## **REVIEWS OF TOPICAL PROBLEMS**

PACS number: 73.22.-f

## Quasi-two-dimensional transition metal dichalcogenides: structure, synthesis, properties, and applications

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DOI: https://doi.org/10.3367/UFNe.2017.02.038065

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<u>Abstract.</u> Electron states in quasi-two-dimensional (2D) metal and semiconductor crystals can have unusual characteristics and can therefore exhibit unusual electronic and optical properties. In this paper, the results recently obtained for a new class of 2D compounds — transition metal dichalcogenides — are presented, including those on the structure, preparation methods, the electronic, mechanical, and optical properties, defects and their influence on material properties, and conditions facilitating the formation of defects. We consider the unique properties of mono- and multilayer materials, examine their dependence on external factors, and discuss their further application prospects. Various applications of 2D transition metal dichalcogenides are described, ranging from nanolubricants, nanocomposites, biosensors, memory cells and supercapacitors to optoelectronic, spin, and photovoltaic devices.

**Keywords:** two-dimensional structures, transition metal dichalcogenides, electronic and optical properties, spin polarization, valleytronics, heterostructures, defects

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Received 19 December 2016, revised 5 February 2017 Uspekhi Fizicheskikh Nauk **188** (1) 3–30 (2018) DOI: https://doi.org/10.3367/UFNr.2017.02.038065 Translated by S N Gorin; edited by A M Semikhatov

## 1. Introduction

Soon after the discovery of fullerenes in 1985, inorganic layered structures of transition-metal dichalcogenides (TMDs), which also had a fullerene-like structure, were obtained [1]. After the creation and study of materials based on carbon nanotubes [2-4], their inorganic analogs MoS2 and WS<sub>2</sub> were revealed and investigated [5, 6]. Recently, beginning with the pioneering work on graphene [7], researchers have been paying intensive attention to quasi-two-dimensional (2D) materials. Among them, the dichalcogenides of transition metals are attracting great attention because they are some of the most promising semiconducting materials for nanoelectronics, optics, and spintronics due to their unconventional electronic and optical properties [8]. The most studied material, MoS<sub>2</sub>, demonstrates good electronic and transport properties, having an indirect band gap with a width of 1.2 eV in the multilayer version, whereas singlelayered  $MoS_2$  has a direct band gap equal to 1.8 eV, high mobility of charge carriers (about 500 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), and a high (up to  $10^8$ ) ON/OFF ratio in the transistor element [8, 9].

The first study devoted to methods for obtaining diverse 2D materials was published in 2005 [10]; in it, the authors demonstrated the principle of exfoliation of 2D monolayers from a three-dimensional material of not only graphene but also other monolayers (h-BN, complex oxides, TMDs).

The dichalcogenides  $MoS_2$  and  $WS_2$  are encountered in small amounts in Earth's crust, and in 2016 a new mineral was discovered, which resembles a roll twisted from a sheet of sulfides of molybdenum, lead, vanadium, and antimony [11]. Many other three-dimensional (3D) dichalcogenides of transition metals were already obtained in the 1960s [12] and, because of their interesting electronic properties, already then attracted the attention of researchers [13]. The synthesis of 2D materials started in the first decade of the 21st century; to date, more than 40 compounds of the family of dichalcogenides have been obtained. The dichalcogenides with tellurium, thallium, and niobium have been studied insufficiently because of their high costs.

Because graphene does not have an energy gap, its application in electronics and optics is limited. At present, semiconducting  $MX_2$  compounds of transition metals (M) from Group VI (for example, W, Mo) with sulfur (S) and selenium (Se) are assumed to be the most promising, but the most investigated is MoS<sub>2</sub> [14, 18]. These materials are relatively inexpensive. They also manifest specific optical properties: optical transitions between valleys with a change in the electron spin are possible in them [19]. Therefore, the search for 2D materials of new compositions, which can become a basis for the next generation of nanodevices in different fields besides electronics [12, 20–22], has now become promising. Some TMDs ( $MX_2$ , M = Nb, Ti, Ta, Mo; X = Se, S) have superconducting properties.

In the last six years, special attention has been given to  $MoS_2$ -based heterostructures. A variety of methods for preparing them have been developed [23]. Another promising material is  $MoSe_2$ , which has a smaller energy gap, but a larger mobility of charge carriers, and also a larger stability than those of  $MoS_2$ , which makes it a more attractive material for the mass production of nanodevices. There are also other versions of the application of TMDs; for example,  $MoS_2$ , since its discovery in 1960 up to now, has been used as a dry lubricant and as a thermoelectric material. It enters the composition of many industrial lubricants (Beslux Molyfilm, MIPO LM 14, MIPO M 15, etc.) with operating temperatures from -185 to 500 °C. This makes it possible to think about the use of such 2D structures for similar purposes, but in nanosize systems.

In the electron spectrum of 2D TMDs, because of a large separation of valleys in the momentum k space, the index of the valley can be considered an additional degree of freedom of charge carriers. Special features such as an additional degree of freedom allow the appearance of an interrelation of the valleys and the phenomenon of circular dichroism, which are actively being investigated currently with the purpose of developing new applications of valleytronics, an analog of spintronics [12]. It was recently shown that the optical alignment of excitons (exciton–valley coherence) can be achieved via the single-photon or two-photon excitation of layers of TMDs [13].

As another subject, it is worth mentioning the class of materials such as monochalcogenides of transition metals, which differ from TMDs only in the stoichiometric ratio of the metal and chalcogen. Their 3D crystals have long been known, and 2D samples were obtained somewhat later than those of 2D TMDs [24–26]. The monochalcogenides of transition metals have ferroelectric properties and ferroelasticity, which makes it possible to speak about their application in memory devices and ultra-high-speed nanotransistors. These materials also have interesting properties that are attracting the attention of researchers and engineers for their potential applications in nanoelectronics and nanooptics.

This review includes six sections: the first is the Introduction. Section 2 is devoted to a description of the structure of single-layer and multilayer TMDs. In Section 3, various methods for preparing 2D TMDs are described, including obtaining TMD-containing composites. Section 4 is devoted to defects in TMD structures and to their doping. Section 5 contains a description of the properties of related materials and their changes under the action of ambient conditions. Section 6 contains information on possible applications of these materials, including the latest information on newly developed devices [27].

## 2. Structure of transition-metal dichalcogenides

The dichalcogenides of transition metals are materials that have the chemical formula  $MX_2$ , where M is a transition metal (molybdenum, tungsten, niobium, vanadium, etc.), and X is a chalcogen (sulfur, oxygen, tellurium, etc.). The atomic bond of the metal and chalcogen is predominantly covalent. The M and X atoms form a two-dimensional hexagonal lattice. Bulk TMD crystals have been known already for more than 40 years [28]. They consist of sandwiches of two layers of chalcogen atoms covalently bound with an interlayer of metallic atoms located between them. Such  $MX_2$  sandwiches are connected by van der Waals forces. Such a structure determines the strong anisotropy of the properties of the materials along and across the layers. Because the interaction between the  $MX_2$  layers is weak, it is not surprising that the properties of such crystals are mainly determined by the properties of the lattice of the quasi-twodimensional sandwich.

At present, two basic phases of  $MX_2$  are known: a thermodynamically stable 2H phase and a metastable 1T phase (space group P3m1) [29], where H and T denote hexagonal and trigonal symmetries. The 2H and 1T phases of  $MoS_2$  have radically different electronic properties because of the different symmetry of their crystal lattices [27–30]. The crystal 2H-MoS<sub>2</sub> is a semiconductor [31], while the 1T-MoS<sub>2</sub> phase is metallic [32]. The transition from one phase to the other is accomplished via shifts of layers (Fig. 1). It is important to note that the 1T-MoS<sub>2</sub> phase does not exist in nature and can be obtained, for example, via the intercalation of multilayer 2H-MoS<sub>2</sub> by atoms of alkaline elements, such as lithium [33], or by components based on lithium (butyl lithium [34] or lithium borohydride [32, 35]). The transformation from the 2H to 1T phase can occur in an MoS<sub>2</sub> monolayer also under the action of an electron beam [31]. Furthermore, in [36], an intermediate 2H - 2H'/1T phase and a T' phase with a structure resembling the anisotropic layers of  $ReS(Se)_2$  and black phosphorus were observed in the polycrystalline films of MoS<sub>2</sub> and MoS<sub>2</sub> [37].



**Figure 1.** (Color online.) (a) 2H and (b) 1T configurations of TMDs [48]. (c, d) Structure of  $\text{ReS}_2$  (schematic) [44]. Notation: gray color stands for a transition metal (Mo or W) (1); red, for a chalcogen (Se or S) (2); yellow, for sulfur (3), dark blue, for rhenium (4).

In the majority of TMDs, the unit cell consists of two atoms of a transition metal and four atoms of a chalcogen. Each metal atom is connected to six chalcogen atoms (see Fig. 1) (space group P63/mmc) [38]. In the ideal MoS<sub>2</sub>, each molybdenum atom is connected to six sulfur atoms. But there are materials in which a displacement of the metal atom from the center of the cell is observed. For example, in WTe<sub>2</sub>, the six nearest metal–metal bonds are divided into two short (2.85 Å), two intermediate (3.477 Å), and two long (4.37 Å) nearest-neighbor bonds [39]. In a layer of WTe<sub>2</sub>, the unit cell contains two nonequivalent W atoms and four equivalent Te atoms.

The adsorption of lithium [40, 41] or rhenium on the surface of  $MoS_2$  or  $WS_2$  can lead to a phase transition of the semiconducting 2H phase to the metallic 1T phase. A similar phenomenon can be observed upon heating the structure to 400-700 °C or under the effect of an electron beam using a high dose of irradiation [32].

In the bulk material, in bilayer and multilayer structures, indirect transitions are observed that result from tunneling of electrons between the molecularly bonded layers. For example, the indirect band gap in bulk  $Mo(W)S_2$  materials is approximately 1.2 eV, and the direct gap in their monolayers is about 1.8 eV. Recently, the previously predicted band structure of a WSe<sub>2</sub> bilayer was confirmed directly [42] by the methods of angle-resolved photoelectron spectroscopy (ARPES) (Fig. 2).

Some TMDs, for example,  $\text{ReS}_2$  and  $\text{ReSe}_2$ , have a triclinic symmetry [43, 44] similar to that of black phosphorus [45], anisotropic in the plane. We also mention the structure of  $\text{ReS}_2$ , in the unit cell of which a Peierls distortion is observed, which leads to a triple increase in the calculated cell. This distortion is manifested in the bend of a layer of sulfur and in the displacement of the rhenium atom in such a way that all sulfur and rhenium atoms become nonequivalent in the calculated cell [46].

The structural parameters and energies of the formation of many single-layer TMDs have been calculated with the aid of the electron density functional theory (DFT) [47] (Table 1).

The relative energy of formation, which is important for estimating the structural stability of materials, was calculated by the formula

$$E_{\rm f} = \frac{E_{\rm 2D}}{N_{\rm 2D}} - \frac{E_{\rm 3D}}{N_{\rm 3D}} \,, \tag{1}$$

where  $E_{2D}$  and  $E_{3D}$  are the respective total energies of the single-layer and multilayer  $MX_2$  materials, and  $N_{2D}$  and  $N_{3D}$  are the numbers of atoms in the calculated cells for the 2D and 3D structures.

According to the estimations given in [47], all the materials examined proved to be stable. Even more compounds were investigated in [48]. All the compounds examined, the 52 2D TMDs, are also stable.

Besides the TMD structures, compounds exist with the structural formula MX: these are monochalcogenides of transition metals, a constantly increasing group of 2D materials. The crystal structures of SnS, SnSe, GeS, and GeSe refer to the orthorhombic subgroup of the space group  $D_{2h}^{16}$ . The crystals of these compounds have been known since the 1970s [49], and already then they drew the attention of researchers due to their unconventional properties; the unique semiconductor-metal and metal-semiconductor phase transitions in SmS and solid solutions based on it began to find practical use, including in devices for recording and storing information [50, 51]. However, experimenters only recently were able to grow and to separate isolated bilayers and monolayers [24–26] of these compounds.

The following monochalcogenides were examined with the aid of the DFT: SnS, SnSe, GeS, GeSe, and their stable conformations have been found. The experiments showed that these compounds are resistant to oxidation [52].

Tin selenide SnSe is a new 2D material with the indirect energy gap equal to 1.45 eV, a mobility of 10,000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, Young's modulus 20-40 GPa, and a very low thermal conductivity (< 3 W m<sup>-1</sup> K<sup>-1</sup> at 300 K). The lattice parameters are a = 4.41 Å and b = 4.27 Å; each atom of Sn (Se) is connected to three atoms of Se (Sn); the bond lengths are equal to 2.73, 2.90, and 2.90 Å. The formation energy, 32 meV Å<sup>-2</sup>, is more than that in graphene (17.8 meV Å<sup>-2</sup>). The geometric, mechanical, and electronic properties of tin selenide are currently being actively studied. It has been shown that they are very sensitive to mechanical loads. The low stress (1.6 GPa) along the x axis causes a geometrical phase transition. The axial deformations (< 0.5 GPa) are the reason for the asynchronous shift of the extrema of the energies of the valleys, which leads to a change in the direct band gap into an indirect one. Such properties give grounds to assume that SnSe should become an outstanding material for nanomechanics, thermoelectric devices, and optoelectronics [53].



Figure 2. Angle-resolved photoelectron spectroscopy (ARPES) of a WSe<sub>2</sub> bilayer [42]: (a) experiment setup; the numbers *I* and *2* correspond to the numbers of the layers; (b) ARPES spectra recorded with various time differences  $\Delta t$  (-400 and + 20 fs) between the probing pulse and the pumping pulse.

