

Stabilization of hBN/SiC heterostructures with vacancies and transition-metal atoms

Arsalan Hashemi^{1,2,3,*}, Nima Ghafari Cherati^{4,5}, Sadegh Ghaderzadeh⁶, Yanzhou Wang,⁷
Mahdi Ghorbani-Asl⁸, and Tapio Ala-Nissila^{7,9,†}

¹*Department of Applied Physics, MSP Group, Quantum Technology Finland Center of Excellence,
Aalto University, P.O. Box 15600, FI-00076 Espoo, Finland*

²*European Laboratory for Learning and Intelligent Systems (ELLIS) Institute Finland, Maarintie 8, 02150 Espoo, Finland*

³*Department of Technical Physics, University of Eastern Finland, P.O. Box 1627, FI-70211 Kuopio, Finland*

⁴*HUN-REN Wigner Research Centre for Physics, PO Box 49, H-1525 Budapest, Hungary*

⁵*Department of Atomic Physics, Institute of Physics, Budapest University of Technology and Economics,
Műegyetem rkp. 3, H-1111 Budapest, Hungary*

⁶*School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom*

⁷*Department of Applied Physics, MSP Group, Quantum Technology Finland Center of Excellence,
Aalto University, FI-00076 Espoo, Finland*

⁸*Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany*

⁹*Department of Mathematical Sciences and Interdisciplinary Centre for Mathematical Modelling, Loughborough University,
Loughborough, Leicestershire LE11 3TU, United Kingdom*



(Received 14 September 2025; revised 11 January 2026; accepted 16 March 2026; published 13 April 2026)

When two-dimensional atomic layers of different materials are brought into close proximity to form van der Waals (vdW) heterostructures, interlayer interactions can strongly influence their physicochemical properties. These effects are particularly pronounced when the interface exhibits local order and near-perfect structural alignment, giving rise to moiré patterns. Using density-functional theory calculations, we investigate a bi-layer heterostructure composed of hexagonal boron nitride (hBN) and silicon carbide (SiC). We predict that introducing a boron vacancy, V_B , at specific lattice sites alters the interlayer interaction from weak vdW coupling to localized silicon-nitrogen covalent bonding. Motivated by this mechanism, we examine the binding of transition-metal adatoms and identify principles for enhancing surface reactivity and stabilizing isolated single-metal atoms. Machine-learning molecular dynamics at finite temperature further demonstrate rapid and effectively irreversible trapping of Cu at V_B sites, and show how the V_B :Cu ratio governs the transition from single-atom isolation to vacancy-directed aggregation. These results suggest the hBN/SiC heterostructure as a versatile platform for atomically precise transition-metal functionalization, with implications for catalytic energy-conversion materials.

DOI: [10.1103/PhysRevMaterials.10.045801](https://doi.org/10.1103/PhysRevMaterials.10.045801)

I. INTRODUCTION

Since the discovery of graphene [1], the two-dimensional (2D) allotrope of carbon, atomically thin materials have become a central theme in modern materials science. A broad range of elements and compounds can now be realized in either flat or corrugated 2D forms, including graphene and its allotropes, silicene (Si), phosphorene (P), hexagonal boron nitride (hBN), and transition-metal dichalcogenides such as MoS_2 . These systems host a wide variety of magnetic and

(opto)electronic phenomena driven by reduced dimensionality and strong correlations [2,3].

Beyond individual monolayers, combining dissimilar 2D materials into van der Waals (vdW) heterostructures provides a controlled route to engineer new functionalities that are absent in the constituent layers [1,4,5]. Such heterostructures have enabled, for example, tunable charge-carrier injection in diodes [6], reconfigurable memory behavior in transistors [7], and subthermionic switching in tunneling field-effect transistors [8]. When 2D layers are vertically stacked [9–11], interlayer hybridization, strain induced by lattice mismatch, and charge transfer across interfaces can substantially modify their electronic structure [12–14]. This process creates a multifunctional platform that may not only enhance the performance of the parent materials but also enable the emergence of new properties [15,16].

Among the 2D materials commonly employed in vdW heterostructures, hBN occupies a unique and central role. Owing to its mature fabrication techniques [17], wide electronic band gap [18], high lattice thermal conductivity [19], optical

*Contact author: arsalan.hashemi@aalto.fi

†Contact author: tapio.ala-nissila@aalto.fi

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

transparency [20], and exceptional mechanical strength [21], hBN has been widely adopted in applications ranging from (opto)electronics [22] to environmental sensing [23] and energy storage and conversion [24]. In the context of layered heterostructures, these properties have made hBN a preferred insulating and encapsulating layer, motivating its integration with other 2D materials such as graphene and transition-metal dichalcogenides [25,26].

A prototypical example appears when hBN is stacked onto semimetallic graphene: two structurally similar sheets form a seamless interface [27–33]. This heterostructure exhibits several emergent properties, including the opening of an electronic band gap in graphene that effectively transforms it from a semimetal to a semiconductor [34], ultrahigh charge-carrier mobility in graphene facilitated by hBN phonon contributions [35], and enhanced spin-orbit coupling, which extends the spin lifetimes to 1–10 ns [36]. Importantly, twisting one layer introduces a tunable moiré superlattice, adding an additional degree of freedom that renders the heterostructure both more complex and intriguing [37–40].

Motivated by the rich interfacial physics observed in hBN/graphene heterostructures, increasing attention has turned to identifying other 2D materials that can be compatibly integrated with hBN to form functional vdW heterostructures. Progress in this direction is governed by both synthetic feasibility and potential application advantages, factors that are often difficult to assess experimentally as the space of candidate materials rapidly expands. In this context, computer-aided modeling provides an effective preliminary screening tool to systematically narrow the material space, reducing experimental complexity while guiding the selection of promising heterostructure combinations [41,42]. Using such approaches, several studies have explored hBN-based heterostructures incorporating materials such as MoS₂, WS₂, and borophene, revealing diverse interfacial effects and application-relevant properties [43–47].

Beyond material selection and moiré engineering, which can induce local strain [48], point defects introduce an additional and often decisive degree of freedom in vdW heterostructures [49,50]. In semiconducting 2D materials, defects are ubiquitous and can introduce localized states within the band gap, thereby strongly modifying optical, electronic, and charge-transport properties [51–53]. In hBN, point defects may be intrinsic, arising primarily from atomic vacancies such as the boron monovacancy (V_B), or extrinsic, introduced via substitutional dopants or metal atoms anchored at vacancy sites [54–58]. These defects can significantly alter the electronic and optical response of hBN and enhance surface activity by promoting charge localization and electron transfer [59–65]. Despite their demonstrated relevance for applications ranging from catalysis and sensing to quantum and optoelectronic devices [66–71], the role of point defects within moiré superlattices of hBN-based vdW heterostructures remains largely unexplored.

In this work, we propose and investigate a bilayer heterostructure with tunable electronic properties formed by coupling a monolayer hBN with a semiconducting silicon carbide (SiC) monolayer, hereafter denoted as hBN/SiC. Despite their similar bonding character, the substantial lattice mismatch between the two layers gives rise to moiré superlattices.

In contrast to hBN, monolayer SiC has been realized in only a limited number of experimental studies [72,73], motivating a systematic computational investigation of its stability and interfacial behavior. While SiC surfaces are widely recognized as promising substrates for the epitaxial growth of 2D materials [74,75], realistic interfaces may involve reconstruction or passivation effects that are beyond the scope of the present idealized bilayer model. The isolated SiC monolayer adopts a flat honeycomb lattice, in contrast to bulk hexagonal SiC, where individual layers are buckled and cleaved surfaces exhibit enhanced chemical reactivity due to unsaturated bonds.

We employ quantum mechanical density-functional theory (DFT) to examine the combined effects of interfacial coupling, point defects in hBN, and metallic impurity atoms on the electronic structure. Specifically, we address (i) the structural stability and electronic properties of pristine hBN/SiC, (ii) the impact of boron and nitrogen vacancies on lattice geometry and emergent physical behavior, (iii) electronic tuning via transition-metal (TM) implantation, and (iv) the feasibility of stabilizing isolated single atoms. Based on these results, we outline design principles for translating defect- and interface-driven modifications into targeted functional applications.

II. COMPUTATIONAL DETAILS

Our spin-polarized DFT calculations were performed with VASP [76], employing projector augmented-wave pseudopotentials [77]. Exchange-correlation effects were treated using the Perdew-Burke-Ernzerhof (PBE) functional [78], and, where necessary, the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [79,80]. A plane-wave kinetic-energy cutoff of 500 eV was employed. Total energy and ionic force convergence thresholds were set to 10^{-6} eV and 0.01 eV/Å, respectively. The Brillouin zone of the pristine primitive unit cells of hBN and SiC was sampled using a $9 \times 9 \times 1$ Monkhorst-Pack grid, ensuring accurate electronic structure convergence. To suppress spurious interactions between periodic images, we added a 25-Å vacuum gap along the out-of-plane direction.

Among the available vdW correction schemes (see Table S1 of the Supplemental Material (SM) [81]), the Grimme DFT-D3 method with Becke-Johnson damping [82] best reproduces the experimental hBN interlayer spacing (≈ 3.3 Å) [83,84]. This method yielded interlayer distances of 3.26 Å for bilayer hBN and 3.23 Å for bilayer SiC, respectively. The experimentally reported lattice constants for monolayer hBN and SiC are 2.5 Å [85] and 3.12 Å [72], respectively, which are in close agreement with our PBE/HSE-calculated values of 2.51/2.49 and 3.09/3.07 Å. Furthermore, our calculated electronic band gap of monolayer hBN using the HSE functional is 5.46 eV, in agreement with experimental values ranging from 5.5 to 5.9 eV [86–88]. This validation confirms the reliability of our computational approach for achieving the objectives of this study.

