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A Review of Intercalation of Rare Gas Solids on Graphene and Hexagonal Boron Nitride

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Intercalation has recently emerged as a powerful tool due to its unique capability of modifying the properties of materials without breaking their chemical bonds. The ultrathin lattice structure of two-dimensional (2D) materials with strong in-plane covalent bonding and weak out-of-plane bonding between neighboring layers allow for the successful utilization of this powerful technique. The physics and chemistry of intercalated foreign species in 2D host materials, especially graphene and hexagonal boron nitride (h-BN), are the focus of this review article. Among many foreign species, special attention is given to rare gas solids that introduce unprecedented physical and chemical properties in the targeted host materials. The historical background of intercalation is briefly discussed, and a comprehensive review of the very recent progress in the intercalation of rare gas solids in graphene and h-BN is then provided. Different technologies used for the growth of the host materials and for the intercalation of rare gas species are also described. The remarkable potential of the resulting hybrid materials is outlined for diverse applications, including sensing, water filtration, and nanoelectromechanical devices.

1. Introduction

With the advancement of nanotechnology, the demand for finding new methods to advance the structural, optical, and electrical characteristics of materials is now greater than ever before. The concept of introducing foreign particles into a host material is known as intercalation. It is a reversible process whereby a range of foreign species, including atoms, molecules, and ions are inserted into the host material. Such insertions typically occur at ambient temperature, but sometimes process temperatures must be sufficiently high to facilitate the mobility of foreign species while ensuring no structural damage occurs to the host lattice.[1] Intercalation has recently garnered popularity and interest among researchers due to several reasons. For instance, it enables achieving the highest possible doping in host materials due to their ability for charge transfer. Conventional doping techniques,[2,3] such as substitutional, chemical, electrical/magnetic field, strain-effect-induced doping, and organic molecular doping are not viable for 2D materials because they damage the atomically thin crystal structure.[4] In fact, the intercalated species transfer charge to materials and this causes shifting of the Fermi level which increases the density of energy states and subsequently the charge carrier density. Other reasons include the reversibility of the entire process and its associated changes, the introduction of structural (e.g., increased interlayer spacing in 2D layers) and phase changes (hexagonal to rhombohedral in transition metal dichalcogenides) to improve physical and chemical properties, and the generation of outstanding electrical, thermal, magnetic, and catalytic properties.[5] Hence, intercalation has been involved in a wide range of real-world applications including in batteries, electrochromic displays, solid electrolytes, and sensors.[6]

Among host materials, 2D materials are atomically very thin and they range from a monolayer (≈0.33 nm) to a few layers in thickness. Due to such confined, atomically thin nature, and a high surface-to-volume ratio, these materials are the ideal platform for intercalation.[7–9] This facilitates the insertion of various foreign species without breaking the in-plane covalent bonds.[1,10] In other words, intercalation is easy to achieve in such layered materials due to the presence of large interlayer gaps.[11,12] **Figure 1** schematically shows the presence of van der Waals (vdW) interactions between 2D layers on three-dimensional (3D) substrates that help sustain the host structure and confine intercalants. Unlike 2D materials, 3D materials as host structures trigger chemical reactions with foreign species which limit the controllability of material properties. Interestingly, intercalants in 3D systems appear as donors and acceptors (turn into electrons and holes) in the host material and form covalent bonds which disrupt structural properties and create defects. In 2D materials, the structural bonding is not disturbed; guest species are allowed to reside on the atomic surface and ions can easily migrate to interlayer sites.[13]

Graphene and h-BN are considered to be among the most promising 2D materials because of several fascinating

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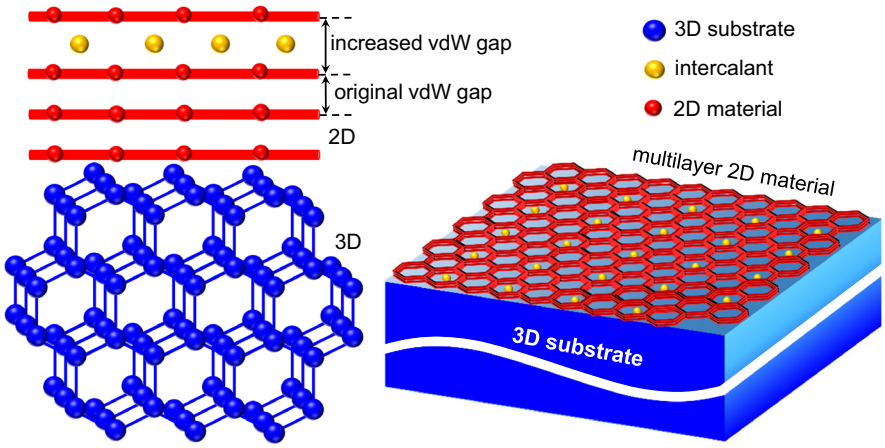

Figure 1. Atomic geometry of intercalants/multilayer 2D material/3D substrate (left), and schematic view of a structure with multilayer 2D material/3D substrate where foreign particles are intercalated (right).

properties. While graphene is a zero-bandgap semiconductor, h-BN has a bandgap of around 5.97 eV and is very useful as an electrical insulator[14] as well as a quantum- and classical-light-emitting material at the same time.[15] The quality of graphene-based electronic and optoelectronic devices has undergone significant enhancement in recent years and this has opened up new avenues for exploring the physics to create heterostructured devices with h-BN as a substrate.[16] Graphene-encapsulated h-BN has recently demonstrated the behavior of electrons as viscous fluids that exhibit hydrodynamic behavior.[17] As for h-BN, also known as white graphene, it is also a layered material with a structure analogous to that of graphene with around 1.8% lattice mismatch, which allows for the formation of superlattices with a periodic moiré potential that influences the electronic spectrum of graphene.[18–23] Due to the presence of optically addressable defects, h-BN is an ideal platform for intercalation by rare gas species for applications in quantum photonics that are relatively unexplored. Moreover, due to the presence of nonzero nuclear spin in rare gas atoms[24] and optically addressable spin defects in h-BN,[25–27] one hypothetically considers that such an intercalated system could be useful for quantum information science (QIS) applications. Our review mainly focuses on these two important 2D materials and recent developments in their intercalation using rare gas atoms.

