Review

Two-dimensional hexagonal semiconductors beyond graphene

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Abstract

The rapid and successful development of the research on graphene and graphene-based nanostructures has been substantially enlarged to include many other two-dimensional hexagonal semiconductors (THS): phosphorene, silicene, germanene, hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMDCs) such as MoS\textsubscript{2}, MoSe\textsubscript{2}, WS\textsubscript{2}, WSe\textsubscript{2} as well as the van der Waals heterostructures of various THSs (including graphene). The present article is a review of recent works on THSs beyond graphene and van der Waals heterostructures composed of different pairs of all THSs. One among the priorities of new THSs compared to graphene is the presence of a non-vanishing energy bandgap which opened up the ability to fabricate a large number of electronic, optoelectronic and photonic devices on the basis of these new materials and their van der Waals heterostructures. Moreover, a significant progress in the research on TMDCs was the discovery of valley degree of freedom. The results of research on valley degree of freedom and the development of a new technology based on valley degree of freedom—valleytronics are also presented. Thus the scientific contents of the basic research and practical applications on THSs are very rich and extremely promising.

Keywords: graphene, phosphorene, silicene, transition metal dichalcogenides van der Waals heterostructures

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1. Introduction

The discovery of graphene by Novoselov, Geim \textit{et al} \cite{1} not only led to the emergence and the development of an extremely promising scientific area as ‘a rapidly rising star on the horizon of materials science and condensed matter physics’ and revealed ‘a cornucopia of new physics and potential applications’ \cite{2}, but also stimulated the development of a wider scientific area—that of the research and applications of two-dimensional hexagonal semiconductor (THS) materials beyond graphene, such as phosphorene \cite{3–5}, silicene \cite{6, 7}, hexagonal boron nitride (h-BN) \cite{8, 9}, transition metal dichalcogenide (TMDC) \cite{10–12} and their van der Waals heterostructures \cite{13, 14}.

Some year ago Xu \textit{et al} \cite{15} published a comprehensive review in graphene-like two-dimensional materials. Since that time a significant progress has been achieved in the research and applications of this particular type of THSs. The purpose of present work is to review scientific results obtained after the submission of the article \cite{15}.

A review on recent advances in the research and applications of phosphorene and silicene is the content of section 2. Also in recent years the research and applications of...
TMDCs were very active, a large number of experimental works on these interesting and extremely promising two-dimensional hexagonal semiconducting materials were carried out. Their results are summarized in section 3. The content of section 4 is a review on van der Waals heterostructures of various two-dimensional hexagonal semiconducting materials (including graphene). The conclusion and discussion are presented in section 5.

2. Recent advances in the research on phosphorene and silicene

In a very interesting and important article [3] Reich remarked that although graphene possesses enticing electrical properties allowing electrons to flow freely across its surface, it lacks a natural bandgap that could be used to switch this flow on and off. This deficiency reduces graphene’s usefulness as a replacement for the semiconductor switches in computer circuits. Phosphorene, an atom—thick layer of elemental phosphorus that does have a natural bandgap could be an alternative to overcome above-mentioned deficiency of graphene, and at the same time, might be also useful for developing flexible electronics. From phosphorene layers Churchill and Jarillo-Herrero fabricated transistor devices [4], while Chen, Zhang et al fabricated field-effect transistors (FETs) [5].

Strain-induced gap in black phosphorus (BP) was studied by Castro Neto et al [16]. Using density functional theory and tight-binding models the authors predicted the band structure of single-layer BP and the effect of strain. Having determined the localized orbital composition of the individual bands from first principle, the authors used the system symmetry to write down the effective low-energy Hamiltonian at the point. From numerical calculations and arguments based on the crystal structure of the material the authors showed that the deformation in the direction normal to the plane can be used to change the gap size and induce a semiconductor-metal transition.

A computational study on semiconducting layered blue phosphorus was carried out by Tománek et al [17]. The authors investigated a previously unknown phase of phosphorus that shares it layered structure and high stability with the BP allotrope. They found the in-plane hexagonal structure and bulk layer stacking of this structure, and called it ‘blue phosphorus’. Unlike graphite and BP, blue phosphorus displays a wide fundamental bandgap. Moreover, it should be easily exfoliated to form a quasi-two-dimensional structure suitable for electronic applications.

In [18] Tománek et al demonstrated the phase coexistence and metal-insulator transition in few-layers phosphorene by using a computational study. Based on ab initio density functional calculations the authors proposed γ − P and δ − P as two additional stable structural phases of layered phosphorus besides the layered α − P (black) and β − P (blue) phosphorus allotropes. Monolayers of some of these allotropes have a wide bandgap, whereas others, including γ − P, show a metal-insulator transition caused by in-layer strain or changing the number of layers. An unforeseen benefit was the possibility to connect different structural phases at no energy cost. This becomes particularly valuable in assembling heterostructures with well-defined metallic and semiconducting regions in one continuous layer.

Electron–phonon coupling in two-dimensional silicene and germanene was studied by Chou et al [19]. Following work in graphene the authors performed the first principles calculations of electron–phonon coupling in low-buckled monolayer silicene and germanene. Despite the similar honeycomb atomic arrangement and linear band dispersion, the electron–phonon coupling matrix element squares of the $\Gamma$ − $E_g$ and $K$−$A_1$ modes in silicene are only about 50% of those in graphene. However, the smaller Fermi velocity in silicene compensates for this reduction by providing a larger joint electronic density of states near the Dirac point, giving rise to comparable phonon linewidths. The authors predicted that Kohn anomalies associated with these two optical modes are significant in silicene. In addition, the electron–phonon coupling induced frequency shift and linewidth of the Raman-active $\Gamma$ − $E_g$ mode in silicene were calculated as a function of doping. The results are comparable to those in graphene, indicating a similar nonadiabatic dynamic origin.

In [20] Yang et al investigated layer-controlled bandgap and anisotropic excitons in few-layer BP. The authors observed the quasiparticle bandgap, excitons and highly anisotropic optical responses of few-layer BP. It was shown that this material exhibits unique many-electron effects, and its electronic structure is dispersive essentially along one dimension, leading to particularly enhanced self-energy corrections and excitonic effects. Additionally, within a wide energy range, including infrared light and a part of visible light, few-layer BP absorbs light polarized along the armchair direction, and is transparent to light polarized along the zigzag direction, making them potentially viable linear polarizers for applications. Finally, the numbers of phosphorene layers included in the stack controls the material’s bandgap, optical absorption spectrum, and anisotropic polarization energy window across a wide range.

Scaling laws for the bandgap and optical response of phosphorene nanoribbons (PNRs) were establised by Yang and Tran [21]. The authors studied electronic structure and optical absorption spectra of monolayer PNRs by using first-principles simulations. The bandgap of PNRs is strongly enhanced by quantum confinement. However, differently orientated PNRs exhibit distinct scaling laws for the bandgap versus the ribbon width. The bandgaps of armchair PNRs scale as $1/W^2$, while zigzag PNRs exhibit a $1/W$ behavior. These distinct scaling laws reflect a significant implication of the band dispersion of phosphorene: electrons and holes behave as nonrelativistic particles along the zigzag direction but resemble relativistic particles along the armchair direction. This unexpected merging of nonrelativistic and relativistic properties in a single material may produce novel electrical and magnetotransport properties of few-layer BP and its ribbon structure. Finally, the respective PNRs host electrons and holes with markedly different effective masses
and optical absorption spectra, which are suitable for a wide range of applications.

In [22] Castro Neto, Özyil Maz et al investigated electric field effect in ultrathin BP. The authors demonstrated few-layer BP field effect devices a Si/SiO2 and measured charge carrier mobility in a four probe configuration as well as drain current modulation modulation in a two point configuration. The authors found room temperature mobilities up to 300 cm² V⁻¹ s⁻¹ and drain current modulation of over 10⁴. At low temperature the ON/OFF ratio exceeded 10⁵, and the device exhibited both electron and hole conduction. Using atomic force microscope the authors observed significant surface roughening of thin BP crystals over the course of 1 h after exfoliation.

A superior gas sensor based on phosphorene was proposed by Kou et al [23]. Using first principles calculations the authors studied the adsorption of CO, CO₂, NH₃, NO and NO₂ gas molecules on a monolayer of phosphorene and predicted superior sensing performance of phosphorene rivaling or even surpassing that of other 2D materials. The authors determined the optimal adsorption positions of these molecules on phosphorene and identified molecular doping, that is, charge transfer between the molecules and phosphorene, as the driving mechanism for the high adsorption strength. Further the authors calculated the current–voltage (I–V) relation using nonequilibrium Green’s function formalism. The transport features showed large (1–2 order of magnitude) anisotropy along different (armchair or zigzag) directions, which is consistent with the anisotropic band structure of phosphorene. Remarkably, the I–V relation exhibits distinct responses with a marked change of the I–V relation along either the armchair or the zigzag directions depending on the type of molecules. Such selectivity and sensitivity to adsorption make phosphorene a superior gas sensor that promises widely ranging applications.

The anisotropic electrical conductance of few-layer BP can be generated by strain-engineering. In [24] Yang et al applied first principles calculations to demonstrate that the anisotropic electronic mobility can be controlled by using simple strain conditions. With the appropriate biaxial or uniaxial strain (4%–6%) the preferred conducting direction can rotate by 90°. This will be useful for exploring unusual quantum Hall effects and exotic electronic and mechanical applications based on phosphorene.

Few-layer BP is a high-mobility layered semiconductor with a direct bandgap strongly dependent on the number of layers, from 0.35 eV (bulk) to 2.0 eV (single layer). Therefore BP is an appealing candidate for tunable photodetection from the visible to the infrared part of the spectrum. The fast and broadband photoresponse of few-layer BP FETs was demonstrated by Buscema, Castellanos-Gomez et al [25]. The authors studied the photoresponse of FETs fabricated from few-layer BP (3–8 nm thick) as a function of excitation wavelength, power, and frequency. In the dark state, the BP FETs could be tuned both in hole and electron doping regimes allowing for ambipolar operation. The authors measured mobilities in the order of 100 cm² V⁻¹ s⁻¹ and a current ON/OFF ratio large than 10⁷. Upon illumination, the BP FETs showed a response to excitation wavelengths from the visible region up to 940 nm and a rise time of about 1 ms, demonstrating broadband and fast detection. The responsivity reached 4.8 mA W⁻¹, and it could be drastically enhanced by engineering a detector based on a p–n function. The ambipolar behavior coupled to the fast and broadband photodetection makes few-layer BP a promising two-dimensional material for photodetection across the visible and near-infrared part of the electromagnetic spectrum.

