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Two-dimensional material templates for van der Waals epitaxy, remote epitaxy, and intercalation growth **p**

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ABSTRACT

Epitaxial growth, a crystallographically oriented growth induced by the chemical bonding between crystalline substrate and atomic building blocks, has been a key technique in the thin-film and heterostructure applications of semiconductors. However, the epitaxial growth technique is limited by different lattice mismatch and thermal expansion coefficients of dissimilar crystals. Two-dimensional (2D) materials with dangling bond-free van der Waals surfaces have been used as growth templates for the hetero-integration of highly mismatched materials. Moreover, the ultrathin nature of 2D materials also allows for remote epitaxial growth and confinement growth of quasi-2D materials via intercalation. Here, we review the hetero-dimensional growth on 2D substrates: van der Waals epitaxy (vdWE), quasi vdWE, and intercalation growth. We discuss the growth mechanism and fundamental challenges for vdWE on 2D substrates. We also examine emerging vdWE techniques that use epitaxial liftoff and confinement epitaxial growth in detail. Finally, we give a brief review of radiation effects in 2D materials also and contrast the damage induced with their 3D counterparts.

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I. INTRODUCTION

The combination of crystals with different physical properties offers the capability of integrating them into functional systems. Numerous epitaxial growth techniques have been developed to realize the crystallographically modulated integration of different crystals. Epitaxy refers to the phenomenon in which grown crystals or films are fabricated with the crystalline orientation relative to the growth substrate when a crystalline material is grown on a different crystalline substrate. The chemical bonding of dangling bonds between the crystalline substrate and atomic building blocks is responsible for the lattice ordering in epitaxial growth, causing the epilayer to mimic the crystalline structure of the substrate. Despite different lattice parameters and thermal expansion coefficients of the grown material and the substrate, strong chemical bonds at the heterointerface forces the formation of lattice matching of the two materials. This causes numerous mismatch-related defects, such as misfit dislocations and interface disorder (buffer layer) at the heterointerface.^{1,2} Therefore, specific conditions need to be satisfied for conventional epitaxial growth with strong chemical bonds at the heterointerface, such as growth of GaAs on GaN. To fabricate high-quality heterointerfaces with low defect density, artificial buffer layers have been introduced at the interface.^{3,4} However, the formation of a buffer layer is not universally applicable to all epitaxial growth systems. Moreover, heterointerfaces with a buffer layer possess a disordered structure, which deteriorates the electrical properties of epitaxially grown films.

Van der Waals epitaxy (vdWE), which refers to epitaxial growth on a dangling-bond-free substrate, relaxes the restriction of lattice matching and thermal expansion owing to weak van der Waals interaction between grown materials and the substrate. In contrast to that in conventional heteroepitaxy, the grown epilayer with van der Waals (vdW) interaction exhibits incommensurate/incoherent in-plane lattices at the heterointerface, thereby enabling an alternative bond-free integration with minimized lattice-mismatch strain.^{5.6} The recent emergence of two-dimensional (2D) materials and vdW heterostructures has sparked considerable interest in vdWE. For example, a previous work has proposed remote epitaxy,⁷ that is, the epitaxial growth of a single-crystalline film on a graphene-coated growth substrate.⁸ In addition, the intercalation growth of quasi-2D crystals, such as Au, Ga, and GaN with a thickness of several atoms, has been demonstrated as a confinement-heteroepitaxial-growth method.^{9–11}

In this paper, we review recent progress in the vdWE, remote epitaxy, and intercalation growth using 2D templates (Fig. 1). First, we introduce the features of vdWE growth of 3D and 2D materials on the 2D templates. Then, we discuss the growth mechanism and limits of vdWE on 2D templates and provide the approaches to solve the issues for vdWE, such as defect control and functionalization. We also highlight the emerging research field based on vdWE, such as remote epitaxy and intercalation growth. Finally, a brief review of radiation damage effects in 2D materials is given, since there is strong interest in using these in lightweight systems with novel electronic and photonic applications, such as space-borne sensing and monitoring.



FIG. 1. Two-dimensional material templates for (a) 2D/2D van der Waals epitaxy, (b) 3D/2D van der Waals epitaxy, (c) remote epitaxy, and (d) intercalation growth.^{7,10,53,112} Reproduced with permission from Balushi *et al.*, Nat. Mater. **15**, 1166 (2016). Copyright 2016 Springer Nature. Reproduced with permission from Domask *et al.*, Cryst. Growth Des. **18**(6), 3494–3501 (2018). Copyright 2018 The Royal Society of Chemistry. Reproduced with permission from Li *et al.*, Nature **579**, 368–374 (2020). Copyright 2020 Springer Nature.

II. Van der WAALS EPITAXY ON 2D TEMPLATES

vdWE is the growth of the epitaxial layer on a crystalline substrate, where the grown crystalline layer is held together with the substrate by a weak vdW interaction. This contrasts with conventional epitaxy, where the crystalline layer is attached to the substrate by a strong chemical bond [Figs. 2(a) and 2(b)]. Substrates used in conventional epitaxy possess a highly active surface with several dangling bonds. Due to the formation of the strong chemical bonds at the heterointerface, the in-plane lattice parameter of the epilayer should be modified to match that of the substrate. A high lattice mismatch between the epilayer and the substrate induces high interfacial strain and a number of mismatch-related defects, such as misfit dislocations and interface disorder.¹ By contrast, the vdW surface has no dangling bonds, and a vdW gap is generated at the heterointerface, leading to a negligibly small strain.⁷ The epilayers in the vdWE have incommensurate in-plane lattices and a crystallographic orientation relationship with the vdW substrate.^{5,6} Therefore, vdWE enables the formation of numerous heterostructure combinations between two materials with different crystal structures and symmetries. When conventional bulk crystals with dangling bonds are grown on a vdW substrate, quasivdWE (QvdWE) is possible due to the dangling-bond-free bottom substrate, as shown in Fig. 2(c).

2D materials have recently attracted interest because of their unique physical and chemical properties and potential technological applications. Owing to the weak vdW interactions between the layers,

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atomically thin layers can be isolated from the bulk materials.¹² The lack of surface dangling bonds on 2D materials provides new opportunities for studying unprecedented, dimensionality-driven physical properties.^{13–15} Recent theoretical studies estimate that more than a thousand materials are exfoliable,^{16,17} including the group IV and V crystals (e.g., silicene and phosphorene), transition metal dichalcogenides (TMDs), (e.g., MoS₂, WSe₂), transition metal carbides, and nitrides (e.g., $Ti_3C_2T_x$, where T = O, OH, F), composite materials of the groups III-V, II-VI, and I-VII [e.g., GaN, hexagonal BN (hBN), and GaAs], and transition metal halides (e.g., CrI₃).¹⁸⁻²¹ Therefore, exfoliable materials with different basal plane structures of square, hexagonal, and rectangular shapes can provide varied potential landscapes for different epilayers without chemical bonds.²² Epilayers grown on the vdW substrates with vdWE have atomically abrupt interfaces with a vdW gap, which prevents interdiffusion between the epilayers and the vdW substrates. The vdWE heterostructures of 2D and 3D materials with ultraclean heterointerfaces offer a rich library of materials with unprecedented and superior electronical, magnetic, and optical properties and enables the investigation into new physics and fabrication of high-performance electronic devices.²²

A. Van der Waals epitaxial relation on 2D materials

1. 2D/2D van der Waals epitaxy

2D/2D vdW heterostructures have been demonstrated using mechanical exfoliation and stacking processes. However, the stacking process is not scalable for practical applications.^{24,25} Thus, vdWE has been studied to scale up 2D/2D vdW heterostructures. Among various deposition techniques, molecular beam epitaxy (MBE) has been used to fabricate a clean heterointerface and minimize impurity concentration in the grown film.²⁶⁻³⁴ For example, in situ growth of MoSe₂/ MoTe₂ superlattices on GaAs (111) was demonstrated as shown in Fig. 3(a). Owing to their ultrathin thickness and excellent crystallinity, the MBE-grown 2D heterostructures are promising templates for investigating novel physical properties at the atomic scale, such as bandgap transition and quantum spin Hall states.^{26,35} However, MBE has a low yield and requires extremely purified source materials; thus, considerable effort has been made to utilize direct vapor-phase growth techniques, such as chemical vapor deposition (CVD)³⁶⁻⁴⁷ and metal-organic CVD (MOCVD).^{48,49} For example, the vdWE growth of single-crystalline, atomically thin 2D metallic Mte₂ (M = V, Nb, Ta)

on a Wse₂ (WS₂) substrate was synthesized using CVD, resulting in vdW contacts for 2D semiconductors with minimal interface damage and improved electronic performance [Fig. 3(b)].³⁶ The atomic layer-by-layer epitaxial growth of vdW superlattices composed of more than two kinds of dissimilar TMDs was successfully demonstrated by MOCVD through the kinetic control of heteronucleation in the near-equilibrium limit.⁴⁹ To suppress the unwanted overgrowth and interlayer mixing, low growth temperature (550 °C) and precursor partial pressure ($\sim 10^{-7}$ Torr) were set, leading to full epilayer coverage by decreasing the lateral growth rate to ~ 0.15 nm min⁻¹ [Fig. 3(c)]. The recent demonstrations of the growth of 2D/2D vdWE are summarized in Table I.

2. 3D/2D quasi van der Waals epitaxy

From elemental metals to other complicated 3D materials with more than one element, such as compound semiconductors (III-V and II-VI semiconductors), oxides, and metal halides, the QvdWE of other non-layered 3D materials on 2D substrates has been achieved. Some metals exhibit a QvdWE interaction with 2D materials when they are directly grown on 2D materials.⁵³⁻⁵⁵ Several face-centered cubic (FCC) metals are known to grow epitaxially on TMDs with an orientational relationship of metal (111)//TMDs (0001). Other sixfold symmetric metals, such as body-centered cubic (111) and hexagonally close-packed (0001), are also grown on TMDs with epitaxial relationships to the (0001) planes of TMDs.^{53,54} Black phosphorus (BP), a low-symmetry 2D material, guides the assembly of metal atoms along the [100] direction, allowing for the epitaxy of single-crystalline film in a different manner from that of TMDs with an orientational relationship of metal (110)//BP (010) [Figs. 4(a)-4(c)].⁵⁶ Figure 4(c) shows the electron back scattering diffraction mapping of single-crystalline Au on a BP flake formed by E-beam evaporation.

The realization of the vdW interface and orientational relationship between 2D materials and metals is essential to increase the performance of 2D material-based devices by reducing the contact resistance and Fermi level pinning at the vdW interface. Based on the reduced Fermi level pinning, contact resistance is simply controlled by the work function difference between 2D materials and metals, approaching the Schottky–Mott limit for a vdW metal–semiconductor junction.^{57,58} The crystallographic alignment of semimetal Bi on MoS₂ with vdW gap shifts the Bi p_z orbital to the conduction band of MoS₂



FIG. 3. (a) Growth diagram of the MoTe₂/MoSe₂ superlattices on the GaAs substrate by molecular beam epitaxy (MBE) and high angle annular dark field-scanning transmission electron microscope (HAADF-STEM) image of the superlattices and atomic resolution electron energy loss spectroscopy (EELS) map of the Te M_{4,5} edge.³⁴ Reproduced with permission from Vishwanath *et al.*, J. Mater. Res. **31**, 900–910 (2016). Copyright 2016 Springer Nature. (b) Optical microscope (OM) images of V(Ta)Te₂ nanosheets grown on the WSe(S)₂ substrates by chemical vapor deposition (CVD) and the corresponding atomic force microscopy (AFM) images. The scale bar of OM and AFM images are 5 and 2 µm, respectively.³⁶ Reproduced with permission from Wu *et al.*, Adv. Funct. Mater. **29**, 1806611 (2019). Copyright 2019 Wiley-VCH GmbH. (c) Flow-rate modulations of metal-organic (MO) precursors for the growth of MoS₂/WS₂ superlattices by metal–organic chemical vapor deposition (MOCVD) and a series of cross-sectional HAADF-STEM images of the MoS₂/WS₂ superlattices from 1 to 7 monolayer stacks.⁴⁶ Reproduced with permission from Jin *et al.*, Nat. Nanotechnol. **16**, 1092–1098 (2021). Copyright 2021 Springer Nature.

while greatly suppressing the metal induced gap states of MoS₂, resulting in an ultralow contact resistance of 123 $\Omega \mu m$ [Fig. 4(d)].

