Magnetoresistance of Carbon Nanotubes: From Molecular to Mesoscopic Fingerprints

Stephan Roche[1,*] and Riichiro Saito[2]
[1]*Commissariat à l'Énergie Atomique, DRFMC/SPSMS, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*
[2]*Department of Electronic Engineering, University of Electro-communications, 1-5-1 Chofugaoka Chofu, Tokyo 182-8585, Japan*
(Received 2 August 2001; published 26 November 2001)

A magnetoresistance study of carbon nanotubes demonstrates that, for small diameters, the location of the chemical potential and the orientation of the magnetic field are parameters that enable tuning from positive to negative magnetoresistance, a phenomenon not related with weak localization. For larger diameters ($\geq$10 nm), the conventional mesoscopic behavior of magnetotransport is recovered.

DOI: 10.1103/PhysRevLett.87.246803 PACS numbers: 73.63.Fg, 73.22.–f

Single-walled carbon nanotubes (SWNTs) exhibit either a metallic or a semiconducting character depending on their helicity [1]. Metallic tubes have μm long mean free paths [2] and behave as long ballistic conductors [3–5]. Conversely, the intrinsic properties of conducting multiwalled carbon nanotubes (MWNTs) are elusive. Indeed, reported ballistic, diffusive, or insulating experimental behaviors [4,6–9] remain difficult to relate with the number and helicities of constitutive shells and the relevance of interlayer coupling. It is usually assumed that the outermost shell, in contact with metallic electrodes, determines the metallic or semiconducting character of the MWNTs [4,8–10].

Two fundamental issues are the role of the magnetic field on transport mechanism and the understanding of sign and oscillations of magnetofingerprints. Measuring magnetoresistance in mesoscopic systems is a formidable tool to investigate quantum coherent phenomena beyond the classical effects. An elegant perturbation theory of localization has been developed for metallic cylinders [11] when the mean free path ℓ_e is smaller than the cylinder circumference. By applying a magnetic field, time reversal invariance is broken and dephasing of the electronic pathways reduces the enhancement of the probability of "return to the origin" (weak localization). Accordingly, a decrease of the resistance with magnetic field results (*negative magnetoresistance*). If ℓ_e becomes much larger than the circumference, the electronic conduction is referred to as quasiballistic and a larger magnetic field is needed to suppress weak localization because boundary scattering induces flux cancellation [12]. The conduction is finally referred to as ballistic as soon as ℓ_e becomes larger than the distance between electrodes.

An early study of magnetoresistance of MWNTs with average diameters $d \sim 20$ nm, was performed by Langer *et al.* [7] applying a magnetic field perpendicular to the tube axis ($\mathcal{B}_\perp$). Negative magnetoresistance together with reproducible universal conductance fluctuations was obtained. More recently, Bachtold *et al.* [13] succeeded in measuring, at low temperature, the magnetoresistance of MWNTs by applying a magnetic field parallel to the tube axis ($\mathcal{B}_\parallel$). Again, negative magnetoresistance was reported together with $\Phi_0/2$-periodic Aharonov-Bohm oscillations ($\Phi_0 = hc/e$ the quantum flux). The theory of weak localization developed for mesoscopic systems accounts reasonably well for these results, *assuming a diffusive electronic conduction* restricted to the outermost shell of the MWNT, with a mean free path smaller than the tube circumference.

On the other hand, several studies [14–16] have reported both negative and positive magnetoresistance, and given the low values of resistance found at zero field, the authors have concluded that a quasiballistic conduction was taking place and that the sign of magnetoresistance was driven, not by localization effects, but by a flux-dependent electronic structure [17]. In particular, Fujiwara *et al.* [15] performed the first study of the magnetoresistance of an individual MWNT (with diameter of $\sim$19 nm), as a function of the orientation of the magnetic field. Surprisingly, negative magnetoresistance was found at low field for $\mathcal{B}_\perp$, whereas positive magnetoresistance was obtained for $\mathcal{B}_\parallel$. In such an experiment, standard weak-localization theory was obviously not sufficient to fully explain the data, and the recourse to the superimposed effect [17] of the magnetic field on the density of states (DOS) was suggested [16] but strongly criticized by other authors [18]. Ballistic transport together with quantization of conductance has been clearly observed in clean MWNTs in the absence of a magnetic field [9]. It is thus necessary to evaluate the effect of the magnetic field on the electronic conduction regime, depending on the concentration of defects that usually favors localization.

