

Strong covalent bonding between two graphene layers

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We show that two graphene layers stacked directly on top of each other (AA stacking) form strong chemical bonds when the distance between planes is 0.156 nm. Simultaneously, C–C in-plane bonds are considerably weakened from partial double bond (0.141 nm) to single bond (0.154 nm). This polymorphic form of graphene bilayer is metastable with an activation energy of 0.16 eV/cell with respect to the standard configuration bound by van der Waals forces at a larger separation between planes (0.335 nm). Carbon atoms form four single bonds in a geometry mixing 90° and 120° angles, intermediate between the usual sp^2 and sp^3 , but similar to the one found in molecules like the cubane, pentaprismene, or hexaprismene. Under an in-plane stress of 9 GPa, this carbon allotrope becomes the global energy minimum. As a function of the separation between layers, the electronic band structure goes through different regimes: It is a semimetal at van der Waals-like distances, a wide gap semiconductor at covalentlike distances, and in between it displays metallic behavior.

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I. INTRODUCTION

Carbon shows one of the richest chemistry in the Periodic Table and it is often found in allotropic forms. Diamond and graphite have a place in textbooks of solid-state physics. The discovery of fullerenes and nanotubes has raised even more interest in carbon-based materials for their potential applications. Recently, the realization of two-dimensional periodic systems made by the stacking of a few graphene layers (FGLs), going down to the single layer, has attracted further interest as the basis for new electronic devices.¹ Several preparation techniques are currently used giving rise to samples showing important differences,^{1–5} most notably, charge accumulation regions associated with physical corrugation found in freestanding graphene,⁵ new properties induced in the graphene layers by the epitaxial growth on a SiC substrate,⁴ or a modification of the stacking, from Bernal AB phase to AA, found in carbon nanofilms grown from graphite oxide.³ Most recently, the possibility to substrate-induced band gaps in epitaxial FGL, or the development of metallic and/or semiconducting properties in bilayers under stress, has increased hopes of finding useful applications for these systems.⁶ Theoretical work that mimics the experimental search for better, new, or more convenient samples has led us to find another type of graphene bilayer that is substantially different from present forms of FGL both because of the type of chemical bonding involved and its characteristic semiconducting electronic band structure. State-of-the-art theoretical total-energy methods show how strong covalent bonds form between graphene layers stacked directly on top of each other (AA) at a distance that is less than half the typical one for an alternating (AB) stacking based on weak van der Waals forces (~ 0.335 nm). On this metastable polymorphic form of a graphene bilayer, each carbon is bonded to the four nearest neighbors, at 0.154 and 0.156 nm for in-plane and out-of-plane bonds, respectively (Fig. 1). Due to the fact that all electrons are allocated in covalent bonds, the bilayer becomes a wide gap semiconductor (indirect gap of 0.91 eV). Intermediate structures between these two limiting cases can be stabilized by external forces. As a function of

the separation between layers, transport properties of the undoped AA stacking are rich: At large distances between planes (e.g., as found in conventional FGL samples), the system is very close to a semimetal, mostly dominated by the single graphene layer properties. As the distance between layers decreases, the bilayer becomes a good metal.

II. THEORETICAL METHODS

Our results are based on *ab initio* calculations taking advantage of density functional theory (DFT).⁷ Exchange and correlation have been computed within a local approximation (LDA).⁸ Including gradient corrections to improve the description of the exchange and correlation functional⁹ (GGA) does not qualitatively change our conclusions; it merely modifies the fine details (GGA overestimates bonding distances by a similar amount as LDA underestimates them and increases the stability of the polymorph by predicting a 26% increase in the barrier). Therefore, LDA has been preferred as a simpler formalism affording a simpler physical

