Spin-polarized electron transmission through B-doped graphene nanoribbons with Fe functionalization: a first-principles study

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Abstract

In this study, we investigate the electron transport properties of a B-doped armchair graphene nanoribbon (AGNR) suspended between graphene electrodes based on first-principles calculations. Our calculations reveal that one of the electron transmission channels of a pristine AGNR junction is closed by the B-doping. We then proceed to explore the effect of the B-doping on the spin-polarized electron transport behavior of a Fe-functionalized AGNR junction. As a result, transmission channels for majority-spin electrons are closed and the spin polarization of the electron transmission is enhanced from 0.60 for the Fe-functionalized AGNR junction to 0.96 for the B- and Fe-codoped one. This observation implies that the codoped AGNR junction can be employed as a spin filter. In addition, we investigate the electronic nature of the transmission suppression caused by the B-doping. A detailed analysis of the scattering wave functions clarifies that a mode modulation of an incident wave arises in the B-doped AGNR part and the incident wave connects to an evanescent wave in the transmission-side electrode. For pristine and Fe-functionalized AGNR junctions, such a mode modulation is not observed and the incident wave connects to a propagating wave in the transmission-side electrode. Tuning of electron transport property by exploiting such a mode modulation is one of promising techniques for designing functionality of spintronics devices. We also discuss the general correspondence between the electron transmission spectrum and the density of states of a junction.

1. Introduction

Graphene nanoribbons (GNRs), a form of quasi-one-dimensional graphene nanostructures, are known to have various electronic structures depending on the ribbon width and the edge geometry [1]. Therefore, in the last two decades the physical and chemical properties have been strenuously studied from both theoretical and experimental points of view [2–13]. Nowadays, in addition to the application of a conductive GNR to wiring between electronic device elements, a GNR is considered as a promising platform for building up electronic, spintronic, and quantum device elements on and in itself.

In 2011, Zhang et al theoretically studied spin-polarized electron transport property of a Fe monatomic chain deposited on a zigzag GNR (ZGNR), in which Fe atoms weakly interact with each other via the ZGNR [14]. The authors revealed that when a Fe chain is formed on an edge of a ZGNR, the spin polarization of the electronic conductance around the Fermi energy $E_F$ is enhanced due to the coupling between the edge states of the ZGNR and the electronic states of the Fe atoms. Therefore, their study suggests a potential application of Fe-functionalized GNRs for spintronic device elements.
Tuning the electronic properties of GNRs has been achieved not only by deposition of heteroatoms on GNRs but also by substitutionally implanting heteroatoms in GNRs [15–21]. In 2015, Cloke et al [22] and Kawai et al [23] independently synthesized a B-doped armchair GNR (AGNR), which has a width of seven C atoms, and therefore, the host GNR is referred to as 7AGNR throughout this paper. In the B-doped 7AGNR, a pair of B atoms are substitutionally embedded in a specific position of a hexagon of the honeycomb structure in a periodic manner so that the B-doped 7AGNR is characterized by a superlattice structure in the direction of the ribbon axis. Their studies reveal that a B-doped 7AGNR has the band gap narrower than a pristine 7AGNR, and the B-atom sites are chemically reactive as a Lewis acid. Therefore, a B-doped 7AGNR is considered as one of promising p-type semiconductor platforms in which the p-type dopants appear periodically along the ribbon axis. Indeed, since the first synthesis of the B-doped 7AGNR, the electronic structure [22–24], electron transport properties [25], chemical reactivity [26], and other properties [27, 28] have been strenuously investigated in details so far.

In a recent study, we investigated the structural and electronic properties of the aforementioned B-doped 7AGNR deposited on an Au(111) substrate [24]. As the result of our previous study, the valence and conduction bands of the B-doped 7AGNR are revealed to contain contribution from the dopant states. On this basis, in this study we theoretically investigate the spin-polarized electron transport property of a B- and Fe-codoped 7AGNR junction, where a fragment of a B-doped 7AGNR is suspended between a pair of graphene electrode and is functionalized by adsorption of a single Fe atom on it. The single magnetic atom is placed so as to be chemically combined with the reactive site of the platform. This complex junction is referred to as a (B + Fe)-codoped 7AGNR junction for convenience throughout this paper. The electron transport property of the codoped junction is evaluated based on first-principles calculations within the framework of the density functional theory [29–31]. To clarify the influence of each of the dopant and the adsorbate on the electron transport property of a pristine 7AGNR junction, we carry out electron transport calculations for pristine, B-doped, and Fe-functionalized 7AGNR junctions as well. For further understanding of the electronic nature of the electron transport properties characteristic of respective junctions, we examine the electron transmission in details together with the density of states (DOS), the electronic band structures, and the scattering wave functions of the junctions.

