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Abstract. If graphene is a promising material in many respects, its remarkable properties may be impaired by unavoidable defects. Chemical vapor deposition-grown graphene samples are polycrystalline in nature, with many grain boundaries. Those extended defects influence the global electronic structure and the transport properties of graphene in a way that remains to be clarified. As a step forward in this direction, we have undertaken quantum mechanical calculations of electron wave-packet dynamics in a multigrain self-supported graphene layer. Our computer simulations show that a grain boundary may act as a reflector at some energies and for some incidences of the Bloch waves. In addition, our calculations reveal that when two grain boundaries run parallel to each other, the graphene ribbon confined between them may behave like a channel for the charge carriers. We emphasize therefore the possibility of creating nanoscale electronic waveguides and nanowires on the graphene surface by a controlled engineering of its grain boundaries. [DOI: 10.1117/1.JNP.6.061718]

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1 Introduction

Electromagnetic waveguides have important applications in modern technology, e.g., the fiber optic cables in telecommunications. A waveguide is a structure that presents very little attenuation for propagation in one spatial dimension while confining spatially the propagating wave in the other two directions. Similar structures—sometimes also called nanowires—can be designed for electron waves and will become essential building elements of nanoelectronic circuits. One of the promising candidates to do so is graphene,[1] a single sheet of graphite. It is a one-atom-thick sheet of sp^2-bonded carbon atoms arranged in a honeycomb lattice. Electronic transport in graphene is shown to be ballistic,[2] even in the micrometer[3] range and at room temperature. The presence of grain boundaries (GBs)[4,5] originating from independently growing together nucleated graphene grains[6] and line defects,[7] however, affects the propagation of charge carriers. Electron mobility of chemical vapor deposition (CVD) graphene—which is known to contain a large number of GBs—can be considerably smaller[8] than that for, e.g., cleaved graphene. According to scanning tunneling spectroscopy (STS) measurements and *ab-initio* calculations, conductivity of the defect region can either increase[9] or decrease[10] compared with graphene, depending on the atomic structure of the defect.

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Using quantum mechanical dynamics based simulation, we investigated, in atomic resolution, the spreading of electronic wave packets on graphene containing various configurations of grain boundaries. Our recent experiments and simulations showed that, in the regions in which an accumulation of graphene structural defects is found—like in graphene grown by CVD—the charge-spreading phenomena are dramatically altered.[11] Wave packet dynamical (WPD) simulations demonstrated that reflection and refraction phenomena occur in the charge spreading on graphene by a line defect. Motivated by the fact that graphene GB structures could be good candidates for building waveguides in nanoelectronics, we use the same simulation technique to study the behavior of a pair of parallel GBs and investigate in what circumstances this system behaves as a waveguide for electron waves.

The methodology is summarized in the next section, which also contains the results of calculations performed for a graphene sample with two parallel GBs. Each grain boundary is a linear chain of periodically reproduced pentagon—heptagon pairs separated by one row of hexagons. Such a linear defect changes the orientation of the graphene network by about 39 deg. The time evolution of an electronic Gaussian wave-packet launched in the graphene ribbon bounded by the two GBs is illustrated and analyzed by time-Fourier transform, allowing us to scan the transmission and reflection properties of the GB in a large energy spectrum. Conclusions deserve a separate section.

2 Calculation and Results

In our simulation, we study a graphene sheet with two parallel GBs. The waveguide effect is investigated by placing a simulated metallic scanning tunneling microscope (STM) tip above the nanoribbon between the two GBs (Fig. 1). A Gaussian wave packet is injected into the graphene sheet from the tip, and its time development is calculated by wave packet dynamics.[12] The graphene sheet was modeled by a local one-electron pseudopotential[13] matching the *ab-initio* band structure of graphene as best as possible. The 38.9-deg GBs[14] are formed by a linear chain of abutting pentagons and heptagons separated by one row of hexagons, relaxed by a molecular mechanics potential. The STM tip is represented by a jellium background model. The tip is taken as a hyperboloid of 0.5-nm apex radius and 15-deg aperture angle. The jellium potential is zero outside the effective surface of the tip and −9.81 eV inside (see Ref. 15 for details).