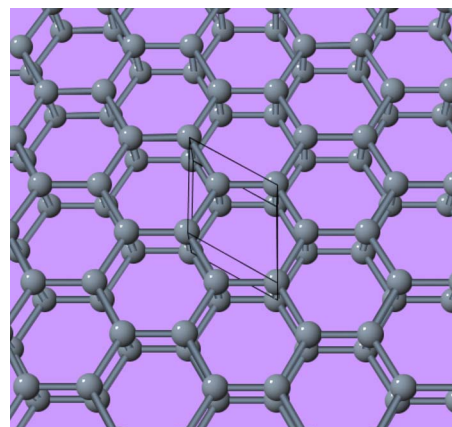


FIG. 1. (Color online) Metastable extended 2D carbon allotrope formed by two graphene layers at covalent C–C bond distance and direct on-top stacking (AA). The 2D unit cell is shown ($a=b=0.267$ nm, $\gamma=120^\circ$).

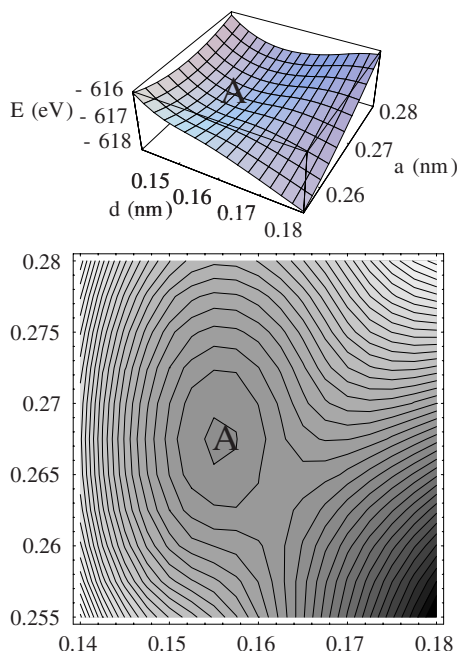


FIG. 2. (Color online) First-principles total-energy landscape for the graphene bilayer as a function of the distance between layers (d) and the 2D lattice parameter (a). Label A shows the local minimum reported in this work at $d=0.156$ nm and $a=0.267$ nm corresponding to the formation of covalent bonds across layers. Contour lines start at -618 eV and go up in steps of 0.05 eV (the minimum in A is at -617.208 eV). Axis on the contour plot closely corresponds to the landscape one.

interpretation. The two-dimensional (2D) periodic graphene layer has been described by using norm-conserving pseudopotentials¹⁰ ($2s^2 2p^2$) and a plane-wave basis of fixed quality, as implemented in the CASTEP code.^{11,12} We have used an energy cutoff of 750 eV for geometry optimization, transition state search, and band structure calculations (Figs. 1, 2, and 4, respectively) and 660 eV for phonon calculation (Fig. 3). A supercell with a c axis of 3 nm has been used to avoid interactions between graphene layers. Wave functions have been sampled in the irreducible part of the Brillouin zone with sets including 98 k points [Monkhorst-Pack grid $14 \times 14 \times 1$ (Ref. 13)], except for phonon calculations where a $12 \times 12 \times 1$ grid has been used. Convergence accuracy

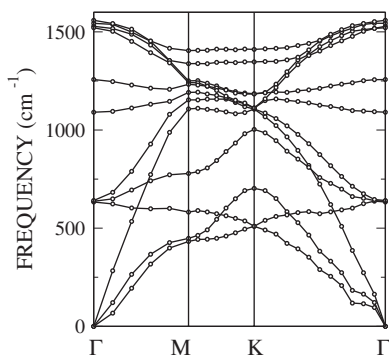


FIG. 3. Phonon spectrum calculated at the local minimum A in Fig. 2. The x axis samples the boundary of the irreducible 2D Brillouin zone. Lines between points are only meant to guide the eye.

