

## *Chapter 1*

### An Introduction to 2D Materials

The successful isolation of monolayer graphene in 2004 prompted an explosion of research in the field of two-dimensional (2D) electronics. Graphene has been the subject of extensive research to understand and modulate its electronic properties because of its ballistic-level carrier mobility<sup>1</sup> and ambipolar field effect,<sup>2</sup> coupled with its 2D nature and remarkable strength.<sup>3</sup> While people have long claimed that graphene will revolutionize technology, this revolution has yet to occur due to the difficulty of designing scalable, reproducible graphene syntheses<sup>4</sup>, the fundamental limitations imposed by the lack of a bandgap in graphene<sup>5</sup>, and the challenge of integrating this material in devices while maintaining its unique properties.

While graphene still dominates work in this field, a large number of new materials has been isolated or grown in the past decade, including 2D semiconductors like the transition metal dichalcogenides (TMDs) and topological insulators like hexagonal boron nitride (h-BN). These discoveries have been driven by the need to isolate 2D materials that overcome the device limitations imposed by the semimetal character of graphene, while retaining high carrier mobilities for integration in a variety of fast, flexible electronics. Still, graphene serves both as a useful comparison to the other materials and a model for the behavior of a 2D semimetal. Graphene and its derivatives have been proposed for use in numerous applications, from advanced flexible electronics to components in polymer composites. This chapter will introduce a basic understanding of 2D material behavior and describe the three different areas within the field of 2D materials covered by this thesis: the ability of graphene and its derivatives to protect semiconductors from deleterious surface reactions, to control the band energetics at semiconductor/liquid junctions, and to enhance signal response in chemiresistive vapor sensors.

### *Properties of 2D Materials*

Monolayer graphene is a semi-metallic 2D material composed entirely of carbon atoms (Figure 1). The atoms in the lattice are bonded together by  $sp^2$ -hybridized orbitals, making graphene a planar material with a thickness of only 3 Å.<sup>2</sup> The  $p_z$  orbitals, which are not involved in the C–C bonds of the lattice, stick up from the basal plane of the material. The overlap of these orbitals form bands that meet at the Dirac point, which allows the ballistic lateral transport of electrons and holes.<sup>2</sup> As a result, graphene has no bandgap and has a linearly decreasing density of states near the Fermi level. This honeycomb lattice of  $sp^2$ -hybridized carbon atoms is also chemically stable and impermeable to oxygen and water.<sup>6,7</sup> Its atomically thin nature makes it highly transparent, transmitting 97% of impinging light in the visible spectrum.<sup>8</sup> The uniformity of atoms within the basal plane contribute to the high stability and low reactivity of the lattice. Thus, pristine graphene is effectively inert.

Aggressive methods are needed to functionalize the basal plane of graphene. Due to the stability of the pristine lattice, it has been established that structural irregularities are critical for applications of graphene.<sup>6</sup> These defects can detract from the other beneficial properties of graphene—particularly charge mobility—as defective graphene has much lower conductivity than pristine graphene.<sup>7</sup> While these irregularities manifest as permanent defects to the lattice, electronic irregularities like those introduced by strain do not damage the network of C–C bonds in the basal plane.<sup>8</sup> Many methods have been designed to tune the bandgap of graphene, including but not limited to: substitutional doping of the graphene lattice during growth, noncovalent interactions with electron-rich and electron-poor molecules,<sup>9</sup> and covalent functionalization.<sup>7</sup> Researchers commonly prefer the last of these methods because it has proven the most effective for permanently altering the electronic properties of graphene.<sup>7</sup>

While no covalent functionalization can fully maintain the pristine nature of the lattice – the carbon atoms by necessity become tetravalent upon successful functionalization – the limitations that arise from the creation of permanent defects in the graphene lattice have prompted the search for functionalization methods that can lead to different electronic properties in the resulting lattice. One such modification is fluorination of monolayer graphene, which generates a corrugated, insulating lattice. Fully-fluorinated graphene has a bandgap of 3.0 eV and is very stable over time.<sup>10</sup> With such a large bandgap, this material has no density of states near its Fermi level. This characteristic makes fully fluorinated graphene a superior material to unfluorinated graphene, as it can be integrated into conventional electronics as a dielectric, whereas graphene has no direct analog in the field of semiconductor processing.<sup>11</sup>

