Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics Letters 453 (2008) 97–100
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Tailoring of amorphous SiO_x nanowires grown by rapid thermal annealing

Yi-Sheng Lai [a,*], Jyh-Liang Wang [b], Sz-Chian Liou [c], Chia-Hsun Tu [d]

[a] Department of Materials Science and Engineering, National United University, Miaoli 36003, Taiwan
[b] Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu 30050, Taiwan
[c] Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan
[d] Department of Electrical and Computer Engineering, Microelectronics Research Center, The University of Texas, Austin, TX 78758, USA

Received 9 October 2007; in final form 9 January 2008
Available online 16 January 2008

Abstract

The growth of Pt-catalyzed SiO_x nanowires by rapid thermal annealing at 900 °C is demonstrated in the study. The growth of the nanowire is found to occur via a catalyst driven VLS mechanism. The seed particle composed of Pt–Si alloy is observed from the reaction between SiO_2 and the catalytic Pt film. When the annealing time exceeds 60 s, the SiO_x nanowires first agglomerate, and then collapse to form dendritic islands on the surface. The dendritic islands may result from the reaction between Pt–Si seed particle and SiO_x nanowires, and are identified to be the Pt–Si compound.

1. Introduction

One-dimensional nanostructures have received increasing attention due to their unique electronic, optical, and magnetic properties as a result of their large surface-to-volume ratio and quantum confinement effect. Numerous studies of the growth of metal-catalyzed nanowires have been investigated by different groups using various growth techniques. The vapor–liquid–solid (VLS) mechanism first proposed by Wagner has been suggested as the mechanism for nanowire growth [1]. Recently, the characteristics of the VLS mechanism has been revisited by Cheyssac et al. [2]. In addition, Persson et al. also proposed the vapor–solid–solid (VSS) mechanism, where the Au seed particle does not exceed the melting temperature during the nanowire growth [3]. Furthermore, nanowires can also be grown without a metal seed, for example in the presence of an oxide or by masking a substrate [4,5].

Novel fabrication technology of nanowires is versatile and includes a wide range of vapor, liquid and solid state processing routes. Elechiguerra et al. deposited Pd/Au films as a catalyst to synthesize SiO_x nanowires by thermal heating at 1100 °C [6]. Zhang et al. demonstrated that SiO_x nanowires could be grown directly from a SiO_2 substrate by annealing at 1100 °C in an Ar/methane flow [7]. Lee et al. reported the fabrication of silica nanowires by solid state diffusion of silicon from the silica films [8]. The growth of SiO_x nanowires via VLS mechanism or solid state diffusion is usually conducted at high temperature (1050–1100 °C). To our knowledge, rapid thermal annealing (RTA) has rarely been used for the nanowire growth. In this Letter, we demonstrate the growth of Pt-catalyzed SiO_x nanowires by a simple procedure, i.e., rapid thermal annealing. The effect of growth parameters on the evolution of SiO_x nanowires, as well as its characterization, will be addressed.

2. Experimental

SiO_2 films with a thickness of 11 nm were grown on p-type silicon (100) substrates by thermal oxidation. A 50-nm-thick Pt layer was then deposited on SiO_2 by thermal evaporation. The $Pt/SiO_2/Si$ structure was subjected to

* Corresponding author. Fax: +886 37 324047.
E-mail address: yslai@nuu.edu.tw (Y.-S. Lai).

0009-2614/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2008.01.026

RTA in nitrogen ambient at 700, 800, and 900 °C for 60, 180, and 300 s, respectively. The surface morphology was examined by field emission scanning electron microscopy (FESEM) (S-4000, Hitachi). The crystallinity of the nanostructure was analyzed by glancing incident angle X-ray diffraction (GIAXRD) (D/MAX2500, Rigaku, using Cu Kα, $\lambda \sim 0.154$ nm) with a fixed incident angle of 2°. The transmission electron microscopy (TEM) experiments were carried out on a JEM-2000FX (JEOL Ltd.) operated at 200 kV. The TEM was equipped with a Gatan image filter (GIF, Model 2000, Gatan) which provides the fingerprint of chemical bonding states with high lateral/energy resolution (i.e. electron energy loss spectroscopy (EELS) spectra), recorded with an energy resolution of 1.2 eV (full width at half maximum, FWHM, of zero-loss peak) and an energy dispersion of 0.3 eV per channel. Electron energy-loss spectroscopy when performed in a nanoanalytical electron microscope provides one route to this information via analysis of the energy-loss near-edge structure (ELNES) present on the ionization edges. The ionization edge onsets and EELS near-edge fine structures (ELNES) are sensitive to the local coordination and electronic structure.

