Synthesis and characterization of germanium nanowires on flexible substrates

Síntese e caracterização de nanofios de germânio em substratos flexíveis

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ABSTRACT
Nanoscience is an area of study based on the production, use and application of materials and technologies on a nanometric scale (Mamani, 2009), i.e. on a scale of 10-9 meters (Rangel; Ferreira, 2009), which in practice represents a unit around 10,000 times smaller than the diameter of a strand of hair. Nanotechnology has been used on a large scale in various areas of knowledge, including nanoscience and its applicability in physics. Thus, structures on a nanometric scale can be used to form semiconductors, materials that can act in the electrical conductivity of electronic equipment.

Keywords: Germanium Nanowires, Nanoscience, Synthesis.

RESUMO
A nanociência é uma área de estudo que se baseia na produção, utilização e aplicação de materiais e tecnologias em escala nanométrica (Mamani, 2009), isso é, em uma escala de 10-9 metros (Rangel; Ferreira, 2009), o que, na prática, representa uma unidade cerca de 10.000 vezes menor que o diâmetro de um fio de cabelo. A nanotecnologia tem sido utilizada em larga escala em várias áreas do conhecimento, dentre elas, pode-se citar a nanociência e sua aplicabilidade na física. Assim, as estruturas em escala nanométrica podem servir de uso para a formação de semicondutores, materiais que podem atuar na condutividade elétrica de equipamentos eletrônicos.

Palavras-chave: Nanofios de Germânio, Nanociência, Síntese.

1 INTRODUCTION

Nanoscience is an area of study based on the production, use and application of materials and technologies on a nanometric scale (Mamani, 2009), i.e. on a scale of 10^{-9} meters (Rangel; Ferreira, 2009), which in practice represents a unit around 10,000 times smaller than the diameter of a strand of hair. Nanotechnology has been used on a large scale in various areas of knowledge, including nanoscience and its applicability in physics. Thus, structures on a nanometric scale can be used to form semiconductors, materials that can act in the electrical conductivity of electronic equipment.

These semiconductors can be used on a nanometric scale, based on structures called nanowires. Semiconductor devices are commonly made of silicon, but germanium has proven to be a very useful chemical element for the nanotechnology market due to its physical, chemical and electronic properties, especially in a miniaturized state. The use of germanium nanowires resumes the initial trend in electronics to use this element in the manufacture of devices. The characteristics of germanium are important in studies relating to the efficiency of electrical devices, especially sensors and energy converters (Gouveia, 2016).

The application of semiconductor nanowire networks in flexible devices brings a new technological proposal for these structures, since it is possible to preserve electrical and opto-electronic characteristics, even with a degree of movement between their elements (individual nanowires), which makes these structures flexible. The synthesis of germanium nanowires on flexible substrates is still a recent but promising area of study, since it is possible to synthesize them without too many technical and material difficulties.

2 OBJECTIVE

The general objective of the project is to promote the synthesis of germanium nanowires on flexible substrates, in addition to their structural, morphological and crystalline characterization, as well as the study of their electrical properties, with the aim of applying them in electronic devices with the possibility of flexibility.

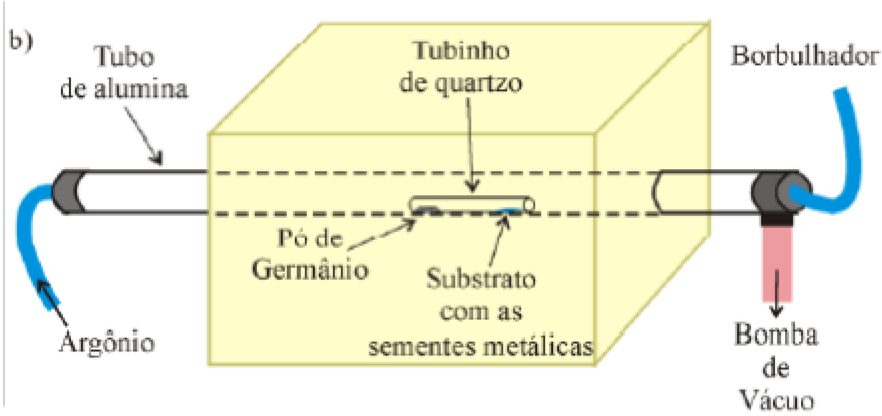
To achieve this goal, the following are specific objectives:

- Inducing the growth of germanium nanowires on flexible ceramic fiber tape substrates using the vapor-liquid-solid method;
- Characterize the dimensions and morphology of the nanowires obtained using optical and scanning electron microscopy;
- To build electronic devices with germanium nanowires and verify electrical properties related to their conductivity that may be flexible;
- Disseminate the results obtained in the syntheses in the scientific literature and the community, as well as their scientific and technological applications.

