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PERSPECTIVE

# Graphene and other two-dimensional materials

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Over the last few years, research on graphene [1–3] has progressed significantly, and as a result, a number of real-life applications of graphene have been realized [4, 5]. This carbon allotrope (for a review on other forms of carbon, see [6]) resulted in a number of novel physical phenomena already discovered (ranging from new types of quantum Hall effect to universal optical conductivity) and dramatically expanded the range of possible applications for such materials (from transparent conductive coating to ultrafast photodetectors). Currently, there are hundreds of products in the market that have graphene playing a significant (sometimes, dominant) role in improving the properties and the functionalities of the products. For example, graphene and other 2D materials can be used to design microwave shields and absorbers with predefined properties [7]. In addition, due to the absence of a band gap and the very high mobility of the charge carriers, graphene can be used for broad-band, ultrafast optoelectronic devices [8] and optical modulators [9]. Moreover, new details about graphene continue to be discovered on a regular basis.

The most important benefit of graphene has been that it paved the way for the discovery and study of more two-dimensional materials [10]. There are dozens of such materials [11] with different characteristics available currently: insulators, semiconductors, semimetals, and metals. Recently, superconductivity [12] and ferromagnetism [13–15] have been observed in two-dimensional materials. In the monolayer form crystals often behave very differently compared to their 3D counterparts. Thus, for instance, monolayers of many transition metal dichalcogenides (TMDC) act as direct-band-gap semiconductors, whereas they exhibit indirect band gap in the bilayer or thicker forms [16], which makes such materials particularly suitable for optoelectronic applications [17]. Further, the catalytic properties of $MoS_2$ can be enhanced by assembling monolayers into the hierarchical structure [18–20].

The multitude of 2D crystals resulted in the concept of van der Waals heterostructures [21–24]. With saturated chemical bonds, the 2D crystals can interact with each other only through the van der Waals forces, thus preserving the major electronic and structural characteristics of the individual crystals.

In the simplest possible manner, such a concept was used to encapsulate atomic crystals sensitive to environment. Thus, graphene encapsulated with hexagonal boron nitride (hBN) demonstrates electronic properties [25] comparable to those of the suspended devices [26–29]. Such encapsulation proved crucial when studying the properties of air-sensitive materials, for instance, $NbSe_2$ for superconductivity [13] or $MoTe_2$ for silicon photonics applications [30].

More complex heterostructures have been achieved with two graphene monolayers separated by a thin layer of hBN. In such structures, the interaction between electrons in the two layers led to Coulomb drag [31] and electron-electron correlation effects [32]. Furthermore, if the hBN layer is sufficiently thin, tunnelling current can be observed in the heterostructures [33–35]. Since the work function of graphene can be readily controlled by an external gate (due to the low density of states in graphene), such tunnelling devices can work as tunnelling transistors, as demonstrated by several groups [36, 37]. Interestingly, the tunnelling current in such heterostructures is strongly dependent on the misorientation between the two graphene electrodes. If the two graphene layers are crystallographically aligned, tunnelling can occur with momentum conservation. This effect, however, depends resonantly on the gate and bias voltages and leads to a negative differential resistance [38–41]. If the two electrodes are crystallographically misoriented, the momentum conservation can only be realized by scattering on impurities [34–42] or phonons [34, 43, 44], since the difference in the momentum between the initial (source) and the final

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(drain) states can be damp to a third particle (phonon) of to the lattice, as in the case of scattering on impurities.

Generally, the ability to control the electronic characteristics and even the electronic structure of such devices by modifying the relative angle between the crystals in the stack is a unique characteristic of the van der Waals heterostructures. Even in the simplest case of graphene on hBN, the difference in the lattice constants between-graphene and hBN lead to the appearance of a moire pattern with a period of 14.5 nm if both types of crystals are aligned. Electron scattering on such a structure lead to a strong spectrum reconstruction and appearance of the secondary Dirac points both on electron and hole sides [45–49]. Furthermore, in a magnetic field, when the integer number of the magnetic flux quanta occupy an integer number of moire unit cells - pronounced Brown–Zak oscillations become observable up to room temperatures [50]. Similarly, the relative angle between two different TMDC crystals is crucially important for the observation of the indirect excitons [51]. Furthermore, not only the electronic structure but also the phonon structure can be modified by stacking different crystals together [52].

