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Schottky contacts in germanium nanowire network devices synthesized from nickel seeds

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HIGHLIGHTS

- Ge nanowires were grown by VLS method using Ni as catalysts.
- All nanowires presented reduced diameters and high single crystalline quality.
- The small size of the nanowires led to phonon localization effect.
- Temperature dependent Schottky barriers were observed on GeNWs network devices.

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ABSTRACT

This paper presents reliable process to the synthesis of germanium nanowires by the vapor–liquid–solid method using nickel as an alternative catalyst to gold, the most commonly used metal, without toxic gas precursors. The structural study showed single-crystalline germanium nanowires with diamond structure, lengths of tens of microns and diameters smaller than 40 nm. The reduced dimensions of the nanowires led to phonons localization effect, with correlation lengths of the same order of the nanowires diameters. Additionally, the analysis of electronic properties of metal-nanowire-metal devices indicated the presence of Schottky barriers, whose values depend linearly on temperature. This linear dependence was assigned to the tunneling process through an insulator layer (mostly GeO_x) at the metal-semiconductor interface. These results point to the existence of another channel for electrons transference from metal to semiconductor being very significant to electronic devices fabrication.

1. Introduction

Group IV semiconductors are part of electronic devices history since its beginning until the latest advances. Germanium, in particular, presents some interesting properties: high holes and electrons mobility, small indirect and direct bandgaps, and large excitonic Bohr radius [1–3]. Because of these properties it is considered a promising material for electronic and opto-electronic applications in nanoscale, especially in building nanowire devices.

One common technique to produce germanium nanowires (GeNWs) is the vapor–liquid–solid (VLS) method. In this method the precursor material, in vapor form, is catalytically incorporated to a metal nanoparticle surface, usually gold [2,4], forming a liquid droplet; the droplet continues do adsorb the precursor material evolving to a supersaturated state when crystallization of the semiconductor occurs then resulting in the nanowire. Although metal is used only as a catalyst for the synthesis process some metal atoms can diffuse into the nanowires affecting their properties [5].

Recently, several works are being conducted with the aim of analyzing different metal catalysts, such as Ag [6,7], Cu [5,8] or In [9,10]. Thombare et al. [11,12] explored the use of nickel as metal catalyst in vapo–solid–solid (VSS) grown method for synthesis of germanium nanowires using GeH_4 (a toxic compound) as precursor gas. Their studies emphasize the effect of the metal on the synthesis process and showed that the growth rate and the activation energy were different from the Au catalyst. Barth et al. [13] and Lu et al. [14] also used nickel as catalyst metal, but in

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supercritical-fluid grown process, studying structural and electrical properties of produced germanium nanowires. They verified that the use of Ni-seeds allowed a beneficial control of nanowires diameter but also promoted a dopping effect, particularly in supercritical-fluid-solid-solid (SFSS) method, which affected electrical properties.

Taking in to account the simplicity of VLS growth technique, this study was aimed to investigate the nickel as seed metal for growing GeNWs by this method, without use of toxic precursors. In addition, the present paper reports on structural properties of the produced germanium nanowires, especially phonon localization phenomenon that occurred due to the reduced size of the nanostructures. Also, the dependence of the Schottky barriers as a function of temperature in nanowire network devices, whose architecture favors the application in gas or light sensors [15], was studied.

2. Synthesis and characterization

The GeNWs were synthesized by the VLS mechanism on Si/SiO_2 (oxide layer 500 nm thick) substrates in a tube furnace (Lindberg/Mini Mite).

Previously, a nickel thin film (2 nm) was deposited on the substrates under high vacuum (better than 10^{-6} mbar) using electron-beam evaporation (Edwards AUTO 306 equiped with EB3 source) and treated by thermal annealing at 800 °C in order to generate the nanoparticles. In sequence, germanium powder of high purity (Aldrich, purity $>99.999\%$) was put in the center of the tube furnace that was heated at 950 °C; at the same time, nanoparticles covered substrates were put in a specific position with temperature of 800 °C, which is higher than the eutectic temperature of the Ge–Ni alloy. Pure Argon (White Martins, purity $>99.998\%$) was used to carry the germanium vapor to the substrates during growth. After one hour of synthesis the furnace was turned off and naturally cooled to room temperature.