In this Letter, by means of an exact numerical computation of the Kubo conductivity for noninteracting electrons, it is shown that magnetotransport in SWNTs or MWNTs with small diameters cannot be understood only from the weak-localization scenario. We first demonstrate that the metal-insulator transition related to the flux-dependent DOS in the $\mathcal{B}_\perp$ configuration is strongly dependent on the value of the chemical potential that is usually difficult to estimate experimentally. By further consideration of the combined effects of the flux-dependent DOS with the diffusion coefficients, we outline several behaviors of the

magnetoresistance that confirm the richness and complexity of magnetofingerprints in small diameter nanotubes. Although these results are consistent with Fujiwara's anomalous magnetoresistance [15], we demonstrate that the hypothesis of the predominant spectral contribution to the magnetoresistance (for nanotubes with diameter $\geq$10 nm) is misleading, if restriction of the electronic conduction to the outermost shell is assumed.

Our systems are described by tight-binding Hamiltonians $\mathcal{H}$ with one $p_\perp$ orbital per carbon atom, and nearest neighbors hopping factors $\gamma_0 e^{i\varphi_{ij}}$ with $\varphi_{ij} = \frac{e}{h}\int_i^j \mathbf{A}\cdot\mathbf{dr}$ ($\mathbf{A}$ is the vector potential and $\gamma_0 = 2.9$ eV). Random on site energies distributed within $[-V_{\rm dis}/2, V_{\rm dis}/2]$ ($V_{\rm dis}$ is the disorder strength) simulate the effect of static disorder. In a first approximation the coupling between layers is neglected, and the magnetoresistance is evaluated assuming a conduction restricted to the outermost metallic shell of the MWNT. We calculate the Kubo conductivity of a weakly disordered nanotube coupled seemlessly to two disorder-free nanotube leads of the same type. In that way, the contacts formed by the two semi-infinite pure nanotubes are Ohmic, so that our numerical approach is equivalent to the Landauer method used by other authors [19]. The two-terminal magnetoconductance of a nanotube of length $L_{\rm tube}$ reads [20]

$$G(\tilde{\nu}, L_{\rm tube}) = \frac{2e^2}{L_{\rm tube}} \lim_{t\to\tau} {\rm Tr}[\delta(E - \mathcal{H})\hat{D}(t)]$$