2. Calculation models and methods

2.1. Calculation model

A schematic representation of a 7AGNR junction employed in this study is depicted in figure 1. The junction is composed of three parts, i.e., a 7AGNR part as a scattering region, and left and right graphene sheets as a pair of semi-infinite electrodes. The 7AGNR part is made of four zigzag C lines aligned along the junction axis, which is indicated by thick line with the arrows in figure 1(a). Each of the zigzag edge of a 7AGNR is connected to either left or right graphene electrode. The remaining dangling bonds are terminated by H atoms. The transition region, in which scattering wave functions are calculated, is defined as the rectangle enclosed by the dashed lines in the middle of figure 1(a). The transition region includes not only the 7AGNR part but also five zigzag C lines composing a part of the graphene electrode for each side so that the effective potential converges to that of the graphene electrode at the both ends of the transition region. Assuming the C–C bond length in the junctions before geometrical optimization to be 1.42 Å, we set the length of the transition region in the z direction to \( L_z = 29.82 \) Å. In the x direction, the side length of the transition region is set to \( L_x = 14.76 \) Å and the periodic boundary condition is imposed. The unit cell of the graphene electrode has the same length in the x direction to that of the transition region, as indicated by a small rectangle enclosed by the dashed lines in figure 1(a). In the y direction, an electrode unit cell contains two zigzag C lines, and therefore, the unit-cell length is set to \( L_y^{(elec)} = 4.26 \) Å. When B atoms are included in a junction, the C atoms indicated by the blue balls in figure 1 are replaced by B atoms. When a Fe atom is included in a junction, following a preceding study by Valencia et al [32], a Fe atom is placed at a hollow site in the middle of the 7AGNR, as indicated by the red balls in figure 1.

2.2. Geometrical optimization

The geometrical optimization of the transition region is performed using VASP code [33–36], a plane-wave-based implementation of the projector-augmented wave (PAW) pseudopotentials originally proposed by Blöchl [37, 38]. The exchange-correlation interactions are treated by the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (GGA-PBE) [39, 40]. In the geometrical optimization of pristine and B-doped 7AGNR junctions, we relax the atoms in the 7AGNR part and those at the interface between the 7AGNR part and the graphene electrode only in the x and z directions under the assumption of periodic boundary conditions in these directions. For the y direction, the atomic
positions are fixed for preserving the planar shape, and the length of the computing unit cell is set to $L_y = 9.12$ Å so that interaction between the graphene planes in neighboring unit cells is negligible. The rest of the atoms in the transition region, i.e., the C atoms in the four zigzag C lines in each end of the transition region, are fixed so as to keep the ideal honeycomb geometry of a graphene. For the 7AGNR junctions including a Fe atom, the six atoms composing the hexagon below the Fe atom are relaxed also in the $y$ direction.

In the geometrical optimization, we employ an energy cutoff of 500 eV and a $Γ$-centered $k$-point mesh of $6 \times 1 \times 1$. The convergence criteria for electronic and geometrical optimization are set to $1.0 \times 10^{-4}$ eV and 0.01 eV Å$^{-1}$, respectively.

2.3. Transport calculation

Employing the optimized geometries, electron transport calculations of the four junctions are performed using JuTrans code \cite{41–43}, which is an implementation of the wave-function matching method \cite{44–46} based on the real-space finite-difference formalism \cite{47, 48}. To keep consistency with the geometrical-optimization calculations, the PAW pseudopotentials are used for describing the interaction between ion cores and valence electrons, and the GGA-PBE is used for treating the exchange–correlation interaction. Scattering wave functions in a transition region are determined in a non-self-consistent manner to a set of given effective potential and pseudopotential parameters. Therefore, the effective potential and pseudopotential parameters of a transition region are determined in advance by using the electronic structure calculation code RSPACE \cite{44, 49–51}. Since RSPACE code is based on the real-space finite-difference formalism as well as JuTrans code, one can treat physical quantities on the same footing. In the electron transport calculations we assume that incident electron waves are injected from the left electrode (see figure 1). The real-space grid spacing is set to 0.18 Å.

The DOS and electronic band structure of a transition region that referred to in the following discussion are calculated under imposition of the periodic boundary conditions using the RSPACE code. In addition, we employ eigenchannel decomposition technique \cite{52–55} to discuss electron transport properties in terms of eigenchannels, which represent scattering states independent of each other and without any interchannel scattering. Channel-decomposed transmissions $T_i$ are obtained by diagonalizing a transmission matrix using a unitary transformation:

$$U^\dagger T^\dagger TU = \text{diag}\{T_i\},$$

where $T$ and $U$ are a transmission-coefficient matrix and a unitary matrix, respectively. A set of scattering wave functions is also decomposed and reconstructed into multiple channel wave functions using $U$. 

Figure 1. Schematic representation of a calculation model used. (a) and (b) show the top and side view, respectively. The black (white) balls represent C (H) atoms. When calculating a B-doped (Fe-functionalized) system, B (Fe) atom is placed at the position of the blue (red) ball. The dashed lines represent the boundaries of the computational unit cell. The large rectangle defined by the dashed lines represents the transition region, and the tall rectangle the electrode unit cell. The thick line indicated by the two arrows denotes the junction axis.
3. Results and discussion

3.1. Geometry and electronic structure

Firstly we discuss the optimized geometries and electronic structures of the junctions. The C–C bonds lengths in the 7AGNR part of the optimized pristine 7AGNR junction are almost identical to those of an infinite AGNR, which are reported by Wang et al [56]. The electronic structure is, however, significantly different from that of an infinite 7AGNR: a preceding study by Linden et al shows that an infinite 7AGNR has the band gap between the valence and conduction bands of \( \approx 1.5 \) eV and the energy dispersion of each band is more than 1 eV [57]. Compared with their result, the DOS of a pristine 7AGNR junction drawn in figure 2(a) exhibits the narrower band gap of \( \approx 0.4 \) eV, and each of the valence and conduction bands is flatter with energy dispersion of \( \approx 0.2 \) eV. A detailed investigation on the electronic structures is presented in section S1 of supplementary material (https://stacks.iop.org/NJP/22/063022/mmedia). We speculate that these flat bands originate from the heterojunction composed of a graphene and a 7AGNR. Indeed, such a small band gap and flat bands are reported for a quasi-one-dimensional periodic heterojunction composed of 7AGNR and 9AGNR by Rizzo et al [58].

