The Reemergence of Chemistry for Post-Graphene Two-Dimensional Nanomaterials

The ascent of graphene over the past decade has been attributed to its superlative and exotic electronic properties that resulted in the Nobel Prize in Physics only 6 years after the pioneering experiments by Novoselov and Geim.[1] While its importance to condensed matter physics is undeniable, the astounding rate at which graphene was adopted and studied by laboratories worldwide can also be explained by its chemical inertness. In particular, since graphene is stable in air at room temperature and remains intact following exposure to all but the most caustic chemicals, it can be straightforwardly exfoliated from graphite *via* micromechanical methods or ultrasonication in an array of commonly available solvents. Following exfoliation, the chemical stability of graphene implies that it can be further subjected to subsequent processing and characterization with minimal precautions. Consequently, nearly any laboratory can get into the graphene business quickly, leading to tens of thousands of papers that have employed graphene in nearly every conceivable fundamental study or application.

Although interest in graphene remains high, it is also evident that graphene cannot solve every problem. For example, the lack of a significant band gap for graphene limits its applicability in digital electronics. While covalent modification schemes have attempted to address this issue,[2] the requisite chemistries for graphene are highly aggressive and have invariably resulted in inhomogeneous functionalization that compromises the high charge carrier mobilities that made graphene interesting in the first place. This quandary has led many researchers to explore other two-dimensional nanomaterials that intrinsically possess a finite band gap. The most popular candidates thus far include the transition metal dichalcogenides (*e.g.*, MoS_2, WS_2, $MoSe_2$, and WSe_2) and elemental two-dimensional nanomaterials such as two-dimensional silicon (often referred to as silicene) and black phosphorus (often referred to as phosphorene).[3]

Much of the early work on transition metal dichalcogenides (TMDs) has attempted to mimic the trajectory of graphene with initial experiments performed on micromechanically exfoliated samples followed by later work based on solution-based exfoliation or growth by chemical vapor deposition. Since TMDs are also relatively inert chemically, reasonable results have been achieved with minimal precautions in handling or processing. However, since TMDs are compounds (as opposed to elemental materials), the stoichiometry of TMDs represents a new chemical parameter that is particularly challenging to control in chemical vapor deposition growth as well as in patterning lithographies. While often not measured or acknowledged in many studies, recent work has shown that stoichiometry is a key parameter that can influence electronic properties in unexpected ways.[4] Furthermore, defect structures that are a strong function of stoichiometry (*e.g.*, grain boundaries) have led to charge transport phenomena qualitatively different than those observed in traditional field-effect transistors.[5] The fundamental chemical concept of stoichiometry thus presents new challenges and opportunities for post-graphene two-dimensional compounds.

While the elemental two-dimensional nanomaterials based on black phosphorus and silicon largely avoid the stoichiometry issue, their significantly higher chemical reactivity compared to that of TMDs or graphene necessitates larger changes in standard operating procedures. For example, the chemical reactivity of silicon has limited the preparation of two-dimensional films to ultrahigh vacuum on single-crystal substrates (most commonly silver). Even in this idealized environment, silicon can interact strongly with the substrate, leading to evidence of substrate atoms being incorporated into the growing two-dimensional silicon film (see Figure 1a).[6] Attempts to passivate two-dimensional silicon for *ex situ* characterization have achieved limited success with the only report of a silicene field-effect transistor showing irreversible chemical degradation in ~2 min in air.[7]

