Pressure-induced semiconducting to metallic transition in multilayered molybdenum disulphide

Avinash P. Nayak1,*, Swastibrata Bhattacharyya2,*, Jie Zhu3,4, Jin Liu3, Xiang Wu3, Tribhuwan Pandey2, Changqing Jin4, Abhishek K. Singh2, Deji Akinwande1 & Jung-Fu Lin3

Molybdenum disulphide is a layered transition metal dichalcogenide that has recently raised considerable interest due to its unique semiconducting and opto-electronic properties. Although several theoretical studies have suggested an electronic phase transition in molybdenum disulphide, there has been a lack of experimental evidence. Here we report comprehensive studies on the pressure-dependent electronic, vibrational, optical and structural properties of multilayered molybdenum disulphide up to 35 GPa. Our experimental results reveal a structural lattice distortion followed by an electronic transition from a semiconducting to metallic state at ~19 GPa, which is confirmed by ab initio calculations. The metallization arises from the overlap of the valance and conduction bands owing to sulphur-sulphur interactions as the interlayer spacing reduces. The electronic transition affords modulation of the opto-electronic gain in molybdenum disulphide. This pressure-tuned behaviour can enable the development of novel devices with multiple phenomena involving the strong coupling of the mechanical, electrical and optical properties of layered nanomaterials.

1 Department of Electrical and Computer Engineering, The University of Texas at Austin, Austin, Texas 78712, USA. 2 Materials Research Center, Indian Institute of Science, Bangalore 560-012, India. 3 Department of Geological Sciences, The University of Texas at Austin, Austin, Texas 78712, USA. 4 Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China. * These authors contributed equally to this work. Correspondence and requests for materials should be addressed to D.A. (email: deji@ece.utexas.edu).
Recent advances in the preparation of atomically thin layers of van der Waals (vdW) bonded crystalline solids by mechanical exfoliation or chemical synthesis have allowed for renewed investigations of two-dimensional (2D) materials beyond graphene but with a similar layered hexagonal structure. Within this class of 2D materials, transition metal dichalcogenides (TMDs), such as molybdenum disulphide (MoS2), which have been increasingly explored to access a wealth of phenomena including opto-electronics, valleytronics, spintronics and coupled electro-mechanics. All of these phenomena arise from the complex thickness-dependent physical and electronic structures of the multilayered materials, in which the coupled electro-mechanics can be regarded as straintronics. Multilayered MoS2, having a band gap ($E_g$) of $\sim$1.2 eV, is composed of stacked tri-atomic sheets where each tri-atomic monolayer exhibits a sandwiched structure with a plane of transition metal molybdenum atoms covalently bonded to, and sandwiched between, two planes of chalcogen sulphur atoms (Fig. 1a). Unlike monoatomic multilayered graphene with $sp^2$ hybridization, the diatomic composition of multilayered MoS2 coupled with its $d$-orbital electronic states and the small 6.5 Å vdW interlayer gap raises the prospects of strong sulphur–sulphur interlayer interactions under axial compression that might lead to an electronic phase transition.

Previously, several approaches have been undertaken to alter the solid-state properties of MoS2, including chemical doping, intercalation, surface functionalization and defect engineering. Furthermore, previous theoretical studies have suggested that an iso-structural semiconducting to metallic (S–M) transition in multilayered MoS2 can be induced by pressure or strain. Despite the broad interest in this phenomenon in layered nanomaterials, previous experimental results only reported a limited reduction in the electrical resistance with no clear evidence for the pressure-induced S–M transition.

In the present study, we have investigated high-purity exfoliated single crystalline MoS2 with a stoichiometric chemical composition to evaluate the structural, vibrational, electrical and optical dependence at pressures up to 35 GPa. These results show a lattice distortion involving anisotropic c/a axial compression beginning at $\sim$10 GPa in multilayered MoS2, leading to an intermediate state (IS) followed by a pressure-induced S–M transition at $\sim$19 GPa. First-principle theoretical calculations, which are performed to shed light on the underlying physics responsible for the S–M transition, attribute the origin of the metallic electronic states to sulphur–sulphur interactions as the vdW gap closes at high pressures. Our combined experimental and theoretical results here open a new window of opportunity for the development of nanoscale pressure switches, sensors and multi-physics devices with coupled electrical, vibrational, optical and structural properties using multilayered MoS2 and semiconducting TMDs.