When B atoms are substitutively doped into a pristine 7AGNR junction, the B–C bond indicated by P (Q) in figure 1(a) stretches from 1.41 Å (1.43 Å) to 1.49 Å (1.52 Å) while the C–C bond indicated by R in figure 1(a) slightly shortens from 1.43 Å to 1.40 Å. These geometrical changes are consistent with a report by Di Valentin et al [59]. As the result of the elongation of the bond Q, the width of the 7AGNR part increases by \( \approx 0.17 \) Å. It is known that the p-states of the B atoms contribute to the \( \pi \)-characteristic valence and conduction bands of a B-doped 7AGNR [22, 24]. The contribution of the B atoms to these bands is confirmed in the DOS of the B-doped 7AGNR junction shown in figure 2(b).

The optimized distance between the Fe atom and the 7AGNR plane is 1.54 Å for the Fe-functionalized 7AGNR junction, and 1.58 Å for the (B + Fe)-codoped one. The former agrees with a preceding work on Fe adsorption onto a graphene by Liu et al [60]. The 7AGNR parts preserve the planar shape upon the Fe

![Figure 2. Total and projected density of states (DOS) of the transition regions of (a) pristine, (b) B-doped, (c) Fe-functionalized, and (d) (B + Fe)-codoped 7AGNR junctions. The total DOSs are shown by the gray area, and the contribution of the \( \pi \)-states from the 7AGNR part including the B atoms, of the d-states from the Fe atom, and of the \( \pi \)-states from the B atoms are drawn by the red, blue, and green curves, respectively. For the spin-polarized systems, the DOSs for the up- and down-spin electrons are separately depicted.](https://stacks.iop.org/NJP/22/063022/mmedia)
adsorption. This is contrast to a study by Fan et al [61], which report significant deformation of a planar C-based scattering body upon an Au adsorptions. The adsorption energies of a Fe atom onto pristine and B-doped 7AGNR junctions are 0.70 and 1.92 eV, respectively. Consequently, our calculations reveal that although the Fe-7AGNR distance is almost identical for the two junctions, the Fe atom is more strongly bound to the B-doped 7AGNR junction than to the pristine one. The difference can be understood from the reactivity of the B site: Pizzochero et al compared the adsorption energy of a H$_2$ molecule onto the pristine and B-doped graphenes, and revealed that the adsorption onto the B-doped graphene is 0.74 eV more stable than that onto the other [62]. Indeed, Kawai et al points out that the electron-deficient B site has Lewis acidity and is chemically reactive [23].

Now, we speculate the electron transport properties of the junctions from the DOSs in figure 2. In general, an electron transmission spectrum has a peak or a finite value at the energy where the corresponding DOS exhibits significant intensity. Therefore, it is supposed that pristine and B-doped 7AGNR junctions exhibit finite transmission in certain energy ranges at both sides of $E_F$. For a Fe-functionalized 7AGNR junction, one may expect finite transmission in certain energy ranges at both sides of $E_F$ for both up- and down-spin electrons. In addition, one expects transmission peaks originating from the three DOS peaks of the Fe d states observed at energy $E = E_F - 0.4$, $E_F - 0.25$ and $E_F + 0.27$ eV. The DOS of a (B + Fe)-codoped 7AGNR junction suggests finite transmission for up-spin electrons in energy ranges at both sides of $E_F$. For down-spin electrons, the transmission spectrum is supposed to have finite values for $E > E_F - 0.3$ eV, and a peak corresponding to the DOS peak just below $E_F$. The validity of the speculation is to be assessed in the following discussion.

### 3.2. Electron transport property

Firstly, we focus on the electron transport properties only of pristine and (B + Fe)-codoped 7AGNR junctions. Since the graphene electrode has periodicity in the x direction as seen in figure 1, we take into account multiple $k$-points in the x direction, $k_x$, for discussing the transport properties properly. Figure 3 shows the total electron transmissions of the two junctions as functions of $k_x$ and $E$ with respect to $E_F$. As a graphene has the Dirac-cone band structure around $E_F$ and the K (K') point of the first Brillouin zone$^2$, propagating waves that are used for incident waves in transport calculation do not exist at $E$ between the upper and lower cones. The $(k_x, E)$ area without incident wave is indicated by the shaded areas in figure 3.$^3$

Therefore, we calculate the electron transmission only at $(k_x, E)$ in the non-shaded areas in figure 3. According to figure 3(a), the electron transmission of the pristine 7AGNR junction varies in the range from 0.23 to 0.36 over the $(k_x, E_F)$ plane, except for large $|k_x|$ with relatively large transmission around 0.55. For the (B + Fe)-codoped 7AGNR junction, the up-spin transmission is not more than 0.1 except for $E = E_F + 0.5$ eV, while the down-spin transmission is larger than 0.55 for $E > E_F - 0.3$ eV. These observations suggest that due to the B doping and Fe adsorption, the up-spin transmission probability is suppressed, while down-spin one significantly increases. Consequently, the (B + Fe)-codoped 7AGNR junction exhibits highly spin-dependent electron transport and the spin-polarization is significantly large.