TMD	Lattice para- meter <i>a</i> <sub>0</sub> , Å	Length of the metal–chalco- gen bond, Å	Length of the chalcogen– chalcogen bond $b_{X-X}$ , Å	Angle of the chalcogen- metal- chalcogen bond $\Theta_{X-M-X}$ , deg	Formation energy $E_{\rm f}$ , eV	Energy-band gap $E_g$ , eV ( $M$ — metal)	Bottom of the conduc- tion band, eV	Top of the valence band, eV
				Phase 2H				
MoS <sub>2</sub>	3.18	2.41	3.13	80.8	0.077	1.68	-3.92	-6.28
MoSe <sub>2</sub>	3.32	2.54	3.34	82.18	0.08	1.45	-3.58	-5.62
MoTe <sub>2</sub>	3.55	2.73	3.61	82.77	0.083	1.08	-3.58	-5.12
WS <sub>2</sub>	3.18	2.42	3.14	81.05	0.077	1.82	-3.47	-6.11
WSe <sub>2</sub>	3.32	2.55	3.36	82.46	0.08	1.55	-3.20	-5.46
WTe <sub>2</sub>	3.55	2.74	3.63	83.02	0.12	1.07	-3.35	-4.97
NbS <sub>2</sub>	3.36	2.49	3.14	77.97	0.093	М		
NbSe <sub>2</sub>	3.48	2.62	3.37	79.9	0.097	М		
NbTe <sub>2</sub>	3.69	2.82	3.7	81.85	0.1	М		
TaS <sub>2</sub>	3.34	2.48	3.13	78.11	0.087			
TaSe <sub>2</sub>	3.47	2.61	3.35	79.87	0.09			
TaTe <sub>2</sub>	3.7	2.81	3.66	81.19	0.14			
				Phase 1T				
TiS <sub>2</sub>	3.4	2.43	3.46	89.08	0.09	М		
TiSe <sub>2</sub>	3.52	2.56	3.71	87	0.097	М		
TiTe <sub>2</sub>	3.74	2.78	4.1	84.71	0.11	М		
VS <sub>2</sub>	3.17	2.35	3.46	85.04	0.09	М		
VSe <sub>2</sub>	3.32	2.48	3.7	83.81	0.09	М		
VTe <sub>2</sub>	3.55	2.69	4.05	82.54	0.097	М		
ZrS <sub>2</sub>	3.68	2.57	3.6	91.36	0.09	1.19	-4.58	-7.14
ZrSe <sub>2</sub>	3.8	2.71	3.85	89.16	0.097	0.5	-4.60	-6.14
ZrTe <sub>2</sub>	3.97	2.92	4.27	85.83	0.113			
HfS <sub>2</sub>	3.64	2.55	3.57	91.02	0.087	1.27	-4.53	-6.98
HfSe <sub>2</sub>	3.76	2.68	3.82	89.05	0.093	0.61	-4.56	-5.95
HfTe <sub>2</sub>	3.96	2.89	4.21	86.54	0.107			
PtS <sub>2</sub>	3.57	2.4	3.21	96.18	0.093	1.81	-3.97	-6.80
PtSe <sub>2</sub>	3.75	2.53	3.4	95.63	0.107	1.41	-3.98	-6.08
PtTe <sub>2</sub>	4.02	2.71	3.62	95.96	0.143	0.79	-3.81	-4.95

Table 1. Structural parameters and the formation energies of TMD monolayers.

SnS and SnSe are promising materials for the production of high-speed transistors. Switching can be achieved with the aid of electrical, thermal, mechanical, or optical methods, or even by acting on the spin system via the anisotropy of the structure. Another potential application of these materials is in memory devices. However, their operating temperature is expected to be considerably lower than room temperature. These materials are ferroelastics [54]: they have a spontaneous elastic deformation, which appears with a temperature decrease, and in a specific temperature range spontaneous polarization can appear in them [55] even in the absence of an external electric field, i.e., a ferroelectric phase transition can occur [56]. Recently, a variety of studies have appeared on the phase transitions in 2D monochalcogenides of transition metals [57–62] and in some dichalcogenides of

transition metals. This subject deserves a separate consideration.

# 3. Methods of production of single-layer and multilayer materials

Some dichalcogenides of transition metals are encountered in nature. For example molybdenum disulfide is encountered in the form of the mineral molybdenite or in an amorphous form, jordisite. The disulfide of tungsten is encountered in the form of the tungsten mineral.

The methods of synthesis of 3D TMDs were developed as early as the 1970s–1980s; more than 40 substances were obtained at that time. The basic method was high-temperature synthesis for a long time [63]. After the discovery of graphene-the first 2D material [7]-interest in obtaining other 2D materials that have a layered structure in 3D samples, in particular, quasi-two-dimensional dichalcogenides of transition metals, grew sharply. At present, different methods for obtaining them are actively being developed: exfoliation of layers from a crystal, chemical etching of a crystal, deposition from the gas phase, etc. The exfoliation of layers can be performed by different methods: mechanically, with the aid of ultrasound; by washing with a liquid; by mixing via grinding. It is important that an isolated layer have thermal and chemical stability and not be destroyed immediately, for example, because of corrosion. The different methods of synthesis allow obtaining materials that differ from each other in quality, size, and the number of 2D layers. These parameters influence the properties of the materials and the fields of their possible application.

The list of 2D TMDs that can potentially be obtained (or already have been obtained) from layered materials is sufficiently large; besides the most known MoS<sub>2</sub> [64], WS<sub>2</sub> [64, 65], MoSe<sub>2</sub> [66, 67], WSe<sub>2</sub> [67, 68], these are VSe<sub>2</sub>, NbSe<sub>2</sub>, TiS<sub>2</sub>, ZrS<sub>2</sub>, HfS<sub>2</sub>, ReS<sub>2</sub>, PtS<sub>2</sub>, TiSe<sub>2</sub>, ZrSe<sub>2</sub>, HfSe<sub>2</sub>, ReSe<sub>2</sub>, PtSe<sub>2</sub>, SnSe<sub>2</sub>, TiTe<sub>2</sub>, ZrTe<sub>2</sub>, VTe<sub>2</sub>, NbTe<sub>2</sub>, TaTe<sub>2</sub>, MoTe<sub>2</sub>, WTe<sub>2</sub>, CoTe<sub>2</sub>, RhTe<sub>2</sub>, IrTe<sub>2</sub>, NiTe<sub>2</sub>, PdTe<sub>2</sub>, PtTe<sub>2</sub>, SiTe<sub>2</sub>, NbS<sub>2</sub> [69], TaSe<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, MoTe<sub>2</sub> [70], SnSe<sub>2</sub>, SnS<sub>2</sub>, NoTe<sub>2</sub>, WTe<sub>2</sub>, ZrS<sub>2</sub> [69], ZrSe<sub>2</sub>, NbSe<sub>2</sub> [71], NbS<sub>2</sub>, TaS<sub>2</sub> [67], TaSe<sub>2</sub> [67], NiSe<sub>2</sub> [72, 73], and others.

#### 3.1 Exfoliation methods

The highest-quality samples consisting of one or two layers are obtained by mechanical exfoliation of layers, similarly to the method applied by Geim's group to graphite [10, 74]. However, this method is quite difficult to control; in particular, it is difficult to obtain large samples. Only very recently, a study appeared that reports on the exfoliation of MoS<sub>2</sub> and WSe<sub>2</sub> nanolayers of large sizes (of the order of hundreds of micrometers) by the use of a gold substrate [75]. The obtained TMD samples have larger adhesion to gold than to traditional silicon substrates, and this is why the size of the exfoliated sheet is large.

MoS<sub>2</sub> and WS<sub>2</sub> were obtained by methods of chemical separation of a 3D material into layers [76]. The layers of LiMS<sub>2</sub> (where M = Mo, W) were synthesized by the interaction of 2H- $MS_2$  with an excess amount of LiBH<sub>4</sub> at 300–350 °C for three days. The  $MS_2$  layer was obtained by washing LiMS<sub>2</sub> with water. The solution was washed several times to remove LiOH and to initiate the process of peeling and deposition of the material onto a copper lattice covered with carbon. There are also other studies on lithium intercalation into dichalcogenides of transition metals. In many of them, good monolayers are reported to have been obtained [39]. The method for obtaining TMD layers with the aid of intercalation by lithium is the most efficient industrial method of mass production. However, it is difficult to control the shape and size of the obtained samples using this method.

Recently, a new scheme was proposed of exfoliation of layers from a crystal with the aid of a tandem-type intercalation first by short 'initiating' molecules and then by long 'primary' molecules without the use of ultrasound or increased temperature [69]. The scheme of the experiment is presented in Fig. 3a. As the initiating molecules, propylamine  $C_3H_9N$  was used; as the primary molecules, hexylamine  $C_6H_{15}N$ . The crystals of TMD, propylamine, and hexylamine were intermixed and were held at room temperature for 10 h. The obtained suspension was centrifuged, chloroform



**Figure 3.** (a) Tandem molecular intercalation (schematic), (b)  $\text{TiS}_2$  intercalated by propylamine (layers separated by 9.5 Å can be seen), and (c)  $\text{TiS}_2$  intercalated additionally by hexylamine (layers separated by 21 Å are visible) [69].

was added, and the mixture was again centrifuged. This procedure was repeated several times. Then the material was dried for 2 h in a vacuum at room temperature. A TEM image obtained after intercalation with the initiating molecules and initiating and primary molecules is shown in respective Figs 3b and c. In this manner, the nanostructures of TMDs of group IV metals (TiS<sub>2</sub>, ZrS<sub>2</sub>), group V metals (NbS<sub>2</sub>), and group VI metals (WSe<sub>2</sub>, MoS<sub>2</sub>) have been obtained.

One more method for obtaining high-quality single-layer materials is the etching of a crystal by gases. By applying a special etching mask that protects part of the material against the action of the gas, it is possible to obtain structures of different geometries and to form periodic openings. The part of the TMD structure not covered with the mask is etched away, and the remaining part of the surface is untouched. The authors of [77] reported obtaining an  $MoS_2$  monolayer by etching a crystal of molybdenum sulfide with gaseous xenon fluoride (XeF<sub>2</sub>). XeF<sub>2</sub> was chosen because of its high oxidizing power and also because the associated reaction products can easily be removed in the form of gases. In [77], various complex nanostructures were obtained, such as nanoribbons of molybdenum sulfide and MoS<sub>2</sub> structures of different geometries by using graphene masks with periodic openings of various diameters.

#### 3.2 Method of chemical vapor deposition

A quite simple way of obtaining TMDs is the method of chemical vapor deposition (CVD) from the gas phase. It allows growing separate layers [67, 78, 79] and combinations of some TMDs on others [80]. The TMDs of two different layers have drawn the interest of researchers because their properties can potentially differ significantly from those of layers taken separately [81, 82]. The size of the obtained

materials depends on the size of the substrate and can reach several centimeters [78, 83]. Films grown on  $SiO_2$  can easily be separated from the substrate and are suitable for further use.

Very many studies have been devoted to the growth of sulfur-containing TMDs by sulfurization of thin films [65, 78, 84]. This method allows obtaining samples of fairly large sizes (of the order of several micrometers). These materials differ in their structure and are not ideal single-layer materials, but nevertheless have unique physicochemical properties [65].  $WS_2$  films were grown by the deposition of  $WO_3$  molecules on  $SiO_2/Si$  substrates using thermal evaporation of WO<sub>3</sub> powder in a high vacuum. Further, they were placed into an atmosphere rich in sulfur in a quartz reactor at 800 °C. Thin WO<sub>3</sub> films (5–10 Å) formed triangular two-dimensional islands on SiO<sub>2</sub>, which corresponded to the initial stages of growth of WS<sub>2</sub>. The structural changes of the obtained composites investigated by an atomic-force microscope showed that for the most part, the thickness of  $WS_2$  on  $SiO_2$ was 1 nm, while the distance between the first and second  $WS_2$  layers was approximately 0.6 nm. The composites differed in structure depending on the experimental conditions.

WS<sub>2</sub> and MoS<sub>2</sub> films were also grown by chemical vapor deposition [64]. In producing WS<sub>2</sub> films, powder of WO<sub>3</sub> (MoO<sub>3</sub> in the case of MoS<sub>2</sub>) was evaporated at high temperature and low pressure  $(10^{-5} - 10^{-6} \text{ Torr})$  and deposited onto a substrate. Further, at a temperature of 200 °C, a pressure of 35 mTorr, and a flow of argon of 50 st. cm<sup>2</sup> min<sup>-1</sup>, the sulfur powder began to evaporate. Then the temperature was raised to 900 °C and the pressure increased to 450 mTorr. Images of the obtained films are shown in Fig. 4. The WS<sub>2</sub> monolayer contains a small number of defects, mainly large atomic rings (heptagons and octagons). The single-layer films, under irradiation with light with a wavelength of 488 nm, demonstrate a photoluminescence signal located at around 2 eV.

To obtain seleniferous TMDs, the method of seleniumization is used. For example,  $WSe_2$  on a quartz substrate was grown from a  $WO_3$  film [68], and  $MoSe_2$ , from  $MoO_3$ and gaseous selenium in an atmosphere of argon and hydrogen [83]. In several experiments, it was established that selenium is not introduced into the films in the absence of hydrogen [68, 83].



Figure 4. Images obtained by the fast Fourier transform using a transmission electron microscope: (a) monolayer  $WS_2$  (defects are marked by arrows); (b, c) two-layer and three-layer  $WS_2$ , respectively; and (d) a photograph of  $WS_2$  on an  $SiO_2/Si$  substrate [64].

A distinctive feature of the method of chemical vapor deposition from the gas phase is the fact that it allows obtaining TMDs of a given shape: triangular, hexagonal, orthorhombic, etc. [85]. Typical data of different experimental studies on obtaining TMDs by this method are given in Table 2. However, there are materials that can hardly be obtained by the CVD method, for example, MoTe<sub>2</sub>, because of a low metal-chalcogen binding energy, which leads to the formation of a shapeless (amorphous) substance [86].