3. Results and discussion

Fig. 1a and b shows the morphology of the Pt/SiO_2/Si structure after RTA at 800 °C and 900 °C, respectively. It is noted that the formation of Pt nanoparticles occurs at 800 °C, while that of nanowires appears at 900 °C. The formation of Pt nanoparticles is also observed for samples after RTA at 700 °C. Consequently, the critical temperature for the growth of nanowires is above 900 °C. The growth temperature of the nanowire is above the eutectic melting point (847 °C) of Pt–Si alloy [9]. It is reported that annealing of SiO_2/Si film stacks will lead to the formation of gaseous SiO at temperatures above approximately 800 °C [10]. The 11-nm-thick SiO_2 thin film may act as the source for the SiO_x nanowire growth. On the other hand, the nonequilibrium nature of heat transfer in the nanoparticles/film system should be taken into account [11]. The nanoparticles may have higher temperature rise than the film or substrate. As a result, it is evident that the growth of the nanowire is driven by the VLS mechanism. Moreover, the length of the nanowire is around 500 nm. The diameter of the nanowires ranges from 50 nm to 110 nm, which are probably connected with the size of the Pt catalyst [12,13].

Fig. 2a shows the TEM micrograph of the nanowire grown after RTA at 900 °C. The seed particles, for the most part, are attached to the top of the grown nanowires. However, a few of them are embedded in the wire during growth [10]. When the catalyst particle is on the wire tip, the VLS mechanism seems to be responsible. However, the VLS mechanism may not account for the catalyst, which remains in between the wire top and wire bottom. As a result, the growth behavior of the nanowire in this study still needs further investigation. Energy-dispersive

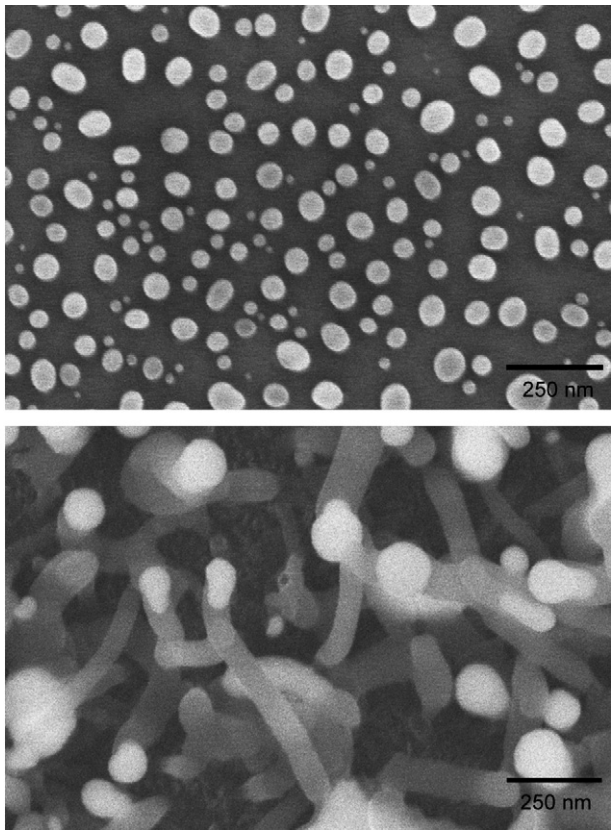

Fig. 1. Scanning electron microscopy images of (a) Pt nanoparticles on the surface after rapid thermal annealing at 800 °C for 60 s. (b) Pt assisted SiO_x nanowires grown after rapid thermal annealing at 900 °C for 60 s.