In the following, we further investigate how the B doping and the Fe adsorption affect the transport property of a pristine 7AGNR junction. One can see from figure 3 that if a small bias voltage is applied between the two electrodes, the transport property is dominated only by the transmission probability around $E_F$, where incident waves exist only at $k_x = 0$. Therefore, in the following we focus on electron transmission only at $k_x = 0$, and investigate in detail the transport properties of pristine, B-doped, Fe-functionalized, and (B + Fe)-codoped 7AGNR junctions.

#### 3.2.1. Pristine 7AGNR junction

Figure 4(a) shows the channel-decomposed electron transmission spectra of the pristine 7AGNR junction. Only two transmission channels are obtained for this junction, and also for the other in figures 4(b)–(f). This can be understood from the fact that a graphene sheet provides only two $\pi$-characteristic incident waves around the Dirac point [41]. One of the two incident waves is symmetric with respect to the principal axis indicated by the arrows in figure 1, and the other is antisymmetric, through the both are antisymmetric with respect to the mirror plane identical to the graphene plane$^4$. Quoting the Mulliken symbols [63, 64], adjectives $A_2$- and $B_1$-channel are prefixed to the quantities derived from the former and latter incident waves, respectively.

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1. In this study, the apex of the Dirac cone appears at the $\Gamma$ point in figure 3, because we employ a unit cell with the side length in the x direction being three times as large as the primitive one.
2. This can be seen by projecting the Dirac cone onto a $(k_x, E)$ plane.
3. Symmetry with respect to a mirror plane and a rotational axis perpendicular to the principal axis is ignored, because a resultant scattering wave has no symmetry with respect to the symmetry operations, though the atomic structure has symmetry with respect to them.
Figure 3. Total electron transmission map as functions of \( k_x \) and \( E \). The panel (a) shows the electron transmissions of the pristine 7AGNR junction. The panels (b) and (c) show the up- and down-spin transmissions of the \((B + Fe)\)-codoped 7AGNR junction, respectively. The band structure of a graphene sheet is drawn by the solid lines. The gray areas represent the \((k_x, E)\) areas without propagating waves of a graphene sheet. \( E_F \) denotes the Fermi energy.

From figure 4(a) one can see that the \( A_2 \) channel hardly contributes to electron transport through the pristine 7AGNR junction, while the \( B_2 \) channel partially opens to contribute to the transport. To understand the difference, we examine the local DOS (LDOS) and band structure of the transition region shown in figures 5(a)–(c). The small \( A_2 \)-channel transmission is understood as follows: According to the LDOS shown in figure 5(a), the \( A_2 \)-channel states are localized only at the graphene part, and hardly penetrate into the 7AGNR part. Besides, the relatively flat \( A_2 \)-channel bands shown in figure 5(b) indicate that the \( A_2 \)-channel states have less interaction between the neighboring unit cells and electron hopping between adjoining unit cells in the \( z \) direction hardly occurs. Therefore, we can expect large reflection of the \( A_2 \)-channel incident wave at the interface between the left electrode and the 7AGNR part. Indeed, the reflection is clearly seen in the linear density profiles of the scattering waves drawn in figure 6(a) for \( E = E_F - 0.3 \) eV and in figures S4(a)–(c) of supplementary material for \( E = E_F - 0.5 \) eV, and \( E_F + 0.5 \) eV. The linear density is obtained by integrating the absolute square of a wave function over each \( xy \) plane. In figure 6(b), one can see that the \( A_2 \)-channel scattering wave decays in the 7AGNR part and the faint transmission wave connects to the \( A_2 \)-channel propagating wave in the right electrode depicted in figure 6(c).

In figure 5(c) the \( B_2 \)-channel states are found to be delocalized over the transition region. This is consistent with the large energy dispersion of the \( B_2 \)-channel bands in figure 5(b). In general, if an electronic state is delocalized and the electrons are not subjected to backscattering, the electron transmission is quantized to be \( T = 1 \). However, this is not the case, because the transmission is not quantized as seen in figure 4(a). To interpret the partially opened \( B_2 \) channel, we investigate the electronic structure only of the pristine 7AGNR part. Figure 5(d) shows the complex band structure [66, 67] of an infinite pristine 7AGNR. The calculation model is taken from the geometrically optimized pristine 7AGNR junction, as indicated by the round rectangle in figure 1. The complex band structure shows that there is no propagating states in the energy range considered here, and only evanescent states exist. The \( B_2 \)-channel evanescent waves have the decay constant \( \kappa \approx 0.18 \) Å\(^{-1}\). In this paper, the imaginary part of a complex
wave number, i.e., \( \kappa = \text{Im}(k_z) \), is defined as decay constant. Therefore, B\(_2\)-channel electrons are subjected to backscattering as passing through the pristine 7AGNR part, resulting in the partially opened B\(_2\) channel. Note that the A\(_2\)-channel evanescent waves have smaller \( \kappa \) than the B\(_2\)-channel ones, implying that the A\(_2\)-channel scattering wave does not decay in the 7AGNR part as much as the B\(_2\)-channel one. However, this does not mean that the A\(_2\)-channel has larger transmission than the B\(_2\) channel, because the A\(_2\)-channel incident waves are largely reflected at the interface between the left electrode and the 7AGNR part, as discussed above. Indeed, comparing the spatial distributions of the A\(_2\)- and B\(_2\)-channel scattering waves in figures 6(b) and (d), the B\(_2\)-channel transmission wave in the right electrode is found to have larger amplitude than the A\(_2\)-channel one.