2.1. Network nanowire characterization

The resulting nanoparticles, whose image made by scanning electron microscopy (SEM, JEOL JSM 6510) is depicted in Fig. 1(a), presented diameters smaller than 40 nm and fairly uniform distribution in the substrate. Fig. 1(b), produced by field emission scanning electron microscopy (FEG-SEM, Zeiss Supra 35), show the obtained germanium nanowires. All analyzed samples showed a region covered by a dense layer of nanowires. The nanowires presented diameters ranging from 5 nm to 40 nm (agreeing to the nanoparticles dimensions), and lengths of tens of microns.

The average diameter (18.2 nm) and diameter distribution (standard deviation of 6.6 nm) of the nanowires grown from Ni-seeds by VLS method was smaller and straighter than those obtained by the VSS mechanism [11,12]. In relation to the germanium nanowires grown by SFSS synthesis [13,14], they present even smaller diameters and narrower distribution, but only because the nickel nanoparticles used are smaller and have fixed diameters (3.0 nm and 4.4 nm).

Regarding the composition of the nanowires, X-ray diffraction (XRD) pattern of the samples (Shimadzu, 6100, 40 kV, 30 mA, Cu

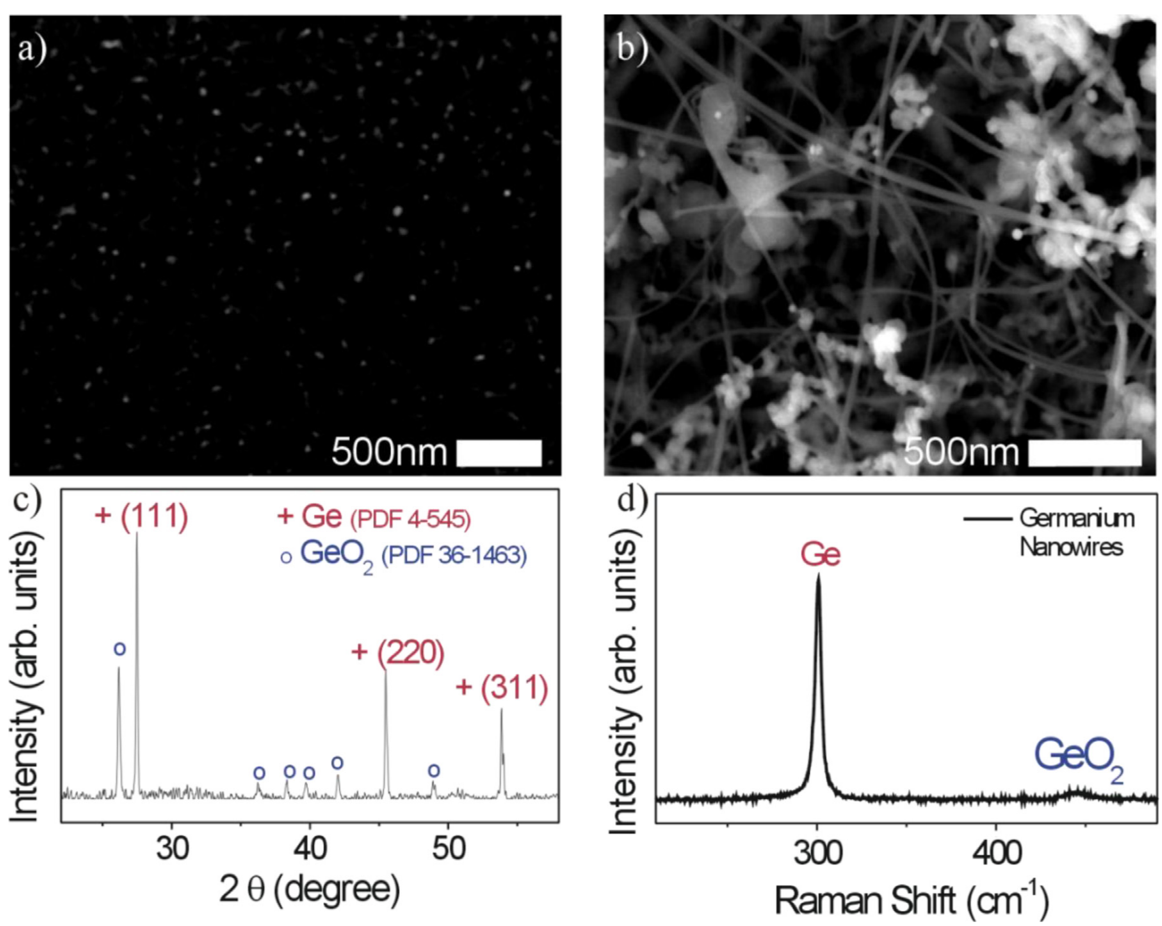

Fig. 1. Germanium as grown nanowire network characterization: (a) SEM image of Ni nanoparticles; (b) FEG-SEM image of the nanowires; (c) XRD pattern of the nanowire network showing Ge and GeO_2 peaks; (d) Raman spectra of germanium network nanowires showing a pronounced peak referring to germanium optical vibrations and a small peak related to A_1 vibrations in GeO_2.