Compound semiconductors can be grown on 2D materials by QvdWE. Graphene is typically used as a 2D substrate for the growth of compound semiconductors because it meets the temperature requirements for the growth conditions (up to 1000 °C) of compound semiconductors due to their high melting temperature and chemical inertness.^{59–63} TMDs are also used as 2D substrates in the QvdWE of compound semiconductors. However, given the low thermal stability and high reactivity of TMDs relative to graphene, only a few experimental demonstrations of vdWE on TMDs have been reported.⁶⁴ Controlling the heat-up procedure and carrier gas is important to preserve the integrity of the TMDs layer during growth. GaN layers were grown on WS₂ substrates by ramping up to the growth temperature in the N₂ atmosphere and switching the carrier gas to hydrogen immediately before the growth of the GaN layer.⁶⁴

The absence of dangling bonds at the surface of 2D substrates suppresses nucleation, thus hindering the growth of the thin-film structure. However, a nanowire structure can be successfully grown on 2D substrates due to its small footprint. The QvdWE growth of III–V semiconductors, such as InAs [Fig. 5(a)], GaAs, and GaN nanowires, on 2D substrates has been demonstrated.^{59,60,65,66} The direct

applications of nanowires/graphene in hybrid systems have been focused on optoelectronic devices such as photodetectors, solar cells, and light emitting diodes.^{61,63,67} Infrared photodetectors, fabricated from graphene/InAs nanowires with a vertically stacked heterojunction, exhibited strong photoresponsivity due to the rectifying behavior of the graphene/InAs nanowire heterojunctions and the tunable Schottky barrier can be used to control charge transport across the vertically stacked heterostructure. QvdWE of vertical nanowires (InGaAs/ InAs core-shell P-N junction) on graphene was employed in a novel solar cell architecture.⁶¹ Graphene functioned as the conductive back contact and growth template for QvdWE of vertical nanowires. The radial junction geometries are beneficial for mitigating surface defects and Shockley-Read-Hall recombination, leading to moderate enhancement in the power conversion efficiency compared to that of the axial junction geometries. Core-shell InGaAs/InAs junction nanowire arrays demonstrate a high conversion efficiency of 2.51%. The other QvdWE of GaN/ZnO core-shell nanowire heterojunction was grown directly on graphene, which was employed for light emitting diodes.⁶⁷ First, ZnO nanowires were grown directly on graphene; then, $In_xGa_{1-x}N/GaN$ multi quantum wells were grown epitaxially on the ZnO core. Finally, a Mg-doped p-GaN layer was deposited. The GaN-based coaxial light emitting diode nanostructures emitted blue

| | | | Lattice s | system | | |
|-------------------|-------------------|----------------|---------------|-----------|----------------------|------------|
| 2D substrates | Epilayers | Growth methods | 2D substrates | Epilayers | Lattice mismatch (%) | References |
| Graphene | MoSe ₂ | MBE | Hexagonal | Hexagonal | -33.5 | 26 |
| | | | | | | 27 |
| | MoS_2 | | | | -27.8 | 28 |
| | | | | | | 29 |
| | Wse ₂ | | | | -33.4 | 30 |
| | | | | | | 31 |
| hBN | MoSe ₂ | | | | -31.3 | 32 |
| WS ₂ | MoS_2 | | | | 0.2 | 33 |
| | MoSe ₂ | | | | -4.3 | |
| | Wse ₂ | | | | -4.2 | |
| MoS_2 | MoSe ₂ | | | | -4.5 | |
| | WS_2 | | | | -0.2 | |
| MoSe ₂ | WS_2 | | | | 4.1 | |
| | MoS ₂ | | | | 4.3 | |
| Wse ₂ | WS_2 | | | | 4.0 | |
| | MoS_2 | | | | 4.2 | |
| Graphene | WS_2 | CVD | | | -28 | 37 |
| | Wse ₂ | | | | -33.4 | 38 |
| hBN | Graphene | | | | 1.6 | 39 |
| | MoS_2 | | | | -25.7 | 40 |
| | WS_2 | | | | -26.0 | 41 |
| | ZrS_2 | | | | -46.2 | 42 |
| WS_2 | MoS_2 | | | | 0.2 | 43 |
| | | | | | | 44 |
| Wse ₂ | MoS_2 | | | | 4.2 | 45 |
| | SnS ₂ | | | | -10.8 | 46 |
| MoSe ₂ | GaSe | | | | -13.7 | 47 |
| Graphene | Wse ₂ | MOCVD | | | -33.4 | 50 |
| | | | | | | 48 |
| | | | | | | 51 |
| | hBN | | | | -1.6 | 52 |
| | MoS_2 | | | | -27.8 | 51 |
| MoS_2 | Wse ₂ | | | | -4.4 | 49 |
| Wse ₂ | MoS_2 | | | | 4.2 | |

TABLE I. Summary of recent examples of 2D/2D van der Waals epitaxy. Note: Lattice mismatch (%) = (a_{epi} - a_{sub})/a_{sub} × 100% (a: d-spacing).

light and could also be transferred to flexible substrates. No significant degradation of the device performance on flexible substrates was observed, owing to the flexibility of the graphene substrate.

Low nucleation density makes the direct growth of thin-film compound semiconductors on 2D substrates difficult to achieve; thus, epitaxially-grown epilayers are used as thin-film growth templates. GaN nanowires grown on graphene assisted the coalescence of a single-crystalline GaN film on an amorphous silica glass substrate.⁶² At the interface between the nanowires and thin film, the top of the nanowires showed an inverted pyramid shape formed in the process of epitaxial lateral overgrowth [Figs. 5(b)–5(d)].⁶² A light emitting diode fabricated using a GaN thin film grown on GaN nanowires

showed a record internal quantum efficiency of 48.67%. No defectrelated emissions were found in the spectra even at low temperature (5 K), indicating the high quality and low defect density of the GaN thin film. It was also demonstrated that the single-crystalline GaN film can be grown on a graphene/Cr substrate by using the epitaxial AlN seeding layer. This can be effective approach to fabricate the singlecrystalline GaN film on a flexible polycrystalline Cu substrate.⁶⁸

The fabrication of thin films directly on 2D substrates usually needs the adequately control of defect or functional groups on 2D substrates to increase the nucleation density. This is described in Sec. II C.

QvdWE of oxides and metal halides on 2D substrates has been demonstrated recently. Oxides with various crystal structures



FIG. 4. (a) Schematic illustration of the metal atom adsorption and film formation process on black phosphorus (BP). (b) Selected area electron diffraction (SAED) pattern of the Au/BP heterostructure. Diffraction spots from Au and BP are marked by blue and red circles, respectively. (c) Electron back scattering diffraction (EBSD) mapping of single-crystalline Au on a BP flake formed by e-beam evaporation.⁵⁶ Reproduced with permission from Lee *et al.*, Chem. Mater. **33**(10), 3593–3601 (2021). Copyright 2021 The Royal Society of Chemistry. (d) Schematic of the side view of Bi–MoS₂ and SAED patterns of MoS₂ (3.6 cm⁻¹), Bi (4.3 cm⁻¹) and Au (6.8 cm⁻¹) circled in yellow, pink, and orange, respectively.⁷⁸ Reproduced with permission from Shen *et al.*, Nature **593**, 211–217 (2021). Copyright 2021 Springer Nature.

including rock salt (NiO), gallium oxide (Ga₂O₃), wurtzite (ZnO), inverse spinel (CoFe₂O₄), and perovskite (lead zirconium titanate, PZT) have an epitaxial relationship with 2D muscovite (mica) substrate.^{69–72} For example, the epitaxial relationships between mica and CoFe2O4 is determined as CoFe2O4(111)//mica(001), which serves same epitaxial relationships other functional oxides grown on CoFe2O4. The magnetoelectric coupling from ferroelectricferrimagnetic bulk heterojunction was demonstrated by epitaxially grown bulk heterojunction (BiFeO₃-CoFe₂O₄) structure on mica.⁷ In addition, single-crystalline flexible ferroelectric PZT films grew on $CoFe_2O_4$ with assistance of mica as a 2D material [Fig. 6(a)]. Scalable epitaxial growth of orthorhombic molybdenum oxide (a-MoO₃) nanosheets on various 2D substrates was demonstrated [Figs. 6(b) and 6(c)].⁷³ High-quality lead halide perovskites (CsPbBr₃) single crystals were grown on highly oriented pyrolytic graphite (HOPG).⁷⁴ Figures 6(d) and 6(e) show the optical image and calculated relaxed supercell structure of CsPbBr₃ on HOPG. Different orientations of CsPbBr3 resulting from the sixfold orientations of HOPG have equal probability for nucleation.

A weak vdW interaction between the functional oxides and inorganic perovskites 2D substrate can reduce the effects induced from the interaction between substrates and epilayers. PZT grown on mica shows better piezoelectric coefficients than others grown by conventional epitaxy due to the absence of structural deformation at the interface between PZT and the substrate.⁷² VO₂ grown on hBN shows sharper metal—insulator transition (MIT) dynamics than that of VO₂ grown on the conventional epitaxial substrate, c-Al₂O₃.⁷⁵ Owing to the weak nature of vdW interaction at the VO₂/hBN interface, MIT proceeds via a single grain within a narrow temperature range of 2 K. Recent works that have demonstrated the growth of 3D/2D QvdWE are summarized in Table II.

B. Effect of growth factors on van der Waals epitaxy*1. Adhesion energy and cohesive energy*

In epitaxial growth, the morphology of epilayers is determined at the early stages of nucleation and by the dispersion of atoms on the surface at the particular growth temperature and mechanism. The adhesion energies and diffusion barriers of adatoms are important parameters in the nucleation process.⁸⁷ The morphology of the nucleus is determined based on the competition between the adhesion energy (E_{ads}) of the adatom to substrate and the cohesive energy (E_{coh}) of adatom to adatom. The evolution of their morphology during growth is influenced by kinetic factors, which determine whether newly deposited adatoms are likely to form a new nucleus or grow on an existing nucleus. When the diffusion barriers of adatoms are low, adatoms diffuse rapidly on the surface to form large crystalline islands. Conversely, when the diffusion barriers of adatoms are high, the nucleus forms finely dispersed islands with a small volume. In the thermodynamic limit, epitaxial growth can follow three major growth types according to E_{ads}/E_{coh} and the diffusion barriers [Fig. 7(a)]: (1) Frank-van der Merwe type, which consists of layer-by-layer growth of the epilayers for large E_{ads}/E_{coh} and low diffusion barriers; (2) Volmer-Weber type, which describes the 3D clustering of adatoms on a bare substrate for small E_{ads}/E_{coh} and low diffusion barriers; and (3) Stranski-Krastanov type, which is an intermediary growth type



FIG. 5. (a) Tilt/top-view FE-SEM image of InAs nanowires grown epitaxially on single layer graphene and schematic images of the atomic configuration presenting the nearly coherent epitaxial relationship of zinc blende InAs [-110]//Gr [1-210].⁵⁹ Reproduced with permission from Hong *et al.*, Nano Lett. **12**(3), 1431–1436 (2012). Copyright 2012 The Royal Society of Chemistry. (b) Schematic illustration of the nanowire-assisted vdWE method for the growth of the GaN film. (c) The tilted-view scanning electron microscope (SEM) image of vertically aligned GaN nanowires with uniform height; the inset shows the high-magnification SEM image of hexagonal-shaped nanowires between which the relative rotation angles of about 0°, 10°, and 30° are labeled by red, green, and blue lines, respectively. (d) The SEM image of a continuous and planar GaN film. At the interface between the nanowires and planar film, the top of nanowires shows an inverted pyramid shape, formed during the epitaxial lateral overgrowth process, shown in the inset of Fig. 1(d) labeled by orange dotted lines. Scale bars, 5 μ m (d), 0.5 μ m [(c), inset of (c)].⁶² Reproduced with permission from Ren *et al.*, Sci. Adv. **7** eabf5011 (2021). Copyright 2021 American Association for the Advancement of Science.

characterized by both Frank–van der Merwe and Volmer–Weber types. Transition from the layer-by-layer growth to island-based growth occurs at a critical layer thickness, which is related to the interface strain between the substrate and epilayer.

In general, 2D substrates provide low diffusion barriers and $E_{\rm ads}$ to adatoms due to the dangling bond-free inert surface. Therefore, adatoms can quickly diffuse and add on to the fastest growth front at the growing epilayer to extend it. Meanwhile, the Frank–van der Merwe type growth mode during 3D/2D QvdWE is difficult to see because of the low $E_{\rm ads}$ of adatoms [Fig. 7(b)]. For example, in QvdWE of metals on 2D substrates, only Li, Na, and K are predicted to follow Frank–van der Merwe-type growth mode due to the large $E_{\rm ads}/E_{\rm coh}$ and low diffusion barrier energy. Meanwhile, other group metals follow either Stranski–Krastanov-type or Volmer–Weber-type growth mode.⁸⁷

In 2D/2D vdWE, E_{coh} of adatoms is anisotropic for growing 2D materials, which results in the layer-by-layer growth of the 2D epilayers.^{88–91} The edge site of the 2D epilayer is more active than that of the plane; consequently, adatoms preferentially merge at the edge site of the growing 2D epilayer, leading to the extension of the 2D epilayer in ultrathin structures following the Frank–van der Merwe type growth mode [Fig. 7(b)]. By contrast, the 3D substrates possess high surface roughness and dangling bonds on the surface, which result in high diffusion barriers that prevent the layer-by-layer growth of 2D epilayers and increase the thickness of the 2D epilayer and the number of 2D islands. Figure 7(c) shows the optical images of NbTe₂ nanoplates grown on substrates WSe₂ and SiO₂. The optical contrast of NbTe₂ indicates that a thinner layer of NbTe₂ is grown on WSe₂ in comparison to that grown on SiO₂. Figure 7(d) shows the thickness distribution of NbTe₂ nanoplates grown on WSe₂ and on SiO₂.



