

Electronic Transport Properties of Graphene Channel between Au Electrodes

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We study the electronic transport properties of armchair graphene nanoribbons with a width of up to 12 nm bridged between two Au electrodes using first-principles calculations. The transport properties sensitively depend on the ribbon width, even though the width reaches 12 nm. The variation of transport properties is ascribed to the detailed electronic structures of graphene ribbons, which sensitively depend on their width. The band structure and the symmetry of π state of the graphene play important roles in determining the transport properties.
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I. INTRODUCTION

Graphene has attracted much attention in the field of nanoelectronics because of its unique electronic and geometric properties. A honeycomb network with atom thickness leads to a massless electron/hole around the Fermi level that allows the material to be applied to high-speed electronic devices in the post-silicon era. On the other hand, electronic properties of graphene are fragile when hybrid structures are formed with other foreign materials, such as insulating substrates [1-8] and metal electrodes [9-18], because the electron system of graphene is distributed normal to their atomic network that intrinsically forms interfaces with such foreign materials. This fragility of the electronic structure is a serious problem for realizing graphene-based electronic devices. For example, experiments have shown the degradation of the carrier mobility [1-3] and the variation of the transport properties [4] of graphene adsorbed on SiO₂. Theoretical calculations have also demonstrated that graphene possesses finite energy gap with a few tens meV by adsorbing on surfaces of α -quartz [5-7]. Moreover, our first-principles electronic transport study of graphene nanoribbons (GNRs) on SiO₂/Si uncovered the variation of the transmission probability depending on the surface morphologies [8].

In addition to the fragility of the electronic structure, high contact resistance between graphene and metal electrodes is another problem in designing graphene-based electronic devices. As well as the high contact resistivity, resistance has also been experimentally reported to depend on the metal species [9-11] and the process conditions [12]. Several theoretical studies reported geometries, electronic structures [13-15], and transport properties [16-18] of interfaces between graphene and metal surfaces. Although these theoretical works revealed that the

transport properties depend on the detailed atomic arrangements of GNRs with a few nm width, little is known about the transport properties of GNRs with over 10 nm width. Therefore, this is motivating us to gain theoretical insight into the fundamental properties of wider GNR channels bridged between metal electrodes for advancing graphene/metal interface science.

In this study, we investigate the electronic transport properties of the graphene channels bridging two Au electrodes using first-principles calculations for providing fundamental understanding of transport properties of armchair GNR bridged between metals. Our calculations show that current density throughout the graphene channel still depends on the width of the GNR channel, even though the width reaches 12 nm. The variation of transport properties is ascribed to the detailed electronic structure of graphene ribbons bridging two electrodes, which sensitively depend on their width and detailed atomic arrangements [19, 20].

II. COMPUTATIONAL METHODS

All calculations were performed in the framework of the density functional theory (DFT) using the DFT code, OpenMX [21, 22], which allows us to perform large-scale calculations on massively parallel computers [23, 24]. We use the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof functional form for describing the exchange-correlation energy among interacting electrons [25]. The electron-ion interaction is described by norm-conserving pseudopotentials [26] with partial core correction [27]. Pseudoatomic orbitals (PAOs) centered on atomic sites are used as the basis function set [21]. For geometrical optimizations and energy band structure calculations, we use the PAOs specified by C6.0-*s2p2d1*, H5.0-*s2p1*, and Au7.0-*s2p2d2f1*. C, H, and Au are atomic symbols, 6.0, 5.0 and 7.0 represent the cutoff radii (Bohr), and *s2p2d1*, for example, indicates the employment of

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two, two, and one orbitals for the s , p , and d component, respectively. Geometric structure of interfaces of graphene and metal surfaces are optimized under a repeated slab model with 13 Å vacuum spacing to exclude the effects arising from periodic images. The convergence criterion for forces acting on atoms is 0.1 eV/nm. For transport calculations, we employ the non-equilibrium Green function (NEGF) method under the finite bias voltage between two electrodes [22]. We use a smaller set of PAOs, i.e. C- $s1p2$, H- $s1p1$, and Au- $s1p2d1$, to reduce the computational cost. Note that the reduced set of PAOs can maintain the quantitative and qualitative accuracy of the transport calculations. The cutoff radii are the same as those used in the band calculations. We use 151 k -points along the perpendicular to the transport direction. The electronic temperature is 300 K.