with $\delta(E - \mathcal{H})$ the spectral operator (whose trace gives the density of states) and $\hat{D}(t) = [\hat{X}(t) - \hat{X}(0)]^2/t$ stands as the diffusivity operator ($\hat{X}$ is the position operator along the tube axis). The parameter $\tilde{\nu}$ is a measure of the dimensionless strength of the magnetic field applied to the tube and depends on the measurement geometry. For $\mathcal{B}_\parallel$, $\tilde{\nu} = \Phi/\Phi_0 = (B|C_h|^2)/4\pi\Phi_0$, whereas for $\mathcal{B}_\perp$ it writes $\tilde{\nu} = \nu = |C_h|/(2\pi\ell_m)$ with $\ell_m = \sqrt{\hbar/eB}$, the magnetic length ($|C_h| = 3a_{\rm cc}N$ is the circumference of the (N, N) tube, with $a_{\rm cc} = 1.44$ Å the distance between carbon atoms). Finally, the factor $L_{\rm tube}$ gives the voltage probe separation, whereas τ is the associated relevant time scale that fixes the value of the conductivity. In the ballistic regime $L_{\rm tube} = v_F\tau$, and the diffusion coefficient scales linearly in time, i.e., $D(t) \simeq v_F^2 t$, so that a length independent resistance $R = 1/G \sim h/2N_{\rm c}e^2$ is obtained (DOS $\sim N_{\rm c}/2\pi\hbar v_{\rm F}$, with $N_{\rm c}$ the number of independent channels). In the presence of disorder, elastic scattering produces a diffusive regime up to the scale from which localization effects fully dominate the electronic motion. The diffusive regime is related to a saturation of the diffusion coefficient of electronic wave packets, i.e., $D(t \geq \tau) = \ell_e v_F$ (v_F is the Fermi velocity, ℓ_e is the mean free path, and τ is here the elastic mean free time) corresponding to a resistance at zero flux $R \sim h/2N_{\rm c}e^2(L_{\rm tube}/\ell_e)$. It is, however, incorrect to extrapolate the value of the conductance from such a formula since it neglects quantum interferences that produce localization, and exponential increase of the resistance [$R(L_{\rm tube}) \sim (h/2N_{\rm c}e^2)\exp(L_{\rm tube}/\xi)$] as soon as $L_{\rm tube} \geq \xi \sim N_{\rm c}\ell_e$ (ξ is the localization length).

In our numerical procedure, the time-dependent Schrödinger equation is solved by using a polynomial expansion of the evolution operator, from which the diffusion coefficient of wave packet $|\psi\rangle$ can be deduced [20]. From different $|\psi\rangle$ initially localized at the center ($x = 0$) of the nanotube, the diffusion coefficient $\langle\psi|\hat{D}(t)|\psi\rangle$ is computed and provides the representative energy averaged diffusion coefficient $D(\tau)$ at a given computational step. To evaluate the magnetoresistance, we further assume that ${\rm Tr}[\delta(E - \mathcal{H})\hat{D}(\tau)] \sim \rho(E, \tilde{\nu}) \times D(\tilde{\nu}, L_{\rm tube})$ (with ρ the DOS at the considered chemical potential). When applying a magnetic field, both the DOS and the diffusion coefficients are modified. If applied parallel to the tube axis, a Φ_0-periodic metal insulator transition occurs in small diameter nanotubes owing to a flux modulated shifting of all the Van Hove singularities [17]. For the configuration ($\mathcal{B}_\perp$), the formation of Landau levels also affects the DOS, but in a different fashion [17]. In experiments, the precise position of the chemical potential can be shifted away from the charge neutrality point (CNP) either undesirably (because of donors or acceptors impurities) or in a controlled manner upon electrochemical doping [21,22] or field-effect doping [23]. We thus investigate the flux-dependent DOS as a function of the Fermi energy and magnetic field, first for the (10, 10) metallic armchair nanotube (diameter $\sim$ 1.37 nm). In Fig. 1, the DOS are given for a Fermi energy at the CNP and for different values of the chemical potential: CP1 $\simeq 0.316\gamma_0$, CP2 $\simeq 0.452\gamma_0$, and CP3 $\simeq 0.972\gamma_0$. One notes that it is experimentally possible to induce a shift of the chemical