As far as intercalants are concerned, rare gas elements, also known as noble or inert gases, i.e., helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), radon (Rn), and the newly found oganesson (Og), exhibit important properties. They are found in minimal amounts in the atmosphere and solidify under atmospheric pressure at very low temperatures (around 83.7 K except He which requires 1.4 GPa), in which case they are termed rare gas solids. The rare gas atoms have also been observed to form closely-packed solids under immense pressure, even at very high temperatures.[28] To stabilize these elements at room temperature (RT), for instance, helium requires a pressure of 12.1 GPa to solidify, while neon and argon require pressures of 4.8 and 1.4 GPa, respectively.[29] Interestingly, one could leverage the intrinsic van der Waals pressure exerted by sandwiching the rare gas solids within 2D materials, e.g., graphene and h-BN. The van der Waals forces between 2D materials, while weaker than covalent bonds, are strong enough to result in pressures estimated to be as high as 70 GPa for encapsulated species.[30]

Previously published review papers have focused on various intercalation species, 2D host materials, and intercalation methods. Comprehensive reviews on intercalated 2D materials have also focused on their applications in high-power and flexible electronic devices.[6] The impact of intercalation on crystal structure and its applications in next-generation energy storage, optoelectronics, and thermoelectrics have also been surveyed.[5] Several reviews have worked on the growth of 2D materials based on intercalation chemistry and the tuning of electrical, optical, and magnetic properties resulting from intercalation.[6,10,31] In this review paper, we discuss the importance of rare gas solids and their novel properties. In light of recent developments, this discussion on rare gas solids and their promise will open the door to several other interesting research areas and is expected to trigger the development of novel and unexpected uses of intercalation where such unique properties could produce significant enhancements. Despite examining a variety of techniques for material growth, achieving intercalation, and subsequent material characterizations, we strive to make this review accessible to individuals with different backgrounds.

We begin with a brief discussion on the importance of rare gas solids in Section 2 followed by a review of the history of intercalation in Section 3. Section 4 describes the recent developments in the growth of 2D host materials for intercalation. The technical challenges associated with the deposition of rare gas solids are described in Section 5. We next present all experimental demonstrations of intercalated systems with rare gas solids that are reported to date as well as their characterization details. Finally, we conclude with a broader outlook on the intrinsic properties of rare gas solids that may lead the way in quantum research.

2. Usefulness of Rare Gas Solids

Intercalated rare gas solids have revolutionized intercalated 2D systems, showcasing exceptional thermal stability and pressure resistance. These solids can withstand temperatures up to

1000 K[32] and pressures exceeding 70 GPa,[30] making them ideal for high-temperature and high-pressure applications. Additionally, their ability to facilitate phonon excitations and enhance electron tunneling beyond the phonon energy threshold makes them highly suitable for nano-electromechanical devices.[33] Their physical dimensions also facilitate accurate measurement of adhesion energy between graphene and graphite layers, providing valuable insights into their mechanical and electronic properties.[34]

The remarkable properties exhibited by intercalated rare gas solids in the 2D system make them highly promising for various applications. One such area is gas sensing, where the stable and leak-proof nature of intercalated systems, facilitated by the presence of these solids, makes it an ideal platform for sensitive gas sensors.[32] The pressure sensitivity of the intercalated 2D system, driven by the presence of these solids, opens up possibilities for pressure sensor applications.[30] Additionally, the unique structure of the intercalated 2D systems with these solids can be exploited for filtration applications. The controlled dimensions and stable nature of these structures make them suitable for filtering particles or molecules of specific sizes. This capability can be harnessed to develop efficient filtration membranes for water purification or separation processes.[35]

Besides these applications, rare gas solids also offer a promise in QIS because of their enclosed electronic shells that protect the nuclear spins from the external environment. While diamond requires material engineering, such as doping and high-temperature annealing, to achieve long coherence time, rare gas solids can preserve their spin without any further processing.[36–42] Some rare gases such as ^{3}He and ^{129}Xe show long coherence time due to the presence of a nonzero nuclear spin which is optically inaccessible and well protected from the external environment.[36] Such gas spins of ensembles can generate long coherence for a few hundred hours above RT. These collective nuclear spins find applications in medical imaging,[43] QIS, and sensing technology,[24,44,45] and in conjunction with controlling quantum excitations lead to long-lived entanglement at RT. Maintaining and generating such entanglement requires precise control and isolation that has been achieved in trapped atoms and ions,[46,47] alkali-metal spins,[46,48,49] high-quality mechanical oscillators, and quantum defects in crystals.[50] Very recently, strong coherent coupling between optically-accessible spins of a rare gas (^{3}He) has been demonstrated.[36] This approach adds a variety of atomic and molecular spin defects through the insertion of several rare gas solids into host 2D materials. The demonstration of quantum emitters by the irradiation of MoS_2 with helium was also reported.[51] The ion irradiation technique is required for intercalation followed by the resulting spin defects that could be interfaced with optical, electrical, mechanical, and magnetic devices (see **Figure 2**). Hence, this intercalation-based novel approach will build a foundation for an extended effort in all three major fields of QIS: sensing, computing, and communication.

3. Overview of Recent Progresses in Intercalation of Rare Gases

The history of intercalation chemistry is very old; the first intercalation was observed by Schafhautl in 1840 when the term "intercalation" was not introduced.[52] Ninety years later, Hoffman et al. from the Technical University of Berlin contributed to the development of intercalation chemistry[53] but the terminology "intercalation" was not used till then. The term "intercalation" was first used by McDonnell et al. in 1951.[54,55] Since then, solid-state physicists and chemists have provided a major push to the field of intercalation chemistry with a significant interest in tuning the physical properties of materials. This push was further amplified by the work on layered 2D materials in 1969.[56] Rare gas intercalation was first performed by Kwei et al. on a fullerene structure in 1997 and the ease of using Ne atoms and their interactions with the host material were

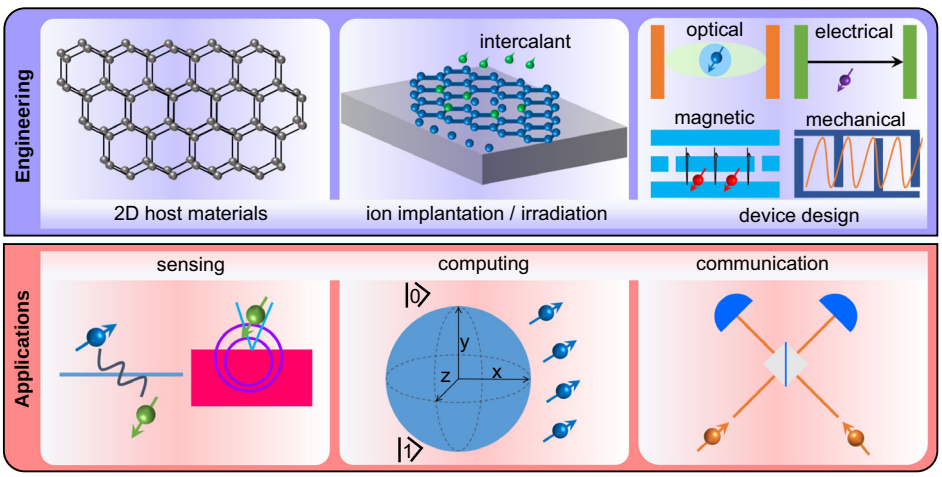

Figure 2. The blue engineering panel (top) displays 2D host materials, atom intercalation by irradiation, and device design via optical, mechanical, electrical, and magnetic devices for interfacing with spin defects. The red application panel (bottom) shows three major quantum applications including quantum sensing, quantum computing, and quantum communication enabled by the electronic or nuclear spins of intercalation-induced defects to enable quantum information science.

reported.[57] With advances in nanotechnology, 2D materials, in particular graphene and h-BN, started receiving massive attention due to their unusual characteristics and the research area of intercalation in these layered materials grew rapidly.