To obtain the most stable configuration of graphene adsorbed on Au electrodes, we structurally optimize graphene adsorbed on Au(111) surfaces. The interface between Au and graphene is simulated by the repeated slab model consisting of four atomic layers of Au and a single graphene sheet. The optimum spacing between graphene and the topmost Au atom is $d = 0.37$ nm indicating the fact that the graphene is weakly bound to the Au(111) surface. We impose a commensurability condition between lateral periodicities of graphene and of Au(111) surfaces. Accordingly, the rectangle unit cell contains the $2 \times 2\sqrt{3}$ lateral periodicity of conventional graphite and the $\sqrt{3} \times 3$ lateral periodicity of the (111) surface. Since there are lattice mismatches between graphite and metal surfaces, the lateral lattice parameter of the Au(111) surface is compressed by about 3.23% from the equilibrium lattice parameter. The artificial lattice compression caused only a slight change in the work function of Au(111) surface (5.30 to 5.18 eV). Under the optimum structure, one carbon atom is situated above the topmost Au atom and the other is on a bridge site [13]. By forming the complex, the Dirac point of graphene shifts upward by 0.4 eV, keeping its characteristic band structure. Thus holes are injected into graphene by the Au(111) surface.

III. RESULTS AND DISCUSSION

Figure 1 shows a structural model for simulating transport properties of GNR-based field effect transistors (GNR-FETs) that consists of Au electrodes and an arm-chair graphene nanoribbon (AGNR). The AGNRs ranging from 2.7 nm to 12.1 nm wide of W are bridged between two Au electrodes with the contact length $L_{\text{con}} = 0.86$ nm to elucidate the W dependence of the transport properties of AGNRs. All edge carbon atoms along the y direction are terminated by hydrogen atoms. The interlayer distance between the AGNR and the Au electrodes is set to 0.37 nm, corresponding to the optimum spacing between graphene and bulk Au(111) surfaces.

Figure 2 shows the calculated current density I as a function of the ribbon width W under the bias voltage $V_b = (\mu_L - \mu_R)/e = 0.1$ V, where μ_L (μ_R) is the chemical potential of the left (right) electrode. The current density sensitively depends on the width of AGNR. The current density basically decreases as the ribbon widens. Furthermore, the current density rapidly oscillates with

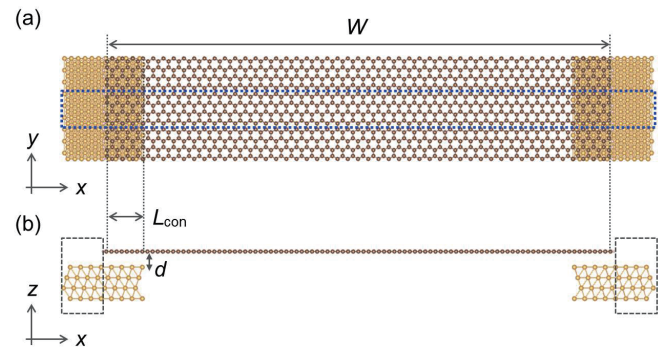


FIG. 1. (a) Top and (b) side views of the GNR-FET model consisting of the AGNR with the width $W = 12.10$ nm ($N = 99$) bridged between two Au electrodes. The contact length L_{con} is fixed to be 0.86 nm. The blue dotted rectangle in (a) indicates the unit cell of the model. The dashed rectangles in (b) indicate the unit cells of leads. The interlayer distance d is set to 0.37 nm. Although both sides in the transport direction (x) are connected to semi-infinite leads in actual calculations, only atoms of the center region are given. The khaki, white, and orange spheres represent the carbon, hydrogen, and gold atoms, respectively.

