

DEVELOPMENT AND ANALYSIS OF MONOLAYER SEMICONDUCTORS FOR PHOTODETECTOR APPLICATIONS

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ABSTRACT

Fabrication of devices with ultrahigh switching speed, low power consumption, tunable emission with vanishingly small footprint size requires replacement of silicon and germanium with new novel semiconducting materials. Meeting such requirements need materials having ballistic conduction, direct-band structure, defect free growth and compatibility with current CMOS based device fabrication procedures. Interestingly experiments on few atoms thick monocrystalline graphitic films was found to show strong ambipolar electric field effect such that electrons and holes upto concentration of 10^{13} per square centimeter and with room temperature mobilities of $\sim 10,000$ cm²/V-s can be induced by applying gate voltage. This work paved the way for atomically thin film of carbon – Graphene discovered by A. K. Geim and K. S. Novoselov in 2005 which showed wide range of properties desired to achieve devices with excellent properties. Two – dimensional (2D) electron and hole gases (2DEG and 2DHG) were found to show surprisingly long mean free path = $1 \mu\text{m}$ (due to the continuity and quality of the last few atomic layers at the surface of graphite, where 2D carriers are resides) ballistic transport on mm scale in addition to Shubnikov-de Haas oscillations. Shubnikov-de Haas oscillations are observed due to existence of two types of charge carriers both electron and holes. In 2008, in case of graphene and its bilayer, they showed mobilities $> 200,000$ cm²/Vs. Interestingly 2D-graphene offered a test ground in solid state systems for many predictions of quantum electrodynamics, where electron transport was found to be governed by Dirac's (relativistic) equation. Interestingly, the charge carriers in the graphene were found to mimic relativistic particles with zero rest mass and have an effective 'speed of light' $c \approx 3 \times 10^8$ ms⁻¹. Experiments show that (a) Graphene's conductivity never falls below a minimum value corresponding to the quantum unit of conductance, even when concentrations of charge carriers tend to zero, (b) the integer quantum Hall effect in graphene is anomalous i.e, it occurs at half-integer filling factors, and (c) the cyclotron mass m_c of massless carriers in graphene is described by $E = m_c c^2$. Interestingly, the opacity of the graphene was found to be governed by the fine structure constant: one of the fundamental constant $e^2 / hc \approx 1/137$, Where, c is the speed of light, the parameter that describes coupling between light and relativistic electrons and that is traditionally associated with quantum electrodynamics rather than material science.

KEYWORD:**INTRODUCTION**

In 2005 group of Philip Kim from Columbia University showed feasibility of device fabrication using micromechanically exfoliated graphite of thickness 10 to 100 nm and lateral size $\sim 2 \mu\text{m}$, for the first time opening up the possibility of device fabrication with layered 2D materials. Although graphene showed strong promise for use in future electronic devices in terms of properties like ballistic transport on the micrometer scale at room temperature, possibility to be doped chemically and its tunability of conductivity with an electric field but has no band-gap. It has linear gapless spectrum and exhibits metallic conductivity even in the limit of nominally zero carrier concentration. At the same time, most electronic applications rely on the presence of a gap between the valence and conduction bands. This inspired researchers to look for other layered materials having electronic band-gaps in particularly transition metal di-chalcogenides (TMDs). Meanwhile in 2008, Meric et al. came with an idea of top-gated graphene field-effect transistor (GFET) based on a high-k gate dielectric with bandgap engineering. Despite poor $I_{on}/I_{off} \approx 7$, high trans conductance and current saturation are achieved making this device suitable for analog applications. With reduced intrinsic disorder, mobilities as high as $2,00,000 \text{ cm}^2/\text{Vs}$ was achieved. Recently identified 2D-crystals covers the complete range of energy band-gap from metallic conductors (like graphene, graphene oxide, fluoro-graphene etc), semiconductors (like transition metal dichalcogenides: MoS₂, WS₂, MoSe₂, Silicene, Phosphorene, Borophene, Stanane) to insulators (like h-BN).

