Pressure-Induced Charge Transfer Doping of Monolayer Graphene/MoS₂ Heterostructure

Tribhuwan Pandey, Avinash P. Nayak, Jin Liu, Samuel T. Moran, Joon-Seok Kim, Lain-Jong Li, Jung-Fu Lin, Deji Akinwande,* and Abhishek K. Singh*

Graphene, a 2D sp²-hybridized carbon sheet has been reported as one of the most fascinating 2D materials^[1,2] because of its outstanding properties including flexibility,^[3-5] high mobility,^[5,6] and transparency.^[7] Recently, graphene has also shown potential to be applied to the application in broadband optoelectronics^[8] and flexible electronics,^[9] due to its unique band structure, electrical tunability, and mechanical strength. To employ graphene for practical application in electronic devices, it is necessary to modify its conductivity, which can be achieved through various doping methods, such as in-plane atomic substitution,^[10,11] molecular adsorption,^[12,13] chemical functionalization,^[14,15] and substrate-induced doping.^[16] The substitution of carbon atoms with boron or nitrogen,^[17] as well as the covalent functionalization,^[18] is favorable for long-term stability; however, the performance of the chemically doped graphene is hindered due to a significant decrease in carrier mobility and conductivity.^[10,11,19]

So far, many studies have focused on increasing the carrier concentration of graphene by the application of an electric field^[20–23] or chemical functionalization.^[13,24] Another novel way to dope graphene is to create van der Waals (vdW)

Dr. T. Pandey, Prof. A. K. Singh Materials Research Centre Indian Institute of Science Bangalore 560012, India E-mail: abhishek@mrc.iisc.ernet.in Dr. A. P. Navak, S. T. Moran, J.-S. Kim, Prof. D. Akinwande Department of Electrical and Computer Engineering The University of Texas at Austin Austin, TX 78712, USA E-mail: deji@ece.utexas.edu Dr. J. Liu, Prof. J.-F. Lin **Department of Geological Sciences** The University of Texas at Austin Austin, TX 78712, USA Dr. L.-J. Li Physical Science and Engineering Division King Abdullah University of Science and Technology (KAUST) Thuwal 23955, Saudi Arabia Prof. J.-F. Lin Center for High Pressure Science and Technology Advanced Research (HPSTAR)

Shanghai 201203, P. R. China

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heterostructures, which augment interlayer interactions between the two layers. These 2D heterostructures show great promise for nano- and opto-electronic applications.^[25,26] Several studies have reported stacking of graphene with other insulating 2D materials, such as SiO₂,^[27,28] mica,^[29] or hexagonal boron nitride.^[2,28,30] Although these substrates enhance the carrier concentration of graphene,^[31,32] this gain comes at a price, such as spatial modulation (Moiré pattern formation)^[32,33] or reduction in carrier mobility,^[34] which hamper the electronic properties. Alternatively, stacking graphene on top of a monolayer 2H-MoS₂ has been shown to provide an effective means to tune the intrinsic electronic structure of graphene without altering its Dirac cone.^[26,35] The carrier density of such heterostructure can be varied via application of a gate voltage.^[26,35] Applying hydrostatic pressure onto the graphene-based heterostructure can also be used to bring further tunability of the carrier density without introducing any impurities into the system. A number of experiments and predictions have been performed on individual monolayer of graphene and MoS₂, respectively, under hydrostatic pressure to investigate their fundamental characteristics, such as electronic band structure and Raman spectra.^[36-38] The electronic structures of transition metal dichalcogenides and graphene have been found to be very sensitive to applied pressure.^[36,39] Previous experimental and theoretical studies have suggested that an isostructural semiconducting to metallic (S-M) transition in multilayered MoS₂^[39,40] and a band gap increase in monolayer 2H-MoS₂ can be induced by hydrostatic pressure.^[41] On the other hand, application of ≈1.0% uniaxial tensile strain on monolayer graphene opens up a small band gap of 100 meV.[36,42,43] Therefore, applying hydrostatic pressures onto the heterostructured graphene and monolayer 2H-MoS₂ stacked layers has the potential to fine tune the electronic and electrical properties of graphene, and can help in uncovering the physics of monolayer materials in extreme environments.[36,43]

