Pressure-Modulated Conductivity, Carrier Density, and Mobility of Multilayered Tungsten Disulfide

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ABSTRACT Tungsten disulfide (WS₂) is a layered transition metal dichalcogenide (TMD) that differs from other two-dimensional (2D) compounds such as graphene due to its unique semiconducting, tunable-band-gap nature. Multilayered WS₂ exhibits an indirect band gap E_g of ~1.3 eV, along with a higher loadbearing ability, that is promising for strain-tuning device applications, but the electronic properties of multilayered WS₂ at higher strain conditions (*i.e.*, static



strain >12%) remain an open question. Here we have studied the structural, electronic, electrical, and vibrational properties of multilayered WS₂ at hydrostatic pressures up to \sim 35 GPa experimentally in a diamond anvil cell and theoretically using first-principles *ab initio* calculations. Our results show that WS₂ undergoes an isostructural semiconductor-to-metallic (S-M) transition at approximately 22 GPa at 280 K, which arises from the overlap of the highest valence and lowest conduction bands. The S-M transition is caused by increased sulfur-sulfur interactions as the interlayer spacing decreases with applied hydrostatic pressure. The metalization in WS₂ can be alternatively interpreted as a 2D to 3D (three-dimensional) phase transition that is associated with a substantial modulation of the charge carrier characteristics including a 6-order decrease in resistivity, a 2-order decrease in mobility, and a 4-order increase in carrier concentration. These distinct pressure-tunable characteristics of the dimensionalized WS₂ differentiate it from other TMD compounds such as MoS₂ and promise future developments in strain-modulated advanced devices.

KEYWORDS: transition metal dichalcogenides · 2D materials · pressure engineering · strain · diamond anvil cell

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wing to the rich two-dimensional character of the transition metal dichalcogenides (TMDs), interest in both the electronic and structural aspects of these materials has been growing rapidly.^{1–4} TMDs afford a variety of electronic states, such as superconducting,⁵ semiconducting, and metallic states,^{3,6} in addition to Mott transition⁷ and Anderson localization phenomena.⁸ By changing the level of interaction in the multilayered TMDs, as in our previous study, we have shown the emergence of an isostructural semiconductor to metal (S–M) transition in MoS₂ that is associated with significant changes in vibrational, optical, electrical, transport, and elastic properties.^{6,9} Of the semiconducting TMD materials, tungsten disulfide (WS₂) has attracted significant interest due to its unique structural,¹⁰ optical,^{11,12} thermal,¹³ and electronic¹⁴ properties. Unlike monolayer graphene, which

has sp² hybridization, multilayered semiconducting WS₂ has an indirect band gap $E_{\rm q}$ of ~1.3 eV. Similar to other TMDs such as MoS₂, WS₂ is a layered TMD in the hexagonal crystal structure, in which tungsten has a trigonal prismatic coordination to sulfur and strong in-plane covalent bonds exist between the transition metal (W) and the two chalcogen (S) atoms, while weak outof-plane van der Waals (vdW) forces exist interstitially between layers. Since the outof-plane atoms along the c-axis are interacting via weak vdW forces, compression is easier along this axis in comparison to the covalently bonded basal plane. This has therefore enabled experimental preparation of WS₂ by means of mechanical exfoliation for fundamental studies. Applying hydrostatic pressure allows for control over the vdW interlayer spacing and therefore affords modulation of the electronic properties.

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VOL. XXX . NO. XX . 000-000 . XXXX ACSNA

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Figure 1. Pressure-induced metalization of the multilayered WS₂. (a) Electrical resistivity (ρ) as a function of pressure at representative temperatures. The results show a resistivity reduction by 6 orders of magnitude, leading to a gradual metalization from the semiconducting (SC) to the semimetallic (SM) state at approximately 20 GPa, while the metallic state (Metal) completely occurs at above ~32 GPa. (b) Temperature-dependent resistivity at each given pressure. The change in the d ρ /dT slope from negative to positive trend is used to ascertain the transition from the semiconducting to the metallic state, respectively.

53 Along with the higher density and molecular weight,

54 the load-bearing ability of WS_2 is higher than MoS_2 .