Kα radiation), presented in Fig. 1(c), clearly shows the peaks (111), (220) and (311) of germanium with diamond structure (space group Fd-3m), agreeing with the powder diffraction card PDF 4-545 [16]. Some germanium oxide with a hexagonal structure in accordance with PDF 36-1463 diffraction card [17] was also detected.

In accordance with X-ray analyses, Raman spectra [Fig. 1(d)] taken from nanowires network present pronounced peaks centered at 300 cm^{-1}, attributed to Ge optical phonons, and a small peak at 443 cm^{-1} related to the A_1 vibration of the α-quartz phase of native GeO_2 [18]. Raman scattering experiments were performed in a triple grating spectrometer equipped with microscope facilities. Liquid nitrogen cooled CCD was used as detector. Spectrometer slits were adjusted in order to provide a spectral resolution of 1.5 cm^{-1}. The line 514.5 nm of an argon laser was used as excitation source with a controlled power lower than 1 mW, in order to avoid heating of the samples.

Based on these initial investigations GeNWs can be successfully synthesizes from Ni seeds by VLS method getting nanowires with smaller diameters and more uniform distribution than those obtained by the same growth process but using gold as catalyst [4]. The produced nanowires also presented large aspect ratio (10^3) and were basically composed of crystalline germanium.

2.2. Characterization of individual nanowires

A more accurate analysis of individual nanowires using high resolution transmission electron microscopy images (HRTEM, TecnaiF20G2, FEI equipped with an energy-dispersive X-ray spectrometer - EDS) and Micro-Raman spectroscopy provided experimental data for a better understand of structure, composition and vibration properties of the nanowires.

A metal drop on the tip of the germanium nanowire is clearly observed from HRTEM images (Fig. 2a), confirming the VLS growing mechanism. The images, particularly those in Fig. 2(b), also allow verify the good crystalline quality of the GeNWs. In addition, EDS analysis of the GeNWs, whose spectrum is depicted in Fig. 2(c), evidences that the nanowire are really composed by germanium with a small content of oxygen, once other elements were not detected along the nanostructure; this also means that no significant amount of the nickel catalyst was diffused throughout the nanowire. The Si, C and Cu peaks refer to the residues of substrates and the support grid of HRTEM equipment.

For micro-Raman analyses, five individual nanowires were picked up (randomly) from Si/SiO_2 synthesis substrates and were put in quartz substrates. In this setup the laser used as excitation was focused to a spot size with diameter smaller than 1 μm. For measurements, the power of laser was reduced below 800 μW,

