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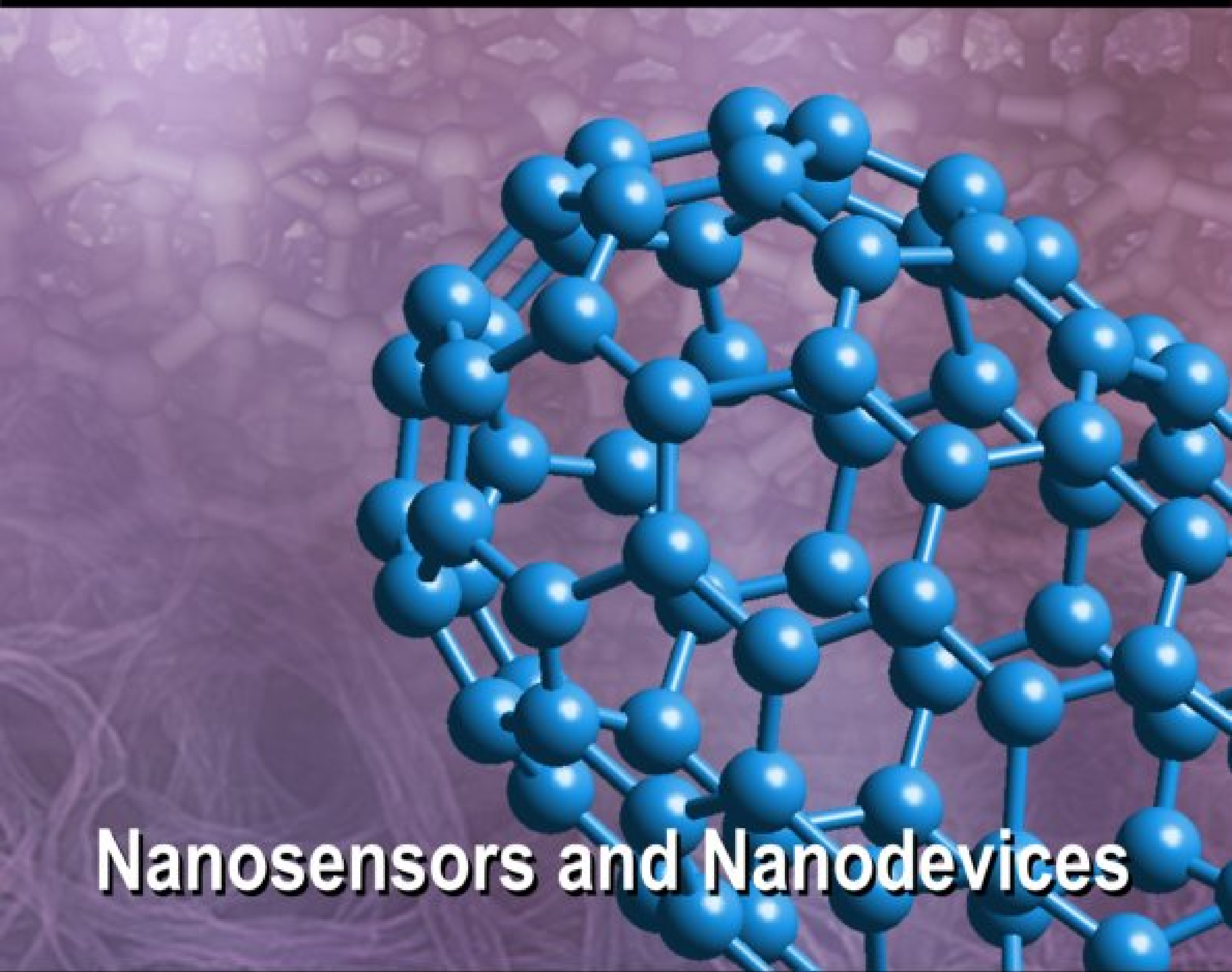

Nanosensors and Nanodevices

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New Theoretical Results for High Diffusive Nanosensors Based on ZnO Oxides

