Substitutional doping of graphene: The role of carbon divacancies

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The most common approach to dope an electronic material is to substitute a constituent atom with a suitable impurity. Here we show with first-principles calculations that this is not the best recipe for doping graphene with Al, P, Ga, or As impurities. Instead, substitution of two C atoms by one of these species is preferred (the ideal choice is phosphorus), as it shifts the Fermi level in the valence band without affecting significant changes in the electronic properties of low-energy carriers. This alternative way of doping could help optimize graphene-based devices and provide analogous doping schemes in other graphenelike materials.

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In traditional Si-based electronics, the replacement of one Si atom by a group-III (V) impurity turns the material into *p* type (*n* type) with excess holes (electrons). This approach has been pursued also for modern graphene-related systems. Indeed, experimental and theoretical studies [1–7] have shown that substitution of one carbon atom by a nitrogen or boron impurity is accompanied by an increase of the number of electrons or holes, respectively.

There are, however, several reasons to look also for other structures that may act as efficient dopants for graphene. Substitutional doping with boron or nitrogen requires the trapping of deposited impurities at single carbon vacancies (V1). Unfortunately, V1's are very mobile and often agglomerate to double- or multivacancy formations [8]. It would thus be advantageous if doping could be achieved also with double vacancies (V2) which are stable and practically immobile due to high diffusion barriers [3]. Moreover, deposition of boron from molecular precursors is problematic because of limited suitable options of B-containing molecules. Finally, using different elements in dopant configurations would definitely increase the possibilities to optimize key properties, such as catalytic and sensing efficiencies, of these structures.

Based on the B and N scenario and the experience with Si systems, it seems plausible that other group-III and -V elements could play the role of graphene dopants. In fact, there is unequivocal evidence based on a plethora of studies [9–19] that the insertion of such species (namely, Al, P, As, and Ga) at V1 sites of graphene functionalize the system in many interesting ways through the modification of its electronic and chemical properties. Likewise, several functionalization scenarios [20–24] for the enhancement of the electronic, magnetic, and catalytic characteristics of graphene have been proposed based on trapping of transition and noble metals atoms at graphene monovacancies.

Nevertheless, functionalization is not tantamount to doping. In order for a particular doping approach to be deemed successful, at least for employment in electronic devices, the insertion of dopants should not lead to large changes of the electronic properties of the host system, particularly of the carriers close to the valance-band maximum (VBM) or the conduction-band minimum (CBM). In this respect, a systematic validation of graphene substitutional group-III and -V dopants (other than B and N) is largely missing.

In this paper we use first-principles calculations to examine the role of Al, P, As, and Ga impurities as dopants for graphene. We find that, in contrast to B and N, substitution of one C atom by an aforementioned impurity is accompanied by undesired modification of the electronic densities of states in the immediate neighborhood of the VBM and CBM of graphene. By the same token, we show that an alternative, satisfactory *p*-type doping scenario pertains to trapping of Al, P, As, and Ga atoms at carbon double vacancies. The simple factors behind the success of this unconventional doping scheme are the correct valence of dopants, appropriate coordination of dopant and carbon atoms, and minimal modification of the planar π-bonding network.

The results were obtained with the plane-wave-based density-functional theory (DFT) code VASP [25]. We used a generalized gradient approximation functional [26] for exchange-correlation and projector-augmented waves [27] in the description of interactions between valence electrons and ionic cores. All calculations were performed on a large graphene supercell with 160 C atoms in the defect-free case, were spin unrestricted, and used a $3 \times 3 \times 1$ mesh for k-point sampling [28]. The energy cutoff for the plane-wave basis was set at 400 eV. Electronic density of states (DOS) calculations used a dense $9 \times 9 \times 2$ k-grid ($7 \times 7 \times 2$ k-grid for the spin-polarized P@V1 and As@V1 cases discussed below) and the tetrahedron method for integration in reciprocal space [29]. We have employed similar methodology in several previous DFT studies on graphene and graphene-related materials [30–33].

In the following we report and analyze the results about trapping of Al, P, As, and Ga atoms at monovacancies and divacancies of graphene and the concomitant effects on the DOS profile of the host system. We start with data on single-vacancy trapping, followed by results about dopants at double C vacancies.