3 METHODOLOGY

The first procedure adopted was a literature review. The topic covered was researched and texts (theses, articles, etc.) on nanoscience and nanotechnology, and particularly on germanium nanowires, were read to familiarize them with the scientific content and procedures involved in the research. After this theoretical framework, the practical procedures began.

FIGURE 1 Representation of the Germanium nanowire synthesis system (Gouveia, 2016).



The nanowire synthesis system on campus, shown in Figure 1, was in disuse due to the pandemic. For this reason, the larger alumina tube, which serves as the base for the entire synthesis system, and the smaller quartz tube, where the germanium powder and the substrate are placed, were cleaned with aqua regia solution for 30 minutes.

After cleaning, it was necessary to maintain certain materials for the synthesis. In this way, the cylinder hose that passed argon was replaced, as it was damaged. Similarly, the germanium powder for the synthesis, the growth substrates, the argon system that would flow through the alumina tube, the bubbler that controlled the argon flow and the other items needed to handle the process were organized.

With all the materials prepared, it was also necessary to characterize the temperature profile of the oven, since it heated unevenly along its length. To do this, a thermocouple was used to measure the temperature of each position of the oven, checking the value every centimeter, from one side of the oven to the other.

The system was then assembled and prepared for the actual synthesis. Initially, the materials that would carry the germanium powder (aluminum foil) and the substrate were cleaned with acetone to remove impurities that could hinder the deposition of the nanowires on the substrate. Approximately 50mg of germanium powder was weighed and then placed in the inner quartz tube. The germanium powder was placed in a region of the furnace where the temperature was close to 950°C, while the substrate was placed at the end of the same inner tube, at a temperature of approximately 700°C. Once this was done, the ceramic tube was placed in the larger alumina tube, already in the ideal position. The argon pump and bubbler were shut off, so that the synthesis could be started later. The preparation procedure was the same for the 3 syntheses that were carried out.

The syntheses took place as follows: the vacuum pump was initially switched on for around 5 minutes, while the argon flow was regulated via a bubbler to reach 10 bubbles every 6 seconds. The vacuum pump remained on during this period. The furnace had to reach a temperature of 120°C before reaching the

950°C required for synthesis, and remained there for at least 30 minutes to remove impurities. After this period, the vacuum pump was switched off and the argon flow rate was adjusted again until it reached the flow rate previously indicated - 10 bubbles every 6 seconds - waiting around 5 minutes for the argon to fill the alumina tube. Once this was done, the furnace was set to reach 950°C and remain there for 60 minutes. After this period, the entire system, including the furnace, was turned off and cooled to room temperature.

After each synthesis, the results were characterized using an optical microscope. The microscope lenses were projected onto a computer where images could be recorded and the structure formed on the substrate discussed.

In summary, the syntheses differed only in the position of the substrate and the amount of germanium powder used: in the first, the substrate was placed in a horizontal position, while in the second and third it was placed in a vertical position. With regard to the amount of germanium, the first synthesis was carried out with 33mg of powder, the second with 53mg and the last again with 33mg.

After characterization using an optical microscope, electrical resistivity measurements were made using a multimeter. The analyses were carried out according to the length of the substrate and its thickness.

4 DEVELOPMENT

For the literature review stage, a search was carried out on the internet (Scholar Google) for nanoscience and nanotechnology and articles were selected that provided an overview of the topic and possible applications (Mamani, 2009; Rangel; Ferreira, 2009). A thesis was also read which deals specifically with the synthesis of germanium nanowires using the VLS method and the morphological and electrical characterization of these nanostructures (Gouveia, 2016).

The cleaning, organization, selection and maintenance of the materials for synthesis was essential for obtaining accurate and correct results. Figures 2a and 2b show how the system was assembled, with the smaller ceramic tube with germanium powder and the substrate inside the alumina tube, the latter of which can also be seen in Figure 2.