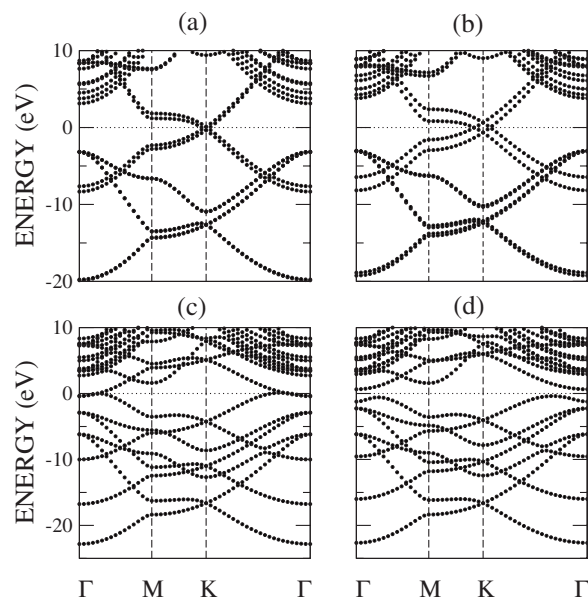


FIG. 4. Evolution of the electronic band structure for the bilayer as separation changes from van der Waals-like distance (a) to the small separation allowing the chemical bonding of graphene sheets (d). (a) $d=0.358$ nm, $a=0.243$ nm (global minimum Γ , semimetallic); (b) $d=0.300$ nm, $a=0.250$ nm (2D metal); (c) $d=0.1625$ nm, $a=0.2645$ nm (near the transition state, 2D metal); and (d) $d=0.156$ nm, $a=0.267$ nm (local minimum A, insulator). Fermi energy is used as the origin for energies.

achieved with these parameters has been better than 0.01 eV for absolute values of total energies and better than 0.001 eV for relative differences in energies (e.g., barrier determination). The electronic band structure displayed in Fig. 4 has been computed assuming that the system is metallic with a smearing width of 0.01 eV and an all-band minimization method (ensemble density-functional theory).¹⁴ Clusters and molecules of interest to elucidate the chemical interactions have been computed using double and triple-zeta basis (depending on the size) and a B3LYP functional,¹⁵ e.g., as implemented in the GAMESS code.¹⁶

LDA describes very well the strong sp^2 bonds inside the graphene layer. Theoretical calculations predict as the most stable configuration a honeycomb lattice with a C-C distance of 0.141 nm and a bond population of 1.53 . Experimental value is 0.142 nm (fractional error less than 1%), in between a carbon double bond (typical length of 0.133 nm) and a single one (0.154 nm). A negligible charge transfer (0.3%) takes place from $2s$ to $2p$ orbitals. These geometrical results, together with those obtained for electronic and vibrational properties, demonstrate the ability of DFT to describe the C-C bond at typical distances allowing the formation of covalent bonds. A rough electron-counting picture for the graphene layer would be each C atom sharing one electron with each of the in-plane three nearest C neighbors, while the fourth electron is delocalized among them, making three stronger C-C bonds with a character somewhere in between a single and a double bond. In bulk graphite, this fourth electron would be responsible for the appearance of pockets near the Fermi energy and the in-plane conductivity. This scenario makes using this extra electron to establish single

bonds between carbons across the layers plausible. While van der Waals interaction is weak and not accurately described by a local DFT, the formation of the new allotropic form of graphene bilayer rather involves interactions between carbons at shorter covalent bonding distances where the DFT formalism is accurate and realistic. This is independent of the basis chosen to solve the equations; we have checked that quantum chemistry calculations made with localized basis sets and mixed functional methods in small clusters concur with the ones derived from plane-wave basis for extended 2D systems.