To construct the hBN/SiC supercell, the crystalline axes of the hBN and SiC monolayers were aligned with a 5:4 ratio of their lattice constants. This alignment corresponds to $5 \times 5 \times 1$ and $4 \times 4 \times 1$ supercells for hBN and SiC, respectively, resulting in a lattice mismatch of 1.5%. To facilitate defect studies while minimizing fictitious defect interactions,

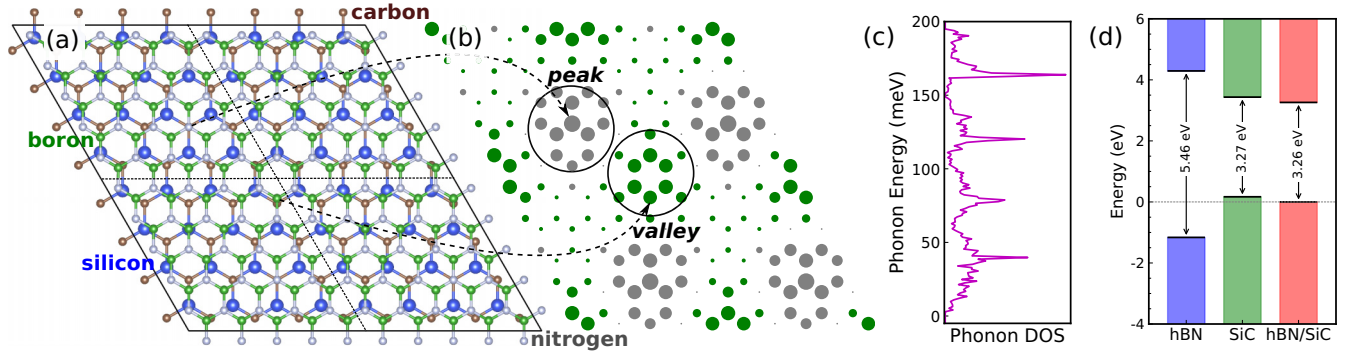


FIG. 1. (a) Heterostructure supercell model. Boron, nitrogen, silicon, and carbon are represented in green, gray, blue, and brown, respectively. (b) Out-of-plane displacements of hBN layer in response to the lattice mismatch of 1.5%. The size of each symbol represents the deviation of an atom's z coordinate from the average value. Green symbols indicate atoms with z coordinates below the average ($\Delta z^{\min} = -0.17$ Å), while gray symbols represent atoms with z coordinates above the average ($\Delta z^{\max} = 0.23$ Å). For the SiC layer $\Delta z^{\min}$ and $\Delta z^{\max}$ are about -0.05 and 0.05 Å, which were not depicted. (c) Phonon density of states (DOS) of the hBN/dosSiC system, shown in units of states/meV. (d) Energy levels and band gap for hBN, SiC, and the hBN/SiC heterostructure. Energy levels are shifted to valence-band maximum (VBM) of the heterostructure system and set as zero.

the supercell was duplicated along each in-plane axis [see Fig. 1(a)]. The final supercell consists of 100 boron (B), 100 nitrogen (N), 64 silicon (Si), and 64 carbon (C) atoms. For calculations involving the supercell, reciprocal space was only sampled at the Γ point.

In the supercell employed, removing or adding a single atom produced a defect density of 0.046 nm^{-2} . Defect formation energies were computed, following the protocol described in Sec. II of the SM, to evaluate the stability of various charge states of V_B and V_N defects. Subsequently, binding energy of a TM atom to the surface is defined as

$$E_{\text{bind}} = E_{\text{TM@surface}} - (E_{\text{surface}} + E_{\text{TM}}), \quad (1)$$

where $E_{\text{TM@surface}}$ is the electronic energy of the optimized complex, while E_{surface} and E_{TM} represent the electronic energies of the V_B -containing defective system (hBN/SiC heterostructure or hBN monolayer) and the isolated TM atom, respectively. A more negative E_{bind} indicates a stronger bond to the surface.

When needed, the lattice vibrations were evaluated using the PHONOPY package [89]. To reach larger system sizes and longer timescales, we carried out machine-learning molecular dynamics (MLMD) simulations using the GPUMD package [90]. The neuroevolution potential (NEP) framework [91] was used to represent the potential-energy surface, with radial and angular cutoffs of 5.0 and 3.5 Å, respectively. The NEP model was trained on DFT reference energies and forces and was employed to run stable MD for pristine and defected hBN/SiC (including V_B , V_N , and Cu adatoms and substitutions) across the temperature and strain ranges considered. A detailed explanation of the dataset can be found in Sec. III of the SM.

III. RESULTS

A. Pristine hBN/SiC

Structurally, hBN resembles graphene, but the B–N bonds exhibit partial double-bond character due to π -electron delocalization between nitrogen's lone p_z electrons and the empty p_z orbitals of boron. This broken sublattice symmetry opens

a wide band gap, making hBN an electrical insulator, in contrast to graphene's semimetallic behavior. The in-plane B–N network in hBN consists of three polarized σ bonds per atom arising from sp^2 -hybridized orbitals, yielding a trigonal-planar coordination with bond angles of around 120° . Table S2 compares the fundamental properties of pristine hBN and SiC with those of graphene. The B–N bond length in hBN is 1.45 Å, shorter than the sum of the covalent radii of B and N (1.55 Å), and comparable to the C–C bond length in graphene (1.42 Å). SiC exhibits a larger lattice constant and bond length (1.78 Å), consistent with the greater covalent radii of Si and C atoms (1.84 Å).

Structural symmetry reduces the elastic tensor to only three independent components: C_{11} , C_{12} , and C_{66} . According to the Born-Huang stability criteria [92], where $C_{11} > C_{12} > 0$ and $C_{66} > 0$, the SiC monolayer and the other systems in Table S2 are elastically stable. Notably, SiC exhibits a lower Young modulus than both graphene and hBN, indicating greater mechanical flexibility. As a result, monolayer SiC is expected to undergo larger deformation under strain induced by lattice mismatch.

The hBN/SiC interface has a binding energy of $-17.9 \text{ meV}/\text{\AA}^2$, comparable to the hBN bilayer ($-16.9 \text{ meV}/\text{\AA}^2$) but less in absolute value than that of a SiC bilayer ($-28.7 \text{ meV}/\text{\AA}^2$). Note that the magnitudes depend on the choice of vdW correction (see Table S3). To minimize the initial mismatch of 1.5%, the optimized lattice constant of the hBN/SiC supercell undergoes strains of -0.7% on the hBN layer and 0.9% on the SiC layer, relative to their respective monolayers. The pronounced mismatch of 18.8% (calculated as $\frac{a_{\text{SiC}} - a_{\text{hBN}}}{a_{\text{SiC}}} \times 100\%$ where a is the in-plane lattice constant) between unit cells naturally induces a long-period moiré pattern, resulting in structural nonuniformity across the bilayer [see Fig. 1(b)].

The interlayer distance between hBN and SiC sheets varies from 3.21 to 3.60 Å, depending on the local stacking pattern. While the SiC plane is under tensile strain, it exhibits a slight displacement along the z axis of about 0.05 Å; when the stacking resembles AA' stacking, where N(C) and Si(B) are

positioned over each other, the layers come closer together, forming a valley. The interlayer distance reaches its maximum when a B atom is positioned at the center of the SiC hexagon, and N atoms are aligned above C atoms, as shown in Fig. 1(b). The variation in interlayer spacing is primarily attributable to the buckling of the hBN layer.

To explore the alternative configuration (different stacking) to the one shown in Fig. 1(a), we swapped the positions of B and N atoms and subsequently assessed the relative stability of the resulting configuration. In this case, the total energy of the supercell increased slightly (by about 0.13 eV), which is negligible for 328 atoms. In what follows, we focus on the most stable configuration, which is dynamically stable [see Fig. 1(c)].

Our MLMD simulations (see Fig. S2 and Movie S1 [81]) show that the hBN/SiC interface is mechanically robust yet elastically compliant. Because of weak interlayer coupling, the monolayers slide readily past one another. The time-averaged interlayer spacing increases by 3% across the entire 25–900 K temperature range, underscoring interfacial stability. Meanwhile, the distribution of interlayer distances broadens markedly with temperature, reflecting enhanced out-of-plane rippling of the sheets. Bader charge analysis [93] reveals that in a monolayer hBN, $0.72e$ is transferred between B and N atoms to form a covalent bond, with B acting as the donor and N as the acceptor. In a SiC monolayer, Si donates $0.84e$ to the bonded C atom, indicating that the Si–C bond has a greater ionic character, while the B–N bond is more covalent in nature. We point out that the absolute magnitude of such partitioned charges is not unique and can vary with the chosen charge-partitioning scheme and the computational setup [94,95]. In the hBN/SiC system, a total charge transfer of $10^{-3}e$ ($\sim 1.859 \times 10^{10} e/\text{cm}^2$) occurs from the hBN layer to the SiC layer, which is negligible [96–98]. Thus, there is almost no redistribution of charge across the interface.

The electronic band gap of the heterostructure is 3.26 eV, which is almost identical to that of pristine SiC [see Fig. 1(d)]. The band alignment analysis indicates that the heterostructure exhibits type-I alignment, in which the band gap of SiC is fully nested within the band gap of hBN. As a result, both electrons and holes are confined within the SiC layer. Nevertheless, this study focuses on hBN, where defect incorporation is experimentally more accessible due to the extensive, long-term efforts devoted to this system [53,99,100].

B. Monovacancies in hBN/SiC

The response of hBN to vacancy creation is site specific: Both the identity of the missing atom and its crystallographic position dictate the local geometry, underscoring the intrinsic interfacial heterogeneity. Energetically, the stability of V_B is strongly influenced by the local environment, particularly the proximity of N atoms to Si atoms and, more prominently, B to C atoms in the adjacent layer. The introduction of neutral V_B at specific sites in hBN leads to the formation of strong chemical bonds between layers that were formerly bound by dispersive vdW interactions. This covalent interlayer coupling occurs only at certain positions, with the largest effect observed for vacancies located at or near regions of quasi-ideal stacking within the heterostructure.