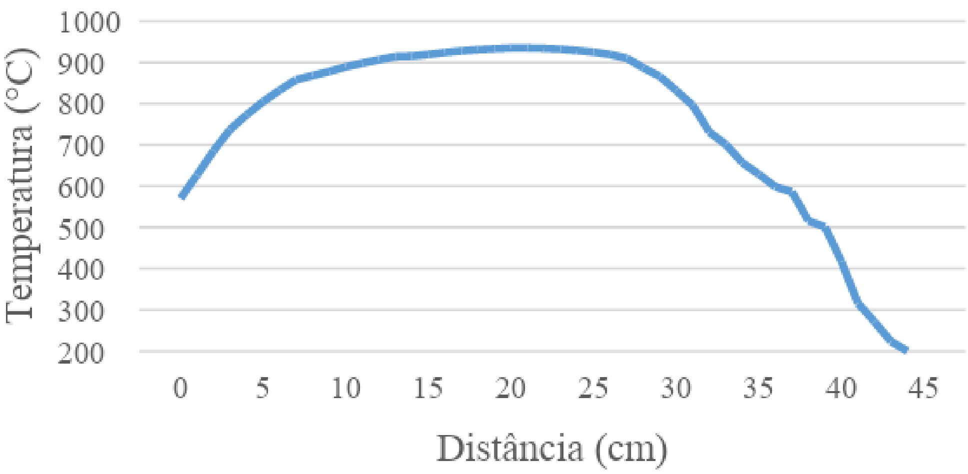
FIGURE 2 View of the synthesis system: a) Argon inlet and part of the furnace, including the programmable one which was switched off; b) furnace outlet, vacuum pump and bubbler. Source: the author.

a) b)

Subsequently, the characterization of the furnace profile allowed us to know where the smaller quartz tube should be placed. The results obtained experimentally were placed on a graph, as shown in Figure 3, for better visualization and analysis of where it should be positioned.

It was found that the ideal region for synthesis - around 950°C - was approximately in the middle of the furnace, so the 23 cm region on the x-axis was adopted for the position of the germanium powder. As the smaller tube was 12 cm long, the substrate was placed 11 cm from the germanium powder, a position corresponding to 35 cm on the x-axis.

FIGURE 3 Characterization graph of the furnace temperature profile. Source: the author



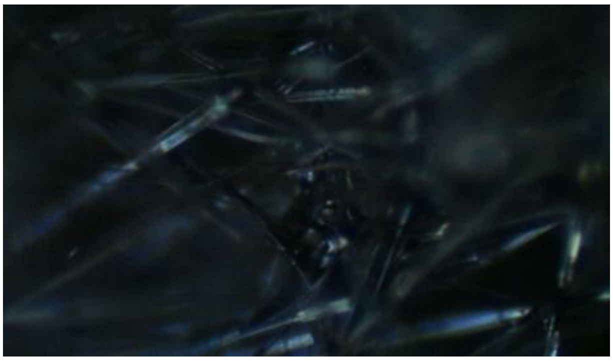
To provide a comparison parameter, the microscopic situation of the substrate before the synthesis took place was analyzed, duly identified by figure 4a.

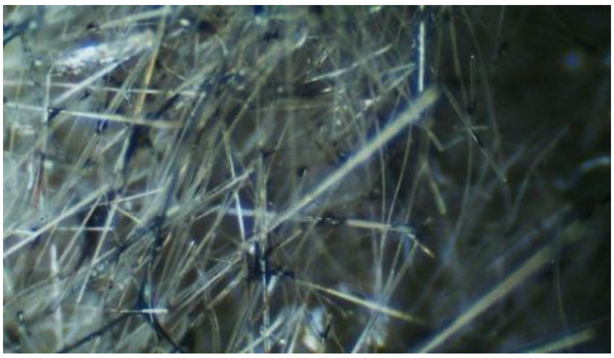
Figure 4b shows an image of the first nanowire synthesis. It is possible to see the presence of germanium deposition in the dark regions of figure 4b, but the formation of nanowires could not be characterized. These apparently more solid structures are areas where germanium has been deposited, but where nanowires are unlikely to be present. However, places in the background that appear to have a more "gelatinous" consistency and are difficult to characterize are those with the greatest possibility of nanowire growth.

Also in this same synthesis, it was noticed that there were regions of the substrate where the germanium had not been correctly deposited, characterized by places with little or no dark regions, similar to the original substrate, as shown in figure 4c.

FIGURE 4. Initial characterizations of the substrates before and after synthesis: a) before synthesis; b) after the first synthesis, with germanium; c) after the first synthesis, where no deposition took place. Source: the author

a) 

b) 

c) 

These analyses showed that the places with little or no deposition of germanium required an important change during the preparation of the synthesis: only part of the substrate was at the synthesis temperature, since the piece of substrate used was a few centimeters long, resulting in part of it being after the ideal temperature, a position in which there was little or no deposition.

This factor was therefore taken into account when preparing for the other synthesis attempts. The substrate would now be placed vertically in order to ensure that every part of it was in the ideal position for nanowire growth. Figure 5 shows this change.

FIGURE 5 Position of the substrate in the quartz tube before and after alteration. Source: the author

The other syntheses occurred with this change. The main change observed in the second synthesis was a greater uniformity of the dark regions, covering a large part of the substrate fibers, something that did not occur in the first synthesis due to the position of the substrate. It was also possible to see larger, rectilinear and apparently shiny and crystalline structures, attesting to the greater possibility of nanowire growth. Finally, we noticed a small amount of solid germanium in the smaller ceramic tube, with a crystallized appearance that was not deposited on the substrate.

