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Band gap tuning in BN-doped graphene systems with high carrier mobility
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The outstanding electronic properties of graphene have led to huge interest in this material although the absence of a band gap strongly restricts the applicability in electronic devices as an alternative to the present Si technology. Therefore, great efforts have been devoted to the opening of a tunable gap in graphene. The proposed routes include superlattices of graphene and hexagonal boron nitride, sheets of interacting graphene, and hexagonal boron nitride domains, as well as bilayer, nanowires, and twisted geometries. Graphene multilayers under an external electric field have been studied in Refs. 10 and 11. In gated bilayer graphene a band gap of 250 meV and in graphene nanowires one of 24 meV have been reported while by means of the substrate a band gap of 52 meV and by twisting one of 270 meV can be imposed. Other approaches proposed to open a band gap in graphene are oxidation, hydrogenation, fluorination, and further adsorbates. Recent experiments indicate the possibility to achieve a tunable band gap by controlling the domain size of in-plane heterostructures of graphene and hexagonal boron nitride.

Hexagonal boron nitride is a wide band gap insulator with the same two-dimensional honeycomb structure as graphene. It is known for a high in-plane mechanical strength, excellent chemical inertness, and high thermal conductivity. For forming hybrid structures with graphene the material is particularly suitable due to a minimal lattice mismatch of 1.6% as it has been demonstrated experimentally in Refs. 6 and 20. Experimentally and theoretically, B and N doping of graphene has been attempted by various groups. On the other hand, charge neutrality can be maintained by BN doping. Although in this case a semiconducting nature has been demonstrated, the details of the band gap opening, in particular, the electron effective mass and mobility, are not settled. Motivated by the recent synthesis of BN-doped multilayer graphene and BN domain structures in monolayer graphene, we investigate in the following the effect of BN doping on the electronic properties of monolayer, bilayer, trilayer, and multilayer graphene. In addition, we address superlattices of pristine and BN-doped graphene. The calculated values of the band gap are in good agreement with the available experimental and theoretical data, which supports the reliability of our predictions. We calculate the electron effective mass and mobility as these are key quantities from the application point of view.

Our results are obtained from first-principles density functional theory in the generalized gradient approximation of Perdew, Burke, and Ernzerhof, using the Quantum ESPRESSO code with a plane-wave cutoff energy of 45 Ry. This approximation gives for monolayer hexagonal boron nitride a band gap of 4.9 eV, which is close to the value obtained by the hybrid functional of Heyd, Scuseria, and Ernzerhof (5.7 eV) as well as the experimental value (5.8 eV). The van der Waals interaction is taken into account via the Grimme scheme, which can be expected to provide correct interlayer spacings. A Monkhorst-Pack $8 \times 8 \times 1$ k-mesh is used for a $4 \times 4$ supercell of graphene. For all structures under consideration, the atomic positions are fully relaxed until an energy convergence of $10^{-5}$ Ry and a force convergence of $10^{-2}$ Bohr/Ry are achieved.

We investigate BN concentrations of 12.5% (2B2N), 25% (4B4N), 43.75% (7B7N), 56.25% (9B9N), and 75% (12B12N), with an equal number of B and N atoms, see Figure 1. Concerning the stacked structures (bilayer, trilayer, multilayer, and superlattice), there are different stacking schemes possible. It has been demonstrated that for bilayer and trilayer graphene the AA stacking is favorable whereas for superlattices of graphene and hexagonal boron nitride the N-centered AB stacking is favorable. We assume that this is also the case for our doped bilayer, trilayer, and superlattice systems. In addition, we assume that the multilayer systems follow the AB stacking scheme. All our supercells have an in-plane extension of $a = b = 9.94$ Å. The BN-doped monolayer, bilayer, and trilayer systems include in the $c$-direction a vacuum slab of 12 Å thickness. In these cases the interlayer distance is found to be 3.34 Å, which equals the spacing in graphite. For the multilayers of BN-doped graphene we obtain an interlayer distance of 3.36 Å. Finally, we find for our superlattices of alternating pristine and BN-doped graphene a distance of likewise 3.36 Å. The relaxed C-C bond lengths of the systems under study vary from 1.40 Å, to 1.43 Å, the C-B bond lengths from 1.46 Å to 1.49 Å, the C-N bond lengths from 1.36 Å to 1.40 Å, and the B-N bond lengths from 1.40 Å to 1.45 Å. Pristine graphene exhibits a C-C bond length of 1.42 Å and hexagonal boron nitride a
B-N bond length of 1.44 Å. The bond angles deviate less than 3° from the 120° angle of the pristine systems.