3.2.2. B-doped 7AGNR junction

As seen in figure 4(b), the two transmission spectra of the B-doped 7AGNR junction are both structureless. However, one can see that when incorporating B atoms into the 7AGNR part, the B\(_2\)-channel transmission is significantly suppressed, while the A\(_2\)-channel one is not significantly affected. Figures 7(a)–(c) show the LDOSs and electronic band structure of the transition region. One can see from figures 7(a) and (b) that the A\(_2\)-channel states are localized at the graphene part and the A\(_2\)-channel band has the energy dispersion of \( \approx 0.1 \) eV. These observations are similar to those of the pristine 7AGNR junction (see figures 5(a) and (b)), indicating less influence of the B-doping on the A\(_2\) channel. Therefore, we can expect large reflection of the A\(_2\)-channel incident waves at the interface between the left electrode and the 7AGNR part, as discussed above. Indeed, the reflection is clearly seen from the linear density profiles of the scattering waves for \( E = E_F - 0.3 \) eV drawn in figure 8(a) and for other energies drawn in figures S4(d)–(f) of supplementary material.

In figure 4(b), the A\(_2\)-channel transmission slightly increase as lowering energy. This increase can be understood from the complex band structure of an infinite B-doped 7AGNR drawn in figure 7(d), which is calculated for the model taken from the geometrically optimized B-doped 7AGNR junction (see the round rectangle in figure 1): in \( E < E_F - 0.2 \) eV, the A\(_2\)-channel band is composed of propagating states. In
Figure 5. Electronic structures of the transition region of the pristine 7AGNR junction and of the infinite 7AGNR. The LDOSs and band structure of the transition region is shown in the panels (a)–(c), and the complex band structure of the infinite 7AGNR is shown in the panel (d). The $A_2$- and $B_2$-channel LDOSs are separately drawn in the panels (a) and (c), respectively. The insets in the panel (d) depict the spatial distributions of the evanescent Bloch states at $E = E_F$, and are visualized by VESTA [65].

Figure 6. Spatial distribution of channel-decomposed scattering waves of the pristine 7AGNR junction for $E = E_F - 0.3$ eV. The linear density profiles of the waves are drawn as a function of $z$ in the panel (a). The inset shows the magnification of the right electrode. The panels (b) and (d) show the isosurfaces of the $A_2$- and $B_2$-channel waves. The panels (c) and (e) show isosurfaces of the propagating Bloch waves of a graphene sheet, to which the $A_2$- and $B_2$-channel transmission waves connect, respectively. For clarity, the Bloch wave function is multiplied by a phase factor derived from the transmission coefficient of the scattering wave function. In each panels, the real and imaginary parts are depicted in the upper and lower halves, respectively. Positive (negative) values are represented in blue (yellow). The vertical dashed lines are guides for the eyes. The wave functions are visualized by VESTA [65].
Figure 7. Electronic structures of the transition region of the B-doped 7AGNR junction and of the infinite B-doped 7AGNR. The LDOSs and band structure of the transition region is shown in the panels (a)–(c), and the complex band structure of the infinite B-doped 7AGNR is shown in the panel (d). The $A_2$- and $B_2$-channel LDOSs are separately drawn in the panels (a) and (c), respectively. The insets in the panel (d) depict the spatial distributions of the evanescent Bloch states at $E = E_F$, and are visualized by VESTA [65].

contrast, the $A_2$-channel band of the infinite pristine 7AGNR drawn in figure 5(d) is composed only of evanescent states. These observations suggest that the $A_2$-channel incident wave into the B-doped 7AGNR junction is subjected to less decay in the 7AGNR part than that into the pristine 7AGNR junction, though a large portion of the incident wave is backscattered at the interface between the left electrode and the 7AGNR part. Indeed, the decay of a $A_2$-channel scattering wave in the 7AGNR part for $E = E_F - 0.3$ eV is seen in figure 6(a) for the pristine 7AGNR junction and in figure 8(a) for the B-doped one. The decay constants estimated from the envelope functions of the density profiles are $-0.26$ and $-0.16$ Å$^{-1}$ for the pristine 7AGNR and B-doped junctions, respectively (for other energy, see also section S2 in supplementary material). Therefore, the $A_2$-channel transmission of the B-doped 7AGNR junction is larger than that of the pristine one for $E < E_F - 0.2$ eV.