To obtain a comprehensive picture of vacancy behavior, we evaluated 15 symmetry-inequivalent neutral V_B sites afforded by the chosen supercell. Sorting them by the number of interlayer covalent bonds formed reveals five families: (i) Nonbonded (or vdW bonded): A V_B positioned almost directly above a Si atom leaves three neighboring N atoms with dangling bonds that point toward the hollow sites of the SiC layer. These N atoms sit at the centers of the bottom-layer SiC' hexagons. Lacking suitable bonding partners, the N radicals neither dimerize nor form additional bonds, and the resulting configuration is 5.4 eV higher in energy than the ground-state defect. (ii) One bonded: Because only one adjacent Si–N pair is available, a single Si–N bond forms, raising the total energy by 3.1 eV relative to the ground-state configuration. The resulting defect shows strong magnetic correlations: its lowest manifold is a superposition of eigenstates (i.e., $|\Psi\rangle = \alpha|S = \frac{1}{2}\rangle + \beta|S = \frac{3}{2}\rangle$). Such spin mixing is typical of highly correlated electronic systems [101]. The two remaining N atoms stay isolated and do not participate in additional bonding. (iii) Two bonded: This configuration forms two Si–N bonds, lies 0.42 eV above the ground state, and carries total spin $S = \frac{3}{2}$. (iv) Three bonded: The defect makes three equivalent Si–N bonds of length 1.81 Å, which are 0.03 Å ($\approx 1.7\%$) longer than the native Si–C bond (1.78 Å). Its spin is $S = \frac{3}{2}$, and its energy is only 0.35 eV higher than the ground state [Fig. 2(a)]. (v) Four bonded (i.e., fourfold coordination in the extended solid-state environment): The energetically preferred structure contains four bonds: three Si–N bonds (1.79, 1.79, and 2.10 Å, respectively) and one C–N bond (1.61 Å). It exhibits total spin $S = \frac{1}{2}$ and defines the zero of the relative-energy scale [Fig. 2(b)]. The relative energies quoted above translate directly into differences in formation energy.

The lowest-energy configuration [the four-bonded defect, shown in Fig. 2(b)] arises when the absence of a B atom allows two neighboring N atoms to relax toward adjacent Si atoms, while the third N atom settles on the Si–C bond axis between the two sublattices. These findings reveal that at the hBN/SiC interface, the V_B defect nucleates preferentially at sites where the local stacking registry promotes Si–N bonding. The driving force is the donor-acceptor character of the elements involved: Si is a stronger electron donor than C, which makes Si–N bonds energetically more favorable [102].

Bond analysis of the four-bonded configuration reveals that the in-plane B–N bonds within the hBN layer are the strongest in the system, whereas the native Si–C bonds in the SiC substrate are roughly 20% weaker. The three interlayer Si–N bonds represent the weakest interactions in the structure: Two equivalent Si–N bonds are approximately 30% weaker than the native Si–C bonds, whereas the third Si–N bond is about 70% weaker. In contrast, the corresponding C–N bond associated with this configuration exhibits a strength comparable to that of the native Si–C bonds. A detailed bond analysis is provided in Fig. S4.

We performed MLMD simulations across a range of V_B densities. For multivacancy cases, defects were randomly distributed. The results are summarized in Fig. S3 and dynamically illustrated in Movie S2 (monovacancy) and Movie S3 (multivacancy). At the lowest density ($\rho = 0.046 \text{ nm}^{-2}$), introducing a single B vacancy induces layer sliding, aligning Si atoms with opposing N radicals and spontaneously forming

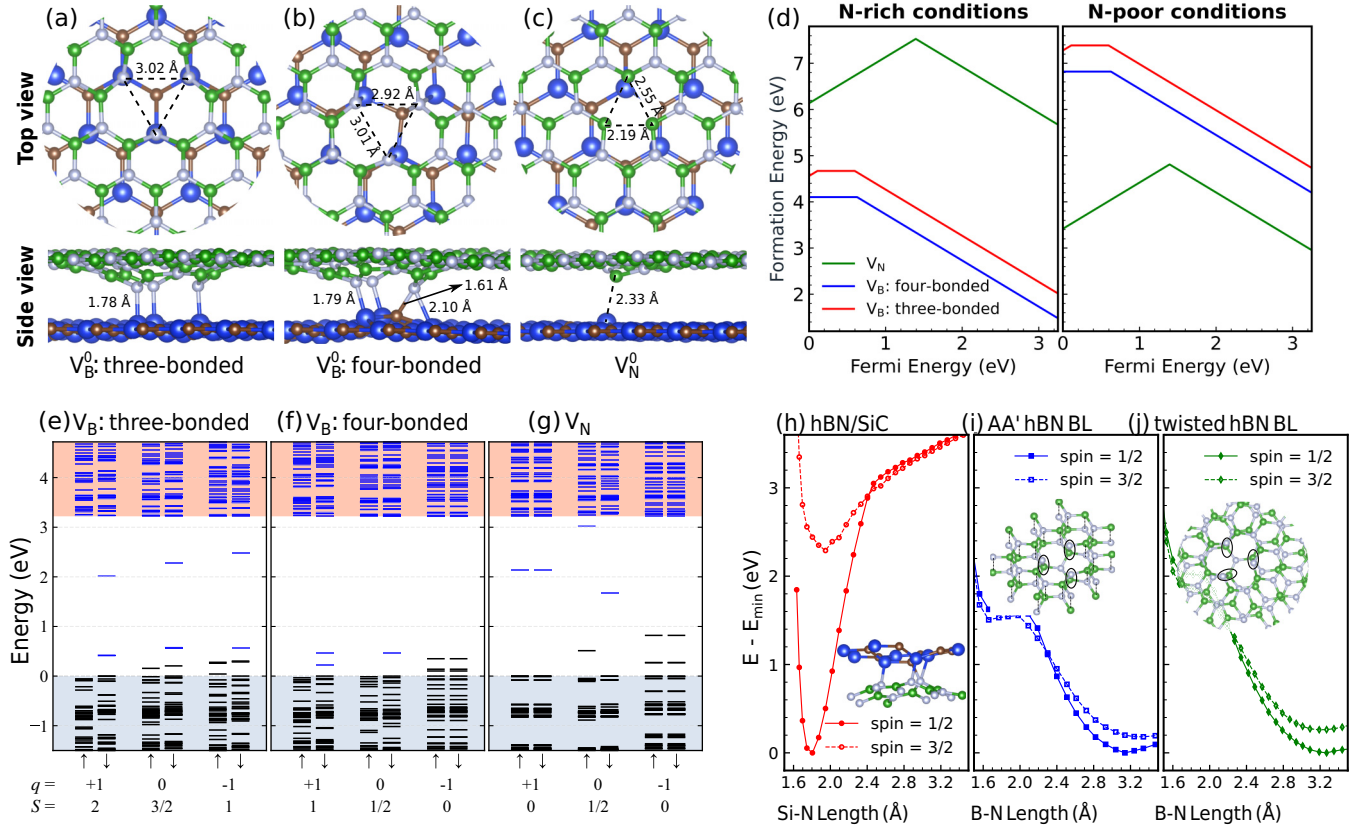


FIG. 2. Local defect structures of the (a) three-bonded V_B , (b) four-bonded V_B , and (c) V_N are presented along with detailed structural information. (d) Formation energy of the defects as a function of the position of the Fermi level under N-rich and N-poor conditions: The VBM is aligned to zero for the sake of simplicity. The conduction-band minimum (CBM) is at 3.26 eV. For each defect the (+), (0), and (−) charge states may appear. The N-rich and N-poor conditions are defined in Sec. II of the SM. (e)–(g) Electronic structure for the ground states of the defects. Kohn-Sham levels are represented in spin-up ($\uparrow$) and spin-down ($\downarrow$) channels. Energy levels at or below the VBM are shown in blue band, while those at or above the CBM are shown in orange. The occupied and unoccupied levels are represented in black and blue, respectively, for each charge state (q). The number of unpaired electrons can be determined from the spin state (S). For example, $S = 1$ indicates two unpaired electrons. (h)–(j) Energy profile for interlayer distance (bond length) scan of the V_B defect in different systems: the hBN/SiC heterostructure, AA' stacking, and the 14° twisted bilayer. Total energies are shifted for simplicity. Both low and high spin states are investigated, and a four-bonded system is considered for the heterostructure.

an interlayer Si–N covalent bond that persists throughout the 5-ns run. These bonds pin the hBN monolayer to the SiC layer and suppress further sliding. At higher vacancy concentrations, competing N radicals generate additional local strain; consequently, most form stable bonds, while the remainder fluctuate between transiently coordinated and dangling states.

A similar analysis for V_N reveals no interlayer chemical bond formation, only a weak tendency for B to remain near Si. Overall, the total energies of different V_N defects are comparable, varying by at most 0.4 eV across different sites. The most stable configuration exhibits a Si–B distance of 2.33 Å [see Fig. 2(c)]. All the V_N defects display a spin state of $\frac{1}{2}$.

By comparing the formation energies of defects [see Fig. 2(d)], we find that V_B is most stable under N-rich conditions, while V_N is most stable under N-poor conditions. However, V_N does not exist in a charge-neutral form. Defect stability in monolayer hBN depends sensitively on the nitrogen chemical potential. Under N-poor conditions, V_N is energetically preferred over V_B throughout the entire chemical-potential range. In contrast, under N-rich

conditions, the two formation energies intersect at about 2.4 eV above the valence-band maximum (VBM), beyond which V_B becomes the lower-energy defect [103,104]. The large band gap of hBN further permits stabilization of a wider spectrum of charge states than is typical in narrower-gap hBN/SiC. Our analysis of the positively charged V_N reveals a significant weakening of the B–Si interaction, with both the hBN and SiC monolayers remaining almost flat (i.e., B–Si distance ≈ 3.2 Å). For the negatively charged V_N defect, one B atom relaxes toward a neighboring Si, shortening the Si–B distance to 2.09 Å. At the same time, the two remaining B atoms approach one another, reaching an interboron separation of 2.05 Å, indicative of B–B dimerization. The (+|−) charge-transition level lies 1.47 eV above VBM. As expected, the four-bonded V_B is more stable than the three-bonded form. The latter is stable in the +1 charge state at very low Fermi levels, up to VBM+0.137 eV. We focus on the most stable V_B , where a charge transition from (0|−) occurs at VBM+0.67 eV. Comparison of the optimized geometries shows that only the longer Si–N bond length shortens by 2 pm, while the others remain unchanged.

