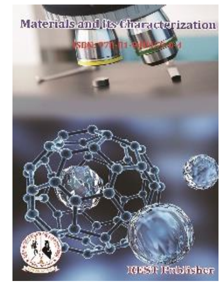
Materials and its Characterization

Vol: 3(1), 2024

REST Publisher; ISBN: 978-81-948459-0-4

Website: https://restpublisher.com/book-series/mc/

DOI: https://doi.org/10.46632/mc/3/1/1



Heating Effect on The Ge/GeO$_X$ Nanoneckless by Electron Gun in Situ TEM

Amar S. Katkar

Dr. B. N. Purandare Arts, Smt. S. G. G. Commerce and Smt. S. A. M. Science college, Lonavala-410403, (MS), India.

*Corresponding Author E-Mail: amarkatkar@gmail.com

Abstract: *Uniform Ge/GeOX nanoneckless were synthesized by optimization of experimental conditions in vapor deposition methos. Germanium nanowires decorated with the Germanium oxide spheres formed nanoneckless kind of structure. The as prepared sample was utilized to investigate structural variations in a single nanoneckless by heating it using electron gun in In- Situ TEM. The dynamic alterations of Ge nanowire and GeOX sphere was observed under electron beam irradiation using in situ transmission electron microscopy (TEM). The morphological changes occurred because of a combination of temperature and electron beam effects.*

***Keywords**: Germanium nanostructure, Nanoneckless, In Situ TEM, Annealing treatment, Nanowires, Polycrystalline*

1. INTRODUCTION

From last few decades, there has been a lot of interest is generated in nanoscale one-dimensional (1D) structures because of their new features and quantum size effects, which could be used in a variety of electrical and optoelectronic devices [1], chemical [2] and biological sensors [3], and photovoltaic systems [4]. Group IV semiconductor nanowires and their heterostructures stand out among the wide variety of materials from which NWs may be produced because they provide material compatibility and easy integration with traditional Si-based circuitry. Germanium, one of the intriguing group IV semiconductors, has been contemplated for use in high-speed electronics. In device applications, Ge provides several advantages over Si, including greater carrier mobility and stronger quantum confinement in a NW, and the potential for lower processing temperatures and simpler integration with traditional devices [5]. Because it is scalable and uses solid pellets or powders as source materials rather than dangerous precursor gases, thermal evaporation is one of the most intriguing synthesis pathways for Ge NWs and a straightforward method of creating large amounts of Ge NWs [6,7]. Numerous synthesis techniques, such as laser ablation, vapor transfer, low-temperature chemical vapor deposition (CVD), and supercritical fluid-liquid-solid synthesis, have been documented for the fabrication of Ge nanowires [8–11]. One of the most crucial elements in the growth of nanowires is growth temperature. It affects both the integration of nanowire devices and the physical characteristics of nanowires, including their shape and crystal structure.

Even at temperatures hundreds of degrees below the material's melting point, surface atom diffusion can cause morphological changes in NWs over extended heat treatment (lasting minutes or longer) [12-14]. Using In-Situ TEM heat treatment by e-beam onto a Si nanowire was investigated [15,16]. It was observed that after conducting a number of heat-treatment the behaviour of adherent and suspended NW components varies with heat treatment.

In our work, Ge nanostructures were synthesized using a simple thermal evaporation technique. Variables such as the growth temperature, carrier gas pressure, and growth sources were employed to study the growth of Ge nanostructures. By variation in the substrate temperature (500^0C to 600^0C) inside three zone furnace germanium nanowires with GeO$_X$ particles was grown successfully. After its characterization using FESEM and HRTEM the annealing effect onto the single nanowire with particles has been investigated using e-beam of TEM for different time period.