In this study, we report a combined theoretical and experimental investigation on the effects of hydrostatic pressure on the vertically stacked heterostructure composed of monolayer graphene and monolayer 2H-MoS₂. The charge transfer between graphene and MoS₂ leads to p-type doping of graphene, even at ambient pressure. A diamond anvil cell (DAC) with a soft neon pressure medium in a sample chamber made of a Re gasket was used to apply a hydrostatic pressure uniformly across the stacked structure. This study allows for







Figure 1. Structural and electronic properties of graphene/MoS₂ heterostructure. a) Top view and b) lateral view of graphene/MoS₂ heterostructure. c) Band structures of freestanding monolayer 2H-MoS₂ and monolayer MoS_2 stacked on top of a monolayer graphene. In the graphene/MoS₂ heterostructure, the conduction band of 2H-MoS₂ falls down in energy reducing the band gap by 0.14 eV.

probing the intrinsic response of the strain-property relations in a controlled environment. The electronic structure calculation confirms a linear shift in Dirac point of graphene with respect to Fermi level under hydrostatic pressure. This shift in Dirac point was quantified in terms of doping concentration as a function of hydrostatic pressure. The doping concentration exhibits an exponentially increasing dependence upon pressure, providing a route to an unprecedented tunability. This leads to a doping of $\approx 3.2 \times 10^{13}$ cm⁻² at 30 GPa, which is higher than the previously reported values for graphene/MoS₂ heterostructure at ambient conditions.^[22] To confirm this charge transfer-doping phenomenon, we further carried out in situ Raman measurements and measured the intensity ratio of the 2D and G Raman peaks of graphene. Raman studies show that the G band of graphene is strongly dependent on pressure and increases by 5.3 cm⁻¹ GPa⁻¹, a rate much higher than that of the freestanding graphene (3.5 cm⁻¹ GPa⁻¹) thereby indicating a charge transfer from graphene to MoS₂. Analysis of the intensity ratio of the 2D and G band (I_{2D}/I_G) demonstrates strong pressure dependence and confirms the theoretically predicted heavy p-type doping in graphene. Pressure-dependent Raman studies and theoretical insights show that applying hydrostatic pressure strongly influences the charge transfer doping between graphene and MoS₂, making pressure a prominent factor in tuning the doping concentration of graphene and potentially other van der Waals solids.

In order to study graphene/MoS₂ heterostructure, we constructed a commensurate cell by taking $5 \times 5 \times 1$ graphene (50 atoms) and $4 \times 4 \times 1$ MoS₂ (48 atoms) supercell (**Figure 1**a,b). The two monolayers are arranged in such a way that one carbon atom positioned exactly above a molybdenum atom (Figure 1a), which is found to be most energetically favorable stacking for graphene/MoS₂.^[44] The electronic structure of the monolayer-graphene does not vary significantly with biaxial-strain (Figure S1a, Supporting Information); however, the electronic structure of monolayer

2H-MoS₂ is highly sensitive to strain (Figure S1b, Supporting Information). Hence, the lattice commensurability of the graphene/MoS₂ heterostructure was ensured by applying a small biaxial strain of 1.9% in *x* and *y* directions to graphene while keeping the lattice constant of MoS₂ fixed at the optimized value of 3.21 Å.