The intercalation of rare gas ions on h-BN was first reported in April 2008 by Dil et al. when they observed the trapping of Xe atoms on their h-BN/Rh(111) samples.[58] In April 2013, the same research group comprising Cun et al. intercalated Ar^+ ions onto h-BN on Rh substrates and observed the trapping of Ar atoms at the 2D/metal interface which led to the formation of blisters.[59] In August and October of the same year, Blanc et al. and Åhlgren et al. worked on intercalating graphene on iridium (Ir) substrate using Ar atoms and eventually obtained similar results by observing the trapping of intercalated atoms at the graphene/Ir interface, also known as blisters.[60,61] In June 2014, Cun et al. published a new work on h-BN intercalation using Ar atoms.[35] Here, the trapping of Ar atoms at the interface was similarly observed with a further examination of the structural and morphological properties of the system after annealing, and finally two new interesting effects, so-called "can-opener" and "self-healing", were reported.

In December 2014, Herbig et al. mistakenly reported the formation of blisters at the 2D/metal interface due to the trapping of carbon atoms when they separately intercalated He, Ne, Ar, and Xe atoms on graphene/Ir samples.[62] Six months later, they invalidated their previous results by explaining that the formation of blisters was due to the trapping of rare gas intercalants instead of carbon atoms.[63] The same authors continued their study on Xe intercalation in graphene/Ir and in August 2015 they published a detailed experimental and theoretical study on the trapping of Xe atoms at the graphene/Ir interface to validate their previous statements.[64]

In June 2015, Kim et al. published their work on intercalating Ar ions on graphene/platinum (Pt) samples to achieve controlled phonon excitations in graphene.[33] They observed the formation of blisters at the graphene/Pt interface due to the Ar intercalation process and found that these blisters helped realize high-performance graphene-based electronic devices. Three months later, Zamborlini et al. also reported the formation of blisters when they intercalated graphene/Ir with Ar ions and observed multiple blisters merging to form a blister larger in size and height.[30] In January 2016, Späth et al. and Larciprete et al. reported their works on the intercalation of Ar ions on graphene/nickel (Ni) samples, and both of them observed the Ar-blister formation.[32,65] Späth et al. reported that the blisters turned out to be thermally stable whereas Larciprete et al. reported the reason for strained blisters forming in the interface. Later in October 2016, Wang et al. also observed the formation of blisters on their graphene placed on highly ordered pyrolytic graphite (HOPG) substrates.[34]

In July 2018, Yoo et al. investigated the formation of Kr blisters on their graphene placed on a graphite substrate due to intercalation and they found that the blisters' heights varied based on the intercalation site.[66] After roughly 2 years, Längle et al. also reported the intercalation of Kr ions on graphene layers with blister formation.[67] **Figure 3** shows the history of intercalation and its time evolution on graphene and h-BN using rare gases to date.

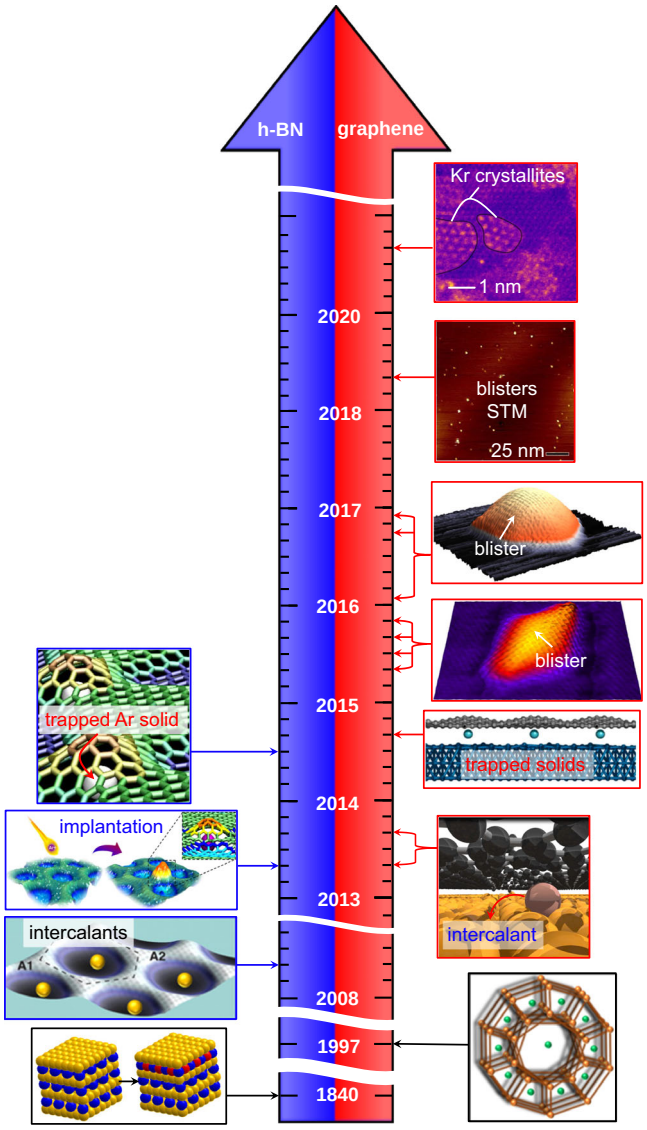

Figure 3. All key demonstrations[30,32–35,52,57–67] of intercalated systems where h-BN and graphene were used as host materials and rare gas solids were used as intercalants.

4. Growth and Intercalation Technology

Several technologies used by the scientific community for growing 2D materials, including exfoliation, chemical vapor deposition (CVD), metalorganic CVD (MOCVD), and molecular beam epitaxy (MBE) are discussed in this section. Ion irradiation is a popular technique to achieve the intercalation of rare gases. We then describe the ion irradiation technique used for the intercalation process.

4.1. Growth of 2D Host Materials

Several methods such as liquid or mechanical exfoliation under ambient conditions, the low-vacuum technique CVD or MOCVD and the high-vacuum technique MBE are widely adopted for the

Figure 4. Various synthesis or growth techniques of h-BN and graphene. These techniques are classified based on the level of vacuum required during material deposition.

epitaxial growth or synthesis of 2D materials. **Figure 4** lists all the possible technologies for the growth of h-BN and graphene. We first discuss different exfoliation techniques used for the synthesis of these two 2D materials, followed by vacuum growth tools used for the same purpose.