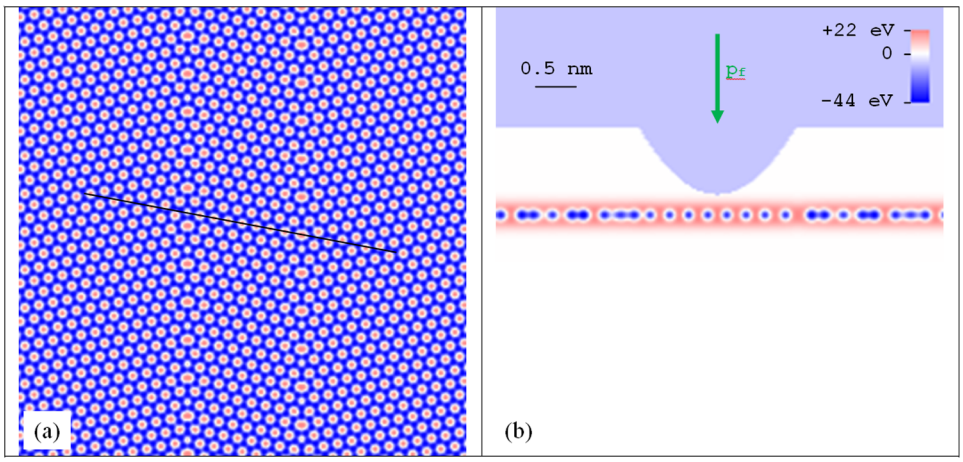

Fig. 1 Model geometry. (a) Two-dimensional (2-D) cross-section of the potential at the graphene plane, shown by color coding. White is the zero potential; blue (red) colors show the negative (positive) values, respectively, see the color bar in (b). (b) 2-D cross section of the potential perpendicular to the graphene plane, taken along the black line in (a). The hyperbolic protrusion on the upper half plane and the horizontal row of blue dots represent the vertical cross-sections of the STM tip and graphene, respectively. Color coding is the same as in (a). The light blue level at the upper part is the negative potential inside the STM tip (−9.81 eV); white is the vacuum potential (zero). The vertical green arrow inside tip shows the momentum of the incoming wave packet.

In the notations of Ref. 16, the particular structure considered in the present paper corresponds to the GB with indices (2,1). In the construction of the (2,1) GB, the two grains are rotated symmetrically in opposite directions by 10.9 deg each (hence a theoretical mismatch angle of 21.8 deg), the initially common armchair direction coinciding with the GB line. The corresponding misorientation angle is defined here as the complement of the mismatch angle to 60 deg (angle between the zigzag directions of each grain closest to the GB line). Relaxation of the structure with Tersoff-Brenner potential[17] slightly modified the misorientation angle from 38.2 to 38.9 deg. Even though such an empirical potential may not be suitable to build the best optimized geometry of the structure, the more so as the energy minimization was constrained to keep a flat sheet, in effect the fine details of the atomic structure do not matter too much here, because the WP dynamic is qualitatively driven by the topology of the system rather than by its detailed structure. For the very same reason, the STM tip can be modeled by a hyperbolic paraboloid rather than by an atomically shaped protrusion.

