Chapter 1
Introduction

Transition metal dichalcogenides (TMDCs) are old; the oldest known samples of MoS_2 date over 2.9 billion years [1]. A comprehensive, even though somewhat outdated, review about structure and properties of three-dimensional TMDCs can be found in [2]. Despite rather similar structure, TMDCs cover a wide spectrum of properties ranging from insulators, to semiconductors, to metals. This diversity of properties is a consequence of the existence of non-bonding *d* bands and the degree to which they are filled with electrons. It is also interesting to note that one of the first reports on monolayer TMDC was published in the mid 1980s [3] while few-layer-thick MoS_2 single crystals were reported even earlier [4] but these publications remained largely unnoticed.

These old materials experienced a renaissance after the discovery of unique electronic properties of graphene, for which K.S. Novoselov and A.K. Geim were awarded the Nobel Prize in 2010. In single-layer graphene's band structure, the linear dispersion at the K points gives rise to novel phenomena, such as the anomalous room-temperature quantum Hall effect, and opened up a new category of Fermi-Dirac physics. Graphene is a fantastic electronic and thermal conductor, and graphene-based materials have been proposed for a host of applications ranging from high-speed electronic and optical devices, energy generation and storage, hybrid materials, chemical sensors, and even DNA sequencing, and a variety of proof-of-concept devices have been demonstrated.

The success of graphene generated explosive interest in other two-dimensional materials, where use of different elements opens novel opportunities for the exciting new physics and ultimately thin devices. Two-dimensional TMDCs [5], which can be easily exfoliated [4] and present very interesting electrical and optical properties, became one of the most intensely studied areas of solid state physics and technology. Among these materials, semiconducting TMDCs are of special interest since the possibilities of gap engineering by varying the number of layers makes them exciting candidates for device applications. Figure 1.1 shows the number of publications per year found in the Web of Knowledge with the key words "MoS_2" and "monolayer", which clearly indicates an exponential increase in interest in the past several years.

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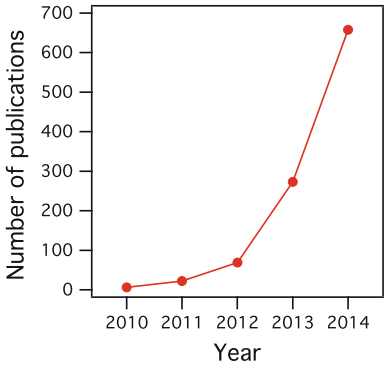

Fig. 1.1 The number of publications found by the Web of Knowledge with the search key words "MoS_2" and "monolayer"

The band structure of those compounds dramatically changes from bulk to single-layer samples, going from indirect gap in bulk materials to direct gap in monolayers, underscoring the important role of interlayer coupling. In addition, their electronic properties are very sensitive to external conditions such as temperature, pressure or strain.

The presence of boundaries, vacancies and/or adatoms in the samples can lead to interesting magnetic properties. Strong spin-orbit interaction in TMDCs alongside with the coupling of the spin, valley and layer degrees of freedom open unprecedented possibilities from both fundamental and applied perspectives. This possibility is especially interesting in single layers where the spin-orbit coupling lifts the spin degeneracy of the energy bands due to the absence of inversion symmetry. Furthermore, reduced dielectric screening in monolayer and few-layer samples of TMDCs makes excitonic effects exceptionally strong.

These and other properties of two-dimensional TMDCs are the subject of this volume. There have been numerous reviews published on this topic [6–21] as well as an edited volume on MoS_2 [22] and the interested readers can check them for details that may be missing here.

The TMDCs are about sixty in number; two-thirds of these assume layered structures. Most of these layered materials are synthetic but some exist naturally, e.g. natural MoS_2 crystals with the $2H$ and $3R$ phases (see Sect. 3.1.2 below for the explanation of the symbols) are quite common. The structure of this mineral, molybdenite, was first determined in 1923 [23]. Bulk TMDC crystals are conventionally grown using the chemical vapor transport method [24–26], where purified dichalcogenide material in the form of powder is mixed with the transport agent, usually bromine or iodine and sealed in a quartz ampoule. The quartz ampoule is introduced into a zone electric furnace, with a temperature gradient formed along the tube [27, 28]. Pure component materials, for example W and Se for the growth of WSe_2 can also be used.