To understand the interlayer interactions when graphene is placed on top of the monolayer MoS₂, we have compared the band structure of MoS2 with and without graphene (Figure 1b). Compared to the monolayer MoS₂, the direct bandgap of MoS₂ supported on the graphene sheet is reduced by 0.14 eV, which is in good agreement with previous experimental^[45] and theoretical studies.^[46] This reduction in the band gap implies that the graphene and MoS₂ monolayers are interacting via charge transfer. The electronic band structures of the graphene/MoS₂ heterostructure shows a linear Dirac-like dispersion relation at the Fermi level (Figure 2a), which is a typical characteristic of graphene.^[4] Owing to the interaction between MoS₂ and graphene layers, we observe a finite upward shift of Dirac point of graphene by 0.14 eV with respect to the Fermi level. This shift in the Dirac point gives an indication of the p-type doping in graphene and is a signature of a strong interaction between layers of graphene and MoS_2 . This relative shift of the Dirac point with respect to the Fermi level ($\Delta E_{\rm D}$) can be quantified as the charge carrier (hole or electron) concentration of the doped graphene by the relation: $N_{h/e} = \frac{1}{\pi} \left(\frac{\Delta E_{\rm D}}{\hbar v_F}\right)^2$ where \hbar is Planck's constant and $|v_{\rm F}| = 1.0 \times 10^8$ cm s⁻¹ is the Fermi velocity in graphene.^[20] At ambient conditions, the calculated 0.14 eV upward shift in the Dirac point corresponds to a p-type doping of 4.5×10^{12} cm⁻². This shift of the Dirac point is shown to double the carrier concentration of graphene, and modifying the interaction between graphene and MoS₂ under applied pressures can be used to further enhance the concentration.

Under pressure due to enhanced interaction between graphene and MoS_2 a large shift of Dirac cone is observed





Figure 2. Electronic structures of graphene/MoS₂ heterostructure under hydrostatic pressure. Band structure for the MoS₂ and graphene heterostructure a) with no applied pressure and b) at 3 GPa pressure. The horizontal dashed black line denotes the Fermi level. The upwards shift of the Dirac point with respect to the Fermi level indicates a p-type doping in graphene. c) The relative shift of the Dirac point of graphene with respect to the Fermi level (ΔE_{D}) upon forming a contact with MoS₂ as a function of the applied pressure and the charge transfer induced carrier concentration of graphene in the graphene/MoS₂ heterostructure as a function of hydrostatic pressure.

(Figure 2b). In order to understand the effect of hydrostatic pressure on doping of graphene, we estimate $\Delta E_{\rm D}$ as a function of hydrostatic pressure. The shift of the Dirac point is referenced with respect to the vacuum level of the graphene/MoS₂ heterostructure (Figure S2, Supporting Information). $\Delta E_{\rm D}$ of graphene upon formation of the interface as a function of the applied hydrostatic pressure shows a linear dependence with a slope of 15.7 meV GPa⁻¹ (Figure 2c). This enhanced shift in $\Delta E_{\rm D}$ indicates that the carrier concentration of graphene can be tuned by application of hydrostatic pressure. For example, at 12 GPa $\Delta E_{\rm D}$ is 0.38 eV, which corresponds to a carrier concentration of $\approx 1.06 \times 10^{13}$ cm⁻². This carrier concentration in the graphene/MoS₂ heterostructure is two orders of magnitude larger than that of the intrinsic carrier concentration of graphene at 1.6×10^{11} cm⁻² under ambient conditions (Figure 2b).^[47,48] Furthermore, the carrier concentration of the monolayer graphene increases exponentially with the hydrostatic pressure (Figure 2b). At 30 GPa, we observe a doping concentration of $\approx 3.2 \times 10^{13}$ cm⁻² which, to the best of our knowledge, is the highest value ever reported for a graphene/MoS₂ heterostructure.^[22] The calculated carrier concentration is compared with other doping methods (Table 1). Our theoretically predicted carrier concentration is higher than the doping reported in graphene/MoS₂ heterostructure

with top-gate bias,^[22] doping in argon pressure medium,^[43] or molecular doping achieved in graphene.^[49] This increase in carrier concentrations under hydrostatic pressure arises from the enhanced interaction between graphene and MoS_2 . Under hydrostatic pressure, the effective distance between graphene and 2H-MoS₂ is reduced by 0.06 Å GPa⁻¹, which allows these layers to interact more strongly. This indicates that the application of pressure can serve as an effective way to enhance the carrier concentration of graphene.