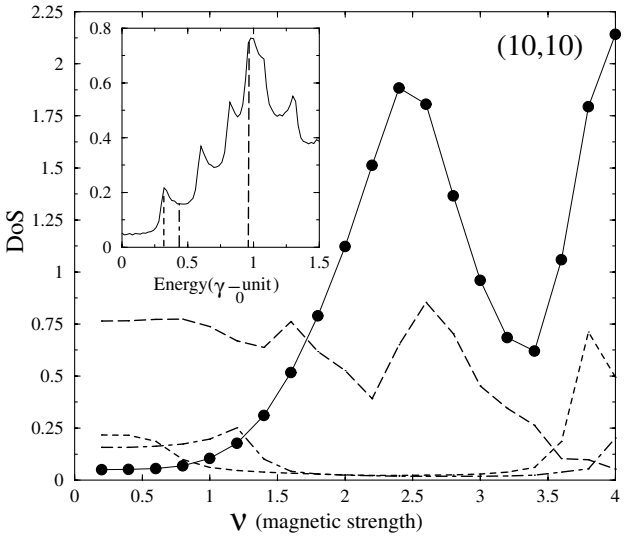

FIG. 1. Flux dependence of the DOS of the (10, 10) nanotube for different locations of the chemical potential, namely, the charge neutrality point (bold line with bullets), CP1 $\simeq 0.316\gamma_0$ (dashed line), CP2 $\simeq 0.452\gamma_0$ (dot-dashed line), and CP3 $\simeq 0.972\gamma_0$ (long-dashed line). Inset: DOS (in $1/\gamma_0$ Å^2 units) for the corresponding chemical potentials.

potential by $0.316\gamma_0$ away from the CNP, as demonstrated by means of an anthraquinone-lithium redox chemical reaction [21]. Our results show that at the CNP, the DOS of the metallic tube is strongly enhanced from $\nu \sim 1$ up to large values of the magnetic field. On the other hand, for the other values of chemical potential, one sees that the DOS may be strongly reduced. This has severe consequences on the magnetotransport.

The magnetoresistance of $(10, 10)$ and $(80, 80)$ tubes is investigated with increasing disorder scattering strength ($V_{\rm dis}$) and for $\mathcal{B}_\parallel$ and $\mathcal{B}_\perp$. We assume as a first approximation that the energy averaged diffusion coefficient well describes the dynamics of propagating wave packets. The mean free path for a (N, N) tube is estimated as [2]: $\ell_e \sim 36 a_{\rm cc} N \gamma_0^2 / V_{\rm dis}^2$. We choose to investigate the behavior of the diffusion coefficient for disorder $V_{\rm dis} = 0.5\gamma_0$, $2\gamma_0$, and $5\gamma_0$ that respectively correspond to $\ell_e \sim 45$, $5 \times |C_h|$, and $\ell_e \sim |C_h|/2$. The value of τ fixes the length of the nanotube, and for $V_{\rm dis} = 0.5\gamma_0$, $\tau = 400, 600, 800\hbar/\gamma_0$ correspond to $L_{\rm tube} \sim 100, 150, 200$ nm $\geq (\ell_e)_x$ [$(\ell_e)_x$ is defined as the projection of ℓ_e along the tube axis]. We remark that by definition $L_{\rm tube}$ is the scale along the tube axis, whereas ℓ_e is a property of the whole tube including the circumferential direction, and care should be taken when comparing ℓ_e with $L_{\rm tube}$. We thus refer to this as the *quasiballistic regime* [12], the regime for which $|C_h| < (\ell_e)_x \leq L_{\rm tube}$, which is nevertheless diffusive at the scale of $L_{\rm tube}$. For $V_{\rm dis} = 2\gamma_0$ and $5\gamma_0$, we also obtain that $(\ell_e)_x \leq L_{\rm tube} \leq \xi$ (for all the considered values of τ). Figure 2 shows the average diffusion coefficient over one quantum-flux period for the $\mathcal{B}_\parallel$ configuration. Two values of $\tau = 600\hbar/\gamma_0$ (solid line) and $800\hbar/\gamma_0$ (dot-dashed line) are reported in order to illustrate the increasing effects of quantum interferences with the system length $L_{\rm tube}$. In all cases, the diffusion coefficient increases at low field, but decreases with $L_{\rm tube}$. Besides, by approaching the limit $\ell_e \lesssim |C_h|$, the $\Phi_0/2$-periodic Aharonov-Bohm oscillations of the diffusion coefficient show up as expected from quantum interference theory [11].