55 These properties of WS₂ allow for pressure or strain

engineering, offering a degree of control in tuning thestructure—property relations of the layered nanoma-

terials that can be exploited in advanced optical
switches,¹⁵ sensors,¹⁶ and mobility engineering of
transistor devices.¹⁷

60 Experimentally, to modify the electronic properties 61 of WS₂, several methods including intercalation,¹⁸ 62 layer confinement,¹⁹ chemical vapor growth,^{20–22} dual 63 gating,¹⁷ and strain²³ have been explored. From a 64 65 theoretical viewpoint, several studies have concen-66 trated their efforts on strain (i.e., uniaxial or biaxial strain) engineering of the electronic properties of 67 WS2,^{10,24,25} uncovering several phenomena such as 68 strain-induced direct-to-indirect band gap (D-to-I) 69 transition⁹ and semiconductor-to-metallic (S-M) 70 transition.^{24,26} Compared to these methods, applying 71 hydrostatic pressure permits studies of larger mechan-72 ical effects on the structural and electronic properties. 73 Despite theoretical studies²⁴ suggesting metaliza-74 tion of multilayered WS₂, no experimental evidence for 75 such a transition has surfaced until now. In this study, 76 using a diamond anvil cell (DAC) apparatus (Figure S1a), 77 we examine the gradual S-M transition of WS_2 up to 78 \sim 35 GPa. With a 6-order decrease in resistivity, semi-79 conducting WS₂ metalizes at ~22 GPa at room tem-80 81 perature, while a 4-order increase in carrier concentration is observed. Along with the experimental evidence, 82 first-principles ab initio theoretical calculations aug-83 ment the experimental results to clearly elucidate the 84 underlying physics responsible for the S-M transition 85 and the increase in the carrier concentration. The 86 electronic changes observed in carrier density and 87 mobility for the first time are discussed in terms of 88 their relevance to the metalization and sulfur-sulfur 89 interactions. The continuous tuning of the optical, 90

structural, and electronic states provides a platform for developing pressure-modulated electronics or pressure-tronics for future material technologies.

RESULTS AND DISCUSSION

The electronic transport measurements over the 95 range of \sim 35 GPa reveal the tunability of the material 96 properties of WS₂. Standard four-point probe in situ 97 electrical resistivity measurements were conducted 98 in a DAC (Figure S1b). Under hydrostatic pressure, 99 the measured electrical resistivity (ρ) shows a gradual 100 decrease with increasing pressure and ultimately un-101 dergoes a metalization at pressures above 22 GPa at 102 280 K (Figure 1a). Our results show that the semicon-103 F1 ducting (SC) to metal (M) transition occurs over a broad 104 pressure-temperature range that is intermediate be-105 tween the two states. The resistivity profiles at different 106 pressures are similar for various temperatures but 107 vary in resistance values owing to thermally activated 108 carriers.²⁷ To uncover the semiconducting and metallic 109 behavior of WS₂ at high pressures, the resistivity of the 110 sample is measured as a function of temperature to as 111 low as 2 K. The temperature-dependent resistivity 112 profile shows that at pressures lower than approxi-113 mately 22 GPa a negative $d\rho/dT$ is observed, indicating 114 the presence of a semiconducting state. At pressures 115 above 22 GPa, a positive $d\rho/dT$ is observed, reflective of 116 a metallic state in the multilayered WS₂ (Figure 1b). 117 Although we do not find evidence of a pressure-118 induced superconducting state up to \sim 35 GPa at 2 K, 119 applying hydrostatic pressure onto multilayered WS₂ 120 shows a 6-order magnitude tunability of the electrical 121 resistivity from the semiconducting to metallic state. 122

Analysis of the pressure-dependent resistivity profile123at representative pressures and temperatures shows that124the S-M transition occurring at a range of 23-28 GPa125exhibits a negative transition boundary (Figure 2a).126 F2At 290 K, the electrical resistivity decreases gradually127

VOL. XXX • NO. XX • 000-000 • XXXX AC





Figure 2. Metalization mechanism of the multilayered WS₂ as a function of hydrostatic pressure. (a) Temperature-pressure contour plot of resistivity showing the transition region from the semiconductor to metallic region that is derived from experimental electrical conductivity measurements in a DAC. The dashed line is plotted to highlight the onset of metalization transition as well as the overall transition boundary that exhibits a negative slope between the semiconducting and the metallic state. (b) Arrhenius plot showing the activation energy exponentially decreases with pressure, indicating the occurrence of the metallic state at pressures above ~22 GPa. Estimates of the activation energy are obtained using ln $R \propto E_a/2k_BT$ in the temperature range between 50 and 100 K, where *R* is the electrical resistance, k_B is Boltzmann's constant, and E_a is the activation energy. (c) Theoretical band structure diagrams at the M, K, and Γ symmetry points at three representative pressures of 0, 20.4, and 39.5 GPa depicting the closure of the band gap. The charge densities at the VBM and CBM increase in interlayer interactions; at 39.5 GPa, the electrons are shown to cross the Fermi level, suggesting a complete metalization.

