Photo-Galvano-Mechanical Phenomena in Nanotubes

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Abstract. We present new effects in nanotubes, as induced by light and friction with fluids. First, we show that atoms intercalated in C nanotubes can be driven by a dc electric current, generated optically by mixing one and two-photon interband electron transitions. In heteropolar BN nanotubes, even monochromatic laser beams can generate electric currents, which are accompanied by depolarization-induced expansion of the BN nanotubes. Piezoelectric effects should be also present in BN nanotubes. Finally, we show that electric currents can be induced in metallic nanotubes immersed in flowing liquids. These phenomena have potential applications in molecular electronics.

COHERENTLY-CONTROLLED ATOM PUMPING

Photovoltaic effects in bulk *non-centrosymmetric* materials are largely based on asymmetric generation of hot carriers at momenta $\pm\mathbf{k}$, giving the so called electrical "ballistic current". The photo-currents can be generated even in *centrosymmetric* materials, if we use a two-beam coherent control [1], giving asymmetric carrier injection due to quantum interference of one and two-photon transitions with frequencies 2ω and ω, respectively. This current can be also generated in semiconductor nanotubes or in higher bands of metallic nanotubes [2].

The photo-generated current J can be calculated from the simple formula

$$J = \frac{2e}{\hbar^2}\, \mathcal{G}\, E_{2\omega_0} (E_{\omega_0})^2 \cos(\delta\theta)\, \tau_{tr}\ .$$

Here, $\mathcal{G}$ is the generation rate for unit light intensities E_{ω_0} and $E_{2\omega_0}$, which depends on interband dipole transition elements and other tube parameters, and τ_{tr} is the electron transport time in the tube. The *current direction* depends on the the relative phase $\delta\theta = \theta_{2\omega_0} - 2\theta_{\omega_0}$ of the two fields. Considering realistic power intensities [2] one can get currents of the order $J \approx 0.1\ \mu A$.

The resulting hot-electron current can drive intercalated and adsorbed atoms on the tube surface. Perhaps the simplest driving mechanism is a direct Coulomb

scattering of free carriers on the atom. The mechanism requires that electrons and holes scatter *differently* from the atoms. Transfer of carrier momenta to the atom generates a force $F \approx 1$ μeV/nm, estimated from the current J, tube and atom parameters [2].

The barriers $E_{barr} \approx 0.12$ eV for inter-site Li atom hopping are shifted by the product of F and the length $l_t = 1.42$ Å, that connects neighboring sites. Consequently, hopping rates towards left and towards right are given by $\nu_{L,R} = \nu_0 \exp\left[-\left(E_{barr} \pm F l_t\right) / \left(k_B T\right)\right]$, where $\nu_0 = \left[(2E_{barr})/(m_{at} l_t^2)\right]^{1/2}$ is the atomic vibration frequency ($\nu_0 = 1.5 \times 10^{13}$ s^{-1} for Li). This yields the drift velocity

$$\langle v_{at} \rangle = \left(\nu_L - \nu_R\right) l_t \approx \frac{2\nu_0 F l_t^2}{k_B T} \exp\left(-\frac{E_{barr}}{k_B T}\right) .$$

Given the above excitation parameters, the drift velocity of Li atom is $\langle v_{at} \rangle \approx 25$ nm/μs for the temperature $T \approx 600$ K.

PHOTO-EFFECTS IN BN NANOTUBES

In heteropolar BN nanotubes even monochromatic light can generate dc electrical currents [3]. In this effect, photo-excited electrons, transferring between conduction and valence bands, asymmetrically shift between B and N atoms.

