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Ab initio simulations are used to show that graphene vacancy sites may offer a means of templated growth of metalloid aluminum clusters from their monohalide precursors. We present density functional theory and ab initio molecular dynamics simulations of the aluminum halide AlCl interacting with a graphene surface. Unlike a bare Al adatom, AlCl physisorbs weakly on vacancy-free graphene with little charge transfer and no hybridization with carbon orbitals. The barrier for diffusion of AlCl along the surface is negligible. Covalent bonding is seen only with vacancies and results in strong chemisorption and considerable distortion of the nearby lattice. Car-Parrinello molecular dynamics simulations of AlCl liquid around a graphene single vacancy show spontaneous metalloid cluster growth via a process of repeated insertion reactions. This suggests a means of templated cluster nucleation and growth on a carbon substrate and provides some confirmation for the role of a trivalent aluminum species in nucleating a ligated metalloid cluster from AlCl and AlBr solutions. © 2016 AIP Publishing LLC. [http://dx.org/10.1063/1.4939594]

I. INTRODUCTION

In addition to its own unique electronic properties,1-5 graphene (GR) has also been considered as a template for small clusters or adsorbates with new functionality. Graphene may offer a high degree of control over the arrangement and separation of nanoclusters, allowing templated growth of systems with specific cluster topologies and electronic structures.6-15 The electronic interactions between graphene and the guest material play a central role in the early growth process.16,17 A Monte Carlo study conducted by Guo et al.12 on ZnO nanoparticle growth on graphene showed that the deformation of Zn clusters and layering on the graphene provides suitable nucleation sites governed mainly by Zn-carbon bond formation. Another study by Zhou et al. found the metal-carbon (M-C) bond strength was a suitable metric for understanding the early cluster formation process.13 A strong bond between carbon and a guest metal typically requires at least one C to change hybridization from sp2 to sp3.18 Structural defects in functionalized graphene arising from the synthesis process can ease this rehybridization and provide natural sites for strong adsorption. Considerable theoretical and experimental efforts have been devoted to understanding the properties of these characteristic defects in graphene.19-25

Here we consider the use of graphene as a template for growing small metalloid aluminum clusters. The pioneering work of Schnöckel and co-workers has led to the development of many striking group 13 metalloid systems,29-35 including the large Al7[SiMe3]292-, Al59Cp2-, and Si@Al59[Si(2,6-iPr2C6H3)SiMe3]12. Metalloid clusters are often conceptualized as metastable intermediates on the way to formation of a bulk metal, and have been considered for use in fast-burning fuels and catalysis.26-28,36,37 In addition to organometallic bonds, these clusters contain many metal-metal bonds in which the Al is in a low formal oxidation state. Synthesis relies on AIX (X = Cl, Br, or I) monovalent aluminum halide precursors formed in a specialized cocondensation apparatus. The AIX solutions, combined with donor-containing solvents, will begin to disproportionate into bulk aluminum and trivalent species (3 AIX → 2 Al(0) + AlX3) upon heating. If bulkier ligands such as Cp* are substituted for the halogen species, the system can become trapped in a kinetic barrier during the disproportionation process, resulting in a metalloid cluster. Little is known about the growth process and the kinetic barrier that traps these clusters in a metastable state, but the growth process is believed to begin at small trivalent impurities (AlCl3, AlBr3) present in the AIX solution.29 Growth towards larger metalloid clusters then proceeds via repeated insertion of AIX into Al-X bonds as well as elimination of AlX3 species. The resulting metalloid clusters are quite distinct from their homogeneous metal cluster counterparts, with ligand effects playing a strong role in altering the symmetry of the metal core.

Here, we use first-principles calculations to study the use of graphene as a template for growth of metalloid clusters from a monohalide AlCl solution. The monohalide lacks the bulky ligands required to kinetically trap large clusters but is expected to exhibit similar behavior during the early stages of cluster formation. We show that monovalent AlCl chemisorbs on graphene with simple structural defects such as a single vacancy (SV) and di-vacancy (DV) with binding energies greater than 3 eV. This results in a surface trivalent Al with strong Al/C bonds that can serve as a nucleus for insertion of additional AlCl monomers from solution. AlCl interacts very weakly with a perfect graphene sheet, and is largely free to diffuse across the surface.