FIG. 6. (a) Schematic illustration of PZT (PbZr_{0.2}Ti_{0.8}O₃)/mica heterostructure via vdW heteroepitaxy and the cross-sectional transmission electron microscope image depicting the PZT/SRO (SrRuO₃) and SRO/CFO (CoFe₂O₄)/mica interfaces along with the selected area diffraction patterns of PZT, SRO, and mica.⁷² Reproduced with permission from Jiang *et al.*, Sci. Adv. **3**, e1700121 (2017). Copyright 2017 American Association for the Advancement of Science. (b) Optical microscopic images of MoO₃ nanosheets grown on graphene, hBN, mica, and MoSe₂. (c) Histogram of relative angles between the edges of MoO₃ grown on various 2D substrates.⁷³ Reproduced with permission from Kim *et al.*, 2D Mater. **6**, 015016 (2019). Copyright 2019 IOP Publishing Ltd. (d) Optical image of CsPbBr₃ on HOPG with different directions. The dotted arrows with the same color between different CsPbBr₃ show an ordered orientation. Different orientations of the CsPbBr₃ result from the sixfold orientations of HOPG. (e) Planar view of atomic stacking of the relaxed supercell used in DFT calculations.⁷⁴ Reproduced with permission from Wang *et al.*, ACS Appl. Mater. Interfaces **12**(17), 19674–79681 (2020). Copyright 2020 The Royal Society of Chemistry.

substrate, which clearly shows that the NbTe₂ nanoplates on the WSe₂ substrate are much thinner than those grown on the SiO₂ substrate.³⁶ Similarly, thinner Bi₂Te₃ was synthesized on hBN in contrast to the growth on SiO₂ substrates.⁹²

2. Growth temperature

The nucleation density in QvdWE is directly related to growth temperature. Nucleation density systematically decreases with increasing growth temperature due to the desorption of adatoms at high temperature.⁹³ In general, MOCVD and CVD growth techniques

systematically yield lower nucleation densities than that of MBE due to the difference in operation temperature. 94

At high temperature, the increased diffusion rate promotes the epitaxial alignment of epilayers. Adatoms with high kinetic energy at high temperature are easily located at a stable position according to surface potential of 2D substrates. When metals deposited on 2D materials with insufficient thermal energy, there are some misalignments of epitaxial orientations due to the limited diffusion of metal adatoms.⁵³ For examples, the crystallographic structure of Au on MoS₂ is changed from polycrystalline to single crystalline by elevating deposition temperature [Fig. 8(a)].⁹⁵ Moreover, Ag and Al are epitaxially grown on MoS₂ with a $\pm 2^{\circ}$ misalignment upon deposition at

TABLE II. Summary of recent examples of 3D/2D quasi van der Waals epitaxy. Note: Lattice mismatch (%) = $(a_{epi} - a_{sub})/a_{sub} \times 100\%$ (a: d-spacing).

| | | | | Enilaver | Lattice | system | | |
|---------------|------------------------|---|----------------------------|--------------|---------------|----------------|--|------------|
| 2D substrates | | Epilayers | Growth methods | morphologies | 2D substrates | Epilayers | Lattice mismatch (%) | References |
| Graphene | Metal | Au (0.3 mm) | Kundsen cells | Island | Hexagonal | Cubic (FCC) | -17.0 | 76 |
| hBN | | Au (0.3 nm) | | Island | Hexagonal | Cubic (FCC) | -15.3 | |
| MoS_2 | | Au (30 nm) | DC magnetron | Film | Hexagonal | Cubic (FCC) | 8.4 | 53 |
| | | Al (30 nm) | sputtering | Film | | Cubic (FCC) | 9.0 | |
| | | Ag (15 nm) | | Film | | Cubic (FCC) | 8.2 | |
| | | Pd (15 nm) | | Film | | Cubic (FCC) | 12.6 | |
| | | Cu (30 nm) | | Film | | Cubic (FCC) | 18.8 | |
| | | Zn (30 nm) | | Film | | Hexagonal | 15.3 | |
| | | Au (2 nm) | E-beam | Island | | Cubic (FCC) | 8.4 | 77 |
| | | Ag (2 nm) | evaporation | Island | | Cubic (FCC) | 8.2 | |
| | | Pd (2 nm) | | Film | | Cubic (FCC) | 12.6 | |
| | | Bi (20 nm) | | Film | | Hexagonal | 16.8 | 78 |
| WS_2 | | Au (30 nm) | DC magnetron | Film | Hexagonal | Cubic (FCC) | 8.5 | 54 |
| | | Ag (30 nm) | sputtering | Film | | Cubic (FCC) | 8.4 | |
| | | Pd (30 nm) | | Film | | Cubic (FCC) | 12.8 | |
| | | Cu (30 nm) | | Film | | Cubic (FCC) | 19.0 | |
| | | Ni (30 nm) | | Film | | Cubic (FCC) | 21.0 | |
| Black | | Au (-) | E-beam | Film | Orthorhombic | Cubic (FCC) | 12.6 (along BP zigzag | 56 |
| phosphorous | | | evaporation | | | | direction) 7.3 (along BP armchair direction) | |
| | | Ag (-) | | Film | | Cubic (FCC) | 12.4 (along BP zigzag direction) 7.1 (along | |
| | | | | | | | BP armchair direction) | |
| | | Bi (-) | | Film | | Hexagonal | 43.9 (along BP zigzag direction) 3.2 (along BP armchair direction) | |
| Mica | Oxide | MoO ₂ (<300 nm) | Pulsed laser deposition | Film | Monoclinic | Monoclinic | 8.8 (mica [100]//MoO ₂ [010]) | 79 |
| Mica | | CoFe ₂ O ₄ (100 nm) | Pulsed laser deposition | Film | | Inverse spinel | 35.7 (mica [100]// CoFe ₂ O, [-1-12]) | 80 |
| Mica | | $VO_2 (50 \text{ nm})$ | Pulsed laser | Film | | Monoclinic | -7.5 (Mica [100])// | 81 |
| | | | deposition | | ; | | VU ₂ [100]) | |
| hBN | | $VO_2 (7 \mu m)$ | Vapor transport method | Nanowire | Hexagonal | Monoclinic | -129 (hBN [11-20]// VO ₂ [100]) | 75 |
| Graphene | | α -MoO ₃ (0.7 – 23 nm) | Vapor transport method | Film | | Orthorhombic | -50.2 (Graphene [11- 20]//MoO ₃ [010]) | 73 |
| hBN | | | Vapor transport method | | Hexagonal | | -58.7 (hBN [11-20]// MoO ₃ [010]) | |
| $MoSe_2$ | | | Vapor transport method | | Hexagonal | | -20.5 (MoSe ₂ [11- 20]//MoO ₃ [010]) | |
| Graphene | Compound semiconductor | InAs $(1 \mu m)$ | MOCVD | Nanowire | Hexagonal | Cubic (FCC) | -0.5 (graphene [1- 210]//InAs [-110]) | 59 |

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| | | | | Entlowe | Lattice | system | | |
|-------------------|--------------|---|-------------------------------|-------------------------|---------------|-------------|---|------------|
| 2D substrates | | Epilayers | Growth methods | гриауег morphologies | 2D substrates | Epilayers | Lattice mismatch (%) | References |
| Graphene | | GaAs (300 nm) | MBE | | | Cubic (FCC) | -8.2 (graphene [11- 20]//GaAs [-110]) | 60 |
| | | | | | | | -6.3 (graphene [1- | 61 |
| - | | | | | | - | 210]//GaAs [-110]) | (|
| Graphene | | GaN (1.1 μ m) | | | | Hexagonal | -2.85 (graphene [11- 20]//GaN [11-20]) | 62 |
| Graphene | | GaAsSb (500 nm) | | | | Cubic (FCC) | -8.53 (graphene [11- 20]//GaAsSb [-110]), | 63 |
| | | | | | | | -6.01 (graphene [1- 210]//GaAsSb [-110]) | |
| WS_2 | | GaN $(50 - 200 \mathrm{nm})$ | MOCVD | Film | | Hexagonal | -1.2 (WS ₂ [11-20]// GaN [11-20]) | 64 |
| MoS_2 | | | | | | Hexagonal | -1.4 (MoS ₂ [11-20]// GaN [11-20]) | |
| Mica | Metal halide | $PbI_2 (90 - 400 nm)$ | CVD | Island | Hexagonal | Hexagonal | 49.4 (mica [310]//PbI ₂ [10-10]) | 82 |
| MoS_2 | | PbI ₂ (monolayer) | Kundsen cells | Film | Hexagonal | Hexagonal | 44 (MoS ₂ [10-10]// PbI, [2-1-10]) | 83 |
| $MoSe_2$ | | | Kundsen cells | Film | Hexagonal | Hexagonal | 38 (MoSe ₂ [10-10]// PbI ₂ [2-1-10]) | |
| NbSe ₂ | | | Kundsen cells | Film | Hexagonal | Hexagonal | 32 (NbSe ₂ [14-50]// PbI ₂ [11-20]) | |
| GaSe | | | Kundsen cells | Film | Hexagonal | Hexagonal | 32 (GaSe [11-20]//PbI ₂ [11-20]) | |
| Mica | | CH ₃ NH ₃ PbCl ₃ (10 nm) | CVD | Nanosheet | Monoclinic | Perovskite | -6 (mica [100]// CH ₃ NH ₃ PbCl ₃ [100] with 5° offset) | 84 |
| Mica | | CsPbCl ₃ (-) | CVD | Nanowire | Monoclinic | Perovskite | -3 (mica [100]// CsPbCl ₃ [100] with a 30° offset) | 85 |
| Graphene | | CsPbBr ₃ | CVD | Nanosheet | Hexagonal | Perovskite | -6 (graphene [11- 20]//CH₃NH₃PbCl₃ [100] with 16° offset) | 74 |
| MoS ₂ | | CH ₃ NH ₃ PbI ₃ (10 nm) | Spin coating and annealing | Film | Hexagonal | Perovskite | 0 (MoS ₂ [11-20]// CH ₃ NH ₃ PbI ₃ [008]) | 86 |

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FIG. 7. (a) Schematic illustrations of the basic growth modes including Frank–Van der Merwe, Volmer–Weber, and Stranski–Krastanov growth. (b) Schematic illustrations of the 3D/2D quasi van der Waals epitaxy and 2D/2D van der Waals epitaxy. Cohesive energy difference between 3D and 2D epilayer induces different growth modes. (c) Optical images of the NbTe₂ nanosheets grown on the WSe₂ and SiO₂/Si substrates. OM image show different thickness NbTe₂ nanosheets on SiO₂/Si. Scale bars are 5 μ m. (d) The histogram shows the thickness distribution of NbTe₂ nanosheets grown on WSe₂ and on SiO₂/Si substrates.³⁶ Reproduced with permission from Wu *et al.*, Adv. Funct. Mater. **29**, 1806611 (2019). Copyright 2019 Wiley-VCH GmbH.

room temperature and that misalignment disappears upon annealing to a moderate temperature [Fig. 8(b)].⁵³

3. Interfacial strain

In 3D/2D QvdWE, the remaining interface strain energy between the epilayer and 2D substrate should be considered. The nucleation density of GaN nanowires on a graphene substrate is related to the number of graphene layers. Owing to increased stiffness, a thicker graphene template releases the strain energy less and leads to elevated nucleation barrier on the graphene.⁹⁶ The growth density of GaN nanowires is dramatically decreased by increasing the number of graphene substrate layers from 1 to 5 [Fig. 9(a)]. In the QvdWE of InP and InAs nanowires on graphene, the thermodynamically less favorable wurtzite phase is grown. The ultrafast diffusion of adatoms on the graphene surface might lower the activation energy barrier for the wurtzite phase nucleation.⁹⁷ The interface strain from the lattice mismatch of InAs/graphene is effectively released by the formation of a wurtzite phase for energy minimization in terms of less in-plane lattice mismatching between wurtzite phase and graphene. The lattice mismatch difference between epi-nanowire and 2D substrates results in the phase separation of nanowires grown on 2D substrates. When InGaAs nanowires are grown on graphene, core–shell phase separation of InGaAs to InAs/InGaAs is observed at the beginning of growth [Figs. 9(b) and 9(c)].⁹⁸ By contrast, no InGaAs phase segregation was observed when the nanowires were grown on MoS₂. The low lattice mismatch between In_xGa_{1-x}As and graphene of only ~0.5% for x = 1(InAs)⁶⁰ and ~5.65% for $x \approx 0.2$ indicates that InAs is close to lattice matched with graphene. However, MoS₂ has a lattice parameter of 3.16 Å (larger than that of graphene by approximately 28%), offering an alternative surface atomic configuration to stabilize the growth of InGaAs.

To relax the interface strain, specific crystallographic alignments between epilayers and 2D substrates are generated in QvdWE. However, the weak vdW interaction induces crystallographic misalignment between epilayers and 2D substrates relative to conventional



FIG. 8. (a) Cross section transmission electron microscope images and atomic force microscope height images of Au on MoS₂ grown at different temperatures. Grain boundaries depicted by the yellow dotted line in the film decrease with higher growth temperatures.⁹⁵ Reproduced with permission from Chen *et al.*, ACS Appl. Nano Mater. **3**(3), 2997–3003 (2020). Copyright 2020 The Royal Society of Chemistry. (b) Selected area diffraction patterns (SAED) of Ag on MoS₂ on deposition showing an epitaxial relationship of Ag(111)// MoS₂(0001). Ag has a $\pm 2^{\circ}$ rotational misalignment, which can be seen where the spots have spread. SAED of Ag on MoS₂ after annealing at 573 K showing the same epitaxy but without the misalignment. The cross-sectional transmission electron microscope image measured after annealing shows epitaxial Ag on MoS₂ with no line defects or grain boundaries.⁵³ Reproduced with permission from Domask *et al.*, Cryst. Growth Des. **18**(6), 3494–3501 (2018). Copyright 2018 The Royal Society of Chemistry.

epitaxy. Figure 10(a) shows the rotation angle distribution for vdWE growth of MoS_2 on hBN substrates. In addition, weak vdW interaction decreases the energy difference of each crystallographic configuration, and several stacking angles appear at the same time. Owing to the minimal difference in relative energies between the 2H and 3R configurations per unit cell for bilayer WSe₂, there is a large probability of finding equilateral triangular crystals with a relative angle difference of 60° [Fig. 10(b)]. Grain boundaries are formed after the coalescence of these grains [Fig. 10(c)].⁹⁴ The coalescence of different crystallographic configurations of GaN nanowire on graphene also induces the

formation of grain boundaries [Fig. 10(d)].⁶² In the QvdWE of PbI₂ on WS₂, a metastable configuration (30° -rotated stacking) is achieved in addition to the most stable configuration, 0° stacking [Fig. 10(e)].⁹⁹

C. Novel approaches toward epitaxial growth on 2D templates

Surface engineering of 2D materials has been studied to enhance nucleation on vdW surfaces. To engineer surface properties, defects or functional groups are commonly generated.^{66,100–112} Defects or



FIG. 9. (a) Scanning electron microscope bird's eye view of the nanowires grown near the central part of a pyramidal monocrystalline graphene flake. The flake consists of distinct terraces bounded by monolayer steps. From periphery to center, the graphene film thickness increases while the nanowires density and height both decrease. Insets show the nanowires at the terrace boundaries.⁹⁶ Reproduced with permission from Kumaresan *et al.*, Nano Lett. **16**(8), 4895–4902 (2016). Copyright 2016 The Royal Society of Chemistry. (b) Schematic illustration of spontaneous phase separation of InGaAs nanowires on the gaphene substrate in contrast to the MoS₂ substrate. (c) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of phase-separated InGaAs. Radial energy dispersive x-ray (EDX) linescan along the white dashed line indicates the formation of coaxially heterostructured InAs/In_xGa_{1-x}As nanowires.⁹⁶ Reproduced with permission from Mohseni *et al.*, Nano Lett. **13**(3), 1153–1161 (2013). Copyright 2013 The Royal Society of Chemistry.

functional groups in 2D materials make the dangling bond-free surface more reactive, thereby promoting the seeding process in epitaxial growth. Moreover, considering the large energy difference between the defect/functional group and the pristine surface, the position of nucleation sites for epitaxial growth can be defined by patterning the defect/functional group on 2D materials.¹¹³ This strategy is hardly applicable to conventional epitaxy substrates because the adatoms are intrinsically attached to 3D materials by a chemical reaction.