The Gaussian wave packet is launched with the Fermi momentum p_f from inside the tip bulk toward the apex of the tip. This Gaussian is the $\psi_0(x, y, z; t)$ initial state of the WPD calculation. The $\psi(x, y, z; t)$ time dependent wave function is developed from the initial wave function by solving the time-dependent three-dimensional Schrödinger equation.[15]

In an earlier, recent calculation,[11] we analyzed the time evolution of a WP injected from an STM tip into a graphene sheet without GBs. Those simulations showed that, as the wave packet reaches the tip apex from inside the tip bulk, it begins to tunnel onto the central hexagon (i.e., that below the tip apex). Then the wave packet begins to spread on the graphene sheet along the C–C bonds, following the hexagonal symmetry. At $t = 3.14$ fs, after spreading 1.2 nm from the center, the direction of the spreading is changed. Further spreading occurs along the 6 ΓK directions of the Brillouin zone, which match the zigzag directions of the graphene sheet in direct space. That is, at small distances the molecular physical behavior dominates, but at larger distances the solid-state physical picture takes over. We also studied the behavior of WP spreading[11] for a graphene sheet containing a grain boundary. The calculations showed a rich variety of transport phenomena, including reflection, beam splitting and states localized[18] on the grain boundary.

Figure 2 shows the details of the time evolution of the WP in our present calculation with the two GBs. To facilitate comparison with the pure graphene case, we display the probability density of the WP for the same time values as used for Fig. 3(b), 3(c), and 3(e) of Ref. 14. The premier stages of the time evolution are similar to the time evolution on a graphene surface without GBs: the simulations show a highly anisotropic in-plane dynamics following a 60 deg angular periodicity. The wave packet first tunnels onto the small graphene clusters below the tip, and the electronic states of these clusters govern the further spreading of the electron on the graphene surface. Upon reaching the GB, however, the spreading pattern is altered, owing to the above-mentioned reflection and refraction phenomena. Part of the WP hitting the GBs is reflected back into the region between the GBs but another part is transmitted to the graphene region outside the graphene stripe defined by the two GBs.

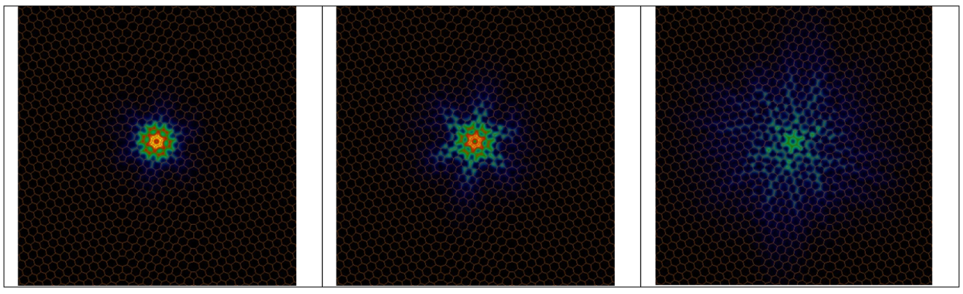

Fig. 2 Selected snapshots (left to right) from the time evolution of the probability density of the wave packet shown as color-coded 2-D sections. Black corresponds to zero probability. We used the same color scale on all images, determined by the maximum probability density on the graphene sheet. The graphene network is shown by thin orange lines. Time values are 2.00 fs, 2.45 fs, and 3.52 fs.