The electronic structures of the defects in the ground state are shown in Figs. 2(e)–2(g). Defects introduce states into the electronic gap. Electron injection into the three-bonded V_B defect draws the lower-energy defect states downward to the VBM and simultaneously pushes the upper defect level upward toward the conduction-band minimum (CBM). In the four-bonded V_B , the unoccupied states are near the VBM, and adding electrons moves them closer to the VBM until they merge. The V_N defect exhibits a different electronic configuration, where two empty states in separate channels remain stable in the positively charged state. Similarly, adding extra electrons brings these states closer to the VBM.

For bilayer hBN, the formation of interlayer covalent bonds between the B–N columns at the edges of monovacancies has been observed in *highly* negatively charged defects, with bond lengths ranging from 1.61 to 1.64 Å [105]; nitrogen vacancies do not form interlayer bonds. To compare the likelihood of interlayer covalent bond formation between hBN/SiC and hBN/hBN in the presence of V_B , we present the configuration-coordinate diagram for the heterostructure, AA'-stacked hBN, and 14° rotated bilayer hBN—chosen for its local AA' stacking and as the smallest twist angle that remains computationally feasible—in Figs. 2(h)–2(j). In the symmetric hBN/hBN systems, the reaction pathway reduces to a one-dimensional coordinate. Accordingly, we rigidly displaced the six atoms that form the prospective interlayer bond (three B and three N stacked directly above one another) along their interlayer difference vector, while allowing all other atoms to relax.

The hBN/SiC heterostructure minimizes energy without a barrier through Si–N bond formation in the low-spin state, as previously discussed. Our partial charge calculations reveal that $2.03e$ ($3.773 \times 10^{13} e/\text{cm}^2$) is transferred from SiC to hBN upon chemical bond formation. In contrast, a neutral V_B in hBN/hBN systems does not induce structural changes in the surrounding atoms, with bond formation occurring only as a metastable state at an energy level approximately 1.5 eV higher. Additionally, the total energies of the low-spin and high-spin states remain close (≈ 0.2 eV), with a transition from low spin to high spin occurring as the atoms move closer together to form bonds.

C. Transition metal-doped hBN/SiC

Introducing V_B leaves the hBN sheet electron deficient. The charge imbalance drives the spontaneous formation of interlayer Si–N bonds. This insight prompts a key question: can a *single* TM atom migrate on the same donor–acceptor pathway to anchor to an isolated V_B site rather than agglomerating into clusters? If successful, it would provide a rational route for dispersing catalytic TM centers at the single-atom limit.

Our calculations show that TM atoms placed at V_B act as local electron reservoirs, compensating for the vacancy's electron deficit while reshaping the interlayer bonding network. Depending on the dopant, the system may preserve, weaken, or altogether break the formed Si–N bridges, creating well-defined structural distortions and a rich spectrum of electronic and magnetic states. A detailed understanding of these TM-decorated point defects, both with and without interlayer bonds, is therefore essential.

To quantify the stability of the interlayer covalent bond and the TM anchoring site, we map the potential-energy profile along the structural transformation pathway. To this end, for each TM species, we could fully relax both the bonded and nonbonded hBN/SiC configurations, verifying that the resulting geometries were true local minima separated by barriers that were not crossed during subsequent DFT optimizations. We then constructed configuration-coordinate diagrams by incrementally displacing the atoms along the geometric difference vector between the bonded and nonbonded structures. Although nudged elastic band [106,107] is the standard approach for locating minimum-energy paths, we instead perform constrained one-dimensional energy scans along the quasi-one-dimensional Si–N bond coordinate to enable high-throughput screening across multiple spin states and transition metals, yielding consistent approximate barrier estimates. All relevant spin multiplicities are treated explicitly. As shown in Fig. S5 [81], this high-throughput protocol yields quantitative insight into the TM-binding stability. There are also the partial charges transferred from a single TM atom to the substrates (denoted as q_{TM}^b and $q_{\text{TM}}^{\text{nb}}$ for bonded and nonbonded configurations, respectively) and E_{bind} . Also, two additional energy-related quantities are reported: the energy difference between the bonded and nonbonded systems ($\Delta E^0 = E^b - E^{\text{nb}}$) and the transition-energy barrier ($\Delta E^* = E^{\text{max}} - E^b$). Here, E^b , E^{nb} , and E^{max} denote the total energy of the optimized structure with interlayer chemical bonds formed, the total energy of the optimized structure without the Si–N chemical bonds, and the maximum total energy along the configuration-coordinate diagrams relative to the bonded system, respectively. These quantities provide insights into the bond formation and dissociation processes. A more negative ΔE^0 indicates a more stable bonded structure, while a smaller ΔE^* suggests an easier transition from the bonded to the nonbonded configuration.

Notably, unlike V_B in hBN/SiC, which spontaneously forms chemical bonds, the presence of TMs introduces an energy barrier to interlayer bond formation [see Fig. 3(a)]. Thus, the larger the barrier, the slower the kinetics of structural transition. We found a direct correlation between the number of d electrons and the value of ΔE^* . The energy barrier ranges from 0.15 to 3.76 eV. Among the TMs studied, the largest barriers are found for Au (3.76 eV), Ag (3.75 eV), Pd (2.75 eV), Cu (2.68 eV), and Pt (2.66 eV).

In contrast to ΔE^* , ΔE^0 decreases as the number of d electrons increases [see Fig. 3(b)]. Negative ΔE^0 values show that the bonded configuration is thermodynamically favored for Cu (−0.11 eV), Ag (−1.37 eV), and Au (−0.85 eV). By comparison, Mo, V, and Cr favor the nonbonded configuration, which lies at 3.68, 3.12, and 3.03 eV, respectively.

Two different fabrication routes may control the bonding at TM-doped hBN/SiC interfaces, focused here on Au, Ag, and Cu, but also applicable to other metals: (i) Bonded interface: A V_B -containing hBN monolayer is first deposited onto the SiC substrate, followed by the introduction of TM atoms. This approach maintains interlayer bonding. (ii) Nonbonded interface: TM atoms are first incorporated into the hBN monolayer, which is subsequently placed onto the SiC substrate. This sequence tends to prevent interlayer bonding.

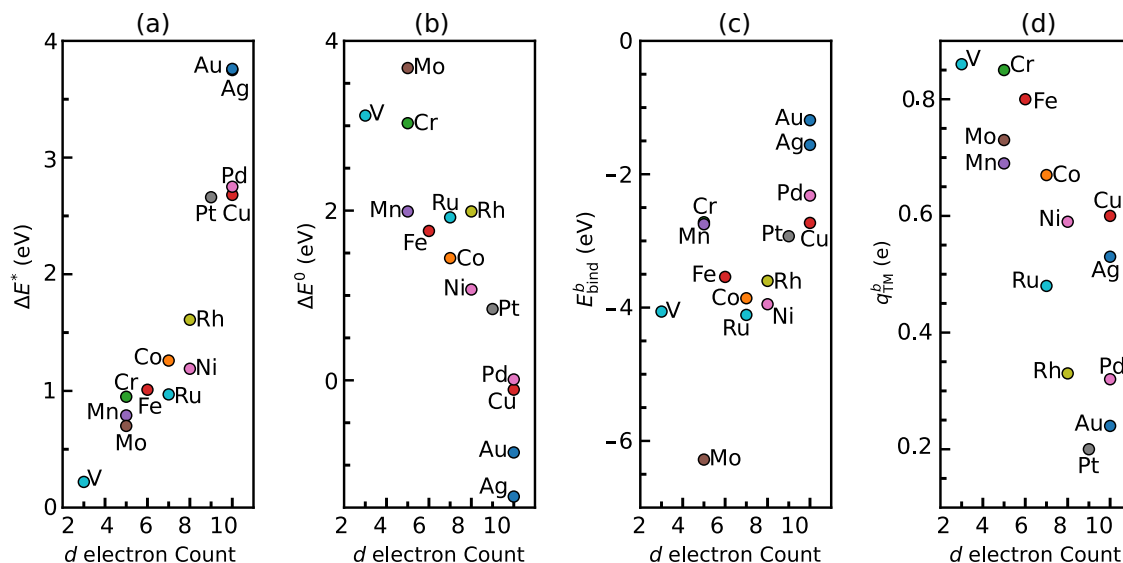


FIG. 3. (a) Activation barrier (ΔE^*) for converting the bonded hBN/SiC configuration to its nonbonded counterpart. (b) Total-energy difference between the bonded and nonbonded minima (ΔE^0). (c) Binding energy of a single-atom transition metal (TM) to the chemically bonded hBN/SiC interface, $E_{\text{bind}}^{\text{b}}$. (d) Net Bader charge transferred from the TM atom to the interface in the bonded configuration, q_{TM}^{b} .

Binding energy is another parameter indicating the strength of metal attachment to the interface and the likelihood of TM rejection. The data can be categorized into three groups: weakly-, moderately-, and strongly bound transition metals [Fig. 3(c)]. For instance, Au and Ag belong to the weakly bound group, suggesting limited orbital overlap with the interface. Comparing the $E_{\text{bind}}^{\text{b}}$ values to those of the hBN monolayer (summarized in Table S4) reveals that TM binding to the V_{B} site is approximately $1.5\text{--}3.5\times$ stronger in the monolayer system compared to bonded hBN/SiC. This difference indicates greater electron sharing between the TMs and the host atoms, resulting in stronger covalent bonding in the hBN monolayer. It is evident that the formation of interlayer chemical bonds partially compensates for the electron deficiency, reducing the need for intense electron donation from the transition metals.

The net Bader charge transferred from the TM atom to the interface (q_{TM}) is a key parameter for assessing electron donation and chemical reactivity at the defect site. Overall, charge transfer decreases as the number of d electrons increases [Fig. 3(d)]. Accordingly, Pt, Au, and Pd atoms, which donate little charge to the bonded hBN/SiC substrate, retain more electrons that can participate in subsequent electrochemical reactions. Our results show that TMs donate $1.4 - 3.6 \times$ more charge to the substrates in both nonbonded hBN/SiC and monolayer hBN compared to bonded hBN/SiC. For example, Pt transfers $0.71 e$ to nonbonded hBN/SiC, $0.70 e$ to monolayer hBN, but only $0.20 e$ to bonded hBN/SiC.