Probably, the dominant effect when assembling van der Waals heterostructures is the charge transfer due to difference in the workfunction of the adjacent crystals. The formation of such an atomically thin p-n junction can be used, for instance, in developing novel photodetectors [53–55].

It is clear that the concept of van der Waals heterostructures is extremely interesting and will enable the study of many more exciting phenomena and the development of novel devices for various applications. Furthermore, as more and more 2D materials are being theoretically and experimentally discovered (for instance, the direct-bangap materials GeAsSe and SnSbTe [56]), the range of possible heterostructures increases dramatically as well. Furthermore, combinations with other nanostructured objects (such as $\gamma$-AlOOH nanosheets [57]) can expand the functionality of such devices even further. However, significant amount of effort is needed to convert the laboratory-scale applications of these stacked-crystal materials to real-life applications.

## References

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Electric field effect in atomically thin carbon films, *Science* 306(5696), 666 (2004)
2. A. K. Geim and K. S. Novoselov, The rise of graphene, *Nat. Mater.* 6(3), 183 (2007)
3. A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, The electronic properties of graphene, *Rev. Mod. Phys.* 81(1), 109 (2009)
4. K. S. Novoselov, V. I. Fal′ko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, A roadmap for graphene, *Nature* 490(7419), 192 (2012)
5. A. C. Ferrari, F. Bonaccorso, V. Fal'ko, K. S. Novoselov, S. Roche, et al, Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems, *Nanoscale* 7(11), 4598 (2015)
6. R. S. Zhang and J. W. Jiang, The art of designing carbon allotropes, *Front. Phys.* 14, 13401 (2019)
7. M. Hu, N. Zhang, G. Shan, J. Gao, J. Liu, and R. K. Y. Li, Two-dimensional materials: Emerging toolkit for construction of ultrathin high-efficiency microwave shield and absorber, *Front. Phys.* 13(4), 138113 (2018)
8. R. Wang, X. Ren, Z. Yan, L. J. Jiang, W. E. I. Sha, and G. C. Shan, Graphene based functional devices: A short review, *Front. Phys.* 14, 13603 (2019)
9. X. Gan, et al., Two-dimensional materials-based optical modulators, *Front. Phys.* doi: 10.1007/s11467-018-0840-9
10. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Two-dimensional atomic crystals, *Proc. Natl. Acad. Sci. USA* 102(30), 10451 (2005)
11. A. H. C. Neto and K. Novoselov, New directions in science and technology: Two-dimensional crystals, *Rep. Prog. Phys.* 74(8), 082501 (2011)
12. Y. Cao, A. Mishchenko, G. L. Yu, E. Khestanova, A. P. Rooney, E. Prestat, A. V. Kretinin, P. Blake, M. B. Shalom, C. Woods, J. Chapman, G. Balakrishnan, I. V. Grigorieva, K. S. Novoselov, B. A. Piot, M. Potemski, K. Watanabe, T. Taniguchi, S. J. Haigh, A. K. Geim, and R. V. Gorbachev, Quality heterostructures from two-dimensional crystals unstable in air by their assembly in inert atmosphere, *Nano Lett.* 15(8), 4914 (2015)
13. D. Zhong, K. L. Seyler, X. Linpeng, R. Cheng, N. Sivadas, B. Huang, E. Schmidgall, T. Taniguchi, K. Watanabe, M. A. McGuire, W. Yao, D. Xiao, K. M. C. Fu, and X. Xu, Van der Waals engineering of ferromagnetic semiconductor heterostructures for spin and valleytronics, *Sci. Adv.* 3(5), e1603113 (2017)
14. S. Jiang, L. Li, Z. Wang, K. F. Mak, and J. Shan, Controlling magnetism in 2D $\mathrm{CrI}_3$ by electrostatic doping, *Nat. Nanotechnol.* 13(7), 549 (2018)
15. D. Ghazaryan, M. T. Greenaway, Z. Wang, V. H. Guarochico-Moreira, I. J. Vera-Marun, J. Yin, Y. Liao, S. V. Morozov, O. Kristanovski, A. I. Lichtenstein, M. I. Katsnelson, F. Withers, A. Mishchenko, L. Eaves, A. K. Geim, K. S. Novoselov, and A. Misra, Magnon-assisted tunnelling in van der Waals heterostructures based on $\mathrm{CrBr}_3$, *Nature Electron.* 1(6), 344 (2018)
16. K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Atomically thin $\mathrm{MoS}_2$: A new direct-gap semiconductor, *Phys. Rev. Lett.* 105(13), 136805 (2010)
17. T. LaMountain, E. J. Lenferink, Y. J. Chen, T. K. Stanev, and N. P. Stern, Environmental engineering of transition metal dichalcogenide optoelectronics, *Front. Phys.* 13(4), 138114 (2018)
18. D. H. Deng, K. S. Novoselov, Q. Fu, N. Zheng, Z. Tian, and X. Bao, Catalysis with two-dimensional materials and their heterostructures, *Nat. Nanotechnol.* 11(3), 218 (2016)