¹²⁸ by 6 orders of magnitude from $2 \times 10^2 \Omega$ cm at 10 GPa

to 3 imes 10⁻⁴ Ω cm at 36 GPa. Unlike the abrupt drop in 129 ρ for MoS₂ in our previous study,⁶ a gradual decrease in 130 131 ρ is observed in WS₂, which suggests the gradual tun-132 ability of the electronic structure and band gap. It is notable that the minimum resistivity observed here 133 $(3 \times 10^{-4} \,\Omega \text{cm}$ at 36 GPa) is comparable to the resistivity 134 $(\sim 10^{-4} \ \Omega \text{cm})$ of semimetallic or metallic TMDs under 135 ambient conditions.³ To understand the S-M depen-136 dence on the transition metal (W or Mo), we compare 137 the optical and electronic structure of WS₂ and MoS₂ 138 (Figure S2). The band diagrams of the bulk WS₂ and MoS₂ 139 are similar and show an indirect band gap of \sim 1.3 eV at 140 ambient pressure. Experimentally, multilayered WS₂ me-141 142 talizes at \sim 22 GPa, in comparison to multilayered MoS₂, which metalizes at \sim 19 GPa at room temperature. In situ 143 X-ray diffraction (XRD) shows that the in-plane compres-144 sion and out-of-plane compression for MoS₂ are more 145 than those for WS₂, which implies that the pressure 146 effects are more prominent on MoS₂ than WS₂. To 147 understand the differences between the two TMDs, we 148 measure the Raman-pressure dependence (cm^{-1}/GPa), 149 150 transition pressure, and the resistivity (ρ) in the semiconducting and metallic region (Figure S2). 151

The extracted activation energy depends on pres-152 sure as shown in Figure 2b, which can be analytically 153 modeled as $E_a = 34.4 - 15e^{0.04P}$ where E_a is the thermal 154 activation energy (in meV) and P is pressure (in GPa). 155 The effective defect energy level in the band gap that 156 typically contributes mobile carriers is directly related 157 to the activation energy, and as the band gap closes, 158 the activation energy approaches zero. The good 159 agreement between the activation energy and the 160 onset of metalization (denoted as semimetallic region 161 in Figure 1a) indicates that the increased charge trans-162 port in WS₂ is pressure activated. Further application 163 of pressure beyond ~22 GPa results in intrinsic band 164 closure and complete metalization (denoted as metal-165 lic region in Figure 1a). The pressure at which metaliza-166 tion occurs is heavily dependent on the number of 167 layers present. From our previous work,⁶ we speculate 168 that the pressure of metalization decreases with an 169 increase in the number of WS₂ layers. Theoretical 170 calculations also confirm the closure of the multi-171 layered WS₂ band gap with applied hydrostatic pres-172 sure (Figure 2c). Beyond 32 GPa, the valence band 173 maxima (VBM) and the conduction band minima 174 (CBM) cross the Fermi level, indicating a complete 175

VOL. XXX = NO. XX = 000-000 = XXXX ACS

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Figure 3. Electronic carrier dynamics of the multilayered WS₂ as a function of pressure. (a) The resistivity ratio (r_{ρ}) at pressures above 22 GPa is $r_{\rho} > 1$, which signifies the onset of metalization, whereas $r_{\rho} < 1$ is observed at lower pressures. The red line indicates the electronic transition between the semiconducting and the metallic state. (b) The carrier density increases by approximately 2 orders of magnitude from 10^{19} cm⁻³ at 15 GPa to 10^{21} cm⁻³ at 35 GPa in the semiconductor and metallic regions, respectively. (c) The Hall mobility decreases by 2 orders of magnitude, indicating the prominent effect of the interlayer scattering.

176 metalization past this pressure point. With increasing pressure, both the VBM and CBM shift their energy 177 levels due to the increased interlayer electronic cou-178 pling, similar to the case of MoS_{2.}⁶ The VBM is contrib-179 uted from the combination of both the antibonding p_z 180 orbitals on S atoms and the d_{z^2} orbitals from W atoms. 181 With increasing pressure, the energy level of the VBM 182 shifts significantly upward.²⁸ The CBM, which is also 183 partially composed of the bonding p_z orbitals from S, 184 185 shifts its energy downward due to the increased overlap 186 upon the decrease of the interlayer distance (Figure S3). 187 In order to probe charge transport under pressure, 188 Hall effect measurements were conducted with a magnetic field (*H*) perpendicular to the a-b plane of 189 the single-crystal WS₂ and the H was swept as a 190 function of pressure at three given temperatures of 2, 191 130, and 290 K, respectively (Figure S4). These results 192 allow us to derive the Hall coefficients and resistivity of 193 WS₂ at high pressures.^{29,30} A gradual increase in the 194 conductivity is observed, which can be understood by 195 the increase in interlayer interactions, and is consistent 196 197 with our theoretical results and prior reports on multilayered MoS₂ with increasing hydrostatic pressure.^{6,28,31} 198 The effect that the structural perturbation has on 199 electron transport can be quantified by the resistivity 200 ratio $r_{\rho r}$ defined as ρ_{280} K/ ρ_{2K} .⁷ The transition of the 201 resistivity ratio r_{ρ} from values smaller than 1 to values 202 203 larger than 1 is indicative of the onset of metalization (Figure 3a). The carrier density increases with applied F3 204 pressure (Figure 3b), showing an about 2-order mag-205 nitude increase in carrier density at 15 GPa compared 206