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Abstract: The approach for converting nanoscale mechanical energy into electrical energy using piezoelectric zinc oxide (ZnO) nanowire arrays has been broadly shown by deflection of the nanowires via a corrugated electrode operated up and down by ultrasounds. From a theoretical viewpoint, we have performed an analytical method for describing the most important quantities concerning transport phenomena. This method predicts very high initial diffusion of charge via mechanical external device stresses, assuming therefore the typical characteristics of a nanosensor. With this model it is possible to deduce important information about the device sensitivity, focusing on the interesting correlation between sensitivity and high initial diffusivity of these materials at nanometric state. *Copyright © 2010 IFSA.*

Keywords: Nanosensors, Semiconducting oxide, Diffusion, Nanodevices, Correlation functions, Frequency-dependent conductivity.

1. Introduction

The sector of sensoristics research and development is actually one of the most dynamic, interesting various application fields, like the industrial, medical and environmental, so as the sector of transports and communications. The micro-electronic technologies allow today the realization of sensors with high miniaturization levels, low consumptions and complex functionality. The micro-nano-sensors and the respective micro-nano-systems are evolving from the specific silicon sphere to the micro-nano-manufacture and micro-nano-engineering technologies, searching to resolve relevant technological problems like the endurance of the developed devices and the difficulties of interconnection and compatibility with the electronic devices. The peculiarities of the environment in which the measures must be performed result often incompatible with the operativity of such devices and demand to find solutions for the measure transfer elsewhere, with contactless and/or wireless technologies. At very small scales there is therefore a big need of energy and technologies for powering implantable biosensors, biomolecular and chemical ultrasensitive sensors, nanorobotics, micro-electro-mechanical systems (MEMS), remote and mobile environmental sensors, portable and resistant personal electronics. The research involves the integration of multifunctional nanodevices in a single nanosystem, appearing like a “living element”, with sensorial, controlling, communication, and answer/action abilities. The development of a nanotechnology able to harvest energy from the environment is therefore very important for the process of self-powering [1]. Various approaches for harvesting environmental energy for mobile and wireless micro-electronics using thermoelectrical, mechanical and piezoelectric vibrations have been developed [2, 3].

2. The Advantages of ZnO

The zinc oxide is one of the most important functional materials, attracting remarkable scientific and technological interests. The one-dimensional ZnO nanostructures, as nanowires and nanobelts [4], are considered fundamental elements for the manufacture of many nanodevices. Using electronical, optical, mechanical and piezoelectric properties, the ZnO nanowires/nanobelts have found useful application as field effect transistors (FET), UV laser, UV photo-detectors, light-emitting diodes (LED), solar cells, piezoelectric transducers and actuators [5]. In particular, through the interesting coupled use of semiconducting and piezoelectric properties of ZnO, it has been possible to obtain nanogenerators [6], piezoelectric field effect transistor [7], piezoelectric chemical sensors [8] and other important devices.

The nanowire-based technology for harvesting energy offers a lot of considerable advantages:

1) the nanowires/nanobelts can be submitted to extremely great elastic deformations without possible fractures, having a big resistance to the strain;
2) they may be easily bent, therefore are sensitive to small mechanical stresses;
3) ZnO nanowire arrays can easily be grown via chemical synthesis and have a good integration with technologically important materials, like silicon or polymers;
4) ZnO exhibits both semiconducting and piezoelectric properties, which form the basis for electromechanically coupled sensors and transducers;
5) ZnO is a not toxic, biocompatible, degradable material and has a wide range of applications;
6) ZnO exhibits the most different and abundant configurations of known nanostructures, such as nanowires, nanobelts, nanosprings, nanorings, nanobows, nanohelices [9-11].

