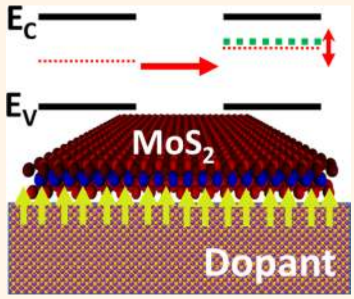
Interfacial Nondegenerate Doping of MoS_2 and Other Two-Dimensional Semiconductors

Sanjay Behura and Vikas Berry*

Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States

ABSTRACT Controlled nondegenerate doping of two-dimensional semiconductors (2DSs) with their ultraconfined carriers, high quantum capacitance, and surface-sensitive electronics can enable tuning their Fermi levels for rational device design. However, doping techniques for three-dimensional semiconductors, such as ion implantation, cannot be directly applied to 2DSs because they inflict high defect density. In this issue of *ACS Nano*, Park *et al.* demonstrate that interfacing 2DSs with substrates having dopants can controllably inject carriers to achieve nondegenerate doping, thus significantly broadening 2DSs' functionality and applications. Futuristically, this can enable complex spatial patterning/contouring of energy levels in 2DSs to form p−n junctions, integrated logic, and opto/electronic devices. The process is also extendable to biocellular-interfaced devices, band-continuum structures, and intricate 2D circuitry.



Carrier confinement by isolating single sheets from layered materials has led to the realization of a wide variety of extraordinary phenomena and applications. This outcome was first recognized in graphene, where, due to the nascent massless Fermions, ballistic carrier transport was achieved. The field has since embraced two-dimensional semiconductors (2DSs), with molybdenum disulfide (MoS_2) being the most studied structure. Monolayer MoS_2, with a stratum of molybdenum atoms sandwiched between two layers of sulfur atoms in a trigonal prismatic (or antiprismatic) lattice, is a direct band gap two-dimensional (2D) material (∼1.8 eV). With a flexible, ultrathin, semiconducting, and photoluminescent structure,[1] MoS_2's versatile functionality is being integrated with other 2D nanomaterials (2DNs) to access new physics. To expand the scope of its applications, it is imperative to control 2DSs' Fermi level, which can enable defined carrier transitions and heterojunction-induced band bending. The applications that will be impacted include optoelectronic devices,[2] catalysis,[3] memory devices,[4] Schottky circuits,[5] controlled photoluminescence,[1] and molecular sensing.

Similar to three-dimensional (3D) semiconductors, the doping density and the position of the Fermi level in 2DNs will influence their electrical and optical properties.[6] While doping in 3D semiconductors such as silicon is achieved *via* ion implantation, such methods cannot be applied toward 2DNs because it leads to significant defect density and deterioration of 2DN properties.[7] This is because 2DNs have large surface areas, which when exposed to ions produce more defects per unit volume.[8] Further, several doping mechanisms on MoS_2 have produced degenerate doping, which leads to MoS_2 behaving like a metal with the resultant Fermi level close to the edge of the conduction band (or valence band).[9] Although degenerate doping is important to tune the Schottky barrier with metal contacts,[9] nondegenerate doping can provide discrete energy levels within the forbidden band gap, thus providing an avenue for optoelectronic transitions and/or carrier recombination processes (Figure 1). In the current issue of *ACS Nano*, Park *et al.*[10] demonstrate a unique and effective mechanism to proxy-dope 2DSs controllably in the nondegenerate regime *via* an interfaced, dopant-rich phosphorus silicate glass (PSG) substrate. The process involves enhancing the intimacy between MoS_2 and the dopants (P_2O_5) *via* (1) dopant out diffusion between 700 and 900 °C, (2) thermal activation at 500 °C, and (3) optical activation above 5 μW laser irradiation (Figure 2).[10]

* Address correspondence to vikasb@uic.edu.

