# **Strain Induced Valley Degeneracy: A route to the Enhancement of Thermoelectric Properties of Monolayer WS<sub>2</sub>**

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# **Supplementary Information**

# SI1. Thermoelectric properties as a function of carrier concentration:

We explained the thermoelectric properties with the help of chemical potential( $\mu$ ). Here, we have discussed the thermoelectric properties of monolayer WS<sub>2</sub> from the point of view of carrier concentration.

The variation of Seebeck coefficient with carrier concentration (N) at 300K, 600K and 900K is shown in Fig.S1.a. The positive and negative values of N represent p-type and n-type doping respectively. Since S is inversely proportional to the carrier concentration so as N increases the value of S decreases. The S value decreases with increase in temperature because carrier concentration near the bandgap region increases with temperature as discussed earlier. There is also a flat region where S=0 at 300K because the carrier concentration is too low in the bandgap region at low temperature. But at 600K and 900K S=0 at only one point not in a range of chemical potential. The highest S value for the n-type doping is found to be 2727  $\mu$ V/K and for p-type doping it is 2821  $\mu$ V/K at 300K and at 600K and 900K the highest S value is found to be 1446 $\mu$ V/K and 969 $\mu$ V/K for n-type and 1429  $\mu$ V/K and 926  $\mu$ V/K for p-type carriers respectively. These values are exactly same when we calculated S as a function of chemical potential.

Fig.S1.b. shows the change in electrical conductivity of monolayer  $WS_2$  varies with carrier concentration at three different temperatures. As carrier concentration increases conductivity also increases and its highest value is obtained at 900K. It is clearly seen that  $\sigma$  value is higher for n-type carriersthan p-type carriers.

The variation of thermoelectric power factor  $S^2\sigma/\tau$  (relaxation time scaled) is shown in Fig.S1.c. The highest thermoelectric power factor of 33.35 x10<sup>10</sup> Wm<sup>-1</sup>K<sup>-2</sup>s<sup>-1</sup>is seen at 900K at a carrier concentration of  $1.4x10^{21}$ cm<sup>-3</sup>for n-type carriers and  $18.40 \times 10^{10}$  Wm<sup>-1</sup>K<sup>-2</sup>s<sup>-1</sup> at a carrier concentration of  $3.13x \times 10^{20}$ cm<sup>-3</sup>for p-type carriers. Both the carrier concentrations are close to the band edge where our transport study is focused. At lower temperature  $S^2\sigma/\tau$  values are low which are 13.34 Wm<sup>-1</sup>K<sup>-2</sup>s<sup>-1</sup> and 5.22 Wm<sup>-1</sup>K<sup>-2</sup>s<sup>-1</sup> for n-type and 6.77Wm<sup>-1</sup>K<sup>-2</sup>s<sup>-1</sup> and 12.90Wm<sup>-1</sup>K<sup>-2</sup>s<sup>-1</sup> for p-type at 600 and 300K respectively and at a lower carrier concentration. These values are also similar to that we calculated from chemical potential approach.



**Fig.S1.** The variation of a) Seebeck coefficient(S) b) electrical conductivity( $\sigma/\tau$ ) c) thermoelectric power factor(S<sup>2</sup> $\sigma/\tau$ ) and d) thermal conductivity (K<sub>el</sub>/ $\tau$ ) due to electrons as a function of carrier concentration(N) at 300K, 600K and 900K.

The thermal conductivity is also one of the important factors that influences the thermoelectric properties. For a good thermoelectric material electrical conductivity must be

higher than thermal conductivity. The variation of thermal conductivity with the carrier concentration is shown in Fig.S1.d. and it is higher at 900K. The electrical conductivity is four orders higher than the thermal conductivity of the material.

From both the approaches we have shown thermoelectric performance of monolayer  $WS_2$  is consistent and our results suggest that both lead to same conclusions.



# SI2. Electronic band structure:

**Fig.S2.** Band structure and DOS of monolayer  $WS_2$  under the application Bi axial strain of a) 0% strain b) -1% strain c) -6% strain d) -10% strain e) +1% strain f) +6 % strain and g) +10% strain. The Fermi levels are shown by red dotted lines.

The electronic band structure of monolayer  $WS_2$  is shown in Fig.S2.a. Monolayer  $WS_2$  exhibits a direct band gap of 1.81 eV with VBM and CBM both lie on K point. When we apply BCS its direct band gap increases to 1.95 eV at 1% of BCS and still VBM and CBM both lie on K point but after 1% of BCS the VBM still remains at K point but CBM shifts to a point between  $\Gamma$  and K point resulting a direct to indirect band gap transition at 2% of BCS and a decrease in indirect band gap and at 10% of BCS the indirect band gap becomes 1.31 eV as shown in Fig.S2.d. However, the effect of BTS in electronic band structure is slightly different. The direct to indirect band gap transition occurs at 1% of BTS where CBM still remains at K point but VBM shifts to  $\Gamma$  point resulting an indirect band gap decreases to a value of 1.59 eV. As BTS increases the band gap decreases very fast and at 6% BTS band gap becomes 0.55 eV only. A semiconducting to metal transition occurs at 10% of BTS where VBM and CBM meet each other at fermi level and band gap becomes almost zero at that point as shown in Fig.S2.g.But in case of BCS there was a finite band gap of 1.31 eV and no semiconductor to metal transitions was found at 10% strain.