The $B_2$-channel states are delocalized over the transition region as seen in figure 7(c), suggesting that the $B_2$-channel incident wave penetrates into the B-doped 7AGNR part. This is, however, intuitively contradictory to the suppression of the $B_2$-channel transmission by the B doping as seen from figures 4(a) and (b). To investigate the electronic nature of the transmission suppression, we hypothesize that the $B_2$-channel incident wave into the B-doped 7AGNR junction decays in the 7AGNR part more than that into the pristine 7AGNR part. This hypothesis is examined based on the complex band structure drawn in figure 7(d): the decay constant $\kappa$ of any $B_2$-channel states is not larger than that for the infinite 7AGNR in figure 5(d), indicating that the $B_2$-channel evanescent states in the B-doped 7AGNR part attenuate more slowly than those in the pristine 7AGNR part. Consequently, the suppression of the $B_2$-channel transmission caused by the B-doping is not explained from the complex band structures, and therefore, is not attributed only to the B-doped 7AGNR part.

To explain the suppression of the $B_2$-channel transmission, we next examine the scattering waves in the right electrode. From the linear density profiles of the $B_2$-channel scattering waves for $E = E_F - 0.3$ eV drawn in the insets of figures 6(a) and 8(a), the $B_2$-channel wave of the B-doped 7AGNR junction is found to decay in the right electrode, while that of the pristine one propagates. Since this is also observed for the other energies as seen in figures S4 of supplementary material, this discussion holds for the other energies considered here. The decay and propagation of the $B_2$-channel waves are more clearly visible in the spatial distribution in figures 6(d) and 8(d), respectively. Further analysis reveals that the $B_2$-channel transmission wave in the right electrode of the B-doped 7AGNR junction is composed mainly of an evanescent generalized Bloch wave of a graphene sheet (see figure 8(e)), while that of the pristine one is composed mainly of a propagating Bloch wave of it (see figure 6(e)). Contrarily, the $A_2$-channel transmission wave is composed mainly of an propagating Bloch wave of a graphene sheet (see figures 6(c) and 8(c)) despite the presence or absence of the B atoms.
Figure 8. Spatial distribution of channel-decomposed scattering waves of the B-doped 7AGNR junction for $E = E_F - 0.3$ eV. The linear density profiles of the waves are drawn as a function of $z$ in the panel (a). The inset shows the magnification of the right electrode. The panels (b) and (d) show the isosurfaces of the $A_2$- and $B_2$-channel waves. The panels (c) and (e) show isosurfaces of the propagating and evanescent Bloch waves of a graphene sheet, to which the $A_2$- and $B_2$-channel transmission waves connect, respectively. For clarity, the Bloch wave function is multiplied by a phase factor derived from the transmission coefficient of the scattering wave function. In each panels, the real and imaginary parts are depicted in the upper and lower halves, respectively. Positive (negative) values are represented in blue (yellow). The vertical dashed lines are guides for the eyes. The wave functions are visualized by VESTA [65].

The propagating-mode wave used as the $B_2$-channel incident wave is depicted in figure 6(e), and the evanescent-mode wave found as a main component of the transmission wave is depicted in figure 8(e). Comparing figures 6(e) and 8(e), one can see that the number of the wave function nodes in the $x$ direction is different. In figure 8(d), the change in the number of the nodes is found to occur gradually in the B-doped 7AGNR part. The change from a propagation mode to an evanescent one is referred to as mode modulation hereafter. Consequently, we conclude that the B-doping into a pristine 7AGNR causes the mode modulation of the $B_2$-channel incident wave, and results in the suppression of the electron transmission. It should be noticed that the zero electron transmission originating from the mode modulation cannot be predicted from the DOS shown in figure 2(b) and is revealed only by electron transport calculations.

3.2.3. Fe-functionalized 7AGNR junction

Here, we discuss in detail the spin-polarized electron transmission spectra of the 7AGNR junction functionalized with a Fe atom, as drawn in figures 4(c) and (d). The up-spin transmission spectra has common features to those of the pristine 7AGNR junction, e.g., the $A_2$-channel transmission is small over the energy range considered here, and the $B_2$-channel one is structureless for $E < E_F + 0.2$ eV. On the other hand, the down-spin transmission spectra are largely different to those of the pristine 7AGNR junction.

Firstly, the up-spin transmission spectra is examined together with the electronic structures of the transition region depicted in figure 9. The LDOS in figure 9(a) shows that the $A_2$-channel states spread only over the graphene part and are forbidden to penetrate into the 7AGNR part. This is the same to the case of the pristine 7AGNR junction (see figure 5(a)). Therefore, the $A_2$-channel transmission for up-spin electrons is as small as that of the pristine 7AGNR junction. The LDOS in figure 9(c) is similar to that in figure 5(c), except for the states localized at the Fe atom around $E = E_F + 0.3$ eV. In particular, below $E_F$ the electronic structures are almost the same, and hence, the transmission spectra of the Fe-functionalized and pristine 7AGNR junctions are comparable for $E < E_F$. At the energy around $E_F + 0.3$ eV, the localized states originating from the s-orbital of the Fe atom appear to hybridize with the $B_2$-channel states delocalized over the transition region. We deduce that because of this hybridization, the $B_2$-channel incident wave is assisted by the s-orbital in passing through the 7AGNR part with less decay constant in comparison to the case of
the pristine 7AGNR junction. Consequently, the B2-channel transmission spectrum of up-spin electrons has the peak at $E = E_F + 0.3$ eV, as seen in figure 4(c).