The site-selective defect engineering of 2D materials has been used to define the nucleation sites of 2D epilayers, which enables to achieve the patterned 2D/2D van der Waals heterostructures. To control the nucleation sites on surface, chalcogen vacancies were periodically generated on WS(Se)₂ substrates by laser irradiation [Fig. 11(a)].¹¹² Owing to the higher volatility of S(Se) than that of W, S(Se) is evaporated under laser irradiation, whereas W-terminated sites remain. Considering that the adhesion energy of W-terminated sites is higher than that of pristine areas, adatoms favor the W-terminated sites for nucleation [Figs. 11(b) and 11(c)]. After nucleation, the epilayer begins to grow laterally, resulting in the perfect vdW interface between WSe₂ and epilayers. The patterned vdWE technique can be applied to other vdW heterostructures, including VSe₂/WSe₂, NiTe₂/WSe₂, CoTe₂/WSe₂, NbTe₂/WSe₂, VS₂/WSe₂, VSe₂/

MoS₂, and VSe₂/WS₂. No interdiffusion or chemical bonds are present in the clean interface between 2D layers and 2D substrates at the overgrown area. An atomically clean interface serves as synthetic 2D/2D vdW contacts without lithography-induced contamination and deposition-induced damage [Fig. 11(d)]. Metallic VSe₂ was selectively grown onto semiconducting WSe₂ for contact formation. Transistors with 2D/2D vdW contacts show improved performance in comparison to conventional metallization contacts [Figs. 11(e) and 11(f)]. Defect-mediated selective-area vdWE can also be realized by a focused He ion beam,¹⁰⁹ which generates carbon vacancies in graphene substrates that serve as preferential nucleation sites for the growth of hBN.¹⁰⁹

Surface engineering of 2D substrates has been used to control the epilayer morphology in 3D/2D QvdWE. The morphology of epitaxially grown ZnO on hBN substrate was controlled by oxygen and argon plasma, which induced linked atomic defects on hBN and consequently promoted the preferential nucleation of ZnO specifically along the linked atomic defects [Fig. 12(a)].¹¹¹ Under the same growth conditions, the pristine hBN surface resulted in ZnO nanoneedle arrays, whereas plasma-treated hBN substrates yielded high-density vertical nanowall networks [Fig. 12(b)].¹¹¹ ZnO nanoneedles were grown on atomic defects (or vacancies) of hBN, whereas the nanowalls were



FIG. 10. (a) Alea probability insolution of the relative rotation angle of single-layer MoS₂ grown on thin bet. a typical selected area electron dimatchin (SALD) patient of a single-layer MoS₂ grown on thin bBN. The green hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from MoS₂ while the purple hexagon shows the sixfold-symmetric diffraction spots from the large probability to find equilateral triangular crystals with a relative azimuthal orientation at respective angles of 15° and 75°. (c) Scanning transmission electron microscopy (STEM) image of the WSe₂ van der Waals homoepitaxy. The green triangle highlights the WSe₂ crystal that is stacked in the 2H phase. The coalescence of such two crystals results in the formation of a 60° grain boundary (GB) as surrounded in the image with the withe rectangle. In the inset of (c), the magnified image of 60° GB is presented. The GB is highlighted using a blue dashed line. The scale bar is 2 nm. Reproduced with permission from Mortelmans *et al.*, Appl. Mater. Today **22**, 1009

grown along with the linked atomic defects. The position and diameter of ZnO nanowire were controlled by modulating the position and size of holes in graphene substrates.¹¹⁴ Hole arrays in multilayer graphene were first patterned by O_2 plasma etching. The exposed edge line of

holes then functioned as the nucleation sites for ZnO nanowires [Fig. 12(c)].¹¹⁴ The position and diameter of the ZnO nanowires were controlled by defining the position and diameter of hole arrays, and then the obtained nanowires were used as a growth template for



FIG. 11. (a) Schematic of the laser-patterning process via focused laser (488 nm) irradiation combined with a raster scan in a confocal laser system. Large-area monolayer or bilayer semiconducting TMDs (for example, WSe₂, MoS₂ and WS₂) were first grown using a chemical vapor deposition (CVD) process and then selectively patterned to create periodic defect arrays that function as exclusive nucleation sites for site-specific growth of metallic TMDs (for example, VSe₂, VS₂, CoTe₂, NiTe₂, and NbTe₂) to form van der Waals heterostructure arrays. (b) The adsorption energy comparison of VSe₂ species on pristine WSe₂ and the W-terminated surface. (c) Illustration of the nucleation and growth of VSe₂ on the W-terminated surface at the patterned sites. (d) Cross-sectional scanning transmission electron microscopy (STEM) image of the van der Waals heterojunction interface with the corresponding atomic model for VSe₂ (upper layers) and WSe₂ (lower layer) and the intensity profile (right), with the white dashed line highlighting the heterojunction interface. (e) Optical microscope image of back-gated WSe₂ transistors with VSe₂ van der Waals contacts. (f) Comparisons of WSe₂ transistors with synthetic van der Waals contacts and directly deposited metal (Cr/Au) contacts on the 285 nm SiO₂/Si substrate by transfer characteristics.¹¹² Reproduced with permission from Li *et al.*, Nature **579**, 368–374 (2020). Copyright 2020 Springer Nature.

lattice-matched GaN and InGaN layers to fabricate InGaN/GaN micro light emitting diodes.

To grow uniform films on 2D substrate, functionalization is generused to increase the surface reactivity of the inert surally face.^{100,101,103–107,110} Such well-regulated groups can be anchored on the 2D surface to work as nucleation sites so that the upper material can grow epitaxially on a large scale. QvdWE growth of high-quality AlN films was conducted on graphene/sapphire substrates [Fig. 13(a)].¹⁰³ The sp³ C-N bonds in N₂ plasma-treated graphene facilitate the AlN nucleation. Density-functional theory (DFT) calculation verified that the adsorption energy of Al atoms to sp^3 C–N bond increased to 5.9 - 8.6 eV compared to that of graphene, 1.1 eV. The N₂ plasmatreated graphene substrate allowed the epitaxial growth of a large-area single-crystal AlN film. A high density of single-crystalline AlN islands was grown on a graphene substrate by the in situ heat treatment of graphene with NH₃ gas during MOCVD to generate sp³ C-N bonds.¹⁰⁷ Single-crystalline AlN islands functions as the direct epitaxial-growth buffer layer to grow single-crystalline GaN thin film. Nucleation induced by artificial dangling bonds is also applied to hBN substrates. A high-quality AlN epilayer was grown on an hBN substrate through O2 plasma treatment.¹¹⁰ A small amount of N atoms in hBN was replaced by O atoms, and some B-O chemical bonds were tilted from the c axis [Fig. 13(b)]. At the nucleation stage, the tilted B–O bonds in O₂ plasmatreated hBN surface induced the tilt of the AlN islands, which merged into uniform films [Fig. 13(c)].¹¹⁰ Recent demonstration samples of surface engineered QvdWE are summarized in Table III.

III. REMOTE EPITAXY ON 2D TEMPLATES

The quality of a material grown through heteroepitaxial growth is determined by the lattice match between the epilayer and underlying substrate. This requirement for closely matched lattice constants limits the substrate—epilayer combinations. Furthermore, the grown epilayer generally includes abundant defects and grain boundaries. These defects act as non-radiative recombination centers that degrade photonic and optoelectronic properties. Therefore, these materials limit the performance of optoelectronic devices such as laser diodes and avalanche photodiodes.^{115,116} By contrast, homoepitaxial growth can be used to obtain a high-quality single-crystalline epitaxial layer aligned with the crystal structure of the substrate. However, this requires a relatively expensive substrate, which hinders the commercial application of these electronic/photonic materials.¹¹⁷

Remote epitaxy is a recently proposed technique that can help compensate for the shortcomings of hetero/homoepitaxy while retaining the advantages of vdWE. Graphene exhibits lattice transparency, which means it cannot completely screen electric fields and electromagnetic waves, due to the single-atom thickness-induced tunneling effect of electromagnetic waves.¹¹⁸ Therefore, information on adjacent crystals penetrates through graphene. The water droplet wetting angle for various substrates under graphene is predominantly determined by the underlying substrate and is barely affected by the graphene.¹¹⁹ It was demonstrated that single-crystalline GaAs, InP, and GaP can be grown on graphene-coated GaAs (001), InP (001), and GaP (001) substrates, respectively, aligned with the substrate despite the presence of



FIG. 12. (a) Cross-sectional schematic showing how ZnO nanoarchitectures are formed on a plasma-treated hBN area. During the metal–organic chemical vapor deposition (MOCVD) process, multiple ZnO nuclei that preferentially dwell along the edge of the plasma-treated area are then connected at their base to form outer nanowalls. (b) Schematic of the fabrication process and tilt-view field-emission scanning electron microscopy images of ZnO vertical nanoneedle arrays and nanowall networks.¹¹¹ Reproduced with permission from Oh *et al.*, NPG Asia Mater. **6**, e145 (2014). Copyright 2014 Springer Nature. (c) Scanning electron microscope (SEM) image of the InGaN/GaN micro crystal array grown on ZnO nanowires. Micro light emitting diodes was fabricated by epitaxial growth of undoped GaN (u-GaN), n-GaN, the InGaN/GaN MQW, and p-GaN on ZnO nanowires.¹¹⁴ Reproduced with permission from Yang *et al.*, ACS Photonics **7**(5), 1122–1128 (2020). Copyright 2020 The Royal Society of Chemistry.

monolayer and bilayer graphene (BIG) interlayers [Figs. 14(a)-14(c)].⁷ These results imply that the crystallographic features of the underlying substrate also can penetrate graphene and remotely determine nucleation and crystallization during the initial epitaxial growth stage.¹²⁰ Their work showed that a heterojunction light emitting diode fabricated using remote epitaxy exhibited electrical and electroluminescence characteristics that were comparable to those of devices grown using conventional homoepitaxy [Figs. 14(d) and 14(e)]. In addition, the epilayer was easily released from the epitaxial substrate, and the characteristics were maintained even after the device was transferred to other substrates. These results illustrate two important findings: first, the electrostatic potential of the substrate is not completely screened by the multiple layers of graphene, which means the crystal alignment of the substrate can be transmitted via remote interactions; and second, the epilayer grown by remote epitaxy can be easily exfoliated and transferred to another substrate without degrading the quality of the epilayer. These findings have encouraged research on the use of the remote epitaxy technique to grow various oxide compounds and metals, as well as III-V, III-N, and I-VII compound semiconductors.^{115,117,120-122} A summary of the recent examples of epilayers grown with remote epitaxy is presented in Table IV.

A. Origin and control factors of remote epitaxy

The remote interaction between an epilayer and a substrate can be explained by charge redistribution on the graphene surface. DFT calculations showed the electrostatic potential modification on the surface of graphene in a graphene/c-ZnO system [Figs. 15(a) and 15(b)].¹²⁰ In the vdW gap between the graphene and substrate, electron accumulation and depletion alternate in the vertical direction according to the lattice arrangement. Depletion of electrons is mainly observed around graphene. By contrast, more electrons are accumulated along c-ZnO. Therefore, a dipole is formed in the vertical direction at the vdW binding interface. When the precursor adatom approaches the graphene surface, adhesion and diffusion can occur at a fixed position owing to the dipole moment. These results suggest that the underlying substrate can influence the adatom across the graphene interlayer by means of the net charge difference along the z-axis direction, which is induced by charge redistribution. Notably, the distance between the monolayer of graphene (MLG) and the c-ZnO substrate decreased from 3.12 to 2.78 Å after remote epitaxial growth, indicating that a strong remote electrostatic attraction still existed between the substrate and the epilayer [Fig. 15(a)]. Similarly, GaN grown on the graphene/SiC system through remote epitaxy possessed a Ga polarity identical to that of GaN grown by direct epitaxy.