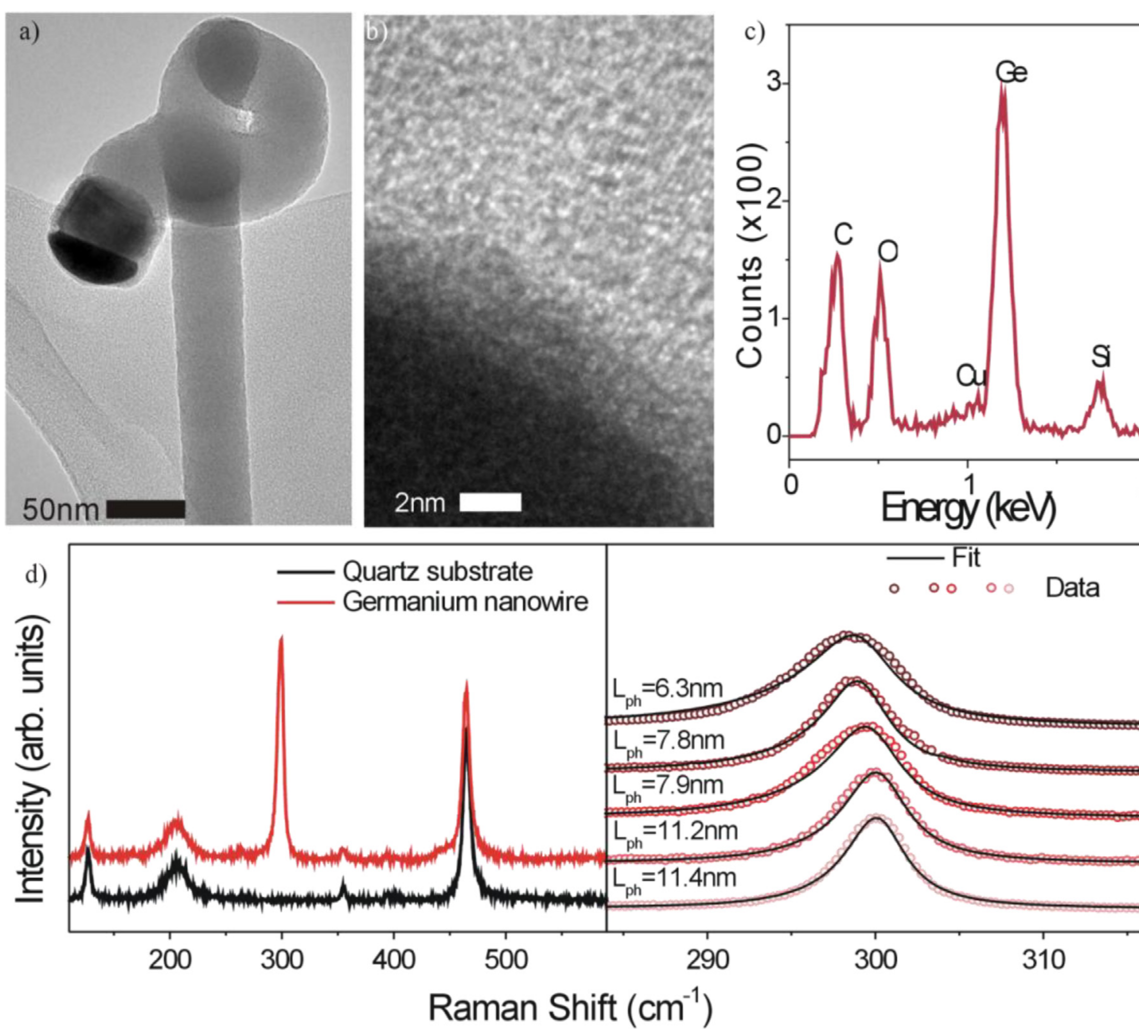

Fig. 2. Characterization of individual germanium nanowires: (a) TEM image of a GeNW showing the nickel drop on the tip of a nanowire; (b) HRTEM image of the same nanowire in metal-nanowire region; (c) EDS spectra of a GeNW grown from nickel catalyst; (d) Left: Raman spectra of the quartz substrate and a individual GeNW; Right: Raman spectra of five individual nanowires grown using Ni as catalyst metal in the range of germanium optical vibrations showing experimental data Ge peak (dots) adjusted to the theoretical spectra calculated for different phonon localization lengths (L_{ph}, straight lines).

preventing heating or damaging of the samples. The Raman spectra obtained from all samples are very similar and present peaks associated to the quartz substrates used as support and peaks in vicinity of 300 cm^{-1}, attributed to germanium optical phonons, as can be observed in Fig. 2(d – left).

More structural information can be achieved by performing a quantitative analysis of the peaks around 300 cm^{-1} of the spectra of each individual nanowire. When the translational invariance is destroyed by the presence of crystalline imperfections or finite size effects, phonons will be localized describing correlation lengths corresponding to the dimension of the structure or the extension of the region which present crystalline order. The decrease in the uncertainty of the localization of the phonons implies in the increasing of the uncertainties of their momenta, and a consequent breakdown in the selection rule for the momentum conservation, allowing the contribution of excitations with $q > 0$ to the Raman intensity. If we are dealing with phonons with negative dispersion relation, as in the case of optical phonons in germanium [19], in the presence of a strong localization, the contribution of phonons with lower wavenumbers will result in a spectral line redshifted and broadened towards lower energies.

Observing the five spectra measured from the samples, showed in Fig. 2(d – right), it can be noticed that the peak associated to Ge optical phonons present different frequencies and broadenings. Then, in order to examine phonon localization effects in these nanowires, we have fitted each one of the experimental data with a calculated spectrum. The calculations were performed using the spatial correlation model [20]. By adjusting the phonon localization lengths (L_{ph}), wich is the only free variable in the fit process, were found the theoretical spectrum that best reproduce the measurements and determined the L_{ph} in each nanowire. The experimental data of the five nanowires (open circles) and the corresponding fit (solid lines) are show in Fig. 2(d – right). The values obtained, around 10 nm, are compatible with the diameters of the nanowires, indicating that the phonon localization is a consequence of the confinement of the phonons due to the small size of the nanowire diameters.