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Car-Parinello molecular dynamics (MD) simulations of liquid AlCl interacting with a single-vacancy site show spontaneous metalloid cluster formation starting from an adsorbed AlCl moiety. Corresponding simulations of liquid AlCl with defect-free graphene show merely free diffusion across the surface. This may provide a means of controlled nucleation and growth of well-dispersed metalloid clusters with unique properties beginning with their precursor monovalent halide liquids.

II. COMPUTATIONAL METHODOLOGY

MD calculations were performed using a Car-Parrinello method as implemented in the CPMD code. Electronic exchange and correlation effects were treated with the Perdew-Burke-Ernzerhof (PBE) functional. Interactions between the nuclei and electrons were described with Vanderbilt ultrasoft pseudopotentials and a plane wave basis set with a cut-off energy of 25 Ry. Simulations were performed in the microcanonical (NVE) ensemble for equilibration for at least 3 ps and followed by canonical (NVT) ensemble runs with Nose-Hoover thermostats and a thermostat frequency of 2600 cm$^{-1}$. A total simulation time of 8 ps at a temperature of 1000 K beyond equilibration was sufficient to observe cluster nucleation from the AlCl liquid. A fictitious mass of 400 amu was used, allowing a time step of 4 a.u. (0.097 fs) for the integration of equations of motion. Periodic boundary conditions were used in the Poisson solver for all calculations with a 12 Å vacuum above the liquid-graphene interface.

All static DFT calculations were performed using the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA), again using the PBE functional. Interactions between the nuclei and electrons were described with norm-conserving Troullier-Martins pseudopotentials. A cut-off energy of 210 Ry was used for the expansion of the band states. K-point sampling of the Brillouin zone was defined using a k-grid cut-off radius scheme of 16 Å (equivalent to 4 k-points in our 64 atom supercell). A double-$\zeta$ plus polarization (DZP) basis set was used for the expansion of the electronic wavefunctions, with an energy shift of 100 meV. Forces and total energy per atom were converged to better than 40 meV/Å and 2 meV, respectively, and an energy smearing of 25 meV was applied. All computations were conducted in spin-polarized mode. No thermal corrections were considered in this study; all calculations were carried out at 0 K. COOP analysis, which sums over all possible overlap states, was performed to distinguish bonding and antibonding orbital interactions between graphene and an adsorbate.

FIG. 1. Snapshots of the liquid AlCl/graphene system after 6 ps simulation time. (a) Metalloid cluster growth around a single vacancy (non-interacting monomers are removed for clarity). (b) Free diffusion of the monohalide over the surface of defect-free graphene (Al = gray, Cl = green, C = black).
The starting graphene sheet was a fully optimized layer with 64 atoms in the cell and periodic boundary conditions. Structural defects were introduced by removing one C atom (SV) and two C atoms (DV). 20 Å of vacuum was present along the z-axis to decouple the system from its periodic images.

(a) $g_{\text{Al-Al}}(r)$ GR-AICl
(b) $g_{\text{Al-C}}(r)$ GR-AICl

FIG. 2. Evolution of coordination number for the initial bound Al atom in the GR(SV) and an average of all Al atoms in the GR(SV).

FIG. 3. (a) Al–Al and (b) Al–C PDFs $g(r)$ and bond distributions $n(r)$ averaged over MD trajectories of perfect GR and GR(CV).
III. RESULTS AND DISCUSSION

We first present ab initio molecular dynamics of the AlCl monohalide liquid interacting with perfect GR and a system with a GR (SV). The supercell of GR (128 atoms) was initially optimized, and then 14 AlCl monomers were randomly placed above the sheet, with the constraint that the Al should start no closer than 2 Å from the graphene and at least 3.2 Å from any nearby Al atom. The GR was held fixed and a 3 ps NVE equilibration was carried out on the AlCl liquid. The wavefunction of the equilibrated structure was then optimized and used for the primary NVT-ensemble simulation. A simulation time of 8 ps was found to be sufficient to observe the nucleation and initial clustering of AlCl on defective GR. Initial molecular dynamics simulations with a single AlCl monomer showed that this group quickly adsorbed into a single-vacancy with the Al–Cl bond orthogonal to the graphene plane and was also confirmed by static DFT calculations of a single monomer adsorbate. The simulation of the graphene with a single vacancy thus began with a lone AlCl bound to the vacancy site. As the simulation evolved, other monomers approached the seed AlCl and begin forming Al–Al bonds. In contrast, the AlCl above the perfect graphene freely diffused above the surface and showed little interaction with carbon or other monomers. A snapshot late in each trajectory is shown in Figure 1, showing a stable metalloid cluster above the vacancy and an unaltered liquid above perfect graphene.