Experimental:

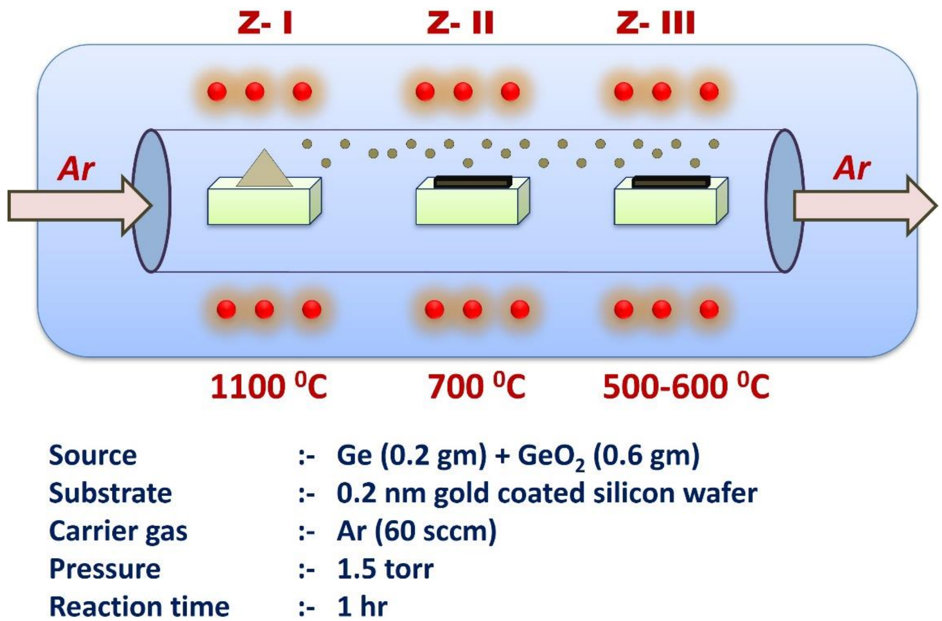


FIGURE 1. Schematic diagram of the vapor deposition method to synthesize Ge nanostructures

Figure 1 depicts experimental method to synthesize Germanium nanowires using simple vapor transport method. As shown in the figure, P-type silicon. (001) wafer was ultrasonically cleaned in ethanol for 10 min. and utilized for experiment. A mixture of commercial Ge (99.999 %, Alfa Aesar), GeO_2 (99.999 %, Alfa Aesar) with 1:3 ratios was used to synthesize Ge nanowires and Ge/GeO_X nanoneckless structures with substrate (Zone III) temperatures of 500^0C and 600^0C respectively. The mixture was placed in an alumina boat, which was heated to a peak temperature of 1100^0C in zone - I. The samples were heated at a rate of 20^0C /min. with the reaction time of 60 min. and with a 60 sccm (1.5 torr) Ar flowing through the tube. The Ge nanowires sheathed with oxide layer and single crystalline Ge nanowires with GeOX nanospheres (nanoneckless structure) were grown by a vapor transport method. The as prepared samples were characterized by using Field emission scanning electron microscope (FESEM), Energy Dispersive X-ray spectroscopy (EDS), Ultra High Vacuum Transmission Electron Microscope (UHV-TEM) etc.

Results and Discussions: At the substrate (Zone III) temperature of 500^0C, the high density of Ge nanowires was observed as shown in FESEM image in figure 2a and b. Both the imaged shows uniform grown Germanium nanowires.