Strain and orientation modulated bandgaps and effective masses in PNRs were investigated by Guo et al [26]. The authors applied the density functional theory to study passivated PNRs, armchair nanoribbon (a-PNR), diagonal nanoribbon (d-PNR) and zigzag nanoribbon (z-PNR). It was shown that z-PNRs demonstrate the greatest quantum size effect, tuning the bandgap from 1.4 to 2.6 eV when the width is reduced from 26 to 6 A. Strain effectively tunes charge carrier of electronic effective mass at +8% strain for a-PNRs or a hole effective mass at +3% strain for z-PNRs, differentiating the m⁺/m⁻ ratio by an order of magnitude in each case. Straining of d-PNRs results in a direct to indirect band gap transition at either ~7% or +5% strain and therein creates degenerate energy valleys with potential applications for valleytronics with potential applications for valleytronics and/or photocatalysis.

In [27] Das et al investigated the tunable transport gap in phosphorene. The authors experimentally demonstrated that the transport gap of phosphorene can be tuned monotonically from ~0.3 to ~1.0 eV when the flake thickness is scaled down from bulk to a single layer. As a consequence, the ON current, the OFF current, and the current ON/OFF ratio of phosphorene FETs were found to be significantly impacted by the layer thickness. The transport gap was determined from the transfer characteristics of phosphorene FETs using a robust technique. By scaling the thickness of the gate oxide, the authors were also able to demonstrate enhanced ambipolar conduction in monolayer and few-layer phosphorene FETs. The asymmetry of electron and hole current was found to be dependent on the layer thickness that can be explained by dynamic changes of the metal Fermi level with the energy band of phosphorene depending on the layer number. The authors also extracted the Schottky barrier height for both the electron and the hole injection as a function of the layer thickness. Finally, the authors discussed the dependence of the hole mobility of phosphorene on temperature and carrier concentration.

Enhanced thermoelectric efficiency via orthogonal electrical and thermal conductance in phosphorene was investigated by Yang et al [28]. Thermoelectric devices that utilize the Seebeck effect to convert heat flow into electrical energy are highly desirable for the development of portable, solid state, passively powered electronic systems. The conversion efficiencies of such devices are quantified by the dimension less thermoelectric figure of merit (ZT), which is proportional to the ratio of a device’s electrical conductance to its thermal conductance. By applying first-principles and model calculations the authors demonstrated that phosphorene possesses a spatially anisotropic electrical conductance and its lattice thermal conductance exhibits a pronounced special-
anisotropy as well. The prominent electrical and thermal conducting directions are orthogonal to one another, enhancing the ratio of these conductances. As a result, $ZT$ may reach the criterion for commercial deployment along the armchair direction of phosphorene at $T = 500$ K and is close to 1 even at room temperature. Ultimately, phosphorene hopefuly stands out as an environmentally sound thermoelectric material with unprecedented qualities. Intrinsiically, it is a mechanically flexible materials that converts heat energy with high efficiency at low temperature ($\sim 300$ K).

The electronic bandgap and edge reconstruction in phosphorene materials were investigated by Meunier, Pan et al [29]. The authors considered atomic scale electronic variation related to strain-induced honeycomb structure of freshly cleaved BP using a high-resolution scanning tunneling spectroscopy (STS) to survey the light ($x$) and heavy ($y$) effective mass directions. Through a combination of STS measurements and first-principles calculations, a model for edge reconstruction was also determined.

Special properties of phosphorene were investigate by Ye et al [30]. The authors showed that single-layer phosphorene is flexible, stable and can be mechanically exfoliated. Unlike graphene, phosphorene has an inherent, direct and appreciate bandgap. By using ab initio calculations the authors indicated that the bandgap of phosphorene is direct, depends on the number of layers and the in-layer strain, and is significantly large than the bulk value of 0.31–0.36 eV. The observed photoluminescence (PL) peak of single-layer phosphorene in the visible optical range also confirmed that the bandgap is larger than that of the bulk system. The transport studies indicated a hole mobility that reflects the structural anisotropy of phosphorene. At room temperature the prepared few-layer phosphorene FET with 0.1 $\mu$m channel length displayed a high ON-current of 194 mA mm$^{-1}$, a high hole field-effect mobility of 286 cm$^2$ V$^{-1}$ s$^{-1}$, and ON/OFF ratio up to $10^4$.

The PL and Raman spectroscopy in few-layer phosphorene were investigated by Lu et al [31]. In this work few-layer phosphorus flakes were fabricated using mechanical exfoliation techniques. The flakes were identified by optical contrast in a microscope. Regions with different colors correspond to phosphorene flakes with different thicknesses. All Raman and PL measurements were carried out in a confocal microscopy setup, which has a 532 nm solid state green laser for excitation. The authors used PL system with two liquid nitrogen cooled detectors which can detect photons with wavelengths ranging from 200 to 1650 nm. Measured PL spectra in few-layer phosphorene were highly dependent on number of layers. Strong peaks at 961, 1268, 1413 and 1558 nm were observed in two-, three-, four- and five-layered phosphorene, respectively, which correspond to energy values of 1.29, 0.98, 0.88 and 0.80 eV, respectively. The measured PL peaks are attributed to the nature of excitons, which represent lower bounds on the fundamental bandgap value in few-layer phosphorene. Thus the energy positions of PL peak increase rapidly, in the consistency with the results of the theoretical calculations of the authors. The strong PL in few-layer phosphorene arises from direct electronic transitions with high radiative recombination rate.

The measured Raman peaks at 359, 437 and 466 cm$^{-1}$ are attributed to the Ag$^1$, B$_{2g}$, and Ag$^2$ phonon modes in the crystalline few-layer phosphorene flakes. The decrease of temperature led to their blue shift. The highly angle-dependent Raman spectra from phosphorene flakes enabled the authors quickly determine their crystalline orientation without TEM or SEM.

The ambipolar phosphorene FET with record high electron mobility was demonstrated by Das et al [32]. By tuning the work function of the contact metal and scaling the thickness of the gate oxide the authors showed that electron transport can indeed be realized in phosphorene. The authors obtained record high electron field-effect mobility of $\sim 38$ cm V$^{-1}$ s$^{-1}$ and hole field-effect mobility of $\sim 172$ cm V$^{-1}$ s$^{-1}$ in phosphorene. The contact resistance values of the Schottky barrier were also extracted and its effects on the device performance were discussed.

Previously silicene has been theoretically predicted as a buckled honeycomb arrangement of Si atoms with an electronic dispersion resembling that of relativistic Dirac fermions in graphene. Le Lay et al [6] provided compelling evidence, from both structural and electronic properties, for the synthesis of epitaxial silicene sheets on a silver (111) substrate, through the combination of scanning tunneling microscopy and angular-resolved photoemission spectroscopy in conjunction with calculations based on density functional theory. Another evidence for Dirac fermions in a honeycomb lattice based on silicon was shown by Wu et al [33]. The authors performed scanning tunneling microscopy studies on the atomic and electronic properties of silicene on Ag (111). Pronounced quasiparticle interference patterns, originating from both the intervalley and intravalley scatterings were observed. From these patterns, in conjunction with theoretical calculations, the authors derived a linear energy–momentum dispersion and a large Fermi velocity, which proved the existence of Dirac fermion in silicene. One more experimental evidence for epitaxial silicene was demonstrated by Yamada-Takamura et al [34]. The authors showed that two-dimen-sional epitaxial silicene formed diboride thin films grown on Si wafer through surface segregation on zirconium. A particular buckling of silicene induced by epitaxial relationship with surface led to a direct electronic bandgap at the $\Gamma$-point. These results demonstrated that the buckling and thus electronic properties of silicene were modified by epitaxial strain.

Although until now the theoretical calculations of the electronic structures of phosphorene and silicene [35–45] still did not reach final confirmed results, there was a significant progress in the applications of this new type of two-dimensional semiconductors. For example, in [46] Xu et al investigated electrical transport and optoelectronic properties of FETs fabricated from few-layer BP crystal down to a few nanometers. The authors explored the anisotropic nature and photocurrent generation mechanisms in BP FETs though spatial-, polarization-, gate-, and bias-dependent photocurrent.
measurements. Obtained results revealed that the photocurrent signals at BP-electrode junctions are mainly attributed to the photovoltaic effect in the OFF-state and photothermoelectric effect in the ON-state, and their anisotropic feature primarily results from the direction-dependent absorption of BP crystals.

Very recently Moller, Akinwande et al [7] successfully fabricated silicene FET corroborating theoretical expectations regarding its ambipolar Dirac fermion transport with a measured room-temperature mobility of 100 cm² V⁻¹ s⁻¹ attributed to acoustic phonon-limited transport and grain boundary scattering. These results were enabled by a growth-transfer-fabrication process that the authors have devised. This approach addresses a major challenge for material preservation of silicene during transfer and device fabrication and is applicable to other air-sensitive two-dimensional materials. Silicene’s allotropic affinity with bulk silicon and its low-temperature synthesis compared with graphene or alternative two-dimensional semiconductors suggest more direct integration with ubiquitous semiconductor technology.

Subsequently Xu, Xia et al [47] observed highly anisotropic and robust excitons in monolayer BP. Although BP has emerged as a promising new two-dimensional material due to its widely tunable and direct bandgap, high carrier mobility and remarkable in-plane anisotropic electrical, optical and phonon properties, current progress of the research on this material is primarily limited to its thin-film form. In above-mentioned work the authors revealed highly anisotropic and strongly bound excitons in monolayer BP using polarization-resolved PL measurements at room temperature. The authors showed that, regardless of the excitation laser polarization, the emitted light from the monolayer is linearly polarized along the light effective mass direction and centers around 1.3 eV, a clear signature of emission from highly anisotropic bright excitons. Moreover, PL excitation spectroscopy suggest a quasiparticle bandgap of 2.2 eV, from which the authors estimated an exciton binding energy of ~0.9 eV, consistent with theoretical results based on first principles. The experimental observation of highly anisotropic, bright excitons with large binding energy not only opened avenues for the explorations of many-electron physics in this unusual two-dimensional material, but also suggested its promising future in optoelectronic devices.