X-ray (EDS) analysis shows that the wire is mainly composed of Si and O, whereas the seed particle is constituted by Pt and Si, as shown in Fig. 2b. The high-resolution TEM micrograph also indicates that the SiO_x nanowire is amorphous (not shown). Analysis of the energy-loss near-edge structure (ELNES) present on the ionization edges can provide information on the local chemistry, structure and bonding. Fig. 2c shows the spatially resolved EEL spectra, indicating the Si L_{23} ELNES of the nanowire and Si substrate, respectively. The Si L_{23} ELNES of the nanowire shows a higher energy than that of the Si substrate. Schulmeister and Mader reported that the Si L_{23} ELNES of amorphous silicon monoxide appears to be a superposition of the spectra of elemental silicon and of SiO_2 [14]. The onset of the near-edge structure of the nanowire is located at a lower energy than that of SiO_2. The shoulder peak near 106 eV is corresponding to the SiO_x, as compared to the reported literatures [14]. As a consequence, it can be concluded that the composition of the nanowire is silicon suboxide (SiO_x).

Next, the effect of annealing time on the growth of SiO_x nanowires is discussed. At the first stage of RTA, the Pt layer starts to agglomerate and forms nanoparticles on the SiO_2 surface. Afterwards, the Pt nanoparticles act as a catalyst and are responsible for initiating the growth

of SiO_x nanowires. The SiO_x nanowires are distributed individually after RTA at 900 °C for 60 s, as shown in Fig. 1b. However, it is seen in Fig. 3a that the sample after annealing at 900 °C for 180 s results in partial agglomeration of nanowires. Furthermore, annealing of the sample for 300 s leads to extinction of wires and forms dendritic islands on the surface, as shown in Fig. 3b. This result indicates that the optimum heating time for the growth of SiO_x nanowires is not longer than 60 s.