III. RESULTS

Recent papers have investigated the electronic structure of the standard alternating *AB* stacking since it is energetically favored over the *AA* stacking.¹⁷ However, the expected energy difference is necessarily small due to the weak interaction between layers, about 0.02 eV/cell in our calculations. The barrier to transform one stacking into the other might be higher, but of the same order. Therefore, we have investigated the *AA* bilayer, searching for new structural configurations; we find a metastable energy minimum at about half the usual distance between layers in graphite. This structure implies an important lateral relaxation of the 2D unit cell and displays electronic properties quite different from the global van der Waals-like minimum. Figure 2 shows a 2D total-energy map for the system near the new minimum: The metastable configuration appears around an interlayer distance $d=0.156$ nm and lattice parameter $a=0.267$ nm (label A in Fig. 2). The alternating Bernal stacking (*AB*) does not show a similar metastable local minimum in our calculations. The reason for the different behavior lies on the different coordination of the C atoms in the bilayer stackings *AA* and *AB*. While *all* C atoms can form an interlayer covalent bond in the *AA* stacking, only half of the atoms have this possibility for the *AB* case. Consequently, when a small separation is forced in the *AB* bilayer, buckling of both planes can release stress efficiently, and sp^3 coordination with nearly tetrahedral angles appears (the resulting structure is a 2D diamond precursor). In the *AA* case, the formation of a metastable configuration is favored because symmetry does not allow the relaxation of structural strain by buckling. A similar idea has been put forward to explain the metastability of *n*-prismanes.¹⁸ Stacking of carbon layers with covalent bonds across layers seems unnoticed; because this configuration is metastable, it should require contributing some external energy to the system. A natural way of doing this is to grow the layers epitaxially on a substrate imposing a stretched length for the 2D unit cell. Until now, most of the structural information about FGL comes from diffraction data, in particular, transmission electron microscopy (TEM). At normal incidence, TEM usually results in a sixfold pattern that cannot distinguish between the *AA* and domains of the *AB* stacking; therefore, off-normal measurements and a theoretical analysis are needed to distinguish both cases.⁵ However, we should mention that the *AA* stacking has been reported in the literature for some related system.³

We have obtained the barrier to escape from minimum A to the global one (G) by applying first a linear synchronous

transit transition state search, followed by a quadratic synchronous transit method.¹⁹ We find a barrier of 0.16 ± 0.04 eV/cell, showing that the minimum around A is topologically stable against small geometrical fluctuations (Figs. 2 and 3). A word of caution is in order here: This barrier cannot be directly used to estimate the stability of A by a simple one-dimensional approach because it would not be enough to separate one unit cell while the surrounding ones remain intact. To prove the stability of A, we introduce a perturbation by displacing a single C atom in a 2×2 unit cell (one over eight atoms are perturbed) along a perpendicular distance to the layer (one-dimensional parameter). From a Debye model,²⁰ we estimate that C atoms in the graphene layer have a root mean square displacement at room temperature of about 0.008 nm. Our calculations on a 2×2 unit cell indicate that moving an atom by 0.01 or 0.018 nm would cost 0.11 or 0.35 eV, respectively (in this region, the energy depends quadratically on the displacement). Those thermal fluctuation relax under its own forces to structure A and are not enough to take the system from A to G. On the other hand, bigger fluctuations can, indeed, destroy A. If the atom is displaced by 0.04 nm (energy cost is 0.82 eV), the system finds its way to the global minimum G. Simultaneous fluctuations of several atoms acting to destroy the bilayer result in combined lower rates. Therefore, these simple one-dimensional estimates allow us to predict that it is possible to stabilize structure A once it is formed. Ruling out more complex mechanisms, the structure would resist, for a very long time, the making of $\frac{1}{8}$ defects (0.35 eV/defect) at liquid nitrogen temperature. The energy barrier for the formation of the metastable state (from G to A) amounts to 4.80 eV/cell, with the A configuration being 4.64 eV/cell higher in energy than the G one. The path from A to the transition state involves a simultaneous modification of parameters d and a (Fig. 2) due to the correlation between bonds formed in and out the planes. Boundary conditions keeping the parameter a fixed to a given value make a scenario with interesting consequences. If a is kept at a constant value of 0.279 nm, the local minimum A is established at $d=0.155$ nm and the barrier grows to 0.8 eV/cell. For a constant value of $a=0.291$ nm, A becomes the global minimum, and the barrier from A to G goes to 1.7 eV/cell, with A being lower in energy than G by 1.03 eV/cell. Therefore, a possible way to induce the proposed bilayer configuration would be to apply stress to the system, maybe by growing epitaxially graphene layers on some appropriate substrate with enough lattice mismatch.