4.1.1. Exfoliation and Drop-Casting

Intercalation-based exfoliation and direct exfoliation are the two types of liquid exfoliation that are popular and promising for synthesizing graphene. Scotch-tape-based mechanical exfoliation is another easy method of synthesizing graphene on a SiO_2-coated silicon substrate.[68] These are low-cost synthesis processes that can yield low-defect graphene from pristine graphite.[69] This technology is, however, not suitable for large-scale production and fabrication of 2D materials. This method also requires the ultrasonic treatment of graphite in expensive solvents, so the extra care for handling required in this method does not contribute to its user-friendliness.[70] Wafer-size, high-quality, and few-layer graphene sheets were produced using aqueous mixtures of graphite.[71] Achievement of low-defect and nonoxide graphene was demonstrated by exfoliating graphite sheets.[72] For the growth or synthesis of h-BN, exfoliation[73] and drop-casting[74] techniques have also been reported. However, none of these techniques are scalable and applicable to industry that requires high or ultra-high vacuum chambers for the growth of h-BN and graphene.

4.1.2. CVD and MOCVD

To date, considerable efforts have been made to achieve single-crystalline graphene and h-BN using CVD, MOCVD, and MBE. Among these, CVD is considered to be a scalable and cost-effective method for the growth of these 2D materials on different catalytic substrates. Various CVD methods including thermal CVD, atmospheric pressure CVD (APCVD), low-pressure CVD (LPCVD), and plasma-enhanced CVD (PECVD) are preferred tools for the growth of large-scale and high-quality graphene. LPCVD and PECVD have received considerable attention due to their capability of growing graphene at low temperatures. Moreover, they are economical, environment-friendly, and ideal for growth on flexible substrates. Metal substrates such as nickel, iridium, ruthenium, platinum, cobalt, and copper are popular for the CVD growth of graphene films because they reduce the reactants' energy barrier. Among these substrates, copper is considered superior because graphene grown on copper exhibits better uniformity and scalability, and higher mobility.[75] However, CVD-grown graphene is limited to large-scale applications as it requires transfer to another substrate which triggers the use of the MOCVD growth tool to eliminate the tedious process of film transfer. Recently, graphene-based nanostructures were grown on SiO_2/Si substrate by MOCVD to leverage the full potential of graphene's outstanding electrical and chemical properties.[76]

Large-area, high-quality h-BN was grown using CVD on an iron coil.[77] A recent review of the synthesis of h-BN by CVD has engaged in an in-depth discussion on the growth mechanism using three steps. However, due to the limited diameter of horizontal tube furnaces and the use of catalytic metal substrates, CVD is not an ideal growth technology for h-BN.[78] In this regard, MOCVD is the preferred choice for commercial use among researchers due to its capacity for high throughput. Bulk h-BN on sapphire substrate grown by MOCVD at 1500 °C has been reported.[79,80] MOCVD is an excellent tool for synthesizing epitaxial h-BN on sapphire.[81]

4.1.3. MBE

A high-vacuum technique like MBE is another alternative approach for graphene growth that does not require the decomposition of hydrocarbons and offers a viable route to grow on a variety of substrates including insulators, other 2D semiconductors, and metals. Additionally, the low growth temperatures required by MBE for graphene significantly reduce production

costs.[82] Unlike MOCVD where the growth temperature is relatively much higher, MBE was found to be suitable for growing large-area and low-defect h-BN at lower growth temperatures. The film was found to be polycrystalline when the growth temperature was lower than 1,000 °C.[83] Moreover, to control the growth of h-BN layers, the temperature of the boron sublimation source should be increased to attain a reasonably high growth rate of h-BN. This effect was explained by achieving streaky reflection high energy electron diffraction (RHEED) patterns at a growth temperature of 1390 °C.[84] The sublimation temperature of the boron cell was fixed at 1925 °C. Such results demonstrated that high-temperature MBE growth is essential for the growth of mono- and few-layer h-BN films with a good, atomically flat surface coverage.[84]

4.2. Technology for Intercalation of Rare Gas Solids

Ion irradiation is one of the commonly-employed techniques for intercalation. To create defects in target 2D materials or alter their properties, this technique is often employed. During ion irradiation, rare gas ions are accelerated to reasonable energies within a high vacuum chamber and subsequently directed toward the 2D materials for intercalation. This process results in the insertion of rare gases into the lattice structure of the 2D materials which is sometimes referred to as ion implantation. Hence, irradiation and implantation are the two terms that are sometimes used interchangeably. Note that the term "implantation" is more appropriate for III–V semiconductors.

Ion beams used in the irradiation process are typically broad and unfocused, leading to damages and vacancies across a large area of the host 2D materials. To address this issue, researchers have focused on the controlled ion beam irradiation process. This process involves changing the angle of incidence of the ion beam, which was shown to reduce the damage to the host material during ion irradiation.[85] A recent study focused on the controlled ion beam irradiation process reported that when the angle of incidence of the ion beam was around 80°, ion irradiation could be achieved with minimal damage to the 2D host material.[85] By controlling the ion beams, the damage in the 2D materials caused during ion irradiation is minimized and the intercalation process is optimized to create the host materials with unique properties. **Figure 5** schematically shows the ion irradiation technique used for intercalation.

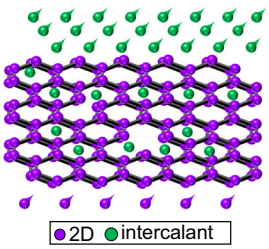

Figure 5. Intercalation technique of rare gas solids: ion irradiation.

5. Technical Challenges

Intercalation in graphene and h-BN is undoubtedly one of the best tools for exploring and tuning the properties of the resulting new materials. Development of novel disruptive technologies via intercalation-enhanced material properties continues to attract scientific interest especially in the field of electronics[86–88] and quantum photonics.[51,89] However, the existence of a handful of problems bottlenecks the opening of new avenues of opportunity to be pursued in quantum applications. Overcoming these challenges requires both more research and technological improvement. The challenges are briefly overviewed below:

1) Single-crystalline h-BN growth by MOCVD is challenging because h-BN crystals nucleate at low temperatures at the edges of substrates.[90] Precursor selection in CVD is also limited due to parameters like pressure, solubility, and temperature sensitivity.[91] Metalorganic precursor and parasitic gas-phase reactions in MOCVD are also major concerns apart from the high-temperature requirement.[92] As far as MBE is considered, extremely high growth temperatures (>1700 °C) and low boron flux ($\approx 1 \times 10^{-8}$ Torr beam equivalent pressure) in a customized MBE can improve the film quality by minimizing crystal nucleation and decomposition which in turn will yield a very poor growth rate.[93] Fine-tuning the growth parameters to realize low-defect and uniform h-BN with a moderate growth rate is still a challenge that researchers experienced in the low-temperature growth of high-quality h-BN.