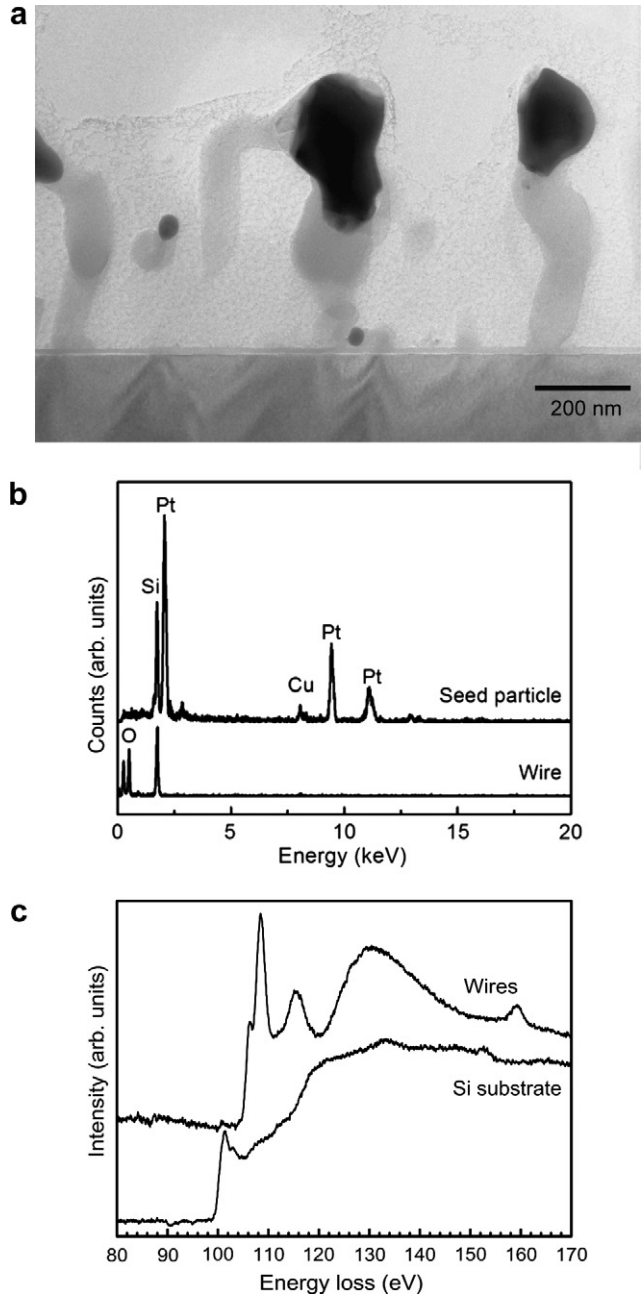

Fig. 2. (a) High resolution transmission electron microscopy images of the nanowire showing the seed particle (dark) and the wire (light gray). (b) The corresponding EDS spectrum of the nanowire, which reveals that the seed particles are mainly composed of Pt and Si, whereas the wires are mainly composed of Si and O. The Cu signal is contributed from the Cu grid. (c) Spatially resolved EEL spectra indicating the Si L_{23} ELNES of the nanowire and Si substrate.

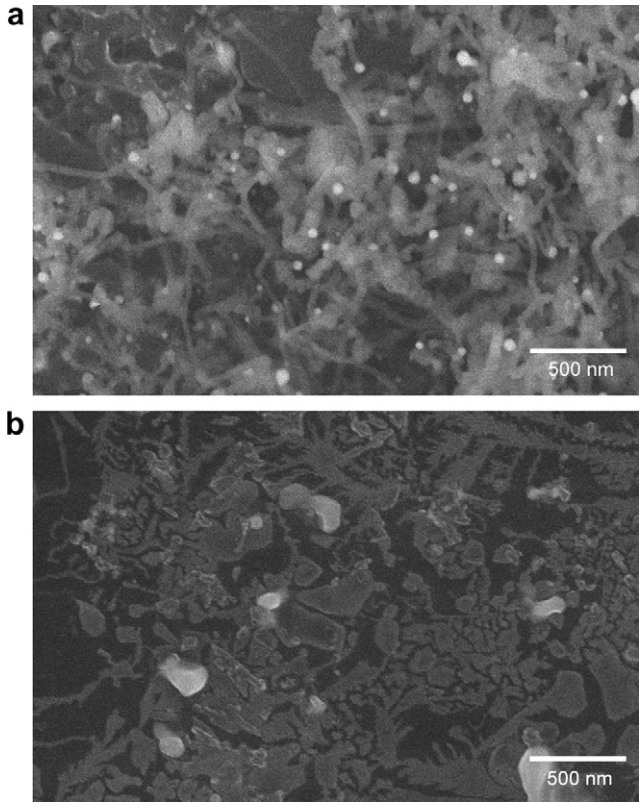

Fig. 3. Scanning electron microscopy images of $Pt/SiO_2/Si$ structures after rapid thermal annealing at 900 °C for (a) 180 s, and (b) 300 s.

Fig. 4a and b shows glancing incident angle X-ray diffraction (GIAXRD) patterns of $Pt/SiO_2/Si$ structures after 900 °C annealing for 60 s and 180 s, respectively. The diffraction peaks in Fig. 4a can be identified as a face-centered-cubic Pt alloy (JCPDS file 04-0802) [15]. From EDS and GIAXRD results, it is revealed that the seed particle in Fig. 2a shall be a solid solution constituted by Pt and Si. As the annealing time increases, the Pt and Si form an orthogonal Pt–Si compound (JCPDS file 07-0251), as shown in Fig. 4b. The dendritic islands in Fig. 3b are identified to be the Pt–Si phase and they may originate from the reaction of Pt with the SiO_x nanowire.

