Synthesis, Characterization and Carrier Transport Properties of Crystalline Ge Nanowires Growth with Ag-Based Catalysts

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Abstract
Ge nanowires were synthesized by VLS method with silver nanoparticles as metal catalysts. The structure and composition of the Ge nanowires were investigated by X-ray diffraction (XRD), scanning electronic microscopy (SEM) and micro-Raman technique showing single crystalline Ge nanowires smaller than 100nm in diameter. The electric properties were characterized in two distinct nanowire devices indicating hopping as the main carrier transport mechanism and we found a Schottky barrier around 0,46 eV for different metals and temperatures.

1. Introduction
Germanium nanowires (GeNW) has received much attention of scientific community in recent years due its interesting properties: high electron and hole mobility, favoring electronic appliances; small bandgap, supporting optical applications in infrared region; and large excitonic Bohr radius (24.3nm), highlighting quantum size effects [1,2].

Vapor-liquid-solid (VLS) is a common technique to grow GeNW, generally using gold as catalyst seed [1, 3, 4]. The diffusion of gold into the nanowire would affect its characteristics, creating deep-level defects and severely impact the electrical properties [5, 6].

This study investigates an alternative route to VLS process, using silver as seed metal for growing GeNW. We also studied the carrier transport in two distinct devices, examining transport process and metal-semiconductor contacts.

2. Experiments
The nanowires were synthesized by the vapor-liquid-solid (VLS) mechanism on Silicon substrates in a tube furnace. Previously thin films of silver (2nm) were deposited on Silicon substrate by evaporation and subject to a heat treatment at 800°C in order to generate the nanoparticles. Germanium powder of high purity was put in center of furnace that was heated at 950°C. Previously prepared Si substrate was put in position with temperature at 800°C. Argon was use to transport the germanium vapor to the substrate. After 1h the furnace was air cooled to room temperature.

Film nanowire devices were built by evaporating Ti metallic contacts on the silicon substrates where the nanowires was grown. Single nanowire devices were fabricated by conventional photolithography techniques, using Ni metallic contacts.

3. Results and Discussion

Fig. 1 (a) SEM image of the as-grown nanowires on the substrate. (b) X-ray diffraction pattern recorded on the Ge nanowires. (c) Raman spectra at 514 nm of Ge nanowires at 1.5mW laser power.
Firstly the samples were submitted to SEM analysis exhibiting a region with high density of nanowires smaller than 100nm in diameters and lengths of tens of microns, as presented in Fig.1(a). In the inset of Fig.1(a) it can be observed a small Ag drop in the tip of a nanowire, indicating the VLS growing mechanism. Hereafter the substrate containing nanowires were examined by XRD, demonstrated good agreement with the diffraction card PDF 4-545 corresponding to a diamond structure of Ge and PDF 36-1463 corresponding to hexagonal structure of GeO₂, as displayed in Fig.1(b).

A more accurate analysis of the region with high density of nanowire by micro-Raman technique, as show in Fig.1(c), present good crystalline quality of Ge and little amount of GeO₂. The Si peak is due to the substrate.

The temperature-dependent resistance measurements in both devices reveal the semiconducting character of the samples. The observed behavior was well fitted to the variable range hopping (VRH) conduction mechanism [7], as shown in Fig.2(a). From this model we found the localization length of ~30nm, which is in reasonable agreement with the Bohr radius of germanium and also it is smaller than the nanowires cross section.

The current-voltage dependence is useful for extraction of electrical parameters of the devices. This dependence is plotted in Fig.2(b) for different temperatures. Two Schottky barriers (in both contacts) were observed in the whole temperature range in the single and multi-(thin film) nanowires’ devices.

This electrical behavior was modeled using the back-to-back Schottky model [8] under the usual thermionic emission theory assumptions. From this model we found barrier heights ranging from 0.41 to 0.51 eV regardless the different contact metals, which can be explained by the influence of surface states in the nanostructures [8, 9].

4. Conclusions

In summary, we present a new route to VLS process using silver as seed metal for growing Ge nanowires. Temperature-dependent resistance and current-voltage measurements were carried out confirming the semiconducting character of the nanowires. Hopping conduction was observed providing us with the localization length in the same order of germanium Bohr radius. Schottky barriers in both contacts were found to be similar for different metals and temperatures, suggesting that surface states are dominating.

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