Orientation-dependent binding energy of graphene on palladium

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Using density functional theory calculations, we show that the binding strength of a graphene monolayer on Pd(111) can vary between physisorption and chemisorption depending on its orientation. By studying the interfacial charge transfer, we have identified a specific four-atom carbon cluster that is responsible for the local bonding of graphene to Pd(111). The areal density of such clusters varies with the in-plane orientation of graphene, causing the binding energy to change accordingly. Similar investigations can also apply to other metal substrates, and suggests that physical, chemical, and mechanical properties of graphene may be controlled by changing its orientation.

Since its isolation in 2004, graphene has attracted a great deal of attention because of its unique technological properties. A remaining technological hurdle that prevents the introduction of graphene into specific applications is a basic, predictable understanding of the interaction of graphene with supporting substrates. The sensitivity of graphene to the substrate material and surface orientation is well established, but even relative azimuthal orientation of graphene on these substrates can affect its properties. These recent works address manifestations of the interactions between graphene and its host substrate, showing that these interactions actually vary with the local environment, that is, the chemical or electronic environment in the immediate vicinity of certain carbon atom(s). Careful bookkeeping of the local structures (and the associated interactions) present within a single spatial period of a moiré superstructure can be compared to variations in the global properties, such as binding energy, to deduce the impact of the orientation of the graphene layer.

In this letter, we study monolayer graphene on Pd(111) for a range of in-plane orientations, and show that the atomic-level carbon–palladium registry affects the binding to the substrate through changes to molecular orbitals at the graphene–metal interface. Furthermore, we uncover a link between the interfacial binding strength and the areal density of certain four-atom clusters centered atop Pd atoms in the first substrate layer. This link provides fundamental insight into the physical origin of the orientation dependence of the binding energy, and can be exploited for understanding the interaction of graphene with other substrates as well.

In order to study the orientation dependence of the binding energy, we start by constructing perfectly periodic moiré patterns of graphene on Pd(111). All moiré patterns are incommensurate when using the equilibrium lattice constants of graphene and Pd, so we have ensured commensurability at each orientation \( \theta \) (defined as in Fig. 1) by applying small strains to the graphene lattice. We have performed density functional theory (DFT) calculations of graphene domains having orientations \( \theta \) between 0 and 30° with respect to the substrate; other angular domains reduce to \( \leq \theta < 30^\circ \) through rotational symmetry. For convenience, we have chose four different orientations, \( \theta = 5.7, 10.9, 19.1, \) and 30.0°, the first three of which have been experimentally identified in Ref. 12; the 30° orientation helps compare our results with those of Giovannetti et al. To understand the impact of atomic registry on the graphene-Pd(111) binding, each carbon atom is designated as a top (T), bridge (B), gap (G), or hollow (H) site, as shown in Figure 1 based on its position relative to the substrate.

Total energy calculations were performed using the Vienna Ab-Initio Simulation Package (VASP) with ultrasoft pseudopotentials in the local density approximation, with a 286 eV plane-wave energy cutoff, and a 12 Å vacuum thickness. The Brillouin zone was sampled using a Monkhorst-Pack grid–7 \( \times \) 7 \( \times \) 1 (5.7°), 9 \( \times \) 9 \( \times \) 1 (10.9°), 17 \( \times \) 17 \( \times \) 1 (19.1°), and 35 \( \times \) 35 \( \times \) 1 (30.0°)–with more...
than 100 points/Å$^2$ along each reciprocal lattice vector. The substrate was modeled with four Pd(111) layers (lowest two kept fixed during relaxation), with the exception of the 5.7° system, which was modeled with three Pd layers due to computational limitations; we have tested that binding energy trends obtained with 3 or 4 substrate layers are indeed consistent with one another. We have computed the binding energy per unit area $E_b$ via

$$E_b = (E_{\text{GrPd}} - E_{\text{GrPd}})/A,$$

(1)

where $E_{\text{GrPd}}$ is the total energy of a system in which the graphene sheet is far from the Pd surface, and $E_{\text{GrPd}}$ is the total energy of a system where the graphene layer was relaxed on the substrate. We express the area $A$ in carbon atoms rather than Å$^2$ ($1 \text{ C} = \sqrt{3}a^2/4$, where $a$ is the lattice constant of graphene).