Published online
10.1021/acsnano.5b01442

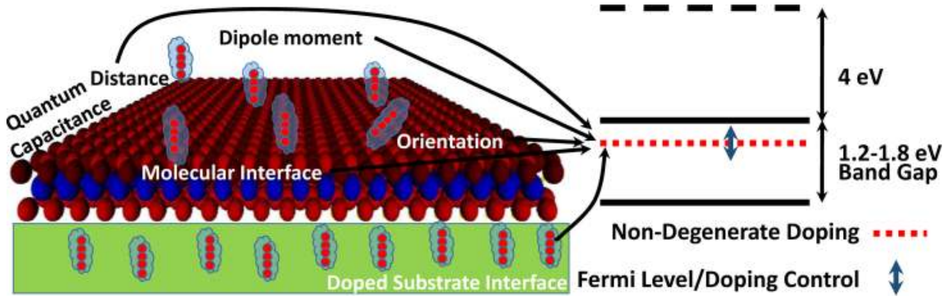


Figure 1. Schematic of the effect of interfacing a doped substrate with a two-dimensional semiconductor (2DS) on its band structure. The dipole moment of the molecule induces doping, which is proportional to the quantum capacitance of the 2DS. The molecular orientation and the distance from the 2DS influence doping density. The figure also shows possible doping from the top face of 2DSs.

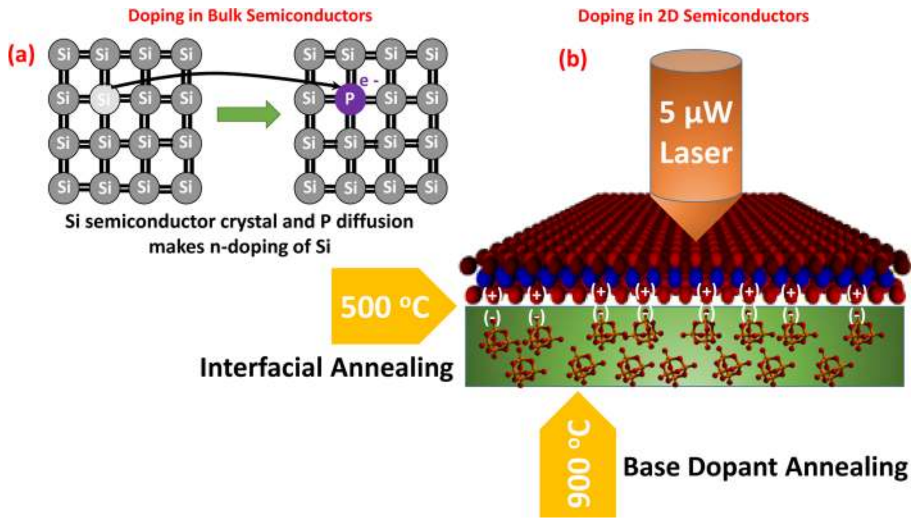


Figure 2. (a) Three-dimensional semiconductors such as silicon can be doped *via* ion implantation. (b) Park *et al.* show that two-dimensional semiconductor (2DS) can be doped *via* an interfaced substrate with imbedded dopant molecules.[10] This can be achieved by a two-step thermal process or a three-step thermal−optical process.

Here, the asymmetry-induced dipole moment of P_2O_5 with negative charge on the O atoms attracts holes to n-dope MoS_2 at the interface. During the optical exposure, the laser's photon energy over the band gap ($h\nu - E_g$) produces equilibrium heat at the PSG−MoS_2 interface to activate n-doping. The increase in the dopant's weight percentage in the substrate increases MoS_2 doping, while the thickness of MoS_2 does not influence the doping process.

The molecular doping mechanism for 2DSs can be influenced by (a) the dipole moment of the interfacing molecule (molecular interfaces influence doping on 2DNs[11]), (b) the quantum capacitance of the 2DSs, (c) the dipolar orientation and distance, and (d) molecular bonding and/or orbital rehybridization. The molecular dipole moment will be associated with an electric field, which will induce doping on 2DSs based on its quantum capacitance: $C_Q = \delta Q/\delta\phi_s$, where Q is the channel charge and ϕ_s is the surface potential from the interfacing molecule. Clearly, the orientation of molecular dipoles and their distance from the 2DSs influence the electric field impinging on the 2DS and, therefore, the level of doping.