19. J. Deng, H. Li, S. Wang, D. Ding, M. Chen, C. Liu, Z. Tian, K. S. Novoselov, C. Ma, D. Deng, and X. Bao, Multiscale structural and electronic control of molybdenum disulfide foam for highly efficient hydrogen production, *Nat. Commun.* 8, 14430 (2017)

20. J. Mao, Y. Wang, Z. Zheng, and D. Deng, The rise of two-dimensional $MoS_2$ for catalysis, *Front. Phys.* 13(4), 138118 (2018)

21. A. K. Geim and I. V. Grigorieva, Van der Waals heterostructures, *Nature* 499(7459), 419 (2013)

22. C. Dean, A. F. Young, L. Wang, I. Meric, G.H. Lee, K. Watanabe, T. Taniguchi, K. Shepard, P. Kim, and J. Hone, Graphene based heterostructures, *Solid State Commun.* 152(15), 1275 (2012)

23. K. S. Novoselov and A. H. C. Neto, Two-dimensional crystals-based heterostructures: Materials with tailored properties, *Phys. Scr. T* 146, 014006 (2012)

24. K. S. Novoselov, A. Mishchenko, A. Carvalho, and A. H. Castro Neto, 2D materials and van der Waals heterostructures, *Science* 353(6298), aac9439 (2016)

25. C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, and J. Hone, Boron nitride substrates for high-quality graphene electronics, *Nat. Nanotechnol.* 5(10), 722 (2010)

26. X. Du, I. Skachko, A. Barker, and E. Y. Andrei, Approaching ballistic transport in suspended graphene, *Nat. Nanotechnol.* 3(8), 491 (2008)

27. X. Du, I. Skachko, F. Duerr, A. Luican, and E. Y. Andrei, Fractional quantum Hall effect and insulating phase of Dirac electrons in graphene, *Nature* 462(7270), 192 (2009)

28. K. I. Bolotin, F. Ghahari, M. D. Shulman, H. L. Stormer, and P. Kim, Observation of the fractional quantum Hall effect in graphene, *Nature* 462(7270), 196 (2009)

29. A. S. Mayorov, D. C. Elias, I. S. Mukhin, S. V. Morozov, L. A. Ponomarenko, K. S. Novoselov, A. K. Geim, and R. V. Gorbachev, How close can one approach the Dirac point in graphene experimentally? *Nano Lett.* 12(9), 4629 (2012)

30. Y. Q. Bie, G. Grosso, M. Heuck, M. M. Furchi, Y. Cao, J. Zheng, D. Bunandar, E. Navarro-Moratalla, L. Zhou, D. K. Efetov, T. Taniguchi, K. Watanabe, J. Kong, D. Englund, and P. Jarillo-Herrero, A $MoTe_2$-based light-emitting diode and photodetector for silicon photonic integrated circuits, *Nat. Nanotechnol.* 12(12), 1124 (2017)

31. R. V. Gorbachev, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. Tudorovskiy, I. V. Grigorieva, A. H. MacDonald, S. V. Morozov, K. Watanabe, T. Taniguchi, and L. A. Ponomarenko, Strong Coulomb drag and broken symmetry in double-layer graphene, *Nat. Phys.* 8(12), 896 (2012)

32. X. Liu, et al., Coulomb drag and exciton condensation in graphene double-layer heterostructures, *Front. Phys.* doi: 10.1007/s11467-018-0838-3

33. F. Amet, J. R. Williams, A. G. F. Garcia, M. Yankowitz, K. Watanabe, T. Taniguchi, and D. Goldhaber-Gordon, Tunneling spectroscopy of graphene-boron-nitride heterostructures, *Phys. Rev. B* 85(7), 073405 (2012)

34. G. H. Lee, Y. J. Yu, C. Lee, C. Dean, K. L. Shepard, P. Kim, and J. Hone, Electron tunneling through atomically flat and ultrathin hexagonal boron nitride, *Appl. Phys. Lett.* 99(24), 243114 (2011)

