JNS 3(2013) 103-108

Journal of
NANOSTRUCTURES

JNS
NANOSTRUCTURES
JNS.kashanu.ac.ir

Gold catalytic Growth of Germanium Nanowires by chemical vapour deposition method

M. Farangi, M. Zahedifar*, M.H. Pakzamir

Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317–51167, Iran

Article history:
Received 19/3/2013
Accepted 22/5/2013
Published online 1/6/2013

Keywords:
Germanium nanowires
CVD method
Au catalyst
Carrier gas composition

**Corresponding author:*
E-mail address:
zhdfr@kashanu.ac.ir
Phone: +98 361 591 2838
Fax: +98 361 551 4005

Abstract

Germanium nanowires (GeNWs) were synthesized using chemical vapor deposition (CVD) based on vapor–liquid–solid (VLS) mechanism with Au nanoparticles as catalyst and germanium tetrachloride ($GeCl_4$) as a precursor of germanium. Au catalysts were deposited on silicon wafer as a thin film, firstly by sputtering technique and secondly by submerging the silicon substrates in Au colloidal solution, which resulted in Au nanoparticles with different sizes. GeNWs were synthesized at 400 °C, which is a low temperature for electrical device fabrication. Effect of different parameters such as Au nanoparticles size, carrier gas (Ar) flow and mixture of H_2 with the carrier gas on GeNWs diameter and shape was studied by SEM images. The chemical composition of the nanostructure was also examined by energy dispersive X-ray spectroscopy (EDS).

1. Introduction

In the last decade, one-dimensional (1D) nanostructures have been widely studied as promising materials for nanoelectronic, and photovoltaic applications [1-4]. These nanostructures such as nanowires and nanotubes, because of their unprecedented properties, have attracted a great deal of attention [5-11]. Compared with silicon as the most prominent material in electronic industry, germanium, having

higher carrier mobility and lower band gap, has received great interest and offers noticeable applications [12-14]. Germanium nanostructures such as GeNWs are amongst the first reported semiconductor nanostructures [15], and excessive amount of researches have been devoted to their characterization and improving the preparation methods. To synthesis GeNWs, various methods have been reported using Au nanoparticles, including CVD, physical vapor deposition (PVD), electron beam evaporation and solvothermal reactions [16-21].

CVD method is one of the most successfully developed techniques to synthesize one-dimensional nanostructures, and it is very favourable method to produce carbon nanotubes. In this technique, reactive materials are decomposed to feed into the catalyst particles, and after reaching to the supersaturated condition, nanowires begin to sprout from the bottom of supersaturated catalyst particles. Compared to other methods, in CVD technique growth parameters can be adjusted in order to prevent the non desirable reagents to deposit on the nanostructures sidewall, meanwhile nanowires location can be specified by managing the catalyst particles location [5]. This mechanism is fulfilled in a horizontal quartz tube. To gain more control on the morphology of the products, one approach is to employ catalyst particles as a preselected deposition sites, which causes the nucleation and growth of nanotubes or nanowires by the VLS growth process [22, 23]. GeI_4 (germanium iodide) or GeH_4 (Germane) are usually consumed as germanium source, however in this work we have used $GeCl_4$ (germanium tetrachloride) as feeding stock which is much unharmed than Germane, and synthesis process can be performed in none high vacuum equipments [24].

2 Experimental

CVD method was employed to produce GeNWs, the gas flow was regulated by mass flow controller (MFC) from Brooks, and Si wafer (100) was used as substrate. Si substrates were cleaned with immersing in acetone, ethanol and HF (5 M) and DI water for 10 min, respectively. Au catalyst was deposited on substrates with two techniques. Using the first method, it was deposited by sputtering technique with 5 nm thickness, and then the samples were treated at 500 ^oC for 10 min in Ar atmosphere. By the second technique, the substrates were immersed in 3-aminopropyltriethoxysilane (APTES) for 20 min and then were washed with DI water. Subsequently, the silicon substrates were submerged in Au colloidal solution for 15 min [24]. Following catalyst deposition process, substrate was placed into the reactor before switching on the main reaction and to purge the reactor, Ar gas flow was used during the system was being heated up to 400 ^oC and then the $GeCl_4$ gas was injected into carrier gas and it was led onto silicon substrate.The growth time was selected about 20 min. SEM (Philips XL30) images were utilized to study GNWs growth peocedure.