to 35 GPa. In comparison to the reported carrier density 207 at room ambient pressure, the carrier density at 35 GPa 208 in this work demonstrates about 4 orders of magnitude 209 tunability.¹⁶ Ab initio calculations also show that the 210 densities of state increase with pressure, and this 211 increase in carrier density is associated with the $d_{x^2-y^2}$ 212 orbital contributing significantly to the carrier concen-213 tration in multilayered WS₂. The Hall measurements 214 also permit us to evaluate the Hall carrier mobility, 215 in which a decrease from ${\sim}240~\text{cm}^2~\text{V}^{-1}~\text{s}^{-1}$ in the 216 semiconducting region to $\sim 60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the 217 metallic region is observed (Figure 3c). We note that a 218 recent report on a high-mobility multilayer WS₂ tran-219 sistor gave an estimate of the field-effect mobility of 220 \sim 90 cm² V⁻¹ s⁻¹ at room temperature.¹⁶ The decrease 221 in the mobility of WS₂ in the metallic phase is due to 222 the pressure-induced doping when the free carriers 223 collide with the confined lattice more frequently, 224 therefore resulting in a decrease in drift velocity.³² 225 The mobility reported in this work is the Hall mobility, 226 a measure of the intrinsic carrier mobility, and is 227 typically higher than the field-effect mobility, which 228 suffers from additional transport effects such as gate-229 oxide interface scattering and contact resistance.^{33,34} 230

Electronic transitions are usually accompanied by 231 crystal structural distortions or transformations. For 232 many pressure-induced structural phase transitions, 233 in situ XRD can be used to decipher the structure 234 modification. For pressure-induced isostructural phase 235 transition, analysis of the bulk and axial incompressi-236 bility may allow a richer understanding of the driving 237 forces of high-pressure phase transitions. Refinements 238 of the XRD patterns of the sample show that it re-239 mains isostructural across the metalization transition 240 (Figure 4a). Although the pressure-volume relation of 241 F4 the multilayered WS₂ does not display a sudden drop 242 across the metalization transition at approximately 243 22 GPa, analysis of the compression data using a 244 third-order Birch-Murnaghan (BM) equation of state 245 (EOS) shows that the metallic state exhibits a distinct 246 EOS behavior from that of the semiconducting state 247 (Figure 4a). Furthermore, the linear compressibility of 248 the out-of-plane *c*-axis is much higher than that of the 249 in-plane *a*-axis in the semiconducting state at pres-250 sures up to 22 GPa, bringing WS₂ layers closer to each 251 other, which eventually leads to enhanced sulfur-252 sulfur interactions and resulting metalization. On the 253 other hand, the axial compressibility of the metallic 254 state does not show a distinct difference between the 255 a- and c-axes. Although we do not observe a structural 256 distortion up to 35 GPa, it has been suggested that 257 further pressure increase could lead to layer sliding 258 from the stable $2H_a$ phase to the $2H_c$ phase at high 259 pressure.35 260

To determine the structural distortion and changes 261 in the electronic states, Raman spectroscopy can be used 262 and has proven to be a powerful tool to determine 263

VOL. XXX = NO. XX = 000-000 = XXXX ACS

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Figure 4. Structural and vibrational properties of the multilayered WS₂ under high pressure. (a) *In situ* XRD showing that the sample remains in the hexagonal structure up to 60 GPa. The *c*-axis is more compressible than the *a*-axis at pressures below approximately 22 GPa but becomes much less compressible at pressures higher than 22 GPa, where the metalization occurs. The dashed gray line shows the S–M transition pressure at ~22 GPa and 280 K. (b) Raman spectra for selected temperatures and pressures showing that with increasing temperature, the A_{1g} mode becomes more prominent while the 2LA(M) is suppressed (left panel). Moreover, hydrostatic pressure suppresses the E_{2g} mode (right panel). (c) Pressure-dependent Raman shifts showing a phonon hardening for both the E_{2g} and A_{1g} modes. The solid lines are the theoretical calculation, which are in good agreement with experimental results. (d) Temperature-dependent Raman shifts indicating a phonon softening at a rate of -0.02 and -0.01 cm⁻¹/K for the E_{2g} and A_{1g} modes, respectively.