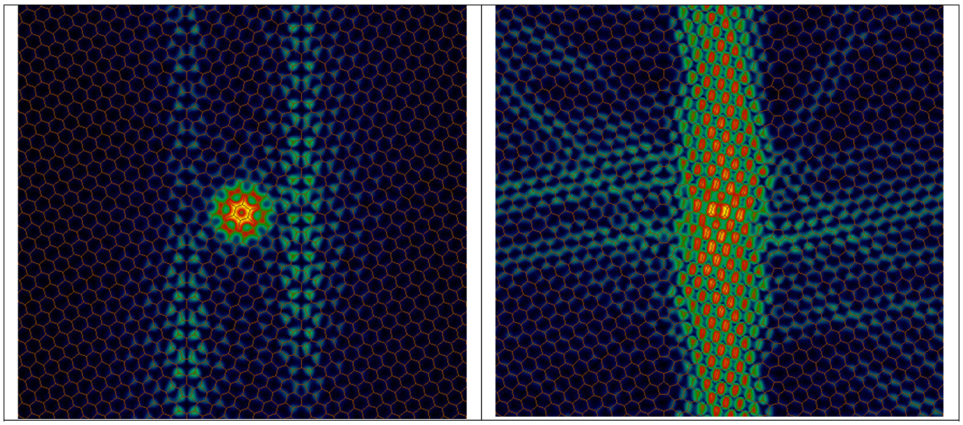

Fig. 3 Probability density on the graphene sheet with the two grain boundaries for selected energies ($E_F + 0.8$ eV and $E_F + 2.9$ eV) shown as color-coded 2-D sections. Black corresponds to zero density, bright yellow to the maximum density. The graphene network is shown by thin orange lines.

To understand the complicated patterns seen in the time evolution, an energy dependent analysis was performed. The energy spectrum of the WP used in our calculation spans to the $[E_F - 3$ eV,$E_F + 3$ eV] range. The time dependent wave function $\psi(x, y, z; t)$ is a complex superposition of the eigenstates of the system. In order to study the behavior of the different energy components of the WP, we calculated the $\psi(x, y, z; E)$ energy-dependent wave function by utilizing a $t \rightarrow E$ Fourier transform. A 0.1 eV energy resolution was used in our calculation. Figure 3 shows the energy-dependent probability density, $\rho(\vec{r}; E) = |\psi(\vec{r}; E)|^2$ for two selected energy values. At $E = E_F + 0.8$ eV localized states are seen at the GBs. This energy value corresponds to a DOS peak at $E = E_F + 0.5$ eV if we take into account the 0.3 eV shift caused by the peak distortion effect of the tunneling.[11] By doping the surrounding graphene lattice,[10] the one-dimensional defect acts as a nanowire. Emergence of states localized on the GB opens up the possibility for using graphene GBs as interconnects in all-carbon nanoelectronic circuits. At $E = E_F + 2.9$ eV, the probability density is confined to the nanostripe between the GBs, hence this structure acts as an electronic waveguide at this energy. Taking into account the 0.3 eV upshift mentioned above, this energy value corresponds to the DOS peak of graphene at $E = E_F \pm \gamma$ where $\gamma = 2.6$ eV is the tight-binding C-C hopping matrix element.

3 Conclusion

In summary, our simulation shows the possibility of creating nanoscale waveguides and nanowires for charge carriers on the graphene surface by a controlled formation of grain boundaries. When injected from an atomically sharp STM tip into a nanoribbon defined by two parallel grain boundaries, electron quasiparticles behave differently according to their energy. For most of the energy values the charge carriers cross the grain boundaries, suffering reflection and refraction. At certain selected energies, however, the electrons are channeled into the grain boundary line, creating extended localized states. There are specific energy values where the two grain boundaries behave as a waveguide: the electron density is confined between them. These effects may have a great significance in the theory of graphene nanoelectronic circuits.

Acknowledgments

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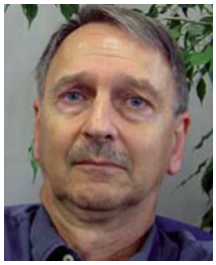

Philippe Lambin is a specialist in theoretical physics of the condensed matter and, more recently, of nanomaterials. He graduated in physical engineering from the University of Liège, Belgium, in 1976 and obtained his PhD in physical sciences in 1981. After having joined the university of Namur, Belgium, he went to the IBM research center of San Jose, California, as visiting scientist (1983 to 1984). After returning to Namur as research associate of the Foundation for Scientific Research of Belgium, he became professor in 1995 and full professor in 2004. He was successively dean of the faculty of sciences (2005-2008) and vice-rector of the University of Namur (2008-2011). He has co-authored about 300 publications, among which half are related to nanocarbons. His research interests include computer simulation of STM/STS experiments and electron diffraction patterns of carbon nanotubes, electronic and vibrational properties of defects in nanotubes, electrodynamics of nanocarbons.

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