In the experimental work [39] Martel et al applied in situ Raman and transmission electron spectroscopies to study the photoexcitation and quantum confinement effects in exfoliated BP. Phosphorene thin layers are exfoliated from lamellar crystal of phosphorus atoms. However, probing the properties of phosphorene thin layer has been challenged by the fast degradation of phosphorene thin layers on exposure to ambient conditions. Therefore a procedure carried out in a glove box was used to prepare phosphorene thin layer in their pristine states for further studies on the effect of layer thickness on the Raman modes. Controlled experiments in ambient conditions were shown to lower the Ag²⁻/Ag²⁺ intensity ratio for ultrathin layers, a signature of oxidation.

3. Recent advances in the research on two-dimensional transition metal dichalcogenides (TMDCs)

3.1. Research on general properties of thin layers of TMDCs

A concise review of the historical development of two-dimensional TMDCs, methods for preparing their atomically thin layers, their electronic and optical properties as well as prospects for future advances in electronics and optoelectronics was presented by Coleman, Strano et al [49]. TMDCs are layered materials with strong in-plane bonding and weak out-of-plane interactions enabling exfoliation into two-dimensional layers of single unit cell thickness. Although TMDCs have been studied for decades, recent advances in nanoscale material characterizations and device fabrication have opened up new opportunities for two-dimensional layers of thin TMDCs in nanoelectronics and optoelectronics. TMDCs such as MoS₂, MoSe₂, WS₂ and WSe₂ are sizable bandgaps that change from indirect to direct in single layer, allowing applications such as transistors, photodetectors, and electroluminescent devices.

PL emission and Raman response of several TMDC monolayers and few-layers were investigated by Bratschitsch et al [50]. The authors mechanically exfoliated mono- and few-layers of MoS₂, MoSe₂ and WS₂. The exact numbers of layers were unambiguously determined by atomic force microscopy and high-resolution Raman spectroscopy. Strong PL emission was caused by the transition from an indirect bandgap semiconductor of bulk material to a direct bandgap semiconductor in atomically thin form. In [51] Meunier et al applied first principles density functional theory to the study of Raman spectra of TMDCs and their heterostructures. The authors quantitatively reproduced existing experimental data and presented evidence that the apparent discrepancy between intensity ratios observed experimentally can be explained by the high sensitivity of the Raman active modes to laser polarization. Furthermore, MoS₂/WSe₂ heterostructures up to four layers were considered in every possible combination and stacking order. Each heterostructure configuration possesses a unique. Raman spectrum in both frequency and intensity can be explained by changes in dielectric screening and interlayer interaction. Obtained results established a set of guidelines for the practical experimental identification of heterostructure configuration.

Tunneling phenomena in TMDCs were investigated by Das et al [52] toward low-power electronics. The authors experimentally explored the impact of band-to-band tunneling on electronic transport of double-gated WS₂ FET and Shottky barrier tunneling of holes in back-gate MoS₂ FET. The authors showed that by scaling the flake thickness and the thickness of the gate oxide, the tunneling current can be increased by several orders of magnitude. The authors also performed numerical calculations based on Landauer formalism and WKB approximation to explain their experimental findings. Based on a simple model the authors discussed the impact of bandgap and effective mass on the band-to-band tunneling current and evaluated the
performance limits for a set of dichalcogenides in the context of tunneling transistors for low-power applications. The findings of authors suggested that WSe$_2$ is an excellent choice for tunneling FETs.

Excited biexcitons in TMDCs were studied by VArga et al [53]. The authors used the stochastic variational method to show that the effective mass model correctly estimates the binding energies of excitons and trions but fails to predict the experimental binding energy of the biexciton. Using high-accuracy variational calculations the authors demonstrated that the biexciton binding energy in TMDCs is smaller than the trion energy, contradicting experimental findings. The authors also showed that the biexciton has bound excited states, and that the binding energy of the $L = 0$ excited state is in very good agreement with experimental data. This excited state corresponds to a hole attached to a negative trion and may be a possible resolution of the discrepancy between theory and experiment.

Until recent time the many-body collective phenomena in two-dimensional systems remain relatively unexplored. In order to study these phenomena Shan, Faimak et al [54] investigated the strongly enhanced charge-density-wave order in NbSe$_2$ monolayer. The authors performed a combined optical and electrical transport study on the many-body collective-order phase diagram of NbSe$_2$ down to a thickness of one monolayer. Both the charge-density-wave and superconducting phase have been observed down to the monolayer limit. The superconducting transition temperature decreased on lowering the layer thickness, but the newly observed charge-density-wave transition temperature increased from 33 K in the bulk to145 K in the monolayer. Such highly unusual enhancement of charge-density-wave in atomically thin samples could be understood to be a result of significantly enhanced electron–phonon interactions in two-dimensional NbSe$_2$, and was supported by the large blue shift of the collective amplitude vibration observed in the experiment of the authors.

A unified description of optical phonon modes in N-layer TMDCs was proposed by Berciaud et al [55]. In general, N-layer TMDCs provide a unique platform to investigate the difference of physical properties of bulk and monolayer materials. Using high-resolution micro-Raman spectroscopy the authors observed series of N-dependent low-frequency interlayer shear and breathing modes (LSM and LBM) below 40 cm$^{-1}$, and well-defined Davydov splitting of the mid-frequency modes in the range 100–200 cm$^{-1}$, which solely involve displacements of chalcogen atoms. In contrast, the high-frequency modes in the range 200–300 cm$^{-1}$, arising from displacement of both the metal and chalcogen atoms, exhibit considerable reduced splitting. The manifold of phonon modes associated with the in-plane and out-of-plane displacements were quantitatively described by a force constant model, including interactions up to the second nearest neighbor and surface effects as fitting parameters. The analysis of authors could readily be applied to other layered materials.

3.2. Research on thin layers of MoS$_2$ and MoSe$_2$

A significant progress of the research on thin layers of TMDCs was the emergence of a new direction in nanoelectronics—the valleytronics (similar to spintronics in electronics). In [56] Wang, Feng et al studied the valley-selective circular dichroism of MoS$_2$ monolayers. The authors remarked that a two-dimensional honeycomb lattice harbors a pair of inequivalent valleys in the $k$-space electronic structure, at the vicinities of inequivalent vertices of a hexagonal Brillouin zone. By applying first-principles calculation the authors showed that monolayer MoS$_2$ is an ideal material for valleytronics, in which valley-selective circular dichroism arising from its unique symmetry. The authors also provide experimental evidence for valley polarization by measuring the circularly polarized PL on monolayer MoS$_2$, which shows up to 50% polarization.

Cui et al [57] applied optical pumping technique to study valley polarization in MoS$_2$. The authors noticed that in order to fabricate a valleytronic device it is necessary to control the number of electrons in different valleys, thereby producing a valley polarization. Monolayer MoS$_2$ is a promising material for valleytronics because both the conduction and valence band edges have two energy-degenerate valleys at the corners of the first Brillouin zone. The authors demonstrated that optical pumping with circularly polarize light can achieve a valley polarization of 30% in pristine monolayer MoS$_2$. Thus the authors demonstrated the viability of optical valley control and valley-based electronic and optoelectronic applications in MoS$_2$ monolayers.

The control of valley polarization in monolayer MoS$_2$ by optical helicity was performed by Heinz et al [58]. In general, if there are two or more minima in the conduction band (or maxima in the valence band) in momentum space, and if it is possible to confine charge carriers in one of these valleys, it should be possible to make a valleytronic device. Valley polarization, as the selective population of one valley is designated, has been demonstrated using strain and magnetic fields, but neither of these approaches allows dynamic control. In the present work the authors demonstrated that optical pumping with circularly polarized light can achieve complete dynamic valley polarization in monolayer MoS$_2$, a two-dimensional noncentrosymmetric crystal with direct energy gaps at two valleys. Moreover, this polarization was retained for longer than 1 ns. Obtained results again demonstrated the viability of optical valley control and suggested the possibility of valley-based electronic and optoelectronic applications in MoS$_2$ monolayers.

Investigation of MoSe$_2$ FETs was performed by Larentis et al [59]. Using ultra-thin, mechanically exfoliated MoSe$_2$ flakes, the authors fabricated black-gate FETs. The MoSe$_2$ FETs are n-type and possess a high gate modulation, with ON/OFF ratios larger than 10$^4$. The devices showed asymmetric characteristics upon swapping the source and drain, a finding explained by the presence of Schottky barriers at the metal contact/MoSe$_2$ interface. Using four-point, black-gated devices, the authors measured the intrinsic conductivity and mobility of MoSe$_2$ as functions of gate bias and temperature.
Samples with room temperature mobility of $\sim$50 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ showed a strong temperature dependence suggesting that phonons play key role in dominant scattering mechanism. In [60] Wang, Palacios et al fabricated integrated circuits based on MoS$_2$ transistors. Two-dimensional MoS$_2$ semiconducting material has been shown to exhibit excellent electrical and optical properties allowing it to overcome the shortcomings of zero-bandgap graphene, while still sharing many of graphene’s advantages for electronic and optoelectronic applications. Discrete electronic and optoelectronic components, such as FETs, sensors, and photo-detectors made from few-layer MoS$_2$ showed promising performance as potential substitute of Si in conventional electronics, and of organic and amorphous Si semiconductors in ubiquitous systems and display applications. An important next step is the fabrication of fully integrated multistage circuits and logic building blocks on MoS$_2$ to demonstrate its capability for complex digital logic and high-frequency ac applications. The authors demonstrated an inverter, a NAND gate, a static random access memory, and a five-stage ring oscillator based on a direct-coupled transistor logic technology. The circuits comprised between 2 and 12 transistors seamlessly integrated side-by-side on a single sheet of bilayer MoS$_2$. Both enhancement-mode and depletion-mode transistors were fabricated thanks to the use of gate metals with different work functions.