35. L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, M. I. Katsnelson, L. Eaves, S. V. Morozov, A. S. Mayorov, N. M. R. Peres, A. H. Castro Neto, J. Leist, A. K. Geim, L. A. Ponomarenko, and K. S. Novoselov, Electron tunneling through ultrathin boron nitride crystalline barriers, *Nano Lett.* 12(3), 1707 (2012)

36. L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, A. Mishchenko, T. Georgiou, M. I. Katsnelson, L. Eaves, S. V. Morozov, N. M. R. Peres, J. Leist, A. K. Geim, K. S. Novoselov, and L. A. Ponomarenko, Field-effect tunneling transistor based on vertical graphene heterostructures, *Science* 335(6071), 947 (2012)

37. H. Yang, J. Heo, S. Park, H. J. Song, D. H. Seo, K. E. Byun, P. Kim, I. Yoo, H. J. Chung, and K. Kim, Graphene barristor, a triode device with a gate-controlled Schottky barrier, *Science* 336(6085), 1140 (2012)

38. L. Britnell, R. V. Gorbachev, A. K. Geim, L. A. Ponomarenko, A. Mishchenko, M. T. Greenaway, T. M. Fromhold, K. S. Novoselov, and L. Eaves, Resonant tunnelling and negative differential conductance in graphene transistors, *Nat. Commun.* 4(1), 1794 (2013)

39. A. Mishchenko, J. S. Tu, Y. Cao, R. V. Gorbachev, J. R. Wallbank, M. T. Greenaway, V. E. Morozov, S. V. Morozov, M. J. Zhu, S. L. Wong, F. Withers, C. R. Woods, Y.J. Kim, K. Watanabe, T. Taniguchi, E. E. Vdovin, O. Makarovsky, T. M. Fromhold, V. I. Fal'ko, A. K. Geim, L. Eaves, and K. S. Novoselov, Twist-controlled resonant tunnelling in graphene/boron nitride/graphene heterostructures, *Nat. Nanotechnol.* 9(10), 808 (2014)

40. M. T. Greenaway, E. E. Vdovin, A. Mishchenko, O. Makarovsky, A. Patanè, J. R. Wallbank, Y. Cao, A. V. Kretinin, M. J. Zhu, S. V. Morozov, V. I. Fal'ko, K. S. Novoselov, A. K. Geim, T. M. Fromhold, and L. Eaves, Resonant tunnelling between the chiral Landau states of twisted graphene lattices, *Nat. Phys.* 11(12), 1057 (2015)

41. J. R. Wallbank, D. Ghazaryan, A. Misra, Y. Cao, J. S. Tu, B. A. Piot, M. Potemski, S. Pezzini, S. Wiedmann, U. Zeitler, T. L. M. Lane, S. V. Morozov, M. T. Greenaway, L. Eaves, A. K. Geim, V. I. Fal'ko, K. S. Novoselov, and A. Mishchenko, Tuning the valley and chiral quantum state of Dirac electrons in van der Waals heterostructures, *Science* 353(6299), 575 (2016)

42. U. Chandni, K. Watanabe, T. Taniguchi, and J. P. Eisenstein, Evidence for defect-mediated tunneling in hexagonal boron nitride-based junctions, *Nano Lett.* 15(11), 7329 (2015)

43. E. E. Vdovin, A. Mishchenko, M. T. Greenaway, M. J. Zhu, D. Ghazaryan, A. Misra, Y. Cao, S. V. Morozov, O. Makarovsky, T. M. Fromhold, A. Patanè, G. J. Slotman, M. I. Katsnelson, A. K. Geim, K. S. Novoselov, and L. Eaves, Phonon-assisted resonant tunneling of electrons in graphene-boron nitride transistors, *Phys. Rev. Lett.* 116(18), 186603 (2016)

44. U. Chandni, K. Watanabe, T. Taniguchi, and J. P. Eisenstein, Signatures of phonon and defect-assisted tunneling in planar metal-hexagonal boron nitride-graphene junctions, *Nano Lett.* 16(12), 7982 (2016)