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FIG. 13. (a) Schematic diagram of the nucleation and film growth of AIN on the N₂-plasma-treated graphene/sapphire substrate. (1) Enhanced AIN nucleation on the plasma-treated graphene/sapphire substrate through AI–N bonding. (2) Then, the fast 2D lateral growth of the AIN islands to form a continuous film due to the reduced diffusion barrier of adatoms on the ideal graphene.¹⁰³ Reproduced with permission from Chen *et al.*, Adv. Mater. **31**, 1807345 (2019). Copyright 2019 Wiley-VCH GmbH. (b) Schematic diagrams of the atom connective structure of hBN before and after the O₂ plasma treatment. O atoms can replace some N atoms in the hBN. (b) Schematic illustration of the growth mechanism of AIN materials on hBN/sapphire and plasma-treated hBN/sapphire.¹¹⁰ Reproduced with permission from Wu *et al.*, CrystEngComm **19**, 5849–5856 (2017). Copyright 2017 The Royal Society of Chemistry.

According to the underlying mechanism of remote epitaxy, the physical distance between the substrate and the epilayer plays a crucial role in determining the lattice alignment by charge redistribution. The seeding effect is weakened by the reduced interaction, resulting in a lowered nucleation density and degraded crystal quality, along with the introduction of polycrystallinity.¹²⁴ For example, although single-crystalline GaAs grew on a GaAs(0001) substrate coated with MLG, a (111)-dominant polycrystal grew when bilayer and tetralayer graphene were used as interlayers [Fig. 16(a)]. These results demonstrate the existence of a "true charge interaction gap" through which crystallographic information from the underlying substrate can be transmitted.⁷ As shown in Fig. 15, the screening effect of graphene for bilayer graphene (BLG) is greater than that for MLG. The screening effect depresses the dipole-induced generation of nucleation sites, consequently disturbing the epitaxial growth of the resulting materials. Therefore, nucleation density decreases with the increasing number of graphene layers owing to the decrease in adhesion energy, which is attributed to dipole momentum damping [Fig. 16(b)]. The adhesion energy at the graphene surface on the

c-ZnO substrate decreased from $-52.0\,meV/{\AA}^2$ with the use of MLG to $-32.3\,meV/{\AA}^2$ with BLG. 120

The use of polar 2D materials, such as hBN and TMDs, results in even lower adhesion energies. The strong polarity of these 2D materials significantly attenuates electrostatic potential propagation, thereby affecting the nucleation and orientation of the epilayer. Kong *et al.*⁸ have theoretically and experimentally demonstrated that the potential fluctuation of the GaN substrate is attenuated more by a hBN (polar) interlayer than by a graphene (non-polar) interlayer. Monolayer hBN disrupts the transmission of the crystallographic information of the substrate, resulting in the growth of an GaN epilayer with two intermixed phases [Fig. 16(c)].⁸ Furthermore, as the number of layers of hBN increases, the effects of vdWE through the hBN template become more dominant than those of remote epitaxy.

In the same context, substrate polarity can also affect the potential fluctuation distance. As the ionicity of the substrate increases, the electric potential of substrate can better penetrate the buffer layer, consequently affecting the growth of upper layer more strongly and enabling remote interaction at greater distances.^{116,132} In the case of Si

| 2D substrates | Epilayers | Growth methods | Surface engineering methods | Defect (functionaliza- tion) type | Epilayer morphologies | References |
|----------------------------------|---|----------------|--|---|-------------------------------------|------------|
| Graphene | AlGaN | MOCVD | Plasma (O ₂) | Oxygen functional group (O– <i>sp</i> ³ C) and C vacancy | Film | 100 |
| Graphene | GaN | MOCVD | Plasma (O ₂) | Oxygen functional group (O- <i>sp</i> ³ C) and C vacancy | Film | 101 |
| Graphene | ZnO | MOCVD | Plasma (O_2) | Linked vacancy | Nanowall | 102 |
| Graphene | AlN | MOCVD | Plasma (N_2) | Nitrogen functional | Film | 103 |
| • | | | | group $(N-sp^{3}C)$ and C | | 104 |
| | | | | vacancy | | 105 |
| Graphene | GaN | MBE | Plasma (N ₂) | Nitrogen functional group (N– <i>sp</i> ³ C) and C vacancy | Nanowire | 66 |
| Graphene | AlN | MOCVD | Plasma (XeF ₂) | Fluorine functional group (F– <i>sp</i> ³ C) | Film | 106 |
| Graphene | AlN | MOCVD | High-temperature NH3 exposure | Nitrogen functional group (N- <i>sp</i> ³ C) | Film | 107 |
| Graphene | GaN | MOCVD | High-temperature NH ₃ exposure | Nitrogen functional group $(N-sp^{3}C)$ | Micro flake | 108 |
| Graphene | hBN | MBE | Focused ion beam (He) | C vacancy | Spatially controlled micro flake | 109 |
| hBN | AlN | MOCVD | Plasma (O ₂) | Oxygen functional group (O- <i>sp</i> ³ B) | Film | 110 |
| hBN | ZnO | MOCVD | Plasma (O ₂) | Linked vacancy | Nanowall | 111 |
| WS ₂ WSe ₂ | VS ₂ , VSe ₂ , NiTe ₂ , CoTe ₂ , NbTe ₂ | CVD | Laser irradiation (433 nm) | S, Se vacancy | Spatially controlled micro flake | 112 |

TABLE III. Summary of recent examples of surface engineered (quasi) van der Waals epitaxy.

and Ge with pure covalent bonds, potential fluctuation rapidly decays by a factor of r-6, where r is interatomic distance (the Lennard-Jones model). Materials with ionic bonds, such as Ga-N, experience dipole field stemming by a factor of r^{-2} . Consequently, longer-distance electrostatic potential transmission is possible for substrates with greater ionicity [Fig. 17(a)] due to the stronger polar cohesive ordering by greater electronegativity difference between the substrate and adatom.⁸ Wang et al.¹³³ showed that the electron charge density of sapphire transmitted through a bilayer hBN interlayer of \sim 7 Å because of the high ionicity of the sapphire substrate, which facilitated the growth of single-crystalline HfS₂ [Fig. 17(b) and 17(c)]. Furthermore, singlecrystalline ZnO was successfully grown even when a trilayer graphene interlayer was used.¹²⁰ The remote interaction of the substrate and adatom depends not only on the polarity of the substrate, but also on the polarity of the adatom. For example, because the diffusion length of Ge adatoms is smaller than that of Ga and As adatoms, the remote interaction between the adatom and the substrate in the Ge/graphene/ GaAs system is larger than that in the Ge/graphene/Ge system and smaller than that in the GaAs/graphene/GaAs system.¹²⁵ Despite the relatively high ionicity of GaAs, single-crystalline GaAs and Ge did not form in the graphene/Ge and graphene/GaAs templates, respectively [Figs. 18(a)-18(d)], indicating that both the substrate and adatom play important roles in remote interaction.

Furthermore, the cleanliness of the graphene/substrate interface and graphene surface is a determining factor for potential propagation. Native oxide and contaminants present at the interface between the graphene and substrate increase the interlayer spacing and cause electrostatic fluctuations, thereby degrading the quality of the epilayer.¹³ For instance, a wet transfer technique for CVD on graphene results in many adsorbates on the graphene surface.^{135,136} These adsorbates hinder lattice transparency, thereby weakening the remote interaction between the adatom and substrate. Therefore, the wet transfer technique can induce more grain boundaries and defects in epilayers than the dry transfer technique.7,125 In addition, when polycrystalline graphene is used as an interlayer, the non-uniform thickness and organic/ metal residues can cause inhomogeneous epitaxial growth.¹³⁷ Notably, these contaminants can be removed through additional annealing steps to improve the conformality of the graphene and substrates.138 ⁻¹⁴⁰ These results provide two general rules for obtaining a single-crystalline epilayer using remote epitaxy: (1) interaction between the underlying substrate and epilayer must be enabled; and (2) the seeding layer should be determined by the epitaxial substrate and not by the 2D interlayer.

Although graphene is chemically and thermally inert, it can be damaged under harsh growth conditions, such as the high temperatures and corrosive precursors employed for compound semiconductors.^{141–143}



FIG. 14. (a) High-resolution x-ray diffraction ω -2 θ scans (top) of the exfoliated semiconductor/stressor stack and large-scale electron backscatter diffraction (EBSD) maps that include GaAs(001) (left), InP(001) (middle), and GaP(001) (right) epilayers. (b) High-resolution STEM images showing excellent remote alignment of the GaAs(001) lattices through the graphene. Convergent-beam electron diffraction patterns from the epilayer (top inset) and the substrate (bottom inset) show identical zinc-blende (001) orientations. (c) Cross-sectional SEM image of heterojunction LEDs. (d) I–V curves of LEDs grown on graphene–GaAs substrates and directly on GaAs. Inset, emitted red light from the LEDs grown on the graphene–GaAs substrate. (e) Electroluminescence spectra of the LEDs grown on graphene–GaAs substrates and directly on GaAs. Inset, photographs of functioning LEDs grown on both substrates.⁷ Reproduced with permission from Kim *et al.*, Nature **544**, 340 (2017). Copyright 2017 Springer Nature.

Considering that surface energy largely fluctuates at the defect sites of graphene, the crystallographic information of the substrate is screened. Therefore, nucleation can occur at the dangling bonds of graphene due to potential fluctuations, resulting in vdWE instead of remote epitaxy.^{125,144,145} In addition, small holes and torn regions induced in graphene in the transfer process form a direct covalent bond for the epilayer with the substrate through opening-mediated nucleation, thereby causing lateral overgrowth or inhibiting exfoliation characteristics.¹²⁰ Several methods have been proposed to overcome this problem. Kum et al. employed bilayer graphene as an interlayer instead of monolayer to prevent the damage of graphene during film deposition process.¹²⁶ This prevented the direct bonding between substrates and epilayers and successfully yielded various single-crystalline complex oxides, such as perovskite SrTiO₃ [Fig. 19(a)], perovskite BaTiO₃, spinel CoFe₂O₄, and garnet Y₃Fe₅O₁₂. Moreover, a multi-step remote epitaxy technique has been proposed, in which an epilayer is grown under harsh conditions after first forming a seed layer at a moderate temperature at which graphene is not damaged [Fig. 19(b)]. A two-step method was proposed for growing the GaN main layer at 1075 °C after nucleation at 700 °C using a low-pressure MOCVD technique.¹²⁷ The GaN epilayer grown using this method with a nucleation step of 2 min possessed comparable structural and optical properties to those of the layer grown directly on the underlying GaN substrate owing to the reduced damage to graphene [Figs. 19(c) and 19(d)]. Similarly, it was reported that dividing pre-nucleation

annealing steps into hydrogen-based initial annealing and ammonia mixture-based nucleation can help minimize damage to the graphene template. $^{\rm 123}$

Based on the experimental results above, three important design considerations for remote epitaxy can be deduced: polarity of the epitaxial materials (adatom, 2D interlayer, and substrate), interfacial properties, and crystal quality of the 2D interlayer. Therefore, to obtain high-quality epilayers by remote epitaxy, further research on various aspects, such as cleaning, transfer, and growth conditions, is required to diminish the formation of residues, defects, and adlayers and to form the conformal contact of the 2D interlayer with the substrate.

B. Applications of remote epitaxial growth

Remote epitaxy can be used to obtain a high-quality epilayer through heteroepitaxial growth. In general, a lattice mismatch between a substrate and an epilayer in heteroepitaxy causes crystalline defects such as a dislocation. Built-in strain energy accumulated in the epilayer by lattice mismatch is released by generating dislocations above a critical thickness [Fig. 20(a)]. Both vdWE and remote epitaxy use slippery 2D layers as an epitaxial template that have weak vdW interactions with adjacent layers. Thus, the misfit strain is spontaneously relaxed during growth [Fig. 20(b)].¹²⁸ It was estimated that the energy required to displace the interface on the surface of graphene is several

| TABLE IV. Summ | ary of recent exam | nples of remote ep | pitaxy. | | | | | | |
|------------------------|--------------------|------------------------------|---------------------------------|------------------------|--------------------------------------|--|---|-------------------------|----------|
| | 2D interlayer | | | | | | | | |
| Number of layers | Interlayers | Transfer methods | Epitaxial substrates | Growth methods | Epitaxial structures | Crystal structures | Dislocation densities | Host substrates Re | ferences |
| Monolayer | Graphene | Dry transfer | GaAs(001) | MOCVD | GaAs film | Single crystalline | : | Thermal release | 7 |
| Bilayer Tetralayer | | | | | | Poly crystalline | | are | |
| Monolayer | | | InP(001) | | InP film | Single crystalline | | Thermal release | |
| Monolayer | | | GaP(001) | | GaP film | | | Thermal release | |
| Monolayer | Graphene | Wet transfer | a-ZnO | Hydrothermal growth | Horizontally-aligned ZnO microrod | Single crystalline | ÷ | iape | 120 |
| | | | c-ZnO |) | Vertically-aligned ZnO microrod | | | | |
| Monolayer | Graphene I | Direct growth | graphene buffer layer/6H-SiC | MOCVD | GaN film | Single crystalline | : | : | 123 |
| Monolayer Monolayer | Graphene | Dry transfer | SiO ₂ /Si SiC | MOCVD | GaN film | Poly crystalline Single crystalline | $2.1	imes 10^7{ m cm}^{-2}$ | : | 124 |
| Tetralayer | | | SiC | | | Poly crystalline | : | | |
| | | | Graphene buffer layer/SiC | | | Single crystalline | $2 \times 10^{8} \text{ cm}^{-2} \text{ (screw)}$ $5 \times 10^{8} \text{ cm}^{-2} \text{ (edge)}$ | Thermal release tape | |
| Monolayer | | | | | | | $4 \times 10^7 \mathrm{cm}^{-2}$ (screw) $2 \times 10^8 \mathrm{cm}^{-2}$ (edge) | • | |
| | | | | Sputter | ZnO film | Single crystalline | | : | |
| Monolayer | hBN | Dry transfer | GaN | MOCVD | GaN film | Poly crystalline Poly crystalline | : | : | ∞ |
| | | | | | | Single crystalline (different phase with epitaxial | | | |
| | Graphene | | | | | substrate) Single crystalline Sinole crystalline | | | |
| | | | | | | Poly crystalline | | | |
| Monolayer | Graphene | Wet transfer | NaCl(001) $CaF_{2}(001)$ | CVD | CsPbBr ₃ film | Poly crystalline Poly crystalline | $3	imes 10^7{ m cm}^{-2}$ | : | 116 |
| Monolayer | Graphene | Dry transfer | GaAs | MOCVD | GaAs film | Single crystalline | : | : | 125 |
| | | Wet transfer Drv transfer | GaAs Ge | | Poly crystalline Ge film | Poly crystalline Poly crystalline | | | |
| | | line |) | | | | | | |