In case of UCS the direct band gap increases first up to a highest value of 1.95 eV as observed at 2% of UCS as shown in Fig.S3.a. Further application of strain results a direct to indirect band gap transition at 3% UCS at which point VBM remains at K point but CBM shifts to a point between  $\Gamma$  and K points as seen for BCS. At 6% UCS the indirect band gap becomes 1.78 eV. It is observed that band gap decreases more for same amount of Bi axial strain than that of for uniaxial strain.

However, the bandgap remains direct up to 1% of UTS and direct to indirect band gap transition occurs at 2% of UTS. The direct band gap with a value of 1.72 eV at 1% of UTS is smaller than that of unstrained one. As the amount of strain further increases band gap decreases very fast but slower than that of BTS. Unlike BTS in this case semiconductor to metal transition was not found at 10% of UTS as shown in Fig.S3.e. There is a finite indirect band gap of 0.77 eV found at 10% of UTS. Semiconducting to metal transition may occur at higher strain than 10%. So, among all types and percentage of strain semiconductor to metal transition occurs very fast for BTS.



**Fig.S3.** Band structure of monolayer WS<sub>2</sub> under a) -2% b)-6% c) +1% d) +6% and e) +10% uniaxial strain. The red dotted lines represent Fermi level.

## SI3. Effect of Uniaxial strain on thermoelectric properties:

The effect of uniaxial strain is slightly different from Bi axial strain. Though the variation in Seebeck coefficient as shown in Fig. S4.a. does not differ very much than that of Bi axialstrain, but the power factor variation is different. The Seebeck coefficient increases with uniaxial compressive strain (UCS) and the highest value is obtained at 2% UCS with a value of  $1067\mu$ V/K for n-type and  $955\mu$ V/K for p-type carriers at 900K which is exactly same that of 1% BCS. But S decreases with the application of uniaxial tensile strain (UTS) for both n-type and p- type carriers. Like Bi axial strain here also S is higher for n-type than that of p-type carriers and the variations of S and band gap follow Goldsmid-Sharp relation. However, variation in S<sup>2</sup> $\sigma$ / $\tau$  (PF) shown in Fig.S4.b.is different from that of Bi axial strain. The PF increases with applied UCS and attains the highest value of 59 x 10<sup>10</sup> W/mK<sup>2</sup>s at 4% of UCS, which is almost 77% higher than the value obtained without strain for n-type carriers. After 4% PF decreases but remains at higher values than that of 0% strain. But with the application of UTS S<sup>2</sup> $\sigma$ / $\tau$  rapidly decreases for n-type carriers up to 4% of BTS and becomes constant with a much lower value than that without strain. It suggests that for n-type doping compressive strain is more effective than tensile strain.



**Fig. S4.** Variation in a) S and b)  $S^2\sigma/\tau$  under the application of uniaxial compressive and tensile strain for n-type doping and p-type doping at 300K, 600K and 900K. c) Variation in S and band gap with applied uniaxial compressive and tensile strain.

For p-type carriers,  $S^2\sigma/\tau$  decreases with application of UCS up to 4% and after that it becomes constant at a lower value than that without strain which is similar to that of BCS. But  $S^2\sigma/\tau$ increases linearly with the application of UTS and attains a value of 24x 10<sup>10</sup> W/mK<sup>2</sup>s at 6% of UTS which is almost 30% higher than that without strain. So, the application of UCS affects more for n-type doping and UTS for p-type doping although the highest power factor at 4% of UCS for n-type is very much higher than that of p-type carriers.



SI4. Electronic Band Structures and valley degeneracy:

**Fig.S5.**Band structure and valleys of monolayer  $WS_2$  under a) -6% Bi axial strain b) -6% uniaxial strain c) +3% Bi axial strain and d) +3% uniaxial strain. The green arrows show indirect transition.

# SI5. Structural stability:

#### SI5.1. Phonon dispersion curve:

We have calculated phonon dispersion curves of monolayer  $WS_2$  and their strained structures along high symmetry points  $\Gamma$ -K-M- $\Gamma$  in hexagonal Brillouin zone to show thermodynamic stability of these structures. Nine branches are found in phonon dispersion curve of monolayer  $WS_2$  corresponding to nine vibrational normal modes. Three lower frequency branches correspond to acoustic vibrational modes represented by in plane longitudinal acoustic (LA) and transverse acoustic (TA) mode and out of plane modes (ZA) as shown in Fig. S6.a. The six upper frequency branches are optical modes. The in-plane LA and TA modes show linear relationship with k vector near the  $\Gamma$  point (k=0) but out of plane ZA branch has a quadratic relationship with k. There are no imaginary frequencies on the negative side for unstrained monolayer WS<sub>2</sub> suggesting thermodynamical stability of the system. We observed monolayer WS<sub>2</sub> is stable with the application of Bi-axial tensile (BTS) and Uni-axial tensile (UTS) strain up to 8% or more as shown in Fig. S6.b. and Fig. S6.c. At 4% Bi axial compressive strain (BCS) the ZA branches show negative imaginary frequency which suggests that instability occurs at 4% or more amount of BCS as shown in Fig. S6.d. But in case of uniaxial compressive strain (UCS) the monolayer WS<sub>2</sub> shows thermodynamical stability up to 4% and after which instability occurs as shown in Fig. S6.e.