Their surfaces are naturally passivated with the absence of dangling bonds, allowing for the integration of 2D materials with photonic structures such as waveguides and cavities. Vertical hetero-structures can also be built using diverse 2D materials without the usual "lattice mismatch" problem. While having atomically thin, many 2D materials have a substantial interaction with light. With having diverse electronic properties, 2D materials can cover a wide electromagnetic spectrum range as shown in Fig. 1.1. Due to the strong Coulomb interactions resulting from low dimensionality and reduced dielectric screening, they exhibit encouraging light emission capabilities, notably in the near-infrared wavelength range dominated by excitons and trions. In 2013, strong light-matter interactions in hetero-structures of atomically thin films were observed in TMDs/graphene stacks due to Van Hove singularities in the electronic density of states of TMDC. This results into enhanced photon absorption and electron-hole creation, allowing development of extremely efficient flexible photovoltaic devices with photo-responsivity above 0.1 ampere per watt corresponding to an external quantum efficiency of above 30 %. In 2012, field-effect tunneling transistor based on vertical graphene heterostructures with atomically thin boron nitride or molybdenum disulfide acting as a vertical transport barrier was realized. These devices exhibited room-temperature switching ratios of ~ 50 and $\sim 10,000$ respectively

opening up the possibility of use of such devices for high-frequency operation and large-scale integration.

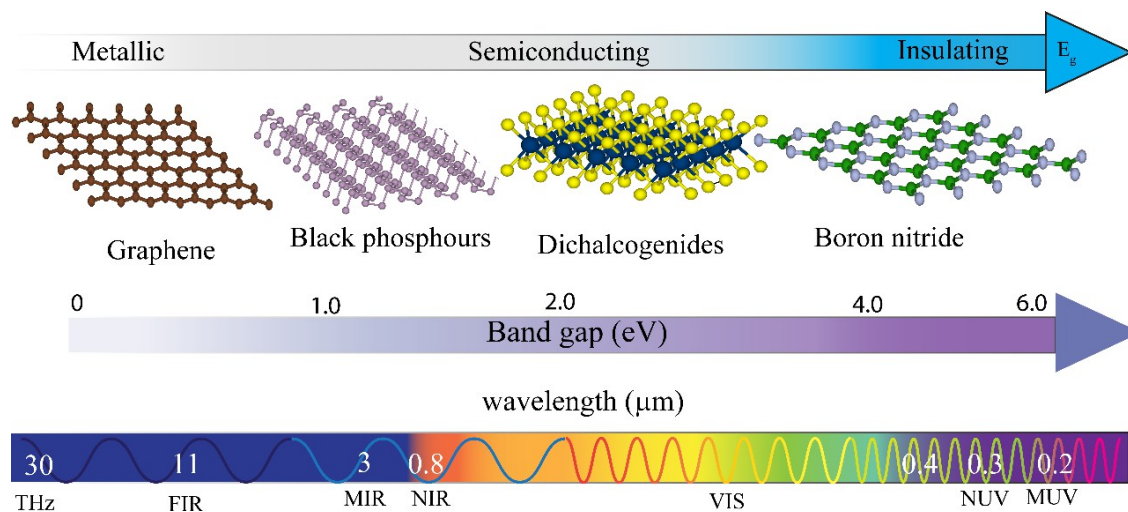


Figure 1.1: A comprehensive collection of two-dimensional layered materials (2DLMs) exhibits diverse chemical compositions, atomic structures, and electronic properties, demonstrating an ascending bandgap trend from left to right. This progression encompasses a spectrum of radiation wavelengths spanning from terahertz to ultraviolet. The applications of these 2D materials extend across a broad range of radiation wavelengths, encompassing the terahertz to ultraviolet spectrum.

Growth of Two –Dimensional materials

2D-materials has been grown using many techniques. Although these methods differ greatly from one another, they can generally be divided into two broad categories: top- down approach, which take an initial bulk material and extract the 2D material, or bottom- up approach, where the desired 2D material grows to the desired specifications.