D. Copper isolation and surface decoration

The performance and cost of electrocatalysts are key factors driving the development and deployment of electrochemical devices [108–110]. Maximizing atomic utilization while minimizing precious-metal content requires precise control of atom coordination and spacing to enhance charge transfer, avoid surface passivation, and prevent agglomeration of active

species. However, designing optimal single-atom catalytic platforms remains a major challenge, as isolated metal atoms tend to coalesce into clusters or three-dimensional structures [111–114].

The hBN/SiC substrate offers a versatile platform for anchoring TM atoms to V_B sites, the chemically active traps of which stabilize adatoms via robust, multidirectional bonds. Yet, practical isolation of single atoms remains unresolved. To probe this hurdle, we first model Cu, Pt, and Pd adatoms migrating toward a boron vacancy on hBN/SiC [Fig. 4(a)]. Geometry optimizations keep the SiC lattice fixed while allowing hBN and metal atoms to relax only along the surface normal (z axis); this constraint can slightly shift binding energies compared with full relaxation. Cu, Pt, and Pd are chosen because prior analysis flagged them as the most integration-ready metals.

Our results indicate that copper binds strongly at (-2.73 eV) yet only weakly to pristine hBN ($E_{\text{bind}}^{\text{b}} > -0.4$ eV). Its diffusion on the pristine surface is virtually barrierless, enabling rapid, thermodynamically favorable migration. Consistent with recent work on monolayer hBN [115], we observe that TMs favor N sites over B sites for binding; for Cu, this preference is ≈ 0.22 eV, and for Pd, adsorption is even stronger (-0.95 versus -0.30 eV for Cu). Pt also shows marked site sensitivity, with the N site about 0.65 eV more stable than the hexagon center. Strong vacancy binding, weak affinity for the pristine surface, and lower material cost make Cu our prime candidate for further MLMD simulations.

Figure 4(b) presents a kinetic map of a Cu atom interacting with V_B sites in hBN/SiC at room temperature and dilute concentration (0.012 nm^{-2}). In nearly all simulations, except for one with a cyan trace, Cu atoms placed at various random initial distances from the vacancy integrate with the vacancy within 5 ns. On the pristine surface, Cu exhibits longer lifetimes at N sites during diffusion, consistent with our earlier binding strength results.

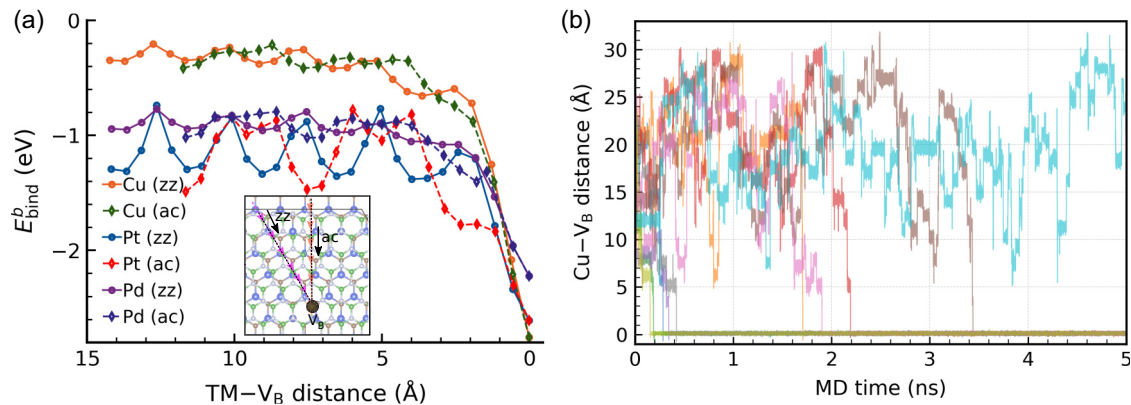


FIG. 4. (a) Binding energies of Cu, Pd, and Pt as a function of their distance from the V_B center along the zigzag (zz) and armchair (ac) directions of the hBN layer. During the geometry optimizations, the SiC substrate is fixed, while atoms in the hBN layer and the transition metal are allowed to relax along the z direction (perpendicular to the surface). (b) Time evolution of the Cu- V_B distance extracted from ten independent MLMD simulations at 300 K. Each trace represents one run, and a separation of zero denotes the Cu atom occupying the vacancy site.

By systematically varying the densities of vacancies and Cu atoms, we identified various scenarios (see Movies S4–S6 as examples): (i) At low density, a single Cu atom rapidly migrates to a V_B vacancy, which acts as a deep potential well that dominates over the flat diffusion landscape of pristine hBN/SiC, enabling single-atom anchoring. (ii) As Cu density increases, the reduced mean-free path between adatoms accelerates aggregation, forming clusters that migrate *en bloc* to vacancies. (iii) Cu atoms sequentially accumulate at a single V_B site, forming a cluster directly at the vacancy. (iv) Cu atoms disperse across multiple V_B sites in varying ratios. Overall, once metals are trapped in vacancies, their migration ceases.

IV. CONCLUSIONS

Using a combination of density-functional theory calculations and machine-learning molecular dynamics, we have mapped the structural, electronic, and (meta)stable defect landscapes of the vdW hBN/SiC heterostructure and shown how selective point-defect chemistry can transform an otherwise mechanically flexible, electronically inert interface into a defect-programmable platform capable of stabilizing isolated metal atoms and enabling substantial electronic tunability.

The creation of a V_B triggers a strong local reconstruction and can generate interlayer covalent bridges (Si–N and C–N), with the bonding motif governed by the local moiré registry. Decorating V_B with a single transition-metal atom systematically reshapes the stability of the bonded versus nonbonded configurations and the available charge reservoir at the defect site. Across the tested d series, the rupture barrier of Si–N bridges generally increases toward the late transition metals, while the thermodynamic preference shifts between bonded and nonbonded geometries depending on metal identity and charge transfer. Focusing on Cu, our results indicate rapid migration on pristine hBN but strong trapping at V_B on the simulated timescales, and reveal a transition from single-atom isolation to vacancy-directed aggregation as the V_B :Cu ratio increases. These insights suggest two practical tuning routes: (i) creating V_B -rich hBN prior to metallization to favor and lock in interlayer bonding, or (ii) predecorating hBN before

interfacing with SiC to suppress interlayer bridge formation while altering the adatom charge state and binding. Taken together, our findings identify the hBN/SiC interface as a mechanically resilient system that can stabilize isolated atoms for catalysis and, with controlled vacancy engineering, support quantum center formation.

To address the stability issue of freestanding monolayer SiC, we use a Si-terminated SiC slab model. More broadly, SiC substrates of various polytypes and orientations provide practical supports for 2D materials [74,75]. The monolayer hBN can, in principle, be physically transferred onto, for example, 4H-SiC(0001) (see Sec. IX, SM). In our preliminary calculations, the hBN/4H-SiC(0001) interface reproduces the key structural and electronic features of the hBN/SiC heterostructure. However, the sample preparation is not straightforward. Experimentally, SiC slab is highly reactive and can undergo adsorption, passivation, and reconstruction; thus, direct hBN–SiC bonding cannot be assumed *a priori*. To minimize parasitic reactions, chemical growth of hBN on a SiC slab can be performed under an inert atmosphere (e.g., in a glovebox), as demonstrated in previous studies [116,117]. However, the large lattice mismatch inevitably introduces interfacial inhomogeneity. Our calculations show that interfacial point defects can locally collapse the vdW gap, promoting nonuniform adhesion and compromising film uniformity. As a practical mitigation strategy, we propose a metal-assisted growth route in which a transition-metal precursor is introduced either cofed with borazine or deposited sequentially [118]. The metal acts as a transient passivating agent for reactive sites, suppresses defect-driven gap collapse, and provides a controlled pathway for intentional single-atom incorporation at the interface.

ACKNOWLEDGMENTS

We acknowledge the CSC–IT Center for Science Ltd. and the Aalto Science–IT project for their generous grants of computer time. A.H., Y.W., and T.A.-N. have been supported by the Academy of Finland through its QTF Center of Excellence program (Project No. 312298). Y.W. and T.A.-N. have also

been supported in part by the Academy of Finland's Grant No. 353298 under the European Union – NextGenerationEU instrument. T.A.-N. further acknowledges support from the Academy of Finland Grant No. 370057.

DATA AVAILABILITY

The data that support the findings of this article are openly available [119], embargo periods may apply.