**Results**

**Diamond anvil cell.** In this work, we have explored applied pressure effects via a high-pressure diamond anvil cell (DAC), as a controllable and reversible degree of freedom to modulate the properties of multilayered single-crystal MoS2. The DAC technique coupled with a hydrostatic pressure medium (Fig. 1b) has been shown to be effective in elucidating the electrical, vibrational, optical and structural properties of a plethora of materials. The optically transparent window of the diamond allows us to conduct a series of in situ high-pressure experiments including accurate pressure calibration from ruby fluorescence, electrical transport measurements and optical Raman and synchrotron X-ray diffraction (XRD) spectroscopy, leading to the observation of S–M transition in multilayered MoS2 at high pressures. Pristine multilayered crystalline MoS2 was transferred onto the DAC using micron-sized tweezers for investigations of the electronic, phononic and structural behaviours at pressures up to 35 GPa (see Methods for details). In addition, first-principle theoretical calculations were performed to elucidate the underlying material physics of the transition.
Electrical conductivity and electronic structures. In situ electrical conductivity measurements at room temperature using standard four-point metallic contacts reveal a gradual decrease in resistivity ($\rho$) with pressure up to 10 GPa, which can be understood in the context of a pressure-activated carrier transport model in good agreement with the experimental data (see Supplementary Note 1 and Supplementary Fig. 1). Between 10–19 GPa an abrupt decrease of about three orders of magnitude (Fig. 1c) is observed. Theoretical ab initio band structure calculations of the multilayer MoS$_2$ corroborates the experimental result with a predicted transition at $\sim$ 20 GPa (Fig. 1c, inset), which was theoretically found to correspond to a vanishing band gap owing to a S–M electronic transition.

In addition, in situ temperature-dependent resistivity measurements were performed in the DAC in order to determine the resistivity profiles before and after the transition. It is well known from classical solid-state physics that resistivity decreases with temperature ($T$) for semiconductors owing to thermally activated carriers, in contrast to increasing resistivity for metallic conductors due to increased electron-phonon scattering$^{27}$. Our resistivity measurements for multilayered MoS$_2$ reflect the aforementioned classical semiconducting behaviour as indicated by the negative temperature coefficient of resistivity at 10 GPa (Fig. 1d, inset) for the semiconducting state, whereas a positive temperature coefficient of $\rho$ is observed at 34 GPa for the metallic state (Fig. 1d). Moreover, the profile of the temperature-dependent resistivity magnitude shown in Fig. 1d follows an exponential decreasing trend at 10 GPa and a linear ($\rho\alpha T$) trend at 34 GPa consistent with the classical behaviours of semiconducting and metallic materials respectively. Calculations using Boltzmann transport theory (BTT) for the temperature-dependent resistivity at $\sim$ 10 GPa and 35 GPa support these experimental findings (Supplementary Fig. 2).

Furthermore, theoretical calculations determine that the semiconducting nature of MoS$_2$ originates from the fact that within a layer, Mo and S atoms are bound by mixed ionic and covalent bonding$^{28}$. Under the application of pressure, the interlayer distance between the atomic planes decreases and the intra- as well as interlayer interactions are expected to alter the electronic properties of MoS$_2$. Along the [0001] direction, MoS$_2$ with anisotropic linear incompressibilities will experience maximum compression, that is, the interlayer distance ($c$ axis) decreases more significantly than the intra-layer distance ($a$ axis). The hydrostatic pressure causes in- and out-of-plane strain. In order to analyse the effect of in-plane strain in achieving the S–M transition, we calculate the charge density redistribution keeping the in-plane strain constant, while varying the out-of-plane strain. Figure 2a,d shows the charge redistribution for a constant out-of-plane strain (6.9%) but at a different in-plane strain of 2.2 and 5.2%, respectively. Figure 2b,c shows the same but at a higher out-of-plane strain (11%). It can be seen that the interlayer interaction is enhanced with the increasing in-plane strain. Although, the S–M transition is caused by interlayer interaction due to the normal or out-of-plane strain, the in-plane strain helps to achieve this transition at a lower pressure.

With increasing pressure, our theoretical calculations show that the electronic charge moves away from the S atoms and accumulates onto the Mo atoms. Near the critical transition pressure, the maximum charge redistribution is predicted to occur in between the MoS$_2$ layers across the vdW gap, indicating enhanced S–S interaction. The change in the interlayer interaction from a weak vdW to a stronger interaction near the critical pressure is also supported by the derived lattice parameters using XRD spectra. However, these results do not give information regarding the orbitals involved in the charge transfer. Therefore, theoretical calculations for the angular momentum resolved density of states (LDOS) as a function of pressure were also performed to understand the contribution from the different orbitals of Mo and S atoms (Supplementary Fig. 3).