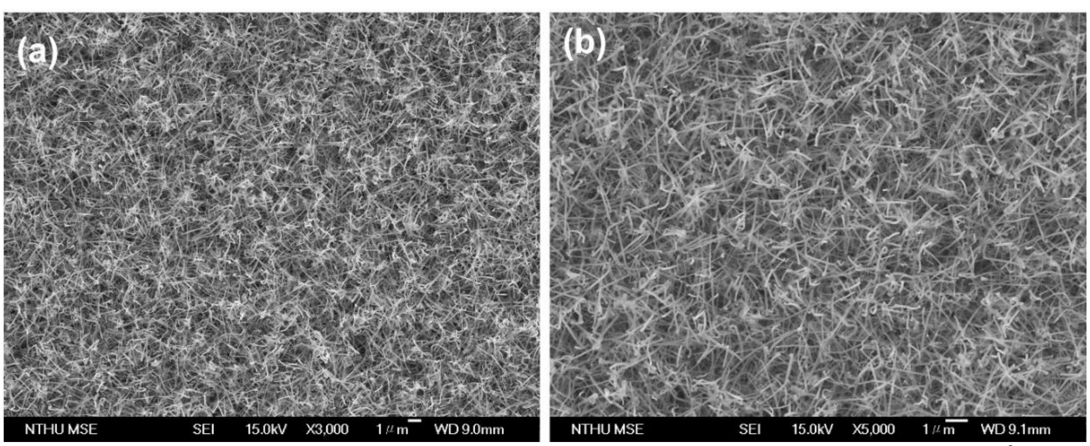


FIGURE 2. FESEM image of germanium nanowires for the substrate temperature of 500^0C.

The structure and composition of obtained product (nanowires) were verified using TEM and EDS data. Figure 3 depicts a TEM image of the nanowire structure. It clearly shows the oxide sheathed layer around nanowire. The diameter of the nanowire from the TEM image is ~60 nm. The thickness of the oxide layer around germanium nanowires is about 5-10 nm. The EDS spectra show germanium and germanium oxide contents at core (Figure 3.5b) and shell (oxide layer) (Figure 3.5c), respectively.

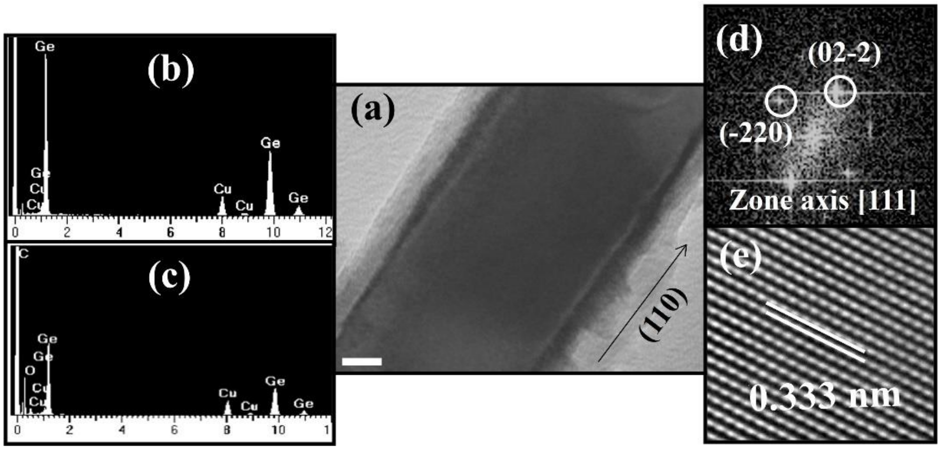


FIGURE 3. (a) TEM image of the germanium nanowire sheathed with oxide layer, (b and c) EDS pattern of core and shell of the nanowire, respectively, (d) corresponding SAED pattern and (e) HR image. The scale bar is 10 nm.

Clearly, the SAED pattern and HRTEM image (zone axis - [111], d spacing – 0.333 nm) revealed that, the nanowire consists of germanium and the growth direction of oxide layer sheathed Ge nanowire is [111].

Further, to investigate dependence of morphological changes in the nanowires on the substrate temperature, the substrate temperature was increased to 600^0C. At the substrate (Zone III) temperature of 600^0C, the high density of Ge nanowires decorated with the GeO_X nanospheres (Ge/GeO_X nanoneckless structure) was observed as shown in FESEM images in figure 3. Both the images show uniform grown Germanium nanoneckless structures.