Binding energy is a fundamental property of epitaxial graphene systems, affecting not only its structural and mechanical stability, but the electrochemical properties as well. While calculations of binding energy have become commonplace, our goal here is to correlate it with simple geometric features that are present in the moiré superstructures characteristic to various orientations. Seeking such correlation involves, in order: (a) identifying the possible locations (coincident sites) that a carbon atom in graphene can occupy with respect to the substrate, (b) tracking the populations of these coincident sites (i.e., their areal densities), or of groups of them, as functions of the orientation of the graphene sheet, and (c) finding which of these tracked populations depend on the orientation angle in a manner similar to the binding energy. Following this plan, we start by selecting four distinct types of coincident sites to describe the positions of a carbon atom relative to the Pd surface–top (T), bridge (B), hollow (H), and gap (G), as described in Figure 1. To avoid counting ambiguities when tracking site populations, we have chosen to identify the regions for which coincident sites are populated by site-centered circles that touch without overlapping, as shown in Fig. 1. This convention ensures that 90.7% of the substrate surface is counted; atoms within the remaining 9.3% of the surface (colored dark blue in Fig. 1) are disregarded.

Tracking changes in coincident site population requires a fixed reference, and we have selected this reference to be the expected fraction of carbon atoms that would lie at a certain coincident site under the assumption of random distribution of carbon atoms. Placed at random, 1/12 of carbon atoms lie on top sites and 1/4, 1/6, and 1/2 at bridge, hole, and gap sites, respectively. Figure 2 shows the variation in the population of each coincident site as a function of angle. Although a given population of single-type coincident site may vary by as much as 45% with respect to its reference, no clear trends emerge for the variation of any coincident site population with the orientation $\theta$ (Fig. 2). On the other hand, as we show below, the binding energy of graphene monolayer on Pd varies monotonically with the orientation angle: therefore, no correlation exists with between binding energy and populations of any of the single coincident sites, T, B, H, or G.

A simple inspection of the moiré patterns corresponding to the orientations $\theta$ studied here (Figure 3) suggests that coincident sites are occupied in a coordinated manner, which is expected since the carbon atoms that occupy them are part of the same graphene lattice (refer to examples given in the caption to Fig. 3). Therefore, we proceed to consider nearest neighbors of a given (central) site, along with the site, in order to create an inventory of single-type coincident site may vary by as much as 45% with respect to its reference, no clear trends emerge for the variation of any coincident site population with the orientation $\theta$ (Fig. 2). On the other hand, as we show below, the binding energy of graphene monolayer on Pd varies monotonically with the orientation angle: therefore, no correlation exists with between binding energy and populations of any of the single coincident sites, T, B, H, or G.

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creases as a function of orientation. The only cluster whose areal density increases monotonously with \( \theta \) is TB\(_3\), which we show to be responsible for the bonding of graphene to the substrate.

![Graph](image)

**FIG. 4.** (Color online) (a) Density of different types of 4-site clusters for the orientations of \( \theta = 5.7^\circ, 10.9^\circ, 19.1^\circ, \) and \( 30.0^\circ \). (b) The binding energy \( E_b \) of graphene on Pd(111) increases as a function of orientation \( \theta \). We have determined the areal density as a function of the binding energy, increasing to 73 meV of clusters that can occur on the substrate. We have identified these clusters by a two-letter abbreviation; for example, HG\(_3\) is a hollow-site (H) carbon surrounded by three gap-site (G\(_3\)) nearest neighbors. Eight such clusters are represented in the moiré patterns shown in Fig. 3 and we have determined the areal density as a function of angle \( \theta \) for all of them [Fig. 3(a)]. As seen in Fig. 3(b), only one of these four-atom clusters, TB\(_3\), has a density that varies with the orientation angle in the same way in which the binding energy does. At small orientations, the graphene sheet physisorsbs to the Pd(111) substrate with a binding energy of only 41 meV. The only cluster whose density of TB\(_3\) reaches its maximum \( \theta \) is TB\(_3\), which we show to be responsible for the bonding of graphene to the substrate.