- [1] A. K. Geim and I. V. Grigorieva, Van der Waals heterostructures, *Nature (London)* **499**, 419 (2013).
- [2] J.-Y. You, B. Gu, G. Su, and Y. P. Feng, Two-dimensional topological superconductivity candidate in a van der Waals layered material, *Phys. Rev. B* **103**, 104503 (2021).
- [3] K. S. Burch, D. Mandrus, and J.-G. Park, Magnetism in two-dimensional van der Waals materials, *Nature (London)* **563**, 47 (2018).
- [4] J. Qi, Z. Wu, W. Wang, K. Bao, L. Wang, J. Wu, C. Ke, Y. Xu, and Q. He, Fabrication and applications of van der Waals heterostructures, *Int. J. Extreme Manuf.* **5**, 022007 (2023).
- [5] A. Castellanos-Gomez, X. Duan, Z. Fei, H. Rodriguez Gutierrez, Y. Huang, X. Huang, J. Quereda, Q. Qian, E. Sutter, and P. Sutter, Van der Waals heterostructures, *Nat. Rev. Methods Primers* **2**, 58 (2022).
- [6] R. Cheng, F. Wang, L. Yin, Z. Wang, Y. Wen, T. A. Shifa, and J. He, High-performance, multifunctional devices based on asymmetric van der Waals heterostructures, *Nat. Electron.* **1**, 356 (2018).
- [7] X. Sun, C. Zhu, J. Yi, L. Xiang, C. Ma, H. Liu, B. Zheng, Y. Liu, W. You, W. Zhang, *et al.*, Reconfigurable logic-in-memory architectures based on a two-dimensional van der Waals heterostructure device, *Nat. Electron.* **5**, 752 (2022).
- [8] Y. Liu, N. O. Weiss, X. Duan, H.-C. Cheng, Y. Huang, and X. Duan, Van der Waals heterostructures and devices, *Nat. Rev. Mater.* **1**, 16042 (2016).
- [9] N. Mounet, M. Gibertini, P. Schwaller, D. Campi, A. Merkys, A. Marrazzo, T. Sohier, I. E. Castelli, A. Cepellotti, G. Pizzi, *et al.*, Two-dimensional materials from high-throughput computational exfoliation of experimentally known compounds, *Nat. Nanotechnol.* **13**, 246 (2018).
- [10] H. Yang, S. O. Valenzuela, M. Chshiev, S. Couet, B. Dieny, B. Dlubak, A. Fert, K. Garello, M. Jamet, D.-E. Jeong, *et al.*, Two-dimensional materials prospects for non-volatile spintronic memories, *Nature (London)* **606**, 663 (2022).
- [11] Y. Liu, X. Duan, H.-J. Shin, S. Park, Y. Huang, and X. Duan, Promises and prospects of two-dimensional transistors, *Nature (London)* **591**, 43 (2021).
- [12] M. S. Hybertsen, Role of interface strain in a lattice-matched heterostructure, *Phys. Rev. Lett.* **64**, 555 (1990).
- [13] Y. Lu, J. Chen, M. J. Coupin, S. Sinha, and J. H. Warner, Lattice-mismatch-driven small-angle moiré twists in epitaxially grown 2D vertical layered heterostructures, *Adv. Mater.* **34**, 2205403 (2022).
- [14] W. Li, T. Brumme, and T. Heine, Relaxation effects in transition metal dichalcogenide bilayer heterostructures, *npj 2D Mater. Appl.* **8**, 43 (2024).
- [15] H. Wang, Z. Li, D. Li, P. Chen, L. Pi, X. Zhou, and T. Zhai, Van der Waals integration based on two-dimensional materials for high-performance infrared photodetectors, *Adv. Funct. Mater.* **31**, 2103106 (2021).
- [16] B. V. Lotsch, Vertical 2D heterostructures, *Annu. Rev. Mater. Res.* **45**, 85 (2015).
- [17] D. N. Futaba, Hexagonal boron nitride heterostructures go large, *Nat. Electron.* **6**, 104 (2023).
- [18] Y. Kubota, K. Watanabe, O. Tsuda, and T. Taniguchi, Deep ultraviolet light-emitting hexagonal boron nitride synthesized at atmospheric pressure, *Science* **317**, 932 (2007).
- [19] C. Wang, J. Guo, L. Dong, A. Aiyiti, X. Xu, and B. Li, Superior thermal conductivity in suspended bilayer hexagonal boron nitride, *Sci. Rep.* **6**, 25334 (2016).
- [20] H. Xu, B. Ding, Y. Xu, Z. Huang, D. Wei, S. Chen, T. Lan, Y. Pan, H.-M. Cheng, and B. Liu, Magnetically tunable and stable deep-ultraviolet birefringent optics using two-dimensional hexagonal boron nitride, *Nat. Nanotechnol.* **17**, 1091 (2022).
- [21] N. Ding, X. Chen, and C.-M. L. Wu, Mechanical properties and failure behaviors of the interface of hybrid graphene/hexagonal boron nitride sheets, *Sci. Rep.* **6**, 31499 (2016).
- [22] S. Moon, J. Kim, J. Park, S. Im, J. Kim, I. Hwang, and J. K. Kim, Hexagonal boron nitride for next-generation photonics and electronics, *Adv. Mater.* **35**, 2204161 (2023).
- [23] M. Li, G. Huang, X. Chen, J. Yin, P. Zhang, Y. Yao, J. Shen, Y. Wu, and J. Huang, Perspectives on environmental applications of hexagonal boron nitride nanomaterials, *Nano Today* **44**, 101486 (2022).
- [24] Y. Gong, Z.-Q. Xu, D. Li, J. Zhang, I. Aharonovich, and Y. Zhang, Two-dimensional hexagonal boron nitride for building next-generation energy-efficient devices, *ACS Energy Lett.* **6**, 985 (2021).
- [25] M. Zahoor, S. Khan, P. M. Ismail, L. Qiao, M. Haneef, J. Akbar, M. Bououdina, C. Zeng, and S. Ali, in *Hexagonal Boron Nitride*, Micro and Nano Technologies, edited by K. Deshmukh, M. Pandey, and C. Mustansar Hussain (Elsevier, Amsterdam, Netherlands, 2024), pp. 3–28.
- [26] Z. Balta and E. B. Simsek, in *Hexagonal Boron Nitride*, Micro and Nano Technologies, edited by K. Deshmukh, M. Pandey, and C. Mustansar Hussain (Elsevier, Amsterdam, Netherlands, 2024), pp. 205–233.
- [27] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, *et al.*, Boron nitride substrates for high-quality graphene electronics, *Nat. Nanotechnol.* **5**, 722 (2010).
- [28] M. Yankowitz, Q. Ma, P. Jarillo-Herrero, and B. J. LeRoy, van der Waals heterostructures combining graphene and hexagonal boron nitride, *Nat. Rev. Phys.* **1**, 112 (2019).
- [29] I. G. Juma, G. Kim, D. Jariwala, and S. K. Behura, Direct growth of hexagonal boron nitride on non-metallic substrates and its heterostructures with graphene, *iScience* **24**, 103374 (2021).
- [30] S. Ogawa, S. Fukushima, and M. Shimatani, Hexagonal-boron nitride/graphene van der Waals heterostructure-based wavelength-selective infrared absorbers using plasmonic metasurfaces for multi-spectral infrared photodetectors, *J. Opt. Soc. Am. B* **39**, 3149 (2022).

