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NANOWIRES AND NANOBELTS: BETWEEN PHENOMENOLOGY AND THEORETICAL MODELLING

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Abstract

This paper describes the most significant properties of nanowires and nanobelts, considering both the phenomenic and the theoretical aspects. ZnO nanostructures are paid a special attention, but interesting considerations related to the most utilized nanomaterials for different applications and topics are also considered.

Keywords *Nanowires, Nanobelts, Phenomenology, Theoretical Modelling, Piezoelectricity.*

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Introduction

Nanowires (NWs) are wire-shaped crystals having a diameter of order of few tens of nanometers (nm) and a length of a few microns (μm). A typical growth process of a nanowire involves a transition vapor-liquid-solid (VLS), in which metal nanoparticles are used as catalysts to increase in a continuous way the one-dimensional (1-D) formation of the semiconductor material. The beauty of this approach lies in the ability to grow a wide range of nanowires formed by different materials, which include elementary semiconductors (Si and Ge), so as compounds and alloys of III-V and II-VI groups. At the same time, the geometry and the alternation of the various materials, incorporated in the nanowires, can be controlled both along the vertical and the radial direction [1]. The fundamental and engineering interest of nanowires is a consequence of the large number of experiments and applications that nanowires allow [2]. Solar cells [3], waveguides, photo-detectors [4], LEDs, lasers [5,6], single photon sources, single electron emitters [7], diodes [8], transistors [9], memory devices [10], integrated circuits [11], chemical and biological sensors [12] are some of the possible applications based on the use of nanowires obtained by semiconductor materials [13-15]. As low-dimensional structures, the semiconductor nanowires are of particular interest for basic scientific research, since they present unique and amazing physical and structural characteristics, significantly different from the corresponding materials in massive form (bulk). Important semiconductors such as Si, GaAs, GaP, InAs, InP, AlAs, AlP, GaSb, InSb are stable in the zincoblend structure (ZB), but they may take the crystal structure of wurzite (WZ), if grown in the form of nanowires [16,17]. This fact constitutes an additional degree of freedom for the formation of heterostructures in which the crystalline phase of the material, rather than its composition, varies.

For all these reasons, the deep understanding of the properties of nanowires and similar nanostructures, as nanobelts, so as the theoretical modelling related to them, are useful and promising for the future of these nanoproducts [18].

Piezoelectric potential on the surface of a bent nanowire

In the typical configuration of a nanogenerator, the basis of the nanowire is attached to a conductive substrate, while the tip is pushed by a lateral force (transverse strength), here denoted by f_y. If the nanowire has approximately a cylindrical shape of radius a, the piezoelectric potential inside and outside the nanowire is, in cylindrical coordinates:

$$\Phi=\frac{1}{8k_\perp}\frac{f_y}{I_{xx}E}\left[2(1+v)e_{15}+2ve_{31}-e_{33}\right]\times$$

$$\times\left[\frac{k_0+3k_\perp}{k_0+k_\perp}\frac{r}{a}-\frac{r^3}{a^3}\right]a^3\sin\theta \tag{1}$$

for $r<a$, $-90°\le\theta\le 90°$;

$$\Phi=\frac{1}{8k_\perp}\frac{f_y}{I_{xx}E}\left[2(1+v)e_{15}+2ve_{31}-e_{33}\right]\times$$

$$\times\left[\frac{2k_\perp}{k_0+k_\perp}\frac{a}{r}\right]a^3\sin\theta \tag{2}$$

for $r\ge a$, $-90°\le\theta\le 90°$,

where $I_{xx}=(\pi a^4)/4$, e_{ij} are the piezoelectric coefficients, k_0 the permittivity in vacuum, E the elastic modulus, $k_\perp$ the dielectric constant in the basis plane (at repose), v the Poisson modulus.

The maximum potential on the surface of the nanowire (r = a), on the stretched (S) (θ = - 90°) and the compressed part (C) (θ = 90°), becomes respectively:

$$\Phi_{\max}^{(S,C)}=\pm\frac{1}{\pi}\frac{1}{k_0+k_\perp}\frac{f_y}{E}\left[e_{33}-2(1+v)e_{15}-2e_{31}\right]\frac{1}{a} \tag{3}$$

or alternatively:

$$\Phi_{\max}^{(S,C)}=\pm\frac{3}{4(k_0+k_\perp)}\times$$

$$\times\left[e_{33}-2(1+v)e_{15}-2ve_{31}\right]\frac{a^3}{l^3}v_{\max}, \tag{4}$$

where $v_{\max}$ is the maximum deflection of the nanowire with respect to the tip. The maximum potential on the surface of the nanowire is therefore directly proportional to the lateral displacement of it and inversely proportional to the cube of the ratio "length / diameter" (Fig. 1).