High-performance multilayer MoS$_2$ transistors with scandium contacts were investigated by Das et al [61]. In this work the authors focused on the contacts and demonstrated that through a proper understanding and design of source/drain contacts and the right choice of number of MoS$_2$ layer, the excellent intrinsic properties of the two-dimensional MoS$_2$ material can be harvested. Using scandium contacts on 10 nm thick exfoliated MoS$_2$ flakes that are covered by a 15 nm Al$_2$O$_3$ film, high effective mobilities of 700 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ were achieved at room temperature. This break though was largely attributed to the fact that the authors succeeded in eliminating contact resistance effects that limited the device performance. The lack of reliable method for the large-scale production of MoS$_2$ nanosheets impeded their practical applications. To overcome this difficulty Yao, Wong et al [62] developed a facile, efficient, and scalable method for the fabrication of high-concentration. The $26.7 \pm 0.7$ mg ml$^{-1}$ concentration achieved was the highest concentration in an aqueous solution previously reported. Grinding generated pure shear forces to detach the MoS$_2$ layers from the bulk materials. Subsequent sonication further broke large crystallites into smaller ones, which promoted the dispersion of MoS$_2$ nanosheets ethanol/water solutions. The exfoliation process established a new method in the top-down fabrication of two-dimensional in aqueous solution. In the meantime, MoS$_2$-based sensing film produced using this approach has successfully demonstrated the feasibility of a low-cost and efficient NH$_3$ gas sensor using inkjet printing as a viable method.

In [63] Ugeda, Crommie et al presented a rigorous experimental observation of the extraordinarily large exciton binding in a MoS$_2$ monolayer by means of STS, as well as the two-particle exciton transition energy using PL spectroscopy. These yielded an exciton binding energy of 0.55 eV for monolayer MoSe$_2$ on graphene-orders of magnitude larger than what was seen in conventional three-dimensional semiconductors and significantly higher than that for MoSe$_2$ monolayers in more highly screening environments. This finding was corroborated by the ab initio calculations of the authors. The renormalized bandgap and large exciton binding observed here will have a profound impact on electronic and optoelectronic device technologies based on single-layer semiconducting TMDCs.

Phase-engineered low-resistance contacts for ultrathin MoS$_2$ transistors were investigated by Mohite, Chhowalla et al [64]. Ultrathin MoS$_2$ has emerged as an interesting layered semiconductor because of its finite energy bandgap and the absence of dangling bonds. However, metals deposited on the semiconducting 2H phase usually from high-temperature. In this work the authors demonstrated that the metallic 1T phase of MoS$_2$ can be locally induced on semiconducting 2H phase nanosheets, thus decreasing contact resistances significantly at zero gate bias. FETs with 1T phase electrodes fabricated and tested in air exhibit mobility values of $\sim$50 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, subthreshold swing values below 100 mV per decade, ON/OFF ratio of $\geq$10$^7$, drive current approaching $\sim\text{100 }\mu\text{A} \cdot \text{m}^{-1}$, and excellent current saturation. The deposition of different metals has limited influence on the FET performance, suggesting that the 1T/2H interface controls carrier injection into the channel. An increased reproducibility of electrical characteristics was also obtained. The direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial MoS$_2$ was reported by Mo, Shen et al [65]. The large enhancement of PL quantum efficiency as well as the potential development of valleytronics in atomically thin layers of TMDCs are closely related to the indirect-to-direct bandgap transition on their monolayers. In this work the authors observed the transition from indirect to direct bandgap in monolayer samples by using angle-resolved photoemission spectroscopy on high-quality thin films of MoSe$_2$ with variable thickness grown by molecular beam epitaxy. The band structure measured experimentally indicated a stronger tendency of monolayer MoSe$_2$ toward a direct bandgap as well as a larger gap size than theoretically predicted. Moreover, the finding of a significant spin-splitting of $\sim$$\text{180 }\mu\text{eV}$ at the valence band maximum of a monolayer MoS$_2$ film could expand its possible application to spintronic devices.

The atomic mechanism of the semiconducting-to-metallic phase transition in monolayer MoS$_2$ was investigated by Suenaga et al [66]. The authors showed that in situ transmission electron microscopy (TEM) can be used to follow the structural transformation between semiconducting (2H) and metallic (1T) phases in single-layered MoS$_2$, with atomic resolution. The 2H/1T phase transition involves gliding atomic planes of sulfur and/or molybdenum and requires an intermediate phase ($\alpha$-phase) as the precursor. The migration of two kinds of boundaries ($\beta$- and $\gamma$-boundaries) was also found to be responsible for the growth of the second phase. Furthermore, the authors showed that areas of the 1T phase can be controllably grown in a layer of the 2H phase using an electron beam.
The coupling between spin and valley degrees of freedom originating from the relativistic spin–orbit interaction is a peculiar physical phenomenon is the valley-dependent spin polarization in MoS$_2$ with broken inversion symmetry investigated by Ishizaka, Iwasa et al [67]. In this work the authors directly observed valley-dependent out-of-plane spin polarization in MoS$_2$, using spin- and angle-resolved photoemission spectroscopy. The result was in fair agreement with a first principles theoretical prediction. This was made possible by choosing a 3R polytype crystal, which has a non-centrosymmetric structure, rather than the conventional centrosymmetric 2H form. The authors also confirmed robust valley polarization in the 3R form by means of circularly polarized PL spectroscopy. Thus non-centrosymmetric TMDC crystals may provide a firm basis for the development of magnetic and electric manipulation of spin=valley degree if freedom.

Valley and band structure engineering of folded MoS$_2$ bilayers was discussed by Wu et al [68]. By folding exfoliated MoS$_2$ monolayers the authors obtained MoS$_2$ bilayer with different stacking orders, as monitored by second harmonic generation and PL. Appropriate folding can break the inversion symmetry and suppress interlayer hopping, evoking strong valley and spin polarizations that are not achieved in natural MoS$_2$ bilayers of Bernal stacking. It can also enlarge the indirect bandgap by more than 100 meV through a decrease in the interlayer coupling. Thus the present work provided an effective and versatile means to engineer TMDC materials with desirable electronic and optical properties.

Using PL spectroscopy Dresselhauß et al [69] probed the interlayer coupling of twisted bilayer MoS$_2$ and revealed its tensility. It was found that the PL intensity ratio of the trion and exciton reaches its maximum value for the twisted angle $0^\circ$ or $60^\circ$, while for the twisted angle $30^\circ$ or $90^\circ$ the situation is opposite. This is mainly attributed to the change of the trion binding energy. The first-principles density functional theory analysis further confirmed the change of the interlayer coupling with the twisted angle, which interpreted the experimental result. Piezoelectricity in free-standing monolayer MoS$_2$ was observed by Zhang et al [70]. It was well-known that piezoelectricity allows precise and robust conversion between electricity and mechanical force, and arises from the broken inversion symmetry in the atomic structure. Reducing the dimensionality of bulk materials has been suggested to enhance piezoelectricity. However, when the thickness of a material approaches a single molecular layer, the large surface energy can cause piezoelectric structures to be thermodynamically unstable. TMDCs can retain their atomic structures down to the single-layer limit without lattice reconstruction, even under ambient conditions. Recent calculations have predicted the existence of piezoelectricity in these two-dimensional crystals due to their broken inversion symmetry. In the present work the authors demonstrated experimental evidence of piezoelectricity in a free-standing single layer of MoS$_2$ and a measured piezoelectric coefficient of $e_{11} = 2.9 \times 10^{-10} \text{C m}^{-1}$. The measurement of the intrinsic piezoelectricity in such free-standing crystals is free from substrate such as doping and parasitic changes. The authors observed a finite and zero piezoelectric response in MoS$_2$ in odd and even number of layers, respectively, in sharp contrast to bulk piezoelectric material. This oscillation is due to the breaking and recovery of the inversion symmetry of the two-dimensional crystal. Through the angular dependence of electromechanical coupling, the authors determined the two-dimensional crystal orientation. The piezoelectricity discovered in this single molecular membrane promises new applications in low-power logic switches for computing and ultrasensitive biosensors scaled down to a single atom unit cell.

Gate-tunable memristive phenomena mediated by grain boundaries (GBs) in monolayer MoS$_2$ were investigated by Lauhon, Hersam et al [71]. Continued progress in high-speed computing depends on breakthroughs in both material synthesis and device architectures. The performance of logic and memory can be enhanced significantly by introducing memristor, the two-terminal device with internal resistance that depends on the history of the external bias voltage. State-of-the-art memristors, based on metal-insulator-metal structures with insulating oxides, such as TiO$_2$, are limited by a lack of control over the filament formation and external control of the switching voltage. In the present work the authors demonstrated a class of memristors based on GBs in monolayer MoS$_2$ devices. Specifically, the resistance of GBs emerging from contacts can be easily and repeatedly modulated, with switching ratios up to $\sim 10^3$ and a dynamic negative differential resistance. Furthermore, the atomically thin nature of MoS$_2$ enables tuning of the set voltage by a third gate terminal in a field-effect geometry, which provides new functionality that is not observed in other known memristive devices.

In [72] Radenovic et al discussed the identification of single nucleotides in MoS$_2$ nanomembranes. The size of the sensing region in solid-state nanomembranes is determined by the size of the pores and the thickness of the pore membrane, so ultrathin membranes such as graphene and monolayer MoS$_2$ could potentially offer the necessary spatial resolution for DNA sequencing. However, the fast translocation speeds ($3000-50000 \text{nt ms}^{-1}$) of DNS molecules moving across such membranes limit their usability. The authors showed that a viscosity gradient system based on room temperature ionic liquids can be to control the dynamics of DNS translocation through MoS$_2$ nanomembranes. The approach can be used to statistically detect all four types of nucleotides, which are identified according to current signatures recorded during their transient residence in the narrow orifice of the atomically thin MoS$_2$ nanopore. The elaborated technique exploits the high viscosity of room-temperature ionic liquids and provides optimal single nucleotide translocation speeds for DNA sequencing, while maintaining a signal-to-noise ratio higher than 10.

In [73] Hofmann, Ulstrup et al reported the observation of ultrafast free carrier dynamics in monolayer MoS$_2$. The dynamics of excited electrons and holes in monolayer MoS$_2$ have so far been difficult to disentangle from the excitons that dominate the optical response of this material. In this work the authors used time-and-angle-resolved photoemission...
spectroscopy for a monolayer of MoS$_2$ on a metallic substrate to directly measure the excited free carriers. This allowed the authors to ascertain a direct quasiparticle bandgap of 1.95 eV and determine an ultrafast (50 fs) extraction of excited free carrier via the metal in contact with monolayer MoS$_2$. This process is of key importance for optoelectronic applications that rely on separated free carriers rather than excitons.