3. Nanopiezotronics and Nanosensoristics

The nanopiezotronics, a new area of the electronics, utilizes the transport properties of a controlled piezoelectric field. The new electronic devices based on such properties are sensitive and well controllable through external strengths as for example a pressure. The piezoelectric effect permits to convert a mechanical vibration in an electric signal and vice versa. Such effect is broadly used in the resonators and in the scanning probe microscopes for the control of the tip movement, so as in the sensors for the vibrational waves in air and water. The piezoelectricity is an intrinsic property of ZnO, which demonstrates to be an interesting material for the applications in the sector of nanosensoristics [9]. A stress-based sensor created with nanowires of piezoelectric ZnO can be built with a not complex and reliable technique, and to accessible costs (see Fig. 1).

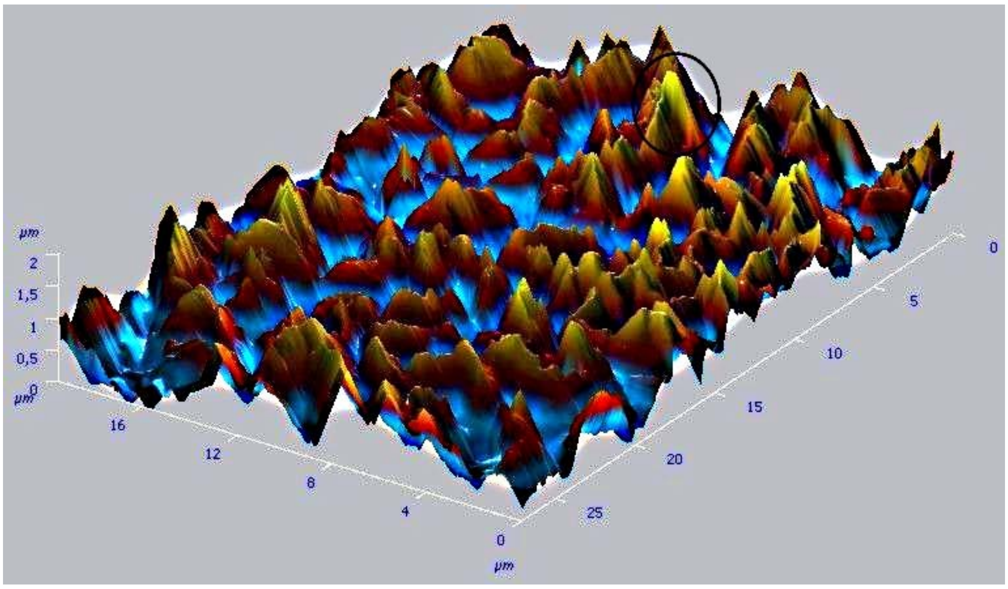

Fig. 1. AFM image of the microstructure of ZnO. In the circle is indicated the typical pyramidal local form of the structure.

One-dimensional nanostructures are very special materials for the creation of ultrasensitive nanosensors. Considering a nanowire or a nanotube as the fundamental unit in the building of the device, we have the typical configuration for the most important sensors, i.e. gas, chemical, and biochemical sensors. These nanowire-based nanosensors are probe-free and highly sensitive in the biological and chemical detection. The obtained electricity is utilizable in a large range of applications, like implantable biomedical devices, wireless sensors, portable electronics [12].

4. Nanodevices with High Initial Diffusivity: Theoretical Aspects of an Interesting Model

One of the most important characteristics of a nanosensor is the sensitivity, resulting in the ability to detect in very high modality. In a nanostructure this aspect is connected to the charge transport and assumes different characteristics with respect to those of bulk. In particular, if the mean free path of charges is larger than the particle dimensions, the system is mesoscopic and the transport depends on the dimensions; the transport bulk theories might therefore be corrected for doing the right results.

One of the most utilized models for describing experimental transport data is the Drude-Lorentz model [13, 14]. An extension of this model was proposed by Smith [15] and successfully applied to fit the conductivity in a large variety of systems. Other interesting models with particular variations with respect to the previously cited are the effective medium theories (EMTs), in which the electromagnetic interactions between pure materials and host matrixes are approximately taken into account [16, 17]. The commonly used EMTs include the Maxwell-Garnett (MG) model and the Bruggeman (BR) model.