The third synthesis, with a smaller amount of germanium, on the other hand, left no loose germanium in the tube, which in itself proved to be advantageous, a factor explained by the smaller amount of germanium used for this one. In addition, it was noticeable that the crystalline structures found in the previous synthesis were much more present, with greater filling, more complex and providing even greater expectations for the growth of the nanowires. These analyses can be seen in the photographic records below. Figures 5 and 6 illustrate the substrate after the second and third synthesis, respectively.

FIGURE 5 Photographic records of the substrate after the second synthesis: a) area showing the uniform deposition of germanium; b) structures with the crystalline appearance found after synthesis. Source: the author

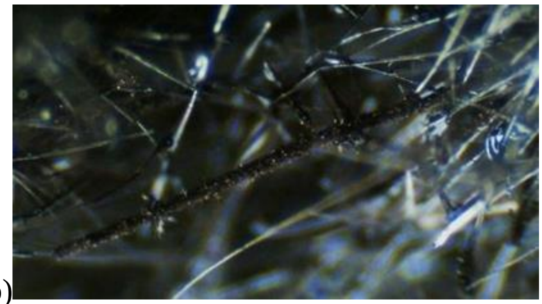
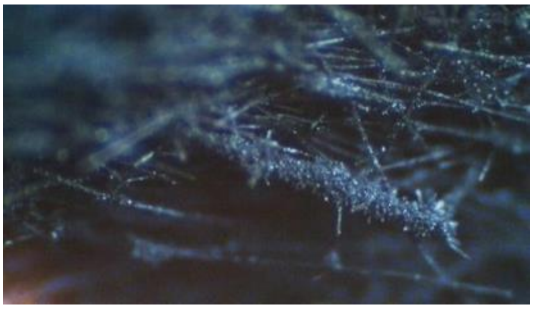
a)  b) 

FIGURE 6 Photographic records of the substrate after the third synthesis: a) region with high deposition of germanium and high expectation of nanowire growth; b) area with crystalline structures that are fuller, larger and more evident than those found in the previous synthesis. Source: the author

a) 

b) 

With these optical microscopy records, it was necessary to take electrical measurements of the substrates in order to ascertain with certainty whether or not the nanowires were growing. The results showed that the first two syntheses had no resistivity measurements, indicating that the nanowires had not grown. However, it was noticeable that the last synthesis attested to the presence of nanowires, given the resistance obtained by the multimeter in this particular sample.

The resistivity results as a function of length are shown in Table 7:

Table 7. Approximate electrical resistivity measurements (kΩ) as a function of substrate length (cm). Source: the author.

Substrate length (cm)	Resistivity (kΩ)
0,25	30
0,45	60
0,60	90

It can be seen that, on average, the resistivity measurements of this last sample show around 120-150kΩ/cm. It was also possible to observe a direct proportional relationship between length and resistance, i.e. the longer the substrate, the higher its resistivity.

Another interesting analysis is resistivity as a function of sample thickness. For a substrate also 0.45cm thick, but with a greater thickness (area), a resistivity of 40kΩ was observed, which indicates an inversely proportional relationship between the two units.

Both relationships can be compared to Ohm's Second Law, shown below:

Figure 8. Ohm's second law

$$R = \frac{\rho . L}{A}$$

As observed experimentally, the theory also shows the direct relationship between resistance and length and the inverse relationship between resistance and area, as explained above.

With these analyses, it was possible to foresee the concrete possibility of constructing electrical devices with this sample, given the electrical measurement presented. One obstacle to this measurement was the fact that the substrate was falling apart due to the brittle appearance of the germanium after deposition. To correct this problem, an attempt was made to glaze the samples to make them firmer. Another possibility tested was to attach the two ends of the sample in order to firm it up and make it easier to measure. This step involved trying to weld the two ends to a piece of acrylic, but this was not effective, as the sample, already worn due to the measurements, did not hold firmly to the acrylic, even with the weld.

Some future possibilities include repeating the synthesis, as was done in the third production, characterizing it via electron microscopy, trying to make the sample a little firmer, either by glazing it or by trying to attach its ends, carrying out current-voltage measurements on the samples and then building the flexible devices.

5 FINAL CONSIDERATIONS

The nanowire synthesis project was successfully resumed after the pandemic. The characterization of the furnace allowed not only this resumption, but also the effectiveness of the experiments. The substrates used experimentally indicated the growth of germanium nanowires due to their morphological characteristics observed microscopically.

This analysis was confirmed by the electrical resistivity measurements of 120-150kΩ which, although they took place, were hampered by the brittle aspect of the germanium. New steps related to the synthesis, characterization and construction of devices must be taken to continue the project.

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