In the down-spin transmission spectra in figure 4(d), one can see a couple of contrasting features, i.e., the A2-channel transmission spectrum has a sharp peak at $E = E_F - 0.3$ eV and the B2-channel one exhibits monotonous increase as energy increases. The former can be simply understood from the LDOS in figure 9(d): around $E = E_F - 0.3$ eV, one can see electronic states localized at the Fe atom. These states have $d_{xz}$ character, and thus, are able to hybridize with the A2-channel states localized in the electrode. Because of the localization, the energy dispersion of the $d_{xz}$-character band is $\approx 0.1$ eV as seen in figure 9(e). Only in this energy range, the A2-channel LDOSs of the both electrodes are connected over the 7AGNR part through the $d_{xz}$-character states. For the other energies, the A2-channel LDOS is similar to those of the pristine and B-doped 7AGNR junctions, and the A2-channel transmission is relatively small.

The increase in the B2-channel transmission can be understood from the B2-channel LDOS depicted in figure 9(f): the electronic states are delocalized over the transition region in the energy above $E = E_F - 0.2$ eV. B2-channel electrons are, therefore, carried by the electronic states forming the band indicated by P in figure 9(e). Therefore, the increase in the B2-channel transmission can be attributed to the dispersive band P. In figure 9(f), one can see electronic states localized at the Fe atom at $E = E_F - 0.4$ eV, which have a $d_{y^2}$ character with the axis perpendicular to the 7AGNR plane (see figure 1). In terms of wave-function symmetry, the $d_{y^2}$ states can hybridize with the delocalized B2-channel states composing the dispersive band P. However, because of the energy difference, they do not hybridize with each other and the $d_{y^2}$ states stay localized to form a flat band, as seen in figures 9(e) and (f). Therefore, the localized states do not contribute to electron transmission, and do not affect the transmission spectra.

3.2.4. (B + Fe)-codoped 7AGNR junction

As mentioned for figures 3(b) and (c), the (B + Fe)-codoped 7AGNR junction is expected to have a large spin-polarized electron transmission around $E_F$. Here, we investigate in detail the transport property based on the transmission spectra in figures 4(e) and (f) and the electronic structure in figure 10. One can see from figure 4(e) that the up-spin transmission is very small for both A2- and B2-channels around $E_F$. The structureless A2-channel transmission spectrum can be straightforwardly understood from the LDOS depicted in figure 10(a): since the A2-channel states are localized at the graphene part and forbidden to penetrate into the 7AGNR part, the A2-channel incident waves into the junction is largely reflected at the interface between the left electrode and the 7AGNR part, resulting in the small transmission. Indeed, the large reflection is clearly seen in the spatial distribution of the A2-channel scattering waves depicted in figures 11(a) and (b).

The B2-channel spectrum drawn in figure 4(e) is also structureless. However, the B2-channel LDOS in figure 10(c) is different from those of the A2-channel one in figure 10(a): the B2-channel states are observed over the transition region, though the B2-channel bands are as flat as the A2-channel ones seen in
Figure 10. Electronic structures of the transition region of the (B + Fe)-codoped 7AGNR junction. The electronic structure for up- and down-spin electrons are shown in (a)–(c) and (d)–(f), respectively. The panels (b) and (e) draw the band structures, and the panels (a), (c), (d), and (f) depict the LDOSs. The LDOS related to the A2- and B2-channel bands are separately shown.

To understand the contradiction between the delocalization of the states and the less dispersion of the band, one should recall the discussion on the B-doped 7AGNR junction, because the electronic structures depicted in figures 7(a)–(c) are similar to those depicted in figures 10(a)–(c). In the discussion on the B-doped 7AGNR junction, we have concluded that a propagating B2-channel incident wave is modulated in the 7AGNR part and connects to an evanescent wave in the right electrode, resulting in a small electron transmission. This mode modulation is supposed to occur also for the (B + Fe)-codoped 7AGNR junction. The spatial distribution of the up-spin B2-channel scattering wave in the (B + Fe)-codoped 7AGNR junction for $E = E_F$ is depicted in figure 11(c). The mode modulation in the 7AGNR part and the decay of the transmission wave in the right electrode are seen. As mentioned for the B-doped 7AGNR junction, this discussion holds for other energies. Therefore, we conclude that the small B2-channel transmission observed in figure 4(e) is attributed to the mode modulation of the up-spin incident wave in the (B + Fe)-codoped 7AGNR part.

We next discuss the down-spin transmission spectra drawn in figure 4(f). The structureless A2-channel spectrum with small transmission can be explained from the down-spin band structure drawn in figure 10(c). The A2-channel bands have less energy dispersion. This is consistent with the A2-channel LDOS depicted in figure 10(d): the A2-channel electronic states are localized only at the graphene electrode part and they are forbidden to penetrate into the 7AGNR part. The electronic structure is almost the same to that for up-spin electrons shown in figure 10(a). Besides, the spatial distributions of the A2-channel scattering waves for up- and down-spin electrons appear similar to each other, as seen in figures 11(b) and (e). Therefore, A2-channel incident waves into the junction are reflected at the interface between the left electrode and the 7AGNR part, and thus, only a small transmission is observed in the energy range considered here.