2) The performance of intercalated films is limited by the random positioning of intercalant atoms or species. The precise control of both the number of intercalants and deterministic intercalation at a particular spatial location is of utmost importance for the targeted quantum technologies. Ion irradiation used for intercalation on h-BN and graphene is not a suitable technology for intercalation because of crystal damage through the formation of point defects, vacancies, and interstitials in these 2D materials due to ion bombardment. Due to such bond rupture and damage, the true benefits of intercalation cannot be achieved using this technique. Moreover, the typical fluence range of 10^9–10^{16} cm^{-2} during irradiation is very high, and control over this parameter is needed and should be incorporated with high spatial resolution.[94]

3) It is important to build a novel material system by encapsulating intercalated rare gas solids in between 2D layered materials, e.g., graphene and h-BN. This also requires deterministic intercalation of the rare gases at a particular spatial location on graphene or h-BN. Such a system will require in situ h-BN or graphene growth followed by rare gas intercalation in a single-growth reactor without breaking the vacuum. This is certainly challenging to accomplish using available technologies. This suggests that further technological advances are necessary to encapsulate rare gases between 2D sheets.

6. Demonstration of Intercalation in 2D Materials

Major efforts have been devoted to the development of intercalated 2D materials. The following section briefly discusses the state-of-the-art intercalation techniques that have so far been used with h-BN and graphene. In the works summarized in the following

paragraphs, the formation of interstitial defects or nanoblisters has been termed bulges, nanoplatelets, nanotents, protrusions, and clusters. Instead of mentioning multiple terms, we will use a common term, "blister", in this review paper to avoid confusion.

6.1. Intercalation in h-BN by Rare Gas Solids

In April 2008, a research group at the University of Zurich reported on the intercalation of Xe ions on monolayer h-BN on Rh(111) substrate.[58] They were the first to experience the trapping of Xe ions on the h-BN/Rh sample. The same group in April 2013 reported the intercalation of Ar ions in a high-temperature CVD-grown monolayer h-BN with a self-assembled corrugated honeycomb structure on Rh(111) substrate.[59] The monolayer h-BN was referred to as a nanomesh. Each nanomesh unit had a periodicity of 3 nm and at the center of each unit cell was a pore with a diameter of 2 nm. These pores were surrounded by wiry regions with weak bonding to the Rh substrate, as shown in **Figure 6**a. Figure 6a also shows the schematic representation of Ar blister creation during the intercalation process. A zoomed-in image of the single Ar atom trapped is also included. Further evidence of the presence of Ar intercalated atoms was found by X-ray photoelectron spectroscopy (XPS) measurements, as shown in Figure 6b, where the green and blue colors represent pristine h-BN/Rh and Ar-irradiated samples, respectively.

More than a year later, the same group published another work on the rare gas intercalation of CVD-grown pristine h-BN on Rh(111) substrate.[35] In this work, they again intercalated the sample using low-energy Ar ions; this created Ar blisters after ion bombardment, shown schematically in **Figure 7**a. The blue circles in Figure 7b show the vacancies created due to the ion bombardment of Ar ions that sputtered out boron and nitrogen atoms. The authors claimed their intercalation scheme to be site-selective since Ar atoms were immobilized only beneath the wire-crossing sites and not in the pores shown in the right bottom inset of Figure 7b, where A and B are wire-crossing sites and P is a pore. The inset also shows the corrugated honeycomb structure. Figure 7c shows the cross-sectional profile of the white arrow, as shown in Figure 7b, giving the differences in height between the structures created along the white arrow after the intercalation process. In Figure 7c, Ar blister is represented by the B* peak followed by the wire-crossing sites A and B. The pink arrow indicates a void, and pores are seen at both ends of the profile. The goal of this study was to explain the can-opener and self-healing effects in monolayer h-BN but since these processes are not relevant to intercalation, we make no mention of it in this review paper.

The intercalation technique used by Cun et al.[35,59] sheds light on the behavior of rare gas intercalants in 2D host materials such as h-BN. The authors claim that their intercalation process is site-selective, as the intercalants are only found at wire-crossing sites in the material and not in the voids. This helps us to understand the intercalant's behavior, as it prefers to be beneath the wire regions rather than in the voids. However, this site-selective process occurs naturally and cannot be manipulated to ensure that the intercalant is present beneath a specific wire-crossing

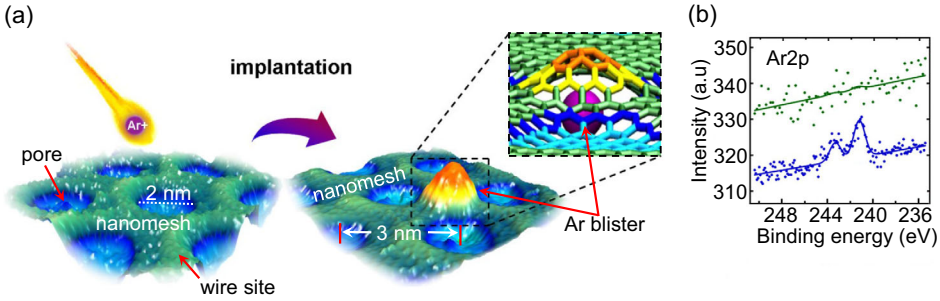

Figure 6. a) Schematic representation of blister formation due to Ar ion irradiation on h-BN, and b) photoemission spectra of pristine h-BN and Ar-irradiated samples. Reproduced with permission.[59] Copyright 2013, ACS.

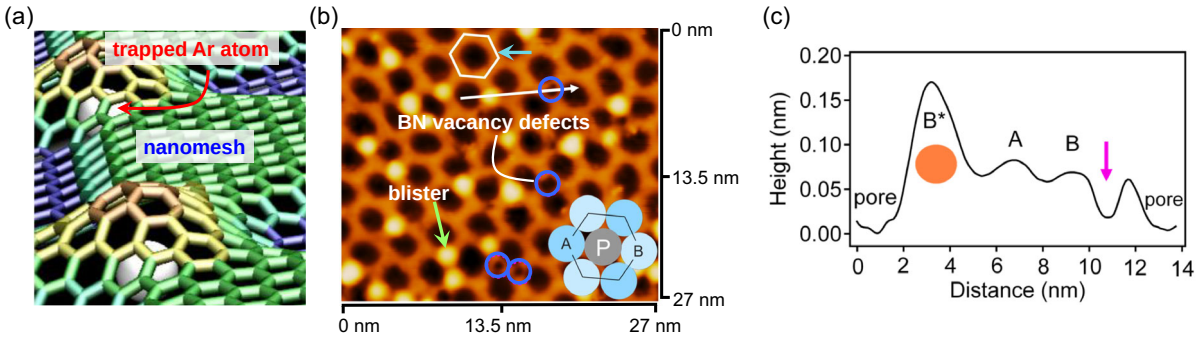

Figure 7. a) Schematic representation of intercalated Ar atoms under the h-BN nanomesh, b) RT-STM image of the intercalated sample, and c) cross-sectional profile along the white arrow drawn in (b) which distinguishes between voids, pores, occupied, and empty sites. Reproduced with permission.[35] Copyright 2014, ACS.

region, as it can be presented anywhere in the wire region and is not selective.