information on the number of layers,³⁶ doping 264 concentration,³⁷ and strain effect² in TMDs. By study-265 ing the Raman pressure dependence, S-M transitions 266 can be further elucidated.^{6,9} Here we have investigated 267 the vibrational modes of WS₂ with varying pressure 268 and temperature. Selected pressure and tempera-269 ture Raman profiles show phonon hardening as well 270 as the $E_{2\alpha}$ mode being suppressed at high pressures 271 (Figure 4b), which has also been observed in other 272 TMDs.^{6,38} Suppression of the intensity ratio between 273 the A_{1q} and E_{2q} modes decreases with pressure (Figure S5a), 274 and the suppressed E_{2g} mode is associated with broad-275 ening of the fwhm at higher pressures (Figure S5b). At 276 277 higher temperatures, the 2LA(M) mode is more prominent (Figure 4b) and the fwhm is observed to increase 278 with temperature for all Raman modes (Figure S5c). 279 The intensity ratio between the two Raman modes has 280 also been shown to decrease with an increase in 281 temperature (Figure S5d). At lower temperatures, there 282 is overlap between the 2LA(M) and E_{2q} modes, and 283 only one integral peak is observed. The pressure-284 dependent Raman shows the A1g mode being promi-285 nent at high pressures, while the $E_{\rm 2g}\xspace$ mode is 286

suppressed (Figure 4c). The temperature-dependent 287 Raman, however, indicates phonon softening (Figure 4d) 288 at a rate of -0.02, -0.01, and -0.01 cm⁻¹/K for the 289 2LA(M), E_{2a}, and A_{1a} modes, respectively. In comparison 290 to the monolayer counterpart,³⁹ an order of magnitude 291 difference in the softening rate is observed in multi-292 layered WS₂. We attribute the difference to the double 293 resonance scattering that is present only in mono-294 layer WS₂.²¹ 295

CONCLUSION

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In summary, we have applied hydrostatic strain as 297 high as 18% to multilayered WS₂ in a high-pressure 298 DAC coupled with electrical (Hall measurements), vi-299 brational, and structural investigations up to approxi-300 mately 35 GPa. Together with the DFT calculations, our 301 results reveal the band gap closure of the multilayered 302 WS₂ that is predominantly modulated via increasing 303 interlayer interactions and sulfur-sulfur s orbital inter-304 actions at pressures above 22 GPa (15% strain), leading 305 to dramatically enhanced conductivity and carrier 306 density while the mobility is drastically reduced. This 307 metallic WS₂ occurs at a higher pressure than that of 308

VOL. XXX • NO. XX • 000-000 • XXXX ACS

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the multilayered MoS_2 and can be understood here in terms of the layer tuning effect on the electronic and transport properties of the TMD compounds. These

results on the electronic structures and carrier den-

313 sity and mobility of strain-tuned WS₂ lead to a better

314 understanding of the multilayered TMDs under high

322 METHODS

323 High-Pressure Laser Raman Spectroscopy. The Raman spectra were recorded with a Renishaw Micro-Raman spectroscopy 324 325 system (Renishaw PLC, Gloucestershire, UK) with a laser wavelength of 532 nm, spectral resolution of $\sim 1 \text{ cm}^{-1}$, and focus 326 327 laser spot on the sample of $\sim 1 \mu m$ with an output power of 328 100 mW. High-pressure Raman experiments were performed 329 using a symmetric diamond anvil cell with silicone oil as the pressure-transmitting medium. The WS₂ single-crystal sample 330 331 was purchased from 2D Semiconductors. The purity of the 332 crystals was characterized and estimated to be greater than 333 99% by 2D Semiconductors. The crystal was placed in a T301 stainless-steel gasket chamber with a diameter of 125 μ m and a 334 335 thickness of 30 μ m. Ruby spheres were loaded close to the 336 sample in the sample chamber of the DAC simultaneously as the 337 pressure calibrant. Pressure was measured based on the shifts of the ruby R_1 and R_2 fluorescence lines.⁴⁰ Considering that 338 339 silicone oil was added as a pressure medium, the estimated 340 pressure errors are \sim 0.5 GPa at pressures less than 10 GPa and \sim 1 GPa at higher pressures. 341