- [31] Z. Wang, Y. B. Wang, J. Yin, E. Tóvári, Y. Yang, L. Lin, M. Holwill, J. Birkbeck, D. J. Perello, S. Xu, J. Zultak, R. V. Gorbachev, A. V. Kretinin, T. Taniguchi, K. Watanabe, S. V. Morozov, M. Andelković, S. P. Milovanović, L. Covaci, F. M. Peeters, *et al.*, Composite super-moiré lattices in double-aligned graphene heterostructures, *Sci. Adv.* **5**, eaay8897 (2019).
- [32] S. Moore, C. Ciccarino, D. Halbertal, L. McGilly, N. Finney, K. Yao, Y. Shao, G. Ni, A. Sternbach, E. Telford, *et al.*, Nanoscale lattice dynamics in hexagonal boron nitride moiré superlattices, *Nat. Commun.* **12**, 5741 (2021).
- [33] R. V. Kamat, A. L. Sharpe, M. Pendharkar, J. Hu, S. J. Tran, G. Zaborski, M. Hocking, J. Finney, K. Watanabe, T. Taniguchi, M. A. Kastner, A. J. Mannix, T. Heinz, and D. Goldhaber-Gordon, Deterministic fabrication of graphene hexagonal boron nitride moiré superlattices, *Proc. Natl. Acad. Sci. USA* **121**, e2410993121 (2024).
- [34] E. M. O'Sullivan, N. Grobert, and M. Swart, Density functional theory investigation of 2D phase separated graphene/hexagonal boron nitride monolayers; band gap, band edge positions, and photo activity, *J. Phys. Chem. C* **129**, 638 (2025).
- [35] P. Huang, E. Riccardi, S. Messelot, H. Graef, F. Valmorra, J. Tignon, T. Taniguchi, K. Watanabe, S. Dhillon, B. Placais, *et al.*, Ultra-long carrier lifetime in neutral graphene-hBN van der Waals heterostructures under mid-infrared illumination, *Nat. Commun.* **11**, 863 (2020).
- [36] K. Zollner, A. W. Cummings, S. Roche, and J. Fabian, Graphene on two-dimensional hexagonal BN, AlN, and GaN: Electronic, spin-orbit, and spin relaxation properties, *Phys. Rev. B* **103**, 075129 (2021).
- [37] J. Li, M. Ghorbani-Asl, K. Lasek, V. Pathirage, A. V. Krashenninnikov, and M. Batzill, A van der Waals heterostructure with an electronically textured moiré pattern: PtSe₂/PtTe₂, *ACS Nano* **17**, 5913 (2023).
- [38] M. K. Jat, P. Tiwari, R. Bajaj, I. Shitut, S. Mandal, K. Watanabe, T. Taniguchi, H. Krishnamurthy, M. Jain, and A. Bid, Higher order gaps in the renormalized band structure of doubly aligned hBN/bilayer graphene moiré superlattice, *Nat. Commun.* **15**, 2335 (2024).
- [39] Y. Ma, M. Huang, X. Zhang, W. Hu, Z. Zhou, K. Feng, W. Li, Y. Chen, C. Lou, W. Zhang, *et al.*, Magnetic bloch states at integer flux quanta induced by super-moiré potential in graphene aligned with twisted boron nitride, *Nat. Commun.* **16**, 1860 (2025).
- [40] Z. Lu, T. Han, Y. Yao, Z. Hadjri, J. Yang, J. Seo, L. Shi, S. Ye, K. Watanabe, T. Taniguchi, *et al.*, Extended quantum anomalous Hall states in graphene/hBN moiré superlattices, *Nature (London)* **637**, 1090 (2025).
- [41] J. Hafner, C. Wolverton, and G. Ceder, Toward computational materials design: The impact of density functional theory on materials research, *MRS Bull.* **31**, 659 (2006).
- [42] R. Dingreville, R. A. Karnesky, G. Puel, and J.-H. Schmitt, Review of the synergies between computational modeling and experimental characterization of materials across length scales, *J. Mater. Sci.* **51**, 1178 (2016).
- [43] Q. Li, L. Xu, K.-W. Luo, X.-F. Li, W.-Q. Huang, L.-L. Wang, and Y.-B. Yu, Electric-field-induced widely tunable direct and indirect band gaps in hBN/MoS₂ van der Waals heterostructures, *J. Mater. Chem. C* **5**, 4426 (2017).
- [44] C.-M. Liu, S.-Y. Hsu, H.-S. Chen, C.-C. Hsu, Y.-W. Lan, H.-C. Chiu, and W.-C. Lin, Enhanced stability of Gr, h-BN and Gr/h-BN protected MoS₂ flakes under laser illumination, *Appl. Surf. Sci. Adv.* **25**, 100687 (2025).
- [45] J.-X. Duan, C.-B. Wang, Y. Tian, and L.-L. Zhang, Augmenting anisotropic gas sensitivity in Borophene/hBN van der Waals heterostructures via transition metal doping for advanced sensing applications, *Mater. Sci. Eng., B* **317**, 118129 (2025).
- [46] X. Zhao, Z. Cui, A. Ge, X. Lu, X. Guan, J. Zhang, H. Zhen, L. Sun, S. Wang, and W. Lu, Exciton-polaritons of hBN/WS₂ heterostructure in cavity observed at room temperature, *Appl. Phys. Lett.* **121**, 231106 (2022).
- [47] Y. Li, P. Jiang, X. Liu, H. Wu, X. Lyu, X. Li, H. Lin, J. Tang, Q. Lyu, H. Yang, C. Wu, G. Lu, P.-H. Tan, L.-Y. Peng, Y. Gao, X. Hu, and Q. Gong, Defect-assisted photoemission in the hBN and TMDs/hBN heterostructures, *J. Phys. Chem. C* **128**, 4286 (2024).
- [48] M. Le Ster, T. Maerkl, P. J. Kowalczyk, and S. A. Brown, Moiré patterns in van der Waals heterostructures, *Phys. Rev. B* **99**, 075422 (2019).
- [49] T. Rakib, P. Pochet, E. Ertekin, and H. T. Johnson, Moiré engineering in van der Waals heterostructures, *J. Appl. Phys.* **132**, 120901 (2022).
- [50] X. Wang, G. Zhao, X. Lv, M. Zhao, W. Wei, and G. Liu, Effect of doping and defects on the electronic properties of MoS₂/WSe₂ bilayer heterostructure: A first-principles study, *Phys. Chem. Chem. Phys.* **26**, 18402 (2024).
- [51] N. Alem, R. Erni, C. Kisielowski, M. D. Rossell, W. Gannett, and A. Zettl, Atomically thin hexagonal boron nitride probed by ultrahigh-resolution transmission electron microscopy, *Phys. Rev. B* **80**, 155425 (2009).
- [52] A. L. Gibb, N. Alem, J.-H. Chen, K. J. Erickson, J. Ciston, A. Gautam, M. Linck, and A. Zettl, Atomic resolution imaging of grain boundary defects in monolayer chemical vapor deposition-grown hexagonal boron nitride, *J. Am. Chem. Soc.* **135**, 6758 (2013).
- [53] N. Alem, Q. M. Ramasse, C. R. Seabourne, O. V. Yazyev, K. Erickson, M. C. Sarahan, C. Kisielowski, A. J. Scott, S. G. Louie, and A. Zettl, Subangstrom edge relaxations probed by electron microscopy in hexagonal boron nitride, *Phys. Rev. Lett.* **109**, 205502 (2012).
- [54] J. He, N. Jiao, C. Zhang, H. Xiao, X. Chen, and L. Sun, Spin switch of the transition-metal-doped boron nitride sheet through H/F chemical decoration, *J. Phys. Chem. C* **118**, 8899 (2014).
- [55] J. Zhang, R. Sun, D. Ruan, M. Zhang, Y. Li, K. Zhang, F. Cheng, Z. Wang, and Z.-M. Wang, Point defects in two-dimensional hexagonal boron nitride: A perspective, *J. Appl. Phys.* **128**, 100902 (2020).
- [56] C. Cholsuk, A. Zand, A. Çakan, and T. Vogl, The hBN defects database: A theoretical compilation of color centers in hexagonal boron nitride, *J. Phys. Chem. C* **128**, 12716 (2024).
- [57] L. Zeng, S. Zhang, J. Meng, J. Chen, J. Jiang, Y. Shi, J. Huang, Z. Yin, J. Wu, and X. Zhang, Single-photon emission from point defects in hexagonal boron nitride induced by plasma treatment, *ACS Appl. Mater. Interfaces* **16**, 24899 (2024).
- [58] T. J. Smart, K. Li, J. Xu, and Y. Ping, Intersystem crossing and exciton-defect coupling of spin defects in hexagonal boron nitride, *npj Comput. Mater.* **7**, 59 (2021).

- [59] H. Chen, Y. Kang, D. Pu, M. Tian, N. Wan, Y. Xu, B. Yu, W. Jie, and Y. Zhao, Introduction of defects in hexagonal boron nitride for vacancy-based 2D memristors, *Nanoscale* **15**, 4309 (2023).
- [60] R. Babar, G. Barcza, A. Pershin, H. Park, O. Bulancea Lindvall, G. Thiering, Ö. Legeza, J. H. Warner, I. A. Abrikosov, A. Gali, *et al.*, Low-symmetry vacancy-related spin qubit in hexagonal boron nitride, *npj Comput. Mater.* **10**, 184 (2024).
- [61] S. Yu, L. Li, Z. Lai, J. Hao, and K. Zhang, A coupling effects of vacancy and Al (Ga, In) dopant on electronic structures of hexagonal boron nitride monolayer, *Mater. Res. Express* **4**, 116302 (2017).
- [62] X. Lian, X. Tang, H. Liao, W. Guo, Y. Zhang, and G. Gao, Theoretical screening of double-atom metals anchored on defective boron nitride for N₂ reduction, *React. Kinet. Mech. Catal.* **137**, 3241 (2024).
- [63] S.-Y. Zhong, S.-Y. Wu, X.-Y. Yu, G.-Q. Shen, L. Yan, and K.-L. Xu, First-principles studies of the adsorption and catalytic properties for gas molecules on h-BN monolayer doped with various transition metal atoms, *Catal. Surv. Asia* **26**, 69 (2022).
- [64] J. Wu, L. Yin, and L. Zhang, Tuning the electronic structure, bandgap energy and photoluminescence properties of hexagonal boron nitride nanosheets via a controllable Ce³⁺ ions doping, *RSC Adv.* **3**, 7408 (2013).
- [65] L. Khalil, C. Ernandes, J. Avila, A. Rousseau, P. Dudin, N. D. Zhigadlo, G. Cassabo, B. Gil, F. Oehler, J. Chaste, and A. Ouerghi, High p doped and robust band structure in Mg-doped hexagonal boron nitride, *Nanoscale Adv.* **5**, 3225 (2023).
- [66] R. Kozubek, P. Ernst, C. Herbig, T. Michely, and M. Schleberger, Fabrication of defective single layers of hexagonal boron nitride on various supports for potential applications in catalysis and DNA sequencing, *ACS Appl. Nano Mater.* **1**, 3765 (2018).
- [67] Y. Lu, B. Li, N. Xu, Z. Zhou, Y. Xiao, Y. Jiang, T. Li, S. Hu, Y. Gong, and Y. Cao, One-atom-thick hexagonal boron nitride co-catalyst for enhanced oxygen evolution reactions, *Nat. Commun.* **14**, 6965 (2023).
- [68] A. Gottscholl, M. Diez, V. Soltamov, C. Kasper, D. Krauß, A. Sperlich, M. Kianinia, C. Bradac, I. Aharonovich, and V. Dyakonov, Spin defects in hBN as promising temperature, pressure and magnetic field quantum sensors, *Nat. Commun.* **12**, 4480 (2021).
- [69] H.-H. Fang, X.-J. Wang, X. Marie, and H.-B. Sun, Quantum sensing with optically accessible spin defects in van der Waals layered materials, *Light Sci. Appl.* **13**, 303 (2024).
- [70] M. Fischer, J. M. Caridad, A. Sajid, S. Ghaderzadeh, M. Ghorbani-Asl, L. Gammelgaard, P. Bøggild, K. S. Thygesen, A. V. Krashennnikov, S. Xiao, *et al.*, Controlled generation of luminescent centers in hexagonal boron nitride by irradiation engineering, *Sci. Adv.* **7**, eabe7138 (2021).
- [71] S. J. White, T. Yang, N. Dontschuk, C. Li, Z.-Q. Xu, M. Kianinia, A. Stacey, M. Toth, and I. Aharonovich, Electroluminescence from pure resonant states in hBN-based vertical tunneling junctions, *Light Sci. Appl.* **11**, 186 (2022).
- [72] C. M. Polley, H. Fedderwitz, T. Balasubramanian, A. A. Zakharov, R. Yakimova, O. Bäcke, J. Ekman, S. P. Dash, S. Kubatkin, and S. Lara-Avila, Bottom-up growth of monolayer honeycomb SiC, *Phys. Rev. Lett.* **130**, 076203 (2023).
- [73] Y. Da, R. Luo, B. Lei, W. Ji, and W. Zhou, Controlled fabrication of freestanding monolayer SiC by electron irradiation, *Chin. Phys. B* **33**, 086802 (2024).
- [74] E. Mokhov, V. Y. Davydov, A. Smirnov, and S. Nagaluk, Growth of hexagonal boron nitride (hBN) on silicon carbide substrates by the physical vapor transport method, *Semiconductors* **57**, 483 (2023).
- [75] J. Zhao, P. Ji, Y. Li, R. Li, K. Zhang, H. Tian, K. Yu, B. Bian, L. Hao, X. Xiao, *et al.*, Ultrahigh-mobility semiconducting epitaxial graphene on silicon carbide, *Nature (London)* **625**, 60 (2024).
- [76] G. Kresse and J. Hafner, *Ab initio* molecular dynamics for liquid metals, *Phys. Rev. B* **47**, 558 (1993).
- [77] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* **50**, 17953 (1994).
- [78] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [79] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, *J. Chem. Phys.* **118**, 8207 (2003).
- [80] J. Heyd and G. E. Scuseria, Efficient hybrid density functional calculations in solids: Assessment of the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid functional, *J. Chem. Phys.* **121**, 1187 (2004).
- [81] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/lymz-nlbf> for validation of the vdW methods; machine-learning datasets; fundamental properties of hBN, SiC, and the hBN/SiC interface; molecular-dynamics trajectory analyses; transition-metal adsorption energy profiles; the influence of bulk SiC(0001) on defective hBN/SiC interfaces; and supplemental movies, which also includes Refs. [72,76,83–85,120,121].
- [82] S. Grimme, S. Ehrlich, and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.* **32**, 1456 (2011).
- [83] R. S. Pease, An X-ray study of boron nitride, *Acta Crystallogr.* **5**, 356 (1952).
- [84] W. Paszkowicz, J. Pelka, M. Knapp, T. Szyszko, and S. Podsiadlo, Lattice parameters and anisotropic thermal expansion of hexagonal boron nitride in the 10–297.5 K temperature range, *Appl. Phys. A* **75**, 431 (2002).
- [85] V. Korsaks, Hexagonal boron nitride luminescence dependent on vacuum level and surrounding gases, *Mater. Res. Bull.* **70**, 976 (2015).
- [86] S. Chahal, T. K. Sahu, S. Kar, S. J. Ray, V. Biju, and P. Kumar, Transition metal-doped boron nitride atomic sheets with an engineered bandgap and magnetization, *J. Phys. Chem. C* **126**, 21084 (2022).
- [87] K. Zhang, Y. Feng, F. Wang, Z. Yang, and J. Wang, Two dimensional hexagonal boron nitride (2D-hBN): Synthesis, properties and applications, *J. Mater. Chem. C* **5**, 11992 (2017).
- [88] D. Chimene, D. L. Alge, and A. K. Gaharwar, Two-dimensional nanomaterials for biomedical applications: Emerging trends and future prospects, *Adv. Mater.* **27**, 7261 (2015).