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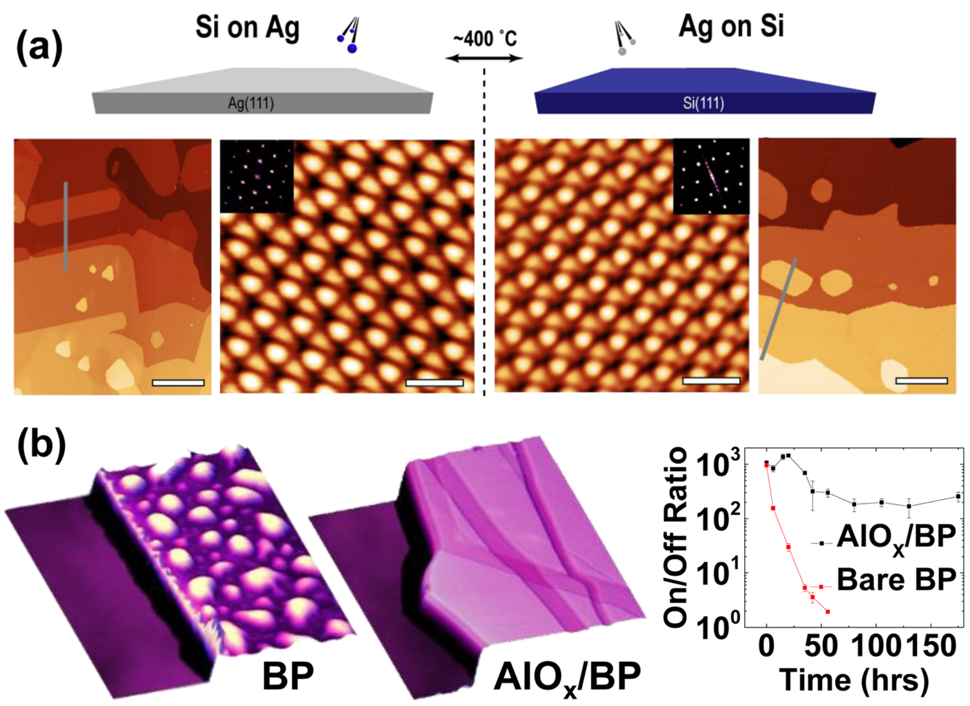

Figure 1. (a) Ultrahigh vacuum scanning tunneling microscopy images of Si on Ag(111) and Ag on Si(111). The latter case is a well-established Ag-mediated reconstruction on Si(111). The close similarity between these two cases suggests that Ag from the substrate is incorporated into the growing two-dimensional Si film on Ag(111). The scale bars in the middle two images are 1 nm, whereas the peripheral two images are 50 nm. This panel is adapted from ref 6. Copyright 2014 American Chemical Society. (b) Atomic force microscopy characterization of bare black phosphorus (BP) shows evidence of ambient degradation, whereas alumina-encapsulated BP remains atomically flat. The ability of alumina to protect BP against ambient degradation is further reinforced by the preservation of the on/off ratio in alumina-encapsulated BP field-effect transistors. This panel is adapted from ref 9. Copyright 2014 American Chemical Society.

Two-dimensional silicon will likely remain relegated to ultrahigh vacuum experiments until stable chemical passivation or encapsulation solutions can be identified.

As the most chemically stable allotrope of phosphorus, black phosphorus would appear to overcome some of the limitations faced by two-dimensional silicon. Indeed, bulk crystals of black phosphorus are stable in ambient conditions on the time scale of multiple months. However, in the two-dimensional limit, black phosphorus readily getters water and oxygen from the environment, resulting in oxidative degradation within days.[8] Fortunately, relatively straightforward encapsulation methods (*e.g.*, atomic layer deposition of alumina) can minimize oxidation and enable reliable two-dimensional black phosphorus characterization in ambient conditions for at least several weeks (see Figure 1b).[9] In addition, careful handling of black phosphorus in inert environments allows solution-based exfoliation and related processing.[10] While this level of stability is sufficient for research laboratory studies, further improvements in passivation and encapsulation will be required for practical deployment of two-dimensional black phosphorus. It should also be noted that most volatile phosphorus precursors are highly toxic, which will present impediments to the development of chemical vapor deposition growth methods for two-dimensional black phosphorus.

> The fundamental chemical concept of stoichiometry thus presents new challenges and opportunities for post-graphene two-dimensional compounds.

In conclusion, chemistry appears destined to play an increasingly significant role as the field expands from graphene to alternative two-dimensional nanomaterials. For two-dimensional compounds such as TMDs, stoichiometry control and characterization will be critical for realizing reproducible experimental results in both fundamental studies and emerging applications. On the other hand, elemental two-dimensional nanomaterials possess chemical reactivity substantially higher than that of graphene or TMDs, which necessitates careful handling in inert environments and the development of encapsulation and passivation schemes. While these chemical complexities of post-graphene two-dimensional nanomaterials represent serious challenges, they also suggest opportunities for controllable chemical functionalization that have thus far eluded graphene. In this manner, the reemergence of chemistry for post-graphene two-dimensional nanomaterials has the potential to motivate productive research and development for the foreseeable future.

Disclosure: Views expressed in this editorial are those of the author and not necessarily the views of the ACS.

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