The visual identification of the atomic layers of many TMDs, including  $MoS_2$ , with an optical microscope is hindered, and Raman spectroscopy (RS) is typically used in these cases: the shift of RS peaks, changes in their intensity, and line broadening indicate an increase in the number of layers [93].

Some of the TMDs obtained demonstrate unstable behavior under normal conditions (room temperature, normal pressure) after prolonged storage; for example, after storage for one month in air, the current–voltage characteristics of  $MoS_2$  and  $WS_2$  worsen by an order of magnitude, and after seven months, strong cracking is observed. The process is described in [94] as follows: first, oxidation at the grain boundaries and stoichiometric defects occur and then oxygen atoms, being connected to sulfur, destroy the layer. As a result, a cracking of the material is observed, which can be

TMD	Precursor	Conditions	Morphology	References
MoS <sub>2</sub>	(NH <sub>4</sub> )MoS <sub>4</sub> in dimethyl furmalate in the presence of argon	200 mTorr to 2 Torr, 400 °C	Flakes of hexagonal shape 2–5 nm thick	[87]
MoSe <sub>2</sub>	$ \begin{array}{c} MoCl_{5} \mbox{ (heated to 255 °C)} \\ C_{8}H_{18}Se \mbox{ (70 °C) or } C_{4}H_{10}Se \mbox{ (90 °C)} \end{array} $	Atmospheric pressure, 450–600 °C	Thin film	[88]
WS <sub>2</sub>	WOCl <sub>4</sub> (heated to 176 °C) HS(CH <sub>2</sub> ) <sub>2</sub> SH (heated to 63 °C)	Atmospheric pressure, 250–600 °C	Thin film	[89]
WSe <sub>2</sub>	WOCl <sub>6</sub> (heated to 260 °C) C <sub>4</sub> H <sub>10</sub> Se (heated to 70 °C)	Atmospheric pressure, 450–600 °C	Platelet crystals mixed with needle-like crystals	[90]
VSe <sub>2</sub>	V(N $M_2$ ) <sub>4</sub> (heated to 130 °C) C <sub>8</sub> H <sub>18</sub> Se (heated to 90 °C)	Atmospheric pressure, 250–500 °C	Thin hexagonal platelets	[91]
TiS <sub>2</sub>	Ti(N $M_2$ ) <sub>4</sub> (heated to 150 °C) 2-methylpropandiol (heated to 57 °C) or tret-butyl disulfide (heated to 115 °C)	Atmospheric pressure, 300–600 °C	Thin film	[92]

Table 2. Data on the preparation of materials by chemical vapor deposition (CVD).

seen in micrographs. To increase the stability, it was suggested that the TMDs be doped with rhenium (Re), technetium (Tc), or manganese (Mn) [95]. Another method of preserving the obtained TMD monolayer is to prevent the access of oxygen to it via its encapsulation between layers of graphene or BN [96]. In this case, a change can be observed in the properties compared with the initial TMD sample. For example, in the case of  $MoS_2$  and  $NbSe_2$ , photoluminescence disappears [97]. Layers of  $Mo(W)Se_2$ , on the contrary, are stable in the ordinary atmosphere, because oxygen barely interacts with selenium.

#### 3.3 Methods for obtaining nanoribbons

There are many theoretical studies predicting that nanoribbons of  $MoS_2$  and  $WS_2$  can demonstrate both metallic and semiconducting properties, depending on their width and edge type [98–100]. For example, nanoribbons with a 'zigzag' edge can demonstrate ferromagnetic and metallic behavior, irrespective of the width and thickness. Nanoribbons with an 'armchair' edge are nonmagnetic semiconductors, whose band gap approaches a constant value of 0.56 eV with an increase in the width. Nanoribbons with a 'zigzag' edge are more stable than those of the 'armchair' type, but the stability of both types exceeds that of separate flat TMD clusters. However, thus far, only multilayer TMD nanoribbons have been obtained.

To date, several methods for obtaining TMD nanoribbons have been developed. The very first method was the cutting of nanoribbons from TMD nanotubes, similarly to obtaining graphene nanoribbons [101]. It was tested on  $WS_2$ multilayer tubes intercalated by lithium [102]. In contrast to graphene nanoribbons, the use of oxygen plasma is hindered in the case of TMDs because the  $WS_2$  nanotubes are highly reactive and are easily oxidized. In [102], large molecules of solvents were used that did not contain oxygen: dodecanethiol (C<sub>12</sub>H<sub>25</sub>SH) and octanethiol (C<sub>8</sub>H<sub>18</sub>S). Supposedly, the mechanism of cutting the tubes consists in introducing molecules into the interlayer spaces through the defects or open ends, which increases stress and leads to the breaking of W-S bonds. The initial 'cut' becomes the target of an even larger number of molecules of solvents, the stress increases, and a longitudinal cut occurs. The described model of cutting has been studied theoretically in [103, 104]. The suggested hypothesis of the cutting mechanism was confirmed. It was shown that both the approach of the octanethiol to the nanotube intercalated by lithium atoms and their subsequent binding are energetically advantageous.

Another method for obtaining ribbons, also borrowed from graphene technologies, is the cutting of a sheet via the selective ionic etching of the corresponding  $MX_2$  monolayers by a focused electron beam of a scanning TEM. This method has already been used to obtain MoS<sub>2</sub> nanoribbons with a width of less than 1 nm and a length of 10 nm. These ribbons have a metallic conductivity and can therefore be used in the production of integrated nanocircuits for flexible nextgeneration nanoelectronic devices [105].

Figure 5 illustrates the preparation and micrographs of samples of  $MoS_2$  nanoribbon arrays on different substrates (glass,  $SiO_2/Si$ ) obtained by a new rapid economic method [106]: the combination of the procedures of micro-molding in capillaries and thermolysis of salt ((NH<sub>4</sub>) 2MoS<sub>4</sub>) as the printing ink. The MoS<sub>2</sub> nanoribbons had a thickness up to 4 nm, a width from 157 to 465 nm, and a length up to 2 cm. The MoS<sub>2</sub> template can be printed on universal substrates,



Figure 5. Preparation (illustration) and microphotographs of nanoribbon arrays of  $MoS_2$  on different substrates (glass,  $SiO_2$  on silicon) [106]. PDMS—polydimethylsiloxane; FTO—fluorine-doped tin oxide; DMF—dimethylformamide.

such as SiO<sub>2</sub>/Si, sapphire, Au film, FTO/glass, and glass with a graphene coating (FTO—fluorine-doped tin oxide). The high-temperature thermolysis (1000 °C) leads to the formation of high-quality conducting samples, with the mobility of carriers comparable to the mobility in thin-film MoS<sub>2</sub>. Field transistors based on such structures are promising for a wide range of applications in nanoelectronics.

Using direct action of a beam of helium ions,  $MoS_2$  nanoribbons with a width of 5–15 nm have recently been obtained (Fig. 6) [107]. The observed Raman modes and optical spectroscopy showed strong optical polarization effects in such ribbons, caused by the appropriate features in the densities of vibrational edge states.

The data in [45, 107], where strongly anisotropic optical properties of nanoribbons from an  $MoS_2$  layer were observed, show the potential of their use in optoelectronics.

#### 3.4 Obtaining planar heterostructures

An analog of the well-known layered 3D heterostructures  $GaAs/Ga_{1-x}Al_xAs$  [108, 109] in the case of quasi-twodimensional materials is planar structures made of two 2D materials with close crystal lattices, whose boundary consists of covalently bonded atoms. Obtaining such a material was first demonstrated with the graphene–h-BN heterostructure [110]. One of the first theoretical papers on the planar TMD superlattice was devoted to the analysis of the variation of the total density of states and the partial density of states of specific atoms in the interfaces of the lateral  $MoS_2 - MS_2$  and  $MoS_2 - MoTe_2$  structures [111].

It has been established that heterostructures have very different properties from separate TMD monolayers. For example, the  $MoS_{2x}WS_{2n-x}$  (x, n = 1, ..., 20) heterostructure is still a semiconductor with the band gap  $\approx 1.6$  eV, which is only slightly less than that in  $MoS_2$  and  $WS_2$  monolayers, but the strong interactions between  $MoS_2$  and  $MoTe_2$  at the phase boundaries lead to the metallicity of the  $MoS_2 - MoTe_2$  heterostructure. Planar heterostructures have also been synthesized on other TMD pairs. For example, after the introduction of W atoms into an  $MoS_2$  layer, a planar  $MoS_2 - WS_2$  structure was obtained (Fig. 7a), but with a not very flat boundary [112].

A monolayer with the vertical stacking of two TMDs,  $MoSe_2-WS_2$ , with an atomically sharp boundary was



**Figure 6.** Nanoribbons made from  $MoS_2$  layers [107]: (a) optical photograph of  $10 \times 10 \ \mu m$  samples of nanoribbons of various widths; (b) image of the surface of a sample with 15 nm nanoribbons, made with an atomic-force microscope; (c) results of height measurements along the horizontal line shown in (b); (d) angular diagram of the second-harmonic signal with a change in the angle of polarization of the incident laser radiation (SHG — second-harmonic generation); (e) model of the atomic structure of a 15 nm nanoribbon of MoS<sub>2</sub> (blue (*I*) and red (*2*) arrows respectively show A and Z directions), used in the qualitative explanation of the modes of Raman scattering from one of the samples.

grown in [113] by chemical vapor deposition on a sapphire substrate (Fig. 7b). The growth of WSe<sub>2</sub> occurred at 925 °C, and that of MoSe<sub>2</sub> at 755 °C. In both cases, the boundary can clearly be determined. The methods are scalable and better control the boundaries of monolayers than the boundaries of TMD nanoribbons. In [82], an analogous method was used to obtain lateral monolayer semiconductors  $MoSe_2 - WSe_2$ .

Simple planar structures — nanoribbons with regions of  $MoS_2$  and  $WS_2$  of different widths situated both perpendicularly and parallel to the 'zigzag' direction — were investigated theoretically in [114]. With an increasing proportion of  $WS_2$ , the band gap decreased in all the heterostructures examined. In the calculated current–voltage characteristics, the effect of negative differential resistance was observed, which increased with an increase in the width of the  $WS_2$  strip.

A different variant of a planar heterostructure was examined in [29], where the authors used DFT methods to study the electronic and transport properties of the periodically alternating phases of  $MoS_2$ —a kind of superlattice formed by 2H-MoS<sub>2</sub> and lT-MoS<sub>2</sub> components—depending on the width of the nanostrip of the 1T phase and the widths of the nanoribbons with a part of the 1T phase incorporated into the 2H phase. The experimental reality of the formation of the 1T phase inside 2H strongly suggests the possibility of the formation of such structures. It was shown that the incorporation of the 1T phase into the 2H-MoS<sub>2</sub> monolayer leads to the formation of electron levels near the Fermi level and the formation of quantum wells in the transverse direction of the superlattices.

Figure 8 presents the results of a study of the dependence of the band gap width on the length of the region of the 1T phase embedded into the 2H-MoS<sub>2</sub> monolayer. Such structures are superlattices with alternating 1T and 2H phases. It has been shown that the introduction of only a small strip of the 1T phase (with a width of 0.6 nm) leads to a sharp reduction in the band gap width, to  $E_{\rm g} \approx 0.5$  eV. It is also worth noting that the formation of periodic strips of alternating phases led to a 'straightening' of the electron spectrum branches in the  $\Gamma$ -X direction (Fig. 8a)—to the formation of levels in the arising quantum wells of the 1T strips. A further increase in the length of the 1T-MoS<sub>2</sub> region (to 2.2 nm) leads to a relative increase in the Fermi energy and the formation of additional energy bands that intersect the Fermi level. This fact, first of all, demonstrates the formation of metallic conductivity in the regions of the strips of 1T-MoS<sub>2</sub> nanostructures of this composition upon the appearance of transverse quantization in them due to the barriers delimiting the transition regions.

Calculations of the thermoelectric characteristics of a planar  $MoS_2-WS_2$  nanoribbon sample in [115] showed that according to their properties, such structures are promising materials for high-performance thermoelectric devices.

Recent theoretical studies [116] of the quasi-two-dimensional alloy  $Mo_{1-x}Fe_xS_2$  (x>0.1) give grounds to hope for the expansion of the class of lateral TMD structures.

It was shown that because of the strong magnetic properties of iron atoms, the Fe-containing  $Mo_{1-x}Fe_xS_2$  film has a



**Figure 7.** Planar single-layer heterostructures: (a) structure of a  $WS_2$ -MoS<sub>2</sub> monolayer (schematic); (b) its microphotography; (c) photovoltaic effect due to the heterojunction (in the inset are shown current–voltage characteristics of a sample upon illumination and without illumination (red curve) [112]); (d) growth of a  $WS_2$ -MoS<sub>2</sub> heterostructure (schematic), images of the interface (scanning TEM), and (to the right) an atomic model of the heterostructure (schematic) [113].



**Figure 8.** Structure (schematic) and electron spectra of heterophase superlattices based on  $MoS_2$  depending on the width of the 1T phase region, ranging from (a) 0.6 nm to (d) 2.2 nm. Red rectangles outline the regions of the 1T-MoS<sub>2</sub> phase. The spectra of the (e) 2H-MoS<sub>2</sub> and (f) 1T-MoS<sub>2</sub> phases of the monolayers are given for comparison [29].

nonzero magnetic moment, which increases to 1.8 Bohr magnetons in the  $FeS_2$  structure (Fig. 9). The alloys of various compositions examined proved to be energetically advantageous, which in principle indicates the possibility of their synthesis in practice.

Thus, the described heterophase lateral TMD structures have immense prospects for constructing new elements of nanoelectronics, optics, and spintronics.

The developed chemical methods of growing heterostructural TMD films allow obtaining materials of large sizes [117].