Trapping of Al, P, As, or Ga atoms at a V1 site of graphene results in threefold coordination for the dopant and saturation of all carbon bonds. Figure 1 shows the configurations for an Al or P atom trapped at a carbon V1. Because of unequal size with respect to carbon atoms, the Al dopant protrudes out of the graphene sheet and is stabilized at a height of 1.9 Å with

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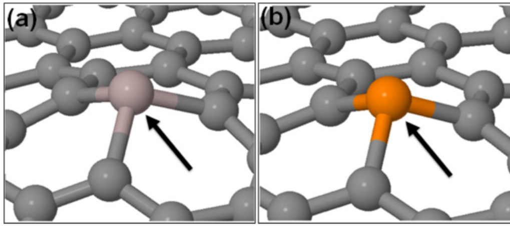

FIG. 1. (Color online) Dopants (shown with arrows) at a single carbon vacancy site of graphene: (a) Al and (b) P.

respect to the graphene layer. The corresponding height values for P, As, and Ga dopants at a V1 trap are 1.75, 2.10, and 2.10 Å, respectively. The results are in agreement with those reported in previous DFT studies about substitutional Al, P, As, and Ga dopants [10–13,19].

Given that similar configurations with B or N atoms dope graphene by shifting the Fermi level seamlessly in the valence and conduction bands, it is, at first thought, reasonable to expect that other elements of columns III and V of the Periodic Table may have the same effect. The DOS plots of Figs. 2 and 3 reveal that this is not true. A phosphorus atom at a V1 site (configuration P@V1) induces a gap of about 0.5 eV (for the concentration of one P impurity per 160 C atoms) and generates two separate strong peaks in the immediate vicinity of the Fermi level. When spin is not included in the calculation these two peaks merge into one right at the Fermi energy. Similar findings have been reported [12,14,16] for P-doped graphene and graphene nanoribbons. Clearly, the P@V1 configuration does not act as a dopant. An As atom trapped at a carbon single vacancy (As@V1) has a similar effect on the DOS profile (Fig. 3), with the difference that the two peaks close to the Fermi level are not separated by an energy gap.

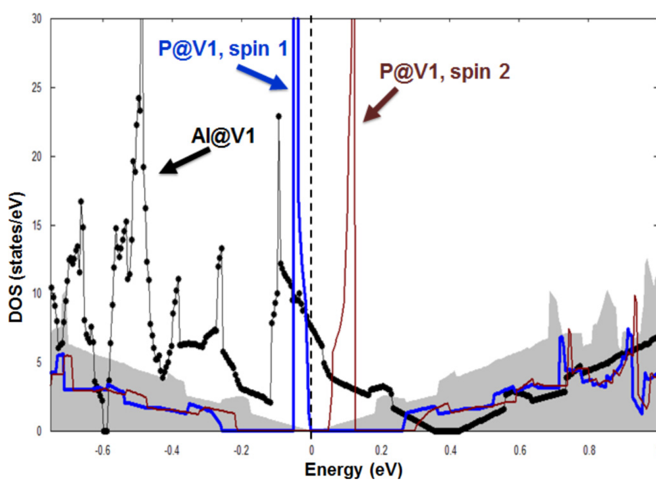

FIG. 2. (Color online) Electronic DOS for pristine graphene (shaded area), and graphene with P [P@V1, thick (thin) solid line for spin 1 (spin 2)] and Al (Al@V1, line with circles) atoms at a carbon single-vacancy (V1) site. Zero of energy is set at the Fermi level. All DOS results are based on supercells with 160 C atoms in the pristine case.