The equilibrium point of the positive charge is located in the center of the tetrahedron. Acting with a pressure on the crystal along the edge of the tetrahedron, it deforms slightly and the gravity center of the positive charge does not coincide with the previous position, thus generating an electric dipole. If all tetrahedra in the crystal have the same orientation, or some other mutual orientations, they do not allow a cancellation among dipoles.

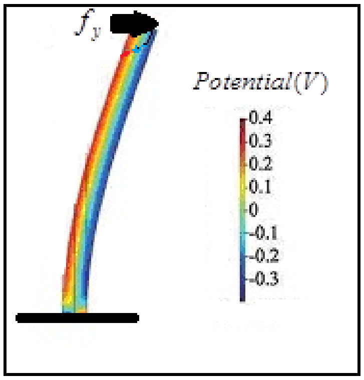

Figure 1: *Distribution of the potential for a ZnO nanowire of diameter d = 50 nm and length l = 600 nm, subjected to a lateral bending strength of 80 nN [19].*

The piezoelectricity is due to polarization at the atomic scale. Let's consider an atom with a positive charge surrounded in a tetrahedral way by anions (Fig. 2).

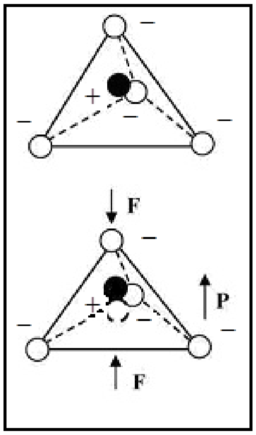

Figure 2: *Diagram showing the piezoelectric effect in "cation-anion" units and tetrahedric coordinates.*

The crystal has a macroscopic dipole and its two opposite faces will have opposite electric charges. The piezoelectricity refers to the opposite process, i.e. a contraction or elongation in the crystal is created when it is immersed in an electric field. Crystals can be piezoelectric only if they have not central symmetry, for ensuring the not compensation among the dipoles created in the tetrahedra. The piezoelectric effect can convert a mechanical vibration into an electrical signal or vice versa. This effect is widely used in resonators, in scanning probe microscopy for the control of the tip movement, in sensoristics for the vibration waves in air and in water. Piezoelectricity is an intrinsic property of some materials, such as the Zinc oxide (ZnO), and its intensity depends on the direction of growth of the nanowires. The piezoelectric coefficient of ZnO nanowires and nanobelts can be measured by an AFM using a conductive tip. Measures did frequency-dependent values ranging from 14.3 pm/V to 26.7 pm/V, much larger than those of bulk ZnO (0001), which is 9.93 pm/V. These informations lead to applications of ZnO nanobelts as nanosensors and nanoactuators [20-22].

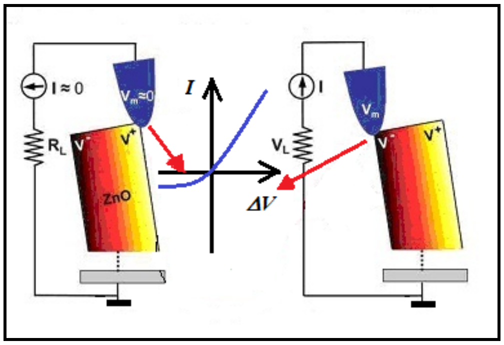

Figure 3: *Creation, separation and accumulation of piezoelectric charges (left), which move for the presence of the piezoelectric potential (right) [19].*

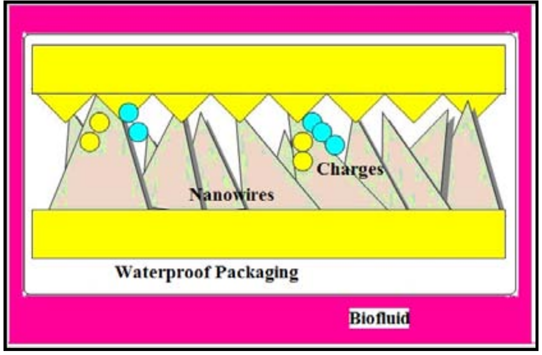

Figure 4: *Schematization of a nanogenerator that can operate in a biofluid. The spheres represent negative and positive charges, arising from piezoelectricity due to the deflection of the nanowires, shown here in a pyramidal shape [1,24,25].*

The Schottky barrier between the metal contact and the ZnO nanowire is another key factor that affects on the power generation and the output process. The physical principle of creation, separation, accumulation of piezoelectric potential in a nanowire is a coupling of piezoelectric and semiconducting properties of the material [23].