In order to understand the mechanism of the dopinginduced phenomenon, we investigated the plane averaged electron density difference $\Delta \rho = \rho(G/MoS_2) - \rho(G) - \rho(MoS_2)$, where $\rho(G/MoS_2)$ is the total electron density of the graphene/ MoS₂ heterostructure, and $\rho(G)$ and $\rho(MoS_2)$ are the individual electron densities of graphene and MoS₂ monolayers, respectively (**Figure 3**a). Even without any applied pressure, the electron density is redistributed from the graphene toward the MoS₂ layer such that some charge depletion and accumulation occur at the graphene and MoS₂ interface. The charge transfer at the graphene/MoS₂ interface increases with increasing hydrostatic pressure (Figure 3a–c). This eventually results in a larger upward shift in the Dirac point leading to an enhanced doping. The Bader charge transfer shows that the charge accumulation at the MoS₂ layer increases with Table 1. Comparison of doping level observed in the graphene/ MoS_2 heterostructure under hydrostatic pressure with previous studies. Our reported doping concentration is two times higher than the values reported under top-gate bias. The interaction between graphene and MoS_2 at applied pressures leads to a high carrier concentration in the graphene/ MoS_2 heterostructure.

System	Doping concentration [cm ⁻²]
Intrinsic monolayer graphene ^[47]	$1.6 imes 10^{11}$
Gated graphene transistor ^[20]	$5.0 imes 10^{13}$
Graphene in alchocol pressure medium ^[43]	$6.0 imes 10^{13}$
Graphene in argon pressure medium ^[43]	1.4×10^{13}
Molecular doping in graphene ^[49]	1.4×10^{13}
Gated bilayer graphene ^[23]	2.3×10^{13}
Intrinsic bilayer graphene ^[50]	2.5×10^{12}
$\label{eq:Graphene} Graphene/MoS_2 \ heterostructure \ with \ top-gate \\ bias^{[22]}$	1.5×10^{13}
Graphene/MoS ₂ heterostructure under hydro- static pressure (this study)	2.7×10^{13}

increasing hydrostatic pressure (Figure 3d), while the charge is being depleted from the graphene layer. As the pressure increases, the charge transfer from graphene to MoS_2 also increases. This is expected, because the interaction between the two materials progressively increases with decreasing



Figure 3. Electronic charge transfer at the monolayer graphene/MoS₂ interface at high pressure. Charge transfer at a) 0 GPa, b) 10 GPa, and c) 20 GPa. With increasing pressure, the charge transfer from graphene to MoS₂ also increases. Blue and green colors represent the charge accumulation and depletion, respectively. d) Bader charge analysis at the graphene/MoS₂ interface as a function of applied pressure. The Bader charge analysis confirms the interaction between graphene and MoS₂, which can be quantified by their charge transfers. Inset in (d) is a schematic describing the relation between the charge transfer and the shift of the Dirac cone (doping). The electrons flow from the Dirac point of graphene to the conduction band minima (CBM) of MoS₂ leaving holes in graphene and giving rise to p-type doping in graphene.



interlayer distance. This suggests that electrons flow from the Dirac point of graphene toward monolayer MoS_2 (inset, Figure 3d). This is also evident from the density of states (DOS) (Figure S3, Supporting Information), where the DOS of the heterostructure is modified significantly such that it does not equal to the sum of the DOS of the isolated layers. Such a charge transfer mechanism confirms the p-type doping of the graphene monolayer, and highlights the benefit of using MoS_2 to enhance its electronic properties.