Therefore, the analysis of individual nanowires have confirmed the crystallinity of the samples and the fact that the GeNWs do not have significant amount of impurities along their length, with nickel virtually limited to the tip of the nanowire (by absence of any content of other compounds along the nanowires). These results also revealed the effect of phonon localization: each spectrum clearly differs in both energy and broadening, which appeared as a natural consequence of the reduced dimensions of these GeNWs.

3. Study of electronic properties

Germanium nanowire network devices used for electrical characterization were built by evaporating metallic contacts (Ti, 80 nm thick) on the Si/SiO_2 substrates where nanowires were grown. Transport measurements were carried out using an electrometer (Keithley 6517) and a closed-cycle helium cryostat (Janis CCS 400H) working at a pressure lower than 10^{-5} mbar. Temperature-dependent resistance curves for all devices revealed the semiconductor character of the samples characterized by an exponential decrease of the resistance as the temperature increases. The semiconductor behavior is depicted in Fig. 3(a).

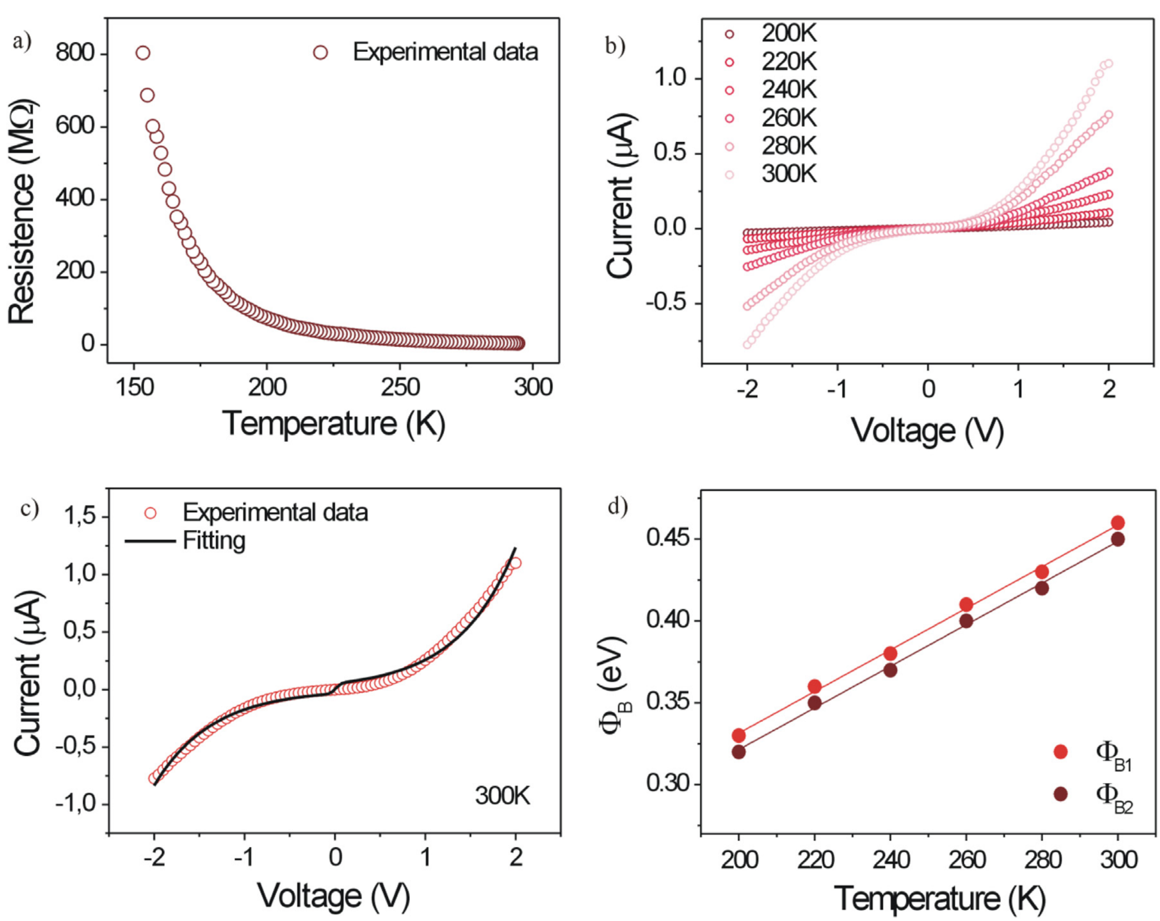

Fig. 3. Electrical analysis: (a) temperature-dependent resistance data showing the semiconductor behavior of the GeNWs; (b) I–V curves for different temperatures evidencing the Schottky barrier in both contacts of the device; (c) fitting the I–V data taken at 300 K to the back-to-back model; (d) barrier height values for different temperatures presenting a linear dependence relation.