45. L. A. Ponomarenko, R. V. Gorbachev, G. L. Yu, D. C. Elias, R. Jalil, A. A. Patel, A. Mishchenko, A. S. Mayorov, C. R. Woods, J. R. Wallbank, M. Mucha-Kruczynski, B. A. Piot, M. Potemski, I. V. Grigorieva, K. S. Novoselov, F. Guinea, V. I. Fal'ko, and A. K. Geim, Cloning of Dirac fermions in graphene superlattices, *Nature* 497(7451), 594 (2013)

46. C. R. Dean, L. Wang, P. Maher, C. Forsythe, F. Ghahari, Y. Gao, J. Katoch, M. Ishigami, P. Moon, M. Koshino, T. Taniguchi, K. Watanabe, K. L. Shepard, J. Hone, and P. Kim, Hofstadter's butterfly and the fractal quantum Hall effect in moire superlattices, *Nature* 497(7451), 598 (2013)

47. B. Hunt, J. D. Sanchez-Yamagishi, A. F. Young, M. Yankowitz, B. J. LeRoy, K. Watanabe, T. Taniguchi, P. Moon, M. Koshino, P. Jarillo-Herrero, and R. C. Ashoori, Massive Dirac fermions and Hofstadter butterfly in a van der Waals heterostructure, *Science* 340(6139), 1427 (2013)

48. G. L. Yu, R. V. Gorbachev, J. S. Tu, A. V. Kretinin, Y. Cao, R. Jalil, F. Withers, L. A. Ponomarenko, B. A. Piot, M. Potemski, D. C. Elias, X. Chen, K. Watanabe, T. Taniguchi, I. V. Grigorieva, K. S. Novoselov, V. I. Fal'ko, A. K. Geim, and A. Mishchenko, Hierarchy of Hofstadter states and replica quantum Hall ferromagnetism in graphene superlattices, *Nat. Phys.* 10(7), 525 (2014)

49. L. Wang, Y. Gao, B. Wen, Z. Han, T. Taniguchi, K. Watanabe, M. Koshino, J. Hone, and C. R. Dean, Evidence for a fractional fractal quantum Hall effect in graphene superlattices, *Science* 350(6265), 1231 (2015)

50. R. Krishna Kumar, X. Chen, G. H. Auton, A. Mishchenko, D. A. Bandurin, et al., High-temperature quantum oscillations caused by recurring Bloch states in graphene superlattices, *Science* 357(6347), 181 (2017)

51. H. Fang, C. Battaglia, C. Carraro, S. Nemsak, B. Ozdol, J. S. Kang, H. A. Bechtel, S. B. Desai, F. Kronast, A. A. Unal, G. Conti, C. Conlon, G. K. Palsson, M. C. Martin, A. M. Minor, C. S. Fadley, E. Yablonovitch, R. Maboudian, and A. Javey, Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides, *Proc. Natl. Acad. Sci. USA* 111(17), 6198 (2014)

52. Y. Liu, H. Zhang, Y. Zhou, F. Ran, W. Zhao, L. Wang, C. Pei, J. Zhang, X. Huang, and H. Li, Probing interlayer interactions in $WSe_2$-graphene heterostructures by ultralow frequency Raman spectroscopy, *Front. Phys.* 14, 13607 (2019)

53. C. H. Lee, G.H. Lee, A. M. van der Zande, W. Chen, Y. Li, M. Han, X. Cui, G. Arefe, C. Nuckolls, T. F. Heinz, J. Guo, J. Hone, and P. Kim, Atomically thin p-n junctions with van der Waals heterointerfaces, *Nat. Nanotechnol.* 9(9), 676 (2014)

54. F. H. L. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, and M. Polini, Photodetectors based on graphene, other two-dimensional materials and hybrid systems, *Nat. Nanotechnol.* 9(10), 780 (2014)

55. Z. Z. Yan, Z. H. Jiang, J. P. Lu, and Z. H. Ni, Interfacial charge transfer in $WS_2$ monolayer/$CsPbBr_3$ microplate heterostructure, *Front. Phys.* 13(4), 138115 (2018)

56. Y. Guo, N. Gao, Y. Bai, J. Zhao, and X. C. Zeng, Monolayered semiconducting GeAsSe and SnSbTe with ultrahigh hole mobility, *Front. Phys.* 13(4), 138117 (2018)

57. C. Yang, Y. Chen, D. Liu, J. Wang, C. Chen, J. Wang, Y. Fan, S. Huang, and W. Lei, Vertically aligned g-AlOOH nanosheets on Al foils as flexible and reusable substrates for $NH_3$ adsorption, *Front. Phys.* 13(4), 138101 (2018)