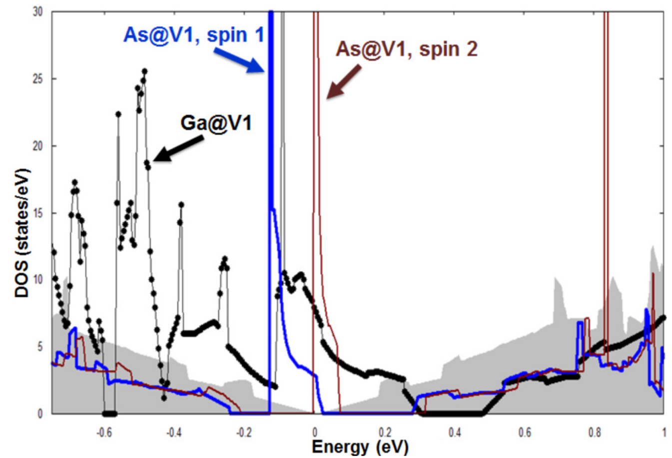

FIG. 3. (Color online) Electronic DOS for pristine graphene (shaded area), and graphene with As [As@V1, thick (thin) solid line for spin 1 (spin 2)] and Ga (Ga@V1, line with circles) atoms at a carbon single-vacancy (V1) site. Zero of energy is set at the Fermi level.

In contrast to P and As, Al and Ga atoms at V1 sites generate excess holes. The pertinent DOS plots of Figs. 2 and 3 show that the Al@V1 and Ga@V1 configurations move the Fermi energy inside the valence band of graphene by 0.3–0.4 eV for this particular dopant concentration. At the same time, however, the Al@V1 and Ga@V1 structures modify the electronic properties significantly, as revealed by the DOS comparison with the defect-free graphene case. Both Al and Ga impurities in these structures open up small band gaps and introduce strong deviations from the pristine DOS profile in the immediate vicinity of the VBM of graphene. Even if the dopant concentration is lowered the results show that the Al@V1 and Ga@V1-related states can act as centers for scattering of holes and degrade carrier mobility.

When two carbon atoms are removed from a graphene sheet, four dangling bonds are created. Consequently, a carbon V2 offers the possibility of capturing impurities in higher, fourfold coordination. Previous studies [34–41] have, indeed, shown that various adatoms are trapped by V2's in very stable configurations similar to the ones depicted for Al and P in Fig. 4. Given that Al, P, As, and Ga all show tetrahedral bonding in silicon, the fourfold structures of Fig. 4 are appealing with respect to the stabilization of dopants with the right coordination. In addition, the size of a graphenic V2 seems to be just about right for the capture of these impurities.

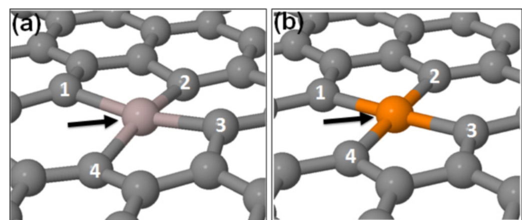

FIG. 4. (Color online) Dopants (shown with arrows) at a double carbon vacancy site of graphene: (a) Al and (b) P.

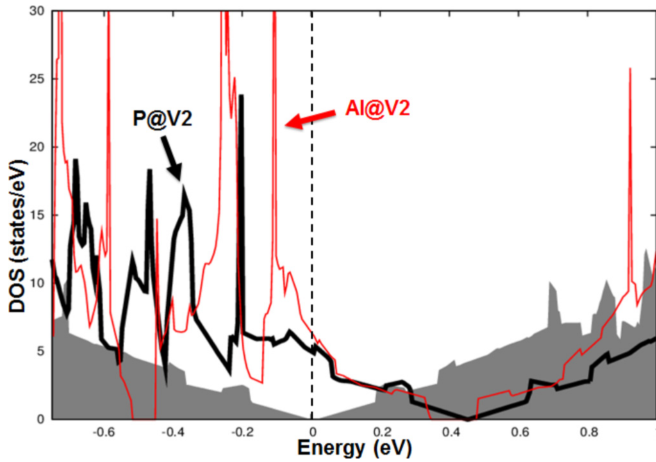

FIG. 5. (Color online) Electronic DOS for pristine graphene (shaded area), and graphene with P (P@V2, thick line) and Al (Al@V2, thin line) atoms at a carbon divacancy (V2) site. Zero of energy is set at the Fermi level.