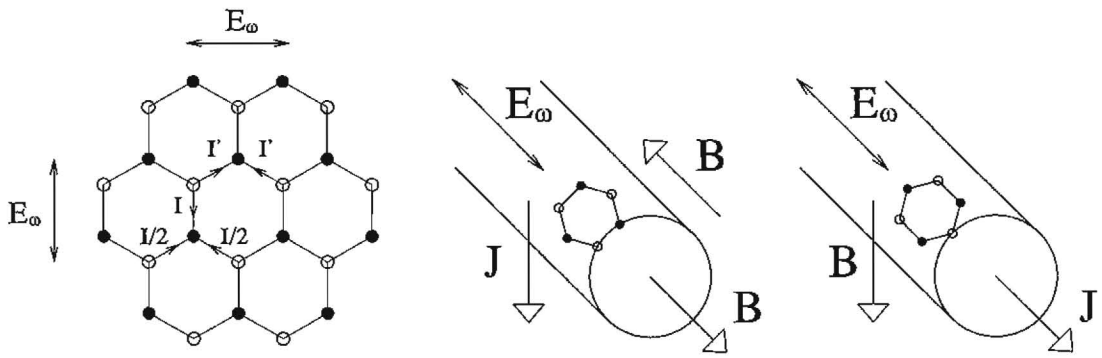

FIGURE 1. (left) Scheme of the shift current generation by light in layered BN. (right) BN armchair and zigzag nanotubes illuminated by light intensity $\mathbf{E}_\omega$ polarized along the tube axis. The induced *macroscopic* shift currents **J** and magnetic fields **B** are symbolized by arrows.

In Fig. 1 (left) we schematically show shift current generation in BN layer illuminated by a normal-incident light beam linearly-polarized in the vertical and horizontal directions. Valence states reside more on black (nitride) atoms, while conduction states on white (boron) atoms. For a vertical light polarization (LP) direction the electric field $\mathbf{E}_\omega$, giving interband electron transitions, goes along one of the three diagonals in the hexagons. The *microscopic* shift current I then runs from each N atom along the bonds to B atoms, oriented parallel with LP. This contribution prevails and determines the direction of the total current. In the horizontal LP orientation, the nonzero contributions I' add and the current flows in the

orthogonal vertical direction. In BN nanotube (right), irradiated by light polarized along its symmetry axis, the situation is qualitatively the same. Thus in armchair and zigzag nanotubes the current runs orthogonal and along the tube axis, respectively, while in chiral nanotubes in runs along a spiral. The detail structure of BN nanotube can further specify the direction [3].

The resulting *shift current* $\mathbf{J}$ can be expressed from the band off-diagonal density matrix $\rho_{\alpha\beta}$, in the second order of the excitation field $\mathbf{E}$, as follows

$$\mathbf{J} = 2e \sum_{\alpha\neq\beta} \sum_{\mathbf{k}} \mathbf{v}_{\beta\alpha}(\mathbf{k})\ \rho_{\alpha\beta}(\mathbf{k},t) = \mathbf{J_e} + \mathbf{J_s} + \mathbf{J_r}\ .$$

Here the current component $\mathbf{J_e}$ is due to light induced interband transitions, $\mathbf{J_s}$ is due to intraband relaxation and $\mathbf{J_r}$ is due to (radiative) transitions to the original bands. The excitation component $\mathbf{J_e}$ usually dominates in bulk materials. If the light is linearly polarized along the tube axis, the current density $\mathbf{J_e}$ can be described by

$$\mathbf{J_e} = e \int \frac{d\mathbf{k}}{2\pi}\ \dot{f}(\mathbf{k})\ \mathbf{R}_{e;vc}(\mathbf{k})\ \approx e\ \dot{n}\ \mathcal{R}\ ,$$

where $\dot{f}$ is the carrier density transition rate and $\mathbf{R}_{e;vc}$ the excitation shift vector. If the shift vector is weakly k-dependent $\mathbf{R}_{e;vc}(\mathbf{k}) \approx \mathcal{R}$, then $\mathbf{J_e}$ can be approximated by the second expression above, where the total carrier generation rate is $\dot{n}$. For the light intensity $I = 100$ kW/cm^2 at $\hbar\omega = 4$ eV one get $\mathbf{J_e} \approx 0.02$ pA in (10,10) BN nanotube.