To understand the stability of the structures and to compare the energetics we calculate the cohesive energy

\[ E_{coh} = \frac{E_{cell} - n \cdot E_C - m \cdot E_B - p \cdot E_N}{n + m + p}, \]

where \( E_{cell} \) is the total energy of the BN-doped supercell and \( E_C, E_B, \) and \( E_N \) are the total energies of isolated C, B, and N atoms (calculated by placing a single atom in a supercell). Moreover, \( n, m, \) and \( p \) are the numbers of C, B, and N atoms, respectively. The results for the cohesive energy are summarized in Table I. For the BN-doped monolayer system it ranges from 7.76 eV/atom (12.5% doping) to 8.02 eV/atom (75% doping). Accordingly, we obtain values from 7.75 eV/atom to 8.00 eV/atom for both the bilayer and trilayer systems and from 7.75 eV/atom to 8.12 eV/atom for the multilayer and superlattice systems. These values are slightly higher than the cohesive energy of graphite (7.41 eV/atom)\(^35\) and close to the results reported for superlattices of graphene and hexagonal boron nitride in Ref. \(^2\). The cohesive energy of hexagonal boron nitride is also similar.\(^36\) We can conclude that all the systems are practically feasible.

Since the band gap of a semiconductor determines its transport and optical properties, it plays a key role in modern device technology. In this context, we probe the sensitivity of the electronic properties of our modified graphene systems. The calculated band structures of pristine graphene and the BN-doped systems under study are given in Figure 2 along the path Γ-K-M-Γ, where the doping grows along the columns from left to right. The top row represents the monolayer, the second the bilayer, the third the trilayer, the fourth the multilayer, and last the superlattice of pristine and BN-doped graphene. We obtain band gaps of 0.42 eV to 2.43 eV for BN concentrations of 12.5% to 75%, see Table I. The increase of the band gap as a function of the doping is addressed quantitatively in Figure 3. The opening of the band gap is a consequence of the broken sublattice symmetry in the presence of B and N and the change in the on-site energy of C due to the isoelectronic co-doping of BN.\(^37\) We note that the doping levels addressed in our work can be achieved in mass production using CH\(_4\) gas as C source and ammonia borane precursor as BN source, introduced as vapor during the sample growth.\(^38\) The BN concentration

![FIG. 1. Supercells used for modeling different BN concentrations.](image)

| Quantity | Concentration (%) | Monolayer | Bilayer | Trilayer | Multilayer | Superlattice |
|----------|-------------------|-----------|---------|----------|------------|-------------|
| \( E_{coh} \) (eV) | 12.5 | 8.02 | 8.00 | 8.00 | 8.12 | 8.18 |
| | 25 | 7.94 | 7.93 | 7.93 | 7.92 | 8.15 |
| | 43.75 | 7.85 | 7.84 | 7.84 | 7.83 | 8.11 |
| | 56.25 | 7.78 | 7.79 | 7.77 | 7.77 | 8.08 |
| | 75 | 7.76 | 7.75 | 7.75 | 7.75 | 8.07 |
| \( E_g \) (eV) | 12.5 | 0.42 | 0.11 | 0.04 | 0.02 | 0.08 |
| | 25 | 0.85 | 0.50 | 0.40 | 0.49 | 0.12 |
| | 43.75 | 1.46 | 1.30 | 1.15 | 0.96 | 0.20 |
| | 56.25 | 1.76 | 1.52 | 1.40 | 1.22 | 0.14 |
| | 75 | 2.43 | 2.20 | 2.08 | 1.90 | 0.13 |
| \( m^* \) (\( m_e \)) | 12.5 | 0.040 | 0.009 | 0.003 | 0.02 | 0.007 |
| | 25 | 0.073 | 0.043 | 0.034 | 0.042 | 0.010 |
| | 43.75 | 0.125 | 0.111 | 0.098 | 0.082 | 0.017 |
| | 56.25 | 0.151 | 0.130 | 0.120 | 0.105 | 0.012 |
| | 75 | 0.209 | 0.189 | 0.178 | 0.163 | 0.011 |
| \( M \) (m\(^2\)V\(^{-1}\)s\(^{-1}\)) | 12.5 | 0.84 | 3.71 | 6.68 | 1.67 | 4.77 |
| | 25 | 0.46 | 0.78 | 0.48 | 0.85 | 3.34 |
| | 43.75 | 0.28 | 0.30 | 0.34 | 0.40 | 1.97 |
| | 56.25 | 0.22 | 0.26 | 0.28 | 0.32 | 2.78 |
| | 75 | 0.16 | 0.18 | 0.19 | 0.20 | 3.04 |
can be controlled and varied by means of the annealing temperature of the precursor, which is monitored by x-ray photoelectron spectroscopy. The authors of Ref. 38 have measured a band gap of 0.6 eV for a low BN concentration, which is very close to our calculated value for 12.5% doping. Figure 3 demonstrates an almost linear growth of the band gap with the BN concentration.

