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Tuning field-induced energy gap of bilayer graphene via interlayer spacing

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Our first-principles calculations reveal surprisingly high sensitivity of the field-induced energy gap of bilayer graphene to changes in its interlayer spacing. Small adjustments in the interlayer spacing near its equilibrium value produce large modulations in the gap over a wide range of field strength. We elucidate the mechanism for the extremely effective gap tuning by examining the interlayer charge redistribution driven by the coupled electric field and nanomechanical effect. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2943414]

Bilayer graphene exhibits properties[1–5] that hold great promise for nanoelectronic applications. Its interlayer bonding states[6] play a key role in producing its exceptional electronic properties.[5,7] An external electric field can open up a gap in its energy spectrum, turning it from a semimetal into a semiconductor with a tunable gap.[8–10] Recent experiments[11] showed that its energy gap can be opened and closed by selective control of the carrier concentration; it was suggested[11] that similar control could be achieved by electric field in a device structure. The electronic structure of few-layer graphene was shown[7,11–14] to be very sensitive to the interlayer interaction that depends on, among other factors, the interlayer spacing, which can be adjusted by nanomechanical control as recently demonstrated in experiments.[15] This raises an intriguing possibility that the energy gap of the bilayer graphene could be tuned via its interlayer spacing. It would provide an approach to modifying the electronic structure of bilayer graphene in a well controlled manner, which is critical to its potential applications.[16,17] In this letter, we report first-principles density functional theory (DFT) calculations that examine the behavior of the field-induced energy gap at reduced or expanded (relative to equilibrium) interlayer spacing. Our calculations show that a relatively small adjustment of the interlayer spacing can produce significant changes in the the field-induced energy gap. Both the range and rate of gap modulation by the interlayer spacing exhibit surprisingly large increase with rising electric field. These results suggest that controlling the interlayer spacing could provide an effective way for tuning the field-induced gap of bilayer graphene.

We examine the bilayer graphene with Bernal ($\tilde{AB}$) stacking in a periodic supercell with a vacuum region larger than 1.6 nm in the direction perpendicular to the graphene planes to avoid any self-interaction of the slabs. The computations were performed using the VASP code with the ultrasoft pseudopotential and local density approximation for the exchange-correlation potential.[18–20] An energy cutoff of 400 eV and special k points sampled on a $30\times30\times1$ Monkhorst–Pack mesh[21] are used to ensure an energy convergence of less than 1 meV/at. The external electric field E_{ext} is modeled by adding a sawtoothlike potential along the direction perpendicular to the graphene planes.[22] In spite of not explicitly accounting for the long-range van der Waals interaction, DFT calculations have consistently produced correct equilibrium interlayer distance in graphite and accurate band structure of few-layer graphene with different interlayer distances.[5,7,10,13,14] Our calculated equilibrium interlayer distance d of 0.334 nm for bilayer graphene is in good agreement with experimental and other theoretical results.[23,24]

Figure 1 shows a selected set of calculated band structures of the bilayer graphene. In the absence of an electric field, the bilayer graphene transforms from a semimetal with a parabolic spectrum near the Fermi energy to a zero-gap semiconductor with a linear spectrum with increasing inter-

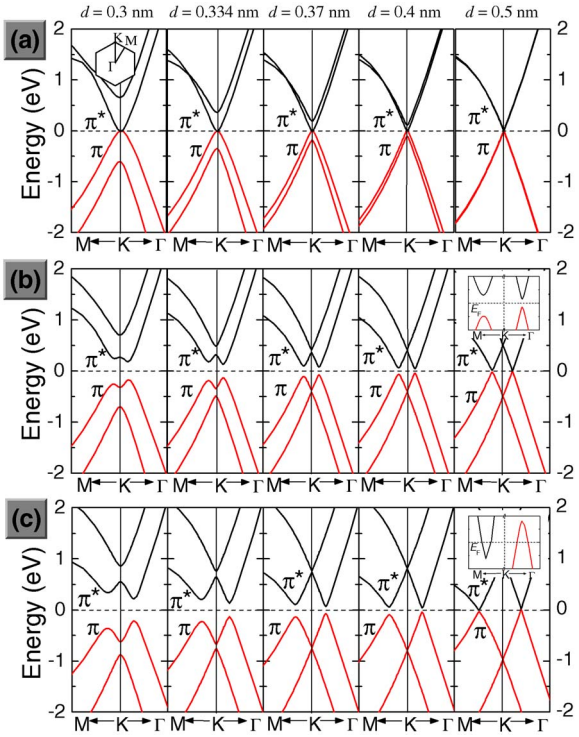

FIG. 1. (Color online) The valence (π) and conduction (π^*) band near the k point of the Brillouin zone (shown in the upper-left panel) of the bilayer graphene with interlayer distances d=0.3, 0.334, 0.37, 0.4, and 0.5 nm in the presence of electric fields (a) 0, (b) 2, and (c) 4 V/nm. The Fermi energy E_f is set to zero. The insets in (b) and (c) show close-up views of the bands near E_f at d=0.5 nm.