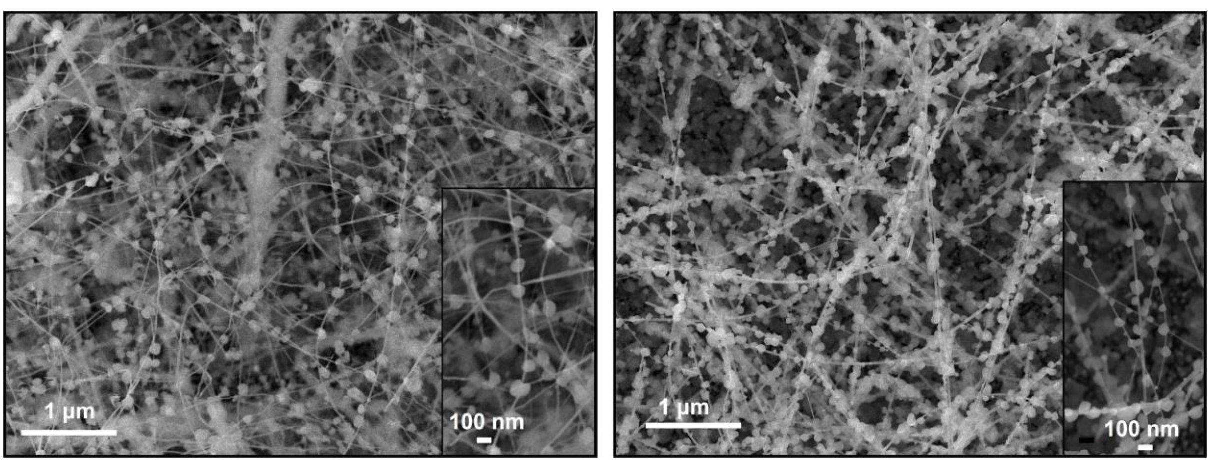


FIGURE 4. FESEM image of germanium nanowires with particles and inset is corresponding magnified image. The scale bars for low and high magnified images are 1 μm and 100 nm, respectively.

As observed from the magnified image (inset of figure 4), the diameter and length of the nanowire is in the range of 50-60 nm and 5-10 μm, respectively. The diameter of the GeO_X Nano spheres was 100 nm.

Figure 5 depicts a TEM image of the nanowire with particle structure. The particle was observed around the nanowire. The EDS (Figure b and c) analysis confirmed that the nanowire and particle around the Ge nanowires consist of germanium and germanium oxide (GeO_X), respectively.

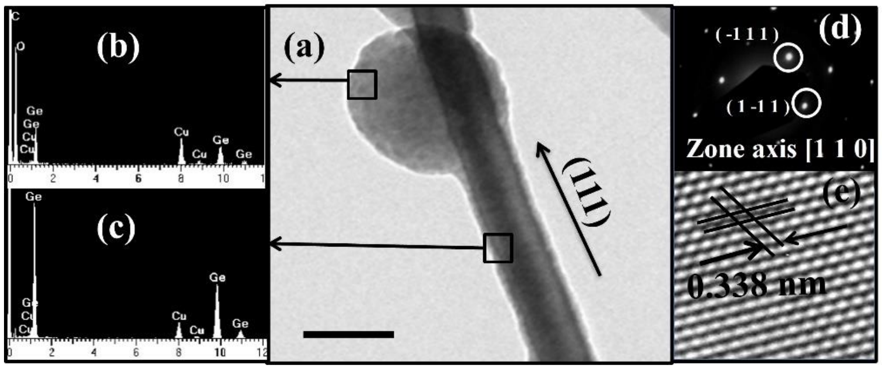


FIGURE 5. (a) TEM image of Ge nanowire with oxide particle, (b and c) EDS data of particle and nanowire, (d) SAED pattern and (e) corresponding high resolution image. The scale bar of TEM image is 100 nm.

The diameter of the nanowire from the TEM image is ~60 nm and that of the particle is ~100 nm. Clearly, the SAED pattern and HRTEM image (zone axis- [110], d spacing – 0.338 nm) revealed that the nanowire consists of germanium. The growth direction of Ge nanowire with oxide particle is [111].