OUTLOOK AND FUTURE CHALLENGES

The process to introduce nondegenerate doping in MoS_2 *via* interfaced substrates can be extended to most of the 2DNs, including $MoSe_2$, WS_2, WSe_2, and WTe_2. However, since the process involves thermal annealing, the chemical stability of 2DNs ($MoSe_2 \approx 980$ °C, $WS_2 \approx 1040$ °C, $WSe_2 \approx 930$ °C, $WTe_2 \approx 700$ °C) at higher temperature will govern the possible extent of doping. It is important to note that 2DSs (and 2DNs) are essentially "surfaces", and therefore, their interface is more sensitive. This is because an interface will influence a larger volume of 2DSs in comparison to a similar interface on 3D semiconductors' surfaces. Moreover, research with other substrate molecules of varied dipole moments is essential to determine if nondegenerate doping can be achieved without thermal or optical annealing. The process can also be employed to study the interfacial potential change in biological cells interfaced with 2DSs. Here, the resultant change in doping (captured *via* Raman spectroscopy) can provide information on cell surface reactions

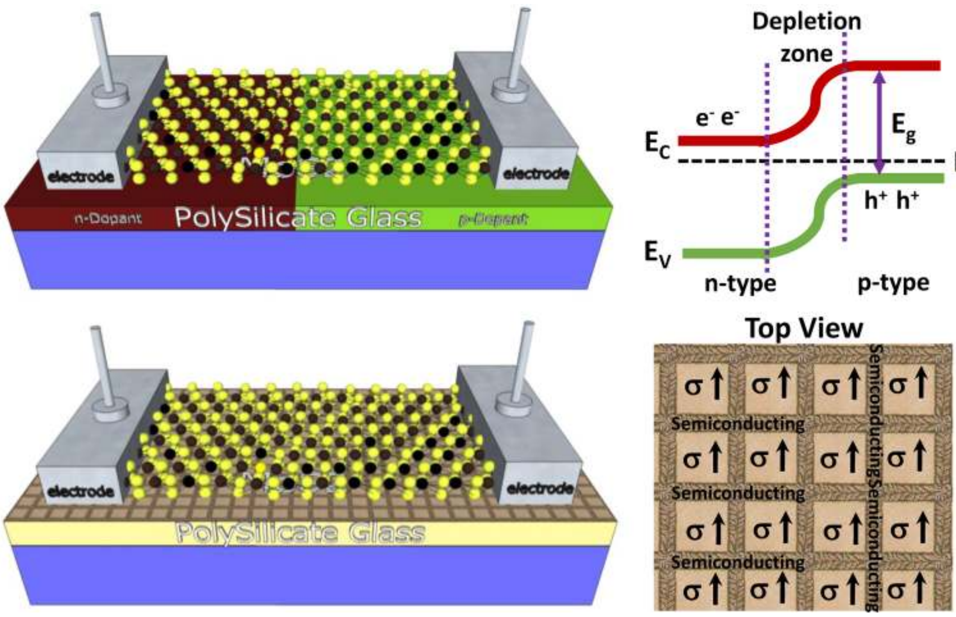


Figure 3. Patterned or gradient doping of the substrate can be employed to produce complex two-dimensional device constructs. (Top left) By patterning n-type and p-type dopants on a substrate, a p−n junction can be achieved on the interfaced two-dimensional semiconductor (2DS) (top right). (Bottom left) With patterning, the substrate high conductivity (high σ) island array can be realized within doped 2DSs (see top view in bottom right). These devices can be employed for a Coulomb blockade, electron tunneling, and/or thermionic emission studies.

and surface potential (due to actuation of ion channels).

A spatially contrasting doping pattern on the substrate can be employed to introduce selective nondegenerate doping levels and/or degenerate doping regions (Figure 3). For example, a 2DS can be deposited on a substrate with patterned dopants, which can induce spatially polarized carrier densities and contrasting Fermi levels to produce complex electronic/optoelectronic devices with predefined band structures. The process proposed by Park *et al.*[10] can be integrated with semiconductor processing techniques (thermal doping, lithographic patterning, epitaxy, atomic layer deposition, plasma functionalization, chemical vapor deposition, and rapid thermal annealing) for analogous device fabrication, bringing 2DS technology closer to practical realization.

As an example, a design of a MoS_2 p−n junction is presented in Figure 3 (top), where lateral polarity contrast is achieved *via* selective p- and n-type doping of the substrate interfaced with 2DSs. This construct can be applied for diodic transistors, tunable optical response devices, or molecular sensors. A rough design of a substrate pattern with degenerate doped islands within the 2DSs' matrix doped in the nondegenerate regime is shown in Figure 3. Here, Coulomb blockade, electron tunneling, negative differential resistance, and/or thermionic emission for 2DS islands can be investigated. Moreover, band continuum *via* gradient doping can be employed for devices responding to a broad optical range (such as solar cells) or for electrokinetic fluid flow.