The magnetoresistance $R(\Phi)$ [respectively, $R(\nu)$] for the configuration $\mathcal{B}_\parallel$ (respectively, $\mathcal{B}_\perp$) are reported in Fig. 3. For each value of the disorder strength $V_{\rm dis}$, a few configurations of disorder have been averaged. For comparison between the case $\mathcal{B}_\parallel$ and $\mathcal{B}_\perp$, we note that the magnetic strength ν corresponding to a magnetic flux $= \Phi_0$ occurs for $\nu \simeq 1.5$. For $V_{\rm dis} = 0.5\gamma_0$, the average value at zero field of the resistance is found to be in order of $15h/2e^2$ (including the effect of quantum interferences for a tube of length $\sim$100 nm). By switching on the magnetic field, the resistance drops $[dR(\nu)/d\nu < 0]$ to $\sim 5h/2e^2$ when $\nu \simeq 1.5$. For $\mathcal{B}_\parallel$, the resistance is found to increase $[dR(\Phi)/d\Phi > 0]$ up to values in order of 1 MΩ at $\Phi = \Phi_0/2$ and returns to its initial zero field value when $\Phi = \Phi_0$. For $V_{\rm dis} = 2\gamma_0$, the magnetoresistance increases by a factor of $\sim$400 for a tube with the same length (see Fig. 3 insets).

These observations demonstrate that magnetoresistance in such carbon nanotubes can be either positive or negative depending on the orientation of the magnetic field with respect to the tube axis, similar to the experiments of Fujiwara *et al.* [15]. In our case, such an unconventional phenomenon stems indeed from the superimposed flux dependence of the DOS. The $\Phi_0/2$ periodic oscillation found for the diffusion coefficient (Fig. 2) is found to be overdamped by the opening of the pseudogap at $\Phi_0/2$, which results in a strong increase of resistance. Another important observation is that the sign of magnetoresistance oscillations of $R(\nu)$ or $R(\Phi)$ strongly depends on the location

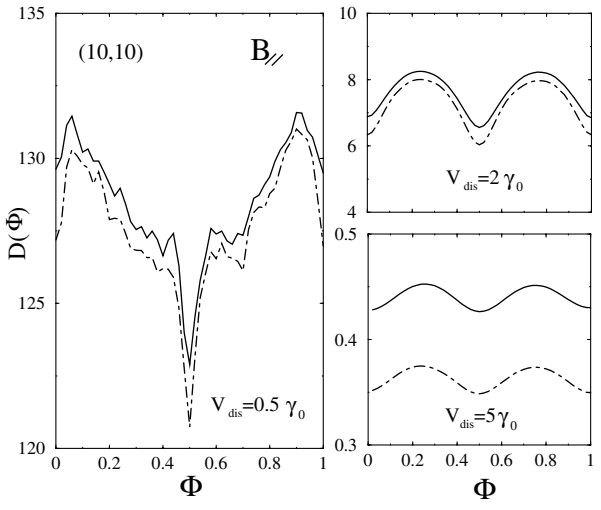

FIG. 2. Averaged flux dependent diffusion coefficient (in $\text{Å}^2\gamma_0/\hbar$ units) for the $(10, 10)$ tube in the $\mathcal{B}_\parallel$ configuration (in Φ_0 units) for several values of disorder, and two values of $\tau = 600\hbar/\gamma_0$ (solid line) and $800\hbar/\gamma_0$ (dot-dashed line).