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Poly crystalline Poly crystalline

GaAs film Ge film

Ge GaAs Ge

Dry transfer Dry transfer Dry transfer

S

П

Ш

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| | Referenc | 126 | | | | 127 | 128 | | 129 | 130 | 131 |
|---------------|-------------------------|--|---------------------|---------|----------|--------------------|------------------------------|-----------|--|----------------------------------|--------------------------------|
| | Host substrates | ··· Free-standing | PMN-PT film | | | : | : | : | Free-standing | Cu plate | Cu tape |
| | Dislocation densities | : | | | | : | $3.72	imes 10^8{ m cm}^{-2}$ | • | : | : | : |
| | Crystal structures | Single crystalline | | | | Single crystalline | Single crystalline | | Single crystalline | Single crystalline | Single crystalline |
| | Epitaxial structures | STO film CoFe ₂ O ₄ film GGG (111) | Sputter | | | GaN film | GaP film | InGaP hlm | ZnO microwire | GaN microrod heterostructure | GaN microcrystal |
| | Growth methods | PLD | YIG film SRO/STO | | | MOCVD | MOCVD | |)Hydrothermal growth | MOCVD | MOCVD |
| | Epitaxial substrates | STO (100) MAO (100) | | | ı | GaN/sapphire | GaAs(001) | | GaN/Al ₂ O ₃ (0001 | c-Al ₂ O ₃ | Al ₂ O ₃ |
| | Transfer methods | Dry transfer | | | BTO film | Wet transfer | Dry transfer | | Wet transfer c | Wet transfer | Dry transfer |
| 2D interlayer | Interlayers | Graphene | | | MBE | Graphene | Graphene | | ned Graphene | Graphene | Graphene |
| | Number of layers | Bilayer | | Ti/PDMS | STO | Monolayer | Monolayer | : | Intalio-patter. monolayer | Monolayer | Monolayer |

orders of magnitude smaller than that required for generating dislocations and delamination due to the weak interface adhesion [Fig. 20(c)].¹²⁸ Therefore, the strain accumulated in the epilayer can be spontaneously relaxed [Fig. 20(b)]. This decoupling of graphene and the epilayer causes the growth of a high-quality epilayer with low dislocation density [Figs. 20(e) and 20(f)]. The dislocation density when InGaN was grown with heteroepitaxial remote epitaxy on a graphenecoated GaAs substrate was $3.72 \times 10^8 \text{ cm}^{-2}$, which was lower than the dislocation density of layers grown on the bare GaAs substrate $(1.49 \times 10^9 \text{ cm}^{-2})$. Moreover, the diffusion of In caused by InGaN strain was suppressed due to strain relaxation during remote epitaxy, facilitating the production of InGaN/GaN multi-quantum-well light emitting diodes with a high level of In incorporation of 30%.¹ Remote epitaxy is expected to help realize highly crystalline epilayers for photonic applications by improving the non-radiative recombination and effective carrier lifetime by minimizing misfit and threading dislocations.116

For an epilayer grown on a 2D material template via vdWE or remote epitaxy, the epitaxial interface exhibits non-covalent vdW bonding. Therefore, as shown in Fig. 21(a), the GaN tetrahedrons grown via remote epitaxy on a graphene/GaN substrate possess a weak adhesion energy and are easily moved to the periphery of the swept zone by atomic force microscopy sweeping.¹²³ The weak adhesion energy enables the detachment of the grown epilayer from the epitaxial substrate via a nondestructive process to obtain a high-quality freestanding membrane.¹²⁹ Several methods for exfoliating the epilayer into a freestanding membrane have been reported.^{120,146,147} The key idea of the proposed methods is to apply a supporting layer, such as polyimide or a metal stressor, onto a grown film and then mechanically peel it off using a flexible handling layer (i.e., thermal release tape) [Fig. 21(c)].^{130,147} The quality of the freestanding membranes obtained through these techniques is maintained because there are no chemical bonds breaking between the layer and substrate. Furthermore, the exfoliated freestanding membrane can be transferred to various functional substrates, providing an additional degree-of-freedom for manufacturing highperformance (opto)electronic devices. The original substrates can be reused for additional epitaxial growth, thereby reducing the cost of the semiconductor manufacturing process [Fig. 21(c)]. The epilayers grown on the reused substrates do not exhibit any performance degradation. The defect density and EL characteristics of GaN light emitting diodes grown with remote epitaxy on reused graphene/c-plane sapphires were comparable to those of GaN light emitting diodes grown on virgin substrates [Fig. 21(b)].¹³⁰ However, the formation of defects such as tears, holes, and wrinkles on the 2D interlayer in the exfoliation and growth processes results in the degradation of the epilayer quality and limited exfoliation. Thus, additional processes such as etching of the 2D material with cleaning and polishing of the substrate are essential to reuse the substrate.¹¹⁷ To overcome these constraints, a graphene buffer layer/SiC system was used as a growth template [Fig. 21(d)].¹²⁴ The strong covalent bond between the graphene buffer layer and the SiC substrate reduces the distance between the substrate and epilayer. The reduced distance not only improves the potential penetration of the substrate [Fig. 21(e)] but also prevents damage to the buffer layer during the epilayer exfoliation process, enabling multiple growth-release cycles at 100% yield [Fig. 21(f)].

Many studies have shown that GaN, GaP, and GaAs epilayers and micro-/nanorods grown via remote epitaxy can be utilized as

TABLE IV. (Continued.)



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FIG. 15. Atomic structure and charge density difference (Δ CD) of remote homoepitaxial (a) c-ZnO/MLG/c-ZnO, and (b) c-ZnO/BLG/c-ZnO heterointerfaces. All the left panels show stable atomic configurations and Δ CD of substrates before remote epitaxy, while the right panels correspond to those of remote epitaxial heterointerfaces after overlayer growth. Δ CDs are depicted at isosurface levels of ± 0.0002 e/ bohr³. The yellow and blue isosurfaces stand for the electron accumulation and depletion regions, respectively. The dotted-line boxes are chosen to represent repeating units, where partial charges resulting from electron accumulation and depletion are denoted with δ^- and δ^+ , respectively. The bond dipoles of "+ \rightarrow " marked in the dot-line boxes denote the electric dipoles with Lewis notation to describe electric field direction and bond polarity.¹²⁰ Reproduced with permission from Jeong *et al.*, Nanoscale **10**, 22970 (2018). Copyright 2018 The Royal Society of Chemistry.

high-quality light emitting diodes and flexible devices [Figs. 22(a)-22(e)].^{7,122,128,130,131} In addition, a multi-dimensional heterostructure system with various structures and orientations can be fabricated by integrating various freestanding membranes. For example, Pb(Mg_{1/3}Nb_{2/3})O₃–PbTiO₃ (PMN-PT) has a significantly high piezoelectric coefficient in its single-crystalline form, and CoFe₂O₄ has a high magnetostriction coefficient.^{148–151} Freestanding PMN-PT and CoFe₂O₄ grown using remote epitaxy have high crystal quality, and the clamping effect by the substrate is excluded; thus, these characteristics can be greatly improved. Moreover, heterostructures integrating PMN-PT and CoFe₂O₄ exhibit extraordinary performance due to the



FIG. 16. (a) Electron Back Scattered Diffraction (EBSD) maps of GaAs grown on and exfoliated from "monolayer" graphene–GaAs(001) substrate (left), showing (001) single-crystallinity, and of GaAs grown on and exfoliated from "bilayer" (middle) and "tetralayer" (right) graphene–GaAs(001) substrate showing (111)-dominant polycrystallinity. On the right is the inverse pole figure color triangle for crystallographic orientations.⁷ Reproduced with permission from Kim *et al.*, Nature **544**, 340 (2017). Copyright 2017 Springer Nature. (b) Schematic (top) and EBSD (bottom) of the exfoliated surface of GaN on MLG/GaN (left), BLG/GaN (middle), and trilayergraphene/GaN (right). (c) Schematic (top) and EBSD (bottom) of the exfoliated surface of GaN on ML-hBN/GaN (left), BL-hBN/GaN (middle), and trilayer-HBN/GaN.⁸ Reproduced with permission from Kong *et al.*, Nat. Mater. **17**, 999 (2018). Copyright 2018 Springer Nature.

coupling effect [Figs. 22(f) and 22(g)].¹²⁶ In addition, the HfS₂ layer grown on the hBN/sapphire substrate can be used for fabricating a high-performance photodetector by weak interface scattering between HfS₂ and hBN [Fig. 22(h)].¹³³ Integration of the freestanding films synthesized using remote epitaxy with various membranes/substrates to produce 3D/3D, 3D/2D, and 2D/3D functional heterostructures can help overcome the functionality and scalability limitations of conventional devices. Moreover, it provides opportunities for exploring new physics and developing unprecedent next-generation electronic and optoelectronic devices.

IV. INTERCALATION GROWTH OF QUASI-2D LAYERS

Although some compounds can be implemented in a 2D form, most compounds with covalent and ionic bonds cannot exist with thicknesses of a few atoms. When materials are scaled down to a fewatom thickness, they transition to another thermodynamically stable



FIG. 17. (a) The schematic of the remote interaction penetration depth depending on ionicity across groups IV, III–V, and I–VII materials shows that graphene transparency increases with material ionicity.⁸ Reproduced with permission from Kong *et al.*, Nat. Mater. **17**, 999 (2018). Copyright 2018 Springer Nature. (b) Crosssectional TEM image of the HfS₂ layer on c-sapphire through a monlayer hBN. The inset shows the corresponding fast Fourier transfer (FFT) pattern. (c) XRD azimuthal scans taken on the HfS₂ (10-11) and sapphire (11-26) reflections for asprepared templates with different hBN interlayers.¹³³ Reproduced with permission from Wang *et al.*, Nanoscale **11**, 9310 (2019). Copyright 2019 The Royal Society of Chemistry.

phase. Moreover, they are easily degraded by environmental molecules.^{10,152,153} This is because the high surface energy caused by unsaturated dangling bonds on the surface constrains reduction of the surface, thereby inducing charge compensation by electron redistribution and surface reconstruction.^{10,153} Due to these limitations, most of the research on non-vdW 2D materials (quasi-2D material) has been focused on theoretical approaches. A growth method for quasi-2D materials that employs the intercalation phenomenon of graphene has recently been proposed.^{154–157} This method overcame thermodynamic and kinetic limitations of the approach and suggested the possibility of expanding a new class of 2D materials that were previously nonexistent. In this part, we briefly introduce the emerging technique of growing quasi-2D atomic crystals by using the intercalation characteristics of graphene.

Recently, Al Balushi *et al.* demonstrated a 2D GaN synthesized by a migration-enhanced encapsulated growth method using a quasi-freestanding epitaxial graphene (QFEG)/SiC(0001) template (Fig. 23).¹⁰ They showed that a 2D GaN with a wurtzite structure is formed when a QFEG/SiC substrate is sequentially exposed to the trimethylgallium precursor and ammonia. These results are of great



FIG. 18. (a) Schematic illustration (left) top-view scanning electron microscopy (SEM) image (middle) and EBSD map (right) of GaAs grown on graphene/GaAs. The scale bar in the SEM image is 10 μ m. The scale bar in the EBSD map is 2 μ m. Top-view scanning electron microscopy (SEM) images (left) and EBSD maps (right) of (b) Ge on graphene/Ge, (c) Ge on graphene/GaAs, and (d) GaAs on graphene/Ge. All scale bars of SEM images and EBSD maps are 2 μ m.¹²⁵ Reproduced with permission from Kim *et al.*, ACS Nano 15, 10587 (2021). Copyright 2021 American Chemical Society.

significance because dimensional scaling of wurzite GaN causes a spontaneous transition into a planar-coordinated graphitic structure through charge compensation. This implies that the graphene layer located at the upper region of quasi-2D GaN plays an important role in stabilizing the 2D-buckled GaN structure, which will be discussed below.

