# Semiconductor Flatland: Metal Chalcogenides in Fewer Dimensions

Sarah White Literature Seminar January 31, 2013

Until very recently it was presumed that two-dimensional, atomically thin materials were thermodynamically unstable, becoming discontinuous or having large atomic dislocations below a few nanometers in thickness. In 2004, the perceptions about the realization of atomically thin two-dimensional materials changed. Novoselov and coworkers not only isolated a single layer of graphene, but they also isolated a perfectly stable, crystalline 10μm sheet with scotch tape. It was an added benefit that this carbon allotrope offered ballistic carrier mobility, huge sustainable currents, and linear current-voltage.[1] However, the layered structure and two-dimensional stability of graphene is not unique. The same year that *Science* published his seminal paper on graphene, Novoselov employed the techniques of micromechanical exfoliation and high throughput identification of single layers to open up an unlikely class of atomically thin two-dimensional crystals. Macroscopic single layers of atomically thin crystals were shown to be air-stable and have carrier mobilities similar to those of the corresponding bulk materials.[2]

Transition Metal Dichalcogenides (TMDCs) have the formula $MX_2$, where M is a transition metal atom and X is a chalcogen (S, Se, or Te). The structure consists of covalently bonded monolayers of the form X-M-X in which two hexagonal chalcogen planes are separated by a hexagonal plane of metal atoms. Interlayer interactions are via weak Van der Waals forces.[3]

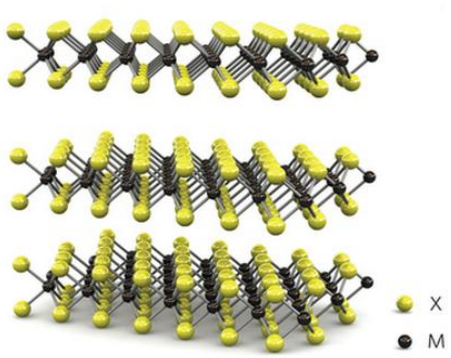

Figure 1. Schematic of TMDC structure.[6]

Among TMDCs, molybdenum sulfide ($MoS_2$) has emerged as a stable, scalable material that combines the benefits of two-dimensional crystals with the large band gap of a semiconductor. Although $MoS_2$ can be produced from several methods such as lithium intercalation exfoliation,[4] CVD[5] and epitaxial growth on silicon substrates, most reported devices using $MoS_2$ today use simple micromechanical cleavage, or the "scotch tape" method.[6]

Several stark electronic properties emerge when monolayers of $MoS_2$ are isolated from the bulk. One of the most exciting changes is a transition in the bandgap that occurs when the interlayer coupling is removed.[7] The consequence of this is that in few-layer $MoS_2$ materials, the bandgap can be tuned from the bulk value by at least 500meV due to quantum size effects. In this sense, few-layer $MoS_2$ materials are like their one-dimensional counterparts, quantum dots, with optical bandgaps, absorbance, and fluorescence properties than can be easily tuned by size.[8]

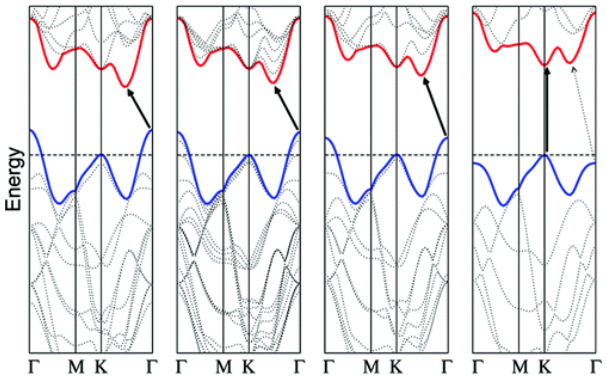


Figure 2. Calculated band structures of bulk (left), quadrilayer, bilayer, and monolayer (right) $MoS_2$ respectively.[9]

Whereas bulk $MoS_2$ is an indirect gap semiconductor, single-layer $MoS_2$ transforms to a direct bandgap semiconductor. Photoluminescence (PL) in $MoS_2$ also displays a strong dependence on layer number with luminescence being strongest for a single layer. In an experiment by Wang et al. strong PL peaks emerge at the direct excitonic transitions in few-layer $MoS_2$ that are completely absent in the bulk.[9]

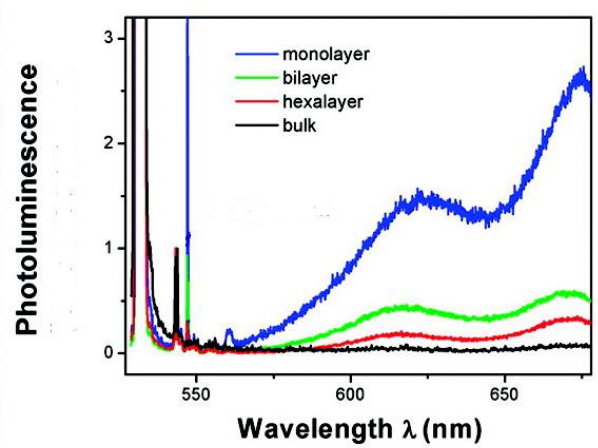


Figure 3. Dependence of PL on layer number in $MoS_2$.[9]

The ability to engineer the bandgap of few-layer $MoS_2$ indicates useful applications in transparent, flexible optoelectronic devices. Single layer $MoS_2$ has already been used to makes a stable phototransistor with highly reproducible photoswitching (when irradiated with light above the direct bandgap energy) and 50 ms switching times.[10] The use of a single layer of $MoS_2$ actually enhanced the phototransistor efficiency (the photo-induced current). Lee et al. demonstrated that by variation of the thickness (layer number) of few layer $MoS_2$ phototransistors, the photoresponsive wavelengths can be tuned from 1.82eV (1L) to 1.65eV (2L) to 1.35eV (3L). For instance, in order to detect red light (680nm), a triple layer device was employed.[11]

An obvious advantage to two-dimensional crystals is that 2D materials are small. Angstrom thick semiconducting channels limit the occurrence of short channel effects simply by virtue of their atomic scale thinness. Flexibility and transparency are also qualities that make 2D materials attractive for electronic applications. Ballistic carrier mobility and linear current voltage make graphene specifically promising for fast electronic applications, but the lack of a bandgap means that graphene cannot have high on/off current ratios and low conductance in the off-state: attributes needed for semiconducting channels in FETs.[12] 2D TMDCs like $MoS_2$ with

a sizeable bandgap offer the high on/off current ratios necessary for digital logic transistors while also offering the 2D attributes of high carrier mobility and atomic scale thinness.[13]

The first implementation of single layer $MoS_2$ in a top gated transistor was reported by Kis and coworkers.[6] Monolayer $MoS_2$ is an intrinsically *n*-doped material that has the same linear current-voltage and high sustainable current that graphene was touted to have. However, by applying a negative gate voltage, $MoS_2$ can be switched to a non-conducting state. The switching ratios, turn-on speed, and low off-state power dissipation of TMDCs compete with those of modern 3D transistors. However, unique attributes from the low dimensionality of TMDCs can be more exciting, such as in the area of chemical sensing. The addition of few adsorbates on the expansive surface of $MoS_2$ can cause large changes in its electrical properties. Few layer $MoS_2$ transistors have been successfully used as sensors for NO gas where *p*-doping from adsorbed NO leads to an increase in resistance and a decrease in drain-source current allowing quantitative detection of NO.[14] As the novel properties of 2D TMDCs are uncovered, there may be a number of other properties among semiconductors that turn out to be more interesting in fewer dimensions.


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