3. Results and discussion

In this work, the growth mechanism is based on VLS process, which is illustrated in Fig. 1. According to this figure, growth mechanism includes three stages: in the first step, precursor molecules including Ge atom are decomposed and Ge atoms feed Au seeds to form Ge_xAu_{1-x} alloy. Au is an excellent catalyst for GeNWs growth due to their low eutectic temperature, which causes

possibility of GeNWs growth at lower

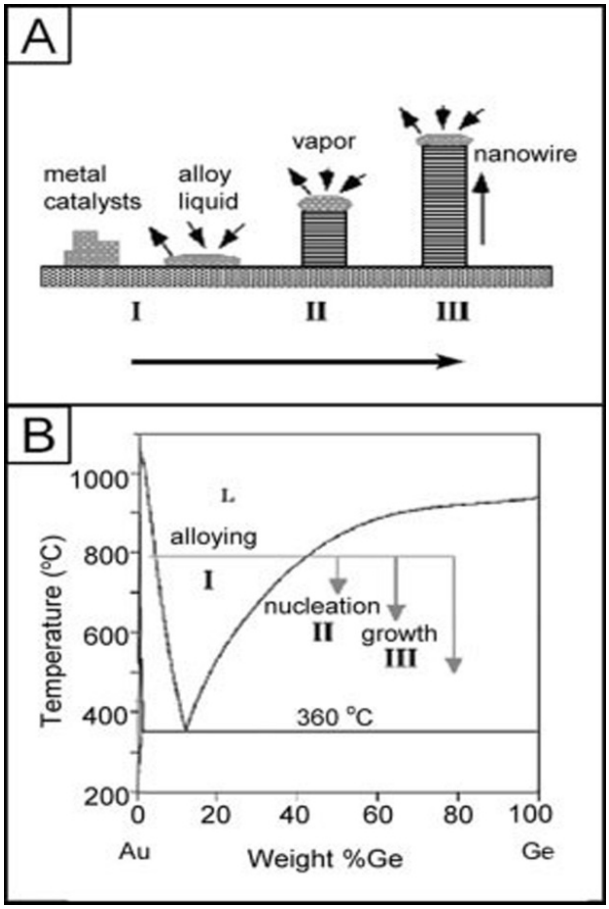

Fig. 1. (a) The VLS mechanism of nanowires growth through catalyst seeds and (b) the binary phase diagram of Ge and Au [25].

temperatures than other catalysts. When this system draws near the eutectic condition, the alloy particles turn into liquid droplets. More feeding by Ge atoms, causes the alloy liquid droplets to reach to a supersaturation condition of Ge atoms, therefore nucleation of Ge takes place. As further Ge atoms are continually provided, this feeding–alloying–nucleation mechanism continues and prolongation of Ge crystals forms GeNWs [25]. In the CVD method, different parameters such as type and size of catalyst, carrier gases, growth temperature and pressure, and crystalline structure of substrate determine the final products.

In the VLS growth, there is better control over

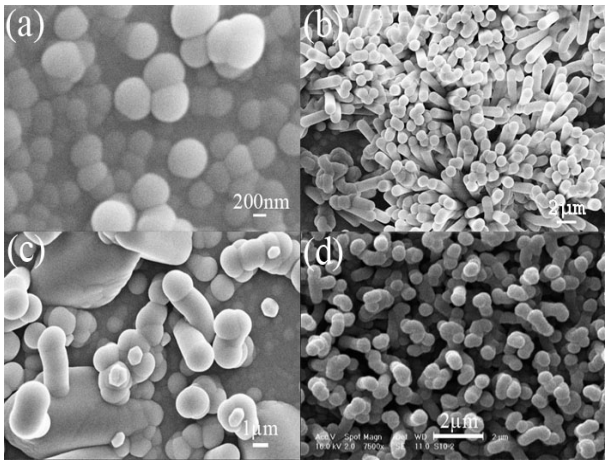

Fig. 2. SEM images of samples (a-c) with Au thin film catalyst for different gas flows: 60, 80, 100 sccm, and (d) with Au colloidal solution catalyst for 80 sccm.