**Figure 9.** (Color online.) (a–h) Atomic structure of  $Mo_{1-x}Fe_xS_2$  at *x* equal to (a) 0, (b) 0.04, (c) 0.06, (d) 0.11, (e) 0.25, (f) 0.5, (g) 0.75, and (h) 1.0 (iron atoms (*I*) are shown in dark blue; molybdenum atoms (*2*), in red; sulfur atoms (*3*), in green); (i) dependence of the magnetic moment  $\mu$  per elementary structural unit of the lateral alloy on the concentration of iron; and (j) dependence of the energy of the system per  $MS_2$  structural unit (M = Mo, Fe) on the atomic concentration of iron in  $Mo_{1-x}Fe_xS_2$  film (values of the energies of the intermediate structures are given in black (*4*); the most energetically advantageous structures are shown in red (*5*)) [116].

The typical synthesis procedure consists in dissolving the appropriate components in deionized water, heating the solution in a reactor, centrifugation, and drying on a substrate. This method does not allow controlling the presence of defects in the materials obtained. However, to date, methods for treating materials that can improve their structure have already been developed. For example, in [117] WS<sub>2</sub> was obtained by mixing tungsten hexachloride (WCl<sub>6</sub>), thioaceta-mide, and trimethoxysilane in deionized water with the subsequent heating of the solution at 265 °C for 24 h, cooling, and centrifugation. The samples were then washed several times in deionized water and dried in a vacuum at 60 °C. The thus synthesized material contained WO<sub>3</sub> impurities, which worsened the electronic properties of the material. The impurities were removed via the sulfurization of the TMDs.

A hybrid structure consisting of ultrathin platelets of WSe<sub>2</sub> and WO<sub>3-y</sub> was obtained on microcrystalline graphite using pulsed laser deposition. The deposition was carried out at room temperature in a mixture of Ar + O<sub>2</sub> (10%) at a pressure of 5 Pa. The WSe<sub>x</sub> films consisted of nanoparticles of a rounded shape with a size of 50–100 nm. The Se/W ratio in the films exceeded the stoichiometric value (x > 2). The WSe<sub>x</sub> films were annealed at 550 °C for 30 min at a pressure of 10<sup>5</sup> Pa. The annealing led to a substantial rearrangement of the film, which was manifested in the formation of a 'flower' morphology, with 'buds' consisting of nanocrystalline petals. The sizes of the platelet crystals did not exceed 200 nm and the thickness was a few nanometers [118].

**3.4.1 Van der Waals heterostructures.** Such structures based on TMDs can also be obtained by the deposition of one layer on another. This method of preparing layered structures is similar to assembling Lego blocks [73]: any sequence of materials can be assembled by placing one layer onto another (Fig. 10). The structure obtained must have stability, just as the initial layers. The layers are connected together by weak van der Waals forces. As a result of the interaction of the layers, the formation of a moire pattern is observed. The preparation of such layered materials encounters a difficulty with controlling the process of the reproduction of multilayers from the structures obtained previously. Thus, the angle of the crystallographic orientation of layers can be reproduced with an accuracy of somewhat less than one degree.

The possibility of combining TMDs with other materials extends the field of application of the obtained junctions due to a change in the properties of their components [119, 120].

**3.4.2 TMD/graphene bilayers.** In practice, the properties of heterostructures always differ from the properties of the initial components. For example, it has been shown that the combination of molybdenum disulfide with graphene strengthens the spin–orbit interaction in the latter, which leads to a weak effect of antilocalization and to a decrease in the spin relaxation time by three orders of magnitude in comparison with other substrates [121].

Two different TMD/graphene heterostructures were obtained in [122]. In graphene deposited on a  $WSe_2$  layer, a



Figure 10. Multilayer crystals: (a) set of 2D structures; (b) model of assembling a heterostructure from 2D structures similar to assembling a material from Lego plates [73]; (c) growth pattern; (d) microphotographs of  $MoS_2$  layers on  $WSe_2$  and of  $WSe_2$  layers on  $MoSe_2$  grown on a substrate of three layers of epitaxial graphene (EG) [119].

very high mobility was observed, 7000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. It was shown that such a sandwich can serve as the basis for tunnel field-effect transistors with a high ON/OFF ratio of the currents. Another heterostructure, Mo<sub>2</sub>/graphene, which is used in the anodes of supercapacitors, is more stable and has a larger capacity than MoS<sub>2</sub>. The SnS<sub>2</sub>/graphene bilayer is restored better than SnS<sub>2</sub>. The enhanced electrochemical characteristics of such a structure are caused by the 2D heterointerface between the metal sulfide and graphene. Moreover, because in Li-ion batteries lithium interacts with both graphene and TMDs, the energy of its adsorption is more than in the single-component system (with graphene or TMDs). The synergistic effect appears to be connected with a charge redistribution over graphene [123].

The  $MoS_2$ /graphene junction under consideration, being a junction of a semiconductor with a semimetal, demonstrates a Schottky barrier. It was theoretically shown that the value of this barrier can change under the action of ambient conditions. For example, with an increase in the distance between graphene and MoS<sub>2</sub>, the n-type barrier decreases because of the decrease in the chemical interaction, which suppresses the transfer of electrons (the barrier potential is  $\Phi_{Bn} = 0.49$ , 0.25, 0.06, and 0.04 eV for the respective distances D = 2.7, 3.0, 3.5, and 4.0 Å). The application of a vertical electric field with a strength of more than 0.6 V  $Å^{-1}$  leads to the transformation of the n-type Schottky barrier into a p-type barrier. A negative electric field whose value is less than  $-0.6 \text{ V} \text{ Å}^{-1}$  leads to a decrease in the barrier to a value less than 0.1 eV; an electric field of more than  $-0.6 \text{ V} \text{ Å}^{-1}$  leads to the transformation of the Schottky contact into an ohmic type [124]. Previously, a similar effect was observed for the WS<sub>2</sub>/graphene heterostructure in [125].

Heterostructures can also be obtained with the aid of a hydrothermal reaction. For example,  $MoSe_2$  sheets and  $MoSe_2/graphene$  hybrids were prepared by this method in [126]. For this,  $Na_2MoO_4$  and selenium hydrate were dissolved in distilled water by heating to 200 °C for 10 h. To

obtain the hybrid, graphene oxide was added to distilled water, and this composition was dried in a vacuum. The obtained composite had a structure resembling a flower, in which thin  $MoSe_2$  films were present. The number of layers was varied from 1 to 10. The peaks present in the Raman spectrum of light indicate a random distribution of films. Most of  $MoSe_2$  had the hexagonal atomic packing. Some particles had a thickness of more than 5 nm while others had smaller sizes (1–2 nm).

3.4.3  $MoS_2/M/graphene$  (G) structures with metal (M) atoms between layers. It is known that rhenium atoms can substitute for molybdenum atoms in an MoS<sub>2</sub> layer to form an  $Mo(Re)S_2$  structure [127], or be located between the layers connected by a van der Waals interaction to form an  $MoS_2/(Re)/G$  structure [128]. New metallic  $MoS_2/graphene$ structures with rhenium atoms introduced between layers were investigated in [129], where it was shown that a change in the electronic properties of the structure can be attained by turning the graphene layer through the angle  $\varphi = 30^{\circ}$  relative to the layer of molybdenum disulfide. The Re atom can substitute for the molybdenum atom in the MoS<sub>2</sub> layer or be located between layers, interacting predominantly with three sulfur atoms and six carbon atoms. In the latter case, a high density of electron states was revealed at the Fermi level, which indicates a high metallicity of the  $MoS_2/(Re)/30^{\circ}$ graphene bilayer in comparison with the previously investigated bilayer structures [130].

The cases of similar structures with a larger number of rhenium atoms were further examined, including configurations with a graphene layer connected to  $MoS_2$  by two atoms of rhenium ( $MoS_2/(2Re)/G$ ) in combinations of the layers with  $\varphi = 0^\circ$  (parallel) and  $\varphi = 30^\circ$  (perpendicular). Figures 11a and 11b schematically show the atomic structures of codirected layers of graphene and molybdenum disulfide in the parallel scheme  $Mo(Re)S_2/(Re)/G$  (an Re layer built into an  $MoS_2$  layer and an Re atom between layers in the orthorhombic  $MoS_2(8Z,8Z)/G(10Z,10Z)$  supercell with zigzag



**Figure 11.** (Color online.) (a, b) 'Parallel' and (c, d) 'perpendicular' setups and the electron spectra of the Mo(Re)S<sub>2</sub>/(Re)/G structures with (a, c) 'close' and (b, d) 'distant' atomic location of rhenium atoms (those on the edge of the supercell replace the atoms of molybdenum in the MoS<sub>2</sub> layer) [129]. (e) Atomic structure of MoS<sub>2</sub>/G without an additional Mo atom and with an Mo atom between the layers. (f) Density of electron states (DOS) near the Fermi level (E = 0) for the appropriate structures in (e): green line (1), the partial DOS for the d orbitals of Mo atoms in the layer; pink line (2), d orbitals of additional Mo atoms; dark blue line (3), p orbitals of S atoms in the layer; red line (4), p orbitals of C atoms in graphene; black line (5) the total DOS [29].

edges with the lattice parameter  $L \approx 21.3$  Å) in the case of a 'close' arrangement (4.33 Å, Fig. 11a) and a 'distant' arrangement (6.88 Å, Fig. 11b) of two rhenium atoms; their electron spectra were also calculated. It was found that in the case of the close arrangement, the structure is a narrow-band semiconductor with the band gap  $E_g = 0.07$  eV, with a significant interaction of rhenium atoms through the MoS<sub>2</sub> layer, and an increase in the interatomic distance between the rhenium atoms in the heterostructure to 6.88 Å leads to the disappearance of the gap (the structure becomes metallic).

In the 'perpendicular' structure with the rotation of one layer relative to another by 30° with the orthorhombic supercell MoS<sub>2</sub>(8Z,8Z)/G(5A,5A) (Figs 11c, d), in which the influence of the interlayer Re atom significantly distorts the electron spectrum of the graphene layer due to the violation of its symmetry and transfer of charge onto it [130], it has been discovered that (1) in the case of a close arrangement of two rhenium atoms (5.32 Å), the structure is a narrow-band semiconductor with the band gap  $E_g = 0.11$  eV, and (2) an increase in the distance between the rhenium atoms to 7.37 Å leads to the vanishing of the gap; the structure becomes metallic with a high density of electron states at the Fermi level.

A similar transformation of TMD/graphene structures into a 2D metal was theoretically studied based on the example of the incorporation of a molybdenum atom into an  $MoS_2$ /graphene structure with the formation of an  $MoS_2$ / (Mo)/graphene structure [131]. In the process of creating a heterostructure, prior to one layer being applied onto another, it was suggested that a small concentration of metallic atoms be adsorbed onto the surface of the first layer and then the next layer be applied on top of it. The authors of [131] first analyzed the process of adsorption of Mo atoms onto the MoS<sub>2</sub> surface. A high binding energy of the molybdenum atom with the sulfur atom of the TMD layer was revealed and the process of migration of the molybdenum atoms over the MoS<sub>2</sub> surface was assessed; the barrier for the transfer of an Mo atom from one S atom to an adjacent S atom was found to be  $\sim 1$  eV. It follows from this estimate that with an increase in the temperature, the molybdenum

atoms can move freely over the surface of the  $MoS_2$  layer. Thus, in the case of a high concentration of Mo atoms on the surface, they should form clusters; these metallic clusters, weakening the van der Waals forces between the  $MoS_2$ surface and graphene, can split the layers of the structure. Upon applying graphene onto the surface of  $MoS_2$  with additional Mo atoms on it (one atom per  $4 \times 4$  cell of  $MoS_2$ with an edge of the 'zigzag' type ), a redistribution of charges occurs and covalent bonding forms between the layers, which converts the bilayer into a metal with a high density of states at the Fermi level.

All the structures examined are energetically stable. The  $MoS_2/M$ /graphene bilayers can find application, for example, as metallic nanowires in nanoelectronic devices.

Results concerning the preparation of other TMD/ graphene heterostructures can be found in recent review [132].

**3.4.4 TMD heterostructures with layers of C**<sub>60</sub> **fullerenes.** At present, interest in composite materials that consist of junctions of fullerene with different nanostructures is growing substantially. An example of such materials is fullerenes inside carbon nanotubes (C<sub>60</sub>@CNT) [133] or between graphene layers [134]. Recently, the authors of [135] obtained similar nanocomposites from C<sub>60</sub> and MoS<sub>2</sub> monolayers by the method of solvent transfer and surface deposition (STSD) of fullerenes onto MoS<sub>2</sub> and subsequently incorporating them into templates. They created hybrid van der Waals heterojunctions (Fig. 12) by combining a layered C<sub>60</sub>/MoS<sub>2</sub> structure (50 nm) with flat electrodes of indium–tin oxide (ITO) and Al.

In such a diode device configuration, a direct transfer of charge and resistive switching was observed with a low SET/ RESET voltage ( $\sim 3$  V) applied perpendicular to the C<sub>60</sub>/MoS<sub>2</sub> layers; the electric bistability was steadily reproduced (> 10<sup>4</sup> times). This effect of rewritable energy-independent 'memory' appeared as a result of the electric-fieldcontrolled tunneling of electrons through effective p–n nanojunctions at the C<sub>60</sub>/MoS<sub>2</sub> boundaries. The high stable ratio of the ON/OFF currents ( $\sim 10^5$ ) in the obtained cell allows predicting the potential of its application in devices with permanent RAM. The suggested method of templating



**Figure 12.** Mechanism of charge transport through the p–n junctions of a system of  $C_{60}/MoS_2$  layers [135]: (a) diagram of energy levels at  $V_g = 0$ ; (b) upon switching on an applied voltage above 2.0 V, when the decrease in the transitional barriers leads to the flow of a high current  $I_{on}$ ; (c) upon switching on the reset voltage below -5.5 V, leading to the flow of a low current  $I_{off}$ ; (d) schematic of the diode device of flash memory; and (e) current–voltage characteristic of one cycle with the scheme of charge distribution before and after the formation of the  $C_{60}/MoS_2$  junction (respective yellow (5) and blue (6) regions).

through STSD opens ways for studying charge transfer through the interface between an organic layer and 2D semiconductor, making it possible to massively produce p-n heterojunctions using TMD/C<sub>60</sub> structures.