342 High-Pressure Electrical Resistance Measurements. The resistance measurement of the WS₂ single-crystal sample under high 343 pressure was conducted using the standard four-point-probe 344 345 electrical technique in a screw-type DAC made of BeCu alloy. To 346 measure the resistivity as a function of temperature of the WS₂ single-crystal sample, the DAC was put inside a Mag Lab system 347 348 upon loading. The temperature was automatically program controlled via the Mag Lab system. The diamond was 300 μ m 349 350 in diameter, with a flat center and an 8 degree bevel out to 500 μ m. A T301 stainless steel gasket was preindented from a 351 thickness of 250 μ m to 40 μ m, and a hole was drilled at the 352 353 center with a diameter of 100 μ m. Fine cubic boron nitride (c-BN) powders were used to cover the gasket to keep the 354 355 electrode leads insulated from the metallic gasket as an insulat-356 ing layer. The c-BN powders were pressed and further drilled 357 into the center chamber. A WS₂ single crystal with dimensions 358 of 40 μ m \times 50 μ m \times 5 μ m was loaded into the sample chamber, 359 together with three ruby spheres as the pressure calibrant and 360 four slim gold wires (18 um) used as electrodes for the electrical resistance measurements. The soft cubic boron nitride (hBN) 361 fine powder surrounded the center chamber as the pressure-362 363 transmitting medium.

The high-pressure Hall effects were measured based on the
van der Pauw method using a piston cylinder-type instrument
that was inserted into the Mag Lab system.

367 Theoretical Calculations. Theoretical calculations were carried 368 out using the Vienna Ab Initio Simulation Package (VASP) 1-3 based on the Perdew-Burke-Ernzerhof (PBE) functional 369 370 4,5 and the projector augmented wave method 4,6. A Monkhorst-371 Pack k-point mesh of 17 imes 17 imes 5 was used to sample the first Brillouin zone, and the plane wave cutoff was set to be 372 950 eV.^{41,42} The ions were relaxed by a quasi-Newton algorithm 373 while keeping the unit cell volume fixed, and the pressure was 374 calculated after relaxation. The convergence criteria are 10^{-6} eV 375 and 10^{-5} eV per unit cell for electronic and ionic relaxations, respectively.⁴³ In Raman spectrum calculations, the Hessian 376 377 378 matrix was calculated using the finite difference method; each ion was displaced 0.015 Å in each direction from its equilibrium 379 position, and the Hessian matrix was calculated from the 380 381 calculated force constants. The vibrational frequencies were 382 calculated from eigenvalues of the Hessian matrix.

Conflict of Interest: The authors declare no competingfinancial interest.

strains and promise future developments in strainmodulated advanced devices. At higher pressures than in this study it is conceivable that a superconducting state in WS₂ may occur similar to recent very high pressure investigations in multilayered MoS₂.³¹

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Comparison of MoS2 and WS2, the carrier density measurements at different temperatures and pressures, and the
diamond anvil cell setup (PDF)388
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REFERENCES AND NOTES

- Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics Of Two-Dimensional Transition Metal Dichalcogenides. *Nat. Nanotechnol.* 2012, *7*, 699–712.
- 2. Akinwande, D.; Petrone, N.; Hone, J., Two-Dimensional Flexible Nanoelectronics. *Nat. Commun.* **2014**, *5*.5678
- Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The Chemistry Of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* 2013, *5*, 263–275.
- Chang, H.-Y.; Yang, S.; Lee, J.; Tao, L.; Hwang, W.-S.; Jena, D.; Lu, N.; Akinwande, D. High-Performance, Highly Bendable MoS2 Transistors with High-K Dielectrics for Flexible Low-Power Systems. ACS Nano 2013, 7, 5446–5452.
- Castro Neto, A. H. Charge Density Wave, Superconductivity, and Anomalous Metallic Behavior in 2D Transition Metal Dichalcogenides. *Phys. Rev. Lett.* **2001**, *86*, 4382–4385.
- Nayak, A. P.; Bhattacharyya, S.; Zhu, J.; Liu, J.; Wu, X.; Pandey, T.; Jin, C.; Singh, A. K.; Akinwande, D.; Lin, J.-F., Pressure-Induced Semiconducting To Metallic Transition In Multilayered Molybdenum Disulphide. *Nat. Commun.* 2014, 5.10.1038/ncomms4731
- Siegrist, T.; Jost, P.; Volker, H.; Woda, M.; Merkelbach, P.; Schlockermann, C.; Wuttig, M. Disorder-Induced Localization in Crystalline Phase-Change Materials. *Nat. Mater.* 2011, 10, 202–208.
- 8. Thouless, D. Anderson Localization in the Seventies and Beyond. *Int. J. Mod. Phys. B* **2010**, *24*, 1507–1525.
- Nayak, A. P.; Pandey, T.; Voiry, D.; Liu, J.; Moran, S. T.; Sharma, A.; Tan, C.; Chen, C.-H.; Li, L.-J.; Chhowalla, M.; et al. Pressure-Dependent Optical and Vibrational Properties of Monolayer Molybdenum Disulfide. *Nano Lett.* **2015**, *15*, 346.
- Duerloo, K.-A. N.; Li, Y.; Reed, E. J., Structural Phase Transitions In Two-Dimensional Mo- And W-Dichalcogenide Monolayers. *Nat. Commun.* 2014, 5.10.1038/ncomms5214
- Jo, S.; Ubrig, N.; Berger, H.; Kuzmenko, A. B.; Morpurgo, A. F. Mono- and Bilayer WS₂ Light-Emitting Transistors. *Nano Lett.* **2014**, *14*, 2019–2025.
 He, J.; Kumar, N.; Bellus, M. Z.; Chiu, H.-Y.; He, D.; Wang, Y.; Zhao,
 - H. Electron Transfer and Coupling in Graphene—Tungsten