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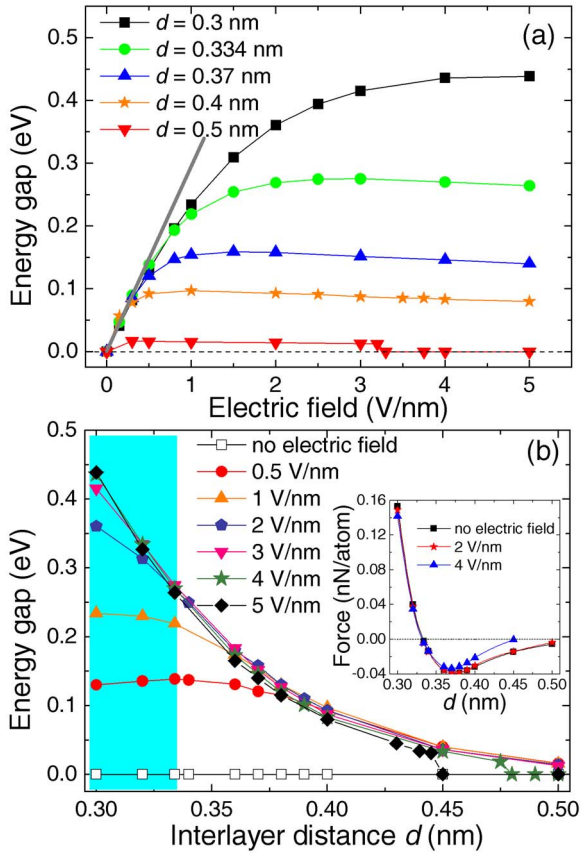

FIG. 2. (Color online) (a) Variation of the energy gap with the electric field at different interlayer spacings d. The gray line on the left side of the curves indicates a universal linear scaling of the gap at low fields (below 0.3 V/nm) with a slope of 0.294 eV per V/nm for $d \leqslant 0.4$ nm. (b) Variation of the energy gap with the interlayer spacing d at different electric fields. The shaded/clear regions on the left/right side correspond to compression/expansion of the interlayer spacing from the equilibrium (d=0.334 nm). The inset in (b) shows the variation of the force between the two graphene layers.

layer spacing. This behavior is consistent with previously reported results.[2,5,25] At compressed interlayer spacing d =0.3 nm, the higher-energy bands are pushed farther apart due to the stronger interlayer coupling between the nearest-neighbor sites,[8–10] while at larger interlayer spacing, they come closer to the low-energy bands. At d=0.5 nm, the band structure of the bilayer graphene is nearly identical to that of a single-layer graphene (except for the degeneracy). When an external electric field is applied, an energy gap opens up by the layer asymmetry.[8–10] Figure 1(b) shows the results for an electric field of 2 V/nm. It is seen that increase in interlayer spacing reduces the field-induced energy gap and, at d=0.5 nm, the gap is almost closed. Under a higher electric field of 4 V/nm, similar processes are observed, as shown in Fig. 1(c). The higher field induces a larger gap at smaller interlayer spacings, but the gap quickly decreases with expanding d and completely closes at d=0.5 nm. These results raise the prospect for an effective tuning of the field-induced gap of the bilayer graphene by adjusting its interlayer spacing and, at the same time, also raise questions concerning the underlying mechanism.

The results in Fig. 2(a) show that, at fields below 0.3 V/nm, the energy gap increases linearly with the field following a nearly universal scaling when the interlayer spacing $d < 0.4$ nm. This behavior can be understood from a

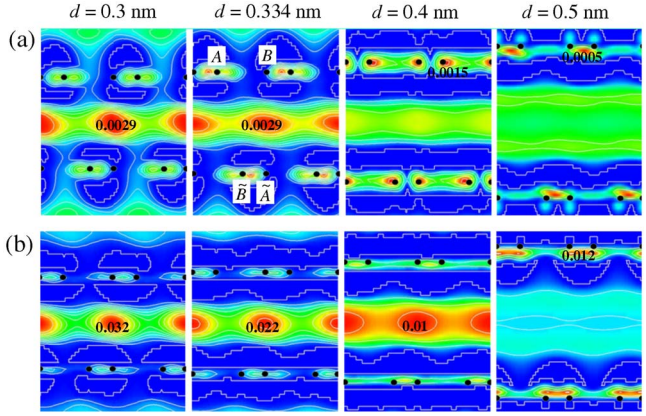

FIG. 3. (Color online) Contour plots of the charge density difference (defined in text) at (a) 1 and (b) 4 V/nm. The black dots denote the carbon atoms. The value and location of the largest charge density difference (in units of $e/\text{Å}^3$) are shown in each panel. The contour step is set to be 1/10 of the largest value in each case.