As a quantitative gauge of cluster formation, we present the evolution of Al–Al bonds (the coordination number) as a function of time along the MD trajectories. In the case of GR(SV), we present the coordination number of the initially adsorbed aluminum which forms the seed of the cluster. For the perfect graphene, we present an average number of Al–Al bonds with respect to every individual Al atom in the system. The calculated coordination numbers are shown in Figure 2. The average coordination number in the perfect GR system is close to one, primarily due to transient interactions in the liquid phase. However, the coordination number of the initially adsorbed Al atom in the GR(SV) system increased along the MD trajectory up to between 4 and 6 towards the end of the 8 ps simulation time. During this process, there is also significant rearrangement of the Cl, which tends to migrate away from the vacancy to the exterior of the growing cluster following insertion of new AlCl monomers. Indeed, this process is quite consistent with the scheme proposed by Schnöckel and co-workers for metalloid cluster growth beginning from a trivalent Al moiety.

Figure 3 shows the Al–Al pair distribution function (PDF) $g(r)$ of perfect and defective GR and AlCl liquid, averaged over the entire molecular dynamics trajectory. In
both cases, Al–Al bonds are observed around an equilibrium bond length of 2.85 Å. The higher peak in $g(r)$ for the GR(SV) system arises due to the small cluster forming near the vacancy. Transient Al interactions in the liquid due to the high temperature of the simulation are primarily responsible for the peak in the pure graphene system. The insets in Figure 3 represent the Al–Al bond distributions as the probability of finding these bonds within a cut-off radius of 3.0 Å of the first coordination sphere for each Al species. Figure 3(b) shows the Al–C PDF and the coordination numbers in both GR and GR(SV). In the case of perfect GR, the PDF shows no evidence of Al–C bonding below 3 Å, consistent with the nearly free diffusion of AlCl above the surface. However, Al–C bonding in the GR(SV) can be seen at 1.9 Å (equilibrium Al–C bond length) and 2.85 Å as shown in the Al–C PDF and the Al–C bonds distribution in Fig. 3(b).

### A. AlCl/graphene interaction

The MD simulations show spontaneous metalloid cluster growth around simple defects, and here, we consider the interaction between the monovalent aluminum halide precursor and the GR in more detail with static DFT calculations.

We begin with the interaction of an individual AlCl unit with a perfect GR sheet and GR with SV and DV defects.

In all configurations, a large number of initial configurations were considered to identify the most favorable adsorption site. Three known sites typically referred to as B (the bridge position, located between two C atoms), H (hollow, the center of one hexagon on the graphene), and T (top, directly above a carbon) were initially tested for the most relevant adsorption site. AlCl was initially placed above the surface defect with a separation distance between Al and carbons at the defect site of 2.3 Å, slightly larger than the equilibrium bond length between Al and C (≈1.9 Å). The local minimum obtained from these initial configurations is followed by full geometry optimization of several rigid translations and rotations of AlCl in the combined systems. The optimized structures revealed that the AlCl monomer generally preferred a nearly planar orientation with respect to the perfect GR and, in sheets with a vacancy, directly bonded to the middle of the vacancy with the Al–Cl bond orthogonal to the graphene.

The Fermi level shift and its relation to the charge transfer between graphene and an adsorbate has been discussed extensively in the literature. It is known that the shift is sensitive to the concentration of dopants and/or adatoms (i.e., the size of the simulation cell). Also, the calculations of charge transfer derived from several methods such as integration of the density of states (DOS), line distribution of the charge density differences, and classical approaches show...
inconsistent results. A correlation between the charge transfer and the Fermi level shift is primarily valid in weak adsorption process in which minimal distortion of the graphene is expected. However, this comparison is less relevant during chemisorption where the spatial distribution of the charge density between the adsorbate and GR is heavily distorted. In this study, will thus use the shift in the Fermi level to classify these configurations as either \( n \)- or \( p \)-type materials based on the shift direction, while the charge transfer is calculated using a simple volume integral of the electron density around the aluminum on the adsorbate. Specifically, we use the difference in volume integrals \( \Delta Q \) within a radius of 1.3 Å around the Al adsorbate,