Figure 2 | Theoretical charge density isosurfaces of multilayered MoS$_2$. Charge accumulation (green) and depletion (orange) at the (a) in-plane and out-of-plane strains of 2.2 and 6.9%, respectively, (b) in-plane and out-of-plane strains of 2.2 and 11%, respectively, and (c) in-plane and out-of-plane strains of 5.2 and 11%, respectively. (d) Same in-plane strain as in (c) but with 6.9% out-of-plane strain.
With increasing pressure, the contribution to the conduction band minima (CBM) from S-\( p_x \) and S-\( p_y \) orbitals decreases, while the contribution from S-\( p_z \) orbitals increases. Similarly, there is a reduction with increasing pressure in contributions from Mo-\( p \) orbitals, while the contribution from Mo-\( d_z^2 \) increases.

**Optical Raman vibrational spectroscopy.** Raman spectroscopy is considered to be a very accurate tool for gaining insight on the lattice vibrations of crystalline materials and has been commonly used to characterize the two prominent vibrational modes (E\(_{2g}\) and A\(_{1g}\)) that are accessible in MoS\(_2\) (refs 29–31). In order to elucidate the S-M electronic transition, Raman measurements were conducted in situ to probe vibrational changes in the multilayered MoS\(_2\) under high pressure. It is well known that inducing pressure in MoS\(_2\) results in an increase in the Raman shift (Fig. 3a) similar to other layered materials\(^{30,32}\). Analyses of the high-pressure Raman spectra reveal that the A\(_{1g}\) mode shows three distinct regions (Fig. 3b): (i) significantly increasing Raman shift up to about 10 GPa, (ii) nearly invariant shift with pressure between 10 GPa and 19 GPa and (iii) pressure-dependent Raman shift above 19 GPa. An evaluation of the Raman intensity ratio (between the E\(_{2g}\) and A\(_{1g}\)) also reveals three distinct regions with the maximum intensity ratio observed in the metallic region (Supplementary Fig. 4). We label these regions starting from low to high pressures as the semiconducting (SC), intermediate state (IS), and metallic regions respectively. In light of these observations, the out-of-plane vibrational mode (A\(_{1g}\)) can be considered the more prominent Raman mode that is correlated with the semiconducting to metallic transition in MoS\(_2\), in contrast to the in-plane mode (E\(_{2g}\) mode) that shows a less distinct character across the transition. The IS can be understood within the context of phonon softening (PS), which describes the electron and A\(_{1g}\) phonon interaction where inter-valence charge transfer between the MoS\(_2\) layers plays an important role in the structural distortion of the crystal symmetry\(^{33}\). Several materials have been previously reported to exhibit an intermediate state with soften phonon behaviour while undergoing a transition from a semiconductor to a metallic state\(^{34,35}\) or when stress or strain is applied\(^{36,37}\). In fact, materials that exhibit superconductivity at high transition temperatures \(T_c\) are often associated with structural distortions that are characterized by PS subsequently resulting in either a structural or electronic phase transition\(^{38}\).

In our study here, the intermediate state ranges from \(\sim 10\) GPa to 19 GPa where both the Raman shift for the A\(_{1g}\) mode (Fig. 3b) and the spacing between the two modes (Fig. 3c) show little dependence on pressure suggesting that the lattice structure is distorted. Moreover, the full-width at half-maximum (FWHM) of the two modes initially increases with pressure followed by a subsequent sharp drop of \(\sim 19\) GPa (Fig. 3d). It should be noted that in a recent report, a drop in the FWHM was also observed during a phase transition in Sb\(_2\)Se\(_3\), a topological insulator that exhibits a metallic state at the surface\(^{39}\).

The effect of pressure on the vibrational properties of MoS\(_2\) can be further understood using theoretically calculated phonon dispersion curves based on the Perdew–Burke–Ernzerhof (PBE) functional method. We note that the calculated dispersion curves are consistent with that calculated using the local density approximation\(^{26}\), justifying the use of the method. Analysis of the A\(_{1g}\) and E\(_{2g}\) modes as a function of pressure (which can be identified at the calculated \(\Gamma\) point as shown in Supplementary Fig. 5) reveal that the splitting in the bands increases with applied pressure, resulting in significant changes in the Raman frequencies of the two modes (Fig. 3b).