tight-binding model[10] that gives the low-energy approximation of the gap $|U|\gamma_1/\sqrt{\gamma_1^2+U^2}$, where U and γ_1 are the interlayer energy difference and the nearest-neighbor interlayer coupling parameter, respectively, with both showing almost linear dependence on the external electric field at low fields for the equilibrium structure. Our DFT results show that this linear scaling also applies to a fairly large range of d. However, when d exceeds a certain limit (around 0.5 nm), this tight-binding description no longer works because of the significantly diminished interlayer coupling, which invalidates the tight-binding description of the interlayer $\tilde{A}$-B dimer state. At higher fields, the energy gap saturates and the value of the saturated gap, which approaches γ_1 in the large-field limit,[10] is very sensitive to the interlayer spacing. At equilibrium interlayer spacing of 0.334 nm, the saturated (at 5 V/nm) gap of 0.27 eV is in good agreement with previous results.[10] The values for d=0.3 and 0.37 nm are 0.44 and 0.14 eV, respectively. In Fig. 2(b), we plot the gap versus the interlayer spacing at different electric fields. The results show that above an electric field of 3 V/nm, the gap decreases almost linearly between the interlayer spacings of 0.3 and 0.37 nm at a high rate of −4.23 eV/nm. These results indicate that adjusting the interlayer spacing, possibly through nanomechanical control,[15] can effectively tune the field-induced energy gap of the bilayer graphene. It is interesting to note that the energy gap closes at high electric fields and the gap closure occurs at decreasing (or, more precisely, less-expanded) interlayer spacing with increasing fields. At first sight, this result appears counterintuitive since higher electric fields initially induce larger gaps, as shown in Fig. 1, which are expected to be more robust against the gap reduction induced by the interlayer spacing increase. A careful analysis reveals that this intriguing phenomenon is caused by a redistribution of the interlayer charge, which is very sensitive to the electric field strength (see below).

We now examine the charge density difference $\Delta\rho_{\text{bilayer}} = \rho^{\text{ext}}_{\text{bilayer}} - \rho_{\text{bilayer}}$, where $\rho^{\text{ext}}_{\text{bilayer}}$ and ρ_{bilayer} are the charge densities of the bilayer graphene with or without the electric field, respectively. The results in Fig. 3 show that at a relatively low field of 1 V/nm, there is an apparent field-driven charge accumulation in the interlayer region, mostly between the $\tilde{A}$ and B sites at the equilibrium d=0.334 nm. At com-

pressed $d=0.3$ nm, the field-driven interlayer charge accumulation is slightly more concentrated, but the overall distribution pattern remains essentially unchanged. It indicates that the low field is unable to drive additional charge from the carbon atoms into the interlayer region. Meanwhile, at expanded interlayer distances, the field-driven interlayer charge accumulation quickly diminishes. These observations explain the behavior of the energy gap versus the interlayer spacing at low fields as shown in Fig. 2: The gap variation is very small when the bilayer graphene is under compression because of a lack of charge redistribution, but it shows more sensitive dependence on the expansion of d when the charge retracts away from the interlayer region. However, the situation changes significantly at higher fields. From Fig. 3(b) it is clearly seen that, at the electric field of 4 V/nm, the interlayer charge accumulation increases by a large amount when the bilayer graphene is compressed to $d=0.3$ nm. Since the field-driven charge accumulation locates right between the $\tilde{A}$ and B sites, it is expected to significantly enhance the interlayer coupling (γ_1),[10] which equals the energy gap at the high-field limit.[8–10] As a result, the gap changes from 0.24 eV at 1 V/nm to 0.44 eV at 4 V/nm, an 83% increase, at $d=0.3$ nm. Between $d=0.3$ and 0.37 nm, the field-driven interlayer charge accumulation decreases quickly, producing a steep drop of the field-induced gap at a rate of −4.23 eV/nm. The results in Fig. 3 also unveil the mechanism for the gap closure at less-expanded d at high fields [see Fig. 2(b)]: At $d=0.5$ nm, the *relative charge disparity* between the intralayer and interlayer regions is larger at the field of 4 V/nm, despite that the absolute amount of the interlayer charge is higher, compared to that at 1 V/nm. It makes the bilayer graphene more decoupled under higher fields at large d, resulting in the "earlier" gap closure.

In summary, our first-principles calculations reveal surprisingly sensitive response of the field-induced gap in bilayer graphene to its interlayer spacing variation. The coupled electricfield and nanomechanical effect produces large gap modulations over a wide range of interlayer spacing and electric field. We unveil the underlying mechanism by examining the interlayer charge redistribution at different interlayer spacings in response to electric field. The present results shed lights on the fundamental behavior of bilayer graphene, which can be explored for innovative applications in mechanical-electric (electronic) devices, such as nanoscale pressure/stress sensors.

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