\[
\Delta Q(-e) = \int_0^r \rho_{\text{comb}}(r) \, d^3r - \int_0^r \rho_{\text{iso}}(r) \, d^3r,
\]

where \( \rho_{\text{comb}} \) is the charge density on Al for the combined AlCl/GR system and \( \rho_{\text{iso}} \) is Al charge density on the isolated AlCl.

The charge transfer values are quite small for the interaction with perfect graphene, consistent with weak physisorption. However, the sign of these values agrees with the shift in the Fermi level and correlates well with the trend in the binding energy of these configurations. The binding energies are calculated in terms of total energies as

\[
E_b = E_{\text{comb}} - E_{\text{GR}} - E_{\text{iso}},
\]

where \( E_b \) is the binding energy of AlCl monomer, \( E_{\text{comb}} \) is the total energy of the combined system, \( E_{\text{GR}} \) is the total energy of the base GR system, and \( E_{\text{iso}} \) is the total energy of the isolated monomer. All configurations have their geometries optimized, and considerable distortion of the graphene occurs in the combined system.

**B. Perfect graphene**

Our calculations show that the AlCl weakly physisorbs onto perfect GR with binding energies less than 0.5 eV, settling into an equilibrium distance approximately 3.5 Å from the sheet. The optimized structures before and after adsorption are provided in Figure S1 of the supplementary material.\(^{49}\)

The strongest binding energy configuration of AlCl with pure graphene is found with aluminum in the hollow (H) site with a relatively weak binding energy (−0.21 eV). The equilibrium distance between Al and center of the hexagon is 3.56 Å. The combined system shows a very small \( n \)-type Fermi level shift toward the conduction band from −4.40 eV before adsorption to −4.30 eV after adsorption. We note that the binding energies in the T and B sites differ by less than 0.1 eV from the hollow site; indeed, a series of static calculations translating the Al between these sites shows that the energy surface is nearly flat. We note that the explicit inclusion of...
van der Waals forces may alter this binding energy slightly, but to remain consistent with other adsorption studies in this manuscript (for which van der Waals interactions are negligibly compared to the strong chemisorption), they are not included.

The DOS before and after adsorption is shown in Figure 4. The electronic structure changes for atomic Al adsorption on perfect GR was previously discussed by Chan and co-workers, who also find a preference for the H site for atomic Al and other group 13 elements. They note hybridization of the Al(3s) electrons with two of the graphene states below the Dirac point. This is not observed with the AlCl adsorbate. Rather, the hybridized Al and Cl states result in new distinct features in the electronic DOS, leaving the graphene states and the Dirac point nearly unchanged. Previous calculations also showed a roughly 1 eV shift in the Fermi level to higher energies following adsorption of an isolated Al. We observe only a small 0.1 eV change in $E_F$ for AlCl, suggesting minimal charge transfer with the graphene; the calculated charge transfer using Equation (1) is indeed nearly zero (0.0032e). Maps of the charge density difference in 2D and 3D are shown in Figure S2 of the supplementary material. The interaction of AlCl with perfect graphene is thus one of the weak physisorption with minimal charge transfer or hybridization, considerably different from an isolated Al adsorbate.

C. AlCl adsorption on SV

We next consider graphene defects which result in strong chemisorption of AlCl, similar to the seed group that nucleated a small cluster in the molecular dynamics simulations. A number of previous studies have considered the electronic state around a single vacancy in graphene. Two of the three dangling bonds on the C atoms around a SV are saturated by means of a Jahn-Teller distortion and the Fermi level shifts toward the valance band (with respect to ideal graphene) in a $p$-type fashion. The AlCl monomer binds strongly with a graphene single-vacancy, preferring an orientation aligned perpendicular to the sheet with the Al atom directly above the defect and equidistant (1.92 Å) from the three C atoms around the vacancy. The Fermi level shifts even further toward the valance band due to interaction with the AlCl, indicating charge withdrawal from the sheet to the monomer as dangling bonds from the carbon hybridize with the Al $p$ orbitals.