**Figure 3 | Raman spectroscopic results of MoS\(_2\) at high pressures.** (a) Raman spectra at representative pressure points. The inset is an illustration of the in-plane and out-of-plane vibrations of the two key modes E\(_{2g}\) and A\(_{1g}\) respectively. (b) The Raman shifts of the two modes with increasing pressures. The solid red and blue lines serve as visual guides. (c) The difference in Raman frequencies between the A\(_{1g}\) and E\(_{2g}\) modes as a function of pressure flattens out in the IS state and rises at a smaller slope in the metallic region. The solid black line is a visual guide. (d) The FWHM for the A\(_{1g}\) and E\(_{2g}\) Raman modes across the electronic transition. A sharp drop is observed at \(\sim 19\) GPa where MoS\(_2\) transitions from the IS to a metallic phase. The solid red and blue lines serve as visual guides for the A\(_{1g}\) and E\(_{2g}\) modes, respectively.
Opto-electronic properties. Photoconductivity measurements have also been performed as a complementary means for understanding the opto-electronic properties of materials, which is dependent on the material's band gap. To provide perspective, the pressure-dependent band gap for multilayered MoS$_2$ (Fig. 4a) can be understood from theoretical analysis using the PBE functional under the generalized gradient approximation (GGA). We note that the calculated unstrained $E_g$ of 1.03 eV is $\sim$ 16% less than the experimental value.\(^{40}\) This underestimation of the bandgap is a well-known problem due to the presence of artificial self-interaction and the absence of the derivative discontinuity in the exchange-correlation potential with the PBE/GGA methods.\(^{41}\) Hybrid Heyd–Scuseria–Ernzerhof functional and DFT with many-body perturbation theory in the GW approximation are among the few methods to correctly predict the band gap of TMDs; however, these methods are computationally very expensive. Nevertheless, our previous study for bilayer MoS$_2$ has shown that the overall nature of the variation in the $E_g$ and the band structure with pressure are independent of the functional used and that the PBE functional gives reasonably accurate results, justifying the use of the PBE/GGA methods for this work. With the increase in pressure, the degeneracy in the bands of the unstrained structure is lifted due to the enhanced interlayer interaction. The split bands in the valence band maxima (VBM) at the $\Gamma$ point and the CBM between the K and $\Gamma$ point start to move toward the Fermi level. The $E_g$ reduces consequently and becomes metallic when the CBM crosses the Fermi level at a pressure of 23.8 GPa (Fig. 4a), which correlates well with the transition pressures of $\sim$ 19 GPa in the experimental resistivity measurements and Raman spectra. Analyses of the band structure in the metallic state indicate the overlap of the conduction and valence bands at the Fermi level (Fig. 4b).

Unlike metals, semiconductors show an increase in the electrical conductivity when illuminated by light, and are therefore considered photoconductive. In particular, semiconducting MoS$_2$ has been found to offer sufficient photo-response that is suitable for practical photoconductive applications.\(^{3,44}\) Opto-electronics require electron-hole generation/recombination, whereas the opto-electronic response of MoS$_2$ under green laser illumination (2.3 eV) in the event of a semiconducting to metallic transition in MoS$_2$ is expected to be significantly diminished in the metallic state (Fig. 4c). As a result, the photocurrent gain (ratio of current under illumination to dark current) was found to decrease with pressure as shown in Fig. 4d. The current gain decreases at a linear rate ($\Delta I_{\text{cur}}/\Delta \text{GPa} = -7.5\%/\text{GPa}$) until $\sim$ 10 GPa where the current gain saturates to unity, indicating that photo-response is vanishing as the band gap begins to close.

XRD and HR-TEM studies. Electronic phase transitions can be accompanied by a structural or iso-structural phase transition. In order to clarify potential structural changes at high pressure, in situ high-pressure synchrotron XRD experiments were conducted to probe the perturbation of the crystal structure of multilayered MoS$_2$ under hydrostatic pressure. Two independent high-pressure angle-dispersive XRD experimental runs were carried out at room temperature using a symmetric DAC. For the entire experimental pressure range, all the diffraction peaks can be refined to the hexagonal $P6_3/mmc$ structure using the Rietveld refinement.\(^{45}\) On the basis of the hexagonal structure model, the crystal lattice parameters for MoS$_2$ from 0 to 28 GPa were calculated (Fig. 5a). The structure of the bulk unstrained MoS$_2$ can be viewed as ABAB stacked single layers of the material.\(^{22}\) Though we did not observe any new peak(s) for multilayered MoS$_2$ up to 24 GPa in the XRD, a change along the
c axis is observed at ~19 GPa, which suggests that the ambient lattice structure of MoS₂ is only weakly distorted. On the other hand, theoretical calculations were performed using the experimental lattice parameters as the reference, which are in close agreement with the GGA values. Results from theoretical pressure-dependent XRD calculations also confirm that there is no structural transition (Supplementary Fig. 6).