In [74] Gies et al discussed the PL of monolayer MoS$_2$ on the basic of experiments and a microscopic theory. The latter connects ab initio calculations of the single-particle states and Coulomb matrix elements with a many-body description of optical emission spectra. The authors studied the PL efficiency at the exciton transitions in terms of carrier populations in the band structure and provided a quantitative comparison to an (In)GaAs quantum well structure. Suppression and enhancement of PL under biaxial strain was quantified in terms of changes in the local extrema of the conduction and valence bands. The large exciton binding energy in MoS$_2$ enables two distinctly different excitation methods: above-bandgap excitation and quasi-resonance excitation of excitonic resonances below the bandgap. In the latter case a nonequilibrium distribution of carriers predominantly in the K-valley led to strong emission from the A-exciton transition and visible B-peak even if the bandgap in indirect. For above-bandgap excitation the emission intensity was strongly reduced.

In [75] Kostantatos et al reported on highly stable and high-performance monolayer and bilayer MoS$_2$ photodetectors encapsulated with atomic layer deposited hafnium oxide. The protected devices showed enhanced electronic properties by isolating them from the ambience as strong n-type doping, vanishing hyteresis and reduced device resistance. By controlling the gate voltage, the strong responsivity and temporal response can be tuned by several orders of magnitude. At strong negative gate voltage, the detector is operated at higher speed and simultaneously exhibits a low-bound record sensitivity. The results of this work lead the way for future application of ultrathin, flexible and high performance MoS$_2$ detectors, and prompt to further investigation in encapsulated TMDC optoelectronics.

Hot electron-based near-infrared photodetection using bilayer MoS$_2$ was demonstrated by Valentine et al [76]. Recently there have been much interest in the extraction of hot electrons generated from surface plasmon decay, as this process can be used to achieve additional band with for both photodetectors and photovoltaics. Hot electrons are typically injected into semiconductors over a Schottky barrier between metal and semiconductor, enabling generation of photocurrent with below bandgap photon illumination. As a two-dimensional semiconductor single- and few-layers MoS$_2$ has been demonstrated to exhibit internal photogain and therefore become an attractive hot electron acceptor. In the present work the authors investigated hot electron-based photodetection in a device consisting of bilayer MoS$_2$ integrated with a plasmonic antenna array. The authors demonstrated sub-bandgap photocurrent originating from the injection of hot electrons in to MoS$_2$ as well as photoamplification that yields a photogain of $10^3$. The large photogain results in a photoresponsivity of 5.2 A W$^{-1}$ at 1070 nm, which is far above similar silicon-based hot electron photodetectors. This technique is expected to have potential use in future ultra-compact near-infrared photodetection and optical memory devices.

3.3. Research on thin layers of WS$_2$, WSe$_2$ and TiS$_2$

THSs WS$_2$ and WSe$_2$ were recently investigated by many authors. In [77] Hwang, Jena et al reported the realization of FETs fabricated by using chemically synthesized multilayer crystal semiconductor WS$_2$. The Shottky-barrier FETs demonstrated ambipolar behavior and a high ($\sim10^5$) ON/OFF current ratio at room temperature with current saturation. The behavior is attributed to the presence of an energy bandgap in the ultrathin layered semiconductor crystal material. The FETs also showed clear photoresponse to visible light. The promising electronic and optical characteristics of the devices combined with the chemical semiconductor crystals such as WS$_2$ make them attractive for future electronic and optical devices.

Subsequently WS$_2$ FETs with enhanced ambipolar characteristics were investigated by Das et al [78]. One of the most relevant features that a semiconducting channel material can offer when used in a FET layout is its capability to enhance both electron transport in conduction band and hole transport in valence band. In the present work the authors demonstrated pronounced ambipolar device characteristics of multilayer WS$_2$ FET using different contact electrodes, and showed that nickel electrodes facilitate electron injection while palladium electrodes are more efficient for hole injection. As an interesting demonstration the authors showed that by using nickel as the source contact electrode and palladium as the drain contact electrode, ambipolar device characteristics with similar on-state performance for both electron and hole branches can be achieved in WS$_2$ FETs. Finally, the authors discussed a technique based on the asymmetry in the ambipolar device transport in valence band. In the present work the authors demonstrated pronounced ambipolar device characteristics to extract the Schottky key barrier height for such metal to WS$_2$ contacts.

Exciton dark states in monolayer WS$_2$ was probed by Louie, Zhang et al [79]. It was well-known than unlike semimetallic graphene, layered TMDCs have a sizeable bandgap. More interestingly, when thinned down to a monolayer, TMDCs transform from indirect-gap semiconductors, exhibiting a number of intriguing optical phenomena such as valley-selective circular dichroism, doping-dependent charged excitons and strong photocurrent responses. However, the fundamental mechanism underlying such a strong light–matter interaction is still under intensive investigation. First-principles calculations have predicted a quasiparticle bandgap much larger than the measured optical gap and an optical response dominated by excitonic effects. In particular, an approach based on Green functions with screened interactions of charge carriers and Bethe–Salpeter equation (GW-BSE) theoretically predicted a diversity of strongly bound excitons. In the present work the authors reported the
experimental evidence of a series of excitonic dark states in monolayer WS\(_2\) using two-photon excitation spectroscopy. In combination with GW-BSE theory the authors proved that the excitons are of Wannier type, meaning that each exciton wavefunction extends over multiple unit cells, but with extraordinary large binding energy (~0.7 eV), leading to a quasiparticle bandgap of 2.7 eV. These strongly bound exciton states were observed to be stable at room temperature. The authors revealed an exciton series that deviates substantially from hydrogen models, with a novel energy dependence on the orbital angular momentum. These excitonic energy levels were experimentally found to be robust against environment perturbations. The discovery of excitonic dark states and exceptionally large binding energy not only shed light on the importance of many-electron effects in this two-dimensional gapped system, but also held potential for the device application of TMDC monolayers and their heterostructure in computing, communication and biosensing.

Optoelectronic devices based on electrically tunable p–n diodes in monolayer WS\(_2\) were investigated by Jarillo-Herrero et al \([80]\). The p–n junction is functional element of many electronic and optoelectronic devices, including diodes, bipolar transistors, photodetectors, light-emitting diodes and solar cells. Ambipolar semiconductors such as carbon nanotubes, nanowires, organic molecules allow for p–n junctions to be configured and modified by electrostatic gating. This electrical control enables a single device to have multiple functionalities. In the present work the authors reported ambipolar monolayer WS\(_2\) devices in which two local gates were used to define a p–n junction within the WS\(_2\) sheet. With these electrically tunable p–n junctions the authors demonstrated both p–n and n–p diodes with ideality factors better than 2. Under optical excitation, the diodes demonstrated a photodetection responsivity of 210 mA W\(^{-1}\) and photovoltaic power generation with a peak external quantum efficiency of 0.2%, promising values for a nearly transparent monolayer material in a lateral device geometry. Finally, the authors demonstrated a light-emitting diode based on monolayer WSe\(_2\). These devices provided building blocks for ultrathin, flexible and nearly transparent optoelectronic and electronic applications based on ambipolar dichalcogenide materials.

Electrically tunable excitonic light-emitting diodes based on monolayer WSe\(_2\) p–n junctions were investigated by Xu et al \([81]\). Previously electroluminescence has already been observed from monolayer MoS\(_2\) devices. However, the electroluminescence efficiency was low and the linewidth was broad due both to the poor optical quality of MoS\(_2\) and to ineffective contacts. In the present work the authors investigate electroluminescence from lateral p–n junction in monolayer WSe\(_2\) induced electrostatically using a thin boron nitride support as a dielectric layer with multiple metal gates beneath. This structure allowed effective injection of electrons and holes, and, combined with the high electroluminescence with 1000 times smaller injection current and 10 times smaller linewidth than in MoS\(_2\). Furthermore, by increasing the injection bias the authors could tune the electroluminescence between regimes of impurity-bound, charged and neutral excitons. This system has the required ingredients for new types of optoelectronic devices, such as spin-and valley-polarized light-emitting diodes, on-chip lasers and two-dimensional electro-optic modulators.

Generation and electric control of spin-valley-coupled circular photogalvanic current in WS\(_2\) were performed by Hwang, Cui et al \([82]\). Previously the achievement of spin-coupled valley polarization in TMDCs remained elusive. In the present work the authors demonstrated a spin-coupled valley photocurrent within an electric-double-layer transistor based on WSe\(_2\), whose direction and magnitude depend on the degree of circular polarization of the incident radiation and can be further modulated with an external electric field. This room-temperature generation and electric control of a valley and spin photocurrent provided a new property of electrons in TMDC systems, and thereby enabled additional degrees of control for quantum-confined spintronic devices.

The electrical control of second-harmonic generation in WSe\(_2\) monolayer transistor was demonstrated by Xu et al \([83]\). In this work the authors studied a mechanism to electrically control second-order optical nonlinearities in monolayer WSe\(_2\) and showed that the intensity of second-harmonic generation at the A-exciton resonance is tunable by over an order of magnitude at low temperature and nearly a factor of 4 at room temperature through electrostatic doping in a FET. Such tenability arises from the strong exciton charging effects in monolayer semiconductors, which allow for exceptional control over the oscillator strengths at the exciton and trion resonances. The exciton-enhanced second-harmonic generation is counter-circularly polarized to the excitation laser due to the combination of the two-photon and one-photon valley selection rules, which have opposite helicity in the monolayer. The study of authors paved the way towards a new platform for chip-scale, electrically tunable nonlinear optical devices based on two-dimensional semiconductors.

In \([84]\) Srivastava, Imamoglu et al reported the observation of zero-dimensional anharmonic quantum emitters in monolayer WSe\(_2\) with an energy that is 20–100 meV lower than that of two-dimensional excitons. The authors referred them to as quantum dots. Photon antibunching in second-order photon correlations unequivocally demonstrated the zero-dimensional anharmonic nature of these quantum emitters. The strong anisotropic magnetic response of the spatially localized emission peak strongly indicated that radiative recombination stemmed from localized excitons that inherit their electronic properties from the host TMDC. The large ~1 meV zero-field splitting showed that the quantum dots have singlet ground states and an anisotropic confinement that is most probably induced by impurities or defects.