Investigation of transition of nanoneckless by In-Situ heating:

To investigate the structural changes in a nanoneckless as it is heated in-situ when they use high-resolution transmission electron microscopy (HRTEM) to study the heating effect of nanowires. This allows to analyze how the nanowire along with the nanospheres morphology, lattice structure, and even atomic arrangement evolve under elevated temperatures. It often reveals phenomena like thermal expansion, phase transitions, or even melting at the nanoscale level. By utilizing a heating stage within the TEM (UHV TEM) and precisely control the temperature of the nanoneckless the simultaneous imaging its structure at atomic resolution, provide real-time insights into the heating process.

Samples for heat-treatment studies were prepared by drop casting Ge/GeO_X Nanoneckless onto the Cu grid from a solution. In the first part of the experiment single nanowire with nanosphere was targeted to investigate annealing effect using In-Situ UHVTEM. The e-beam was focused onto the nanowire and for 5 minutes and its effect was observed as shown in the figure 6. After 30 sec of annealing at annealing temperature 500 ^{0}C nanowire was covered with amorphous oxide layer and step by step after 5 min nanowire has been started to melt and induced into the oxide particle.

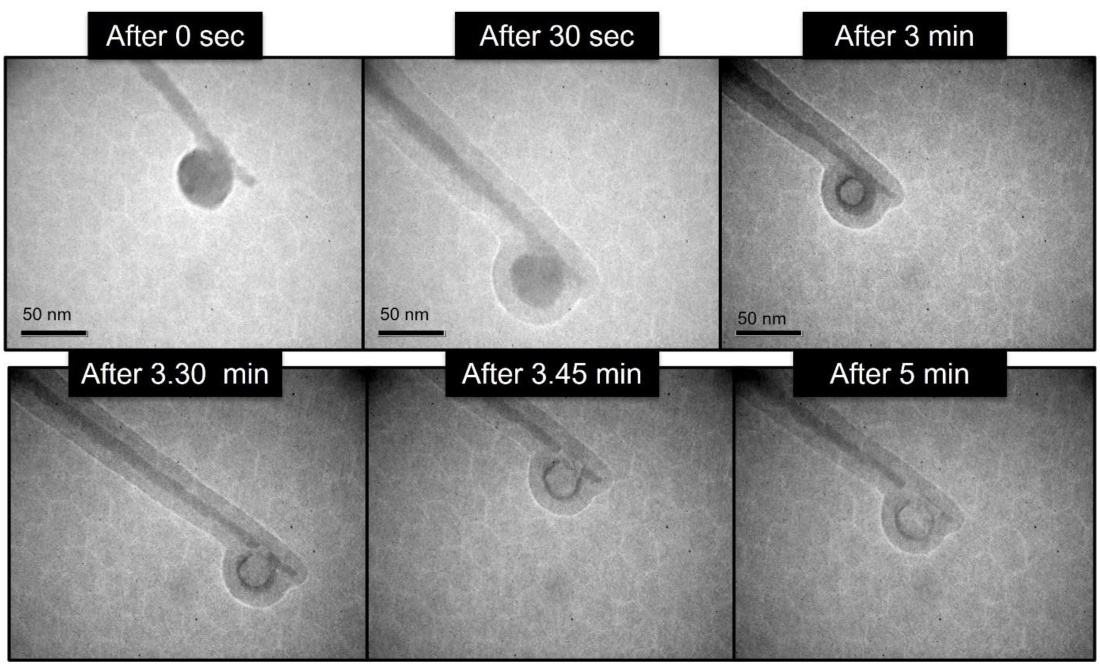


FIGURE 6. TEM images after passing e-beam over the single nanowire after 30 seconds to 5 minutes.

In the second part of the experiment e-beam was passing for long time (30 min) through particle with nanowire (Figure 7), the nanowire inside germanium oxide particle was melted and induced completely into the particle. So, nanoparticle shrinking was observed and it became denser than before.