Let us further characterize the bonding configuration after the formation of chemical bonds between C atoms located in different layers. The building of these bonds produces a weakening of the sp^2 -like in-plane bonds that elongate from 0.141 to 0.154 nm. In A, we observe a 0.1 electron charge transfer from the $2p$ to the $2s$ orbital and the formation of a single bond between carbons across the two graphene layers at 0.156 nm with a calculated bond order of 0.92. This distance is typical of single C–C bonding for substances such as diamond, propane, etc.,²¹ supporting the formation of a chemical bond in place of the previous weak van der Waals interaction. We notice that similar strained carbon structures have been observed in molecular systems known as

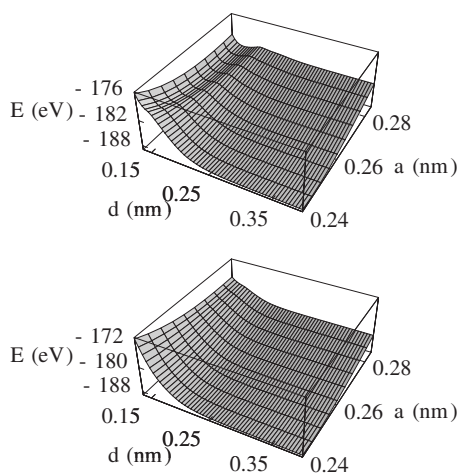


FIG. 5. Total-energy landscape computed in a tight-binding approximation for AA and AB stackings (top and bottom, respectively). For the AB stacking, there is no metastable local minimum at covalent bonding distances between layers.

n-prismanes.²² Quantum chemical calculations performed with the program GAMESS (Ref. 16) confirm the building of single C–C bonds across parallel carbon hexagonal rings saturated with H to form the hexaprismane. C–C bond distances and angles are similar to those found in the graphene bilayer (A). In agreement with our periodic solid-state calculations, this is a metastable molecular configuration with respect to van der Waals-like separation between two benzene molecules. Our calculations give a barrier between the metastable structure and the global minimum (C₆H₆–C₆H₆, one hexagonal ring) of about 0.83 eV per C–C bond. This value decreases consistently as more rings are added; already for three hexagonal rings (C₁₃H₈–C₁₃H₈), it goes down to several tenths of eV per C–C bond. As the number of hexagonal rings increases, this barrier converges to our result for the graphene bilayer. The physical content of our results can be better understood by comparing with the standard Bernal (AB) stacking of graphene layers. Tight-binding calculations can accurately describe the electronic structure of graphene layers, and we have reproduced most of our *ab initio* results by using a suitable tight-binding parametrization.²³ Because these calculations are faster, a larger parameter space can be covered with this approach. Figure 5 shows the behavior of the total energy for the AA stacking (upper panel) compared with the AB stacking (lower panel). The metastable structure is not formed for the latter, probably an indication of the reduced symmetry in the AB stacking, where only half of the carbons find carbons on the other layer at the right distance to form single bonds.

Figure 3 gives the phonon spectra at the minimum A calculated with a linear response formalism.²⁴ The phonon spectra have no dispersion in the direction perpendicular to C layers and show that the new minimum is stable with respect to small displacements that preserve the unit cell area.²⁵ The optical branches around 1600 cm⁻¹ at Γ can be compared with those measured for graphite,²⁶ although bonding in the layer is now weaker than for graphite. Near 1100 and 1250 cm⁻¹, we observe a couple of optical modes related to

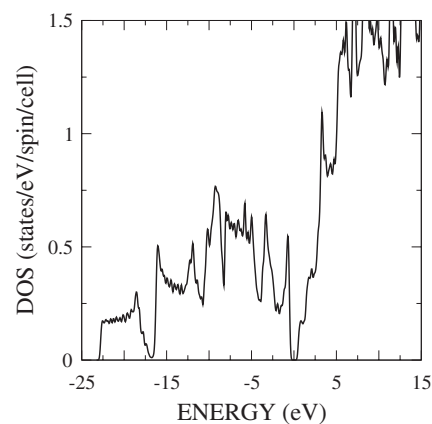


FIG. 6. Total density of states computed for bands shown in Fig. 4(d) (geometrical configuration labeled A in Fig. 2). All the parameters are like in Fig. 4(d), except the Monkhorst-Pack mesh that has been increased to $28 \times 28 \times 1$. An energy gap of 0.91 eV appears around the Fermi energy ($E_F = 0$ eV).

vibrations perpendicular to the layers that are similar in energy to that found for two C₆H₆ rings (hexaprismane) vibrating against each other at C–C covalent distances. These may be used to experimentally identify the bilayer.