A. Growth mechanism of quasi-2D layers through intercalation

In SiC substrates, the Si atoms on the surface are sublimated at temperatures above 1200 °C, and then reconstruction of the $(6\sqrt{3} \times 6\sqrt{3})$ R30° layer follows.¹⁵⁸ The top carbon layer forms a honeycomb structure, generally referred to as the buffer layer or zeroth layer, and one-third of the bottom carbon atoms are covalently bound with the SiC substrate to form a quasi-freestanding epitaxial graphene (QFEG) [Fig. 23(a)]. Subsequently, passivation of the dangling bonds

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FIG. 19. (a) Micrography of the exfoliated SrTiO₃ membrane on graphene-coated SrTiO₃ substrates with varying graphene thickness. Holes are evident (indicated by black arrow) from monolayer graphene compared bilayer graphene. The scale bar indicates 20 μm. The holes are due to macroscopic holes and tears of the graphene during transfer, resulting in homoepitaxy on those areas and ultimately leading to spalling during exfoliation.¹²⁶ Reproduced with permission from Kum *et al.*, Nature **578**, 75 (2020). Copyright 2020 Springer Nature. (b) Schematic illustration of multi-step remote epitaxy techniques. (c) TEM images of GaN epilayers on graphene with the nucleation layer (left) and magnified GaN/graphene/GaN interface (right). (d) XRD rocking curves of GaN epilayers grown on graphene.¹²⁷ The reference indicates the rocking curve width of the GaN epilayer grown directly on the underlying GaN. Reproduced with permission from Badokas *et al.*, J. Phys. D: Appl. Phys. **54**, 205103 (2021). Copyright 2021 IOP Publishing Ltd.

existing at the interface between graphene/SiC through hydrogeneration decouples the QFEG from the substrate, resulting in the generation of an additional graphene layer. Therefore, *n*-layer graphene can be grown into (n + 1)-layer graphene through repeated hydrogen intercalation [Fig. 23(b)].¹⁵⁴ When the QFEG/SiC substrate is exposed to the trime-thylgallium precursor, Ga adatoms are decomposed at the surface of graphene and easily diffused into the QFEG/SiC interface because of the lowered energy by hydrogenation [Fig. 23(c)]. Thereafter, when the substrate is exposed to ammonia at 675 °C, a 2D GaN with a wurtzite structure is formed through a chemical reaction between the decomposed nitrogen and intercalated gallium [Figs. 23(d)–23(g)].

The formation of a quasi-2D material using an intercalation method involves complex interactions of adatom, graphene, and a substrate. Graphene defects, such as grain boundaries, point defects, and wrinkles, act as a pathway through which the adjacent molecules can enter the QFEG/SiC interface. By using DFT calculations, it was demonstrated that the vacancy formation energy of graphene decreases with the cooperative effect of the adatom and substrate [Figs. 24(a) and 24(b)].¹⁵⁹ When an Si adatom is located on the surface of the

freestanding graphene, the defect formation energy of graphene is considerably stable at 8.09 eV [Fig. 24(a)]; however, the energy is significantly reduced to $0.23\,e\mathrm{V}$ when the graphene is supported on a Ru substrate [Fig. 24(b)]. Theoretical simulations and experiments demonstrated that this formation energy reduction is a universal phenomenon in various adatom/substrate systems. In addition, the precursor-derived adatoms break the carbon-carbon bond near the pre-existing defects of graphene, thus causing defect enlargement.^{160,161} Therefore, adatoms dissociated at the graphene surface can be intercalated into the interface between graphene and SiC through the enlarged holes and the newly formed defects from the hydrogenation process [Fig. 24(c)].¹⁶² Defect engineering of graphene can stimulate such intercalation. By controlling the permeability according to the density or configuration of defects formed in graphene through UV/ozone, electron beam, and plasma treatments, it is possible to permeate atoms with large atomic sizes, such as Ga, In, and Sn, or increase the lateral coverage.^{11,163} Hydrogenation of SiC substrates also plays an important role in determining the coverage of 2D materials. In interfaces without hydrogenation, atoms cannot easily diffuse owing to the disturbance of the

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FIG. 20. (a) Schematic diagram of strain relaxation via the introduction of a dislocation. T indicates where a dislocation forms. (b) Schematic diagram of strain relaxation via spontaneous relaxation. (c) Energy barrier required for the interface sliding of epilayers on graphene/substrates and bare substrates (left) and threshold energy for the situations of interface sliding on graphene, the introduction of a dislocation, and interface sliding on bare GaAs (right). (e) Cross-sectional view of GaP grown on bare GaAs and (f) cross-sectional view of GaP grown on graphene/GaAs.¹²⁸ Reproduced with permission from Bae *et al.*, Nat. Nanotechnol. **15**, 272 (2020). Copyright 2021 Springer Nature.

Si dangling bonds with a relatively high diffusion-energy barrier against the intercalants. By contrast, intercalation and diffusion easily occur after the hydrogen intercalation process because of reduced interfacial energy, which enhances the lateral coverage.

Atoms stabilized by the low interface energy cause an interface ordering in the 2D form by spatial restriction and interaction with the underlying substrate. For example, single-layer gold atoms synthesized at the heterointerface between graphene and 6H-SiC(0001) have a highly ordered triangular lattice by imitating the SiC (1 \times 1) registry [Fig. 25(a)].^{9,164} By contrast, Au atoms deposited on the SiC(0001) substrate without a graphene capping layer do not follow the (1×1) order, thereby confirming that graphene stabilizes the unique ordering and electronic structure of the synthesized quasi-2D materials. Intercalated post-transition metals, such as Ga, In, and Sn, at the graphene/SiC interface also can be arranged and stabilized in one to three atomic layer forms according to the chemical potential of each metal [Fig. 25(b)].¹¹ Furthermore, quasi-2D group III-nitrides, such as GaN, InN, and AlN, obtained through the nitridation of quasi-2D single elements show the lattice alignment with the substrates.¹⁰ This finding is due to the altered orbital of an atom or chemical structure of a molecule by the strong interaction between the intercalant and substrate, as well as the confinement effect by the spatial restriction.¹⁶⁷ The electrical and structural properties of the quasi-2D material can be further tuned by manipulating the interfacial properties. The graphene defects generated during intercalation can be recovered by annihilating the carbon vacancies at a relatively low annealing temperature

 $(300-800 \,^{\circ}C)$ after the growth process.^{159,167} The repaired graphene also prevents oxidation and lattice reconstruction by blocking the synthesized quasi-2D materials from oxygen or chemical species. This sealing effect enables the *ex situ* analysis of the intrinsic properties of the quasi-2D materials without degradation by environmental molecules.¹⁶⁷ The resulting quasi-2D materials form a strong covalent bond with the SiC substrate and a non-bonded vdW interface with the graphene overlayer, named the "half vdW" structure [Fig. 25(c)].¹⁰ Overall, the formation of a quasi-2D material through intercalation follows four key steps: formation of defects, intercalation and diffusion of atoms, ordering and growth of intercalants, and repairing of graphene. Many experiments and theoretical results have demonstrated that this phenomenon is universal and can be extended to various adatom/substrate systems.

B. Characteristics of quasi-2D materials and their heterostructures

The quasi-2D materials grown using the intercalation technique exhibit electrical and structural properties that are significantly different from those of their bulk forms. The most common phenomenon is bandgap tuning due to strong quantum confinement. For example, the exciton Bohr radii of InN, GaN, and AlN are 8, 2.4, and 1.4 nm, respectively, and the electronic properties of few-atom-thick 2D InN, GaN, and AlN are modified by the strong quantum confinement effect [Figs. 26(a)-26(c)].¹⁰ The bandgap of 2D InN as measured using scanning tunneling spectroscopy is 2 ± 0.1 eV, which is wider than that of



FIG. 21. (a) SEM images showing the positions of the GaN crystals, respectively, before (left) and after (right) the AFM sweeping of the surface. The swept area is indicated by a square on each image.¹²³ Reproduced with permission from Journot *et al.*, Nanotechnology **30**, 505603 (2019). Copyright 2019 IOP Publishing Ltd. (b) Photographs of blue EL emission of the LEDs fabricated with a virgin wafer (left) and recycled wafer (right) attached on the surface of finger-sized bottle in the bent form at an R_b of 10 mm.¹³⁰ Reproduced with permission from Jeong *et al.*, Sci. Adv. **6**, eaaz5180 (2020). Copyright 2020 American Association for the Advancement of Science. (c) Schematic of the processes of remote epitaxy, exfoliation, and transfer. (d) Modeled atomic structures of the buffer layer on SiC. (e) Potential fluctuation (meV) maps on the GBL/SiC. (f) Photograph of the three-times-reused GBL substrate and the exfoliated GaN epilayers.¹²⁴ Reproduced with permission from Qiao *et al.*, Nano Lett. **21**, 4013 (2021). Copyright 2021 American Chemical Society.

bulk InN (0.7 eV).¹⁶⁸ Similarly, quasi-2D GaN with a buckled structure grown by the intercalation method has a direct bandgap of 5.28 eV, which is larger than the indirect bandgap of freestanding 2D GaN in the planar structure (4.12 eV) and the direct bandgap of the wurtzitestructured bulk GaN (3.42 eV).¹⁰ This shows that the quasi-2D GaN grown by the intercalation method can be used in deep-ultraviolet photonic and optoelectronic applications. Notably, quasi-2D transition metals such as Au and Ag exhibit metal-to-semiconductor transitions depending on thickness.^{9,169} Moreover, the charge transfer and orbital overlap between graphene and quasi-2D materials affect the electronic state of each layer. 2D Ga exhibits superconducting properties owing to the interaction with graphene overlayers.¹¹ Furthermore, the Dirac point of graphene shifts because quasi-2D materials act as an electron donor or acceptor.¹⁶¹ The heterostructure of the graphene/quasi-2D materials naturally formed in the intercalation growth process enables the fabrication of Moiré superstructure, double lateral junction, and Schottky junction devices without additional processes such as exfoliation or transferring [Figs. 26(d)-26(i)].^{9,10,170,171} This new class of 2D materials and their heterostructures are expected to enable the development of new electronic, optoelectronic, superconductor, and plasmonic devices with new physics. However, the synthesis of quasi-2D materials using the intercalation method has the limitations of poor uniformity and low lateral coverage.^{10,170} Therefore, further research

on the tuning of growth factors in combination with defect engineering is required. Overall, expanding this approach for the experimental implementation of a new class of 2D materials that have not been explored to date will be an interesting research topic (Fig. 27).

V. RADIATION DAMAGE IN 2D MATERIALS

Due to the interest in employing them in space-borne and other harsh environment applications, the degradation of thermal, electrical and optical properties of 2D materials through interaction with ionizing and non-ionizing radiation has been the subject of numerous studies over the past decade.¹⁷²⁻¹⁹⁹ Additional structural changes can be caused by ions creating primary defects, which are mostly vacancies and interstitial atoms in the case of ions of low mass number. It is common for these primary defects to have significant diffusion distances at room temperature, and thus, they can form complexes with impurities, dopants, or other defects in the crystal structure. The most common type of radiation exposure of fluxes of high energy protons, alpha particles, and electrons would occur for 2D materials used in space-borne applications such low earth orbit satellites,¹⁷² as well as neutrons or gamma rays if used in radiation-hard nuclear or military systems Each of these forms of radiation produces different types of crystal lattice damage on the crystalline materials.

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FIG. 22. (a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of MQWs in the InGaN/GaN MQWs LED structure and the EDS linear scanning spectrum along the growth direction in MQWs. (b) EL spectra of an LED as a function of injection current.¹²² Reproduced with permission from Zhang *et al.*, Small **17**, 2100098 (2021). Copyright 2021 Wiley-VCH GmbH. (c) EL spectra and photomicrographs of white, blue, green, yellow, and orange emissions obtained from each single microcrystal GaN p–n junction LED. (d) Photographs of EL emission from the microcrystal-white LED with a current injection of 100 mA. The large-area photomicrograph of microcrystal-white LED taken from the boxed area in (d) and enlarged photographs presenting various EL light emission colors. Reproduced with permission from Jeong *et al.*, Nano Energy **86**, 106075 (2021). Copyright 2021 Elsevier Ltd. (e) A series of photographs of cyan microrod LED ($\lambda = 500$ nm) deformed in various shapes, such as twisted, 90°-folded crumpled, and 180°-folded forms, operated at 100 mA. The inset in the rightmost image is a schematic illustrating the geometry of MR arrays in the folded form.¹³⁰ Reproduced with permission from Jeong *et al.*, Sci. Adv. **6**, eaaz5180 (2020). Copyright 2020 American Association for the Advancement of Science. (f) Schematic of the CFO/PMN-PT magnetoelectric device. (g) The voltage induced across the PMN-PT (∂V_{ME}) as a function of the alternating-current magnetic field strength at a frequency of 1 kHz. The inset shows schematics of the freestanding and the clamped devices.¹²⁶ Reproduced with permission from Kum *et al.*, Nature **578**, 75 (2020). Copyright 2017 Springer Nature. (h) Responsivity and detectivity of HfS₂/hBN photodetector as a function of the power intensity at 10 V.¹³³ Reproduced with permission from Wang *et al.*, Nanoscale **11**, 9310 (2019). Copyright 2019 The Royal Society of Chemistry.

For space-based applications, the doses received by electronics depends on many factors, including the altitude and inclination, the amount of shielding, and the solar flare cycles.¹⁷² The main sources of radiation in this case are solar flares and coronal mass ejections, trapped charge in the radiation belts and galactic cosmic rays (GCR). Deep-space missions may also encounter neutrons from background or radio-isotope thermal generators or other nuclear sources. Atmospheric and terrestrial applications are subject to GCRs and their secondaries. A GCR ion is a charged particle (typically H, He, Fe, and heavier) found in free space, whose energies range from MeV to GeV.¹⁷²

An important parameter determining the magnitude of the effect radiation has on 2D materials is how much energy is deposited per unit length by this particle as it passes through the material. This is known as linear energy transfer or LET (dE/dX). The common LET unit is MeV cm²/mg of the material. For one particular type of disruption to a 2D device, known as a single event effect (SEE), immunity is defined as a device having an LET_{th} > 100 MeV cm²/mg. The radiation effects are usually classed into long-term effects due to total ionizing dose (TID) and displacement damage (DD) and transient or single particle effects, which lead to soft or hard errors in microprocessors.