We have performed a method based on a complete Fourier transform of the frequency-dependent complex conductivity of the system.

From a mathematical viewpoint, the Kubo relation of the linear response must be inverted. But, due to the presence of a half Fourier-transform, it is necessary to modify this relation in such a way that the whole time axis ($-\infty$, $+\infty$) occurs. This procedure is not trivial and as "time domain", not "frequency domain" approach, is not previously found in the literature in such a contest. We have started considering a system with an hamiltonian of the form:

$$H = H_0 + H_1 \tag{1}$$

with H_1 having small effects with respect to H_0, and negligible in the remote past (adiabatic representation). In the case of an electric field of frequency ω we have:

$$H_1 = e\vec{E}\cdot\vec{r}\,. \tag{2}$$

For an electric field constant in space and depending on time as:

$$\vec{E} = \vec{E}_0\, e^{i\omega t} \tag{3}$$

the time dependent corresponding current is:

$$\vec{J}(t) = \sigma(\omega)\ \vec{E}(t)\,. \tag{4}$$

Following the standard time-dependent approach [13], we have derived a general formula for the linear response of a dipole moment density $\vec{B} = e\vec{r}/V$ in the β direction with the electric field $\vec{E}$ directed in the α direction, where V is the volume of the system. This permits to deduce the correlation between the susceptibility $\chi(\omega)$ and the conductivity $\sigma(\omega)$:

$$1 + 4\pi\,\chi(\omega) = 1 + 4\pi\, i\,\frac{\sigma(\omega)}{\omega}\,. \tag{5}$$

Deducing from Eq. (5) the real part of $\sigma(\omega)$ (denoted as $\sigma'(\omega)$):

$$\sigma'_{\beta\alpha}(\omega) = \frac{e^2\,\omega\pi}{V\hbar} S_{\beta\alpha}(\omega)\left(1 - e^{-\hbar\omega/KT}\right) \tag{6}$$

with:

$$S_{\beta\alpha}(\omega) = \int_{-\infty}^{+\infty} dt \left\langle \vec{r}^{\,\alpha}(0)\ \vec{r}^{\,\beta}(t) \right\rangle_T e^{-i\omega t} \tag{7}$$

using quantum physical techniques, Eq. (6) can be written in a form containing the velocity correlation function. Assuming the high temperature limit $\hbar\omega << KT$ as usual in systems to be considered in this contest, we obtain:

$$\sigma'_{\beta\alpha}(\omega) = \frac{e^2}{2VKT} \int_{-\infty}^{+\infty} dt \left\langle \vec{v}^{\,\alpha}(0)\vec{v}^{\,\beta}(t) \right\rangle_T e^{-i\omega t} \tag{8}$$

The integral in Eq. (8) spans the entire t axis, so we can perform the complete inverse Fourier transform of this equation. It gives:

$$<\vec{v}^{\alpha}(0)\,\vec{v}^{\beta}(t)>_T = \frac{KTV}{\pi e^2}\int_{-\infty}^{+\infty} d\omega\, \sigma'_{\beta\alpha}(\omega)\, e^{i\omega t} \quad (9)$$

(V is the volume of the system, K the Boltzmann's constant, T the temperature) [18,19]. By integration of Eq. (9), we have deduced all the results for the velocities correlation functions $\langle \vec{v}(0)\cdot\vec{v}(t)\rangle$, the mean squared displacement $R^2(t)$ and the diffusion D, defined in the usual way as the half of $d/dx(R^2(t))$, with $x=t/\tau$.

5. Discussion

In ZnO oxides it has been found that the time required to the charges to traverse a nanoparticle is very small, resulting in rather high current [20]. These results demonstrate that the carriers within nanoparticles deviate from their bulk Drude-like behaviour. We have compared the velocities correlation functions and the diffusion coefficient, calculated through our theoretical results, with the correlation functions deduced from experiments [20]. In Fig. 2 it has reported the mean squared displacement $R^2(t)$ as a function of time for ZnO nanostructures with the average value of τ in the range considered (see Table 1 and Table 2).