The B2-channel transmission spectrum for down-spin electrons has a significant increase at $E = E_F - 0.3$ eV and keeps large transmission for $E > E_F - 0.3$ eV, as seen in figure 4(f). The transmission behavior can be attributed to the B2-channel bands with large energy dispersion for $E > E_F - 0.3$ eV drawn in figure 10(c). According to figure 10(f), the B2-channel states composing the dispersive bands are delocalized over the transition region. This fact indicates nearly coherent propagation of the B2-channel down-spin states through the transition region, implying no mode modulation in the 7AGNR part. Therefore, a B2-channel incident wave of down-spin electrons is able to pass through the 7AGNR part, and connects to a propagating-mode wave in the right electrode. From the spatial distribution of the B2-channel scattering waves shown in figures 11(d) and (f), one can see that the amplitude of the waves in the left and right electrodes is almost the same, indicating less backscattering in the junction. Consequently, the B2-channel transmission spectrum for down-spin electrons exhibits large transmission, while that for up-spin electrons does not. This observation implies that the (B + Fe)-codoped 7AGNR junction acts as a superior spin filter.
Figure 11. Spatial distributions of channel-decomposed scattering wave functions of the (B + Fe)-codoped 7AGNR junction for $E = E_F$. The linear density profiles of the waves are drawn as a function of $z$ in the panel (a) for up-spin electrons and in the panel (d) for down-spin ones. The insets in the panels (a) and (d) show the magnifications of the right electrode. The panels (b) and (c) [(e) and (f)] shows isosurfaces of the $A_2$- and $B_2$-channel waves for up-spin (down-spin) electrons, respectively. In each panels, the real and imaginary parts are depicted in the upper and lower halves, respectively. Positive (negative) values are represented in blue (yellow). The vertical dashed lines are guides for the eyes. The wave functions are visualized by VESTA [65].

It should be noticed that the two electronic bands indicated by P and Q in figure 10(e) are formed as the result of an avoided crossing between the dispersive band ranging from $E_F - 0.1$ eV to $E_F + 0.3$ eV and the flat band just below $E_F$. This is because the electronic states of the flat band have the $d_{yz}$ character of the Fe atom, and is able to hybridize with the $B_2$-channel states of the dispersive band in terms of wave-function symmetry. Therefore, the band structure shown in figure 10(e) exhibits a tiny band gap between the bands P and Q. In addition, there exist Van Hove singularities [68] at the band edges on both sides of the band gap, because the band edges originate from the flat band. The Van Hove singularity is known to cause sudden suppression/opening of a transmission channel at its energy [69–72]. Therefore, a sharp dip in the $B_2$-channel transmission spectrum for down-spin electrons at the energy just below $E_F$ is expected, though the dip is not obtained in the present transport calculation because the energy grids are too coarse to detect the dip. Consequently, it is reasonable to presume that the localized $d_{yz}$ states observed as a DOS peak in figure 2(d) do not contribute to the electron transport as an individual transmission channel additional to the contribution of the delocalized states of the dispersive band, but rather contribute to the depression of the electron transmission associated to the delocalized dispersive-band states.

4. Conclusion

Using first-principles electron transport calculations based on the density functional theory, we investigated the electron transport properties of pristine, B-doped, and Fe-functionalized 7AGNR junctions as well as those of (B + Fe)-codoped one. Our transport calculations revealed that the (B + Fe)-codoped 7AGNR junction exhibits large spin-polarized electron transmission around $E_F$. Interestingly, the spin polarization
obtained for the codoped junction is 0.96, and on the other hand that for the Fe-functionalized 7AGNR junction is only 0.60. Therefore, the B-doping into the 7AGNR part clearly enhances the spin polarization of electron transmission. This observation implies that the (B + Fe)-codoped 7AGNR junction acts as an almost perfect spin filter.

In addition, we tackled the puzzling observation that although B2-channel states of the B-doped and (B + Fe)-codoped 7AGNR junctions are seen to be delocalized over a transition region, the corresponding bands are flat and the electron transmission at the corresponding energy is small. This puzzle was explained from the behavior of scattering waves that a propagating incident wave undergoes modulation of its mode during passing through the B-doped 7AGNR part and connect not to a propagating transmission wave but to an evanescent one in the right electrode. This implies the backscattering of B2-channel propagating waves at the interface between the B-doped 7AGNR part and the right graphene electrode. We also pointed out the possibilities not only that flat-band states characterized by a sharp peak in a DOS do not contribute to electron transmission, but also that their role is to close a transmission channel originating from dispersive-band states as a result of an avoided crossing of the two bands. It was revealed that a broad and gentle hill in a DOS formed by dispersive-band states is associated to large electron transmission more than a tall and sharp DOS peak formed by flat-band states.

To conclude, in this study we demonstrated the enhancement of spin-polarized electron transport through a nanoscale junction by means of incorporating magnetic and non-magnetic heteroatoms, and explained its electronic nature in terms of the mode matching between scattering and transmission wave functions. In particular, we revealed that the tuning of the spin-polarized transport property using the mode modulation leads to an almost perfect spin filter function, and this insight can be promising for finely designing the functionality of spintronics devices.

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