These three main types of radiation damage are summarized below:

(1) Total ionizing dose, which is ionization damage caused by electron-hole pairs that are generated in gate insulators. The damage is the result of trapping of excess carriers at interface



FIG. 23. (a) HAADF-STEM cross section of quasi-2D GaN, consisting of two sub-layers of gallium, between bilayer graphene and SiC(0001). Elemental energy-dispersive xray spectroscopy mapping of (b) silicon, (c) gallium, and (d) nitrogen in 2D GaN. [(e)–(g)] Schematic of the MEEG process that leads to the formation of quasi-2D GaN. (e) The process of silicon sublimation from SiC(0001) to grow epitaxial graphene that consists of an initial partially bounded graphene-buffer layer (bottom) followed by a monolayer of graphene (top). The green halos at the SiC/graphene interface represents Si dandling bonds. (f) Exposing the epitaxial graphene in a to ultrahigh-purity hydrogen at elevated temperatures decouples the initial (bottom) graphene-buffer layer to form bilayer QFEG. (g) The proposed MEEG process for the formation of quasi-2D GaN: first, trimethylgallium precursor decomposition and gallium adatom surface diffusion; second, intercalation and lateral interface diffusion; finally, transformation of gallium to quasi-2D GaN via ammonolysis.¹⁰ Reproduced with permission from Al Balushi *et al.*, Nat. Mater. **15**, 1166 (2016). Copyright 2016 Springer Nature.



FIG. 24. The predicted energy barrier of Si intercalation (a) without and (b) with the Ru substrate, respectively.¹⁵⁹ Reproduced with permission from Li *et al.*, J. Am. Chem. Soc. **137**, 7099 (2015). Copyright 2015 American Chemical Society. (c) Schematic structures for the formation of quasi-2D AIN layers sandwiched between graphene and Si substrates.¹⁶² Reproduced with permission from Wang *et al.*, Adv. Mater. **31**, 1803448 (2018). Copyright 2018 WILEY-VCH GmbH.



FIG. 25. (a) STM topography image over a (5.2×5.2) nm² region. The (13×13) moiré unit cell is indicated as a cyan diamond. Image recorded at U_{sample} = 100 mV and I_{lumnel} = 85 pA. The scale bar is 1 nm. The ball-and-stick model of the gold atoms intercalated between graphene and SiC(0001). Side view and, on the right side, top view showing the (13×13) supercell.⁹ Reproduced with permission from Forti *et al.*, Nat. Commun. **11**, 2236 (2020). Copyright 2020 Springer Nature. (b) Cross-sectional STEM showing three layers of Ga, In, and Sn between EG and SiC. The inset of top figure shows different interlayer spacings of the Ga layers.¹¹ Reproduced with permission from Briggs *et al.*, Nat. Mater. **19**, 637 (2020). Copyright 2020 Springer Nature. (c) Schematic of the buckled 2D GaN structure between SiC and graphene grown with intercalation growth.¹⁰ Reproduced with permission from Al Balushi *et al.*, Nat. Mater. **15**, 1153 (2016). Copyright 2016 Springer Nature.

regions at the interface between the dielectric and 2D material. This is a cumulative long term ionizing damage. In electronic devices, the main effects are threshold shifts, excess leakage current and functional failures. The units are kRads (material). TID can be partially mitigated with shielding.

- (2) Displacement damage, also referred to as non-ionizing energy loss (NIEL) caused by lattice collisions between energetic ionized particles that transfer sufficient energy to the lattice to displace it within the lattice. This is also a cumulative long term non-ionizing damage. Some of the effects include production of defects that degrade device performance by trapping of carriers and reduction of carrier mobility. The unit of interest is particle fluence at a given energy. Shielding can reduce the severity of displacement damage.
- (3) Single event upsets (SEU), which are caused by passage through the materials of incident single ions resulting in an ionized trail of charge that couples to the lattice. This electron-phonon coupling to the atomic structure creates a local thermal spike on a time scale <300 fs. At sufficiently high energy deposition rates, this can progress to formation of localized electronic excitations that can rupture bonds. If the LET of the particle (or reaction) is greater than an energy threshold, transients or destructive errors may occur in device operation.

In the initial stages of entering the material under irradiation, the incident ions lose energy mainly by electronic stopping, and move in fairly straight paths. When the ion has slowed down sufficiently, the collisions with nuclei become more likely. When atoms receive significant recoil energies, they will be removed from their lattice positions, and produce a cascade of further collisions in the lattice. These collision cascades are the main cause of damage production. Ions create mainly point defects, which are most commonly created right after irradiation.

Krasheninnikov recently published a perspective on the reasons for the reported high tolerance of 2D materials to radiation damage.199,200 He suggested that although the free-standing films are indeed radiation-hard, the influence of the substrate can have a major effect and be the determining factor in the response of the 2D to radiation exposure. Of the 2D materials, most radiation damage studies have been performed on graphene. when graphene is irradiated with a proton beam, the defect generation is dependent on the number of graphene layers and is coupled to the interactions with the underlying substrate. At radiation levels common for satellite altitudes up to geostationary orbit, Vogl et al. reported no changes in the characteristics of hBN, MoS₂, and WS₂ after irradiation with protons, electrons, gamma rays, or x rays.¹⁷³ However, under high γ -irradiation doses, WS₂ monolayers exhibited a significant change in optical emission. However, for these WS2 monolayers, the extrapolated effect of increased PL and carrier lifetime after 4 yr in low earth orbit to be <0.15%. Self-healing after γ -irradiation was suggested to be due to reaction of chemisorbed oxygen with chalcogen vacancies. Shi et al. irradiated WSe2/SiC heterostructures with 2 MeV protons, 2.5 and 5 MeV Fe^+ or 4 MeV Ag^+ and found that proton doses of 10^{16} cm^{-2} were necessary before they observed charge transfer into WSe₂.¹⁹³ For the heavy ions, irradiation at high displacement per atom (dpa) levels leads to significant physical damage. Collisions between heavy ions and WSe₂ lead to structural disorder and the preferential ejection of selenium; therefore, the sample is oxidized once exposed to an oxygen-bearing ambient. Kim et al. found that 10 MeV proton irradiation of MoS₂ field effect transistors can induce trap states at interfaces and within the gate oxide, degrading the transistor's performance.¹⁹



FIG. 26. (a) Binding energy calculations of freestanding planar and buckled 2D nitrides (N: nitrogen, M: group-III metal element and H: hydrogen atoms), as a function of layer number (L). (b) Band structure calculations via DFT of freestanding planar and buckled 2D monolayer GaN, (c) diagram of bandgap energy vs in-plane lattice parameter for bulk and buckled 2D nitrides. The dashed lines are to illustrate the potential for E_g tunability via alloying of 2D buckled monolayers. A plot of E_g as a function of number of atomic buckled layers is included as an inset in (c).¹⁰ Reproduced with permission from AI Balushi *et al.*, Nat. Mater. **15**, 1166 (2016). Copyright 2016 Springer Nature. (d) Scanning tunneling microscopy (STM) topography image borophene-graphene vertical heterostructures. (e) Point scanning tunneling spectroscopy (STS) spectra of graphene and borophene-intercalated graphene. (f) Zoomed-in STM image of the graphene-graphene/borophene interface (top) and borophene-intercalated graphene (f) Zoomed-in STM image of the graphene-graphene/borophene interface (top) and borophene-intercalated graphene (f) Zoomed-in STM image of the graphene-graphene/borophene interface (top) and borophene-intercalated graphene domain (bottom).¹⁷¹ Reproduced with permission from Forti *et al.*, Nat. Commun. **11**, 2236 (2020). Copyright 2020 Springer Nature. (h) Current-voltage (I-V_{tip}) characteristics collected with the conductive atomic force microscopy (c-AFM) tip on the graphene/SiC (red) and graphene/InO/SiC (black) regions. The inset shows a semi log plot of the two I-V_{tip} curves under forward bias polarization and the fit with the thermionic emission and with the combined thermionic emission from Kakanakova-Georgieva *et al.*, Appl. Surf. Sci. **548**, 149275 (2021). Copyright 2021 Elsevier Ltd.

The threshold for damage was 10^{13} cm⁻², with higher doses leading to significant decrease in FET current and transconductance. Zhang *et al.* found that 10 keV x-ray irradiation led to decrease in drain current of back-gated MoS₂ transistors.¹⁸⁶ It was suggested that the x-ray irradiation enhanced adsorption of oxygen on the surface of MoS₂ and that these adsorbed atoms function as electron traps. Proton, electron, and ion-beam irradiation of MoS₂ structures. When exposed to an 80 keV electron beam, the MoS₂ layers can be doped when vacancies created

by the irradiation are filled by impurity atoms. After irradiation with 1.14 GeV U^{28+} ions, Ochedowski *et al.* reported that MoS₂ exposedchannel transistors suffered permanent failure.¹⁸⁹ The electrical characteristics of MoS₂ devices have been found to change due to high-energy proton irradiation-induced traps in the oxide layer and/or at the interface between MoS₂ and oxide.^{186,188–190} Kim *et al.* used point defect creation in ambipolar WSe₂ by exposure to an Ar plasma to induce n-type doping in contact regions, while protecting the channel region



FIG. 27. Clockwise from top left are shown a schematic of proton beam irradiation on a MoS₂ FET, change in the threshold voltage of the devices following proton irradiation with different beam fluences (10¹², 10¹³, and 10¹⁴ cm⁻²) and optical image of FET. Reprinted with permission from Kim *et al.*, ACS Nano **8**, 2774 (2014). Copyright 2014 American Chemical Society.

of the transistors with h-BN.¹⁹⁷ The sheet resistance of the exposed areas was much reduced as a result of the point defect introduction, leading to strong n-type conductivity. Similarly, plasma bombardment of 2D MoS₂, was found to create point defect (S vacancies), causing 1T phase transitions.¹⁹⁸ Using a plasma exposure to change the conductivity of 2D materials is a very convenient and controllable method, since the more conventional ion implantation is difficult to implement in such thin layers. In particular, the use of inert Ar plasmas means there is no change due to chemical reactions. Liang *et al.* reported the total ionizing dose radiation response of HfO₂-passivated black phosphorus MOSFETs.¹⁹² Both positive and negative biasing during irradiation with 10 keV x rays led to positive oxide-trap charge buildup in the HfO₂ gate dielectric, with degradation of mobility and subthreshold swing.

Table V shows a summary of reported radiation studies on 2D materials.^{173–199} It is clear that under the types of doses expected to be encountered by 2D materials in space-borne or terrestrial applications, they can be classed as radiation-hard compared to Si devices. Whether or not the films are free-standing or supported by a substrate makes a difference in their response to radiation and more studies are needed that separate these effects.¹⁹⁸

VI. OUTLOOK

We have reviewed the (quasi) vdWE, remote epitaxy, and intercalated quasi-2D material growth using 2D materials as growth templates. Different from conventional epitaxy, material growth using a 2D substrate offers a bond-free integration strategy without the severe

| Material | Radiation treatment | Outcome | References |
|-------------------------------------|--|--|------------|
| WS ₂ , MoSe ₂ | γ rays, 1.28 MeV protons, 1.7 MeV, 10^{12} cm ⁻² | Devices no change, single layers O passivation of S _V | 173 |
| MoS ₂ FETs | Protons, 10 MeV, 10^{13} cm ⁻² | Decrease in conductance and current | 190 |
| MoS ₂ FETs | 10 keV x-rays | Decreases in drain current | 186 |
| MoS ₂ FETs | 1.14 GeV U-238 | FET destroyed at dose of 4×10^{11} cm ⁻² | 189 |
| WSe ₂ | Protons, 2 MeV, 10^{16} cm ⁻² , | Charge transfer to WSe_2 from substrate with protons, | 193 |
| | Ag or Fe, 4 or 5 MeV, 10^{10} cm^{-2} | dissociation with heavy ions | |
| MoS_2 | Remote ICP Ar plasma | $2H \rightarrow 1T$ phase transition | 198 |
| MoS_2 | 2 MeV protons | Magnetic ordering induced | 187 |
| WSe ₂ | Low energy Ar plasma exposure | Creation of Se vacancies | 197 |
| hBN | 2 MeV electrons, 10^{15} cm^{-2} | Increase in density of single photon emitters | 196 |
| BP | 10 keV x-rays | Threshold voltage shifts in MOSFETs | 192 |
| Graphene | 10 keV x-rays 1.8 MeV protons | Hole trapping in gate oxide, decreased drain current, eventual creation of O-related defects | 181 |

consideration of lattice mismatch, thus allowing the experimental validation of the epitaxy in various 3D/2D and 2D/2D heterostructures. The interplay between the symmetries of the 2D material and substrate is critical during conventional epitaxial growth.^{201,202} Moreover, due to the atomically thin nature of 2D materials, the crystallographic features of the 3D substrate can penetrate the 2D overlayer and remotely determine orientation of the epilayer by charge distribution, thereby enabling remote epitaxial growth. The 2D overlayer-covered substrate can also confine atoms penetrated through defects of the 2D overlayer, vielding highly ordered quasi-2D crystals by low interface energy and spatial restriction. Despite the extraordinary potential and considerable progress to date, to the application of 2D template-based growth techniques in practical technologies have several issues. For uniform growth of epilayers on 2D templates, proper surface engineering of various 2D materials is needed. Moreover, the effects of defects and functional groups on the physical properties at the interface between epilayers and 2D templates should be studied. Although remote epitaxy has been successfully demonstrated so far, process conditions should be further optimized to improve crystal quality and throughput and to reduce process cost for commercial applications. The implementation of intercalation growth requires additional studies to increase the uniformity and crystallinity of the quasi-2D materials. Defect engineering in conjunction with interface engineering of 2D overlayer/substrate may help control the quality of quasi-2D materials. The investigation and advances in this review provide opportunities for fundamental studies and technological applications using epitaxial growth on 2D templates.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Huije Ryu: Investigation (equal); Writing – original draft (equal). Hyunik Park: Investigation (equal). Joung-Hun Kim: Investigation (equal). Fan Ren: Funding acquisition (equal); Validation (equal). Jihyun Kim: Supervision (equal); Writing – review & editing (equal). Gwan-Hyoung Lee: Writing – original draft (equal); Writing – review & editing (equal). Stephen J. Pearton: Conceptualization (equal); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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