Materials Chemistry and Physics xxx (2016) 1–7

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Germanium nanowires grown using different catalyst metals

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HIGHLIGHTS

- Ge nanowires were grown by VLS method using Au, Ag, Cu, In and Ni as catalysts.
- All nanowires presented high single crystalline quality and long range order.
- Devices showed semiconducting behavior having VRH as dominant transport mechanism.
- The metal catalyst did not influence structural properties or the transport mechanism.

ARTICLE INFO

Article history:
Received 1 October 2015
Received in revised form
4 August 2016
Accepted 6 August 2016
Available online xxx

Keywords:
Nanostructures
Semiconductors
Raman spectroscopy
Transport properties

ABSTRACT

Germanium nanowires have been synthesized by the well known vapor-liquid-solid growth mechanism using gold, silver, cooper, indium and nickel as catalyst metals. The influence of metal seeds on nanowires structural and electronic transport properties was also investigated. Electron microscopy images demonstrated that, despite differences in diameters, all nanowires obtained presented single crystalline structures. X-ray patterns showed that all nanowires were composed by germanium with a small amount of germanium oxide, and the catalyst metal was restricted at the nanowires' tips. Raman spectroscopy evidenced the long range order in the crystalline structure of each sample. Electrical measurements indicated that variable range hopping was the dominant mechanism in carrier transport for all devices, with similar hopping distance, regardless the material used as catalyst. Then, in spite of the differences in synthesis temperatures and nanowires diameters, the catalyst metals have not affected the composition and crystalline quality of the germanium nanowires nor the carrier transport in the germanium nanowire network devices.

1. Introduction

Semiconductor nanowires attract the interest of scientists because of their wide range of potential applications, such as electronic, photonic, energy and magnetic [1]. Germanium has been receiving special attention as a precursor material in nanostructure manufacturing due to its particular characteristics: high carrier mobility and compatibility with conventional silicon equipments, favoring electronic applications; narrow indirect (0.66eV) and direct (0.8eV) bandgaps, supporting optical devices development in infrared and visible regions; and large excitonic Bohr radius (24.3 nm), highlighting quantum size effects [2,3].

Different experimental methods have been used for obtaining germanium nanowires (GeNWs) such as vapor-liquid-solid (VLS), vapor-solid-solid (VSS) and solution-liquid-solid (SLS) [4]. Among these techniques, the most widely used is the VLS mechanism which relies on a vapor phase precursor of the nanowire material being adsorbed onto a liquid seed and then precipitating at the growth surface, resulting in nanostructures [2,5,6].

In this technique, gold is generally used as catalyst seed, but recent papers have reported investigations of the growth of GeNWs using different catalyst metals. Barth et al. [7] and Biswas et al. [8] studied the use of Ag as growth seed for generating GeNWs via SLS. Kang et al. [9] and Geaney et al. [10] reported a VSS growth of GeNWs using Cu-catalysts. Lu et al. [11] and Thombare et al. [12] studied SLS and VSS Ni-seeded synthesis of GeNWs, respectively.

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http://dx.doi.org/10.1016/j.matchemphys.2016.08.012

Xiang et al. [13] presented a route for GeNWs by In-seeded VLS growth. Furthermore, some authors have discussed the use of other possible catalyst metals such as Bi, Sn and Mn [4].

Despite the great contribution to the understanding of growth process and nanowires properties achieved in each one of these publications, they present different routes for the synthesis of GeNWs making difficult a comparative analysis of how the seed metals influence the nanowire's properties. Therefore, the aim of this study was to provide a comparison between the nanowires growth by the same method (VLS) but using different catalysts (Au, Ag, Cu, In and Ni) regarding to structural characteristics and transport mechanisms. The use of these metals can provide a good overview of this subject, since they have metal-Ge eutectic curves characterized by distinct features, as well as different diffusion coefficients and energy levels in germanium crystals.

2. Synthesis and characterization of the nanowire networks

Initially, thin films of gold, silver, copper, indium and nickel were deposited on Si/SiO_2 (oxide layer 500 nm thick) substrates under high vacuum (better than 10^{-6} mbar). Then, in order to generate the catalyst nanoparticles the substrates with thin (2 nm) metallic films were submitted to thermal treatment under temperatures of 600 °C for Au and Cu and 800 °C for Ag and Ni. For In-based growth the film was 1 nm thick and the thermal treatment was not used.

The synthesis was carried out in a tube furnace system (Lindberg/Mini Mite) where high purity germanium powder (Aldrich, purity > 99.999%) was placed at the center of the furnace and heated to 950 °C. Previously prepared substrates were placed at specific positions with temperatures of 800 °C for Ag, Cu and Ni nanoparticles and 600 °C for Au seeds and In film. All these temperatures are higher than the eutectic point for used metal-Ge alloys. Argon (White Martins, purity > 99.998%) was used for carrying the Ge vapor to the substrates during growth. After 1 h of synthesis the furnace was turned off and naturally cooled to room temperature.