Characterizing the atomic structure and quality of MoS₂ is critical for further understanding of the lattice distortion and electronic phase transition under pressure, and for ruling out the effects of lattice defects (that is, point defects, dislocations, grain boundaries and edges) that could play a role in influencing the experimental results11,16,17. For this purpose, high-resolution transmission electron microscopy (HR-TEM) and electron diffraction techniques were employed to evaluate the crystal structure of the same multilayered MoS₂ before and after the pressure loading experiments. The morphology of the starting sample in HR-TEM shows an atomic MoS₂ lattice having high crystallinity and the expected hexagonal lattice structure with a lattice spacing of 2.7 Å corresponding to the [100] direction (Supplementary Fig. 7a). The cross-section HR-TEM analysis shows the layered structure of MoS₂ having an interatomic c axis spacing of ~6.5 Å (Supplementary Fig. 7b). Transmission electron microscopy energy-dispersive X-ray spectroscopy (TEM-EDX) analyses were performed on both the pristine and decompressed MoS₂ to determine the stoichiometry, which was found to be a 1:2.07 ratio (Supplementary Fig. 7c), very close to the ideal 1:2 Mo:S ratio. Scanning electron microscopy (SEM) and scanning electron-energy-dispersive X-ray spectroscopy (SEM-EDX) for both pristine and decompressed samples also show negligible difference (Supplementary Fig. 7d). The fast Fourier transformation (FFT) of the HR-TEM image shows the reflection spots from (100), (010) and (110), while the selected area electron diffraction (SAED) patterns for both the pristine and decompressed MoS₂ also show negligible difference. The ideal 1:2 Mo:S ratio was also confirmed by electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDX) analyses on both the pristine and decompressed MoS₂. The SAED patterns show that the single-crystal structure with the hexagonal symmetry was not significantly affected by high pressures and can be recovered back to its original crystal structure.

Discussion
Previous studies have shown that loading of a crystal lattice via strain or hydrostatic pressure can cause a sharp reduction in resistivity, which is a precursor for an S–M transition21. In agreement with prior theoretical studies18,19,46, our theoretically predicted band gap is found to depend inversely on pressure and that the critical pressure for the electronic phase transition is predicted to scale down for multilayered films from ~16% normal compressive strain to ~11% for bilayer MoS₂ (Supplementary Fig. 8). For monolayer MoS₂ this transition is predicted to occur at ~10% bi-axial strain19. Reported studies on other materials such as Sb₂Te₃ (ref. 23), WSe₂ (ref. 24), BaNi₂As₂ (ref. 38), Fe₅S (ref. 47), V₃O₅ (ref. 48) and VO₂ (ref. 49) have also shown a drop in resistivity before an electronic or structural phase transition in the material. These results have indicated that applying extremely high pressures onto such materials can even lead to a superconducting state. In MoS₂, this drop in resistivity is correlated with the characteristic phonon modes (E₂g and A₁g), and concurrent with phonon softening in the intermediate state, which has been observed as a precursor for resistivity transition in other materials35–38. We find that both the valence band (VB) and the conduction band (CB) originate from the Mo-d and S-p orbitals with the VB having minor contributions from the Mo-p orbital at zero pressure (Supplementary Fig. 3). With increasing pressure, the contribution from the S-p orbitals increases in both VB and CB, indicating a strong interlayer interaction. This analysis is in agreement with the charge redistribution. Experimentally, the bandgap can be extracted from temperature-dependent resistivity for intrinsic semiconductors; however, for the case of contemporary MoS₂ materials, the prevailing n-type character prevents bandgap extraction directly from resistivity data.

We note that the A₁g mode arises from the out-of-plane vibration of the S atoms with enhanced S–S interactions as the vdW gap closes resulting in the observed metallization. In the intermediate state, vibrational phonon softening phenomenon in the Raman spectra has been studied extensively for other layered materials29, suggesting that it can be used as a clear signature for the electronic phase transition in the multilayered MoS₂. The pressure-dependent Raman frequency increase was observed to be higher for the out-of-plane A₁g mode than that of the in-plane E₂g mode. This clearly indicates an enhancement of interlayer interactions with pressure. The multitude of pressure-dependent
Raman spectra characteristics (FWHM, intensity ratio and peak spacing) are well correlated with the pressure-dependent resistivity, all showing an abrupt or particular response in the IS region. These strong correlations provide unambiguous experimental and theoretical support for the semiconducting to metallic phase transition in multilayered MoS$_2$.

Since the neighbouring planes of the sulphur atoms along the $c$ axis are bonded by weak vdW forces, the $c$ axis contracts two times more than the $a$ axis below 28 GPa, exhibiting strong anisotropic compressional properties. The $c/a$ lattice-parameter ratio decreases monotonically with pressure up to 19 GPa, which indicates that the interactions between the adjacent planes of sulphur atoms become stronger under pressure. We note that the $c/a$ curve profile shows discontinuity at ~ 19 GPa. Similar behaviour was also reported by Aksyov et al.\textsuperscript{50} and can be attributed to a pressure-induced structural distortion in which MoS$_2$ layers slide from the original 2H$_x$-MoS$_2$ to the 2H$_x$-MoS$_2$ structure\textsuperscript{24}. Based on theoretical studies by Hromadova et al.\textsuperscript{22}, the peak positions in Raman measurements under high pressure coincide with the electronic properties of the emergent 2H$_x$-MoS$_2$ phase.