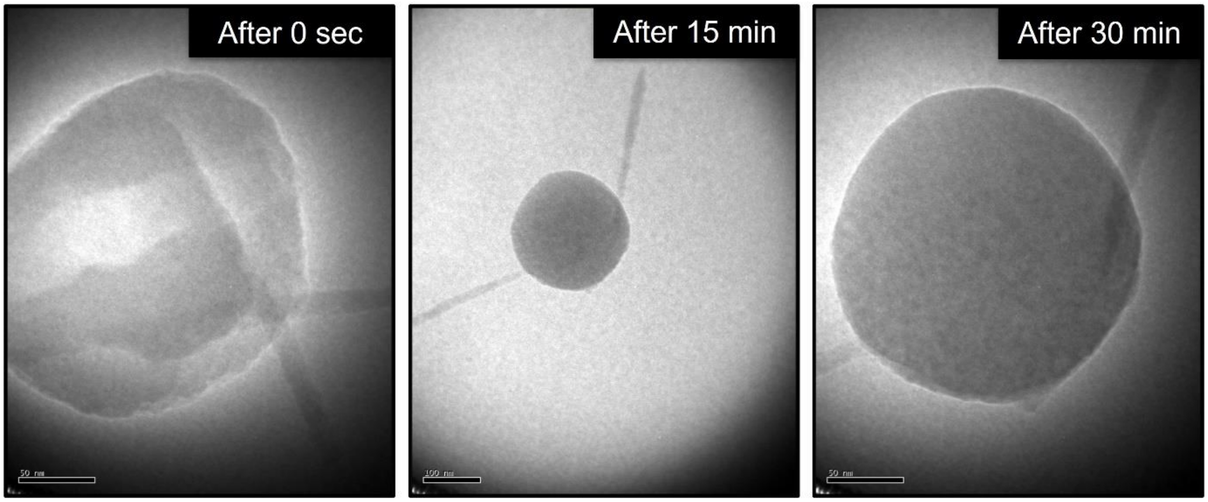


FIGURE 7.TEM images after passing e-beam over the single nanowire further after 15 minutes to 30 minutes.

The formation of grain boundaries was observed after annealing of sphere after 30 minutes. During the period of 30 minutes to 45 minutes as shown in the figure 8 the amorphous sphere due to recrystallization process undergoes rearrangement and transform into polycrystalline nanosphere as shown in the figure 8b. Insets of figure 8a and 8b depicts XRD patterns. XRD pattern of figure 8a (wherein annealing time was 30 minutes) depicts amorphous nature and after 45 minutes of prolonged incidence XRD shows polycrystalline nature of the nanosphere.

