Synthesis and characterization of single crystalline Germanium nanowires

Ramesh Bhise¹, Amar S. Katkar^{2*}, Pandit N. Shelke³, Ravindra Mene³, Tushar Salve⁴

1 Hon. Balasaheb Jadhav Arts, Commerce and Science college, Ale

2 Department of Physics, Dr. B. N. Purandare Arts, Smt. S. G. Gupta Commerce and Smt.

S. A. Mithaiwala Science college, Lonavala, India

3 Annasaheb Magar Mahavidyalaya, Hadapsar, Pune

4 SNJB's KKHA Arts, SMGL Commerce and SPHJ Science College,

Abstract: One-dimensional (1D) Ge nanostructures such as single crystalline nanowires have attracted intense research zeal in the past decade as compared to its bulk form, owing to their wide range of potential applications in sensing, biology, optoelectronics, solar cells and photocatalysis. In this work, by optimizing the experimental conditions using simple vapor transport method, single crystalline germanium nanowires with lowest diameter were successfully synthesized and characterized.

Keywords: Germanium, Nanowires, single crystalline, Nanostructures

Introduction:

Nanomaterials are commonly defined as materials designed and produced to have structural features with at least one dimension of 100 nanometers or less. Various types of nanomaterials attract tremendous attention in recent researchers. New physical properties and new technologies both in sample preparation and device fabrication evoke the development of nanoscience. Dimensionality is an important governing factor in the electronic structures of semiconductor nanocrystals. The quantum confinement energies in two-dimensional quantum wells, one-dimensional quantum wires and zero-dimensional quantum dots are quite different [1-8]. Semiconductor nanocrystals, such as quantum dots (QDs) and quantum wires (QWs), are of intense scientific and technological interest. One-dimensional (1D) nanostructures suchas wires, rods, belts, and tubes have also become the focus of intensive research owing to theirunique applications in mesoscopic physics and fabrication of nanoscale devices [9,10]. It is generally accepted that 1D nanostructures provide a good system to investigate the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction (or quantum confinement). 1D nanostructures can now be fabricated using a number of advanced nanolithographic techniques, such as electron-beam (e-beam) or focusedion- beam (FIB) writing, proximal- probe patterning, and X-ray or extreme-UV lithography. The vapor-liquid-solid method (VLS) is a mechanism for the growth of one-dimensional structures, such as nanowires, from chemical vapor deposition or physical vapor deposition [11]. Growthof a crystal through direct adsorption of a gas phase on to a solid surface is generally very slow. The VLS mechanism circumvents this by introducing a catalytic liquid alloy phase which canrapidly adsorb a vapor to supersaturation levels, and from which crystal growth can subsequently occur from nucleated seeds at the liquid-solid interface. The physical characteristics of nanowires grown in this manner depend, in a controllable way, upon the size and physical properties of the liquid alloy. For the gold germanium system, eutectic

temperature is 361°C and occurs at a Ge:Au ratio of 7:18 [12-14]. Above the eutectic temperature, semiconductor nanowires grow via the VLS mechanism. As a general requirement for the controlled growth of nanostructures, the first step is to control the morphology (or shape)of the nanostructures, since some of the properties depend critically on morphology in additionto the size dependence [15]. The most important parameters need to be controlled are length, radius, tapering, and orientation. The control of these parameters is dependent of both theoretical understanding of morphology evolution and experimental facilities and approaches.

This research is comprised of synthesis of germanium-based nanostructures and addressing interesting and innovative applications towards the advancement of present nanoscience and nanotechnology. This research is focused on the synthesis, characterization, and applications based on the Ge nanostructures. Efforts are invested to modify the morphology of the germanium nanowires by variation of experimental parameters.

Initially the synthesis of germanium nanowires was investigated by tuning the experimental parameters such as pressure, temperature, and reaction time. Growth temperature is one of the most important factors in nanowire-based electronics. It impacts not only the physical properties of nanowires, such as morphology and crystal structure, but also the integration of nanowire devices. In our work, a thermal evaporation system was used to synthesize Ge nanostructures. The growth of Ge nanostructures was investigated by varying parameters like sources used for growth, growth temperature and pressure of carrier gas. This synthesized single crystalline germanium nanowires cab be utilized to investigate their future electronic, optical, and biological applications [16-20].