nanowires size and order by adjusting the size and location of seeds. To study the effect of carrier gas flow on formation of GeNWs, some experiments were conducted by Au thin film catalyst. Gas flow was changed at three steps: 60, 80 and 100 sccm (standard cubic centimeter per minute). According to Fig. 2 (a), there is no nanowire on substrate; it is suggested that due to aggregation of Ge atoms at the entrance wall of reactor, Au seeds cannot attract enough Ge atoms. With increasing gas flow, one can see the formation of Ge wires for 80 sccm, however at higher flux (100 sccm) the growth was reduced owing to passing Ge atoms above the substrate with intensive stream of carrier gas, and Ge atoms cannot be attracted by Au seeds, so subsequent experiments have performed with 80 sccm as optimized carrier gas flow.

As mentioned beforehand, catalyst particles size is an important parameter for controlling nanowires diameter. Due to this fact, we used two types of Au catalyst in our experiments (Fig. 3). In accordance with this figure, Au thin layer turned

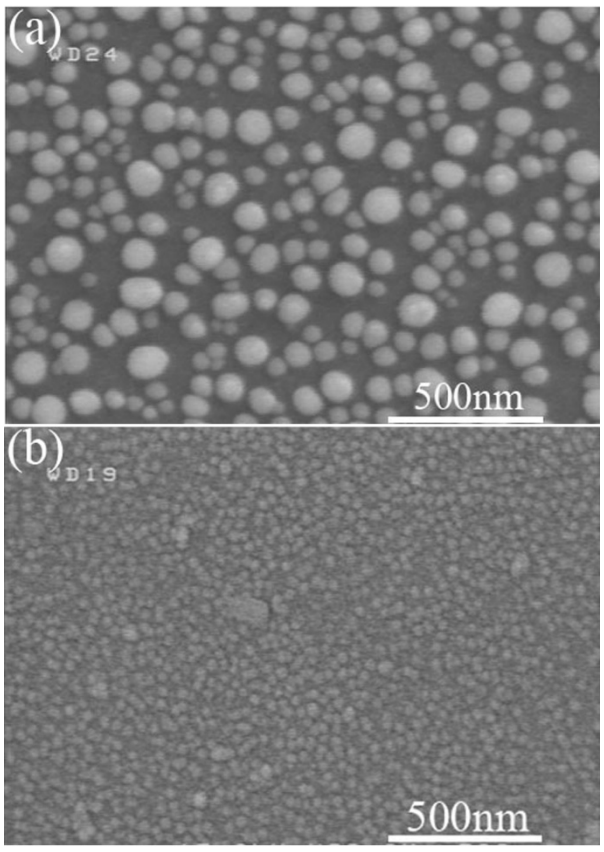

Fig. 3. SEM images of Au nanoparticles from (a) Au thin layer after annealing process at 500 □C and (b) Au colloidal solution.

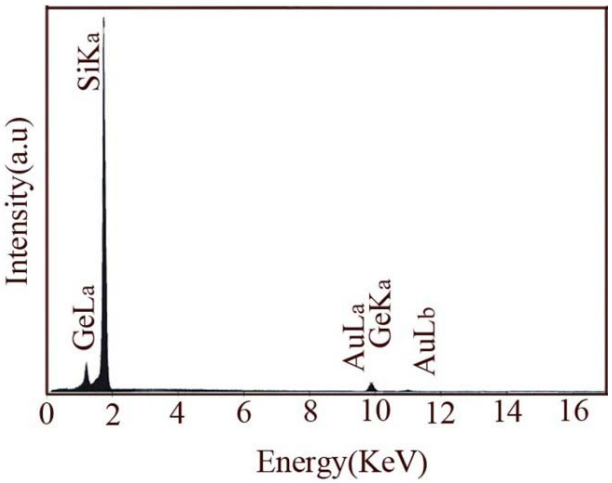

Fig. 4. EDS spectrum of the GeNWs with 80 sccm as carrier gas flow and catalyst of Au colloid solution.

to Au nanoparticles (with a size distribution from 50 to 100 nm) after annealing process at 500°C, but Au colloidal solution gives uniform nanoparticles with diameter about 30 nm. A comparison between Fig. 2(b) and Fig. 2(d) reveals the role of seeds size on nanowires diameters, but formation of large size nanowires, apparently is owing to Au seeds aggregation [26-29].