Photo-excited carriers asymmetrically shifting in the elementary cells also depolarize the walls of the BN nanotubes. This is followed by a *fast readjustment* of atomic positions in the walls (atomic shift current). We can appreciate the atomic shifts in III-V semiconductors GaAs, GaP, GaN, ..., BN, where lattice constants are roughly inversely proportional to their ionicity. Consider that in equilibrium the charge $Q \approx 2.5$ e is transferred from B to N atom, where $d_{BN} = 1.45$ Å. Then the light induced transfer of $\delta q \approx 0.01$ e from N back to the B atom, in the above light intensities, increases the lattice distance by $\Delta d_{BN} \approx 0.4$ %. We can expect that *piezoelectric* effects are also present in heteropolar BN nanotubes.

ELECTRON DRAG IN FLOWING LIQUIDS

Motion of liquids along metallic nanotubes could also generate currents in nanotubes [4]. Fluids coat the tube in a form of layers, which slip along it the faster the further they are from it. The most plausible mechanism for current generation is a transfer of molecular momentum to the phonon bath. The liquid layers give the tube a rough surface, covered by defects, additive molecules, clusters or small islands. The defect boundaries, exposed to the unidirectional flow of molecules, differently absorb momentum from the liquid, and inject phonons with a nonzero average quasi-momentum in the nanotube. The resulting phonon wind *drags* free conduction electrons as shown in Fig. 2.

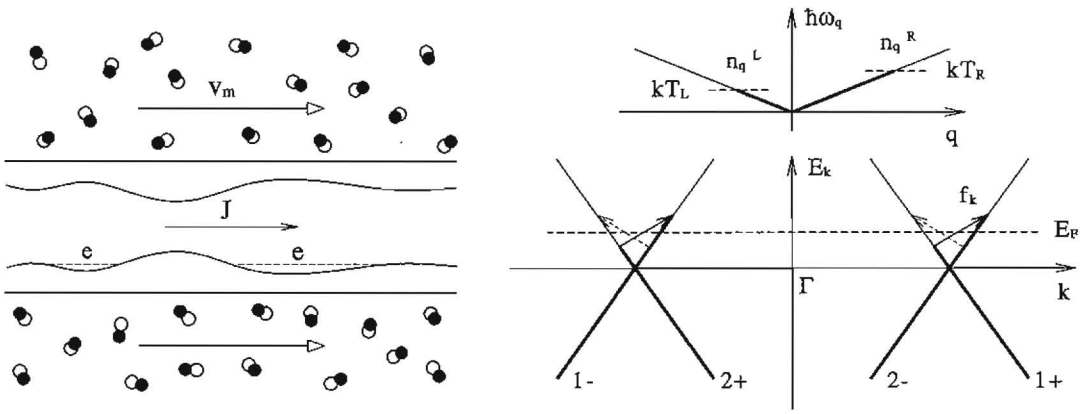

FIGURE 2. (left) Scheme of a metallic nanotube immersed in a liquid, flowing along it with a bulk velocity v_m. The molecules coat the nanotube in a form of slipping layers, which generate a phonon wind in the tube, dragging the free electrons. (right) Electronic structure of the lowest bands in carbon nanotube (10,10), where the Fermi level E_F is shifted up by dopants or the liquid. The populated regions of the carrier distribution f_k are drawn by tick lines. The unbalance in f_k is induced by the phonon population $n_q^{R,L}$ with temperatures T_R, T_L for the right and left propagating LA phonon winds, as shown schematically in the inset.

We consider that the velocity of water falls from $v_m = 1$ cm/s at the distance $d = 10$ nm from the tube to zero at the tube surface. This gives for a nanotube with $l = 1$ μm and periphery 10 nm the friction force $F \approx 10$ pN. If this force would be *only* balanced by generation of phonons with the phonon umklapp time $\tau_{um} \approx 10$ ps, then the momentum density of LA phonons is $p_{fric} = (F/l)\,\tau_{um} \approx 0.6$ ps eV/nm^2. We can use a Boltzmann description to obtain the resulting change of the hot-electron distribution Δn. From Δn we can evaluate the electron current as follows

$$J_{e-p} = \frac{2\,e}{l_0} \sum_{\alpha,k} v_F^\alpha \, \delta f_k^\alpha \approx 8\,e\,v_F\,\Delta n \approx 0.7\ nA\ ,$$

where v_F is the electron velocity at the Fermi surface. The induced electric current should allow building of nanoscale flow detectors or power cells.

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