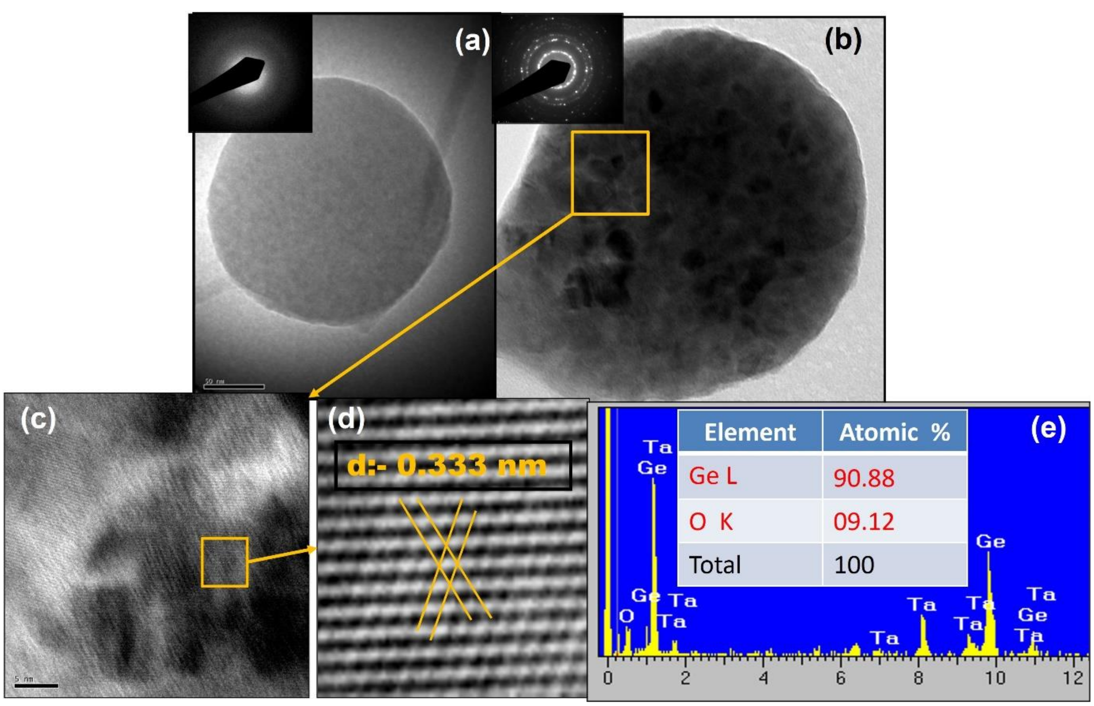


FIGURE 8. TEM images after passing e-beam over the nanosphere for (a) 30 minutes and (b) 45 minutes. Insets are XRD patterns. (c and d) HRTEM images and (e) elemental analysis of highlighted area.

Figure 8c and d for highlighted area is showing d spacing (0.333 nm) of Germanium. Which was confirmed by EDS pattern. Thus, the Grain boundaries, lattice spacing, and defect generation inside the Ge/GeO_X nanoneckless could be investigated using HRTEM, which could provide insight into the material's thermal stability. In-situ heating experiments could capture dynamic processes like diffusion, nucleation and growth of new phases within the nanosphere. It was imperative to consider the interaction of the electron beam with the nanoneckless, as the beam itself contributed to heating. In future it can be possible to design of nanoneckless for specific thermal applications by understanding its deformation in nature (amorphous to crystalline nature) or phase under In-Situ heating treatment.

2. CONCLUSIONS

In this work, initially germanium nanowires sheathed with GeO_X was synthesized using vapor transport method with the substrate temperature of 500^0C. After increase the substrate temperature of 600^0C Ge/GeO_X nanoneckless type of structure was obtained. In the further experimental part nanoneckless was annealed in-situ to 500^0C for different time using e-beam of TEM. During the heating time of 30 seconds to 5 minutes (stage 1) the melting of Ge nanowires to GeO_X and its inclusion into the nanosphere was observed. In the stage 2 of heating the time was increased to 30 minutes. In this stage the initiation in the amorphous nature of sphere to crystalline nature had occurred. In the stage 3 of heating up to 45 minutes complete formation of polycrystalline nature of sphere was observed. In this process nanowire disappeared to form amorphous to polycrystalline nanosphere of Germanium. The improvement in the crystallinity of the nanosphere was verified by the HRTEM image, XRD pattern and elemental analysis. An investigation of In-Situ heating treatment by TEM to single nanowire can be interesting to understand its thermal stability.

REFERENCES

[1]. Ye, C., " Recent Progress in Understanding the Growth Mechanism of One-Dimensional Nanostructures by Vapor Phase Processes" *Sci. Adv. Mater.* 2010, 2, 365.

[2]. Yin, Z. Y.; Garside, B. K., "Low-loss GeO_2 optical waveguide fabrication using lowdeposition rate rf sputtering" *Appl. Opt.* **1982**, 21, 4324.

[3]. Jiang, Z.; Xie, T.; Wang, G. Z.; Yuan, X. Y.; Ye, C. H.; Cai, W. P.; Meng, G. W.; Li, G. H.; Zhang, L. D., " GeO_2 nanotubes and nanorods synthesized by vapor phase reactions" *Materials Letters* **2005,** *59* (4), 416.