The band structures in Figure 2 show that pristine bilayer trilayer graphene is of metallic nature, in agreement with the findings in Refs. 39 and 40. The variation of the band gap follows a similar trend as in the case of the monolayer but with an overall slightly reduced value, see Table I and Figure 3. In general, our results show that the band gap decreases when the number of layers in the slab grows. While a band gap opening in pristine bilayer graphene by the breaking of the inversion symmetry due to the application of a finite electric field has been demonstrated experimentally in Ref. 40, where a value of 250 meV could be achieved, we obtain by BN doping in bilayer and trilayer graphene a strongly tunable band gap. The range reaches from 0.04 eV to 2.20 eV, which can be further enhanced and controlled by the application of an electric field, analogous to the mentioned experimental demonstration for pristine bilayer graphene.

In general, the quantization of energy states in a potential well gives rise to the characteristic features of superlattices. The key quantity thereby is the barrier height. If the barrier height is small then the bands will split into quasi two-dimensional subbands, as it is the case in most conventional superlattices, for example in InAs/GaSb. On the other hand, if the barrier height is large then the overlap of the wavefunctions is suppressed, leading to separated quantum wells. In our case we are in the domain of a large barrier height. We find that the band gap is smaller for the multilayer than for the BN doped monolayer, bilayer, and trilayer, see Figure 2 and Table I. Following the same trend as in the other cases, the band gap increases with the BN concentration, as predicted theoretically41 and confirmed experimentally.33 We next turn to the electronic band structure of the superlattice in the bottom row of Figure 2. In this case, a minimum band gap of 0.08 eV and a maximum band gap of 0.13 eV are observed. These values are in the range expected from data for similar systems.2–4 We note that superlattices are promising candidates for low voltage electronic devices40 and that those with low BN concentration can be interesting for thermoelectric applications.

In the tight-binding approximation the energy spectrum of gapped graphene (the charge carriers are treated as massive Dirac particles) is found as

\[
E(k) = \pm v \sqrt{k_x^2 + k_y^2 + m^2 v^2},
\]
In conclusion, we have performed a comparative study of the electronic properties of BN doped monolayer, bilayer, trilayer, and multilayer graphene, considering also a superlattice of pristine and BN-doped graphene. Our results show that a band gap is induced by the BN doping, due to the broken sublattice symmetry in the presence of B and N atoms, and can be tuned in a large doping range. We provide insight into the quantitative interrelation between the doping and the size of the band gap. Band gaps of 0.02 eV to 2.43 eV are obtained for 12.5% to 75% BN doping. The electron effective masses are found to be low so that a high carrier mobility is achieved, as compared to graphene on a substrate of hexagonal boron nitride, for example. The comprehensive overview presented for the band gaps and carrier mobilities in various structural setups and a wide range of BN concentrations can guide the selection of the right basis system for future graphene devices.

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