The stability of the fully fluorinated material has led some to equate it to 2D Teflon.<sup>10,12</sup> This nickname for fluorinated graphene belies the reactive nature of the more common partially fluorinated graphene derivatives. Partially fluorinated graphene is actually quite reactive, showing the spontaneous detachment of fluorine in a matter of days after fluorination, which has led to its use as a precursor for subsequent functionalization.<sup>13,14</sup> As a result, many methods have been used to try to achieve full fluorination of the basal plane of graphene to achieve greater stability of the lattice. These methods include exposure to various strong fluorine chemistries, including hydrofluoric acid, XeF<sub>2</sub> gas, and CF<sub>4</sub> and SF<sub>6</sub> plasmas.<sup>15</sup> However, the methods that introduce the most fluorine also introduce the most disorder to the lattice and eventually destroy the lattice entirely. Thus, the partially fluorinated material is more widely studied than the fully fluorinated derivative and can take on a range of characteristics, depending on the degree of fluorination of the underlying basal plane.<sup>16</sup>

Similar to fluorinated graphene, hexagonal boron nitride (h-BN) is a topological insulator, but it is a single monolayer of atoms in its pristine forms. While it has the same

crystal structure as graphene, h-BN is formed of an alternating honeycomb lattice of boron and nitrogen atoms with lattice parameters very close to those of graphene and fluorinated graphene ( $r_{\text{B-N}} = 1.45 \text{ \AA}$  while  $r_{\text{C-C}} = 1.42 \text{ \AA}$ ). It has the largest bandgap of the known 2D materials at  $\sim 6.0 \text{ eV}$ .<sup>17</sup> The highly insulating and inert nature of h-BN has made it most commonly used as a passivation layer in devices, as it can stabilize a surface without significantly changing the behavior of the underlying layers.

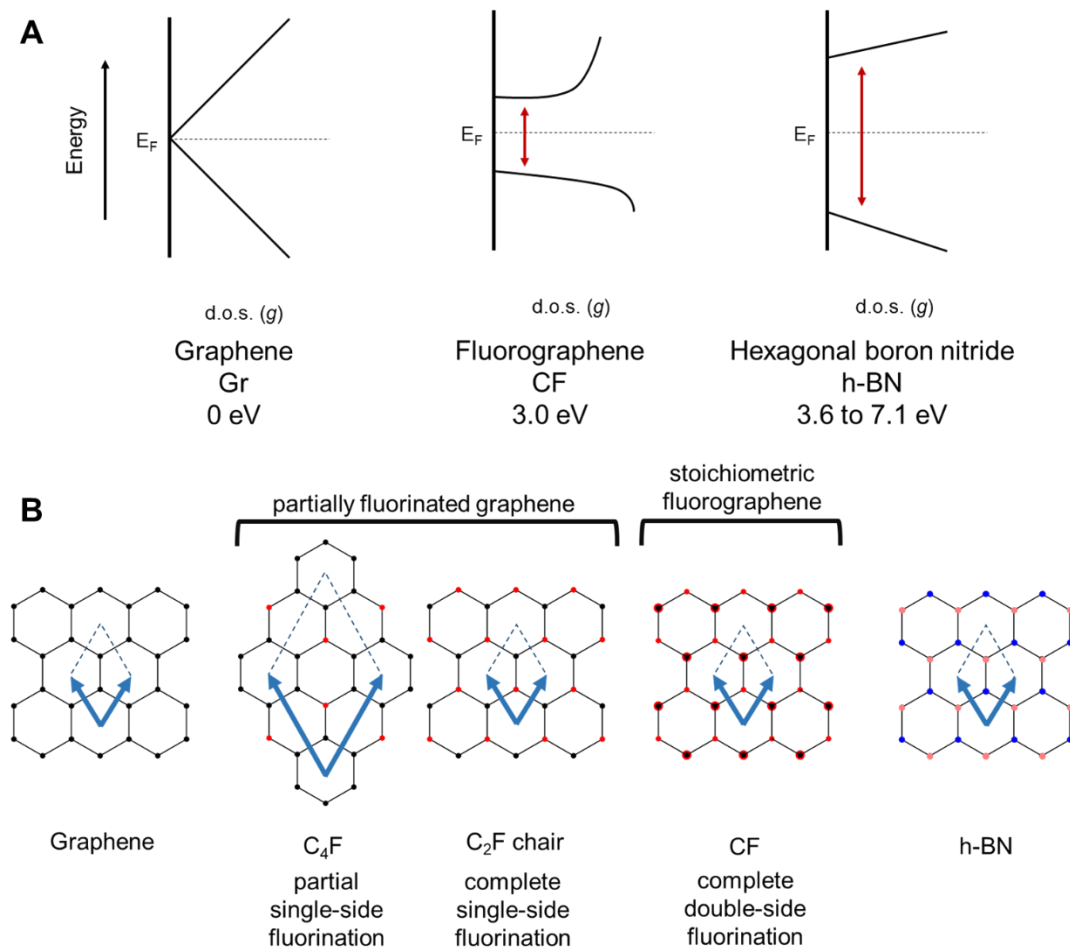


Figure 1. 2D materials used in this thesis. A) Density of states ( $g$ ) for graphene and fully single-side fluorinated graphene ( $C_4F$ ). The D.O.S. for fluorographene is significantly further from the intrinsic Fermi level for graphene while h-BN is completely insulating. B) The unit cells for graphene and fluorinated graphene. There are multiple ways that fluorine can bond to the basal plane to form partially fluorinated graphene.