We can conclude that the observed changes in the electrical and vibrational response can be solely attributed to an iso-structural electronic phase transition.

We have demonstrated for the first time that a drastic drop in resistivity can be attributed to an electronic phase transition from semiconducting to metallic in multilayered MoS$_2$, which is further corroborated by in situ temperature-dependent resistivity measurement and Raman spectroscopy. Our results can be applied to novel MoS$_2$ devices, where pressure can be an external stimulus to dynamically control the band gap and tune the opto-electronic response or photoconductive gain. The experimentally observed transition is in good agreement with \textit{ab initio} theoretical calculations, allowing one to predict the thickness dependence of the critical transition pressure. Based on the similarity in the crystal and band structure of the semiconducting transitional metal dichalcogenides, the observed electronic phase transition in MoS$_2$ is likely to be experimentally accessible in MoSe$_2$, WS$_2$ and WSe$_2$ as predicted in a previous work\textsuperscript{18}. The combined experimental results and theoretical insights indicate a new opportunity for the development of multi-physics device concepts with coupled mechanical, electrical and optical properties based on the tunable and unique material structure of the semiconducting transitional metal dichalcogenides.

**Methods**

**Sample characterization.** MoS$_2$ single crystals were purchased from SPI Supplies (CAS# 1317-33-3). The purity of the crystals was characterized and estimated to be >99% by SPI supplies. The crystals were then thinned down to flakes of ~ 150 nm thick and 100 µm in length. Cross-section HR-TEM analyses of the sample flakes showed chemically and physically homogeneous layer surfaces at the nanometre scale. To understand the characteristics of the pristine as well as pressure-quinched samples (up to ~35 GPa and then quenched to ambient pressure), HR-TEM was used to analyse the lattice structures at the nanometre scale. Pristine MoS$_2$ was exfoliated onto a Cu TEM grid (SPI# 2040C-XA), while the quenched MoS$_2$ was transferred onto the Cu TEM grid using a micro-tip needle for HR-TEM analysis. The beam spot size was 5 nm in the TEM-EDX and an aperture size of 160 nm was used for the selected area electron diffraction (SAED). HR-TEM analyses of the recovered samples from DAC compression experiments show that their crystallinity and hexagonal lattice structure have not been altered drastically by compression and decompression in the DAC (Fig. 5 and Supplementary Fig. 7).

**High-pressure electrical resistance measurements.** Four-point probe electrical technique was employed to measure the electrical resistivity of the single-crystal multilayered MoS$_2$ as a function of pressure. Resistivity measurements as a function of temperature were also conducted in the SC, IS and metallic state. A modified short symmetric DAC having a pair of anvil culets of 400 µm or 500 µm was used in two separate runs to ensure reproducibility. A rhodium gasket was pre-indented from a thickness of 250 µm to 40 µm at ~20 GPa, and a hole with a diameter of 200 µm was drilled in the centre of the pre-indented area. Cubic BN (c-BN) fine powders were used as an insulating layer that was pressed into the pre-indented area and the drilled hole. Consequently, another hole of 100 µm in diameter was drilled at the centre of the 200 µm hole filled with c-BN, which was then further filled with soft h-BN fine powders as the pressure-transmitting medium while neon was used as the gas medium. A MoS$_2$ single crystal of 150 nm thick with dimensions of ~100 µm × 266 µm was loaded into the sample chamber, together with three ruby spheres as the pressure calibrant and four Au electrodes with a length of 12.5 µm for EC measurements. The resistivity of the sample was obtained by measuring the DC current changes in a pair of Au probes while sweeping DC voltages in another pair. The sample resistivity was derived by measuring the slope of the current–voltage ($I$–$V$) plot after taking the sample thickness into account\textsuperscript{3}. Quenched samples were further examined using cross-sectional SEM for potential dimensional changes of the samples to ensure reliable EC correction. For the opto-electronic measurements under high pressure, a green laser with 532 nm wavelength (2.3 eV) was focused down to a 10 µm × 10 µm window to ensure that the laser was exclusively on the sample.