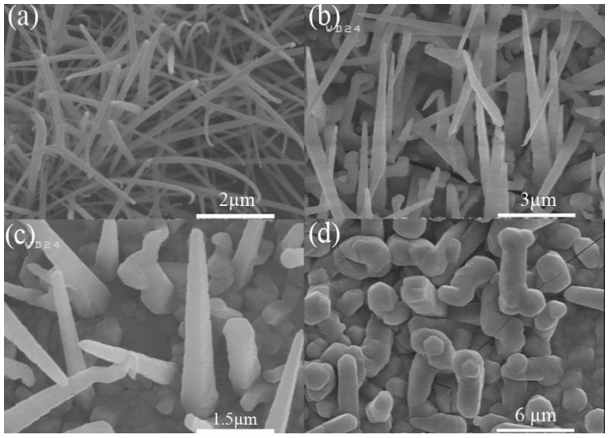

Fig. 5. SEM images of GeNWs with different ratio of Ar and H_2 as carrier gas.

The chemical compositions of structure were examined by energy dispersive X-ray spectroscopy (EDS) connected to the SEM. EDS spectrum of the GeNWs with catalyst of Au colloid solution is shown in Fig. 4. The peaks attributed to Si and Au come from the substrate and catalyst seeds, respectively. This analysis shows that the nanowires are made up of Ge.

To investigate the effect of carrier gas type, we used different complexes of Ar and H_2. At the first part, the relative ratio of Ar:H_2 was 70:10 sccm, which results thinner GeNWs (Fig. 5(a)). According to Fig. 5(b) and 5(c), with increase in the amount of H_2 to 60:20 and 50:30 sccm, pyramidal GeNWs were formed, but lower density of nanowires was gained for the ratio of 50:30 sccm. With escalation of H_2 amount up to 0:80 sccm, formless structures of Ge were produced (Fig. 5(d)). It is suggested that the presence of H_2 gas in reaction medium causes faster decomposition process of $GeCl_4$. Higher quantity of H_2 not only increases the number of Ge atoms

for Au seeds but also introduces a new type of growth mechanisms. In the experiments with low amount or absence of H_2 in carrier gas, the growth process of nanowires is performed only through the Au seeds, however for higher amount of H_2, attraction process of Ge atoms can be conducted by sidewall of nanowires, too. So in the presence of H_2, nanowires grow in axial and lateral directions, bottom sidewall of nanowires has more time than top part of nanowires to gather higher quantity of Ge atoms which results in pyramidal GeNWs instead of cylindrical GeNWs. With increase of H_2 ratio up to 80 sccm, the attraction of Ge atoms through surface, overcomes the attraction through Au seeds; this trend causes the substrate surface to be covered with a layer of Ge. According to these results, we propose fabrication of GeNWs with Au colloidal solution instead of Au thin film as a source of catalyst, and a mixture of Ar:H_2 carrier gas with optimized ratio of 70:10 sccm.

4. Conclusion

In summary, GeNWs have been synthesized using CVD method at 400 °C with $GeCl_4$, Au seeds and silicon wafer as precursor, catalyst and substrate respectively. $GeCl_4$ as a less toxic precursor compared to Germane was proposed to synthesize GeNWs [24]. Influence of carrier gas flow on growth process of GeNWs was studied and 80 sccm was selected as an optimum flow which can feed catalysts seeds with enough Ge atoms. Effect of Au thin film and Au colloidal solution as sources of catalyst on diameter of nanowires was investigated with SEM images. It was realized that adding H_2 gas into Ar as carrier gas, impresses on growth mechanism and causes lateral growth beside axial growth which results in pyramidal GeNWs and changes nanowires shapes. An increase in the quantity of H_2 to 80 sccm, caused undesired deposition of Ge on silicon surface and GeNWs sidewalls.