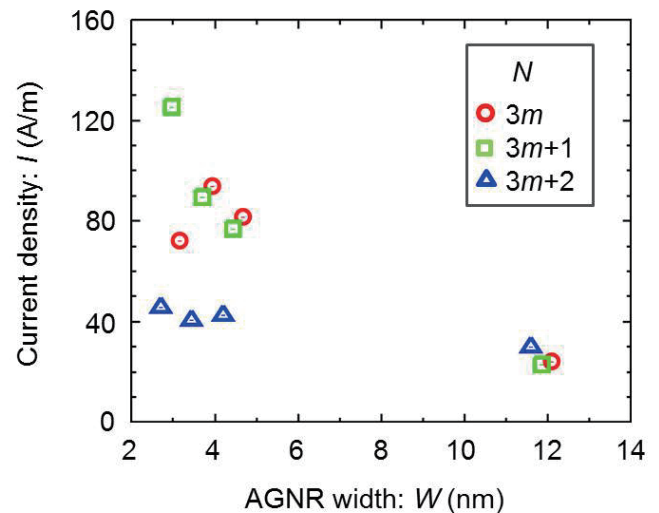


FIG. 2. Current density I as a function of the ribbon width W for the models of the AGNR bridged between two Au electrodes at a bias voltage $V_b = 0.1$ V. The results for three N families of $3m$, $3m+1$, and $3m+2$ are represented by the red circles, green squares, and blue triangles, respectively.

the number of C_2 dimer row N along the ribbon direction in the narrow ribbons: the current density of AGNR with dimer row $N = 3m+2$ is lower than those with $N = 3m$ and $3m+1$. More interestingly, the current densities still depend on the N family in the wide ribbons ($W \sim 12$ nm): they are 24.1 A/m for $N = 99$ ($W = 12.10$ nm), 23.0 A/m for $N = 97$ ($W = 11.85$ nm) and 30.3 A/m for $N = 95$ ($W = 11.60$ nm). The facts indicate that the transport properties of ANGR with Au electrodes sensitively depend on the tiny difference in their atomic structures. Therefore, the current density variation and contact resistance variation are expected to be essential in AGNR-FET with Au electrodes. The spacing between graphene and Au electrode sensitively affects the current density

which is associated with the overlap of the wave functions between them. In the present calculation, the spacing between graphene and Au electrode is slightly overestimated because of the choice of GGA functional which could not reproduce the dispersive force. Indeed, the previous calculation on similar systems showed the narrower optimum spacing between graphene and metal surface [28]. Therefore, the current is expected to increase by taking account the dispersive force into this calculation. However, due to the weak interaction nature of the dispersive force, the quantitative nature of the current thorough the electrode and graphene is expected to retain in calculations containing the dispersive force.

To unravel the N -family dependence observed in current densities, we analyze transmission spectra $T(k_y, E)$ as functions of both wave number along the ribbon k_y and energy E of AGNR with $W \sim 4.5$ nm [Fig. 3(a)-3(c)]. Under the bias voltage $V_b = (\mu_L - \mu_R)/e$, the current density I is evaluated by

$$I = \frac{1}{L_y} \sum_{\sigma} \frac{e}{h} \int_{-\infty}^{\infty} T_{\sigma}(E) [f(E - \mu_L) - f(E - \mu_R)] dE, \quad (1)$$

where $f(E)$ is the Fermi-Dirac function, L_y is the length of the unit cell of the model along the y direction, and σ represents spin degree of freedom. The spin-dependent transmission coefficient $T_{\sigma}(E)$ is defined as

$$T_{\sigma}(E) = \frac{1}{N_{k_y}} \sum_{k_y} T_{\sigma}(k_y, E), \quad (2)$$

where N_{k_y} ($= 151$) is the number of k -points along the y direction. The $T_{\sigma}(k_y, E)$ around the energy integration range from 0 to 0.1 eV smeared with the electronic temperature in the Fermi-Dirac function gives the current density. We found the large $T_{\sigma}(k_y, E)$ within the integration range for AGNRs with $N = 39$ and 37 , while the transmission is small within the range for the AGNR with $N = 35$. Indeed, the AGNRs with $N = 39$ and 37 exhibit high transport properties while the AGNR with $N = 35$ is less conductive than the other two ribbons. Further analyses on the transmission spectra for the AGNRs with the other ribbon width corroborate the fact that the N -family dependence in the current densities originates from the transmission spectra in the integral region determined by the ribbon width or the number of dimer row N . The transmission spectra reflect the characteristic feature of the band structures of the isolated AGNRs as shown in right panels of Fig. 3(a)-3(c). The energies in the band structures are shifted upward by about 0.3 eV simulating the p -doping from the Au electrodes for the comparison with the transmission spectra. The transmission occurs at the particular k_y and E at which electronic energy band emerges in graphene because of the weak interaction between Au and graphene.