### *Protective layers in photoelectrochemical cells*

Photoelectrochemical (PEC) cells are unique in that the charge-separating junction of the device is formed at a semiconductor/liquid interface instead of a semiconductor/solid interface, as is found in standard photovoltaic (PV) cells. Fabrication of a PEC device can be as simple as submerging a semiconductor in an appropriate electrolyte solution. These devices can generate chemical fuel directly via photon-driven water-splitting at the semiconductor surface without a separate electrolyzer (E), as a typical PV strategy would require. By eliminating the need for a separate electrolyzer, we expect the PEC cell to reduce the total cost of the solar water-splitting process compared to the common PV+E strategy.<sup>2</sup>

The protection of semiconductor surfaces from passivation and corrosion upon exposure to aqueous solution under photoanodic conditions is one of the foremost challenges facing the fabrication of stable PEC devices.<sup>3</sup> To prevent these deleterious reactions, several protection strategies have been developed, including various metallic and metal oxide protective layers for photoanodes. However, these layers generally reduce effective light absorption and thus limit energy conversion efficiency.<sup>3,4</sup> Protective metallic layers are limited by loss of majority carriers to the recombination processes that are promoted by thermionic emission at the interface. Protective metal oxide layers are limited by the thickness required for protection; films of promising oxide materials become more porous as they are made thinner to decrease absorption and prevent loss to reflection, which limits their effectiveness. Ideally, a protective layer would be optically transparent, while preventing deleterious surface reactions and still allowing for an efficient charge-separating junction to form.<sup>3</sup>

As a protective layer on n-type silicon (n-Si) under illumination in photoanodic conditions for 1000s, graphene has been shown to only partially pin the graphene/semiconductor interface, due to the lack of states at the Fermi level (Figure 1).<sup>9</sup>

However, current growth methods limit the use of graphene as a protective layer.<sup>9</sup> Exfoliation, or “the Scotch tape method,” produces single-crystal graphene pieces that are small (~100  $\mu\text{m}$ ) and difficult to locate optically. Chemical vapor deposition (CVD) growth can be used to make polycrystalline sheets with variable grain size. However, diffusion through grain boundaries and defects from wet-chemistry transfers have stymied the use of CVD-grown graphene as the ubiquitous, transferable protective layer it could be.<sup>10,11</sup> In addition, small amounts of contaminants left behind after wet transfer are known to dope the graphene sheets, which allows easy access to more deleterious surface states by charge carriers at the interface.<sup>12,13</sup> It would be beneficial to limit the effect of high-energy defect sites and grain boundaries on the performance of graphene-based electrodes through passivation and limit the number of surface states easily accessible to charge carriers at a graphene/semiconductor interface.

Recent work has shown that various protective layers, such as  $\text{HfO}_2$  and  $\text{TiO}_2$ , can react with high energy defect sites and effectively repair some of the damage to the honeycomb structure of graphene, preventing unwanted diffusion through the lattice.<sup>14,15</sup> With this in mind, Chapter 2 will detail work using monolayer fluorographene on a semiconductor photoanode to stabilize the surface and form an efficient charge-separating junction for use in a solar water-splitting device through termination of defect sites with fluorine atoms.

### *Interfacial control at semiconductor/liquid junctions*

To form an efficient charge-separating junction, we need to minimize the number of electronic states introduced by a protective layer with energy mid-gap to the semiconductor. In addition, the initial difference between the electrochemical potential of the semiconductor ( $E_F$ ) and the contacting electrolyte determines the maximum efficiency of a photoanode or photocathode.<sup>18</sup> Efficient photoanodic devices have the edge of the

valence band aligned with the electrochemical potential for the reaction of interest ( $E(A/A^-)$ )), maximizing the extractable energy (Figure 2a). In contrast, photocathodic devices have the conduction band aligned with  $E(A/A^-)$  (Figure 2b). Thus, these interfaces can be optimized with the use of interstitial layers to tune the resulting efficiency for different applications, shown as a dipole in Figure 2. When a 2D material is used as this interstitial layer, the properties of the layer, particularly its density of states, are predicted to have a strong effect on the quality of the resulting interface. Since graphene has a Fermi level that falls between the the band edges of many semiconductors, it is not predicted to make an efficient charge-separating junction. Because h-BN has a large bandgap, there are no mid-gap states and it should produce a more efficient charge-separating junction than graphene would.<sup>17</sup> Chapter 3 will further explain how these interfaces were tested using macroscale and nanoscale techniques.