Single photon emitters in thin layers of WSe\(_2\) were revealed by Potemski et al \([85]\). In this work the authors performed comprehensive optical micro-spectroscopy studies of thin layer of WSe\(_2\), a representative semiconducting dichalcogenide with a bandgap in the visible spectral range. At the edges of WSe\(_2\) flakes (transferred onto Si/SiO\(_2\) substrates) the authors revealed centers that, at low temperatures, give rise to sharp emission lines (100 μeV line width). These narrow emission lines revealed the effect of photon
antibunching, the unambiguous attribute of single photon emitters. The optical response of these emitters is inherently linked to the two-dimensional properties of the WSe$_2$ monolayer, as they both give rise to luminescence in the same energy range, have nearly identical excitation spectra and very similar characteristic large Zeeman effects. With advances in the structural control of edge imperfections, thin films of WSe$_2$ may provide added functionalities that are relevant for the domain of quantum electronics. Magnetoluminescence and valley polarized states of the two-dimensional electron gas in WS$_2$ monolayers were investigated were investigate by Petrou, Hawrylak et al [86]. Materials often exhibit fundamentally new phenomena in reduced dimensions that potentially lead to novel applications. This is true for single-layer, two-dimensional semiconductor crystals of TMDCs. They exhibit direct bandgaps with energies in the visible region at two nonequivalent valleys in the Brillouin zone. This makes them suitable for optoelectronic applications that range from light-emitting diodes to light harvesting and light sensors, and also to valleytronics. In the present work the authors study of the magnetoluminescence of WS$_2$ single-layer crystals in which the strong spin–orbit interaction additionally locks the valley and spin degrees of freedom. The recombination of the negatively charged exciton in the presence of two-dimensional electron gas was found to be circularly polarized at zero magnetic field despite being excited with unpolarized light, which indicated that the existence of a valley polarized two-dimensional electron gas is caused by valley and spin blocking and strong electron–electron–electron interactions. Negative electronic compressibility and tunable spin splitting in WSe$_2$ were observed by King et al [87]. Tunable bandgaps, extraordinarily large excite–binding energies, strong light–matter coupling and a locking of the electron spin with layer and valley pseudospins have established TMDCs as a unique class of two-dimensional semiconductors with wide-ranging practical applications. Using angle-resolved photoemission, in the present work the authors demonstrated that doping electrons at the surface of WSe$_2$, the prototypical strong spin–orbit TMDC, akin to applying a gate voltage in a transistor-type device, induces a counter-intuitive lowering of the surface chemical potential concomitant with the formation of a multivalley two-dimensional electron gas. The measurements of authors provided a direct spectroscopic signature of negative electron compressibility, a result of electron–electron interactions. An accompanying tunable spin splitting of the valence bands further revealed a complex interplay between single-particle band-structure evolution and many-body interactions in electrostatically doped TMDCs. Understanding and exploiting this would open up new opportunities for advanced electronic and quantum-logic devices.

In [88] Gedik et al reported on an effect related to valleytronics—the valley-selective optical Stark effect in monolayer WS$_2$ two-dimensional crystal with broken inversion symmetry leading to valley-selective electron populations. Lifting the valley degeneracy in this material is of great interest because it would allow for valley-specific band engineering and offer additional control in valleytronic applications. In the present work the authors showed the first direct evidence of lifted valley degeneracy in monolayer WS$_2$. By applying intense circularly polarized light which breaks time-reversal symmetry, the authors demonstrated that the exciton level in each valley can be selectively tuned by as much as 18 meV through the optical Stark effect. These results offered a new way to control the valley degree of freedom, and might provide a means to realize new Floquet topological phases in two-dimensional TMDCs.

Flexible n-type thermoelectric materials were prepared by organic intercalation of layered TiS$_2$ in the experimental work of Wan, Koumoto et al [89]. Organic semiconductors are attracting increasing interest as flexible thermoelectric materials owing to material abundance, easy processing and low thermal conductivity. Although progress in p-type polymers and composites has been reported, their n-type counter-part has fallen behind owing to difficulties in n-type of organic semiconductors. In the present work the authors proposed the approach to synthesize n-type flexible thermoelectric materials through a facile electrochemical intercalation method, fabricating a hybrid superlattice of alternating inorganic TiS$_2$ monolayers and organic cations. Electrons were externally injected into the inorganic layer and then stabilize by organic cations, providing n-type carriers for current and energy transport. High power factor and low thermal conductivity contributed to a thermoelectric figure of merit (ZT) of 0.28 at 373 K, which might find application in wearable electronics.

Resonant internal quantum transitions and femtosecond radiative decay of excitons in monolayer WSe$_2$ were investigated by Huber et al [90]. In this work the authors reported the first direct experimental access to all 1s A-excitons, regardless of momentum—inside and outside the radiative cone—in monolayer WSe$_2$. Phase-locked mid-infrared pulses revealed the internal orbital 1s–2p resonance, which is highly sensitive to the shape of the excitonic wave functions and provides accurate transition energies, oscillator strengths, densities and linewidths. Remarkably, the observed decay dynamics indicated an ultrafast radiative annihilation of small-momentum excitons within 150 fs, whereas Auger recombination prevailed for optically dark states. Obtained results provided a comprehensive view of excitons and introduced a new degree of freedom for quantum control, optoelectronics and valleytronics of dichalcogenide monolayers.

Evolution of electronic structure in atomically thin layers of WS$_2$ and WSe$_2$ was investigated by Eda et al [91]. Geometrical confinement effect in exfoliated sheets of layered materials leads to significant evolution of energy dispersion in mono- to few-layer thickness regime. In the present work the authors measured differential reflectance and PL spectra of mono- and few-layer WS$_2$ and WSe$_2$ that indicated that the band structure of these materials underwent indirect-to-direct gap transitions when thinned to a single monolayer. The transition was evidenced by distinctly enhanced PL peak centered at 630 and 750 nm in monolayer WS$_2$ and WSe$_2$, respectively. Few-layer flakes were found to exhibit comparatively strong indirect gap emission along with direct gap
hot electron emission, suggesting high quality of synthetic crystals prepared by a chemical vapor transport method. Fine absorption and emission features and their thickness dependence suggested a strong effect of Se p-orbitals on the d-electron band structure as well as interlayer coupling in WSe₂.

In [92] Javey et al investigated high-performance p-type FETs based on single layered (thickness ~0.7 nm) WSe₂ as the active channel with chemically doped source/drain contacts and high-κ gate dielectrics. The top-gated monolayer transistors exhibited a high effective hole mobility of ~250 cm² V⁻¹ s⁻¹, perfect subthreshold swing of ~60 mV/dec, and $I_{ON}/I_{OFF} > 10^6$ at room temperature. Special attention was given to lowering the contact resistance for hole injection by using high work function Pd contacts along with degenerate surface doping of the contacts by patterned NO₂ chemisorption on WSe₂. Obtained results presented a promising material system and device architecture for p-type monolayer transistors with excellent characteristics.

In [93] Kumar, Gerardot et al showed that strain gradients, either unintentionally induced or generated by substrate patterning, result in spatially and spectrally isolated quantum emitters in mono- and bilayer WSe₂. By correlating localized excitons with localized strain variations, the authors showed that the quantum emitter emission energy can be red-tuned up to a remarkable ~170 meV. The authors probed the fine-structure, magneto-optics, and second-order coherence of strained emitter. These results raised the prospect of strain-engineering quantum emitter properties and deterministically creating arrays of quantum emitters in two-dimensional semiconductors.

4. Recent advances in the research on van der Waals heterostructures of THSs

For the fabrication of electronic, optoelectronic and photonic devices from THSs the formation of multilayer heterostructures owing to the van der Waals interaction between them plays a crucial role. The present section is a review of the research on this topic.

Haigh, Gorbashhev et al [13] indicated that by stacking various two-dimensional atomic crystals on top each other, it is possible to create multilayer heterostructures and devices with designed electronics properties. However, various adsorbates become trapped between layer during their assembly, and this is not only affects the formation of a true artificial layered crystal upheld by van der Waals interaction, creating instead a laminate glued together by contamination. TEM showed that graphene and boron nitride monolayers, the two best characterized two-dimensional crystals, are densely covered with hydrocarbons (even after thermal annealing in high vacuum) and exhibit only small clean patches suitable for atomic resolution imaging. This observation seems detrimental for any realistic prospect of creating van der Waals materials and heterostructures with atomically sharp interface. The authors employed cross-sectional TEM to take a side view of several graphene-boron nitride heterostructures. The authors found that the trapped hydrocarbons segregate into isolated pockets, leaving the interfaces atomically clean. Moreover, the authors observed a clear correlation between interface roughness and the electronic quality of encapsulate graphene.

A general discussion on van der Waals heterostructures was presented by Geim and Grigorieva [14], noting that isolated atomic planes can also be reassembled into designer heterostructures created layer by layer in a precisely chosen sequence. The authors reviewed this emerging research area and identified possible future directions with steady improvement in fabrication techniques and using graphene' springboard, van der Waals heterostructures should develop into a large field of their own.

Jarillo-Herrero, Ashoori et al [94] studied Dirac fermion and Hofstadter band structure engineering in a van der Waals heterostructure. The authors demonstrated band structure engineering in a van der Waals heterostructure composed of a monolayer graphene flake coupled to a rotationally aligned hexagonal boron nitride substrate. The spatially varying interlayer atomic registry results in both a local breaking of the carbon sublattice symmetry and a long-range moiré superlattice potential in the graphene. In the prepared samples this interplay between short- and long-wavelength effects resulted in a band structure described by isolated superlattice minibands and an unexpectedly large band gap at charge neutrality. This picture was confirmed by the observation of fractional quantum Hall states at $\pm 5/3$ filling and features associated with the Hofstadter butterfly at ultrahigh magnetic fields.

A comprehensive commentary on progress, challenges and opportunities in two-dimensional materials beyond graphene was presented by Goldberger et al [95]. The authors reviewed the state-of-the-art of two-dimensional materials beyond different classes of two-dimensional materials and discussed various strategies to prepare single-layer, few-layer and multilayer assembly materials in solution, on substrates and on the wafer scale. Additionally the authors presented an experimental guide for identifying and characterizing single-layer-thick materials as well as outlining emerging techniques that yield both local and global informations. The authors described the differences that occur in the electronic structure between the bulk and the single layer, and discussed various methods of tuning their electronic properties by manipulating the surface. Finally, the authors highlighted the properties and advantages of single-, few- and many-layer two-dimensional materials in FETs, spin- and valleytronics, thermoelectrics, and topological insulators, among many other applications.