In addition to the band structure, the symmetry of π state of graphene also plays an important role in determining the transmission spectra. The isolated AGNR with $N = 39$ is a semiconductor with a band gap of about 0.2 eV as shown in Fig. 3(a). The highest occupied state (HOMO) and the second highest occupied state (HOMO-1) of the isolated AGNR at the Γ -point are located at the energies of 0.2 eV and 0 eV, respectively. The wave functions of these two states are shown

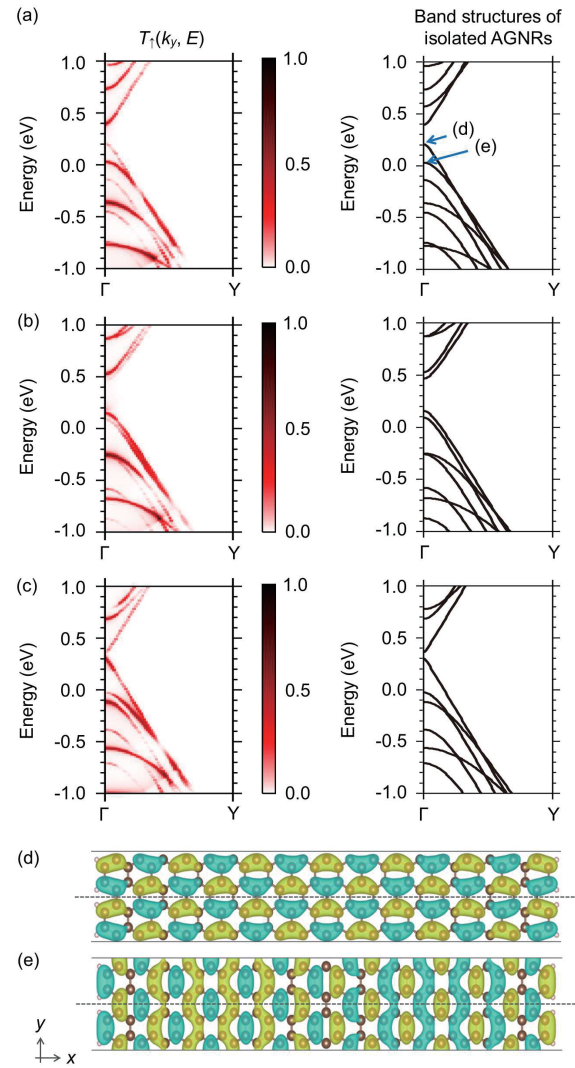


FIG. 3. Transmission spectra $T(k_y, E)$ for the up-spin and band structures of the isolated AGNRs for the model with $N =$ (a) 39, (b) 37, and (c) 35, which belong to the $3m$, $3m + 1$, and $3m + 2$ families, respectively. The energies in the band structures of the isolated AGNRs are shifted upward by 0.3 eV for comparison with $T_{\uparrow}(k_y, E)$. Only the up-spin of the transmission is shown due to no spin-polarization. The chemical potentials of the left-side lead μ_L are set to 0 eV in $T_{\uparrow}(k_y, E)$. The right color bar shows the value of $T_{\uparrow}(k_y, E)$. The wave functions at the Γ -point of (d) HOMO and (e) HOMO-1 of isolated AGNR with $N = 39$, which are indicated by the arrows in (a). The yellow and aqua areas in the isosurfaces denote different signs of the molecular orbitals. The dotted lines in (d) and (e) represent the xz plane.

