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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

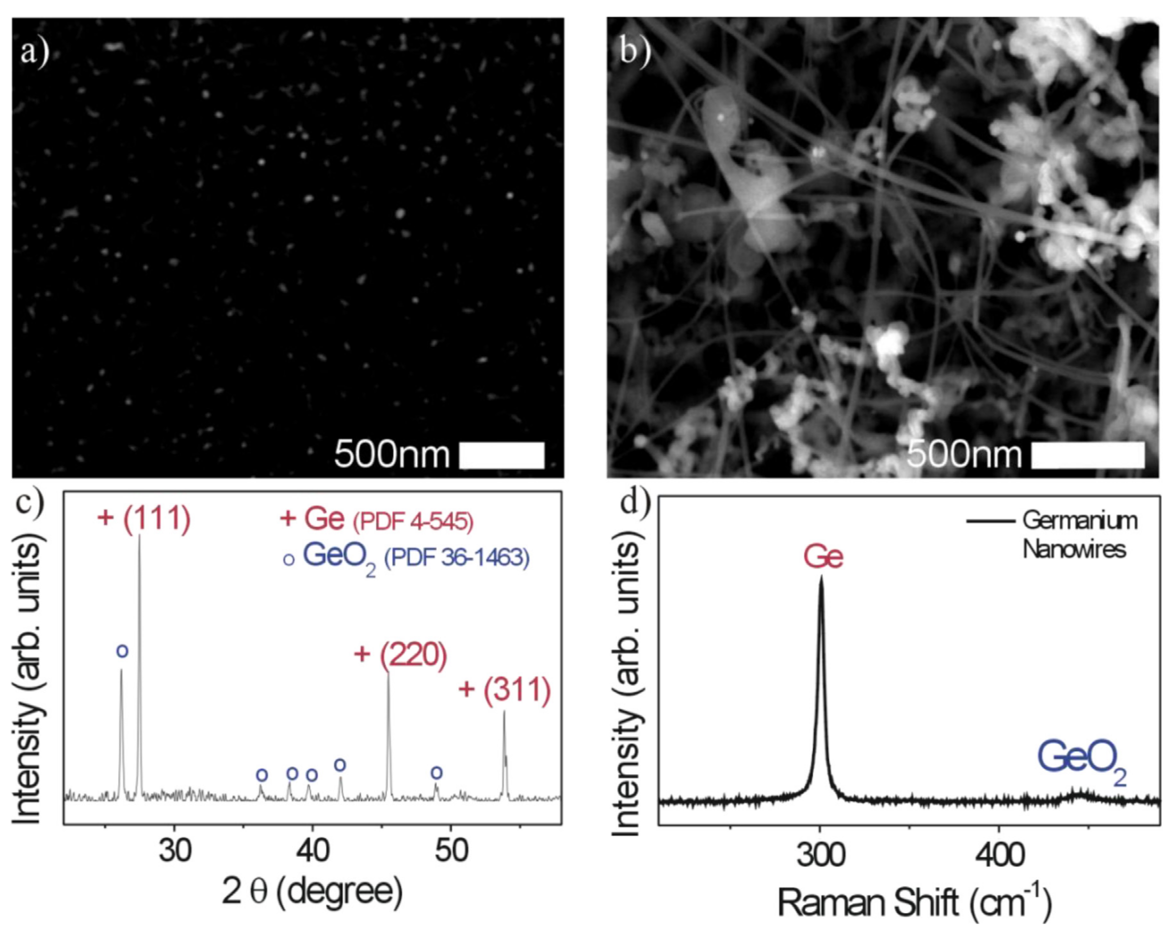

Fig. 1. Germanium as grown nanowire network characterization: (a) SEM image of Ni nanoparticles; (b) FEG-SEM image of the nanowires; (c) XRD pattern of the nanowire network showing Ge and GeO_2 peaks; (d) Raman spectra of germanium network nanowires showing a pronounced peak referring to germanium optical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