We note that earlier, in 2013 [136], a storage cell that works under the application of a transverse electric field was obtained for the first time using a 2D TMD based on an  $MoS_2/$ graphene/h-BN heterostructure on an SiO<sub>2</sub> substrate, albeit with lower characteristics than those in the above-considered  $C_{60}/MoS_2$  system with p–n junctions.

Because the molecules of  $C_{60}$  fullerenes are good acceptors, the electronic properties inherent in separate components of the TMD/ $C_{60}$  system change in the bilayer. Therefore, in [137], some other combined structures (MoS<sub>2</sub>/ $C_{60}$ , G/ $C_{60}$ , G/MoS<sub>2</sub>, and G/MoS<sub>2</sub>/ $C_{60}$ /G) were recently analyzed in terms of the DFT method (Fig. 13).

In the  $MoS_2/C_{60}$  bilayer, because of the weak van der Waals interaction between the  $MoS_2$  film and fullerenes, the energy band structure is a superposition of the energy bands of its component parts (see Fig. 13), but with a shifted Fermi level. The gap width of this bilayer is equal to 0.75 eV. Thus, the presence of a layer of close-packed fullerenes on the surface of molybdenum disulfide leads to its doping and to a decrease in the gap.

In the case of the  $G/MoS_2/C_{60}/G$  sandwich, the energy spectrum can also be represented as a superposition of the energy band structures of a sheet of  $MoS_2$ , a layer of  $C_{60}$ fullerenes, and sheets of graphene. This structure has the metallic conductivity with a low density of electron states (DOS) near the Fermi level that correspond to two outer graphene layers. In this sandwich, the region of high values of the DOS is significantly enlarged compared with other structures (see Fig. 13): there are additional peaks in the energy ranges 0.2-0.6, 1.3-1.6, and 2.1-2.5 eV, and also in the energy ranges from -11 to -1.6 and from -2.1 to -2.5 eV. The fullerenes can play the role of acceptors for the photoelectrons, whereas the graphene monolayers are electrodes for the photocurrent. This allows regarding the  $G/MoS_2/C_{60}/G$  sandwich as an efficient material for photovoltaic elements. It can be concluded that this heterostructure is promising for the use in photovoltaics as elements of solar batteries.

3.4.5 Bilayers made of 2D polar and TMD layers. Graphenelike 2D polar materials are receiving special attention from the standpoint of both their creation and the theoretical substantiation of their stable existence [138, 139]. As long ago as 2005, monolayers of the hexagonal phase of zinc oxide (ZnO) in a form with the sphalerite crystal structure were observed in [140]. Because zinc atoms and sulfur atoms can form a structure similar to ZnO, the Zn/MoS<sub>2</sub> bilayer could be expected to demonstrate the occurrence of a strong rearrangement of the geometry and therefore of the spectrum, compared with the spectra of its components. The small difference between the parameters of the unit cells of molybdenum disulfide and zinc oxide (3.17 and 3.28 Å, respectively) suggests the possibility of obtaining such heterostructures without strong mechanical deformations of the layers.

Using the DFT method with the Perdew-Burke-Ernzerhof (PBE) functional, the authors of [141] investigated the electronic properties of heterostructures based on such bilayers. The most energetically advantageous structure proved to be  $MoS_2/ZnO$ , in which zinc atoms are mainly located over the sulfur atoms. The calculation showed that in contrast to the indirect band gap in the spectrum of the  $MoS_2/ZnO$  bilayer ( $E_g = 0.8 \text{ eV}$ ), the  $G/MoS_2/ZnO/G$ heterostructure has energy spectrum branches related to the graphene layers, with the Dirac point lying higher than the Fermi level and a direct-band dielectric gap with a width of 0.72 eV. The wide regions of high values of the DOS exist in the valence band and in the conduction band, which is related to a significant charge transfer between the layers and with charge localization. The asymmetric charge distribution in the direction across the layers gives grounds to assume that the G/MoS<sub>2</sub>/ZnO/G heterostructure can manifest noticeable photovoltaic and diode effects when a transverse electric field is applied.

We also note recent review [142], where results of an analysis of heterostructures based on TMDs and graphene are given.

## 4. Defect and doped structures

Obtaining defect-free objects is usually a difficult problem from the experimental standpoint. The formation of defects and doping with atoms of other elements can significantly change the physical and chemical properties of materials and open new prospects for their application.

Possible defects in transition-metal dichalcogenides were classified in [143]. They can be divided into 0D, 1D, and 2D types. The 0D defects are the simplest and most common: these are vacancies, adatoms, and impurity atoms that replace the host atoms, as well as agglomerates of defects. The 1D defects are the lines of topological defects, the passivated boundaries of nanoribbons or of flat fragments, and the boundaries of laminar overgrowths of one material on



**Figure 13.** (Color online.) (a) Atomic structure and (b–d) the energy spectrum of the quasi-two-dimensional heterostructure  $G/C_{60}$ : of its components (b, c) and of the entire structure (d). (e) Atomic structure and energy spectrum of  $G/C_{60}/MoS_2/G$ : (f, g) of its components and (h) of the entire structure. The red rectangles outline the unit cell of the structure. (i) Distribution of the density of electronic states (DOS) depending on the energy for the  $G/MoS_2/C_{60}/G$  heterostructure [red, (*I*)], the  $G/C_{60}$  composite structure [green, (*2*)], and  $MoS_2/C_{60}$  [black, (*3*)] in comparison with the  $G/MoS_2$  structure [dark blue, (*4*)] [137].

another. The 2D defects are overgrown single-layered fragments of the same composition, embedded or overgrown fragments of another composition, and swollen or curved regions of the surface, including its ripples. For example, in a separate  $MoS_2$  sheet of a microsize [144], just as in graphene, distortions of the surface are observed in the form of ripples with a height of the order of nanometers.

The main native defects in TMDs are vacancies of the atoms of metals and chalcogens, adsorbed atoms, impurities of other atoms, and interstitials (atoms inserted between the layers) or antisites (substitutions of one atom of the material for another, e.g., Mo for X or X for Mo). At high temperatures, the concentration of vacancies of sulfur atoms in  $MoS_2$  can reach  $10^{10}$  cm<sup>-2</sup>, and even  $10^{11}$  cm<sup>-2</sup> in

the presence of rhenium atoms. An S vacancy is the most frequently encountered native defect in TMDs [145]. Furthermore, the vacancies can be formed by artificial methods, for example, by sputtering  $Ar^+$  when used for the subsequent removal of sulfur atoms in  $MoS_2$  [146]. The presence of vacancies can be revealed visually in images obtained by a scanning electron microscope. Another universal signature of vacancies is an increase in the intensity of light absorption and a red shift of optical absorption [147].

To understand the character of changes in the structure of a 2D TMD layer in the presence of defects, the energies of the formation of basic defects were calculated in [148, 149]. In MoS<sub>2</sub>, the energy of the formation of an S vacancy and of the attachment of an S adatom is approximately 1 eV; for an Mo vacancy and Mo adatom, the formation energy has a larger value ( $\sim 4 \text{ eV}$ ) [148]. The S adatom is electrically neutral. The presence of vacancies influences the electronic and optical properties. It was first predicted in the example of WS<sub>2</sub> that the presence of a vacancy leads to spin polarization near the defect due to the ionic character of W–S bonds and the presence of an unbound electron near the vacancy [147]. This effect can be used to create magnetic 2D materials.

It was shown by combining high-resolution TEM and *ab initio* simulation [150] that the vacancies in an  $MoS_2$ monolayer under external actions have a sufficiently high mobility and tend to agglomeration with the formation of defect lines. The energy barrier for the migration of one vacancy is 2.3 eV. This is a rather high barrier, which can hinder significant diffusion at room temperature, but it can be completely overcome under external actions, for example, under prolonged electron bombardment. It was noted that in the presence of a large number of vacancies in the region under consideration, the value of the barrier decreases significantly (to 0.8 eV), and the speed of migration increases correspondingly. The direction in which the lines of vacancies are formed can be controlled by the application of mechanical stress. An image of a single line of vacancies is presented in Fig. 14. In a layer, the formation of a double defect line, consisting of two rows of sulfur vacancies located above each other, is also possible [150].

The structure of  $MoS_2$  grown by chemical vapor deposition has been studied by a scanning electron microscope [97]. Line defects (with a length up to 100 nm) and local overgrowths of second layers were observed on the monolayers. The majority of such local overgrown regions has a triangular shape. These defects lead to a decrease in photoluminescence [97].

In TMD layers, the formation of another type of defect was also observed: a  $60^{\circ}$  rotation of the Mo–X bond [151], similar to the Stone–Wales defect in the carbon sp<sup>2</sup> structure [152]. It occurs as a result of a local rotation of one C–C bond through 90°, which leads to the formation of two pentagons and two heptagons instead of four hexagons connected to each other. The presence of a Stone–Wales defect in a TMD is highly improbable from the energy standpoint because of the polar nature of the chemical bonds between unlike atoms in such systems. Figure 14 displays the transformation of Stone–Wales defects into a 'trefoil' via the rotation of an Mo–S bond through 60°. Such a defect can migrate similarly to a point defect. The presence of trefoils in an  $MoS_2$  layer significantly influences its electronic properties and changes the elasticity moduli by approximately 4%.

In an  $MoSe_2$  monolayer grown by molecular beam epitaxy under the conditions of a deficit of selenium (the more precise formula being  $MoSe_{1.983}$ ), a dense network of mirror-twin boundaries is observed (Fig. 15), which are thermodynamically stable line defects. In the case of a very large number of selenium vacancies, the 2D sheet becomes unstable and transforms into a nanowire [153].

It is well known that defects significantly change the electron structure of substances and lead to the appearance of intermediate energy states near the Fermi level. These states correspond to a strong localization of the electron density near the defects and act as scattering centers. As a result of a change in the electronic structure, changes in the electron transport occur; namely, the charge mobility can change. In the case of Mo vacancies (with a change in the structure composition by 1.1%), the mobility decreases to 75% compared with the defect-free system. The presence of S vacancies leads to an increase in the electron mobility due to the contribution of localized electrons directly to the conduction band. Besides the defects, the boundary conditions also strongly affect the conductivity of TMDs. The conductivity also strongly depends on the direction of the current because the conductivity is higher along the 'zigzag' lines than in the 'armchair' direction [154].



**Figure 14.** Single line of vacancies in  $MoS_2$ : (a) model (top view and side view), (b) TEM data [150]. Models of rotary defects in graphene and TMDs: (c) atomic model of a sheet, (d) top view of the formation of a Stone–Wales defect, (e) atomic model of graphene with a double vacancy, (f) model of the transformation of a divacancy, (g) atomic model of  $MX_2$ , (h, i) spatial rotation of the M-X bond through 60° (top view and a perspective view); (j) atomic model of a trefoil defect, (k) image of the monolayer of WSe<sub>2</sub> at 500 °C; the density of trefoil defects is approximately 5.1%. Scale bar: 2 nm. (From [151].)



**Figure 15.** (Color online.) (a) Model of mirror-twin boundaries in the network of an  $MoSe_2$  monolayer, (b) their real image in TEM in the triangular region of the layer after irradiation by electrons with an energy of 80 keV [153]. The lines are drawn along the single (red, *I*) and double (yellow, *2*) vacancy. The number '10' indicates the number of defects.

The formation of defects in the structures can also depend, for example, on a change in the experimental conditions in the process of chemical deposition. The action of high temperature or ion/electron treatment leads to the appearance of defects in samples already prepared [155]. The values of the energies necessary for the formation of some defects, e.g., the removal of atoms from  $MoS_2$ , and also from graphene and h-BN, are given for comparison in Table 3 [156]. It can be seen that the lower the chalcogen is located in the periodic table, the smaller the value of the energy that is necessary for its displacement. There are no such dependences for the atoms of transition metals. The authors of [157] calculated analogous parameters for many other TMDs.

Figure 16 presents a series of photographs illustrating the growth of a defect: an example of the formation of an opening in an  $MoS_2$  layer under the bombardment by an 80 kV electron beam from a transmission electron microscope. It can be seen that the amorphous phase accumulates at the edges of the opening. The influence of electron and ion irradiation on 2D TMDs is considered in recent review [161].

### 4.1 Doping

Another method that can alter the structure and properties of a material is doping by atoms of other elements. For example, doping can lead to an increase in the density of states at the Fermi level [162]. A distinctive feature of TMDs is that they can be doped only by donors of electrons. This is most probably caused by the fact that the acceptor impurities, when located between the negatively charged atoms of

**Table 3.** Structural data of monolayers of graphene, h-BN, and 2H-MoS<sub>2</sub> with a hexagonal lattice [156].

Material	Atomic number	Lattice parameter, Å	Threshold energy of displacement of an atom, eV	Reference
Graphene	C: 6	2.46	17	[158]
h-BN	B: 5 N: 7	2.51	B: 19 N: 23	[159]
2H-MoS <sub>2</sub>	S: 16 Mo: 42	3.2	S: 6.9 Mo: 20	[160]
MoSe <sub>2</sub>	Se: 34 Mo: 42		Se: 6.4	[160]
WS <sub>2</sub>	S: 16 W: 74		S: 7	[160]
WSe <sub>2</sub>	Se: 34 W: 74		Se: 6	[160]

chalcogens, cause strong electrostatic repulsion, making the existence of such compounds impossible. Doping by atoms from Group I (alkali metals Li, Na) was investigated theoretically and experimentally in [163]. Doping by alkali metals does not change the conductivity type of the 2H and 1T phases. But the electron doping destabilizes the 2H-MoS<sub>2</sub> crystal structure and leads to its transformation into the 1T' phase. The heterostructures of TMDs doped by lithium can be used as anodes in the elements of ion batteries; this application is discussed in more detail in Section 6.