- [89] A. Togo and I. Tanaka, First principles phonon calculations in materials science, *Scr. Mater.* **108**, 1 (2015).
- [90] Z. Fan, W. Chen, V. Vierimaa, and A. Harju, Efficient molecular dynamics simulations with many-body potentials on graphics processing units, *Comput. Phys. Commun.* **218**, 10 (2017).
- [91] P. Ying and Z. Fan, Combining the D3 dispersion correction with the neuroevolution machine-learned potential, *J. Phys.: Condens. Matter* **36**, 125901 (2024).
- [92] F. Mouhat and F. -X. Coudert, Necessary and sufficient elastic stability conditions in various crystal systems, *Phys. Rev. B* **90**, 224104 (2014).
- [93] W. Tang, E. Sanville, and G. Henkelman, A grid-based Bader analysis algorithm without lattice bias, *J. Phys.: Condens. Matter* **21**, 084204 (2009).
- [94] T. A. Manz, Seven confluence principles: A case study of standardized statistical analysis for 26 methods that assign net atomic charges in molecules, *RSC Adv.* **10**, 44121 (2020).
- [95] S. Mahmoudi, T. Gruene, C. Schröder, K. D. Ferjaoui, E. Fröjd, A. Mozzanica, K. Takaba, A. Volkov, J. Maisriml, V. Paunović, *et al.*, Experimental determination of partial charges with electron diffraction, *Nature (London)* **645**, 88 (2025).
- [96] Y.-C. Lin, A. Motoyama, S. Kretschmer, S. Ghaderzadeh, M. Ghorbani-Asl, Y. Araki, A. V. Krashennnikov, H. Ago, and K. Suenaga, Polymorphic phases of metal chlorides in the confined 2D space of bilayer graphene, *Adv. Mater.* **33**, 2105898 (2021).
- [97] S. Back and S. Siahrostami, Noble metal supported hexagonal boron nitride for the oxygen reduction reaction: A DFT study, *Nanoscale Adv.* **1**, 132 (2019).
- [98] I. S. S. de Oliveira and R. H. Miwa, Organic molecules deposited on graphene: A computational investigation of self-assembly and electronic structure, *J. Chem. Phys.* **142**, 044301 (2015).
- [99] I. V. Vlassiuk, Y.-C. Wu, A. Puretzky, L. Liang, J. Lasseter, B. Dryzhakov, I. Gallagher, S. Ghosh, N. Lavrik, O. Dyck, A. R. Lupini, M. Checa, L. Collins, H. M. Meyer III, H. Zhao, F. Likhi, K. Xiao, I. Ivanov, D. Glasgow, A. Tselev, *et al.*, Defect engineering in large-scale CVD-grown hexagonal boron nitride: Formation, spectroscopy, and spin relaxation dynamics, *Small* **22**, e06874 (2026).
- [100] M. Längle, B. M. Mayer, J. Madsen, D. Propst, A. Bo, C. Kofler, V. Hana, C. Mangler, T. Susi, and J. Kotakoski, Defect-engineering hexagonal boron nitride using low-energy Ar⁺ irradiation, [arXiv:2404.07166](https://arxiv.org/abs/2404.07166).
- [101] G. m. H. Thiering and A. Gali, Characterization of oxygen defects in diamond by means of density functional theory calculations, *Phys. Rev. B* **94**, 125202 (2016).
- [102] H. I. Rasool, C. Ophus, and A. Zettl, Atomic defects in two dimensional materials, *Adv. Mater.* **27**, 5771 (2015).
- [103] C. Linderälv, W. Wieczorek, and P. Erhart, Vibrational signatures for the identification of single-photon emitters in hexagonal boron nitride, *Phys. Rev. B* **103**, 115421 (2021).
- [104] L. Weston, D. Wickramaratne, M. Mackoīt, A. Alkauskas, and C. G. Van de Walle, Native point defects and impurities in hexagonal boron nitride, *Phys. Rev. B* **97**, 214104 (2018).
- [105] N. Alem, O. V. Yazyev, C. Kisielowski, P. Denes, U. Dahmen, P. Hartel, M. Haider, M. Bischoff, B. Jiang, S. G. Louie, and A. Zettl, Probing the out-of-plane distortion of single point defects in atomically thin hexagonal boron nitride at the picometer scale, *Phys. Rev. Lett.* **106**, 126102 (2011).
- [106] H. Jónsson, G. Mills, and K. W. Jacobsen, *Classical and Quantum Dynamics in Condensed Phase Simulations* (World Scientific, Singapore, 1998), pp. 385–404.
- [107] G. Mills, H. Jónsson, and G. K. Schenter, Reversible work transition state theory: Application to dissociative adsorption of hydrogen, *Surf. Sci.* **324**, 305 (1995).
- [108] Y. Zhou, Y. Jiang, Y. Ji, R. Lang, Y. Fang, and C.-D. Wu, The opportunities and challenges in single-atom catalysis, *ChemCatChem* **15**, e202201176 (2023).
- [109] D. Liu, X. Wan, T. Kong, W. Han, and Y. Xiong, Single-atom-based catalysts for photoelectrocatalysis: Challenges and opportunities, *J. Mater. Chem. A* **10**, 5878 (2022).
- [110] S. Weon, D. Huang, K. Rigby, C. Chu, X. Wu, and J.-H. Kim, Environmental materials beyond and below the nanoscale: Single-atom catalysts, *ACS ES&T Eng.* **1**, 157 (2021).
- [111] J. Wu, H. Shi, K. Li, and X. Guo, Advances and challenges of single-atom catalysts in environmental catalysis, *Curr. Opin. Chem. Eng.* **40**, 100923 (2023).
- [112] J. Dong, L. Gao, and Q. Fu, Hexagonal boron nitride meeting metal: A new opportunity and territory in heterogeneous catalysis, *J. Phys. Chem. Lett.* **12**, 9608 (2021).
- [113] H. Jeong, S. Shin, and H. Lee, Heterogeneous atomic catalysts overcoming the limitations of single-atom catalysts, *ACS Nano* **14**, 14355 (2020).
- [114] J. Li, C. Chen, L. Xu, Y. Zhang, W. Wei, E. Zhao, Y. Wu, and C. Chen, Challenges and perspectives of single-atom-based catalysts for electrochemical reactions, *JACS Au* **3**, 736 (2023).
- [115] Y. Zhang, C. Qin, L. Zhu, Y. Wang, and J. Cao, Adsorption of NO₂, NO, NH₃, and CO on noble metal (Rh, Pd, Ag, Ir, Pt, Au)-modified hexagonal boron nitride monolayers: A first-principles study, *Langmuir* **40**, 1058 (2024).
- [116] Y.-R. Lin, M. Franke, S. Parhizkar, M. Rath, V. Wen-zhe Yu, T.-L. Lee, S. Soubatch, V. Blum, F. Stefan Tautz, C. Kumpf, and F. C. Bocquet, Boron nitride on SiC(0001), *Phys. Rev. Mater.* **6**, 064002 (2022).
- [117] A. Biswas, R. Xu, G. A. Alvarez, J. Zhang, J. Christiansen-Salameh, A. B. Puthirath, K. Burns, J. A. Hachtel, T. Li, S. A. Iyengar, T. Gray, C. Li, X. Zhang, H. Kannan, J. Elkins, T. S. Pieshkov, R. Vajtai, A. G. Birdwell, M. R. Neupane, E. J. Garratt, *et al.*, Non-linear optics at twist interfaces in h-BN/SiC heterostructures, *Adv. Mater.* **35**, 2304624 (2023).
- [118] S. Lu, P. Shen, H. Zhang, G. Liu, B. Guo, Y. Cai, H. Chen, F. Xu, T. Zheng, F. Xu, *et al.*, Towards *n*-type conductivity in hexagonal boron nitride, *Nat. Commun.* **13**, 3109 (2022).
- [119] A. Hashemi, Stabilisation of hBn/SiC heterostructures with vacancies and transition-metal atoms (v.1), Zenodo (2025), doi: 10.5281/zenodo.17102508.
- [120] C. Freysoldt and J. Neugebauer, First-principles calculations for charged defects at surfaces, interfaces, and two-dimensional materials in the presence of electric fields, *Phys. Rev. B* **97**, 205425 (2018).
- [121] R. Nelson, C. Ertural, J. George, V. L. Deringer, G. Hautier, and R. Drnaskowski, LOBSTER: Local orbital projections, atomic charges, and chemical-bonding analysis from projector-augmented-wave-based density-functional theory, *J. Comput. Chem.* **41**, 1931 (2020).