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Substitutional impurity in the graphene quantum dots



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HIGHLIGHTS

- We discuss the effect of the substitutional doping of graphene dot on its eigenstate energies and total energy change.
- For O the effect of lattice distortion was included.
- According to our model B, N, and O can form stable substitutional defect in graphene quantum dot.

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ABSTRACT

The process of formation of the localized defect states due to substitutional impurity in sp^2 -bonded graphene quantum dot is considered using a simple tight-binding-type calculation. We took into account the interaction of the quantum dot atoms surrounding the substitutional impurity from the second row of elements. To saturate the external dangling sp^2 orbitals of the carbon additionally 18 hydrogen atoms were introduced. The chemical formula of the quantum dot is $H_{18}C_{51}X$, where X is the symbol of substitutional atom. The position of the localized levels is determined relative to the host-atoms (C) ϵ_p energies. We focused on the effect of substitutional doping by the B, N and O on the eigenstate energies and on the total energy change of the graphene dots including for O the effect of lattice distortion. We conclude that B, N, and O can form stable substitutional defects in graphene quantum dot.

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1. Introduction

Graphene, just one layer of carbon atoms, is an isolated graphite layer. It is the first example of truly two dimensional crystals Carbon atoms arranged in a two-dimensional honeycomb lattice form a building block for three dimensional graphite, as well as “one-dimensional” carbon nanotubes and “zero-dimensional” fullerenes. It is a gapless semiconductor with unique electronic properties resulting from a charge-conjugation symmetry between electrons and holes and it possesses an internal degree of freedom similar to a “chirality” for ultrarelativistic elementary particles. The high electron mobility in graphene and its unique electrical properties make it a prospective material for next-generation, carbon-based electronics. The prospects for future application in nanoelectronics have put graphene in the focus of many theoretical and experimental studies (see Ref. [1] and references therein).

Following the progress in the fabrication of graphene based devices [1], lower dimensional structures such as graphene ribbons [2,3], and more recently graphene quantum dots [4], are attracting increasing attention due to their nontrivial electronic and

magnetic properties. In particular, it was shown that when an electron is confined to a triangular atomic thick layer of graphene with zigzag edges, its energy spectrum collapses to a shell of degenerate states at the Fermi level (Dirac point) [5] similar to the edge states in graphene ribbons [2,3], but isolated from the remaining states by a gap. This opens up the possibility to design a strongly correlated electronic system as a function of fractional filling of the shell, in analogy to the fractional quantum Hall effect [6], but without the need for a magnetic field.

Applications exploiting graphene's unique electronic properties require an understanding of impurity effects in this material. Adsorbates on graphene as well as the intentionally introduced impurities are sources of a free electron or a hole and they create scattering centers. Among the scattering mechanisms limiting the electron mobility in graphene under discussion there are charged impurities [7] and resonant states related to adsorbates on graphene (see Refs. [8–13] and references therein). Wehling et al. [13] discussed the influence of adsorbates on the electrical properties of graphene. According to this survey open-shell adsorbates like NO_2 , alkali and halogen adatoms (except for fluorine) are very reactive and they act as direct dopants. They accept or donate one electron and bind ionically to graphene but they hybridize weakly with the graphene bands and they experience very low migration

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barriers. Recent theoretical and experimental studies on graphene doping showed the possibility of substituting C atoms with B and N atoms [14–16]. Substitutional doping can modify the electronic band structure of graphene.

In Ref. [14] the authors reported on doping graphene by substituting some C atoms with N atoms. N-doped graphene was obtained by NH_3 annealing after N^+ -ion irradiation of graphene samples. The authors observed a transition of graphene from p-type to n-type after an annealing of irradiated samples in NH_3 . In Ref. [15] the authors reported that substitutional doping during growth could be used to alter the electronic properties of monolayer graphene. They used scanning tunneling microscopy, Raman spectroscopy, X-ray spectroscopy, and first-principles calculations to characterize individual nitrogen dopants in the monolayer graphene grown on a copper substrate. They found that nitrogen atoms occupied the place of carbon atoms, and that the extra electron introduced together with the nitrogen changed properties of the electronic structure of graphene, but only in the range of a few lattice spacing of the nitrogen dopant site. In Ref. [16] the authors performed an ab initio total-energy calculations to investigate the effect of substitutional B and N doping in the electronic and structural properties of graphene with grain-boundary defects. Their results indicated that the incorporation of N and B atoms into the defective region was an energetically favorable process. The calculated electronic properties showed that the incorporation of a single substitutional B (N) atom produced p-type (n-type) doping in all investigated grain-boundary structures.

In our previous paper [17] we have presented the results of calculations of the energy levels introduced by doping of graphene layers by substitutional impurities of the second period of the periodic table using the Green's-functions framework and the tight-binding method. We discussed the possibility of the existence of well-defined resonant states that coincide with the valence band and the conduction band near the Dirac point. We concluded that in the case of a high substitutional doping by O the Fermi level could be attached to the appropriate energy level and the resonant motion of the conduction electrons may be significantly disrupted.

In this paper we present the results of energy-level calculations associated with the substitutional impurities in graphene quantum dots. The ideal unrelaxed substitutional impurities are defined by replacing carbon atom at the center of a quantum dots by an impurity atom and considering the positions of all other atoms to be unchanged. According to that simple model we discuss the effect of substitutional doping by B, N, and O on the total energy change of the graphene dots, as well as the energy levels introduced by the dopants.