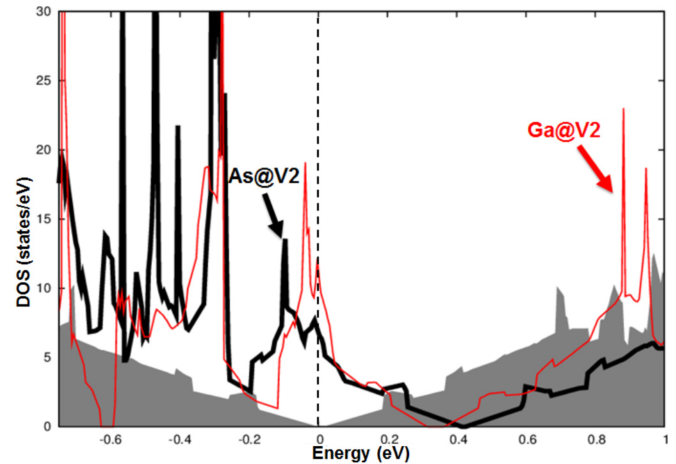

FIG. 6. (Color online) Electronic DOS for pristine graphene (shaded area), and graphene with As (As@V2, thick line) and Ga (Ga@V2, thin line) atoms at a carbon divacancy (V2) site. Zero of energy is set at the Fermi level.

When a phosphorus atom is trapped by a V2 (P@V2 configuration), the impurity resides at the same level (within 0.1 Å) as all surrounding carbon atoms. The system thus retains the planar character of graphene, contrary to the case of large protrusions encountered for P trapping at V1 sites. The Al@V2 structure, on the other hand, shows signs of tetrahedral bonding. Specifically, the carbon atoms 1 and 3 (2 and 4) of Fig. 4(a) are located above (below) the Al impurity with a height difference of 0.20–0.25 Å. Similar nascent tetrahedral geometries are obtained for the Ga@V2 case with the same height differences (0.20–0.25 Å) between the dopant and the neighboring carbon atoms. The As@V2 configuration is reminiscent of the P@V2 geometry with a local corrugation of less than 0.1 Å.

Figure 5 compares the electronic DOS of pristine graphene and graphene sheets with one P@V2 or Al@V2 structure per 160 C atoms. The phosphorus results are particularly interesting. They show that the P@V2 configuration generates excess holes, while the associated changes in the DOS profile become significant far away (by more than 0.6–0.7 eV) from the valence-band maximum. In this sense, the P@V2 configuration is an effective hole dopant for graphene, the best performer among the impurities considered in this work.

The second-best choice for V2-related doping is arsenic. The corresponding DOS data of Fig. 6 show that the As@V2 structure has effects similar to those of P@V2. It turns graphene into a p-type material, while the energy difference between As@V2-induced states and the VBM is about 0.5 eV, slightly lower than that of the P@V2 case. Al@V2 and Ga@V2 configurations also shift the Fermi level inside the valence band of graphene. Nonetheless, their effect on the DOS profile is more pronounced for low-energy carriers as they open small band gaps and create states within 0.3 eV from the VBM.

An additional important issue is the sensitivity of particular dopant configurations to irradiation. This sensitivity can be characterized by the displacement threshold energy, which is the minimum kinetic energy E_K that must be delivered to an atom in a collision with an energetic particle, in order for the former to be knocked out of its position [42]. In pristine graphene we obtain an E_K of 22 eV. Notably, E_K drops to 17–18 eV for the ejection of a C atom that is bonded to P in the P@V1 and P@V2 cases. The threshold electron energy E of the electron beam can be estimated based on the classical binary collision formula, which gives $E \approx m_C E_K/4m_e$, where m_C (m_e) is the mass of a carbon atom (an electron) [42]. Since E is proportional to E_K, using the upper limit of the threshold energy of 100 eV for pristine graphene found in the experiments [43], one can obtain the threshold energy of 77–82 keV in the P@V1 and P@V2 cases.

Therefore, by tuning the e-beam energy one can use electron irradiation to transform P@V1 structures to P@V2 geometries, when graphene samples have initially a majority of P@V1 species. On the other hand, irradiation can also transform P@V2 configurations to structures with P dopants trapped at carbon trivacancies. We should also note that the relevant E_K for the ejection of a P atom from the P@V1 configuration is only 14 eV. However, due to the larger mass of P, the corresponding e-beam energy threshold is about 200 keV.