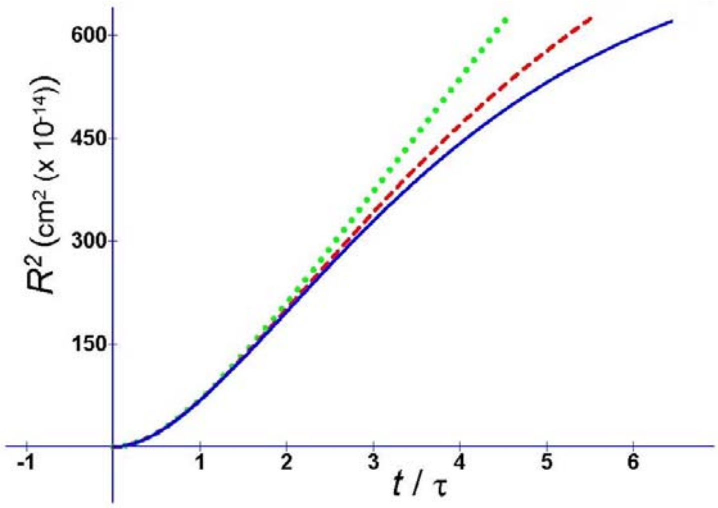

Fig. 2. $R^2(t)$ vs. t/τ for three different values of $\alpha_I = \sqrt{1-4\tau^2\,\omega_0^2}$, a parameter of our model (0.1 blue solid, 0.5 red dashed, 0.9 green dots) with the average value $\tau \cong 0.7\cdot 10^{-13}\, s$.

Table 1. Data of transport parameters for ZnO native electrons [23].

ZnO (native electrons) ($m^* = 0.24\ m_e$, T = 300 K)		
N (cm^{-3})	ω_p (s^{-1}) ($\times 10^{13}$)	τ (s) ($\times 10^{-13}$)
19×10^{17} Nanowires	15.8	0.28
6.1×10^{17} Film	8.98	0.35
0.25×10^{17} Annealed film	1.82	0.39

Table 2. Data of transport parameters for ZnO photoinduced electrons [23].

ZnO (photoinduced electrons) ($m^* = 0.24\ m_e$, T = 300 K)		
N (cm^{-3})	ω_p (s^{-1}) ($\times 10^{13}$)	τ (s) ($\times 10^{-13}$)
2.0×10^{16} Nanowires	1.63	0.84
1.1×10^{16} Film	1.2	0.93
2.3×10^{16} Annealed film	1.75	1.01
6.6×10^{16} Annealed nanowires	2.96	0.88
2.0×10^{16} Nanoparticles	1.63	0.77

We observe that the plateau of $R^2(t)$ becomes larger than the size of the nanoparticles composing the structure [21]. These features indicate that carriers created at time $t = 0$ will have enhanced mobility at small times on the order of few τ, in contrast with a commonly expected low mobility in the disordered network. Our results can therefore give an explanation of the ultra-short times and of high mobilities, with which the charges spread in mesoporous systems, of big and increasing interest in sensoristics sector. The short times, with which charges can reach very long distances with respect to the typical nanoparticle dimensions, indicate easy charge diffusion inside them. The unexplained fact found experimentally of ultra short injection of charge carriers can be related to this phenomenon.

In Fig. 3 it is presented the diffusion *D* as a function of time for a ZnO nanostructure constituting a nanosensor with $\tau \cong 0.7 \cdot 10^{-13}\ s$ for different values of the parameter $\alpha_I = \sqrt{1-4\tau^2\omega_0^2}$ resulting to our theoretical results. Fig. 4 represents the diffusion *D* as a function of time for fixed α_I and the extreme values of τ in the interval $[0.28 \cdot 10^{-13}\ s, 1.01 \cdot 10^{-13}\ s]$ (see Table 1 and Table 2).