Doping by the atoms of Group IV transition metals (Ti, Zr) is interesting from the standpoint of tribological applications. Because the atoms of Group IV metals have the maximum degree of oxidation, an ion of such a metal can be isovalently substituted by another ion (IV). For  $MoS_2$ , there are data showing a decrease in friction in the case of a small level of Ti doping (the optimum level of doping for these purposes is 15%). The high concentration of impurities leads to a distortion of the lattice [164, 165].

Doping the structures with Group V atoms (V, Nb) leads to a 20-fold increase in the electric conductivity and a 40-fold increase in the concentration of charge carriers in TMD materials [166, 167].

Doping TMDs with Group VI atoms (Cr) leads to structural changes in the geometry of the material, enhances elastic properties, and makes its morphology more clearly granular [168]. Doping SnSe with Ga, As, or Sb leads to the



Figure 16. TEM images of a hole that appears under the sequential action of a beam of 80 kV electrons on an MoS<sub>2</sub> layer. Scale bar is 1.5 nm [161].

appearance of semiconducting properties; doping with In gives semimetallic properties [169]. The selection of the doping element, its concentration, and the method of introducing the dopant both for the monochalcogenides and for the dichalcogenides of transition metals can considerably change a range of properties of the material, making its application more interesting for one field of science and technology or another.

There are many studies on the physical adsorption of thiols on  $MoS_2$  [170, 171]. Because of the absence of chemical bonding, the thiols can subsequently be easily extracted. Thus, TMD layers can serve as substrates for the transfer of biomolecules.

## 5. Properties of transition-metal dichalcogenides

### 5.1 Electronic properties

At present, there are numerous papers devoted to the study of the electronic structure of TMDs both theoretically [172-178] and experimentally [179-182]. The electronic properties of TMDs highly depend on the number of layers and their arrangement [183]: with a decrease in the number of layers, an indirect band gap transforms into a direct one, which lies lower by approximately 0.6 eV [178, 179, 184-191]. For example, in the case of an MoS<sub>2</sub> monolayer, the splitting of the crystalline field of d orbitals leads to a direct band gap equal to 1.8 eV at the K point (Fig. 17). This material can be used in photon detectors. In the MoS<sub>2</sub> monolayer, the band splitting is observed because of the absence of a center of inversion. For the valence band, the maximum and minimum values are attained at the respective  $\Gamma$  and K points. For the conduction band, the minimum value corresponds to the K point; the maximum value corresponds to the  $\Gamma$  and M points [38]. The effective masses near the K point are  $m_{\rm e}^* = 0.54$  for electrons in the conduction band and  $m_{\rm p}^* = 0.44$  for holes in the valence band. The precise values of the energy gaps and effective masses in  $MX_2$  are still debated because of the lack of direct measurements of these parameters.

Multilayer structures have an indirect gap (the  $\Gamma$ -K transition from the  $\Gamma$  point of the valence band to the K point of the conduction band (Fig. 17a)). The change in the band structure upon, for example, a change in the number of MoS<sub>2</sub> layers is caused by the effect of quantum tunneling

between the layers and is the result of changes in the hybridization of the pz orbitals of the sulfur atoms and of the d orbitals of the molybdenum atoms [179]. The direct optical transition in monolayer MoS<sub>2</sub> occurs at the K point of the Brillouin zone [192]. This was experimentally confirmed for the first time by an American-Chinese group [180]. Using molecular beam epitaxy, they obtained a set of high-quality MoS<sub>2</sub> films with thicknesses ranging from one to eight monolayers. In the samples obtained, they measured angleresolved photoemission spectra (ARPES) in situ, which give information about the dispersion laws of valence-band electrons. They confirmed the results of the theoretical calculations in [192, 193]. An exception among the 2D TMD layers is only the structure of  $\text{ReS}_2$ , in which the band gap does not change with an increase in the number of layers because of the weak interaction between the layers, which is due to the absence of an ordered stacking of layers [46].

By applying a uniaxial extension and causing shearing strains, it is possible to significantly decrease the band gap of monolayer TMDs [192]. For example, monolayer MoS<sub>2</sub> can become metallic under a biaxial tension by more than 10% or under a compression by more than 15% [193]. The lengthening can also increase the mobility of carriers in single-layer MoS<sub>2</sub>. The photoluminescence spectra for several MoS<sub>2</sub> layers showed that the gap width decreases by 120 meV for every 1% uniaxial extension of bilayer MoS<sub>2</sub> [194], whereas in three-layered MoS<sub>2</sub>, it increased by approximately 300 meV upon a 1% biaxial compression [195].

In 2D layers, the transfer and scattering of charge carriers are limited to the plane of the material. Therefore, the mobility of charge carriers in TMD layers has a stronger dependence on the temperature than in bulk samples. At low temperatures, scattering on acoustic phonons is dominant, whereas at high temperatures, the leading contribution comes from scattering on optical phonons [196].

The electronic structure of TMDs clearly depends on the coordination environment of the transition metal and on the number of its d electrons. The metal atoms donate four electrons, and therefore the oxidation degree of the respective metal and chalcogen atoms is +4 and -2. The half-filled d orbital of a transition metal (Cr, Mo, W) leads to the appearance of semiconducting properties of the TMDs; moreover, a decrease in the band gap is observed with an increase in the atomic number of the chalcogen. 2D TMD



Figure 17. Energy-band structure of (a) bilayer and (b) monolayer  $MoS_2$ . (c) Calculated values of their direct and indirect optical band as a function of biaxial deformation [192]. Teg red branch (*1*) corresponds to the valence band; the dark blue branch (*2*) corresponds to the conduction band.



Figure 18. Optical band gaps depending on the number of layers for main TMDs and other 2D materials: graphene (G), black phosphorus (BP),  $SnS_2$ , and h-BN [197].

materials can be dielectrics (HfS<sub>2</sub>), semiconductors (MoS<sub>2</sub>, WS<sub>2</sub>), semimetals (WTe<sub>2</sub>, TiSe<sub>2</sub>), and true metals (NbS<sub>2</sub>, VSe<sub>2</sub>), as well as superconductors (NbSe<sub>2</sub>, TaS<sub>2</sub>). The band gaps of many  $MX_2$  compounds were previously calculated by the DFT [47, 197]. Figure 18 depicts the values of the band gaps for many TMDs as functions of the number of layers.

As noted above, the electronic properties of TMDs depend not only on the number, arrangement, and combination of layers in the material but also on the presence of defects [198]. For example, the most frequently encountered defect in an exfoliated  $MoS_2$  layer of high purity is a sulfur vacancy [199]. Such a vacancy leads to the appearance of unpaired electrons in the lattice and n-type doping of the layer of the material; the excess of sulfur leads to p-type conductivity of the semiconductor. The p- and n-type regions can be encountered simultaneously in different regions of a sample; in experiment, it is therefore always necessary to pay attention to the local stoichiometry of the material [200].

Monolayer TMDs, just like graphene, are very sensitive to the ambient conditions. For example, upon treating films with oxygen plasma, a reduction is observed in charge mobility and in the conductivity because of the impregnation of nonconducting domains of  $MO_3$  (*M* is a metal) into the structure. These parameters, which depend linearly on the time of treatment of the films, can decrease by four orders of magnitude [201]. A clear dependence of the change in the charge density on the temperature was established: the conductivity of the films increases with an increase in the temperature [202].

#### 5.2 Mechanical and piezoelectric properties

Mechanical deformation significantly affects the electronic and optical properties of TMD layers. In [194, 203, 204], a linear dependence of changes in the optical band gap  $E_g(\varepsilon)$  of an MoS<sub>2</sub> layer on mechanical deformations ( $\varepsilon$ ) was established. This dependence can be used for the production of mechanically controlled photodiodes. The realization of different modes of loading on MoS<sub>2</sub> layers is shown in Fig. 19 [205, 206], where the results of calculations are compared with the experimental data for the  $E_g(\varepsilon)$  dependence. A similar effect is also predicted for nanoribbons of  $WX_2$  (X = S, Se) subjected to mechanical stresses [207], in which both a redistribution of the electron density and a shift of the Fermi level occur (Fig. 19b).

With a relatively small increase in deformations (< 0.5%), a linear dependence of the decrease in the peak energies of the exciton absorption of the  $MoS_2$  layer is also observed [203]. The computed values of the direct and indirect band gaps in MoS<sub>2</sub> structures as a function of biaxial stress are given in [192] (Fig. 17c). It was revealed that the gap width decreases under the effect of an external mechanical stress or external electric field up to the achievement of metallic conductivity for MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> monolayers, and bilayer heterostructures based on them [208], as well as for TiS<sub>2</sub>, CrS<sub>2</sub>, CrSe<sub>2</sub>, and CrTe<sub>2</sub> [209]. However, by no means does this apply to all TMDs. The band gap of ZrS<sub>2</sub>, ZrSe<sub>2</sub>, HfS<sub>2</sub>, and HfSe2 increases upon applying mechanical loads up to 6-8%, and then it decreases [209]. In the compounds with tellurium, ZrTe<sub>2</sub> and HfTe<sub>2</sub>, the gap width does not change under stress until the load reaches 4% and 2%, respectively, and then increases. In the recent study [210], a simulation was carried out (in the framework of the tight-binding approximation) of a change in the electronic properties near the K point of the Brillouin zone for various monolayer TMDs under their mechanical deformations, including bending. For the first time, a change in the effective masses and band gap  $E_{\rm g}$ , and the appearance of an effective magnetic field upon curving a lattice was described.

It was shown in [211] that the compression and stretching of  $SnS_2$  and  $ZrS_2$  monolayers leads to various nonlinear changes in the magnetic moment and in the gap width. This dependence is shown in Fig. 20. For  $SnS_2$ , the magnetic moment can reach  $4\mu_B$ .

**5.2.1 Piezoelectricity in TMD structures.** Piezoelectric materials are currently finding wide application in energy sensors and converters and in electromechanical and other devices. There is a great variety of natural and synthetic piezoelectric crystals; layered TMD materials have now joined this family.

The authors of [212] calculated the piezocoefficients for relaxed and unrelaxed atomic configurations of some monolayer TMDs, which are given in Table 4. They revealed a



Figure 19. Load applied to layers: (a) the compressive biaxial stresses with the use of a piezoelectric substrate [205] (PMN-PT —  $[Pb(Mg_{1/3}Nb_{2/3})O_3]_{0.7}$ ,  $[PbTiO_3]_{0.3}$ ; (b) bending of an MoS<sub>2</sub> ribbon, change in the charge distribution, and shift of the Fermi level before and after the bending; and (c) axial stretching [206].



Figure 20. Dependence of (a) the magnetic moment and (b) the gap width on deformation in ZrS<sub>2</sub> and SnS<sub>2</sub> monolayers [211].

Material	Relaxed structure, $e_{11}(10^{-10} \text{ Cm}^{-1})$	Unrelaxed structure, $e_{11}(10^{-10} \text{ C m}^{-1})$
2H-MoS <sub>2</sub>	3.06	3.64
2H-MoSe <sub>2</sub>	2.80	3.92
2H-MoTe <sub>2</sub>	2.98	5.43
2H-WS <sub>2</sub>	2.20	2.47
2H-WSe <sub>2</sub>	1.93	2.71
2H-WTe <sub>2</sub>	1.60	3.40

Table 4. Piezocoefficients, theoretical estimation [212].

periodic variation of the changes in the piezoelectric coefficients depending on the position of the atoms in the periodic table: moving transition metals upward inside Group VI or chalcogens upward in the group of chalcogens increases the coefficient.

In 2014, a piezoelectric effect was demonstrated for the first time in  $MoS_2$  with odd numbers of atomic layers [213]. The structures with even numbers of layers are not piezoelectric crystals. One  $MoS_2$  monolayer generates a current of 20  $\mu$ A or a voltage of 15 mV under compression by 0.53%; the corresponding electromechanical energy conversion is 5.08%. With an increase in the number of layers, the piezoelectric effect decreases.

### **5.3 Optical properties**

A change in the electronic structure of TMD layers is directly reflected in their optical properties. The presence of a direct band gap inherent in many TMDs makes these materials very promising for the development of electro-optical devices [197]. Under the transition from the multilayer semiconductor  $MoS_2$  with an indirect band gap to the monolayer structure (a direct-gap semiconductor), the photoconductivity, absorption spectra, and photoluminescence change [176, 184]. The deformations of the TMD layers lead to a softening of phonons in the Raman spectrum (degeneracy of the E' mode), to a decrease in the optical band gap and the intensity of photoluminescence, and to the transformation of the direct band gap into an indirect one. The red shift of the photoluminescence peaks is an indicator of a deformationinduced decrease of the gap width for both monolayer and bilayer  $MoS_2$  [185].

The electroluminescence in various layered heterostructures, which include TMD layers such as  $MoS_2$ ,  $WS_2$ , and  $WSe_2$ , has been observed by several groups of researchers [186–188]. Light-emitting diodes based on these materials demonstrate an efficient emission of light in a wide range of wavelengths.

TMDs are promising materials for photo-voltaic devices because they efficiently absorb light. An important characteristic of these materials is the transfer of charge through the interface. Heterostructures with TMDs demonstrate ultrahigh-speed and highly efficient transfer. For example, the time of charge transfer from the  $WS_2$  layer onto graphene was approximately 1 ps [189].