The success of doping by Al, P, As, and Ga atoms trapped at divacancies raises the question whether other impurities trapped at these defects can play a similar role. The results discussed above offer useful guidelines for this search. The potential dopants should be stabilized in fourfold coordination and have the right size so as to induce minimal protrusions with respect to the surrounding graphene sheet. Of course, these are only search guidelines, not guarantees of efficient doping. For example, silicon and germanium fulfill both coordination and size conditions [44]. Yet, we have found that substitutional Si and Ge atoms, either at a single vacancy, or at a double vacancy, do not shift the Fermi level inside the conduction or valence bands of graphene. Instead, they open small energy band gaps of the order of 0.1 eV.

Future studies can explore the potential of different impurities to act as graphene dopants when trapped at divacancies, or, perhaps, suitable multivacancy sites. Likewise, it is interesting

to investigate whether this doping scheme works for other systems. Several emerging two-dimensional materials (for example, silicene [45] and graphane [46,47]) have bonding networks that resemble the hexagonal honeycomb lattice of graphene. Hence, these systems are good candidates for the alternative divacancy-based doping approach discussed in the above.

In summary, using density-functional theory calculations, we have identified an efficient way to dope graphene with holes by trapping Al, Ga, and, especially, P or As atoms at C divacancy sites. Because this substitution is associated with small changes in the electronic density of states profile of low-energy holes, divacancy-related graphene doping with Al, P, Ga, and As is superior to the conventional approach that relies on substitution of one C atom by one impurity. Under certain irradiation conditions [8], double vacancies are created in larger numbers than single vacancies. Combined with the fact that the former are more stable and less mobile than the latter, the best scenario to achieve doping using divacancies is to first create them through irradiation and then deposit the dopant atoms.