6.2. Intercalation in Graphene by Rare Gas Solids

In 2013, Blanc et al. worked on exploring the strain properties of CVD-grown graphene on Ir(111) substrate.[60] Intercalation was performed on a graphene/Ir(111) sample using high-energy Ar ions. The trapping of Ar atoms at the graphene/Ir(111) interface was confirmed by observing the RHEED profile. The trapping was also experienced by Åhlgren et al. in 2013 which they confirmed using STM.[61]

In 2014, Herbig et al. from the University of Helsinki intercalated low-energy He, Ne, Ar, and Xe ions on the epitaxial graphene layer deposited on Ir(111) substrate at RT.[62] At first, the authors reported that the intercalation of rare gas ions knocked out a few carbon atoms from the graphene layer by creating vacancies and that these knocked-out carbon atoms get trapped at the graphene/Ir(111) interface forming blisters. Later in 2015,[63] they nullified their previous claim by proving those blisters were caused by the agglomeration of rare gas solids. To confirm this, they exposed a bare Ir substrate to Xe ions at RT followed by high-temperature annealing. XPS measurements confirmed the presence of Xe $3d_{3/2}$ signal which got reduced postannealing due to thermal excitation, as shown in **Figure 8**a. The presence of a residual Xe signal after annealing at 1,300 K was attributed to the accumulation of Xe atoms which was also justified by other two reports.[95,96] However, graphene deposited on Ir yielded a different photoemission spectrum when exposed to the same ions. A substantial increase of the integrated Xe 3*d* peak intensity by a factor of 2 compared to the same peak for the bare substrate is shown in Figure 8b. This was attributed to the diffusion of irradiated Xe atoms from the substrate and their eventual trapping beneath the graphene monolayer, enhancing the corresponding intensity.[63] Figure 8c,e represents the 2D schematics of ion irradiation on bare metallic Ir(111) and graphene/Ir(111) at 300 K, respectively, and Figure 8d,f represents the high-temperature annealing of Ir(111) and graphene/Ir(111), respectively.

In 2014, they intercalated four different types of rare gas ions, namely He, Ne, Ar, and Xe, on graphene/Ir(111) and found that the trapping of carbon atoms at the graphene/Ir(111) interface increased substantially with the increasing atomic number of rare gas intercalants, based on STM images for the different intercalants, as shown in **Figure 9**a–d.[62] But based on their 2015 comment, we can infer that Figure 9a–d represented the

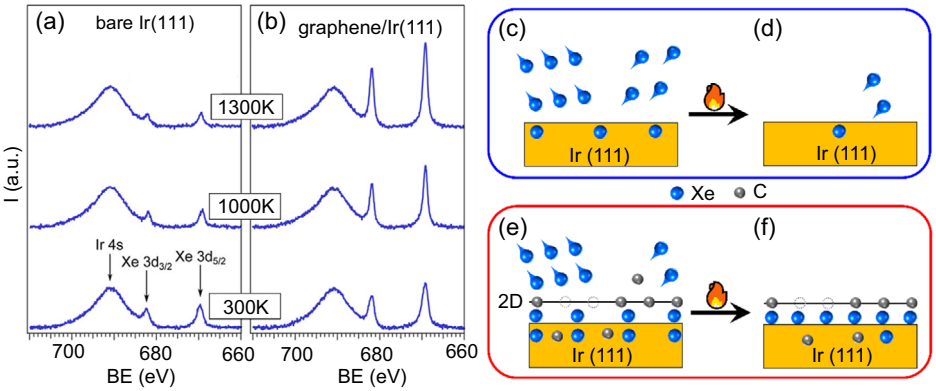

Figure 8. XPS spectra showing a) the presence of 3*d* peak of Xe atoms, and b) the intensified 3*d* peak after annealing at 1,000 and 1,300 K. Schematic image of ion irradiation c) on bare Ir (111), e) on graphene/Ir (111) at 300 K d,f) after subsequent annealing. Reproduced with permission.[63] Copyright 2015, ACS.

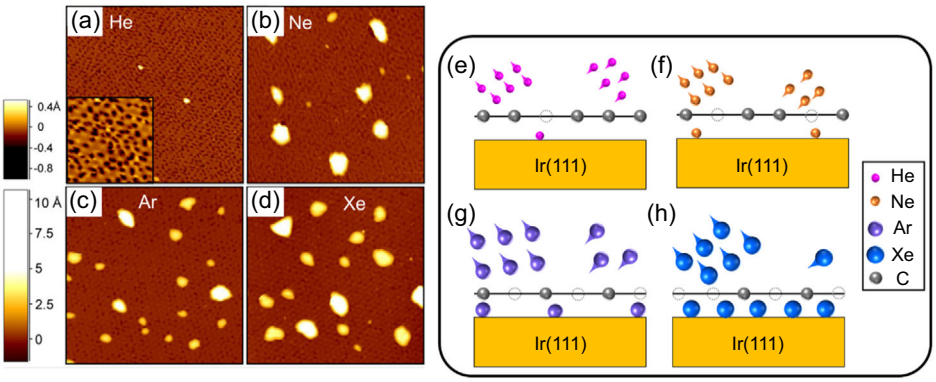

Figure 9. STM images showing trapped a) He, b) Ne, c) Ar, and d) Xe atoms (The image sizes are 80 nm × 80 nm, with the inset in (a) - 20 nm × 20 nm). Schematic representation of intercalation of e) He, f) Ne, g) Ar, and h) Xe atoms, respectively. Reproduced with permission.[62] Copyright 2015, ACS.

trapping of rare gas intercalants instead of carbon atoms,[56] and the dependence of rare gas trapping on atomic numbers can be attributed to the size of atoms. He atoms, with an atomic number of 2 and an atomic size of 31 pm, can penetrate carbon layers without creating vacancies. As a result, He atoms with high kinetic energy and small size do not interact much with carbon, allowing them to escape to the vacuum. However, Xe atoms, with an atomic number of 54 and an atomic size of 108 pm, strongly interact with carbon atoms upon incidence on the graphene layer, causing them to lose energy and be trapped at the substrate/2D interface upon hitting the substrate. Figure 9e–h shows the 2D representation of the intercalation of different rare gas ions on graphene/Ir(111) based on the authors' 2015 revision.