For O we examined the effect of lattice distortion resulting from replacement of the central carbon atom by O atom. In our calculations we assumed that the distortion is a function of the atomic radius.

2. Methodology

We consider two dimensional honeycomb lattice composed of N ($N=51$) carbon atoms placed at the positions \vec{r}_i ($i=1, 2, N$) of two different kinds of atoms ($\kappa=\kappa(i)=1,2$) and an substitutional impurity atom placed at \vec{r}_0 position and an $M=18$ hydrogen atoms which task is to saturate dangling sp^2 orbitals of the outside carbon atoms (see Fig. 1). We consider the both the unrelaxed and relaxed lattice around the substitutional impurity by considering the positions of the atoms surrounding the impurity are unchanged and changed, respectively.

The calculations were carried out using tight-binding method. As a basis for the expansion of electron wave function of

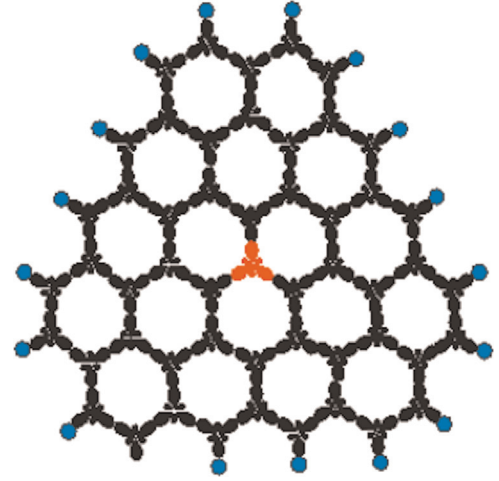


Fig. 1. Red – the sp^2 orbitals of the substitutional impurity, black – the 51 carbon host atoms surrounding the impurity, blue – 18 surrounding hydrogen atoms.

substitutional and host atoms we used p_z atomic orbitals and sp^2 hybrids. For the atom at the positions \vec{r}_i , with \vec{r}_0 included, we have.

$$\varphi_{in}^{(\kappa)} = \varphi_n^{(\kappa)}(\vec{r} - \vec{r}_i) = \frac{1}{\sqrt{3}} \left[s^{(\kappa)}(\vec{r} - \vec{r}_i) + \eta_i^{(\kappa)} \vec{e}_n \vec{p}^{(\kappa)}(\vec{r} - \vec{r}_i) \right] \quad (1)$$

where $\varphi_n^{(\kappa)}(\vec{r} - \vec{r}_i)$ is a hybrid centered on the i th site with the positive lobe pointing toward the n th nearest-neighbor site ($n=1, 2, 3$). Here $\vec{e}_1 = \left(\frac{\sqrt{6}}{2}, \frac{\sqrt{2}}{2} \right)$, $\vec{e}_2 = \left(-\frac{\sqrt{6}}{2}, \frac{\sqrt{2}}{2} \right)$, $\vec{e}_3 = (0, -\sqrt{2})$ and $\vec{p}^{(\kappa)} = (p_x^\kappa, p_y^\kappa)$. The factor $\eta_i^{(\kappa)} = \pm 1$ for $\kappa=1$ and 2 respectively see also Fig. 2a. For the substitutional atom ($1', 2', 3'$) in Fig. 2a, $\eta_i^{(\kappa)} = \eta_i^{(1)} = 1$. For $n=4$ we have

$$\varphi_{i4}^{(\kappa)} = p_z^{(\kappa)}(\vec{r} - \vec{r}_i) \quad (2)$$

For both kind of atoms, and for the hydrogen atoms

$$\varphi_j = s(\vec{r} - \vec{r}_j) \quad (2a)$$

The one-electron wave function may be written as

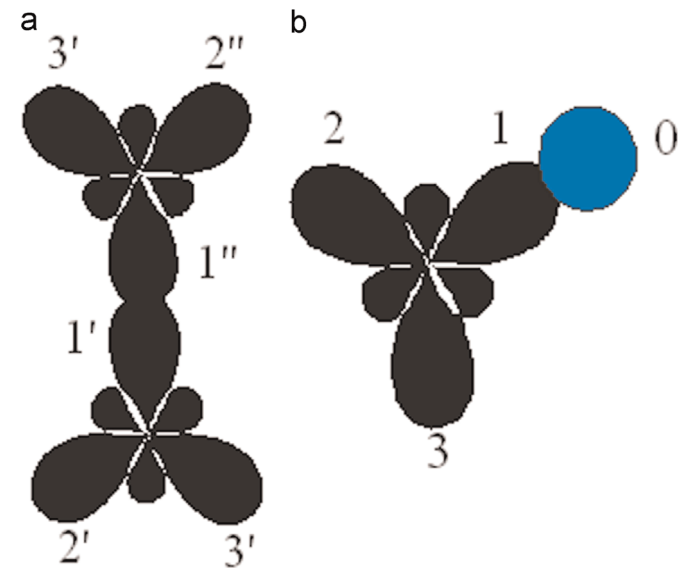


Fig. 2. Schematic illustration of geometric settings for (a) sp^2 orbitals of the substitutional atom or host (C) atom ($1', 2', 3'$) relative to the surrounding C atoms ($1'', 2'', 3''$), (b) s orbital of hydrogen (H) atom (0) relative to the nearest sp^2 orbitals of the C atom ($1, 2, 3$).

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