Experimental:



To grow single crystalline germanium nanowires sources were changes to mixture of Ge (99.999 %, Alfa Aesar) and C (99.999 %, Alfa Aesar). The mixture with ratio of 2:3 and substrate temperature of 500 °C was used to grow nanowires. The samples were heated to 1100°C at a rate of 20 °C /min with the reaction time of 60 min and with a 60 sccm Ar flowing through the tube. As in above experiment 2-nm thick gold film was deposited on to Si wafer and used as a substrate. After completion of reaction, the furnace was allowed to cool to roomtemperature. The as synthesized film was further characterized by using X-ray diffractometer (XRD) (Shimadzu 6000) with Cu K α radiation (λ =0.154 nm), UV-VIS spectrometer, field emission scanning electron microscope (FE-SEM) (JEOL JSM-6500F SEM) operating at 10 kV accelerating voltage and JEOL JEM-2010 transmission electron microscope (TEM) (200 kV), equipped with an energy-dispersive spectrometer (EDS).

Results and Discussions:

As the final aim of the experiments was to synthesis the single crystalline germaniumnanowires with small diameter and long length i.e., with high aspect ratio, it was essential to tune the experimental parameters and conditions. But to tune the diameter of the germanium nanowires in a controlled way it was necessary to use catalysis. So, for further experimental part 2 nm gold coated Si wafer was used as a substrate. Also, the substrate temperature was varied from 500-600 °C.

By using Ge and C as a source and substrate temperature of 500 °C the high density of nanowires was obtained as shown in FESEM image in Figure 1. Inset is its high magnificationFESEM image. FESEM image depicts nanowires with diameter and length in the range of 10 to 20 nm and 1 to 2 μ m. The above FESEM image clearly shows uniform growth of germaniumnanowires with gold cap at the top. At the specific temperature of 500 °C germanium nanowireswith smallest diameter was grown successfully.



Figure 1: FESEM image of Ge nanowires and inset is corresponding magnified image. The scale bars of low and high magnified images are 1 µm and 100 nm, respectively.

To confirm the crystallinity and contents of nanowires TEM analysis with elemental analysis and SAED analysis was carried out. Figure 2a and b depicts a low and high magnification of TEM images of the nanowire structure. From TEM image the single crystalline nanowire was observed. The EDS (Figure 2c) analysis confirmed that the nanowireconsists of pure germanium.



Figure 2: (a) TEM image of the germanium nanowire and corresponding, (b) EDS spectrum (c) SAED pattern and (d) HR image. The scale bars for (a) and (b) are 100 nm and 10 nm, respectively.

The diameter of the nanowire from the TEM image is about ~ 15 nm. The SAED pattern and HRTEM image (zoneaxis-[111], d spacing – 0.32 nm) revealed that the nanowire consists of germanium. The growthdirection of Ge nanowire with oxide particle [110].

Thus, by using mixture Ge and C (2:3 ratio), the single crystalline germanium nanowires were synthesized successfully. As we know that, the electrical transport property of germanium nanowires dependent on their diameters, it will be interesting to investigate electrical properties of these smallest diameter germanium nanowires in detail for future electronic applications.

Summary and Conclusions:

Thus, the variation in experimental parameters such as source amount, substrate temperature can play vital role in formation of different morphological changes. Also, the increment in substrate temperature from 500-600 °C could cause the oxidation along the nanowires, which is reasonable because at high temperature oxidation will be prominent process during the growth of nanostructures. In conclusion, a simple vapor transport has been employed to synthesize single crystalline germanium nanowires with high yield and high purity.

References:

1. Bae, W. K.; Char, K.; Hur, H.; Lee, S., "Single-Step Synthesis of Quantum Dots withChemical Composition Gradients" Chem. Mater. 2008, 20, 531. 2. Gallagher, S. J.; Rowan, B. C.; Doran, J.; Norton, B., "Quantum dot solar concentrator: Deviceoptimisation using spectroscopic techniques" Solar Energy 2007, 81, 540. 3. Asryan, L. V.; Luryia, S., "Temperature-insensitive semiconductor quantum dot laser" Solid-State Electr. 2003, 47, 205. 4. Zhuang, L.; Guo, L.; Chou, S. Y., "Silicon single-electron quantum-dot transistor switchoperating at room temperature" Appl. Phys. Lett. 1998, 72, 9. 5. Cooke, M., "Flash fast forward to quantum dot memory" Semicon. Today 2008, 3, 45. 6. Costa-Fernandez, J. M., "Optical sensors based on luminescent quantum dots" Anal. Bioana.lChem. 2006, 384, 37. 7. Kerim M.; Asfura G.; Leblanc, R. M., "Peptide-coated CdS quantum dots for the optical detection of copper(II) and silver(I)" Chem. Commun. 2003, 2684. 8. Zhao, J.: Bardecker, J. A.; Munro, A. M.; Liu, M. S.; Niu, Ding, Y. K.; Luo, J.; Chen, B.; Jen, A. K. Y.; Ginger, D. S., "Efficient CdSe/CdS Quantum Dot Light-Emitting Diodes Using a Thermally Polymerized Hole Transport Layer" Nano Lett. 2006, 6, 463. 9. Roper, S. M.; Davis, S. H.; Norris, S. A.; Golovin, A. A., "Steady growth of nanowires via the vapor-liquid-solid method" J. Appl. Phys. 2007, 102, 034304. 10. Schmidt, V.; Gösele, U., "How Nanowires Grow" Sci. 2007, 316,698. Greytak, A. B.; Lauhon, L. J.; Gudiksen, M. S.; Lieber, C. M., " Growth and transport properties of complementary germanium nanowire field-effect transistors" Appl. Phys. Lett. 2004, 84, 4176. 9. Xiang, Y.; Cao, L.; Conesa-Boj, S.; Estrade, S.; Arbiol, J.; Peiro, F.; Hei, M.; Zardo, I.; Morante, J. R.; Brongersma, M. L.; Morral, A. F., "Single crystalline and core-shell indiumcatalyzed germanium nanowires a systematic thermal CVD growth study "Nanotech. 2009, 20, 245608. 10. Zhou, Z.; Li, Y.; Liu, L.; Chen, Y.; Zhang, S. B.; Chen, Z., "Size- and Surface-dependent Stability, Electronic Properties, and Potential as Chemical Sensors: Computational Studies on One- dimensional ZnO Nanostructures" J. Phys. Chem. C 2008, 112 (36), 13926. 11. Yu, B.; Sun, X. H.; Calebotta, G. A.; Dholakia, G. R.; Meyyappan, M., " OnedimensionalGermanium Nanowires for Future Electronics" J. Clust. Sci. 2006, 17, 579. 12. Ge, M.; Liu, J. F.; Wu, H.; Yao, C.; Zeng, Y.; Fu, Z. D.; Zhang, S. L.; Jiang, J. Z., "Synthesis

- of Germanium Nanowires" J. Phys. Chem. C 2007, 111 (30), 11157.
- 13. Kim, B.-S.; Koo, T.-W.; Lee, J.-H.; Kim, D. S.; Jung, Y. C.; Hwang, S. W.; Choi, B. L.; Lee, E. K.; Kim,

J. M.; Whang, D., "Catalyst-free Growth of Single-Crystal Silicon and Germanium Nanowires" *Nano Letters* **2009**, *9* (2), 864.

14. Korgel, B. A., "Synthesizing silicon and germanium quantum dots and nanowires" *SPIE Newsroom*, **2006**, 1.

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

16. Chui, C. O.; Kim, H.; Chi, D.; McIntyre, P. C.; Krishna C., "Nanoscale Germanium MOSDielectrics—Part II: High-κ Gate Dielectrics" *IEEE Trans. Elect. Dev.* **2006**, 53, 1509.

17. Bojarczuk, N. A.; Copel, M.; Guha, S.; Narayanan, V.; Preisler, E. J.; Ross, F. M.; Shang, H., "Epitaxial silicon and germanium on buried insulator heterostructures and devices" *Appl. Phys. Lett.* **2003**, 83, 5443.

18. Khakaniand, M. A. E.; Yi, J. H., "The nanostructure and electrical properties of SWNT bundle networks grown by an _ all-laser growth process for nanoelectronic device applications"*Nanotech.* **2004**, 15, S534.

19. Ang, K. W.; Lo, G. Q.; Kwong, D. L., " Germanium Photodetector Technologies for OpticalCommunication Applications" *Semicon. Techn.* **2010**, 16, 373.

20. Greytak, A. B.; Lauhon, L. J.; Gudiksen, M. S.; Lieber, C. M., " Growth and transport properties of complementary germanium nanowire field-effect transistors" *Appl. Phys. Lett.* **2004**, 84, 4176.