Transport properties on FGL-based devices are determined by the band structure of the material. Therefore, we study the electronic structure of the bilayer for different structural parameters (size of the 2D unit cell a and separation between layers d). A single graphene layer displays a semimetallic character with valence and conduction bands touching in the corners of the Brillouin zone $\{\mathbf{K}\}$ and the dispersion relation being linear. At the van der Waals-like separation between layers (0.358 nm), the interaction is weak, and a marginal 2D metal starts to form. The 2D Fermi circle is centered at the corners of the Brillouin zone, \mathbf{K} , with a very small radius, and the density of states at the Fermi energy is nearly zero [Fig. 4(a)]. We notice that in the AA stacking, the bands near \mathbf{K} are still linear, unlike the AB stacking where the bands approach \mathbf{K} quadratically.²⁷ A new situation emerges if the two layers are forced to get closer to each other. Figure 4(b) shows the band structure for such a nonequilibrium configuration ($a = 0.250$ nm, $d = 0.300$ nm). For this geometry, repulsive forces on atoms on each layer are 0.024 eV/nm. A comparison between panels (a) and (b) in Fig. 4 shows how the radius of the Fermi circle increases, yielding a distinctively nonzero density of states and making the bilayer a quasi-2D metal. This picture is still valid near the transition state, where the Fermi line is approaching the symmetry point Γ in the Brillouin zone [Fig. 4(c)]. Further down the distance between the two layers, the system develops strong single covalent bonds, and the bilayer becomes a wide gap semiconductor [Figs. 4(d) and 6].

Finally, we have explored the role of external stresses on the bilayer by applying in-plane tensile stresses of $\sigma_{xx} = \sigma_{yy} = 3, 6,$ and 9 GPa (all other components are set to zero). These stresses correspond to forces per unit length of 9, 18, and 27 N/m, respectively, applied in the x and y directions (the supercell c axis is 3 nm). As expected, by forcing the 2D unit cell to extend, the minimum at A is stabilized and the

barrier grows to 0.43, 0.88, and 1.4 eV/cell, respectively. The local minimum A changes so the 2D unit cell size grows from 0.267 to 0.273, 0.280, and 0.289 nm, respectively, while the two layers come closer together by a small distance (0.0008 nm for 6 GPa). For 0.289 nm, the allotrope has become the global total-energy minimum, being the energy of reaction necessary to create the now metastable van der Waals-like configuration around 1 eV/cell. Finally, we notice that around G , the strain is approximately half the value around A (from 0.243 to 0.249 nm for the 6 GPa stress), a consequence of the existence of stronger sp^2 bonds.

IV. CONCLUSIONS

We have found another polymorphic form for two extended flat graphene layers stacked with AA sequence where carbon atoms located in atop positions establish strong covalent bonds. Although this configuration is metastable with respect to the one bound by weak van der Waals forces at much larger distances, the activation energy necessary to destroy this phase is large enough to make it feasible at room

temperature. This carbon allotrope shows semiconducting properties, making conventional doping with impurities (B, N, etc.) possible. This property opens a new well-defined way toward strict 2D electronics. Between the van der Waals and the covalent regimes, several interesting structures can be stabilized by external pressure and/or in-plane stresses. As a function of the separation between the two layers, their electronic properties range from a semimetal (layers far apart) to a weak 2D metal (van der Waals distances, low density of states at the Fermi energy), to a stronger 2D metal (intermediate distances, higher density of states at the Fermi energy), and finally to a wide gap semiconductor (covalent bonding distance).

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