A. Top-down approach

Fig. 1.2 illustrates a flowchart demonstrating Top-down methodologies, encompassing mechanical exfoliation, electromechanical exfoliation and solution processing techniques utilized for the fabrication of 2D materials. Top-down approaches are relatively simple compared to bottom-up approaches. Top-down approach is limited in terms of controlling the size and thickness of the grown 2D material. Mechanical exfoliation is the simplest method for exfoliating bulk 2D material into monolayer, bilayer or few-layer structures. It is achieved by constantly peeling the bulk material with adhesive tape.

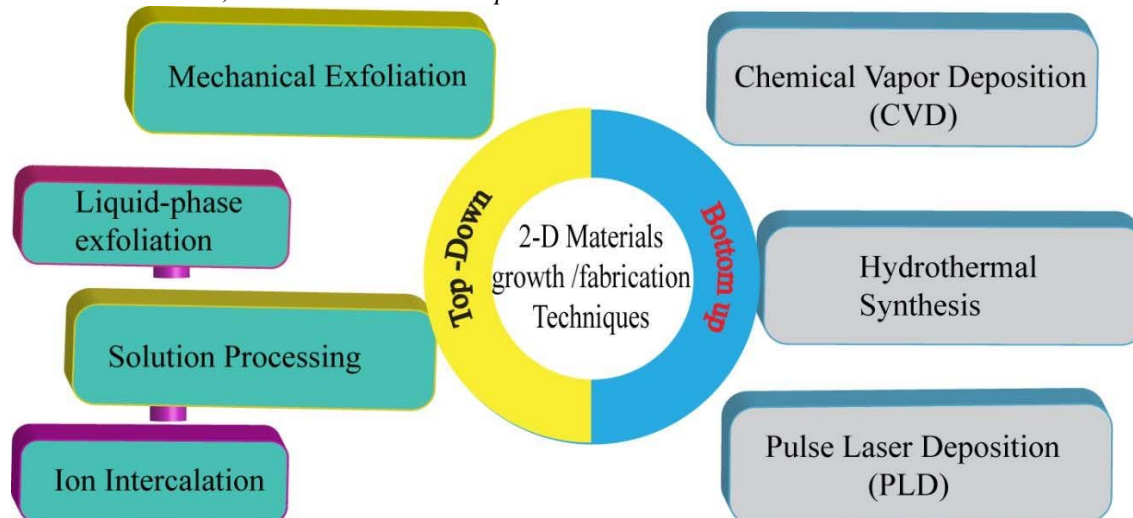


Figure 1.2: Overview of 2D Transition metal dichalcogenides fabrication techniques.

While the solution processing techniques are categorized into two sub-categories: liquid-phase exfoliation and ion intercalation. The liquid-phase exfoliation technique employed in the synthesis of 2D materials comprises distinct processes, including: (i) dispersion of the bulk material into a solvent, (ii) sonication, and (iii) centrifugation. Solvent having lowest mixing enthalpy are preferred, so that 2D material can be spread out properly. Lithium-ion is frequently used intercalant in the intercalation process due to its high efficiency. The lithium-ion works to improve the interlayer separation of the bulk material, which facilitates the subsequent hydrothermal exfoliation process. The lithium ions between layers actively react with the water during exfoliation to release H₂ gas. H₂ gas creates tiny bubbles that divide the layers of 2D materials.

CONCLUSION

Increasing demand to miniaturize electronic devices has generated interest of researchers into physics and growth of atomically thin semiconductors. Experimental demonstration of stability of atomically thin layer of carbon i.e graphene in 2004 and its ballistic conductivity set the researcher on hunt for monolayered semiconductor materials with natural band-gap. Observation of near unity photoluminescence in case of MoS₂ (a member of TMDs) showed the path of monolayered semiconductors for opto-electronic devices. Realization of commercial production of devices based on such atomically thin semiconductors depends upon crystalline quality of the material grown and their batch production. The compatibility of existing fabrication techniques and integration process parameters optimized for Silicon CMOS devices with 2D semiconductors also plays a deciding role. In spite of more than hundred articles dedicated towards growth of MoS₂ and another ten for the growth of WS₂, no unique recipe exists to achieve monolayered structure with nearly 100 % coverage area.

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