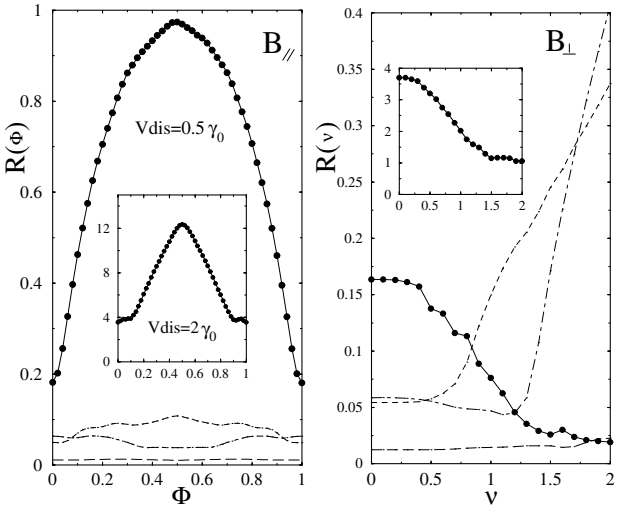

FIG. 3. Magnetoresistance $R(\Phi)$ (left) and $R(\nu)$ (right) for the disorder parameter $V_{\rm dis} = 0.5\gamma_0$, $\tau = 400\hbar/\gamma_0$, and values of the chemical potential corresponding to Fig. 1. Inset: Magnetoresistances for $V_{\rm dis} = 2\gamma_0$ at the CNP.

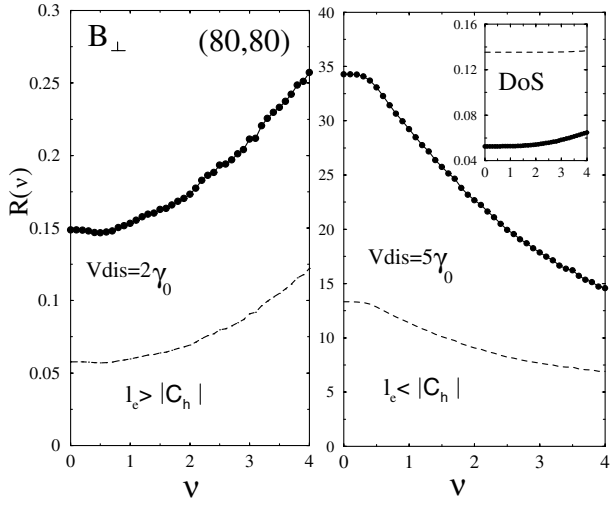

FIG. 4. Magnetoresistance $R(\nu)$ of the $(80, 80)$ nanotube, for $V_{\rm dis} = 2\gamma_0$ (left) and $V_{\rm dis} = 5\gamma_0$ (right) at the CNP (bold line with bullets) and at CP1 (dashed lines). Inset: Magnetic field dependent DOS for $V_{\rm dis} = 2\gamma_0$.

of the chemical potential. For the $\mathcal{B}_\perp$ configuration, at the charge neutrality point, the magnetoresistance is negative and the decrease is seen up to large values of the magnetic field, whereas for a doping corresponding to a shift of chemical potential by $\sim$0.9 eV with respect to the CNP, the opposite behavior is established.

We show now that for similar parameters, the increase of nanotube diameter yields completely different magnetotransport patterns. First, one notes that the tube $(10, 10)$ with disorder strength $V_{\rm dis} = 0.5\gamma_0$ has a mean free path of the order of the one of the $(80, 80)$ tube (diameter $\sim$ 11 nm) with disorder $V_{\rm dis} = 2\gamma_0$. Note also that in the case $\mathcal{B}_\perp$, we have $B \simeq 21\nu^2$ (tesla). The typical magnitude of resistance for $\mathcal{B}_\perp$ is roughly $R(\nu) \sim 200\ {\rm k}\Omega$, whereas $R(\Phi) \sim 2\ {\rm M}\Omega$ for $\mathcal{B}_\parallel$, weakly dependent on the magnetic strength (not shown here). Compared to the $(10, 10)$ tube, the behavior of magnetoresistance of the $(80, 80)$ tube for $\mathcal{B}_\perp$ is opposite from a chemical potential at the CNP. No dependence is found as a function of doping. Positive magnetoresistance is found at the CNP for the regime $\ell_e \sim 5|C_h| \leq L_{\rm tube}$ (Fig. 4 left), whereas negative magnetoresistance prevails in the case where there is diffusive conduction at a scale lower than the tube circumference, i.e., $\ell_e \sim |C_h|/2$ (Fig. 4 right). In the large diameter case, the DOS weakly depends on the magnetic strength for $\mathcal{B}_\perp$ (Fig. 4 inset). Analytical calculations show that the oscillations of the Van Hove singularities for the case of $\mathcal{B}_\parallel$ are irrelevant in such larger diameter shells, the DOS being identical to that of the graphene sheet. Actually, the distance between consecutive Van Hove singularities is in order of $\gamma_0 a_{\rm cc}/r_{\rm nt}$ ($r_{\rm nt}$ is the nanotube radius). This yields an average distance of $\sim$0.6 eV (respectively, $\sim$0.076 eV) between singularities for the $(10, 10)$ [respectively, $(80, 80)$] tube.

