Strong covalent bonding between two graphene layers

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Abstract

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 meta-stable w.r.t. the one bound by van der Waals forces at a larger separation (0.335 nm) with an activation energy of 0.16 eV/cell. Similarly to the structure found in hexaprismane, C forms four single bonds in a geometry mixing 90° and 120° angles. Intermediate separations between layers can be stabilized under external anisotropic stresses showing a rich electronic structure changing from semimetal at van der Waals distance, to metal when compressed, to wide gap semiconductor at the meta-stable minimum.

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Carbon shows one of the richest chemistry in the periodic table and it is often found in allotropic forms. In molecules it is the basis for organic compounds, being central to different fields from biology to electronics in new materials. In solid state it shows very different properties drifting from a soft metal (graphite, the most stable phase at P=0 GPa, T= 0 K) to a hard wide gap semiconductor (diamond). New forms like fullerenes and nano-tubes have raised even more the interest in carbon for their potential applications. Recently, the realization of two-dimensional periodic systems made by the stacking of few graphene layers (FGL), going down to the single layer, has attracted much interest as the basis for new electronic devices[1]. The peculiar linear dispersion found in the electronic band structure near the charge neutrality point (Dirac Point), where the carriers behave like mass-less chiral relativistic particles, translates in all sort of new phenomena related to transport properties on these systems[2]. Moreover, a variety of preparation techniques have been used giving rise to samples showing important differences[1, 3, 4, 5, 6]; most notably: charge accumulation regions associated with physical corrugation found in free standing graphene[6], new properties induced in the graphene layers by the epitaxial growth on a SiC substrate[5], or a modification of the stacking, from Bernal AB phase to AA, found in carbon nanofilms grown from graphite oxide[4]. Accurate and detailed information on these samples obtained from structural techniques is sometimes difficult to interpret; state-of-the-art theoretical total-energy methods are necessary to understand the precise atomic and electronic structure of these films. In this paper, we report on the formation of strong covalent bonds between graphene layers stacked directly on top of each other (AA) at a distance that is much smaller than ~ 0.335 nm, that is, the typical distance for an alternating (AB) stacking based on weak van der Waals forces (Fig. 1). On this metastable polymorphic form of a graphene bi-layer each carbon is bonded to the four nearest neighbours, at 0.154 and 0.156 nm for in-plane and out-of-plane bonds respectively. Under these conditions, the bi-layer is a wide gap semiconductor (indirect gap of 0.91 eV). As a function of the separation between layers, transport properties of the un-doped AA stacking are rich: at large distances between planes (e.g., as found in graphite) the system is very close to a semi-metal, mostly dominated by the single graphene layer properties. As the distance between layers decreases it is possible to find interlayer distances and/or different 2D unit cell sizes where the bi-layer becomes metallic.

Our ab-initio calculations are based in Density Functional Theory (DFT)[7] and a local
FIG. 1: (Color online) Meta-stable 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, $\gamma = 120^\circ$).

approximation to describe exchange and correlation (LDA)\textsuperscript{8, 9}. LDA calculations performed with CASTEP\textsuperscript{10, 11, 12} reproduce very well distances and angles for the strong $sp^2$ bonds inside the graphene layer, predicting 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 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 neighbours, 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 plausible to use this extra electron to establish single bonds between carbons across the layers. While van der Waals interaction is weak and not accurately described by a local DFT, the formation of the new allotropic form of graphene bi-layer 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-waves basis for extended 2D systems.

Recent papers have investigated the electronic structure of the standard alternating AB stacking since it is energetically favoured over the AA stacking\cite{13}. 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 bi-layer, searching for new structural configurations; we find a meta-stable energy minimum at about half the usual distance between layers in graphite. This new 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. Fig. 2 shows a 2D total energy map for the system near the new minimum: the meta-stable 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 meta-stable local minimum in our calculations. The reason for the different behaviour lies on the different coordination of the C atoms in the bi-layer stacking 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 bi-layer, 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 meta-stable configuration is favoured because symmetry does not allow the relaxation.
FIG. 2: (Color online) First-principles total energy landscape for the graphene bi-layer 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).
of structural strain by buckling. A similar idea has been put forward to explain the meta-stability of n-prismanes \[14\]. Stacking of carbon layers with covalent bonds across layers seems unnoticed; because this configuration is meta-stable 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. However, we should mention that the AA stacking has been reported in the literature for some related system \[4\].