**High-pressure laser Raman spectroscopy.** Raman spectra were measured using a green 532 nm Coherent Verdi V2 laser. The scattered light was dispersed by a 1,800 groves per mm grating and collected by an EMCCD (Andor Technology) in situ temperature-dependent resistivity measurement and Raman spectroscopy. Our results can be applied to novel MoS$_2$ devices, where pressure can be an external stimulus to dynamically control the band gap and tune the opto-electronic response or photoconductive gain. The experimentally observed transition is in good agreement with \textit{ab initio} theoretical calculations, allowing one to predict the thickness dependence of the critical transition pressure. Based on the similarity in the crystal and band structure of the semiconducting transitional metal dichalcogenides, the observed electronic phase transition in MoS$_2$ is likely to be experimentally accessible in MoSe$_2$, WS$_2$ and WSe$_2$ as predicted in a previous work\textsuperscript{18}. The combined experimental results and theoretical insights indicate a new opportunity for the development of multi-physics device concepts with coupled mechanical, electrical and optical properties based on the tunable and unique material structure of the semiconducting transitional metal dichalcogenides.

**First-principle theoretical calculations.** Theoretical calculations were carried out using first-principle \textit{ab initio} DFT using Vienna \textit{Ab initio} Simulation Package (VASP)\textsuperscript{35}. All-electron projector augmented wave potentials\textsuperscript{36,37} and the PBE\textsuperscript{38} GGA were used to account for the electronic exchange and correlation. The weak vdW interaction was incorporated by adding a semi-empirical dispersion potential (D) to the conventional Kohn–Sham DFT energy, through a pairwise force field following Grimmes DFT-D2 method\textsuperscript{39}. The crystal structure was optimized by employing a conjugate gradient scheme until the forces on every atom were below 0.005 eV Å$^{-1}$, and that a well-converged Monkhorst–Pack k-point set (7 × 7 × 6) was used for this procedure. The phonon dispersion of MoS$_2$ was calculated using density functional perturbation theory\textsuperscript{40} implemented in VASP. An additional tool, Phonopy\textsuperscript{41}, which supports the VASP interface, was used for extracting the phonon frequencies. The force-constants were calculated with a supercell of 2 × 2 × 2 and the k-point set of 9 × 9 × 3. The criterion for the force convergence used for the phonon calculations was 10$^{-6}$ eV Å$^{-1}$.

Electrical conductivity of MoS$_2$ is calculated using BTT within the constant scattering time approximation (CSTAA)\textsuperscript{62}, as implemented in the BoltzTraP programme\textsuperscript{61}. In the CSTA, it is assumed that the scattering time ($\tau$) determining the electrical conductivity does not vary strongly with temperature. In the BTT, the motion of an electron is treated semi-classically. The group velocity of an electron in a particular band can be described as:

$$v_{g}(k, \omega) = \frac{\hbar}{m^*} \text{Re} \left( k \cdot E(k) \right)$$

where $v_{g}(k, \omega)$ is the $n$th energy band at point $k$ and $m^*$ is the effective mass of the carriers.
From the group velocity $v_{\text{g}}(i, \mathbf{k})$, the electrical conductivity tensor can then be calculated by the following equation:

$$\sigma(\mathbf{T}, \mathbf{E}) = \frac{1}{\gamma} \sum_{\mathbf{k}} v_{\text{g}}(i, \mathbf{k}) v_{\text{g}}(i, \mathbf{k}) |\text{c}(i, \mathbf{k})| - \frac{\partial \sigma(\mathbf{T}, \mathbf{E})}{\partial \mathbf{T}} \text{dE} \cdot (3)$$

where $\mathbf{T}$ is the relaxation time, $\alpha$ and $\beta$ are the Cartesian indices, $N$ is the total number of $k$ points of the sampled $\mathbf{k}$, $V$ is the volume of the unit cell, $f_s$ is the Fermi Dirac distribution function and $e$ is the elementary charge.

In order to estimate the electrical transport properties of bulk MoS$_2$, the calculations for the electronic structure were performed using a denser $k$-point set of $32 \times 32 \times 8$. This was followed by the calculation of group velocities by Fourier integration of the band energies as a function of $k$. Consequently, the transport properties were calculated by using equation (3). From the electronic structure it is possible to calculate $\sigma/\tau$ as a function of temperature ($T$) and carrier concentration ($n$), but it is not possible to calculate $\sigma$ without relaxation time ($\tau$). To approximate the relaxation time, we used experimental data from Mahalawey et al. (2010). The reported experimental electrical conductivity is $0.03 \Omega^{-1} \text{cm}^{-1}$ at room temperature, which combined with the calculated $\sigma/\tau$ yield $\tau = 7.5 \times 10^{-14}$.

We then calculate $\sigma$ as $n/\tau \times \mathbf{T}$.

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Author contributions

A.P.N initiated this collaborative research project. J.Z., J.L., X.W. and J.-F.L. designed the experiment. A.P.N, D.A, J.Z., J.L. and X.W performed the measurements. D.A., S.B., T.P. and A.K.S. conducted the theoretical modelling and correlation with experimental data. D.A. led the writing of the paper. All the authors participated in the discussion of the results and the whole project was supervised by A.K.S., D.A. and J.-F.L.