Hereafter, the composition of resultant nanowire networks was analyzed by X-ray diffraction (Shimadzu, XRD 6100,40 kV, 30 mA, Cu Kα radiation) and Raman spectroscopy; also the nanowires' dimensions were statistically studied using images taken by scanning electron microscopy (SEM, JEOL JSM 6510) and field emission scanning electron microscopy (FEG-SEM, Zeiss Supra 35). 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. All measurements were performed keeping the same experimental parameters.

An initial inspection of the as-grown samples by XRD and Raman spectroscopy indicates that the structures are composed mainly of crystalline germanium with a small amount of germanium oxide, without significant presence of any other compounds.

XRD patterns of samples grown using different metal seeds are shown in Fig. 1(a) where it is possible to observe the peaks (111), (220) and (311) of germanium, agreeing with the powder diffraction card PDF 4–545 [14] which corresponds to a diamond structure (space group Fd-3m). GeO_2 peaks with a hexagonal structure in accordance with PDF 36–1463 diffraction card [15] were also detected, mostly for GeNWs synthesized at higher temperatures (using Ag, Cu and Ni nanoparticles); this germanium oxide could be located in the nanowires, possibly forming a shell [5], or in the microcrystals present in the growth substrates.

In agreement with x-ray analyses, Raman spectra [Fig. 1(b)] taken from all samples presented pronounced peaks centered at 300 cm^{-1}, attributed to Ge optical phonons. The spectra measured from the samples grown with Au, Ag, Cu and Ni also show peaks with wave numbers around 443 cm^{-1} related to the A_1 vibration of the α-quartz phase of native GeO_2 [16] present in the substrates. This feature cannot be found in the spectra of the sample prepared using indium and gold nanoparticles, as an indication that no significant volume of germanium oxide was produced during the growth process at a lower temperature, which also agrees with XRD pattern.

Regarding the generation of the nanoparticles by treatment of previous evaporated thin metallic film, Fig. 2 (a and b) shows that the Au, Ag, Cu and Ni films produced catalyst seeds with dimensions and densities proper for nanowires synthesis. The differences in size and distribution of the nanoparticles on the substrates may be caused by differences in the physical properties of the metals such as melting point, viscosity, etc. Indium thin films were subjected to annealing process at a wide range of temperatures (70 °C–800 °C) and no nanoparticles were observed, probably due to the low melting point and high viscosity of this metal.

SEM and FEG-SEM images [Fig. 2(c)] revealed that in each type of sample there is a region covered by a high density of nanowires characterized by a large aspect ratio (~10^3). Some variation in the nanowires morphology was also noticed, probably due to the differences in the density and distribution of the nanoparticles on the substrate [2]. For the same reason, in those substrates prepared with Cu, In and Ni thin films, the presence of microcrystals in addition to nanowires were observed; these structures are also composed of germanium and/or germanium oxide, as indicated in XRD and Raman analyses, which have not detected the presence of any other elements.

As expected from the VLS mechanism [17] and evidenced in histograms of Fig. 2 (b and d) the grown nanowires exhibited diameters distribution compatible with that of the corresponding metallic nanoparticles. By analyzing more deeply the data in the histograms in Fig. 2(a and c) one notice that the average of nanowire diameters ($\overline{D}$) are higher for Ag catalyst (98.3 nm) and lower for Ni catalyst (18.2 nm), while for other metals in this study the mean value was found to be 55.9 nm (Au), 52.4 nm (Cu) and 89.1 nm (In). Concerning to the variance of the diameters, In-seeded GeNWs showed broadened cross-section distribution (standard deviation around 43.8 nm) since the synthesis was conducted using non-previously annealed thin film (instead of nanoparticles with defined sizes). On the other hand, nanowires grown from Ni nanoparticles are quite homogeneous in diameters, presenting a standard deviation (σ) of only 6.6 nm. Gold and copper catalysts generated nanowires with similar distribution; the difference lies on the fact that for gold the quantity of nanowires with diameters larger than 90 nm is negligible but for copper a small portion of nanowires with diameters reaching 120 nm is still observed.

Therefore, despite the catalyst metal has not interfered in the composition of nanowires network, as shown by XRD and Raman analysis, considerable differences in the dimensions of nanostructures were produced, which possibly have influence on mechanical, optical and electronic properties.

3. Structural characterization of individual nanowires

For better understanding the crystalline parameters and composition of the nanowires that were grown using the five catalyst metals and investigating the influence of nanowire dimensions in vibrational properties, high resolution transmission electron microscopy (HRTEM, TecnaiF20G2, FEI, measurements at room temperature with an acceleration voltage of 200 kV, equipped