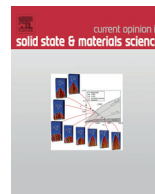




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Emerging opportunities in the two-dimensional chalcogenide systems and architecture

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ABSTRACT

Inspired by the triumphs - and motivated by the need to overcome the limitations - of graphene, the science and engineering community is rapidly exploring the landscape of other potential two-dimensional materials, particularly in their single - or few layer form. Dominating this landscape are the layered chalcogenides; diverse in chemistry, structure and properties, there are well over 100 primary members of this materials family. Driven by quantum confinement, single layers (or few, in some cases) of these materials exhibit electronic, optical, and transport properties that diverge dramatically from their bulk counterparts. The field has evolved considerably since the time when single or few layer flakes were “synthesized” by the scotch-tape mechanical cleavage method. New and more sophisticated methods for controlled synthesis (or thinning), deposition and chemical exfoliation have been developed that can “dial” the number of layers with large areal coverage on diverse substrates. Further, the 2D chalcogenide layers are being used as “substrates” onto which other dimensionally confined structures are being integrated in the spirit of nanoscale composites. Some composite structures exhibit synergy of multiple functionalities of the individual components, while in other cases they represent quantum coupling or unusual behavior that is contrary to nominal synergy or the proportional contribution of individual components. Last but not the least, there remain many structural and chemical combinations that are yet to be explored with deeply intriguing properties or phenomena that are waiting to be revealed. Thus, it is timely to review the status of the field; particularly in the context of synthesis, geometric architecturing and characterization of 2D layered systems.

Herein we review the evolving architecture of two-dimensional chalcogenide materials. We outline classes of specific materials and the evolution of their properties as they transition from nominally three to two-dimensionality, and especially in their single (or few) layer form. A variety of vapor-phase synthetic methods for the direct growth of large area single layers and the typical techniques for their characterization are presented. Lastly, we examine the potential of these materials as the fundamental building blocks of two-dimensional heterostructures and multi-dimensional nanocomposites. However, we also emphasize the need for fundamental experimental and theoretical undertaking to probe the classical problems like basic characterization and the dynamics of nucleation and growth in these 2D systems for realizing complex architecturing and resultant technologically useful phenomena and properties.

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1. Introduction

1.1. Two-dimensional materials

Over the past several decades, the concept of dimensionality, and the engineering of materials *via* changes in dimensionality, has captured the collective imaginations of the materials science, physics, and chemistry communities. This stems from the potential for advanced technological applications anchored by the expected

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novel physical phenomena in materials under extreme dimensional constraint. Nowhere has this been more evident than in the recent rise of two-dimensional (2D) materials following the discovery of graphene in 2004 [1]. Since then, the search has begun for additional 2D materials with properties that can both complement and supplement those of graphene. The layered crystal structure necessary for the isolation of single, atomically thin layers is ubiquitous in nature and recently the catalogue of 2D materials has expanded to include hexagonal boron nitride (h-BN) [2], black phosphorous (BP) [3], transition metal oxides [4], perovskites [5], and chalcogenides [6]. It is this last family, the layered chalcogenides, which presents the greatest diversity of available materials, crystal structures and properties. This review focuses on the key issues with the layered chalcogenide materials in their various forms and stoichiometries. Below, we classify the different chalcogenide compounds by chemistry and structure, highlighting the diversity of both. We also address the emergent properties of the materials as they transition to two-dimensionality. Vapor phase techniques for the direct growth of chalcogenide monolayers are presented along with the advantages and disadvantages of each. To close, we address the opportunities and challenges in the integration of 2D materials into multi-dimensional architectures like heterostructures and nanocomposites, where we believe the greatest potential for these materials lies.

1.2. Layered chalcogenides and their structures

The layered chalcogenides, compounds containing group 16 elements, can be further classified by chemistry and stoichiometry, as shown in Fig. 1. Atomic planes of these materials exist as self contained units, with no dangling bonds at the surface; it is this property that allows individual layers to be isolated from the bulk. The largest subset of the chalcogenide family is the transition metal dichalcogenides (TMD). These are compounds of the form MX_2 , where M is a transition metal (Mo, W, Nb, Ti, Ta, Hf) and X represents the chalcogen (S, Se, Te), e.g. MoS_2 or WSe_2 . Monolayer TMDs exhibit three polymorphs: 2H, 1T, and 1T'; each with unique properties [7]. The trigonal prismatic, 2H, phase is the thermodynamically