Lateral heterojunctions within monolayer MoSe₂-WSe₂ semiconductors were investigated by Wu, Sanchez et al [96]. The authors demonstrated that high-quality in-plane heterojunctions can be grown between monolayer semiconductors MoSe₂ and WSe₂. The junctions grown by lateral hetero-epitaxy using physical vapor transport were visible in an optical microscope and showed enhanced PL. Atomically resolved TEM revealed that their structure is an undistorted honeycomb lattice in which substitution of one transition metal by another occurs across the interface. The growth of
such lateral junctions will allow new device functionalities, such as in-plane transistors and diodes, to be integrated within a single atomically layer.

Vertical and in-plane heterostructures from WS$_2$/MoS$_2$ monolayers were fabricated and investigated by Zhou, Ajayan et al [97]. Layer-by-layer stacking or lateral interfacing of atomic monolayers has opened up unprecedented opportunities to engineer two-dimensional heteromaterials. Fabrication of such artificial heterostructures with atomically clean and sharp interfaces, however, was challenging. In the present work the authors report a one-step strategy for the creation of high-quality vertically stacked as well as in-plane interconnected heterostructures of WS$_2$/MoS$_2$ via control of the growth temperature. Vertically stacked bilayers with WS$_2$ epitaxially grown on top of the MoS$_2$ monolayer were formed with preferred stacking order at high temperature. A strong interlayer excitonic transition was observed due to the type II band alignment and to the clean interface of these bilayers. Vapor growth at low temperature, on the other hand, led to lateral epitaxy of WS$_2$ on MoS$_2$ edges, creating seamless and atomically sharp in-plane heterostructures that generated strong localized PL enhancement and intrinsic p–n junctions. Thus the fabrication of heterostructures from monolayers, using simple and scalable growth, paved the way for for the creation of unprecedented two-dimensional materials with exciting properties.

Photoinduced doping in heterostructures of graphene and boron nitride was performed by Wang et al [98]. The design of the stacks of layered materials in which adjacent layers interact by van der Waals forces has enabled the combination of various two-dimensional crystals with different electrical, optical and mechanical properties as well as the emergence of novel physical phenomena and device functionality. In the present work the authors reported photoinduced doping in van der Waals heterostructures consisting of graphene and boron nitride layers. It enabled flexible and repeatable writing and erasing of charge doping in graphene with visible light. The authors demonstrated that this photoinduced doping maintains the high carrier mobility of the graphene/boron nitride heterostructure, thus resembling the modulation doping technique used in semiconductor heterojunctions, and can be used to generate spatially varying doping profiles such as p–n junctions. The authors showed that this photoinduced doping arises from microscopically coupled optical and electrical responses of graphene/boron nitride heterostructures, including optical excitation of defect transitions in boron nitride, electrical transport in graphene, and charge transfer between boron nitride and graphene.

Atomically thin p–n junctions with van der Waals heterointerfaces were investigated by Kim et al [99]. In conventional p–n junctions, regions depleted of free charge carriers are formed on either side of the function, generating built-in potentials associated with uncompensated dopant atoms. Carrier transport across the junction occurs by diffusion and drift processes influenced by the spatial extent of this depletion region. With the advent of atomically thin van der Waals materials and their heterostructures, it is now possible to realize p–n junctions at the ultimate thickness limit. Van der Waals junctions composed of p- and n-type semiconductors-each just one unit cell thick—are predicted to exhibit completely different transport characteristics than bulk heterojunctions. In the present work the authors reported the characterization of the electronic and optoelectronic properties of atomically thin p–n heterojunctions fabricated using van der Waals assembly of TMDCs. The authors observed gate-tunable diode-like current rectification and a photovoltaic response across the p–n interface, and found that the tunneling-assisted interlayer recombination of the majority carriers was responsible for the tenability of the electronic and optoelectronic processes. Sandwiching an atomic p–n junction between graphene layers enhanced the collection of the photoexcited carriers. The atomically scaled van der Waals p–n heterostructures presented in this work constituted the ultimate functional unit for nanoscale electronic and optoelectronic devices.

Ultrafast charge transfer in atomically thin MoS$_2$/WS$_2$ heterostructures was studied by Wang et al [12]. Van der Waals heterostructures have recently emerged as a new class of materials, where quantum coupling between stacked atomically thin two-dimensional layers, including graphene, hexagonal-boron nitride and TMDCs give rise to fascinating new phenomena. TMDC heterostructures are particularly exciting for novel optoelectronic and photovoltaic applications, because two-dimensional TMDC monolayers can have an optical bandgap in the near-infrared to visible spectral range and exhibit extremely strong light–matter interactions. Theory predicted that many stacked TMDC heterostructures form type I semiconductor heterojunctions that facilitate eficient electron–hole separation for light detecting and harvesting. In the present work the ultrafast charge transfer in photoexcited MoS$_2$/WS$_2$ heterostructures was experimentally observed by using both PL mapping and femto-second pump-probe spectroscopy. The authors showed that hole transfer from MoS$_2$ layer to WS$_2$ layer took place within 50 fs after optical excitation, a remarkable rate for van der Waals coupled two-dimensional layers. Such ultrafast charge transfer in van der Waals heterostructures can enable novel two-dimensional devices for optoelectronics and light harvesting.

Twist-controlled resonant tunneling in graphene/boron nitride/graphene heterostructures was investigated by Novoselov et al [100]. Recent development in the technology of van der Waals heterostructures fabricated from two-dimensional atomic crystals have already led to the observation of new physical phenomena, such as the metal-insulator transition and Coulomb drag, and to the realization of functional devices such as tunnel diodes, tunnel transistors and photovoltaic sensors. An unprecedented degree of control of the electronic properties was available not only by means of the selection of materials in the stack, but also through the additional fine-tuning achievable by adjusting the built in strain and relative orientation of the component layers. In the present work the authors demonstrated how careful alignment of the crystallographic orientation of two graphene electrodes separated by a layer of hexagonal boron nitride in a transistor device can achieve resonant tunneling with the conservation of electron energy, momentum and, potentially, chirality. The
authors showed how the resonance peak and negative differential conductance in the device characteristics induce a tunable radiofrequency oscillator current that has potential for future high-frequency technology.

In [101] Lee, Hone et al preformed multi-terminal transport measurements of MoS2 using a van der Waals heterostructure device platform. Atomically thin two-dimensional semiconductors such as MoS2 hold great promise for electrical, optical and mechanical devices and display novel physical phenomena. However, the electron mobility of mono- and few-layer MoS2 has so far been substantially below theoretically predicted limits, which has hampered efforts to observe its intrinsic quantum transport behaviors. Potential sources of disorder and scattering include defects such as sulfur vacancies in the MoS2 itself as well as extrinsic sources such as charged impurities and remote optical phonons from oxide dielectrics. To reduce extrinsic scattering, the authors have developed a van der Waals heterostructure device platform where MoS2 layers were fully encapsulated within hexagonal boron nitride nitride and electrically contacted in a multi-terminal geometry using gate-tunable graphene electrodes. Magneto-transport measurement showed dramatic improvement in performance, including a record-high Hall mobility reaching 34 000 cm2 V−1 s−1 for six-layer MoS2 at low temperature. The authors also observed Shubnikov–de Haas oscillations in high-mobility monolayer and few-layer MoS2. Modeling of potential scattering sources and quantum lifetime analysis indicated that a combination of short-range and long-range interfacial scattering limited the low-temperature mobility of MoS2.

A phosphorene-graphene hybrid material was used by Cui et al [102] as a high-capacity anode for sodium-ion batteries. Sodium-ion batteries have recently attracted significant attention as an alternative to lithium-ion batteries because sodium sources do not present the geopolitical issue that lithium sources might. Although recent reports on cathode materials for sodium-ion batteries have demonstrated performance comparable to their lithium-ion counterparts, the major scientific challenge for a competitive sodium-ion battery technology was to develop viable anode materials. In the present work the author showed that a hybrid material composed of a few phosphorene layers sandwiched between graphene layers possessed a specific capacity of 2.440 mA h g−1 at a current density of 0.05 A g−1 and an 83% capacity retention after 100 cycles while operating between 0 and 1.5 V. Using in situ TEM and ex situ x-ray diffraction technique, the authors explained the large capacity of fabricated anode through a dual mechanism of intercalation of sodium ions along the x-axis of the phosphorene layers followed by the formation of a Na3P alloy. The presence of graphene layers in the hybrid material as a mechanical backbone and an electrical highway ensured that a suitable elastic buffer space accommodated the anisotropic expansion of phosphorene layers along the y and z directions for stable cycling operation.

Another graphene-hexagonal boron nitride heterostructure to be used as a tunable hyperbolic metamaterial was studied by Basov et al [103]. Hexagonal boron nitride (h-BN) is a natural hyperbolic material in which the dielectric constants are the same in the bassal plane (ε' = ε'' = ε0) but have opposite signs (ε'ε'' < 0) in the normal plane. Owing to this property, finite-thickness slabs of h-BN act as multimode waveguide for the propagation of hyperbolic phonon polariton modes that originate from the coupling between photons and electric dipoles in phonons. However, control of these hyperbolic phonon polariton modes has remained challenging, mostly because their electrodynamic properties are dictated by the crystal lattice of h-BN. Using direct nano-infrared imaging, the authors showed that these hyperbolic polaritons can be effectively modulated in a van der Waals heterostructure composed of monolayer graphene on h-BN. Tunability originated from the hybridization of surface plasmon polaritons in graphene with hyperbolic phonon polaritons in h-BN, so that the eigenmodes of the graphene/h-BN heterostructure are hyperbolic plasmon–phonon polaritons. The hyperbolic plasmon–phonon polaritons in graphene/h-BN suffer little from Ohmic losses, making their propagation length 1.5–2.0 times greater than that of hyperbolic phonon polaritons in h-BN. Therefore, graphene/h-BN can be classified as an electromagnetic metamaterial as the resulting properties of these devices are not present in its constituent elements alone.

The band offset and the negative compressibility in graphene–MoS2 heterostructures were observed by Tutuc et al [104]. The authors used electron transport to characterize monolayer graphene-multilayer MoS2 heterostructure. Prepared samples showed ambipolar characteristics and conductivity saturation on the electron branch that signaled the onset of MoS2 conduction band population. Surprisingly, the carrier density in graphene decreased with gate bias once MoS2 was populated, demonstrating negative compressibility in MoS2. The authors quantitatively interpreted the results of measurements by accounting for disorder and using the random phase approximation for the exchange and correlation energies of both Dirac and parabolic-band two-dimensional electron gases. This interpretation allowed the authors to extract the energetic offset between the conduction band edge of MoS2 and the Dirac point of graphene.