Finally, it is critical to account for or to study the quantum capacitance of the 2DSs and their heterostructures because C_Q represents the interaction between the molecular dipole moment and the resultant doping induced in 2DSs. Strategies have to be developed to enhance the mobility by employing substrates (doped) without dangling bonds, as they introduce scattering sites. Further, it is well-known that the 3D semiconductors undergo a slight reduction in band gap upon doping.[12] This phenomenon is still to be characterized for 2DSs, where the interface-induced doping process can be effectively leveraged. Another mechanism that requires further research is the electromagnetic interaction-induced phonon scattering near impurities in 2DSs, which is known to modify the band structures of 3D semiconductors.[13] In conclusion, interface-induced proxy-doping of 2DSs can be employed to control doping density and Fermi level. Further, patterning the substrate with polarized dopants or dopant gradients can produce unique electronic architectures for a wide range of systems, including optoelectronics, biocellular interfacing, potential integrated circuits, and logic devices.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. V.B. acknowledges financial support from National Science Foundation (Grants CMMI-1503681 and CMMI-1030963) and University of Illinois at Chicago.

REFERENCES AND NOTES

1. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS_2. *Nano Lett.* **2010**, *10*, 1271–1275.

PERSPECTIVE

2. 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.
3. Wang, H.; Lu, Z.; Kong, D.; Sun, J.; Hymel, T. M.; Cui, Y. Electrochemical Tuning of MoS_2 Nanoparticles on Three-Dimensional Substrate for Efficient Hydrogen Evolution. *ACS Nano* **2014**, *8*, 4940–4947.
4. Choi, M. S.; Lee, G.-H.; Yu, Y.-J.; Lee, D.-Y.; Lee, S. H.; Kim, Ph.; Hone, J.; Yoo, W. J. Controlled Charge Trapping by Molybdenum Sisulphide and Graphene in Ultrathin Heterostructured Memory Devices. *Nat. Commun.* **2013**, *4*, 1624.
5. Tian, H.; Tan, Z.; Wu, C.; Wang, X.; Mohammad, M. A.; Xie, D.; Yang, Y.; Wang, J.; Li, L.-J.; Xu, J.; et al. Novel Field-Effect Schottky Barrier Transistors Based on Graphene−MoS_2 Heterojunctions. *Sci. Rep.* **2014**, *4*, 5951.
6. Sreeprasad, T. S.; Nguyen, P.; Kim, N.; Berry, V. Controlled, Defect-Guided, Metal-Nanoparticle Incorporation onto MoS_2 *via* Chemical and Microwave Routes: Electrical, Thermal, and Structural Properties. *Nano Lett.* **2013**, *13*, 4434–4441.
7. Lucchese, M. M.; Stavale, F.; Martins Ferreira, E. H.; Vilani, C.; Moutinho, M. V. O.; Capaz, R. B.; Achete, C. A.; Jorio, A. Quantifying Ion-Induced Defects and Raman Relaxation Length in Graphene. *Carbon* **2010**, *48*, 1592–1597.
8. McDonnell, S.; Addou, R.; Buie, C.; Wallace, R. M.; Hinkle, C. L. Defect-Dominated Doping and Contact Resistance in MoS_2. *ACS Nano* **2014**, *8*, 2880–2888.
9. Fang, H.; Tosun, M.; Seol, G.; Chang, T. C.; Takei, K.; Guo, J.; Javey, A. Degenerate n-Doping of Few-Layer Transition Metal Dichalcogenides by Potassium. *Nano Lett.* **2013**, *13*, 1991–1995.
10. Park, H.-Y.; Lim, M.-H.; Jeon, J.; Yoo, G.; Kang, D.-H.; Jang, S. K.; Jeon, M.-H.; Lee, Y.; Cho, J. H.; Yeom, G.-Y.; et al. Wide-Range Controllable n-Doping of Molybdenum Disulfide (MoS_2) through Thermal and Optical Activation. *ACS Nano* **2015**, 10.1021/acsnano.5b00153.
11. Sreeprasad, T. S.; Berry, V. How Do the Electrical Properties of Graphene Change with Its Functionalization? *Small* **2013**, *9*, 341–350.
12. Mocatta, D.; Cohen, G.; Schattner, J.; Millo, O.; Rabani, E.; Banin, U. Heavily Doped Semiconductor Nanocrystal Quantum Dots. *Science* **2011**, *332*, 77–81.
13. Mazur, E. *Spectroscopy and Dynamics of Collective Excitations in Solids*; Springer: Berlin, 1997; pp 417−470.