**Fig.S6.** Phonon dispersion curve of monolayer  $WS_2$  with the application of a) 0% strain b) +8% Bi axial strain c) +8% uniaxial strain d) -4% Bi axial strain e) -4% uniaxial strain.

#### SI5.2. Cohesive energy:

The cohesive energy  $(E_{coh})$  has been calculated further for monolayer WS<sub>2</sub> to show structural stability with the view point of experimental synthesis as predicted for two dimensional materials. Cohesive energy per atom of monolayer WS<sub>2</sub> has been calculated by using the formula

$$E_{coh} = \frac{E_{WS_2} - E_W - 2E_S}{3}$$

where  ${}^{E_{WS_2}}$  is the total energy of monolayer WS<sub>2</sub> and  ${}^{E_W}$  and  ${}^{E_S}$  are the energies of an isolated W atom and S atom. The value of  $E_{coh}$  of monolayer WS<sub>2</sub> has been found to be -2.872 eV from our calculation which is slightly less negative as previously calculated value of  $C_4N_4$  monolayer<sup>1</sup> and is also stable. The variation of  $E_{coh}$  with applied Bi axial and Uni axial strain are shown in Fig.S7.a and S7.b.which indicates that application of tensile strain is more stable than that of compressive strain and similar trends was observed in phonon dispersion curves.



Fig.S7. variation in Cohesive energy per atom with a) Bi axial and b) Uni axial strain.

# **SI6. ZT Product:**

The variation in ZT product of unstrained monolayer WS<sub>2</sub> at 300K, 600K and 900K is shown in Fig.S8.a. We found that at 300K lattice thermal conductivity<sup>( $k_{ph}$ )</sup> of unstrained monolayer WS<sub>2</sub> is 72W/m-K. The variation of  ${}^{k}{}_{ph}$  with temperature is shown in Fig.S8.b. The highest ZT product of unstrained monolayer WS<sub>2</sub> has been found to be 0.52 for n-type carriers and 0.49 for p-type carriers at 900K. With applied BCS ZT product increases and highest ZT product with a value 0f 0.70 at 900K has been observed at 2% of BCS which is 35% higher than ZT value of unstrained WS<sub>2</sub> for n-type carriers. After 2% of BCS the variation is almost constant having avalueofZT = 0.62 at 6 % of BCS which is still19% higher than ZT of unstrained WS<sub>2</sub>.



**Fig.S8.** a) Variation of ZT product with chemical potential ( $\mu$ ) at 300K, 600K and 900K where VBM, CBM and Fermi level are shown by dotted lines and b) Variation of lattice thermal conductivity due to phonon  $(k_{ph})$  with temperature in monolayer WS<sub>2</sub>. Variation in ZT product with applied c) Bi axial strain (compressive and tensile) d) uniaxial strain for n-type and p-type doping at 300K, 600K and 900K.

We have shown that monolayer  $WS_2$  is thermodynamicallystable below 4% of BCS(SI Fig. S6.d). But for the p-type carriers ZT products first decrease then becomes almost constant with the application of BCS. The variation of ZT values at different amount of Bi axial strain and uniaxial strain has been shown in Fig. S8.c. and S8.d. at different temperatures. With the application of BTS ZT value for p-type carriers slightly increases up to 4% of BTS with a value of ZT=0.56 and then decreases but for n-type carriers it does not vary much and slightly decreases at 900K.

The highest ZT products of ZT = 0.72 among all types of strain has been found for -4% uniaxial compressive strain (UCS) at 900K which is 38.5% higher than that of unstrained monolayer WS<sub>2</sub>. The effect of UCS is almost similar to that of BCS but highest ZT product has

been found at 4%, 3%, and 2% of UCS at 900K, 600K and 300K respectively. Phonon dispersion curve at 4% of UCS (SI Fig. S6.e) shows monolayer  $WS_2$  is stable at 4% of UCS. The effect of UTS is slightly different from that of BTS. For n-type carriers ZT value slightly decreases and then remains constant with the application of UTS but for p-type carriers ZT value changes very slowly up to 6% of UTS.

So, it is clear that ZT product increased to 38.5% at 4% UCS and 35% at 2% BCS than that of ZT value of unstrained monolayer WS<sub>2</sub>. Also, from phonon dispersion curves at different strain it has been observed that monolayer WS<sub>2</sub> is thermodynamically stable at 4% of UCS and 2% of BCS. The value of Seebeck coefficient, power factor, and ZT product at different temperatures for different doped materials under both uniaxial and Bi axial strain is shown in table-1.

## References:

1 T. Li, C. He and W. Zhang, J. Mater. Chem. A, 2019, 7, 4134–4144.