Figures 5 and 6 show the DOS and structure before and after AlCl adsorption in this configuration. Unlike the perfect GR discussed above, the DOS shows clear evidence of this hybridization between the AlCl and the carbon 2$p$ states near the Fermi level. The distances between C atoms at the defect site increase and tilt out of the plane by $\approx 0.2$ Å upon AlCl adsorption. The AlCl chemisorbs on this defect with a binding energy of $\sim 4.676$ eV and a $+1.72e$ charge transfer.
D. AlCl adsorption on DV

A double vacancy is also a common defect in graphene as a result of coalescence of two SVs or by simple removal of two C atoms. Consistent with previous calculations, the four C atoms around the DV defect undergo a reconstruction into one octagon and two pentagons. The Fermi level is shifted toward the valance band compared to pure graphene. As with the single vacancy, the AlCl monomer chemisorbs (binding energy of $-3.35$ eV) into the middle of the double vacancy in a perpendicular position with the Al atom pointing toward the GR. The average bond length between Al and these carbons is 2.06 Å. Here, the Al is coordinated with all four atoms surrounding the DV, unlike the triply coordinated state in the single vacancy. Upon AlCl adsorption, the Fermi level also shifts further towards the valence band similar to the SV and consistent with charge withdrawal. Figures 7 and 8 show the DOS and structural measurements of the optimized structures before and after AlCl adsorption in this configuration. A side view showing AlCl adsorbed in this configuration is given in Figure S3 of the supplementary material.

As with the SV, considerable hybridization between the AlCl orbitals and the carbon 2$p$ states is observed (maps of the charge density difference in SV-DV-GR configurations are given in Figure S4 of the supplementary material). The DOS of SV- and DV-GR configurations (Figures 5 and 7) show localized $p$ states of Cl atoms between $-6.8$ eV and $-8.0$ eV and deep $s$ states localized around $-18.0$ eV. A COOP analysis of the Al-C interactions in both the SV- and DV-GR is given in Figure 9. The Al-C interactions are almost entirely bonding in character and arise from a combination of Al(3$p$)–C(2$p$), Al(3$s$)–C(2$p$), and Al(3$p$)–C(2$s$) hybridizations. In all cases, the Al(3$s$)–C(2$s$) hybridization is negligible. The Cl–C interactions (in the form of orbital hybridizations) in graphene with single and double vacancies are shown in Figure S5 of the supplementary material. The overall Cl–C interactions are significantly smaller than that of Al–C interactions and are primarily anti-bonding in character. The origin of these anti-bonding states is mainly Cl(3$p$)–C(2$p$) with smaller contributions from Cl(3$s$)–C(2$p$) and Cl(3$p$)–C(2$s$) hybridizations.

The charge transfer is consistent in all cases, showing charge donation to the AlCl as the dangling bonds on graphene vacancies bind with the aluminum and form a trivalent core.
FIG. 9. COOP analysis of Al–C interactions in (a) AlCl-SV-GR and (b) AlCl-DV-GR configurations. Interactions were terminated beyond $R = 2.4 \text{ Å}$.

This donation to the adsorbate is consistent with the small $p$-type shifts observed in the Fermi level and the considerable increase in binding energies in the presence of the vacancy.

IV. CONCLUSIONS

Simple graphene vacancies may provide a means of growing well-dispersed metalloid clusters from the same monohalide solution used for large known metalloid systems. Our \textit{ab initio} molecular dynamics and static DFT simulations suggest the following general picture for this process. The monohalide AlCl interacts very weakly with defect-free graphene regions, showing weaker physisorption than pure atomic Al. The monohalide is thus largely free to diffuse across the sheet until encountering a characteristic vacancy, at which point a single AlCl unit chemisorbs and provides an Al(III) moiety. Additional monohalide units can then grow a cluster via repeated AlCl insertion reactions, similar to the mechanism proposed by Schnöckel and co-workers for metalloid cluster growth starting at an Al(III) impurity in solution.\textsuperscript{29} This process occurs spontaneously in Car-Parrinello molecular dynamics simulations, leading to a well-defined metalloid cluster above a graphene single vacancy. Further experimental studies exploring these processes using graphene/reduced graphene oxide materials and aluminum monohalide solutions are ongoing.

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