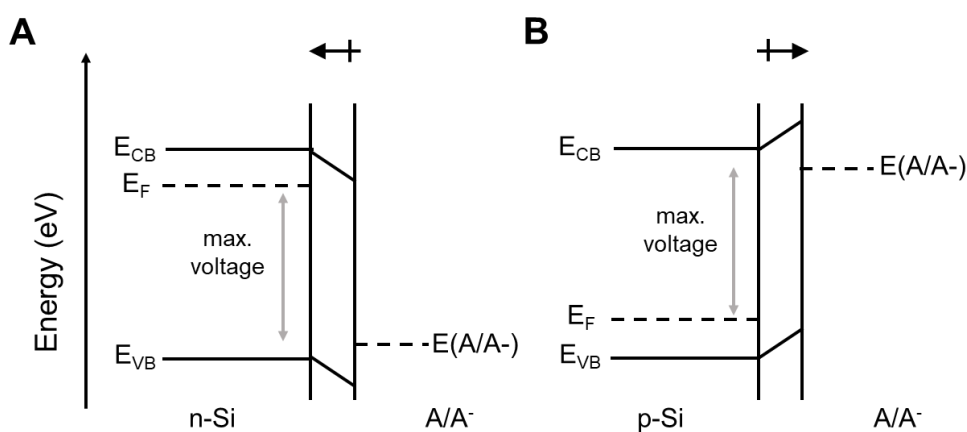


Figure 2. Energy diagrams for efficient charge-transfer in semiconductor/2D material/liquid junctions. An efficient semiconductor/2D material/liquid junction places the electrochemical potential of the contacting electrolyte ( $E(A/A^-)$ ) close to the appropriate band given the dopant type in the semiconductor. A) For the n-Si/2D material/liquid junction,  $E(A/A^-)$  is moved closer to the the valence band. B) A p-Si/2D material/liquid junction has  $E(A/A^-)$  close to the conduction band. Note that the direction of the necessary surface dipole has switched for the two interfaces.



### *Strain-based sensing with graphene*

Strain-induced reactivity of graphene is a promising method that explores the effect that controlled tensile and compressive strain of the basal plane of graphene has on reactivity. This technique relies on the strain-induced change in electron density along the basal plane to increase reactivity. In the same way that dangling bonds along grain boundaries or edges promote reactivity, these strain-induced hot spots have been shown to be highly reactive to graphene functionalization methods.<sup>18–20</sup> Unlike other methods for covalent functionalization, the generation of these reactive hot spots should also be fully reversible with the removal of strain from the lattice. Since strain significantly changes the conductivity of graphene, strain-based methods should allow the reversible changes to the conductivity of graphene with minimal damage to the underlying lattice.

Even with only minor rippling of the lattice, the lability of the C–C bonds still substantially increases because of reduced orbital overlap and increased localization of electron density.<sup>21</sup> From  $\pi$ -orbital angle vector (POAV) analysis – frequently used in discussions of fullerenes or other intrinsically strained carbon allotropes – deviation from  $sp^2$  hybridization decreases electron delocalization and increases the chemical potential of the strained atoms.<sup>22</sup> That is, as the s-orbital character of the  $p_z$  orbital increases, the delocalization of the  $\pi$ -bond network decreases. The deformation of graphene and the resulting charge localization alter the conductivity through the monolayer, creating a detectable change in the resistance across the lattice.

This reversible and detectable change in conductivity makes graphene an ideal material to study as part of a chemiresistive sensor. These sensors detect the adsorption of particular chemicals through a change in the resistance of the sensing material. As the graphene lattice is very sensitive to perturbations, a sensor made with pristine graphene should have high sensitivity to molecule adsorption in contrast with the

amorphous conductive carbon commonly used today. However, as highlighted previously, pristine graphene is relatively inert. Clean graphene actually shows very low selectivity to gases. In fact, most of the sensitivity attributed to graphene has been shown to be attributable to polymer contamination on the surface. Rather than excluding graphene from use in chemiresistive sensors though, this lack of selectivity has inspired the work detailed in Chapter 4, where a sensor is developed to amplify small changes in strain to large changes in resistance across the lattice through the integration of a textured substrate with and polymer-coated graphene layer.

### Summary

Together the three materials used herein bridge a wide range of bandgaps currently accessible in 2D materials. The diverse work in this thesis characterizing the interfacial behavior of graphene, fluorinated graphene, and h-BN will allow scientists to elucidate the pattern of behavior expected as the density of states of these materials and to better predict the behavior of new 2D materials in the future.

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