To further confirm the MoS₂ and graphene interaction and doping of graphene, we conduct in situ Raman measurements at hydrostatic pressures in a DAC. Raman spectroscopy has been shown to be a powerful tool for deciphering the doping phenomenon in graphene and other 2D materials.^[20,21,43,51] As shown in previous studies on graphene^[20] and MoS_2 ,^[52] the shift of Raman frequency can be used as an efficient means for the evaluation of the doping concentration. We first discuss the Raman spectra of the monolayer 2H-MoS₂ and compare the out-of-plane A1g and in-plane E2g modes for monolayer 2H-MoS₂ with and without graphene (Figure 4a). Both the Raman peaks of the monolayer 2H-MoS₂ display a nominal shift when the layer is supported on graphene. Due to the presence of an additional layer of graphene, E_{2g} peak slightly shifts from 384 to 385 cm⁻¹ while A_{1g} shifts from 405 to 407 cm⁻¹ at ambient conditions. This observation is in good agreement with previous experimental studies which showed that these Raman shifts are not affected in presence of a second layer of graphene on top of MoS₂,^[53] indicating that the frequency shifts in E_{2g} and A_{1g} mode of the monolayer 2H-MoS₂ are caused by the interaction with graphene. The E_{2g} mode is associated with the in-plane vibration of the Mo and S atoms that vibrate in opposite direction from one another, whereas the A1g mode corresponds to opposing outof-plane vibrations of the two S atoms with respect to the Mo atom. The presence of graphene hardly affects the in-plane interaction such that E_{2g} mode remains unaffected in the monolayer 2H-MoS₂. For the A_{1g} mode, however, the shift observed in the graphene/MoS₂ heterostructure can be associated with the interlayer interaction between graphene and MoS₂. For the monolayer 2H-MoS₂, the intra-layer interaction term dominates the out-of-plane A1g mode. In the presence of graphene, the additional vdW interaction between graphene and MoS₂ also contributes to the A_{1g} mode, which leads to a slight increase in its frequency. Under hydrostatic pressure, the E_{2g} and A_{1g} modes increase linearly at a rate of 1.6 and 2.7 cm⁻¹ GPa⁻¹, respectively, for monolayer 2H-MoS₂ in graphene/MoS₂ heterostructure, whereas these rates are 1.6 and 2.6 cm⁻¹ GPa⁻¹ for the monolayer 2H-MoS₂. Therefore, the rate of increase is similar for heterostructure and 2H-MoS₂ monolayer for both the A_{1g} and the E_{2g} modes.

On the other hand, the G band of the freestanding graphene and the G band measured in the graphene/MoS₂ heterostructure as a function of hydrostatic pressure show a noticeable difference (Figure 4b). Due to the semi metallic nature of graphene, the atomic vibrations are partially screened by electrons via the electron-phonon interaction. This screening changes rapidly for vibrations associated with K and Γ point of the Brillouin zone, leading to a variation of the optical phonon-frequencies much larger than





Figure 4. Experimental Raman spectroscopy of the stacked heterostructure. a) The A_{1g} and E_{2g} Raman shift for monolayer 2H-MoS₂ with pressure exhibits similar behavior indicating that the out-of-plane and in-plane modes of MoS₂ are not affected by the graphene. b) The pressure dependence of the in-plane G band of graphene and stacked graphene/MoS₂ heterostructure. The G band of stacked heterostructure increases at a faster rate of 5.3 cm⁻¹ GPa⁻¹, indicating the p-type doping of graphene. c) The Raman spectra of the G and 2D peaks showing the 2D and G intensity differences at two different pressures. d) The change in intensity ratio (I_{2D}/I_G) as a function of applied pressure. The intensity ratio has been correlated with the carrier concentration^[20,43] showing the doping of graphene via charge transfer to MoS₂.

that in conventional systems.^[54] The consequent anomalous behavior of the phonon dispersion is called Kohn anomaly.^[55] The Kohn anomaly can be suppressed by changing the Fermi level, as the electrons or holes occupied by doping suppresses the electron–phonon interaction. As reported in previous studies, the Raman peaks of graphene are strongly sensitive to doping, in particular for the G peak, because of the removal of the Kohn-anomaly at Γ point.^[55,56] Thus, any doping via the charge transfer between graphene and 2H-MoS₂ can be captured by analyzing the shift in G band.

The G band peak position in the graphene/MoS₂ heterostructure at ambient conditions is at 1586 cm⁻¹, which is 6 cm⁻¹ larger than the freestanding graphene and is also observed in the theoretically calculated phonon spectra (Figure S4, Supporting Information). This shift in the G band suggests that the graphene is slightly doped and interacting with MoS₂. We compare pressure dependence of the G band in the graphene/MoS₂ heterostructure with other systems (Table 2). With increasing hydrostatic pressure, the G band increases at a rate of 5.3 cm⁻¹ GPa⁻¹, which is higher than the 3.5 cm⁻¹ GPa⁻¹, rate observed for freestanding graphene or graphene in alcohol/argon pressure medium.^[43] The higher rate of increase of G-band for graphene/MoS₂ heterostructure than that of freestanding graphene confirms the interaction between graphene and MoS₂ via charge transfer. This indicates that with the increasing hydrostatic pressure the doping of graphene also increases, which is in good agreement with the theoretical results. Analysis of the pressure-dependent Raman shifts shows that pressure effects on the in-plane (G-band) Raman frequencies of graphene are more prominent than the out-of-plane (2D band), while the intensity of the 2D band decreases markedly under pressure because of charge transfer (Figure 4c). Similar effects are observed on the interaction of graphene with electrondonor and electron-acceptor molecules.^[14,24,49]