For a ZnO vertically disposed nanowire, its deflection with an AFM tip creates a voltage field, with the stretched outer surface (positive stress ε^+) and the compressed inner surface (negative stress ε^-). The asymmetric stress introduces an asymmetric potential on the two surfaces, with the compressed surface having a negative potential V^- and the stretched surface having a positive potential V^+.

Considering an array of ZnO aligned nanowires, with an upper electrode which can bend them, we have a typical nanogenerator of “dc” current. Such nanogenerators can be operated through the use of ultrasonic waves, through mechanical vibrations or even using body fluid flows. For this reason, these devices may also operate in liquids or fluids in general (Fig. 4).

The physical principle regarding the process of energy generation, observed in a piezoelectric ZnO nanowire, uses the coupling of piezoelectric and semiconductive properties by means of a metal-semiconductor Schottky barrier, which governs the transport process. The deflection of a nanowire through the tip of an AFM microscope involves an internal longitudinal distribution of stress ε_i. In correspondence with that, a distribution of induced piezoelectric longitudinal electric field E_i is observed in the nanowire, so as a corresponding distribution of potential as result of the piezoelectric effect [12,14].

The metal-semiconductor contacts between the tip of the AFM and the semiconductor nanowire exhibit a rectifying Schottky type inverse and direct behaviour, which allows: 1) avoiding the dispersion of the piezoelectric charges; 2) the production of the output discharge (Fig. 3).

Mechanical properties

The atomic force microscope (AFM) is a powerful tool for characterizing the mechanical properties of nanostructures. Using the tip of an AFM for deflecting for example a carbon nanotube, the displacement of the nanotube is directly attributable to the force acting on the tip, from which one can measure the Young’s modulus of the nanotube. In relation to the resonant excitation of the induced electric field, it has been developed an alternative technique for the measurement of mechanical properties of individual structures of type of a nanowire through the "in situ" transmission electron microscope (TEM).

Using this method it has been quantified the mechanical properties of carbon nanotubes, of Si nanowires, and Si and carbite-silica composite nanowires. The TEM is also used for obtaining measurements of the mechanical properties of nanobelts. It was demonstrated a AFM-based technique for measuring the elastic properties of individual aligned ZnO nanowires [26].

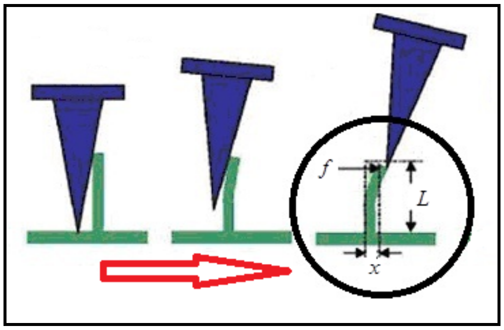

Figure 5: *Schematization of the technique for the measurement of mechanical properties [19].*

Through the simultaneous measurement of the topography and of the lateral force in AFM-contact modality (when the AFM tip passes through the array of aligned nanowires), it is possible to determine the elastic modulus of individual nanowires. This technique allows the measurement of the mechanical properties of individual nanowires of different lengths in an array, without destroying or manipulating the sample (Fig. 5).

The displacement and the lateral force are determined by the topographic map and by the image of the corresponding lateral force. Measurements of ZnO nanowires grown on sapphire surfaces, with an average diameter of 45 nm, gave an elastic modulus of 29 ± 8 GPa. The used technique allows a direct observation of the mechanical properties of aligned nanowires, of great importance for their applications in electronics, optoelectronics, sensoristics, actuatoristics [1,27].

