Available online at www.sciencedirect.com

ScienceDirect

Progress in Crystal Growth and Characterization of Materials 62 (2016) 9–28

www.elsevier.com/locate/pcrysgrow

Review

Recent progress in chemical vapor deposition growth of two-dimensional transition metal dichalcogenides

Swee Liang Wong, Hongfei Liu, Dongzhi Chi *

*Institute of Materials Research and Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Singapore 138634, Singapore*

Available online 28 July 2016

Abstract

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have received significant attention recently due to their unique properties such as a transition from indirect to direct band gap when thinned down to a monolayer and also valley-dependent photoluminescence. In addition, being a semiconductor with considerable mobility, it has been touted as a candidate in next generation electronics. However, a major hurdle to its implementation is the difficulty in producing large areas of these 2D TMDCs with well-defined thicknesses. In this review, we will first introduce the basic properties as well as the various synthesis methods of 2D TMDCs. Focus will be placed on recent advances in chemical vapor deposition (CVD) growth as they currently yield the largest areas. Obstacles present in CVD growth will be presented and existing solutions to them will be discussed in tandem with current characterization methods for evaluation of crystal quality. Through our presentation on the latest approaches to issues in CVD growth, we hope to present the readers a perspective on recent developments as well as providing an outlook on the future of CVD growth of TMDCs.

Keywords: Transition metal dichalcogenides; Two-dimensional; Chemical vapor deposition; Material modification

1. Introduction

In recent years, since the Nobel Prize was awarded for graphene in 2010, there has been considerable research in the field of two-dimensional (2D) materials [1–5]. One particular class of 2D materials, transition metal dichalcogenides (TMDCs) has garnered much attention. TMDCs, like graphene, are layered materials which can be thinned down to a single layer, albeit being three atoms thick instead of one [6]. TMDCs have exhibited considerable charge mobility with a semiconducting band gap [7–10], allowing significant intrinsic on–off current ratios compared to graphene as well as photoluminescence [8]. Furthermore, TMDCs have also shown remarkable physical and optoelectronics properties such as high tensile strength [11] as well as exhibiting intrinsic spin-valley polarization of its electronic bands [8]. Thus, 2D TMDCs have been touted to be a promising component in advanced device technology and optoelectronics. TMDCs have also been applied as a biocompatible platform in a variety of biomedical applications [12].

However, a bottleneck to widespread application of these materials is the cost and yield of its production. Hence, much effort has been placed in the research on the various production methodology of these 2D TMDCs

* Corresponding author. Institute of Materials Research and Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Singapore 138634, Singapore. Fax: +65 64168918.

E-mail address: dz-chi@imre.a-star.edu.sg (D. Chi).

http://dx.doi.org/10.1016/j.pcrysgrow.2016.06.002
0960-8974/

to improve its yield while maintaining sufficient quality. At the moment, the most promising way to have high quality large area yield of 2D TMDCs is through chemical vapor deposition (CVD) [13–15]. Thus, in this review, we first aim to provide readers with a background overview of the basic properties of 2D TMDCs as well as the different synthesis techniques currently available. Following which, an in-depth review on the current progress in CVD growth of TMDCs will be conducted, taking into account the challenges faced and the solutions employed to tackle them. Lastly, a general outlook on the future direction of CVD based synthesis of TMDCs will be provided.

2. Basic properties of 2D TMDCs

TMDCs are layered materials consisting of a hexagonal arrangement of transition metal atoms sandwiched between two layers of group six chalcogenide atoms such as S or Se [6,8]. The positions of the elements in the periodic table are highlighted in Fig. 1a [6]. Depending on the elemental makeup, the electronic structure of these TMDCs can range from an insulating character in the case of HfS_2 to semiconductors such as WS_2 and MoS_2 as well as metallic in nature for NbS_2 and VSe_2 [6]. In this review, we will place our attention on semiconducting TMDCs as much of the CVD based growth are focused on them.

In TMDCS, the transition metal atoms are covalently bonded to a triagonal arrangement of chalcogenides within the same layer while individual layers are held together through non-covalent van der Waals forces. Fig. 1d describes the physical structure for a particular TMDC, MoS_2 [10]. As the interlayer van der Waals forces are much weaker, the individual layers of the bulk 3D material can be easily separated from each other, leaving behind a single layer which is only three atoms thick (≈0.7 nm), revealing a true two-dimensional nature. Furthermore, no dangling bonds are available on the surface of each layer for reaction with the ambient environment, enabling significant stability of the material even when it is thinned down to a single layer.

Unlike graphene which only has a single phase as it contains only a single element and is a single atom thick, a single layer of TMDC which consists of three layers of atoms (a central transition metal sandwiched between chalcogenides) can exist in two different phases, depending on the relative arrangement of the three atomic layers. Fig. 1b and c describes the two phases that a monolayer of TMDC can be in. The trigonal prismatic (D_{3h}) phase has a non-centro-symmetric configuration while the octahedral (O_h) or also known as antiprismatic point group (D_{3d}) phase has a centro-symmetric configuration. There are also distinct stacking polytypes for multilayer TMDCs. A 2H polytype is made up of stacking sequences of AbA BaB (where the capital case and lower case represents the chalcogen and metal atom respectively) while a 3R phase can be observed when the layers are stacked in the sequence of AbA CaC BcB. For monolayer TMDCs, only the trigonal prismatic or octahedral phases exist as no layer stacking is involved, commonly known as the monolayer 1H (for D_{3h} point group) or monolayer 1T (for D_{3d}) phases. Such phases have implications on the electronic structure of the material. For example, the 1T phase of monolayer MoS_2 is metallic while its 1H phase is semiconducting [6].

A striking feature of 2D semiconducting TMDCs is the change in electronic band structure from one with an indirect band gap to one with a direct band gap when the material is thinned to a single layer [8]. This occurs due to the absence of inversion symmetry in monolayer TMDC when its top layer is removed. The electronic band gap of the material also increases as the vertical dimension is reduced due to quantum confinement. For materials such as MoS_2, the initial indirect band gap of 1.3 eV with a valence band maximum at $\mathbf{\Gamma}$ and a conduction band minimum at the midpoint along $\mathbf{\Gamma}$-$\mathbf{K}$ symmetry lines transits to a direct band gap of 1.8 eV [16,17] with both conduction band minimum and valence band maximum present at the $\mathbf{K}$ point of the Brillouin zone when its thickness is reduced from bulk to a monolayer as depicted in Fig. 2a [17]. Such a transition from an indirect electronic band gap to a direct one results in observation of an enhanced photoluminescence (PL) yield in monolayer TMDCs compared to the usually low PL yields when they are in their bulk. This is evidenced for MoS_2 by Mak et al., where an increase in magnitude of PL yield of multiple orders of magnitude is observed as MoS_2 is thinned down to a single layer [16]. This is described in Fig. 2b [16], where the clear increase in PL with decreasing number of MoS_2 layers is demonstrated.

Another interesting aspect of TMDCs is the presence of valley polarization as described for MoS_2 in Fig. 2c [18], where the spin of the electron in the 2D TMDC is coupled with the valley quantum number which is defined by the crystal momentum of the electron, $\mathbf{k}$. In Fig. 2c, the first Brillouin zone of monolayer TMDC is presented with the electronic band gaps present at two inequivalent momentum valleys present at the K and K′ (-K) points. In TMDCs, spin-orbit coupling (SOC) results in a splitting in energy of the previously degenerate spin-up and spin-down electronic states at the valence bands present in the K and K′ valleys. This split varies with the elemental composition of the TMDC, with MoS_2 having a SOC split of 0.16 eV [18] while WS_2 has a split of