in Fig. 3(d) and 3(e). By comparing the transmission spectra and the band structure, we find that one of two states gives the small $T_{\sigma}(k_y, E)$ while the other leads to the large $T_{\sigma}(k_y, E)$. The former state (HOMO) shows the anti-symmetric nature of their wave function with respect to the xz plane, while the later state (HOMO-1) shows its symmetric nature. On the other hand, surface electron states around the Fermi level of Au comprise s orbital of Au atoms possessing the symmetric nature with respect to the surfaces. We also find that the values of $T_{\sigma}(k_y, E)$ are fluctuated along the k_y even in the same π state, be-

cause the symmetry of the π state changes with respect to the k_y . Thus, the π states with symmetric nature mainly contribute to the transmittance through the contact between Au and graphene. The same analysis is applicable to the other AGNR with different ribbon widths or the N family: the state possessing the symmetric nature with respect to the surfaces leads to the large transmission irrespective to the ribbon width or the number of dimer row N .

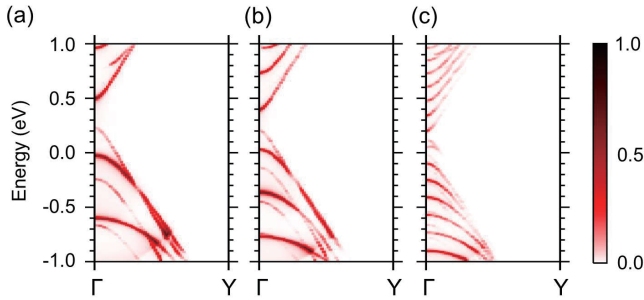


FIG. 4. Transmission spectra $T_{\uparrow}(k_y, E)$ for the model with $N =$ (a) 27, (b) 39, and (c) 99, which belong to the $3m$ family with $W = 3.15$, 4.68 , and 12.10 nm, respectively.

It is worth investigating how the current depends on the ribbon width in each N family. In all N family cases, the current density asymptotically decreases as the ribbon widens. In the case of the AGNR with the width of $N = 3m$, the current density oscillates within the family. Figure 4 shows the transmission spectra of the AGNR with $N = 27$ ($W = 3.15$ nm), $N = 39$ ($W = 4.68$ nm), and $N = 99$ ($W = 12.10$ nm). The large $T_{\sigma}(k_y, E)$ originating from the HOMO-1 state is not located in the bias range for $N = 27$, while the $T_{\sigma}(k_y, E)$ is observed in the range for $N = 39$, resulting in a higher current density in $N = 39$ than in $N = 27$. The $T_{\sigma}(k_y, E)$ in $N = 99$ is the

smallest among $N = 27$, 39 , and 99 within the integration range from 0 to 0.1 eV, although the band structures correspond with the transmission spectra. This leads to the lowest current density in $N = 99$ among the $N = 3m$ family. As described above, the variation of current density was observed even in the 12 nm ribbons. The energy interval of the π states associating with the transmittance is 0.15 eV for the model with $N = 99$ as shown in Fig. 4(c). The larger energy interval than the integration range of 0.1 eV is likely to cause the variation of current density. Wider AGNRs will suppress the variation because the energy interval decreases inversely with the ribbon width.

Finally, we discuss the contact area effect on the transport properties. As reported in the previous works [9, 16], the current density is expected to depend on the contact area: In the case of Cu electrode [18], transmission spectra shift downward in energy with respect to the Fermi level due to the enhancement of electron transfer from the metal surface to the graphene with increasing the contact area. By the analogy with the Cu electrode, thus, the electron transfer from the graphene to the metal surface is expected to increase with increasing the contact area. Furthermore, the transmission spectra shift upward with respect to the Fermi level.

IV. CONCLUSION

In summary, we have studied the electronic transport properties through armchair graphene nanoribbons with a width of up to 12 nm bridged between two Au electrodes using first-principles calculations. We have found that the current densities sensitively depend on the ribbon width, even though the ribbon width reaches 12 nm. The symmetry of π state of the graphene ribbons as well as the band structure is important for determining the transport properties. These results suggest that the width of graphene material should be precisely controlled for designing the graphene-based FET devices with Au electrodes.

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