Optical properties

The optical properties of nanowires and nanobelts are important for the majority of the technological applications. The ZnO nanobelts are quite narrow, thin and uniform. Their average diameter is about 5.5 nm, with a standard deviation of ± 1.5 nm, indicating a good uniformity of size. For examining the quantum effect induced by the size, it is possible to carry measures of photoluminescence (PL) at room temperature and using, for example, Xe lamps with particular wavelength of excitation (order of 330 nm) [19,27,28]. LEDs based on hybrid heterojunctions of NWs/p-GaN and ZnO-n can be fabricated, by growing arrays of n-type ZnO nanowires directly on GaN-p wafers [29-31]. Also dye sensitized solar cells (DSSC) with organic-inorganic heterojunctions were fabricated, using the large surface offered by the array of nanowires. Vertically aligned ZnO nanowires, with heights of about 10 μm, were grown on a glass substrate covered with ITO via hydrothermal approach, achieving interesting efficiencies [32-35].

Mathematical modelling

The charge transport is actually one of the most important aspects at nanoscale, influenced by particles dimensions and with particular different characteristics with respect to those of bulk [1,36]. In the mesoscopic range, the mean free path of charges can become larger than the particle dimensions, bringing therefore to a transport dependence by dimensions and to corrections of the transport bulk theories.

The techniques considered for the understanding of transport phenomena are both analytical descriptions based on transport equations and numerical approaches, as classical and quantum Monte Carlo simulations [37].

With the Drude-Lorentz model and its succeeding variations and extensions, it is possible to study the dynamics at nanolevel with good approximation. Recently it has appeared a new theoretical approach, which kernel is the complete Fourier transformation of the frequency-dependent complex conductivity $\sigma(\omega)$ of the considered system; with this model it is possible to calculate exactly the analytical expressions of the most important dynamical functions, i.e.:

a) the velocities correlation function $<\vec{v}(t)\cdot\vec{v}(0)>_T$ at the temperature *T*, from which the velocities of carriers are obtainable;

b) the mean square deviation of position $R^2(t)=\left\langle[\vec{R}(t)-\vec{R}(0)]^2\right\rangle$, from which the position and the travelled space of carriers are obtainable;

c) the diffusion coefficient $D(t)=1/2\,(dR^2(t)/dt)$, is a very important parameter, from which interesting informations related to the sensitivity and the global performance of nanobiodevices can be obtained. The new model was performed at classical, quantum and relativistic level [1,38-40]; it holds not only for electrons, but is more general. It contains also a “gauge factor”, which allows its utilization from sub-nanolevel to macrolevel, with interesting amazing general applications [41]. The model was tested in recent years using the experimental data of the most promising nanomaterials today, i.e. Si, ZnO, TiO_2, GaAs, CNTs, CdTe, CdS, CIGS [1,42-46], confirming accurate agreement with experimental results and offering new interesting peculiarities for future validations with currently important experimental techniques, such as TRTS spectroscopy [47-49].

Conclusions and perspectives

The future nanotechnology research will certainly still focus their efforts on the areas related to the integration of individual nanodevices into a nanosystem, that acts as a living organism, i.e. with sensorial, communicative, of control and response abilities.

A nanosystem requires a power source at nanoscale, able to preserve the small sizes of the entire device and working with high performance. One of the ultimate goals is the construction and optimization of nano-powered nanosystems, able to operate wireless. important areas on focusing the future research could be: 1) the increase “in number” of active nanowires, as engaged in generation of electricity, with the aim of increasing the voltage intensity and the output power. A possible approach is the use of arrays of ZnO nanowires with uniform size, in particular of uniform length, and to shape such arrays in accordance with the size and the shape of the upper electrode; 2) modelling in a systematic way the charge generation and the transport processes, considering accurately the dynamics involved in mechanics, piezoelectricity, semiconductor physics, contacts among interfaces [50,51]; 3) to develop effective theories for characterizing the performances of the nanodevices and their efficiency; 4) to optimize the dimensionality and the design for achieving higher energy conversion efficiencies; 5) to improve the packaging technology for integrating the electrode and the nanowires arrays, in order to achieve an optimization of output; 6) to study the possible damage mechanisms; 7) to study the metal-nanowire interface for building a robust and durable structure, which will improve the lifetime of these nanodevices; 8) to integrate three-dimensionally multiple nanogenerators, in order to increase power and output voltage; 9) to develop the storage technology of the generated charges and to increase the voltage for the use in the available electronics; 10) to integrate nanogenerators with nanodevices, in order to create self-powered nanosystems [52].

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