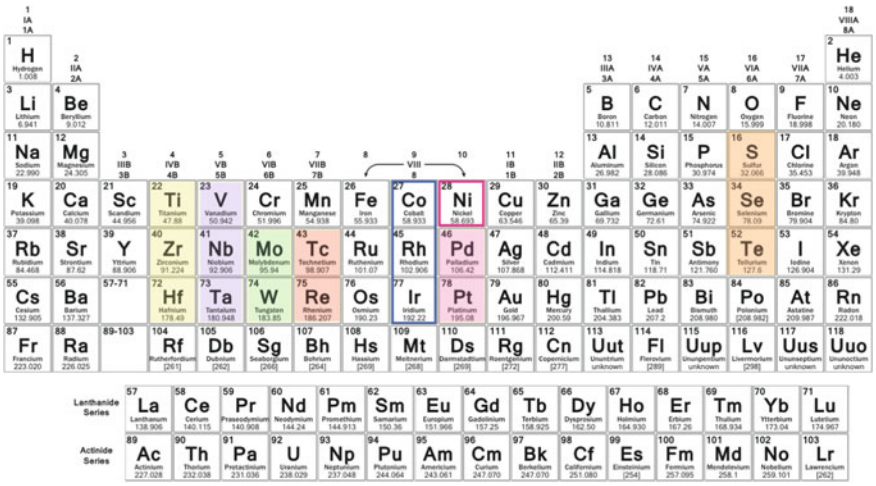

Fig. 1.2 The transition metals and the three chalcogen elements that crystallise into layered structures are highlighted in the Periodic Table. The transition metals that crystallise into layered structures with some chalcogens but not with others are framed. The columns in the Periodic Table show both 'old' and new labels, i.e. chalcogens can be referred to as either group VIA or group 16 elements

In Fig. 1.2 the Periodic Table of elements is shown with the transition metals that form layered structures highlighted in different colours; those metals that form layered structures with some chalcogens but not with others are colour-framed, e.g. while $NiTe_2$ has a layered structures, NiS_2 possesses a three-dimensional pyrite structure. Chalcogen atoms are highlighted in orange. Also shown in the Figure are the "old' and "new" notations for the columns, thus chalcogen atoms will be referred to as either group VIA or group 16 elements. Later in this volume the old and new notations are used interchangeably, following the original publications.

As can be seen from Fig. 1.2, group 4–7 metals are predominantly layered while some of the group 8–10 metals form three-dimensional crystals. Recent interest is mainly associated with semiconducting TMDCs, which form the main body of this volume. At the same time, we would like to mention that there are also reports on other materials, such as noble-transition-metal (Pt and Pd) dichalcogenides [29, 30] and tin disulphide [31], the latter being indirect-gap semiconductors.

The present monograph is organised as follows. In Chap. 2, the readers are introduced to chemistry of chalcogenides and transition metals, which is followed by Chap. 3, where the structure and properties of bulk TMDCs are briefly reviewed. Chapter 4 describes the major fabrication methods to produce two-dimensional TMDCs. In Chaps. 5 and 6, atomic and electronic structures of monolayer and few-layer TMDCs are discussed in detail. Raman scattering, which evolved into a major method of TMDCs characterisation, is the subject of Chap. 7. Luminescence from 2D TMDC and exciton behaviour are subsequently discussed in Chaps. 8 and 9, followed by Chaps. 10 and 11 dedicated to magnetism and spin-valley coupling in 2D TMDCs.

Chapter 12 is dedicated to miscellaneous phenomena observed in 2D TMDC, that are too short to be the subject of dedicated chapters, e.g. second-harmonic generation. Engineered heterostructures based on 2D TMDCs are described in Chap. 13, followed by the conclusive Chap. 14 that discusses emerging applications of 2D TMDCs in nanoelectronics.

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Kolobov, A.V.; Tominaga, J.

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