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Disulfide van der Waals Heterostructures. Nat. Commun. 2014, 5, 5622

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- 13. Gandi, A. N.; Schwingenschlögl, U. WS₂ As an Excellent High-Temperature Thermoelectric Material. Chem. Mater. 2014, 26, 6628-6637.
- 14. Ovchinnikov, D.; Allain, A.; Huang, Y.-S.; Dumcenco, D.; Kis, A. Electrical Transport Properties of Single-Layer WS₂. ACS Nano 2014, 8, 8174-8181.
- 15. Tsai, D.-S.; Liu, K.-K.; Lien, D.-H.; Tsai, M.-L.; Kang, C.-F.; Lin, C.-A.; Li, L.-J.; He, J.-H. Few-Layer MoS₂ with High Broadband Photogain and Fast Optical Switching for Use in Harsh Environments. ACS Nano 2013, 7, 3905-3911.
- 16. Jobal M. W.: Jobal M. Z.: Khan M. E.: Shehzad M. A.: Seo, Y.: 456 457 Eom, J. Deep-Ultraviolet-Light-Driven Reversible Doping 458 Of WS₂ Field-Effect Transistors. Nanoscale 2015, 7, 747–757.
 - 17. Radisavljevic, B.; Kis, A. Mobility Engineering and a Metal-Insulator Transition In Monolayer MoS₂. Nat. Mater. 2013, 12.815-820.
 - 18. Ohuchi, F. S.; Jaegermann, W.; Pettenkofer, C.; Parkinson, B. A. Semiconductor To Metal Transition Of WS₂ Induced By K Intercalation In Ultrahigh Vacuum. Langmuir 1989, 5, 439-442
 - 19. Georgiou, T.; Yang, H.; Jalil, R.; Chapman, J.; Novoselov, K. S.; Mishchenko, A. Electrical and Optical Characterization Of Atomically Thin WS2. J. Chem. Soc., Dalton Trans. 2014, 43, 10388-10391.
 - 20. Yen, P. C.; Huang, Y. S.; Tiong, K. K. The Growth And Characterization Of Rhenium-Doped WS₂ Single Crystals. J. Phys.: Condens. Matter 2004, 16, 2171.
 - 21. Gutiérrez, H. R.; Perea-López, N.; Elías, A. L.; Berkdemir, A.; Wang, B.; Lv, R.; López-Urías, F.; Crespi, V. H.; Terrones, H.; Terrones, M. Extraordinary Room-Temperature Photoluminescence in Triangular WS2 Monolayers. Nano Lett. 2013, 13, 3447-3454.
 - 22. Chen, Y.; Xi, J.; Dumcenco, D. O.; Liu, Z.; Suenaga, K.; Wang, D.; Shuai, Z.; Huang, Y.-S.; Xie, L. Tunable Band Gap Photoluminescence from Atomically Thin Transition-Metal Dichalcogenide Alloys. ACS Nano 2013, 7, 4610-4616.
- 482 23. Voiry, D.; Yamaguchi, H.; Li, J.; Silva, R.; Alves, D. C. B.; Fujita, T.; Chen, M.; Asefa, T.; Shenoy, V. B.; Eda, G.; et al. Enhanced 484 Catalytic Activity In Strained Chemically Exfoliated WS₂ 485 Nanosheets For Hydrogen Evolution. Nat. Mater. 2013, 12, 850-855
- 487 24. Bhattacharyya, S.; Singh, A. K. Semiconductor-metal Tran-488 sition in Semiconducting Bilaver Sheets of Transition-489 metal Dichalcogenides. Phys. Rev. B: Condens. Matter 490 Mater. Phys. 2012, 86, 075454.
 - 25. Amin, B.; Kaloni, T. P.; Schwingenschlogl, U. Strain Engineering of WS₂, WSe₂, and WTe₂. RSC Adv. 2014, 4, 34561-34565.
 - Scalise, E.; Houssa, M.; Pourtois, G.; Afanas'ev, V.; Stesmans, 26. A. Strain-Induced Semiconductor To Metal Transition In The Two-Dimensional Honeycomb Structure Of MoS₂. Nano Res. 2012, 5, 43-48.
 - Streetman, B. G. Solid State Electronic Devices; Pearson 27. Education, Limited, 1972.
 - 28. Cao, B.; Li, T. Interlayer Electronic Coupling in Arbitrarily Stacked MoS₂ Bilayers Controlled by Interlayer S-S Interaction. J. Phys. Chem. C 2015, 119, 1247-1252.
 - 29. van der Pauw, L. J. A Method of Measuring Specific Resistivity and Hall Effect of Discs of Arbitrary Shape. Philips Res. Rep. 1958, 13, 1.
- 505 30. Kong, P. P.; Sun, F.; Xing, L. Y.; Zhu, J.; Zhang, S. J.; Li, W. M.; 506 Liu, Q. Q.; Wang, X. C.; Feng, S. M.; et al. Superconductivity in Strong Spin Orbital Coupling Compound Sb₂Se₃. Sci. 507 508 Rep. 2014, 4, 4.
- 31. Zhenhua Chi, F. Y.; Peng, F.; Zhu, J.; Zhang, Y.; Chen, X.; 509 Yang, Z.; Liu, X.; Ma, Y.; Zhao, Y.; Kagayama, T.; Iwasa, Y. 510 511 Ultrahigh Pressure Superconductivity in Molybdenum Disulfide. Arxiv 2015, 1503, 05331. 512
- 32. Harris, J. J. Delta-Doping of Semiconductors. J. Mater. Sci.: 513 Mater. Electron. 1993, 4, 93-105. 514
- 515 33. Pradhan, N. R.; Rhodes, D.; Xin, Y.; Memaran, S.; Bhaskaran, 516 L.; Siddiq, M.; Hill, S.; M. Ajayan, P.; Balicas, L. Ambipolar 517 Molybdenum Diselenide Field-Effect Transistors: Field-Effect and Hall Mobilities. ACS Nano 2014, 8, 7923-7929. 518