[4]. Kim, H. W.; Lee, J. W.; Kebede, M. A.; Kim, H. S.; Lee, C., "Effect of growth temperature on the ZnO nanowires prepared by thermal heating of Zn powders" *Current Applied Physics* **2009,** *9* (6), 1300.

[5]. Tang, Y. H.; Zhang, Y. F.; Wang, N.; Bello, I.; Lee, C. S.; Lee, S. T., "Germanium dioxide whiskers synthesized by laser ablation" *Appl. Phys. Lett* **1999**, 74, 3824.

[6]. Dang, H. Y.; Wang, J.; Fan, S. S., " The synthesis of metal oxide nanowires by directly heating metal samples in appropriate oxygen atmospheres" *Nanotech.* **2003**, 14, 738.

[7]. Hidalgo, P; M´endez, B.; Piqueras, J., "High aspect ratio GeO_2 nano- and microwires with wave guiding behaviour" *Nanotech.* **2007**, 18, 155203.

[8]. Hidalgo, P; M´endez, B.; Piqueras, J., " GeO_2 nanowires and nanoneedles grown by thermal deposition without a catalyst" *Nanotech.* **2005**, 16, 2521.

[9]. Katkar, A. S.; Chu, Y.-C.; Chu, L.-W.; Chen, L. J., "Chromium-Doped Germanium Nanotowers: Growth Mechanism and Room Temperature Ferromagnetism" *Cryst. Growth & Des.* **2011,** 11, 2957**.**

[10]. Mao, Y.; Huang, J. Y.; Ostroumov, R.; Wang, K. L.; Chang, J. P., " Synthesis and Luminescence Properties of Erbium-Doped Y_2O_3 Nanotubes" J. *Phys. Chem. C* **2008,** *112* (7), 2278.

[11]. Mowbray, D. J.; Martinez, J. I.; García Lastra, J. M.; Thygesen, K. S.; Jacobsen, K. W., " Stability and Electronic Properties of TiO_2 Nanostructures with and Without B and N Doping" *J. Phys. Chem. C* **2009,** *113* (28), 12301.

[12]. Oras, S.; Vlassov, S.; Vigonski, S.; Polyakov, B.; Antsov, M.; Zadin, V.; Lõhmus, R.; Mougin,; "The effect of heat treatment on the morphology and mobility of Au nanoparticles", K. *Beilstein J. Nanotechnol.* **2020,** *11,* 61–67. doi:10.3762/bjnano.11.6

[13]. Vigonski, S.; Jansson, V.; Vlassov, S.; Polyakov, B.; Baibuz, E., Oras, S.; Aabloo, A.; Djurabekova, F.; Zadin, V.; "Au nanowire junction breakup through surface atom diffusion", *Nanotechnology* **2018,** *29,* 015704. doi:10.1088/1361-6528/aa9a1b

[14]. Langley, D. P.; Lagrange, M.; Giusti, G.; Jiménez, C.; Bréchet, Y.; Nguyen, N. D.; Bellet, D.; "Metallic nanowire networks: effects of thermal annealing on electrical resistance" *Nanoscale* **2014,** *6,* 13535–13543. doi:10.1039/c4nr04151h

[15]. Elyad, D.; Sven, O.; Edgars, B.; Allar, L.; Mikk, A.; Boris, P.; Annamarija, T.; Veronika, Z.; Andreas, K.; Loïc, V.; Karine, M.; Siim, P.; Sergei, V.; "Heat-induced morphological changes in silver nanowires deposited on a patterned silicon substrate", *Beilstein J. Nanotechnol.* **2024,** *15,* 435–446.

[16]. Shen, Y.; Xuechun, Z.; Ruiling, Gong.; Eric, Ngo.; Jean-Luc, M.; Pere, Rocai.; Cabarrocas, Wanghua, Chen.; "Influence of the Electron Beam and the Choice of Heating Membrane on the Evolution of Si Nanowires Morphology in Situ TEM", Materials 2022, 15, 5244