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[1] X. Zhou, F. Wang, Y. Zhu, and Z. Liu, J. Mater. Chem. **21**, 3353 (2011).
[2] D. S. L. Abergel, V. Apalkov, J. Berashevich, K. Ziegler, and T. Chakraborty, Adv. Phys. **59**, 261 (2010).
[3] S. T. Pantelides, Y. Puzyrev, L. Tsetseris, and B. Wang, MRS Bull. **37**, 1187 (2012).
[4] R. Lv and M. Terrones, Mater. Lett. **78**, 209 (2012).
[5] L. Tsetseris and S. T. Pantelides, Phys. Rev. B **85**, 155446 (2012).
[6] B. Wang, L. Tsetseris, and S. T. Pantelides, J. Mater. Chem. A **1**, 14927 (2013).
[7] H. Terrones, R. Lv, M. Terrones, and M. S. Dresselhaus, Rep. Prog. Phys. **75**, 062501 (2012).
[8] A. W. Robertson, C. S. Allen, Y. A. Wu, K. He, J. Olivier, J. Neethling, A. I. Kirkland, and J. H. Warner, Nat. Commun. **3**, 1144 (2012).
[9] Z. M. Ao, J. Yang, S. Li, and Q. Jiang, Chem. Phys. Lett. **461**, 276 (2008).
[10] Z. M. Ao, Q. Jiang, R. Q. Zhang, T. T. Tan, and S. Li, J. Appl. Phys. **105**, 074307 (2009).
[11] J. Dai, J. Yuan, and P. Giannozzi, Appl. Phys. Lett. **95**, 232105 (2009).
[12] J. Dai and J. Yuan, J. Phys.: Condens. Matter **22**, 225501 (2010).
[13] J. Dai and J. Yuan, Phys. Rev. B **81**, 165414 (2010).
[14] P. A. Denis, Chem. Phys. Lett. **492**, 251 (2010).
[15] Y. Sun, L. Chen, F. Zhang, D. Li, H. Pan, and J. Ye, Solid State Commun. **150**, 1906 (2010).
[16] E. Cruz-Silva, Z. M. Barnett, B. G. Sumpter, and V. Meunier, Phys. Rev. B **83**, 155445 (2011).
[17] Y. Lv, G. Zhuang, J. Wang, Y. Jia, and Q. Xie, Phys. Chem. Chem. Phys. **13**, 12472 (2011).
[18] Y. Tang, Z. Yang, X. Dai, D. Ma, and Z. Fu, J. Phys. Chem. C **117**, 5258 (2013).
[19] H. Wang, H. Wang, Y. Chen, Y. Liu, J. Zhao, Q. Cai, and X. Wang, Appl. Surf. Sci. **273**, 302 (2013).
[20] E. J. G. Santos, A. Ayuela, S. B. Fagan, J. Mendes Filho, D. L. Azevedo, A. G. Souza Filho, and D. Sanchez-Portal, Phys. Rev. B **78**, 195420 (2008).
[21] E. J. G. Santos, A. Ayuela, and D. Sanchez-Portal, New J. Phys. **12**, 053012 (2010).
[22] Y. Tang, Z. Yang, and X. Dai, J. Chem. Phys. **135**, 224704 (2011).
[23] M. Wu, C. Cao, and J. Z. Jiang, New J. Phys. **12**, 063020 (2011).
[24] Z. Yang, Z. Yao, G. Li, G. Fang, H. Nie, Z. Liu, X. Zhou, X. Chen, and S. Huang, ACS Nano **6**, 205 (2012).
[25] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).
[26] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[27] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[28] D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).
[29] O. Jepson and O. K. Andersen, Solid State Commun. **9**, 1763 (1971).
[30] L. Tsetseris and S. T. Pantelides, J. Phys. Chem. B **113**, 941 (2009).
[31] L. Tsetseris and S. T. Pantelides, Carbon **47**, 901 (2009).
[32] L. Tsetseris and S. T. Pantelides, Appl. Phys. Lett. **99**, 143119 (2011).
[33] O. Ziogos and L. Tsetseris, J. Phys.: Condens. Matter **25**, 085301 (2013).
[34] A. V. Krasheninnikov, P. O. Lehtinen, A. S. Foster, P. Pyykko, and R. M. Nieminen, Phys. Rev. Lett. **102**, 126807 (2009).
[35] B. Sanyal, O. Eriksson, U. Jansson, and H. Grennberg, Phys. Rev. B **79**, 113409 (2009).
[36] O. Cretu, A. V. Krasheninnikov, J. A. Rodriguez-Manzo, L. Sun, R. M. Nieminen, and F. Banhart, Phys. Rev. Lett. **105**, 196102 (2010).
[37] A. T. Lee, J. Kang, S.-H. Wei, K. J. Chang, and Y.-H. Kim, Phys. Rev. B **86**, 165403 (2012).
[38] H. Wang *et al.*, Nano Lett. **12**, 141 (2012).
[39] K. M. Fair, X. Y. Cui, L. Li, C. C. Shieh, R. K. Zheng, Z. W. Liu, B. Delley, M. J. Ford, S. P. Ringer, and C. Stampfl, Phys. Rev. B **87**, 014102 (2013).
[40] M. Kaukonen, A. V. Krasheninnikov, E. Kauppinen, and R. M. Nieminen, ACS Catal. **3**, 159 (2013).
[41] A. W. Robertson *et al.*, Nano Lett. **13**, 1468 (2013).
[42] A. V. Krasheninnikov and K. Nordlund, J. Appl. Phys. **107**, 071301 (2010).
[43] J. C. Meyer *et al.*, Phys. Rev. Lett. **108**, 196102 (2012).
[44] W. Zhou, M. D. Kapetanakis, M. P. Prange, S. T. Pantelides, S. J. Pennycook, and J. C. Idrobo, Phys. Rev. Lett. **109**, 206803 (2012).
[45] D. Kaltsas, L. Tsetseris, and A. Dimoulas, J. Phys.: Condens. Matter **24**, 442001 (2012).
[46] J. O. Sofo, A. S. Chaudhari, and G. D. Barber, Phys. Rev. B **75**, 153401 (2007).
[47] L. Tsetseris and S. T. Pantelides, J. Mater. Sci. **47**, 7571 (2012).