Acknowledgements

The authors gratefully acknowledge the research council of the University of Kashan for financial support.

References

[1] Y. Chaoyi, Y.Ch. Mei, Zh. Tao, S.L. Pooi, J. Phys. Chem. C. 113 (2009) 1705–1708.
[2] Y. Cui, C. M. Lieber, Science. 291 (2001) 851-853.
[3] M.S. Hu, H.L. Chen, C.H. Shen, L.S. Hong, B.R. Huang, K.H. Chen, L.C. Chen, Nat. Mater. 5 (2006) 102-106.
[4] B.Z. Tian, X.L. Zheng, T.J. Kempa, Y. Fang, N.F. Yu, G.H. Yu, J.L. Huang, C.M. Lieber, Nature. 449 (2007) 885-889.
[5] D. Wang, Pure Appl. Chem. 79 (2007) 55–65.
[6] H. Dai. Surf. Sci. 500 (2002) 218-241.
[7] H.J. Dai. Acc. Chem. Res. 35 (2002) 1035-1044.
[8] C.M. Lieber. Mrs Bull. 28 (2003) 486-491.
[9] Y.N. Xia, P.D. Yang. Adv. Mater. 15 (2003) 351-352.
[10] P.D. Yang. Mrs Bull. 30 (2005) 85-91.
[11] J.H. Kim, S.R. Moon, Y. Kim, Z.G. Chen, J. Zou, D.Y. Choi, H.J. Joyce, Q. Gao, H.H. Tan, C. Jagadish, Nanotechnology, 23 (2013) 115603.1-115603.6.
[12] S.M. Sze. Physics of Semiconductor Devices, John Wiley, New York, 1981.

[13] K.C. Saraswat, C.O. Chui, T. Krishnamohan, A. Nayfeh, P. Mcintyre. Microelectron. Eng. 80 (2005) 15-21.

[14] M.A. Sk, M.F. Ng, L. Huang, K.H. Lim, Phys. Chem. Chem. Phys. 15 (2013) 5927-5935.

[15] J.R. Heath, F.K. Legoues. Chem. Phys. Lett. 208 (1993) 263-268.

[16] A.R. Phani, V. Grossi, M. Passacantando, L. Ottaviano, S. Santucci, NSTI Nanotech. 3 (2006)141-144.

[17] Y. Wu, P. Yang, Chem. Mater. 12 (2000) 605-607.

[18] G. Gu, M. Burghard, G.T. Kim, S. Dusberg, P.W. Chiu, V. Krstic, S. Roth, W.Q. Han, J. Appl. Phys. 90 (2001) 5747-5751.

[19] T.I. Kamins, X. Li, R.S. Williams, Nano.Lett. 4 (2004) 503-506.

[20] R. Rakesh Kumar, K. Narasimha Rao, A.R. Phani, AIP Conf. Proc. 1512 (2012) 266-267.

[21] T. Harnath, B.K. Korgel, J. Am. Cerm. Soc. 124 (2001) 14241429.

[22] D.C. Johnson1, W.D. Morris, A.L. Prieto. Nanotechnology 21 (2010) 1-9.

[23] R.S. Wagner, W.C. Ellis, Appl. Phys. Lett. 4 (1964) 89–90.

[24] M. Zahedifar, F. Hosseinmardi, L. Eshraghi, B. Ganjipour, Radiat. Phys. Chem. 80 (2011) 324–327.

[25] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, Adv. Matter. 12 (2003) 353-389.

[26] T. Hanrath, B.A. Korgel. J. Am. Chem. Soc. 124 (2002) 1424-1429.

[27] T. Hanrath, B.A. Korgel. Nano Lett. 4 (2004) 1455-1461.

[28] T. Hanrath, B.A. Korgel. J. Phys. Chem. B. 109 (2005) 5518-5524.

[29] T. Hanrath, B.A. Korgel. Small. 1 (2005) 717-721.