To demonstrate the trapping of rare gas solids on graphene/Ir(111), the authors further continued their 2015 work using the same technique and material but this time they varied the dosage of Xe ions and annealed the samples at different temperatures.[64] The results, however, turned out the same as the blisters formed due to Xe trapping were found to be thermally stable. The authors justified this with DFT calculations. The overall study conducted by Herbig et al.[62–64] showed that the size of intercalant solids has a significant impact on the intercalation process, reducing or increasing host material damages. Smaller intercalants cause less damage without changing the host material's inherent properties. Understanding the intercalation process at the nanoscale is critical for developing effective strategies for intercalation that can be scaled up.

During the same period, Zamborlini et al. also worked on the rare gas intercalation of CVD-grown graphene on an Ir(100) substrate.[30] Low-energy Ar ions were intercalated at RT, shown as a 2D top-view model in **Figure 10**a. Experimental confirmation was provided by RT μ-XPS, as shown in Figure 10b, where Ar atoms are seen to form 2D and 3D blisters by getting trapped in the graphene/Ir(100) substrate. The blisters increased in size, which was likened to ripening, as shown in Figure 10c. The ripening occurred mainly due to the mobility of the trapped Ar atoms causing the merging of two or more blisters to form larger ones; Figure 10d shows the proximity of blisters. Based on the authors' calculations, the pressure in these ripened blisters was above 70 GPa. This work revealed the pressure properties and size variability of Ar blisters on graphene/Ir. Blister size is crucial for determining the strain and pressure properties of intercalated 2D materials. This study also provides insights into the physical processes governing blister formation, including the role of graphene and Ir substrates.

In 2015, Hyo Won Kim et al. reported their work on the controlled phonon excitation of graphene/platinum by intercalation of Ar ions.[33] They intercalated their sample by Ar ions in a controlled manner and observed trapped Ar atoms at the interface forming blisters. These blisters were found to interact with phonons by facilitating their excitation. They also enhanced electron tunneling. This discovery is significant as phonons are a major factor in determining the electronic properties of materials. By clarifying the mechanisms behind Ar blister formation, the authors provided valuable insights into effectively exciting phonons in graphene layers.

In 2016, Späth et al. published their work on the Ar intercalation of graphene/Ni(111).[32] First, they intercalated Ar ions on the Ni(111) substrate which was followed by the growth of graphene layers. The authors were interested in trapping Ar atoms at the graphene/Ni interface due to their potential application in gas sensors. They conducted comprehensive thermal stability experiments on the graphene/Ni intercalated with Ar atoms and found that at high temperatures, nonintercalated graphene layers were less stable and eventually diffused into bulk Ni. This was attributed to the direct bonding of C atoms with Ni substrate and the fact that the catalytic properties of nickel at high temperatures dissolve the graphene layers. Contrary to this, the intercalated graphene layer with Ar atoms was found to be very stable at the same temperature due to the mutual exchange of energies between C and Ar atoms, i.e., Ar protected the graphene from dissolving into the Ni substrate, while graphene retained the Ar atoms desorbing into the vacuum. This study provided significant insights into the thermal stability of nonintercalated and intercalated graphene layers. It was claimed that intercalated graphene layers are highly thermally stable, making intercalation with Ar rare gas solids a promising method for preparing graphene for high-temperature applications.

In 2016, Larciprete et al. reported the rare gas intercalation of CVD-grown monolayer graphene on Ni substrate using intercalated Ar atoms.[65] They also observed the formation of Ar blisters due to Ar trapping on the graphene/Ni interface during the intercalation process, as shown schematically in **Figure 11**a. Figure 11b shows that increasing the dosage of Ar ions increases their coverage of the sample as ions with high dosage can create multiple carbon vacancies paving the way for Ar accumulation on the graphene/Ni interface. The authors explained that as the van de Waals diameter of the Ar atoms was larger than the interlayer spacing of graphene/Ni, the Ar atoms deformed the monolayer graphene elastically, forming blisters. Figure 11b shows the in-plane 3D STM image of the blisters, with two of them marked A

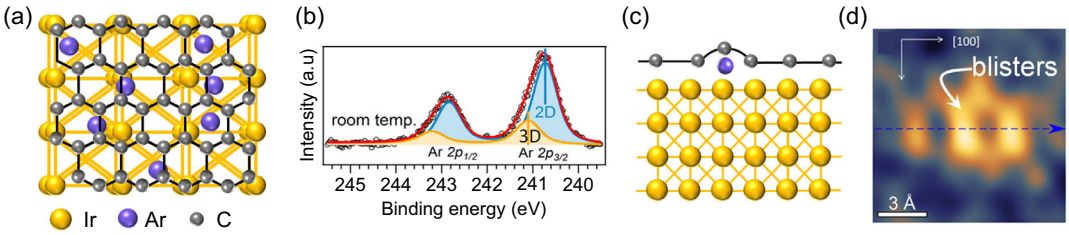

Figure 10. a) 2D top view of Ar ion trapping, b) RT μ-XPS Ar 2*p* spectra with the low and high binding energy doublets correspond to 2D (blue) and 3D (orange) interfacial Ar, respectively, c) 2D model of blister formation, and d) an experimental STM image of Ar blisters. Reproduced with permission.[30] Copyright 2015, ACS.

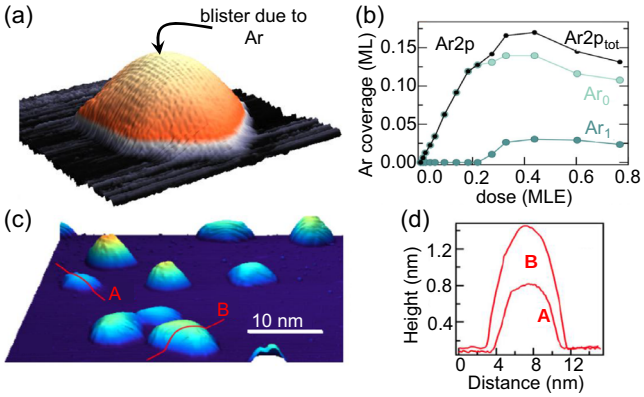

Figure 11. a) Schematic representation of a blister, b) evolution of the Ar 2*p* component intensity with Ar^+ dose, c) STM image of two different blisters A and B, and d) height profiles showing the variation of height between A and B indicated in (c). Reproduced with permission.[65] Copyright 2016, ACS.

and B. Their height difference is displayed in Figure 11d, ranging from 0.7 to 1.5 nm where A is shorter compared to B. This was due to the immobility of certain blisters preventing their merger with others to form larger blisters. Moreover, the formation of Ar blisters at the interface of graphene and nickel, as well as the factors that contribute to their mobility were inferred from the study. The work sheds light on the underlying mechanisms that give rise to blister formation, including the role of nickel and the influence of graphene layer thickness.