In conclusion, the magnetoresistance of the $(10, 10)$ tube cannot be described only by using the localization theory, since it is very sensitive on the position of chemical potential and on the orientation of magnetic field. However, MWNTs with outershell diameter as large as 10 nm follow conventional mesoscopic theories [8,13], as soon as conduction departs from ballistic motion and is restricted to the outermost shell of the MWNT. Other properties of magnetoresistance in bundles or doped nanotubes deserve further consideration [24].

R. S. acknowledges a Grant-in-Aid (No. 13440091) from the Ministry of Education, Japan. F. Triozon and D. Mayou are acknowledged for help on computational issues.

*Email address: sroche@cea.fr

[1] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
[2] C. T. White and T. N. Todorov, Nature (London) **393**, 240 (1998); T. Ando, Semicond. Sci. Technol. **15**, R13 (2000).
[3] M. Bockrath *et al.,* Science **275**, 1922 (1997).
[4] A. Bachtold *et al.,* Phys. Rev. Lett. **84**, 6082 (2000).
[5] R. Martel *et al.,* Appl. Phys. Lett. **73**, 2447 (1998).
[6] T. W. Ebbesen *et al.,* Nature (London) **382**, 54 (1996).
[7] L. Langer *et al.,* Phys. Rev. Lett. **76**, 479 (1996).
[8] C. Schönenberger *et al.,* Appl. Phys. A **69**, 283 (1999).
[9] S. Frank *et al.,* Science **280**, 1744 (1998).
[10] P. C. Collins *et al.,* Science **292**, 706 (2001).
[11] A. Aronov and Y. Sharvin, Rev. Mod. Phys. **59**, 755 (1987).
[12] H. van Houten *et al.,* Acta Electron. **28**, 27 (1988).
[13] A. Bachtold *et al.,* Nature (London) **397**, 673 (1999).
[14] J. O. Lee *et al.,* Phys. Rev. B **61**, R16 362 (2000).
[15] A. Fujiwara *et al.,* Phys. Rev. B **60**, 13 492 (1999).
[16] A. Fujiwara *et al.,* Physica (Amsterdam) **298B**, 541 (2001).
[17] H. Ajiki and T. Ando, J. Phys. Soc. Jpn. **62**, 1255 (1993); W. Tian and S. Datta, Phys. Rev. B **49**, 5097 (1994); S. Roche *et al.,* Phys. Rev. B **62**, 16 092 (2000).
[18] C. Schönenberger and A. Bachtold, Phys. Rev. B **64**, 157401 (2001).
[19] D. Orlikowski *et al.,* Phys. Rev. B **63**, 155412 (2001).
[20] S. Roche and D. Mayou, Phys. Rev. Lett. **79**, 2518 (1997); S. Roche, Phys. Rev. B **59**, 2284 (1999).
[21] E. Jouguelet *et al.,* Chem. Phys. Lett. **318**, 561 (2000).
[22] M. Krüger *et al.,* Appl. Phys. Lett. **78**, 1291 (2001); V. Derycke *et al.,* Nanoletters **1**, 453 (2001).
[23] A. Bachtold *et al.,* Science **294**, 1317 (2001).
[24] H. R. Shea *et al.,* Phys. Rev. Lett. **84**, 4441 (2000); K. Liu *et al.,* Phys. Rev. B **63**, 161404(R) (2001).