4. Conclusions

In conclusion, SiO_x nanowires have been successfully prepared by rapid thermal annealing with the use of Pt as catalysts, which initiate and guide the growth. The SiO_x nanowire can be grown at temperatures of 900 °C. Well distributed nanowires have been found after RTA for 60 s. Further annealing on the sample will lead to the deterioration of the nanowire structure. Considering the experimental results including the presence of catalyst

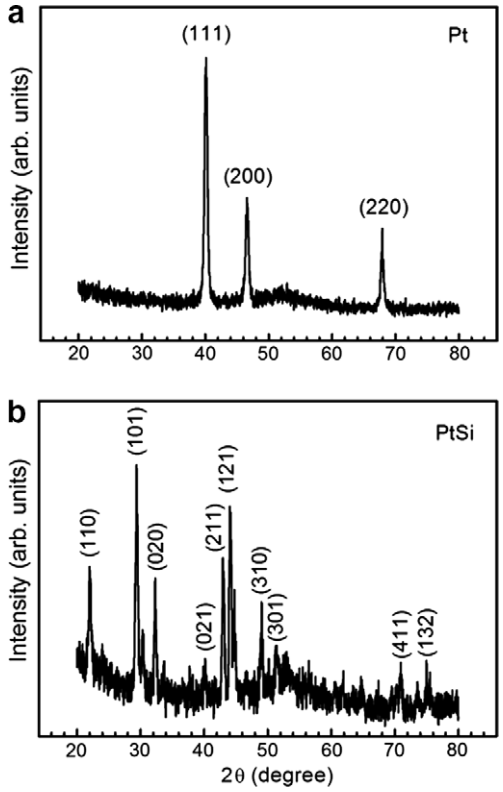

Fig. 4. Glancing incident angle X-ray diffraction (GIAXRD) patterns of $Pt/SiO_2/Si$ structures after rapid thermal annealing at 900 °C for (a) 60 s, and (b) 180 s.

on the nanowire tip, the VLS mechanism seems to be responsible for the SiO_x nanowire growth via RTA.

Acknowledgements

This work was supported by the National Science Council of ROC under the contract 95-2218-E-239-001. The authors are also indebted to the National Nano Device Laboratory (NDL) for technical support.

References

[1] R.S. Wagner, W.C. Ellis, Appl. Phys. Lett. 4 (1964) 89.
[2] P. Cheyssac, M. Sacilotti, G. Patriarche, J. Appl. Phys. 100 (2006) 044315.
[3] A.I. Persson, M.W. Larsson, S. Stenström, B.J. Ohlsson, L. Samuelson, L.R. Wallenberg, Nature Mater. 3 (2004) 677.
[4] W.S. Shi, Y.F. Zheng, N. Wang, C.-S. Lee, S.-T. Lee, Adv. Mater. 13 (2001) 591.
[5] J. Noborisaka, J. Motohisa, T. Fukui, Appl. Phys. Lett. 86 (2005) 213102.
[6] J.L. Elechiguerra, J.A. Manriquez, M.J. Yacaman, Appl. Phys. A 79 (2004) 461.
[7] Z. Zhang, B.Q. Wei, P.M. Ajayan, J. Phys. Condens. Matter 14 (2002) L511.
[8] K.-H. Lee, H.S. Yang, K.H. Baik, J. Bang, R.R. Vanfleet, W. Sigmund, Chem. Phys. Lett. 383 (2004) 380.
[9] B. Predel, in: O. Madelung (Ed.), Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys, Springer, Berlin, 1991.
[10] F.M. Kolb, A. Berger, H. Hofmeister, E. Pippel, U. Gösele, M. Zacharias, Appl. Phys. Lett. 89 (2006) 173111.
[11] G. Chen, J. Heat Transfer 118 (1996) 539.
[12] L. Schubert et al., Appl. Phys. Lett. 84 (2004) 4968.
[13] S.M. Roper, S.H. Davis, S.A. Norris, A.A. Golovin, P.W. Voorhees, M. Weiss, J. Appl. Phys. 102 (2007) 034304.
[14] K. Schulmeister, W. Mader, J. Non-crystal. Solid 320 (2003) 143.
[15] Powder Diffraction File, Joint Committee for Powder Diffraction Standards, International Center for Diffraction Data, Swarthmore, PA, 1997.