Later in the same year, Wang et al. also reported the formation of blisters when they intercalated Ne ions on their multilayer graphene placed on HOPG substrates.[34] The objective of their work was to measure the adhesion energy of graphene layers on a graphite substrate, so they used blisters as a tool to measure the adhesion energy. In 2018, Yoo et al. reported intercalating low-energy Kr atoms on exfoliated multilayer graphene obtained from graphite where the topmost layer acted as a capping layer and the remainder acted as a substrate.[66] Since the authors were more inclined toward studying the growth, they used encapsulated graphene where diffusion did not play a major role and hence the blister gets maximum pressure and erupts leaving a crater. **Figure 12**a shows the clean graphene layer after exfoliation. This clean sample was irradiated with low-energy Kr ions, trapping Kr atoms in the graphene layers which was confirmed by the surface morphology of the intercalated sample, as shown in Figure 12b, where bright spots portray the trapped Kr atoms. The authors observed two different types of blister height, as shown in Figure 12c, where gray bars represent tall blisters and green bars represent short ones. This height difference was due to the intercalation of Kr ions in different graphene layers. According to the authors, Kr intercalation in different layers affected the mechanical and electrical properties of the encapsulated graphene which in turn played a major role in determining the height and Kr atom population in the sites. This work represents a significant advancement in the field of intercalation, deviating from the established methods. The authors' findings on the height and location of Kr rare solids within the graphene layer are particularly noteworthy as they provide insights into the underlying physics of 2D materials intercalation.

Demonstration of intercalation of low-energy Kr ions on exfoliated multilayer graphene layers was also reported by a research group at the University of Vienna in collaboration with another at the University of Helsinki in 2020.[67] During the intercalation process, the authors observed that certain Kr ions with suitable energy were able to penetrate the first layer of graphene and got intercalated in the subsequent layers below which can be inferred from the schematics of **Figure 13**a. The trapped Kr ions between

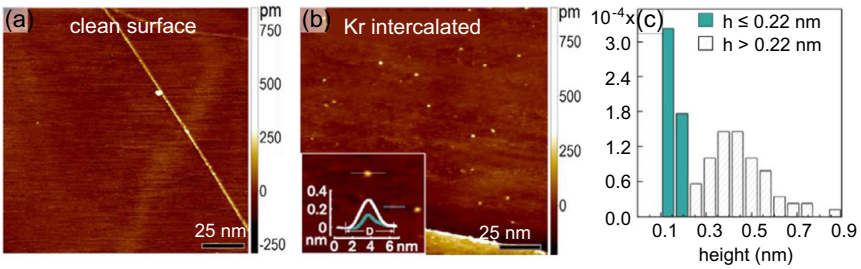

Figure 12. a) STM image of the clean exfoliated graphene, b) STM image of Kr ions intercalated on graphene with an inset representing the line profiles of two representative blisters, and c) the height distribution of the blisters shown in inset (b). The short and tall groups of blisters are displayed in green and gray, respectively.[66]

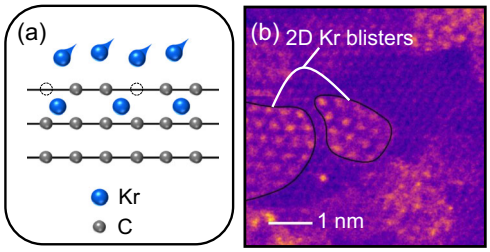

Figure 13. a) 2D representation of Kr trapping in graphene, b) STEM image of Kr-intercalated few-layer graphene. Two crystallites are highlighted by the black boundary lines. Reproduced with permission.[67] Copyright 2020, Cambridge University Press.

the graphene layers form 2D blisters shown in the scanning tunneling electron microscope (STEM) image in Figure 13b. These 2D crystallites were reported to be thermally stable.

7. Conclusion

In this review, we present the emerging field of research of the intercalation of 2D-layered materials with an entire focus on graphene and h-BN as well as rare gas solids to generate novel intercalated systems. Despite the availability of a few experimental studies of intercalation of graphene and h-BN using rare gas solids, vast research opportunities in this nascent and rapidly growing field still exist, especially in quantum photonics which is yet to be unveiled. Intercalation of rare gas solids on these 2D materials and exploiting nonzero nuclear spins of the ions could be possible solutions to enable quantum technologies. Rare gases have isolated spins that remain coherent for several hours above RT[24,97] and can maintain entanglement[37] for a long period of time. These spin ensembles can interact with the optically addressable spin of h-BN-defects in an intercalated environment to advance the stability of single photon emission. Although not investigated yet, the insertion of the intercalants into low-defect graphene h-BN and graphene at a particular spatial location in a controlled manner is promising for the development of high-efficiency deterministic quantum photon emitters. The results presented in Section 6 offer valuable insights into the behavior of rare gas solids in intercalated systems, as well as their capacity to induce exciting physical and chemical changes in 2D materials like graphene and h-BN. These findings provide a foundation for further exploration of rare gas intercalation on these materials, including the measurement of rare gas solid properties and their combined effects with the 2D materials for quantum applications.[54]

Different growth techniques for these 2D materials and insertion techniques for various rare gas solids are also discussed in this review. Growth challenges in CVD, MOCVD, and MBE are also described in detail; close attention is required for their successful implementation to realize low-defect and single-crystalline h-BN at low growth temperatures. For real-world applications, controlled intercalation with a defined fluency is necessary. The state-of-the-art ion irradiation technique that is mostly used for intercalation is not well-controlled and is not suitable for all substrate materials. Given the little progress made in the intercalation of h-BN and graphene over the past decade or so, considerable challenges remain in this field. This is attributed to a lack of not only appropriate technologies but also of fundamental understanding of the intercalation processes and their technological applications in practical devices. Using patterned host substrates and exploiting the correct intercalation techniques are required for realizing application-suited devices. In addition, controlling the beam-spot size and the voltage during irradiation is important for ruling out the possibility of random intercalation and paving the way for deterministic intercalation.

The unprecedented combination of low-defect 2D host materials and the intrinsic spin properties of rare gas solids remains unexplored and is expected to open up fascinating opportunities in material chemistry, fundamental physics, and device engineering. With advances in the field of intercalated 2D materials, more functional systems in other areas will emerge. Continued efforts from the relevant research community are required for enhancing the understanding of intercalated systems which will allow us to gain more control over the chemistry of systems with other 2D materials and intercalants.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

blisters, boron nitride, graphene, intercalation, ion irradiation, rare gases

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