5.3.1 Valleytronics. TMDs are ideal materials for valleytronics (a term formed from 'valley' and 'electronics') [214]. Valleytronics is a new promising alternative to electronics. It is an analog of spintronics, where information is transferred by spin currents via the motion of the spin density of the electron gas. Valleytronics is based on the fact that some semiconductors have several minima of the allowed energy of conduction electrons (in the language of energy band theory, minima in the conduction band, which are called valleys). The key to the creation of valleytronic devices is a nonuniform distribution of charge carriers excited by light between valleys in the first Brillouin zone. The 'left-hand' and 'right-hand' valleys in the Brillouin zone absorb photons with a circular polarization differently; this phenomenon is called circular dichroism. The natural condition for the appearance of circular dichroism is the absence of a center of inversion [215].

The polarization of the valleys opens new opportunities for information processing devices, such as magnetoresistive random-access memory. However, the realization of intentional control of polarization remains a complex problem. In [216], for the first time, with the aid of the injection of spins from ferromagnetic semiconductors (Ga, Mn)As, an electric polarization of valleys in WS<sub>2</sub> was revealed. Earlier, a selective polarization of valleys was demonstrated with the use of circularly polarized light [217]. The lifetime of spinpolarized holes was more than 1 ns. At a temperature up to 90 K, the polarization reached 30%; with an increase in the temperature, the polarization rapidly decreased [218]. The calculation in [219] showed that in the WS<sub>2</sub> layer, a 50% polarization of carriers can be reached. It was also shown in [220] that a decrease in the polarization and photoluminescence can be obtained using mechanical deformations. Recent success in the optical pumping of the polarization of valleys in TMDs to a considerable extent has favored the development of the concept of valleys in information theory and in electronics. Nevertheless, before the new technology can be applied at a large scale, a large number of problems have to be solved, including the valley-assisted supply of long-lived charge carriers. These and other problems connected with valleytronics were considered in recent review [19].

5.3.2 TMD-based nonlinear optics. It is natural to expect the observation of the second harmonic generation on monolayer TMD structures that do not have a center of inversion and the observation of third-order nonlinear phenomena on structures with even numbers of layers with a center of inversion. Recently, a high ability to modulate nonlinear-optical processes near the region of selective resonance birefringence in one- and two-layered samples of WS2 was demonstrated in [221]. The authors observed an uncommon nonlinear refractive index, which, together with the saturation of absorption, depended on the number of layers in the sample (the level of their stacking). The prevailing physical mechanism responsible for the third-order optical nonlinearity appears to be the Kerr effect. It has been shown that WS<sub>2</sub> can serve as an efficient material for 2D devices of nonlinear optics. The nonlinear optical effects also manifest themselves nonstandardly in experiments with excitons.

**5.3.3 Excitons in TMDs.** It is known that the excitation of the electron subsystem of a material by a flux of light with the energy close to the width of the optical gap is accompanied by the appearance of excitons—quasi-particles consisting of coupled electron—hole pairs; their states form a number of levels lying below the bottom of the conduction band. In 2D TMD materials, the energy pattern of excitons that is observed by spectroscopic methods in the reflection and

absorption of light differs significantly from the one for excitons observed in the case of a bulk material, because the excitons are concentrated in the plane of the layer. A decrease in Coulomb screening causes the formation of optically selected excitons with a high energy of coupling. This leads to the existence of nonhydrogen-like Rydberg series of 2s, 3s, 4s, etc. exciton states (Fig. 21a).

The optical spectra of the TMD layers studied are characterized by three main exciton peaks. Exciton A (1s) corresponds to the fundamental optical gap of the material with an energy of approximately 1 eV. Exciton B also corresponds to the transition from the K point, but between bands with opposite spins. Peak C comprises other excitations of quasiparticles, including trions—positively or negatively charged excitons and bi-excitons (see the example in Fig. 21a). Trions with binding energies of 10–110 meV, which do not have analogs in the usual semiconductors, can be observed even at room temperature.

In two-photon experiments, in the photoluminescence spectra of monolayers of WSe<sub>2</sub> (Fig. 21b) and WS<sub>2</sub>, peaks were observed located at large distances from each other. which does not correspond to the usual Rydberg series and is therefore a consequence of not purely Coulomb electron-hole interaction. Furthermore, also observed were biexciton and trion peaks in the range 10-100 meV, which are described well in the framework of the unified Wannier-Mott model [222]. The breaking of inversion symmetry, together with the large spin-orbit coupling in TMDs, leads to the coupling of spins and their carriers in the k space of the valleys; in other words, the circular polarization ( $\sigma^+$  or  $\sigma^-$ ) of the absorbed or emitted photon can be directly related to the selective excitation of carriers in one of two nonequivalent K valleys  $(K^+ \text{ or } K^-)$ . The key role of the exciton exchange interaction is discussed in [223]. It was shown that the optical alignment of excitons (exciton-valley coherence) can be achieved after one- or two-photon excitation.

The authors of [224] used the method of spectroscopy of polarized time-resolved photoluminescence to study the properties of the spin–valley coupling for both neutral and charged excitons in MoS<sub>2</sub>, MoSe<sub>2</sub>, and WSe<sub>2</sub> monolayers. The authors of [225] investigated the dynamics of the process of exciton–valley depolarization in the Kerr effect with a



**Figure 21.** (Color online.) Excitons in 2D structures of WS<sub>2</sub> and WSe<sub>2</sub>: (a) derivative of the contrast spectrum (RCD) of the reflected signal of a WS<sub>2</sub> monolayer; the ground state (transition 1s–AX), the peak due to trions (AX<sub>T</sub>), and the highest excited exciton states are noted by the appropriate quantum numbers (see the diagram to the right); the inset shows the variation of the reflection coefficient  $\Delta R/R$ , which allows correlating the peaks with the exciton transitions corresponding to A, B, and C. (b) Spectrum of the second harmonic generation depending on the energy of two photons; the black (*I*) and green (2) curves are the Gaussian functions of the profiles of the 1s and 2s/2p transitions [224].



**Figure 22.** (Color online.) Dynamics of Kerr rotation at T = 4 K for  $\sigma^+$  and  $\sigma^-$  of the pumping of a WSe<sub>2</sub> monolayer. The insets: to the left, a diagram of the selection rules for the excitons formed by photogenerated charge carriers in the K<sup>±</sup> valleys and coupled due to the long-range exchange interaction; to the right, a schematic of the experiment with circularly polarized pumping light incident perpendicularly to the layer and incident and reflected probing beams; the change in its polarization angle is shown in the main graph [225].

circular pumping in  $WSe_2$  monolayers (Fig. 22). In a later study [226], this Kerr effect was interpreted based on the model of exciton spin dynamics controlled by a long-range interaction. These studies allow developing a strategy of the manipulation of exciton emission, which is valuable for creating new 2D light-emitting devices.

Another method for controlling valley–exciton coherence is the application of a magnetic field. Such control is a first step toward the complete control of qubits based on the degrees of freedom of the valleys. A single qubit is realized, for example, by the rotation of one spin through any angle [227].

Coherent optical control can efficiently change the properties of electronic valleys in TMDs. Very recently [228], a new type of the optical Stark effect in a  $WS_2$  monolayer was investigated. This effect, as was shown, is indirectly related to a rearrangement of intervalley biexcitons under the action of circularly polarized light. This helicoidal optical control not only induces a shift of the exciton energy downward in the excitation valley but also leads to an anomalous shift of the energy in the opposite valley, which is forbidden by the selection rules for excitons in general, but has now become accessible for intervalley biexcitons. These results indicate the critical (thus far disregarded) role of biexcitons in the connection between two seemingly independent valleys. This effect must play an important role in the optical control of valleytronic devices.

**5.3.4 Photoluminescence.** In [229],  $WS_2/MoS_2$  structures epitaxially grown on each other and obtained via the transfer of one layer onto another were considered. In both cases, a decrease in the photoluminescence by two orders of magnitude compared with an  $MoS_2$  monolayer was noted. In both cases, it was noted that the bilayer  $WS_2/MoS_2$  demonstrates an improved absorption compared with  $WS_2$  or  $MoS_2$  taken separately, which opens new opportunities for photonic devices, in particular, for those that require good separation of excitons or strong absorption of light (solar cells, photodetectors, photocatalists). The band structure of a bilayer favors charge separation: electrons go to  $MoS_2$  and

holes, to  $WS_2$ . This charge separation between the different layers decreases the spatial overlap between the wave functions of the electrons and holes, which eventually leads to a decrease in the photoluminescence efficiency. A significant decrease in photoluminescence under other experimental conditions of the preparation of such heterostructures was reported in [230].

For the WSe<sub>2</sub>/MoS<sub>2</sub> heterostructure, the photoluminescence data [231] demonstrate that by forming different heterostructures, it is possible to control the optical properties of the compounds obtained. For WSe<sub>2</sub> and MoS<sub>2</sub>, strong exciton peaks are respectively observed at 1.64 and 1.87 eV, while for the WSe<sub>2</sub>/MoS<sub>2</sub> heterostructure, the peak is at 1.55 eV, which lies lower in energy than those for the components of its layers. A weak photoluminescence signal is also observed that corresponds to the exciton bands of separate layers.

## 6. Application of transition-metal dichalcogenides

In recent decades, researchers from various countries have been actively searching for an alternative to traditional electronics. It is assumed that the new nanoelectronics can be based on 2D dichalcogenides of transition metals [232].

Transistors. In one of the first studies concerning the production of transistors that contain TMDs [125], a  $WS_2$ layer was used in the BN/G/WS<sub>2</sub>/G heterostructure on an  $SiO_2/Si$  substrate obtained by deposition from the gas phase, in which tunneling of current carriers occurred in the vertical direction. Somewhat later, a usual field-effect transistor with the ON/OFF current ratio reaching six orders of magnitude was assembled entirely of 2D materials with an operating  $MoS_2$  layer with a mobility of 33 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [233]. Also reported in [233] was the production of a diode with graphene electrodes and an  $MoS_2/WS_2$  junction, with a high (~ 10<sup>5</sup>) ratio of the forward and reverse currents (with a low value of the latter). On the whole, transistors on the graphene/TMD structure created with the use of WS<sub>2</sub> as the barrier demonstrated better characteristics than those with the use of MoS<sub>2</sub>. Such vertical field-effect transistors open new opportunities for flexible and transparent electronics.

**Phototransistors.** A phototransistor based on an  $MoS_2$  monolayer was obtained by chemical vapor deposition in [234]. Complete switching between the ON and OFF modes occurred in 50 ms and was fully controlled by incident light. The phototransistor demonstrated stable characteristics: the photoconductive response reached 7.5 mA W<sup>-1</sup> under low-power illumination (80  $\mu$ W) and a voltage of 50 V. For comparison, the phototransistor was also prepared on the basis of six-layer MoTe<sub>2</sub>; its photoresponse reached 10<sup>3</sup> mA W<sup>-1</sup>; the ON/OFF ratio of currents was 10<sup>5</sup> at room temperature [70]. The unique characteristics and relatively low production cost of such phototransistors must stimulate the development of new photodevices based on TMDs.

**Power accumulators.** Since the 1990s, work is constantly under way on the study of systems related to the primary (disposable) current sources and on the solution to problems concerning reusable lithium systems. The overwhelming majority of the studies is devoted to the introduction of lithium particles or other materials into lithium storage batteries [236]. Many TMDs with a graphene-like structure are considered alternatives to graphite for the anodes in rechargeable ion batteries. The sulfurized WS<sub>2</sub> [117] and  $SnS_2$  (with a thickness of 3–4 nm) [237] have the respective capacity of 566.8 and 647 mA h g<sup>-1</sup>, even after 50 recharge cycles. The capacity of  $MoS_2$  is 771.9 mA h g<sup>-1</sup>; that of  $MoS_2$ flakes ('nanoflowers') doped with nitrogen is 967.6 mA h  $g^{-1}$ [238]. Titanium disulfide was one of the first cathode materials based on which a reversible lithium source of current was realized as long ago as the 1970s [239]. The theoretical value of the specific capacity of TiS<sub>2</sub> reaches 717 mA h  $g^{-1}$ ; in reality, values 190–240 mA h  $g^{-1}$  have thus far been obtained. The substitution of vanadium for titanium leads to a significant increase in the intercalation capacity of the material; the specific capacity reaches  $260 \text{ mA h g}^{-1}$  [240]. At present, the best characteristics are reached in TMDgraphene composites; for example, the capacity of the  $MoS_2/WS_2/graphene-oxide$  heterostructure with the Mo/Wratio equal to 1:1 is 1032 mA h g<sup>-1</sup> after 100 cycles of recharging [241]; on the MoS<sub>2</sub>/graphene composite, the capacity of 1020 mA h g<sup>-1</sup> was obtained [242]. However, the long-term operation of such super-capacitors has thus far been investigated insufficiently.

**Light absorbers.**  $MoS_2$ ,  $MoSe_2$ , and  $WS_2$  can absorb up to 5–10% of visible light; this is an order of magnitude greater than in the case of GaAs or Si. The comparative characteristics of graphene, TMDs, and some other materials are given in Table 5. The absorbed flux of photons per cm<sup>2</sup> is reduced to the equivalent electric current units [243].

**Photodetectors.** To date, photodetectors based on the graphene/rhenium-doped  $MoS_2$  heterostructure have been obtained [128]. The presence of rhenium leads to the transfer of charge from the molybdenum sulfide to graphene. The photocurrent is generated at the interface between graphene with an uncovered and covered  $MoS_2$  fragment. The molybdenum disulfide integrated with a plasmon antenna is a good acceptor of hot electrons [244]. The photoresponse is 5.2 A  $W^{-1}$  at the light wavelength of 1070 nm, which corresponds to the same level as in silicon photodetectors on hot electrons.