Additional information

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Supplementary Information:

The pressure dependent resistivity in the semiconducting state (SC) can be understood within the context of pressure activated conduction of dopant or defect states, consistent with prior reports of the reduction of dopant activation energy ($E_A$) with increasing pressure in MoS$_2$ crystals [1]. We note that n-type carrier conduction is the dominant transport mechanism in mined natural MoS$_2$ materials [1,2,3]. In a careful study by Hinkle and co-workers on MoS$_2$ obtained from the same supplier (SPI), native defects such as interstitials and vacancies were found to be responsible for the defect or dopant states rather than external impurity atoms. This is consistent with our elemental analysis (Figure S7), and overall the material can be summarized to be of high chemical purity but with native defects. On this basis, the effects of external chemical dopants and intercalated chemical species can be ruled out.

The pressure activated model assumes a weak or negligible mobility dependence on pressure, justified by a prior experimental study of n-type MoS$_2$ [1]. To first order, the activation energy can be described by $E_A = E_{AO} - mP$ in the semiconducting state [4,5]. $E_{AO}$, $m$, and $P$ are the activation energy at ambient pressure, linear coefficient of the pressure dependent activation energy, and applied pressure respectively. Analytically, the resistivity can be captured by an exponential model as is appropriate in the semiconducting state, $\rho = \rho_o \exp((E_A - E_{AO})/E_{th}) = \rho_o \exp(-mP/E_{th})$, where $\rho_o$ is the ambient resistivity and $E_{th}$ is the thermal energy. The pressure activated model proves adequate in understanding the resistivity or resistance dependence on pressure in the semiconducting state and shows good agreement to the experimental data (Figure S1). The best fit value of the linear coefficient is $m \approx 9.7$ meV/GPa within the range of values (~7-26 meV/GPa) of a previous study on MoS$_2$ [1], and within a factor of two of a recent study on WSe$_2$ [4].


Figure S1. Resistance dependence on pressure in the semiconducting region. The pressure activated carrier transport model shows good agreement with the experimental data.
Figure S2. Theoretical temperature-dependent resistivity of MoS$_2$ at selected pressures. (a) Semiconducting state, and (b) metallic state.
Figure S3. Angular momentum projected density of states (LDOS) of Mo and S in multilayered MoS$_2$ at representative pressures. (a) and (b) are LDOS at 0 and 29.6 GPa, respectively. Zoom in of the LDOS at (c) 0 GPa, and (d) 29.6 GPa. The Fermi level is at 0 eV.
**Figure S4.** **Raman intensity ratio.** $I_{A_{1g}}/I_{E_{2g}}$ ratio as a function of pressure shows an increase in the IS region. The maximum intensity ratio is observed in the metallic state. The insets show the relative intensities of the $E_{2g}$ and $A_{1g}$ peaks at selected pressures.

**Figure S5.** **Theoretically predicted phonon bands at representative pressures.** The results indicate that the splitting in the bands increases with increasing pressure. The $E_{2g}$ (blue line) and $A_{1g}$ (red line) modes are identified from the dispersion curves at the $\Gamma$ point and their frequencies at ambient conditions are 375.5 cm$^{-1}$ and 405.5 cm$^{-1}$, respectively.
Figure S6. Theoretically-predicted XRD results for multilayered MoS$_2$ as a function of pressure. The $d$-spacings of representative lattice planes as a function of pressure. No new peaks are observed.
Figure S7. Electron microprobe analyses of the multilayered MoS$_2$ sample. (a) HR-TEM image of the honeycomb structural arrangement of the multilayered MoS$_2$. Inset: FFT image of the pristine multilayered MoS$_2$ sample. (b) Cross-sectional HR-TEM image of a multilayered MoS$_2$ before compression showing the interlayer distance to be approximately 6.5 Å. (c) TEM-EDX spectra of the multilayered crystalline MoS$_2$ after decompression. (d) SEM-EDX spectra for the multilayered MoS$_2$. Inset: SEM images are shown before loading and after decompression.
Figure S8. Pressure-strain relation and the theoretical band gap dependence on strain. (a) Pressure relationship to compressive strain, which allows correlation of the theoretical pressures in this work to strain. The red line is a quadratic fit to the data. (b) Band gap reduction with normal compressive strain applied to multilayered (bi-layer, tri-layer, four-layer, five-layer, six-layer and bulk) MoS$_2$. (c) Predicted critical strain threshold ($|\varepsilon_{th}|$) as a function of the number of layers. The critical strain threshold is the strain corresponding to the closure of the band gap.