Current–voltage characteristics of a germanium nanowire network device taken at six different temperatures are shown in Fig. 3 (b). The presence of a non-linear behavior (Schottky barrier) in both contacts was clearly observed for all measured temperature and a small asymmetry was also detected, indicating two distinct barrier heights. In order to obtain more information about the metal-semiconductor interface properties, the experimental data were fitted to the back-to-back Schottky model [21], under the usual thermionic emission theory assumptions. In this model, the current in a metal-semiconductor junction is written as

$$J=\frac{2J_1J_2\sinh\left(\frac{qV}{2k_BT}\right)}{J_1\exp\left(\frac{qV}{2nk_BT}\right)+J_2\exp\left(\frac{-qV}{2nk_BT}\right)} \quad (1)$$

with

$$J_{1,2}=A^*T^2\exp\left(-\frac{q\Phi_{B1,B2}}{k_BT}\right) \quad (2)$$

where A^* is the Richardson constant, Φ_{B1} and Φ_{B2} are the Schottky barrier heights, n is the ideality factor and the other symbols have their usual meanings.

The good agreement of both theoretical and experimental curves can be seen in Fig. 3(c), measured at room temperature. For all other temperatures a similar behavior was obtained. The fitting allowed estimating the n factor around 1.06. Idealities $n>1$ have been ascribed to several effects, including the presence of interface states distributed in a thin oxide between the metal and the semiconductor [22].

The Schottky barrier heights as a function of temperature are plotted in Fig. 3(d). In this figure the linear temperature dependence of barrier height in the GeNWs network device is quite evident. This linear dependence can be assigned to the presence of an insulator at the interface of metal-semiconductor contact [23] which contributes with localized states leading to a temperature dependent barrier height due to tunneling process.

Under this consideration Φ_{B1} and Φ_{B2} in Eqs. (1 and 2) are calculated by

$$\Phi_{B1,B2}=\Phi_{0B1,0B2}+\beta lk_BT \quad (3)$$

where β and l are the tunneling constants which refer to the tunneling efficiency of electrons through the insulator and to the thickness of the insulator, respectively.

The value of Φ_{0B} was estimated to be approximately 0.1 eV from extrapolation to 0 K of temperature dependent barrier curves (Fig. 3d), which agrees with the expected barrier height for the Ge/Ti devices [23]. Simultaneously, the βl product for these GeNWs (14.7) is very close to that found in organic monolayers used in silicon devices or in modified electrodes in C_{60} field-effect transistors [24] in order to improve the properties displayed for them.

For germanium nanowire network devices studied here the insulator layer between the electrodes and the active germanium nanostructures could be directly formed by the germanium oxide as detected in the structural analysis, which usually originates a nanowire shell [2]. As was observed, the tunneling barrier created at the core/shell (Ge/GeO_x) interface plays an important role in determining the properties of the devices since it contributes to another channel for electrons transference from metal to semiconductor which in turn, induces the barrier dependence on temperature. As GeO_x is naturally formed during the synthesis process this is interesting to the construction of electronic devices as well single electron transistors or field effect transistors.

4. Conclusion

This paper presented a new possibility for the synthesis of germanium nanowires by VLS mechanism using nickel as catalyst metal, without toxic precursor in the process. The structural analysis revealed nanowires composed mainly by single crystalline germanium with a small amount of germanium oxide; also they were found to have diameters around 20 nm with fairly uniform distribution and large aspect ratio. Raman study in individual nanowires indicated that the reduced size of the samples led to phonon confinement effects characterizes by localization lengths of the order of nanowires diameters. In the study of electric characteristics, the metal-semiconductor contacts behavior was investigated in germanium nanowire network devices, whose architecture favors direct electronic application. The I–V experimental data were fitted with back-to-back Schottky barrier model and the temperature dependence of barrier heights revealed the influence of tunneling process in the metal-semiconductor junction, probably due to the presence of a thin layer of germanium oxide forming a shell.

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