The ratio of intensities of the 2D and G bands, (I_{2D}/I_G) , is a sensitive probe used to examine the doping of graphene (Figure 4d).^[20,58,59] A strong variation in I_{2D}/I_G is shown to be related to heavy doping of graphene.^[20,58,59] We plot the pressure dependence of the I_{2D}/I_G ratio for graphene/MoS₂ heterostructure (Figure 4d). The relation between doping and both the G band position and the ratio of intensities of

Table 2. Comparison of the evolution of the G band as a function of hydrostatic pressure with various other reported studies. Graphene/ MoS_2 heterostructure shows the highest rate of increase for the G band with respect to pressure.

System	[cm ⁻¹ GPa ⁻¹]
Graphite ^[57]	3.4
Graphene on Si/SiO ₂ ^[36]	4.7
Few layer graphene ^[37]	4.4
Graphene in alcohol pressure medium ^[43]	3.6
Monolayer freestanding graphene (this study)	3.5
Graphene on MoS ₂ (this study)	5.3

the 2D and G bands have been well characterized for graphene.^[20,21,60] We have used the measured values of I_{2D}/I_{C} and their pressure evolution to quantify the initial doping values as a function of pressure, by comparing I_{2D}/I_{G} with the data of Das et al.^[20,43] As predicated in the theoretical calculation, under pressure the graphene shows an order magnitude $(8 \times 10^{12} \text{ cm}^{-2})$ higher carrier concentration in comparison to pristine graphene $(2 \times 10^{11} \text{ cm}^{-2})$.^[48] This observed carrier concentration is in good agreement with the doping predicted by the Dirac point shift at ambient conditions (Figure 2c). The origin of this initial doping could be associated to the interaction between MoS₂ and graphene in the absence of applied pressure (Figure 3). These observations also allow us to propose that the predicted hole doping takes place through the interaction between graphene and MoS₂ via charge transfer. The strong pressure dependence of I_{2D}/I_{G} leads to an exponential increase in the carrier concentration under pressure; for example, a high carrier concentration of 2.7×10^{13} cm⁻² is observed at 30 GPa. It is important to note that, although the pressure dependence of G band in the graphene/MoS₂ heterostructure is higher than the graphene in alcohol pressure medium,^[43] the higher carrier concentration is observed in the later due to the doping effects of the alcohol pressure medium used.^[43] Due to presence of alcohol in the sample chamber, additional charge to graphene is attributed from the formation of silanol groups (Si-O-H) on the surface of silicon substrates^[43,61] resulting in a higher carrier concentration.

In conclusion, we have demonstrated a new approach to induce the p-type doping in graphene in the graphene/ MoS_2 heterostructure under hydrostatic pressure without introducing any impurities into the system. The main cause of this doping is the strong vdW interactions between MoS₂ and graphene monolayer that increases with increasing pressure. The calculated doping level of $\approx 3.2 \times 10^{13}$ cm⁻² is higher than the previously reported values for the graphene/MoS₂ heterostructure.^[22] The theoretically predicted doping phenomenon was further confirmed by analysis of experimental Raman spectra at hydrostatic pressures measured in a DAC. The G and 2D band of graphene in graphene/MoS₂ heterostructure deviates significantly from the freestanding graphene and exhibit a strong pressure dependence confirming the theoretically predicated doping. Application of hydrostatic pressure on heterostructure enables tuning of the p-type carrier concentration from 0.4×10^{13} to 3.2×10^{13} cm⁻², providing a wide range of carrier concentration for pressure-tunable applications. Our results highlight a unique way of achieving controllable, pressure-induced charge transfer doping in the graphene/MoS₂ heterostructure that can be applied to tune the electronic structures of other van der Waals heterostructures at extreme environments.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.



Acknowledgements

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