In [105] Das, Sumant et al reported on 10 atomic layer thick, high mobility, transparent thin film transistors (TFTs) with ambipolar device characteristics fabricated on both a conventional silicon platform as well as on a flexible substrate. Monolayer graphene was used as metal electrodes, 3–4 atomic layers of h-BN were used as the gate dielectric, and finally bilayers of WSe2 were used as the semiconducting channel material for the TFTs. The field-effect carrier mobility was extracted to be 45 cm2 V−1 s−1, which exceeded the mobility values of start-of-the art amorphous silicon based TFTs by ~100 times. The active device stack of WSe2-h-BN-graphene was found to be more than 88% transparent over the entire visible spectrum, and the device characteristics were unaltered for in-plane mechanical strain of up to 2%. The device demonstrated remarkable temperature stability over 77–400 K. Low contact resistance value of 1.4 kΩ μm, sub-threshold slope of 90 mV/decade current ON/OFF ratio of 107, and the presence of both electron and hole conduction.
were observed in all prepared two-dimensional TFTs. These characteristics are extremely desirable, but they were rarely reported in previous works on organic as well as inorganic TFTs. For large-scale two-dimensional electronics was developed by Wang, Palacios et al [106]. The authors demonstrated a novel technology for constructing large-scale electronics systems based on graphene/MoS2 heterostructures grown by chemical vapor deposition, and fabricated high-performance devices and circuits based on these heterostructures, where MoS2 was used as the transistor channels and graphene as contact electrode and circuit interconnects. The authors provided a systematic comparison of graphene/MoS2 heterojunction contact to more traditional MoS2-metal junctions, as well as a theoretical investigation, using density functional theory. The tenability of the graphene work function with electrostatic doping significantly improved the Ohmic contact to MoS2. These high-performance large-scale devices and circuits paved the way for practical flexible transparent electronics.

Hybrid surface-phonon-plasmon polariton modes in graphene/monolayer h-BN heterostructures were investigated by Atwater et al [107]. Infrared transmission measurements revealed the hybridization of graphene plasmonics and the phonons in a monolayer hexagonal boron nitride (h-BN) sheet. Frequency-wave vector dispersion relations of the electromagnetically coupled graphene plasmon/h-BN phonon modes were derived from measurements of nanoresonators with the widths varying from 30 to 300 nm. It was shown that the graphene plasmon mode was split into two optical modes that displayed an anticrossing behavior near the energy of the h-BN optical phonon at 1370 cm $^{-1}$. The authors explained this behavior as a classical electromagnetic strong-coupling with the highly confined near fields of the graphene plasmons allowing for hybridization with the phonons of the atomically thin h-BN layer to create two clearly separated new surface-phonon-plasmon-polariton modes.

The electronic states at the graphene-hexagonal boron nitride zigzag (ZZ) interface were investigated by Liljeroth et al [108]. The authors proposed the ZZ-terminated, atomically sharp interfaces between graphene and hexagonal boron nitride (h-BN) as experimentally realizable, chemically stable model systems for graphene ZZ edges. Combining scanning tunneling microscopy and numerical methods, the authors explored the structure of graphene/h-BN interfaces and showed them to host localized electron states similar to those on the pristine graphene ZZ edge.

In [109] Loh et al studied lattice relaxation at the interface of graphene and hexagonal boron nitride. Heteroepitaxy of two-dimensional crystals such as h-BN on graphene can occur at the edge of an existing heterointerface. Understanding strain relaxation at such two-dimensional laterally fused interface is useful in fabricating heterointerfaces with a high degree of atomic coherency and structural stability. The authors used in situ scanning tunneling microscopy to study the heteroepitaxy of h-BN on graphene edges on a Ru surface with the aim of understanding the propagation of interfacial strain. The authors found that defect-free, pseudomorphic growth of h-BN on a graphene edge ‘substrate’ occurred only for a short distance (<1.29 nm) perpendicular to the interface, beyond which misfit dislocations occurred to reduce the elastic strain energy. Boundary states originating from a coherent zigzag-linked graphene/h-BN boundary were observed to greatly enhance the local conductivity, thus affording a new avenue to construct one-dimensional transport channel in graphene/h-BN hybrid interface.

In [110] Beschoten et al determined spin lifetimes in single- and few-layer graphene/h-BN heterostructures at room temperature. The authors demonstrated a new fabrication method of graphene spin-valve devices that yielded enhanced spin and charge transport properties by improving both the electrode-to-graphene and graphene-to-substrate interface. First the authors prepared CO/MgO spin injection electrodes onto Si$^{++}$/SiO2. Thereafter the authors mechanically transferred a graphene/h-BN heterostructure onto the prepatterned electrodes, and showed that room temperature spin transport in single-, bi- and tri-layer graphene devices exhibited nanosecond spin lifetimes with spin diffusion lengths reaching 10 μm combined with carrier mobilities exceeding 20 000 cm$^2$V$^{-1}$s$^{-1}$.

The coupling of orbital magnetic moments to the valley degree of freedom in graphene van der Waals heterostructures was investigated by Grujić et al [111]. In honeycomb Dirac systems with broken inversion symmetry, orbital magnetic moments couple to the valley degree of freedom due to the topology of the band structure, leading to valley-selective optical dichroism On the other hand, in Dirac systems with prominent spin–orbit coupling, similar orbital magnetic moments emerge as well. These moments are coupled to spin, but otherwise have the same functional form as the moments stemming from spatial inversion breaking. After reviewing the basic properties of these moments, which are relevant for a whole set of newly discovered materials, such as silicene and germanene, the authors studied the particular impact that these moments have on graphene nanoengineered barriers with artificially enhanced spin–orbit coupling. The authors examined transmission properties of such barriers in the presence of a magnetic field. The orbital moments were found to manifest in transport characteristics through spin-dependent transmission and conductance, making them directly accessible in experiments. Moreover, the Zeeman-type effects appeared without explicitly incorporating the Zeeman term in the model, i.e., by using minimal coupling and Peierls substitution in continuum and the tight-binding methods, respectively.

Interlayer hybridization and Dirac relativistic carriers in graphene/MoS2 van der Waals heterostructures were directly observed by Batzill et al [112]. Artificial heterostructures assembled from van der Waals materials promise to combine materials without traditional restriction in heterostructure growth such as lattice matching conditions and atom interdiffusion. Simple stacking of van der Waals with diverse properties would thus enable the fabrication of novel materials or device structures with atomically precise interfaces. Because covalent bonding in these layered materials is limited to molecular planes and the interactions between planes are very weak, only small changes in the electronic structure are
expected by stacking these materials on top of each other. In the present work the authors prepared interfaces between CVD-grown graphene and MoS₂, and reported the direct measurement of electronic structure of such a van der Waals heterostructure by angle-resolved photoemission spectroscopy. While the Dirac cone of graphene remained intact and no significant charge transfer doping was detected, the authors observed formation of bandgaps in the π-band of graphene away from the Fermi level due to hybridization with states from MoS₂ substrate.

Tunable light–matter interaction and the role of hyperbolicity in graphene/h-BN heterostructure was investigated by Fang et al [113]. In this work the authors examined theoretically the mind-infrared optical properties of graphene/h-BN heterostructures derived from their coupled plasmon–phonon modes. The authors found that the graphene plasmon couples differently with the phonons of two reststrahlen bands, owing to their different hyperbolicity. This also leads to distinctively different interactions between an external quantum emitter and the plasmon–phonon modes in the two bands, leading to substantial modification of its spectrum. The coupling to graphene plasmon allows for additional gate tenability in the Purcell factor and narrow dips in its emission spectra.

In [114] Kim et al carried out electrical and optical characterization of graphene/MoS₂ heterostructures. The few-layer MoS₂ devices with metal electrode at one end and monolayer graphene electrode at the other end showed non-linearity in drain current with drain voltage sweep due to asymmetrical Schottky barrier height at the contacts and were modulated with an external gate field. The doping effect of MoS₂ on graphene was observed ad double Dirac points in the transfer characteristics of the graphene FET with a few-layer MoS₂ overlapping the middle part of the channel, whereas the underlapping of graphene had negligible effect on MoS₂ FET characteristics, which showed typical n-type behavior. The heterostructure also exhibited a strongest optical response for 520 nm wavelength which decreased with higher wavelengths. Another distinct feature observed in the heterostructure was the peak in the photocurrent around zero gate voltage. Thin peak was distinguished from conventional MoS₂ FET, which showed a continuous increase in photocurrent with black gate voltage. These results offered significant insight and further enhance in the understanding of the graphene/MoS₂ heterostructure.

Quantum transport detected by strong proximity interaction at a graphene/WS₂ van der Waals interface was studied by O’Farrell, Özyilmaz et al [115]. Magneto transport measurements demonstrated that graphene in a van der Waals heterostructure is a sensitive probe of quantum transport in an adjacent WS₂ layer via strong Coulomb interactions. The authors observed a large low-field magnetoresistance and a ~lnT temperature dependence of the resistance. In plane magnetic field resistance indicated that the origin is orbital and non classical. The authors demonstrated a strong electron–hole asymmetry in the mobility and coherence length of graphene demonstrating the presence of localized Coulomb interactions with ionized donors in the WS₂ substrate, which ultimately led to screening as the Fermi level of graphene was tuned toward the conduction band of WS₂. The authors concluded that graphene coupled to quantum localization processes in WS₂ via the Coulomb interaction. These results showed that theoretical descriptions of the van der Waals interface should not ignore localized strong localizations.

5. Conclusion and discussion

In this review we have presented fascinating achievements of basic research and applications of most important THSs beyond graphene such as phosphorene, silicene and TMDCs MoS₂, MoSe₂, WS₂, WSe₂. We have seen that the basic research on these new materials led to the discovery of a new degree of freedom in the band structure of these materials—the valley degree of freedom, leading to the emergence of a new high technology—the valleytronics. On the basis of van de Waals heterostructures composed of various pairs of THSs many electronic optoelectronic, photonic, plasmonic and valleytronic devices were fabricated.

Thus the contents of the basic as well as applied researches on THSs are indeed very rich and extremely promising. On the basis of above presented scientific results we can now apply the famous statement of Richard Feynmann at Caltech more than a half of century ago and say that ‘there is still plenty of room in two dimensions’.

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