stable structure at standard temperature and pressure. The TMDs can also exhibit the less stable octahedral, 1T, phase or the 1T' phase, a distorted version of the 1T structure [7]. All three structures have an X-M-X arrangement, with the transition metal sandwiched between chalcogen atoms. In their bulk and monolayer forms, the electronic properties of the TMDs vary widely; for example, they can exhibit insulating (e.g. HfS_2), semiconducting (e.g. MoS_2 , WSe_2), semimetallic (e.g. WTe_2), or metallic (e.g. TiS_2) behaviors. Additionally, some exhibit low-temperature phenomena like superconductivity and charge (CDW) or spin density wave (SDW) behavior (e.g. $NbSe_2$). These characteristics coupled with unconventional monolayer optical properties, like enhanced photoemission [6], second harmonic generation [8], and optical valley selectivity [9], make the TMDs promising materials for new physics and improved opto-electronic device capabilities.

An additional subset within the broad family of the layered chalcogenides, are the AX monochalcogenides, where A represents the element from group III (Ga) or group IV (Ge, Sn), e.g. GaS or SnSe [10]. The Ga based chalcogenides are wide band gap semiconductors (2–3 eV) with hexagonal crystal structures composed of repeating X-Ga-Ga-X units built by six membered Ga_3X_3 rings [11]. There are also the group IV chalcogenides; for example, GeSe and SnSe are both semiconductors and structurally similar to BP. This orthorhombic crystal structure (space group: Pnma) is highly anisotropic, resulting in directionally dependant optical and electronic properties in monolayers. Density functional theory (DFT) calculations have predicted both materials to exhibit anisotropic spin splitting as well as extremely strong visible light absorbance which opens the door to novel spintronic and photovoltaic applications [12].

The group V chalcogenides can also be isolated as single layers and exhibit novel electronic phenomena. These are materials of the form B_2X_3 , where B is a group V element (Bi, Sb), e.g. Bi_2Se_3 or Sb_2Te_3 . Structurally the B_2X_3 compounds are composed of 5 atom thick “quintuple layers”, each approximately 1 nm thick, with an X-B-X-B-X arrangement in the c-direction. These materials are generally narrow band gap semiconductors, which have received a great deal of interest as thermoelectric materials and, more recently, topological insulators [13]. The properties, synthetic methods and emerging opportunities for each of these classes of materials will form the basis of this review.

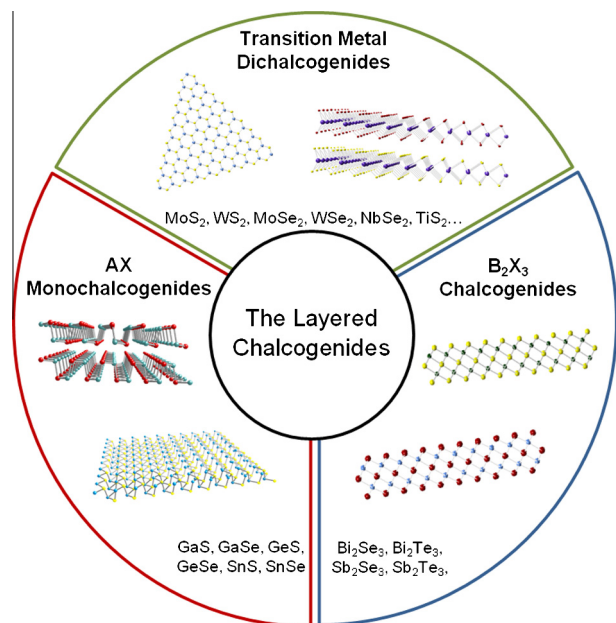


Fig. 1. The layered chalcogenide families: the transition metal dichalcogenides, the AX monochalcogenides, and the B_2X_3 chalcogenides.

2. Emergent properties in monolayer chalcogenides

2.1. From bulk to monolayer: electronic structure changes

As a result of confinement, monolayer chalcogenides exhibit a range of useful properties distinct from their bulk counterparts, as often indicated by their optical and electronic signatures. Electronic structure changes in monolayers are frequently elucidated using DFT calculations and confirmed *via* spectroscopic and transport experiments. As witnessed through DFT predictions and experimental verification, a number of the mono- and dichalcogenide materials experience an indirect to direct band gap change in their electronic structure as a function of monolayer confinement. These direct band gaps lead to characteristic strong luminescence yields in monolayers as compared to their bulk counterparts. Additionally, optical band gaps of monolayer chalcogenides are hundreds of meV larger than bulk values [6], stemming from the standard “particle in a box” confinement physics, in which the energies of electronic states increase with decreasing size. Fig. 2 shows this DFT-calculated indirect to direct band gap widening, along with the corresponding photoluminescence enhancement, for the case of MoS_2 .

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