoS2-Nx under NH3 pressures of 1 mTorr, 10 mTorr, 100 mTorr, and 300 mTorr respectively by Pulsed Laser Deposition (PLD) (KrF, λ = 248). Here we have used c-Al2O3 substrates for the detailed characterization and ITO coated PET for nanogenerator application. The MoS2-Nx films were deposited at 400°C and 150°C on c-Al2O3 and ITO-coated PET substrates, respectively. To make the c-Al2O3 substrate atomically flat, the annealing treatment was given at 1000°C for 1 h in air before the deposition. The distance between the polycrystalline MoS2 target to the substrate was ~40 mm. The substrate temperature was 400°C for all depositions under ammonia-argon gas mixture (30% ammonia) at 5 Hz frequency by using 1.5 J/cm² laser energy density. Pristine MoS2 films were deposited under vacuum with the base pressure of 10⁻⁶ mbar. All films were cooled down naturally.
Structural and chemical characterizations

Raman spectra for all MoS\(_2\) thin-film samples were recorded at \(\sim 2.33\) eV (532 nm) excitation energy laser. Atomic force microscopy (AFM) topography images of thin films were taken using Nanosurf AFM (Switzerland). X-ray photoelectron spectroscopy (XPS) was performed in an ultra-high vacuum chamber (2\(\times\)10\(^{-9}\) mBar) by using an Al K\(\alpha\) x-ray source with 6 mA beam current on a Thermo-Fisher Scientific Instrument, UK, where beam spot size on the thin-film samples were \(\sim 400\) \(\mu\)m. High-resolution transmission electron microscopy (HRTEM) images were recorded using UHR FEG-TEM microscopic instrument, operating at 200 kV accelerating voltage. To record the absorption spectrum of MoS\(_2\)\(_x\)N\(_x\) thin film, an ultraviolet-visible (UV–vis) spectrophotometer (LAMBDA 950, PerkinElmer) was used. Field emission scanning electron microscopy (FESEM) images of the electrodes were recorded using a JEM-2100F (JEOL, Japan) instrument.

X-ray absorption spectroscopy measurement of N K-edges was collected in total electron yield (TEY) mode of MoS\(_2\)\(_x\)N\(_x\), characterization was done using synchrotron radiation source at RRCAT, Indore at ‘polarized light soft X-ray absorption spectroscopy beamline’ (BL-01) in INDUS-2, respectively. Before recording the XAS spectra, the thin film surface was sputtered using high energy Argon ions inside the chamber where base pressure was maintained at \(\sim 1 \times 10^{-10}\) mbar in order to remove any surface contamination.

Electrical characterization

Electrical measurements were performed in standard AC transport four-probe method by using a Quantum Design Physical Property Measurement System (PPMS), over the temperature range of \(T = 5-300\) K, where the dimensions of MoS\(_2\) and MoS\(_2\)\(_x\)N\(_x\) film was 2\(\times\)5 mm\(^2\).

Nanogenerator output performance

Keithley multimeter (DMM7510 7.5 multimeter) was used to measure open circuit voltage at 10 M\(\Omega\) input impedance at 10 N impact force with 21 Hz frequency. For the impact force and frequency source, we used home-made modified sewing machine setup. We measured force using PASPORT Force Sensor. Voltage and current were also measured on Keithley multimeter (DMM7510 7.5 multimeter) with variable resistance.

QUANTIFICATION AND STATISTICAL ANALYSIS

The TENG data were collected on a Kickstart, an oscilloscope testing system (DMM7510). Figures were produced by Origin from the raw data.

ADDITIONAL RESOURCES

Any additional information about the thin-film fabrication, TENG fabrication, tests and data reported in this paper is available from the lead contact on request.