**Catalysts.** TMD materials can become an alternative to platinum as catalysts for specific reactions; their advantages are a relatively low cost and ease of fabricating. Because the atoms of chalcogens retain hydrogen, only the surface of 2D materials is of interest in the reaction of the release of hydrogen, a good characteristic for which is the value of the Gibbs free energy  $\Delta G_{H^*}^0$  [245]. It was theoretically confirmed in [245] that the bulk 3D crystal of MoS<sub>2</sub> is not a catalyst for the release of hydrogen from water. It was also shown there that for the MoS<sub>2</sub> monolayer, the value of the free energy

Table 5. Absorbed flux of photons [243].

Material	Band gap at 300 K, eV	Absorbed flux of photons, mA cm <sup>-2</sup>
Graphene	0	2.0
MoS <sub>2</sub>	1.89	3.9
MoSe <sub>2</sub>	1.64	4.6
WS <sub>2</sub>	1.96	2.3
Si	1.11	0.1
GaAs	1.42	0.3
Polymer R3NT	1.95	0.2

equal to 0.14 eV, which is close to the thermoneutral value, corresponds to the 75% coating of the surface with water. For  $MoS_2$ , this energy is equal to 0.231 eV, which corresponds to 50% coating. The calculations in [126] also showed good activity of an  $MoS_2$  monolayer for the reaction of the release of hydrogen. Therefore, the preparation of catalytic cells from nanosize TMD clusters should be of interest.

The 2D materials  $MoS_2$  and  $MoSe_2$  were also suggested to be used as electrocatalysts for hydrogen evolution reactions [191, 246]. Investigated in [191] were  $MoS_2$  electrocatalysts based on a 3D material and a 2D sheet in which the photocurrent was several times higher than in the bulk material.

As is known, conductivity plays a major role in the productivity of electrocatalysts. It was shown in [247, 248] that the weak conductivity of  $MoS_2$  can be compensated by using composites containing it. For example, an electrocatalyst based on the  $MoS_2/graphene$  composite demonstrated stable behavior even after two-hour static loading (200 mV), which agrees well with theoretical calculations [246].

MoS<sub>2</sub> can serve as a photocatalyst for splitting water [249]. It is stable in aqueous solutions under normal conditions. The width of its optical gap, equal to 1.9 eV, lies in the visible range. A comparison of the redox potentials of water with the energy of the gap edges in the energy band structure of the SnS<sub>2</sub> monolayer indicates that the maximum of the valence band is energetically favorable for oxygen release, and the value of the minimum of the conduction band is sufficient for hydrogen evolution. Therefore, for the photocatalytic dissociation of water to occur, an external bias potential of at least 0.9 V is necessary [249].

**Biochemical applications.** A porous sheet of  $MoS_2$  is an extraordinary material for DNA sequencing. Molecular dynamics and DFT calculations showed that  $MoS_2$  gives a separate clearly pronounced signal with a signal-to-noise ratio equal to 15 in detecting the DNA base [250]. In contrast to graphene, nanoporous  $MoS_2$  membranes do not require special surface treatment to avoid the hydrophobic interaction of the DNA with the surface and show a better productivity of treating the DNA samples [251].

A large array of biosensors based on field-effect transistors made of  $MoS_2$  was grown by chemical vapor deposition. The protein was recognized via comparison/identification with a signal obtained by a different method, when it became immobilized and its electronic signal could be read out [253]. The biochemical applications of layered TMD structures are considered in more detail in [252].

TMDs with quantum dots. In [254], structures with CdSe/CdS quantum dots located on 2D MoSe<sub>2</sub> and on a layer of h-BN that separates the quantum dot from the TMD were obtained and investigated. It was shown that MoSe<sub>2</sub> efficiently suppresses the fluorescent signal when the quantum dot is excited by laser light. The presence of an h-BN layer between the quantum dot and MoSe<sub>2</sub> leads to a decrease in the suppression efficiency. The capacity to control both the refractive index and the absorption offers the possibility of controlling the energy transfer in nanosize structures, which will be used in next-generation optoelectronic devices. Another application of TMDs connected with quantum dots was investigated in detail in [255]. In a system that consists of an MoS<sub>2</sub> or WS<sub>2</sub> layer applied onto CdS(Se) quantum dots, a resonance energy transfer by the Förster mechanism is observed. The adsorption by the TMD layer reaches 75% of the quantum dot photoluminescence.

**Renewable power generation.** An unusual application of  $MoS_2$  as a membrane between fresh water and seawater in a super-power energy source was proposed in 2016 [256]. The semipermeable porous membrane separates two liquids that have different salt concentrations. Until the concentrations become equal, the system attempts to arrive to the osmotic equilibrium, ions pass through the membrane, and electrical power is released. The specific power of such a membrane is 250 times higher than that for the available renewable electrodialysis systems. The authors of [256] assume that molybdenum disulfide can be used in water desalination devices and for the transfer of protons in solutions.

In the recent brief review [257], results obtained with the use of layered 2D materials are given, including TMDs and their potential applications; in [197], advances in the field of optoelectronic devices based on 2D TMD materials (light-emitting diodes, photodetectors, lasers, etc.) are discussed.

Below, we discuss the latest (2016) achievements in the creation of TMD-based nanodevices.

According to recent forecasts, the scaling of silicon transistors has reached its limits. A decrease in the length of the gates to below 5 nm is difficult because of the influence of the narrow channel. As an alternative to silicon, many semiconductors are being considered that can be obtained in the form of thin layers of a uniform thickness (up to a monolayer) and which have lower dielectric constants and band gaps of larger widths. In [258], a transistor is described based on molybdenum disulfide with a gate that has a 1 nm physical length, with a single-layer carbon nanotube used as the gate electrode. These ultrashort devices demonstrate excellent switching characteristics: a switching rate with the ON/OFF ratio ~ 10<sup>6</sup>. A simulation shows the effective length of the channel to be  $\sim 3.9$  nm in the ON state and  $\sim 1$  nm in the OFF state. Very recently, based on an MoSe<sub>2</sub> sheet obtained by the lithography method, a field-effect transistor was prepared with the size of  $10 \times 2 \ \mu m^2$ . Its response rate was less than 25 ms; the switching frequency was 10<sup>6</sup>. The mobility of electrons was 23 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>; the mobility of holes was 15 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [83]. At present, these are record characteristics for TMD-based transistors.

Materials such as activated carbon, carbon nanofibers, carbon nanotubes, and graphene are considered promising for creating supercapacitors. Among them, activated carbon is most frequently used as the material of electrodes because of the large area of its surface. However, the nonuniform distribution of the sizes of pores in activated carbon limits the use of their effective surface in supercapacitors. Recently, carbon-based nanomaterials have been widely studied as electrodes. The integration of 2D TMD layers with other functional nanomaterials pursues the same purpose: to improve their electrochemical parameters. A high workability of hybrid supercapacitors based on an array of nanowires surrounded by 2D TMD layers was recently reported in [259]. Such stable structures were obtained by sequential oxidation and sulfurization. They demonstrated a remarkable reproducibility of the charge-discharge process for more than 30,000 cycles [259].

In [123], adsorption and diffusion processes were theoretically investigated in graphene/metal-disulfide structures ( $MoS_2$ ,  $SnS_2$ , and  $Li_2S$ ). It was established that the adsorption of Li atoms on the metal disulfide is enhanced significantly because of the presence of graphene; this contributes to the additional arrangement of Li atoms. The synergistic effect between graphene and the metal sulfide upon the adsorption of Li atoms at the interfaces appears as a result of the charge distribution on graphene in the  $Li_2S/G$ system. Although the adsorption energies of Li atoms at the interfaces of  $MoS_2/G$ ,  $SnS_2/G$ , and  $Li_2S/G$  structures are increased, the energy barriers for the diffusion of Li at the interfaces can be supported as before at relatively low values because of the uniform accumulation of electrons near graphene upon the atomic adsorption of Li into the interfaces. In storing lithium atoms at the interface, this behavior gives an increase in the capacitance and in the charge accumulation rate.

The variety of the optical properties of 2D layers and TMD combinations with other 2D structures in the visible range (for example,  $E_g \sim 2.0$  eV for WS<sub>2</sub> and  $\sim 1.9$  eV for MoS<sub>2</sub> [17, 184]) (Fig. 23) is promising as regards their use in optical and optoelectronic devices such as displays, night-vision devices, diagnostic medical instruments and terahertz and radio-frequency devices. Sufficiently complete surveys of such applications of TMD structures were made in 2015–2016 [16, 17].

The first array of MoS<sub>2</sub> photodetectors has already been prepared, with the size of elements being 20 and 250  $\mu$ m on a 4 inch substrate of SiO<sub>2</sub>/Si [260]. True, thus far the photocurrent obtained is only about 2  $\mu$ A cm<sup>-2</sup> under the illumination by light with a power of 12.5 mW cm<sup>-2</sup>. However, an improvement in the technology of the production of cheap films of TMD materials will lead to the appearance of new types of highly economical solar batteries [261].

We now note the very latest advances in the application of TMDs in laser optics.

In Fig. 24a, a recently fabricated [262]  $Pr^{3+}$ -based fiber laser is shown, in which a WS<sub>2</sub> film was used to create a high quality factor at the end of the fiber. This film has a nonlinear absorption and strong reflection of orange light; hence, the absorption falls sharply at high radiation power, and the opening of this unique mirror occurs.

Ebessen's group [263] was able to achieve a strong coupling between polaritons and excitons of WS<sub>2</sub> monolayers at room temperature by their insertion into a metallic optical nanocavity. This feature unambiguously manifested itself in radiation and reflection spectra, which showed a large Rabi splitting (101 meV) in the employed Fabry–Pérot cavity (Fig. 24b). The unambiguous influence of the WS<sub>2</sub> monolayer on the strong coupling of modes in easily fabricated metallic resonators at room temperature suggests numerous opportunities to combine spintronics and valleytronics. This should open interesting opportunities in the fields of not only technology but also fundamental physics.

## 7. Conclusions

To summarize, there is substantial progress in the study of diverse quasi-two-dimensional TMD materials, both monolayers and multilayer films. In this review, we presented an analysis of the experimental and theoretical work that appeared in the last few years in the field of preparation and application of the rapidly growing family of TMDs. It has been shown that these structures have diverse physicochemical properties, which already have significant prospects for application in a wide range of technologies, in science, and in engineering. The obtained prototypes of TMD-based devices show a high potential for the application of such 2D materials in optoelectronics and photonics. Some other possible applications of TMDs connected with the task of the



**Figure 23.** (Color online.) (a) Different ranges of the electromagnetic spectrum that cover the allowed energy bands in the electron spectra of quasi-twodimensional materials: (b) hexagonal boron nitride (h-BN), (c) molybdenum disulfide ( $MoS_2$ ), (d) black phosphorus (BP; x and y are the anisotropic directions of its structure), and (e) graphene. TMDC—transition-metal dichalcogenides.



Figure 24. (Color online.) Optical devices with the application of TMDs: (a) fiber orange laser with a compact quality factor insertion cell (installation under operating conditions of the experiment where the  $Pr^{3+}$  fiber laser shines brightly and whose end is covered with a WS<sub>2</sub> film); (b) illustration of the device (film of a WS<sub>2</sub> monolayer in the Fabry–Pérot resonator) for the observation of the spectrum of the strong coupling of the exciton and polariton branches (straight and parabolic dashed lines in the spectrum constructed using the data from the experiment in the form of the black (*1*) and red (2) circles in Fig. 24c); (d) splitting of the transition from the valence band (VB) to the conduction band (CB) at the frequency  $\omega_p$  under microwave irradiation at the frequency  $\Omega_R$  [263].

development of methods of mass production of large defectfree systems were also considered.

We note the most important results that have been obtained to date in the TMD research.

(1) Methods for obtaining macro-size single-layer structures of high quality (with an area up to several cm<sup>2</sup>) have been developed.

(2) Heterostructures based on TMDs with the energy gap in the range from the near infrared to visible light demonstrate a strong sensitivity of properties to the action of light, which makes their application in optical-electronic, spinoptical, and photo-voltaic nanodevices and in catalysis possible and potentially interesting.

(3) On the basis of TMDs, various nanodevices have already been obtained, such as biosensors, photodetectors, microwave generators, and high-speed field-effect transistors.

(4) A number of interesting theoretical predictions have been made. For example, quite recently theoretical studies of zigzag (ZNR) and armchair (ANR) MoS<sub>2</sub> nanoribbons have appeared [264]. In the first case, it is shown that because of the replacement of the channels for the passage of current at high voltages from the central part of the ZNR to the boundary parts (switching-on of states localized at these parts), a negative differential resistive (NDR) effect appears. In the second case, the authors showed that at room temperature the thermoelectric effect is 3 to 4 times higher in doped ANRs than in monolayer  $MoS_2$ , which is promising for applications in thermoelectric generators. The authors of [265] discovered new unexpected opportunities in valley spintronics: based on numerical examples, they have shown that in 2D TMDs the created disorder in the nanoribbons is converted from a harmful factor into a strong source of valley and spin polarization. Strong spin-orbit coupling was shown to be attainable in systems with semiconductor TMDs (MoS<sub>2</sub>,  $WSe_2$ ,  $WS_2$ ) and the SiO<sub>2</sub> substrate [266]. The coupling value is of the order of 10 meV, which is two orders of magnitude greater than the spin-orbit coupling observed in graphene. This makes the graphene/TMD system promising for the realization and studies of different spin-dependent transport phenomena, in particular, the spin Hall effect.

Without a doubt, investigations of 2D dichalcogenides and chalcogenides of transition metals, in spite of the variety of subjects already covered, will also be developed in the coming decades, which will lead to their further introduction into electronics, spintronics, and optoelectronics, including the new branch that was born from their symbiosis, valleytronics.

## Acknowledgments

This study was supported in part by the Russian Science Foundation, grant No. 14-12-01217.

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