We have obtained the barrier to escape from minimum A to the global one (G) by applying first a Linear Synchronous Transit (LST) transition state search, followed by a Quadratic Synchronous Transit (QST) method. We find a barrier of $0.16 \pm 0.04$ eV/cell, allowing us to predict that the structure A is stable at room temperature. The energy

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.
barrier for the formation of the meta-stable state (from G to A) amounts to 4.80 eV/cell, 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 different 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, A being lower in energy than G by 1.03 eV/cell.

Let us further characterize the new 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 nm 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 like diamond, propane, etc.\(^{[15]}\), 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 n-prismanes\(^{[16]}\). Quantum chemical calculations performed with the program GAMESS\(^{[17]}\) 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 bi-layer (A). In agreement with our periodic solid-state calculations, this is a meta-stable molecular configuration w.r.t. van der Waals-like separation between two benzene molecules. Our calculations give a barrier between the meta-stable structure and the global minimum (\(\text{C}_6\text{H}_6-\text{C}_6\text{H}_6\), 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 (\(\text{C}_{13}\text{H}_8-\text{C}_{13}\text{H}_8\)) 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 bi-layer.

Fig. 3 gives the phonon spectra at the minimum A calculated with a linear response formalism\(^{[18]}\). The phonon spectra has no dispersion in the direction perpendicular to C layers and shows that the new minimum is stable with respect to small displacements that preserve the unit cell area\(^{[19]}\). The optical branches around 1600 cm\(^{-1}\) at \(\Gamma\) can be
FIG. 4: Evolution of the electronic band structure for the bi-layer 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 G, semi-metallic); (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.
compared with those measured for graphite[20], 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 vibrations perpendicular to the layers that are similar in energy to that found for two C\(_6\)H\(_6\) 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 bi-layer for different structural parameters (size of the 2D unit cell, \(a\), and separation between layers, \(d\)). A single graphene layer displays a semi-metallic 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, but already a marginal 2D metal starts to form. The 2D Fermi circle is centred 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. 4a). 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[13]. A new situation emerges if the two layers are forced to get closer to each other. Fig. 4b shows the band structure for such a non-equilibrium 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 non-zero density of states and making the bi-layer a 2D metal. This picture is still valid near the transition state, where the Fermi line is approaching the symmetry point \(\Gamma\) in the Brillouin zone (Fig. 4c). Further down the distance between the two layers, the system develops strong single covalent bonds, and the bi-layer becomes a wide gap semiconductor.

Finally, we have explored the role of external stresses on the bi-layer by applying in-plane tensile stresses of \(\sigma_{xx}=\sigma_{yy}= 3, 6 \) and 9 GPa. 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 nm 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). 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.
In conclusion, we have found a new polymorphic form for two extended flat 2D graphene layers stacked with AA sequence where carbon atoms located in atop positions establish new covalent bonds. This meta-stable configuration is not subject to thermodynamic instability and shows a barrier large enough to make it feasible at room temperature. As a function of the separation between the two layers, their electronic properties range from a semi-metal (layers far away 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). External stresses can help to further stabilize these configurations, as well as to control the separation between layers. The new predicted semiconductor should allow traditional doping with impurities (B, N) opening a well-defined way towards strict 2D electronics.

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details (GGA overestimates bonding distances by a similar amount as LDA underestimates them, while the barrier to the global minimum slightly increases to 0.21 eV). We have decided to use LDA because using a simpler formalism yields a simpler physical interpretation.

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