- 34. Chang, H.-Y.; Zhu, W.; Akinwande, D. On The Mobility And Contact Resistance Evaluation For Transistors Based On MoS₂ Or Two-Dimensional Semiconducting Atomic Crystals. Appl. Phys. Lett. 2014, 104, 113504.
- Hromadová, L.; Martoňák, R.; Tosatti, E. Structure Change, Layer Sliding, and Metallization in High-Pressure MoS₂. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 144105.
- Berkdemir, A.; Gutierrez, H. R.; Botello-Mendez, A. R.; Perea-Lopez, N.; Elias, A. L.; Chia, C.-I.; Wang, B.; Crespi, V. H.; Lopez-Urias, F.; Charlier, J.-C.; Terrones, H.; Terrones, M. Identification of Individual and Few Layers of WS₂ Using Raman Spectroscopy. Sci. Rep. 2013, 3.10.1038/srep01755
- 37. Laskar, M. R.; Nath, D. N.; Ma, L.; Lee, E. W.; Lee, C. H.; Kent, T.; Yang, Z.; Mishra, R.; Roldan, M. A.; Idrobo, J.-C.; et al. p-Type doping of MoS₂ thin films using Nb. Appl. Phys. Lett. 2014, 104, 092104.
- 38. Bandaru, N.; Kumar, R. S.; Baker, J.; Tschauner, O.; Hartmann, T.; Zhao, Y.; Venkat, R. Structural Stability of WS₂ Under High Pressure. Int. J. Mod. Phys. B 2014, 28, 1450168.
- M, T.; Late, D. J. Temperature Dependent Phonon Shifts in 39. Single-Layer WS2. ACS Appl. Mater. Interfaces 2014, 6, 1158-1163.
- Mao, H.; Xu, J.; Bell, P. Calibration Of The Ruby Pressure 40. 541 Gauge To 800 Kbar Under Quasi-Hydrostatic Conditions. 542 J. Geophys. Res. 1986, 91, 4673. 543
- 41. Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid 544 metals. Phys. Rev. B: Condens. Matter Mater. Phys. 1993, 47, 545 558-561. 546
- 42. Kresse, G.; Furthmiiller, J. Efficiency of Ab-Initio Total 547 Energy Calculations for Metals And Semiconductors Using 548 a Plane-Wave Basis Set. Comput. Mater. Sci. 1996, 6, 15-50. 549
- 43. Blöchl, P. E. Projector Augmented-wave Method. Phys. Rev. B: 550 Condens. Matter Mater. Phys. 1994, 50, 17953-17979. 551

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