Electronic transfer calculations also reveal a clear signature of the bonding between graphene and Pd for a certain range of the orientations. At small angles (\( \theta \leq 10.9^\circ \)), there is no significant charge transfer, consistent with the low binding energy values shown in Fig. 4(b). However, for \( \theta = 19.1^\circ \) and \( 30.0^\circ \) the electron transfer becomes significant, as shown in Figs. 4(a) and 4(c): this transfer amounts to the formation of chemical bonds (occupied bonding orbitals) between graphene and substrate, which are the physical origin of the binding energy increase computed at large angles \( \theta \) [Fig. 4(b)]. In Figure 4(a), we can identify three bonding orbitals by their shapes: the axially–symmetric TB\(_3\) bond, the ovoid bond that lies below the \( \sigma \)-bond between two carbon atoms, and the oblong bond where adjacent carbon sites are not directly atop a first-layer Pd atom. The “strengths” of the bonds formed, as estimated by the increased electronic charge, \( Q \), in a certain volume are also different with the highest corresponding to the TB\(_3\) case: \( Q_{TB3} = 0.055e > Q_{ooid} = 0.042e > Q_{oblong} = 0.007e \). This reinforces, albeit qualitatively, our earlier observation that the combined effect of the top and bridge-site neighboring carbons is responsible for bonding. Unlike the case of the 19.1° system where three types of bonds are found, in the case of 30° only TB\(_3\) is present [Figure 4(b)]. The TB\(_3\) bonds are \( \sim 24\% \) weaker for \( \theta = 30^\circ \) than their 19.1° counterparts, but are present on 2/3 of...
the surface Pd atoms which accounts for the the higher binding energy.

FIG. 6. (Color online) Electron transfer density for (a) 19.1° and (b) 30.0° orientations, showing regions of charge accumulation (red-orange spectrum) and depletion (blue spectrum). Three types of bonds can be identified at these orientations, marked in (a) as ovoid, oblong, and TB1. Only the TB1 type exists at θ = 30° (b), and no bonds are formed at orientations of 5.7° or 10.9°. Panel (c) shows side-views of the charge transfer regions corresponding to different types of bonds identified in (a).

When bound strongly to a substrate, graphene tends to adopt one predominant orientation, as seen on Ru(0001) and Ni(111). On substrates with weaker binding, including Pd(111), Pt(111), and Ir(111), multiple azimuthal orientations are observed, and are readily identified by the presence of moiré structures with different spatial periodicities. Recently, Merino et al. have catalogued structures of graphene on Pt(111) into minimum-strain “phases”, characterized by their orientation-dependent spatial periodicities. It is worth noting that when applied to the graphene on Pd(111) system, the Merino et al. model describes well the structures we examined here: 5.7°, L = 17.12 Å (same as in Ref. η phase); 10.9°, L = 11.20 Å (10.75 Å in Ref. η phase); 19.1°, L = 7.33 Å (7.25 Å in Ref. β phase); and 30°, L = 4.89 Å (5.00 Å in Ref. α phase). The most stable phases (orientations) are those with stronger binding, i.e., α and β, as shown before in Fig. [11b].

In summary, we have shown that the binding energy of graphene on Pd(111) depends on its orientation, and that this dependence arises not from the population of any single coincident site, but from coincident site four-atom clusters (one top-site C atom surrounded by three bridge-site carbons). The 78% increase in binding energy, from 41 meV/C to 73 meV/C, emphasizes the sensitivity of this property to the carbon–palladium coincidence. The approach presented here can be applied to other metal substrates as well, in order to see if equally simple clusters (and which ones) are responsible for controlling the binding strength between physisorption and chemisorption.

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