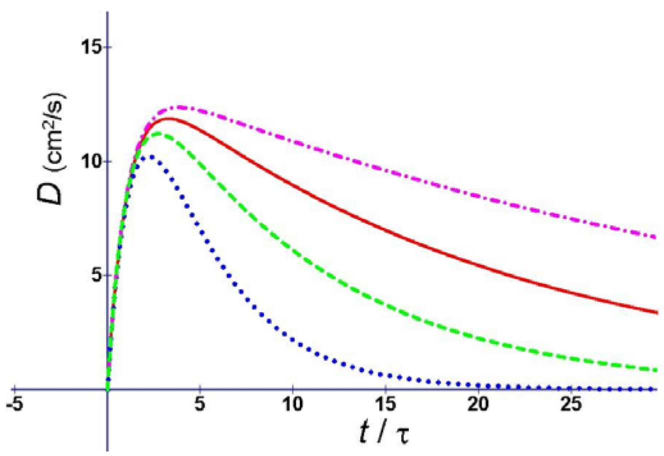

Fig. 3. *D* for variable $\alpha_I = \sqrt{1-4\tau^2\omega_0^2}$ in the interval (0,1) with $\tau \cong 0.7 \cdot 10^{-13}\ s$.

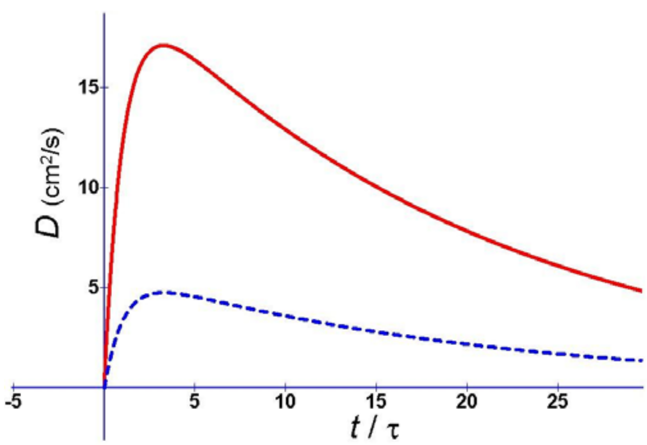

Fig. 4. *D* for fixed α_I and with the two extreme values of τ in the considered range (see Table 1 and Table 2).

We note that *D*→0 for *t*→∞, indicating absence of diffusion at very long times, as expected from theory and experiments.

We deduce the very interesting feature that, for fixed ω_0 the diffusion coefficient vanishes at long times and remains finite in the contrary case. It passes from $D \cong 0$ at large times to 5÷18 times the diffusion coefficient at smaller times. There is therefore a high initial diffusivity, which can adequately support the nanosensor sensitivity. At the beginning of the process the diffusion *D* is very high and the charges can reach the surface of nanoparticles in very short times. This result, derived from the numerical application of our theoretical results, is significantly in agreement with the conclusions obtained by THz spectroscopy [20, 22, 23].

6. Conclusions

The presented theoretical results regard the possibility of a very fast response of the transport of charge carriers, with a direct consequence for the efficiencies of devices based on such systems, like nanosensors. It is possible to explain the unwaited experimental result of high mobility at small times for fixed ω_0 in ZnO nanostructures, which would explain the high efficiency of devices based on this oxide. Our analysis can be useful for a nanostructured system, such as a solar cell composed of nanoparticles, as well as for a single nanotube. These enhanced transport times for nanostructured systems and films may constitute the basis for single nanotube nanosensors, where enhanced currents arising from piezoelectric charges have been shown to occur.

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- SECSED: Sensor circuits and sensor devices
- RIWISN: Radio issues in wireless sensor networks
- SAPSN: Software, applications and programming of sensor networks
- DAIPSN: Data allocation and information in sensor networks
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- Theory, principles, effects, design, standardization and modeling;
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- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
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