

Formation of silicon oxide nanowires directly from Au/Si and Pd–Au/Si substrates

Hyun-Kyu Park^a, Beelyong Yang^a, Sang-Woo Kim^{a,*}, Gil-Ho Kim^b, Doo-Hyeob Youn^c, Sang-Hyeob Kim^c, Sung-Lyul Maeng^c

^a*School of Advanced Materials and System Engineering, Kumoh National Institute of Technology, 1 Yangho-dong, Gumi, Gyeongbuk 730-701, South Korea*

^b*School of Information and Communication Engineering and SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746, South Korea*

^c*Cambridge-ETRI Joint R&D Center, Electronics and Telecommunications Research Institute, 161 Gajeong-dong, Daejeon 305-700, South Korea*

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Abstract

Amorphous silicon oxide (SiO_x) nanowires were directly grown by thermal processing of Si substrates. Au and Pd–Au thin films with thicknesses of 3 nm deposited on Si (001) substrates were used as catalysts for the growth of nanowires. High-yield synthesis of SiO_x nanowires was achieved by a simple heating process (1000–1150 °C) in an Ar ambient atmosphere without introducing any additional Si source materials. The as-synthesized products were characterized by field-emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, and transmission electron microscopy measurements. The SiO_x nanowires with lengths of a few and tens of micrometers had an amorphous crystal structure. The solid–liquid–solid model of nanowire formation was shown to be valid.

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1. Introduction

Studies on the fabrication and characterization of one-dimensional (1D) nanostructures such as nanowires and nanotubes have flourished in recent years because of their fundamental importance to nanotechnology [1,2]. A number of applications using 1D nanostructures have been investigated for nanoscale devices, devices using flexible substrates, and sensor applications [3–5]. Recently, silicon oxide (SiO_x) nanowires have attracted intensive interest due to their novel physical properties and potential applications in realizing multi-functional nanosized devices, such as blue light emitters and optical sensors with high sensitivity [6,7]. Various fabrication methods, including laser ablation, chemical vapor deposition, and evaporation, have been used to produce SiO_x nanowires via a vapor–liquid–solid (VLS) process requiring Si source

materials [8–10]. In this work, we report simple synthesis of amorphous SiO_x nanowires achieved by thermal heating of Au and Pd–Au coated Si substrates in an Ar ambient atmosphere without any additional silicon source supply.

2. Experiments

Si (001) substrates were used in our experiments. The substrates were alternately ultrasonically cleaned in acetone and in methanol for 5 min, and then dried by nitrogen blowing. Each 3 nm thin layer of Au and Pd–Au was deposited on the substrates in a simple sputtering system. For deposition of the Pd–Au catalyst layer, Pd–Au alloy (Pd:Au = 1:1) was introduced as the target material. The substrate was placed in an alumina tube, which was then heated in a tube furnace at 1000–1150 °C. While heating the substrates for 90 min, Ar gas with the flow rate of 50 sccm was introduced in the alumina tube at an atmospheric pressure of 760 Torr. After cooling down to room temperature, a thin layer of white-colored deposit was

*Corresponding author. Tel.: +82 54 478 7745; fax: +82 54 478 7769.

E-mail address: kimsw@kumoh.ac.kr (S.-W. Kim).

found on the substrate surface, indirectly indicating the formation of SiO_x nanowires. Measurements utilizing a field-emission scanning electron microscope (FE-SEM), equipped with an energy-dispersive X-ray spectroscope (EDX) as well as a transmission electron microscope (TEM), were carried out for analysis of the morphology and atomic composition of the grown nanowires.

3. Results and discussion

Fig. 1 shows FE-SEM images revealing the general morphologies of the thermally heated Au deposited Si (001) [Au/Si] and Pd–Au deposited Si (001) [Pd–Au/Si] substrates in the tube furnace. As shown in Fig. 1(a), Au nanoislands with diameters of 10–80 nm were formed on the surface of the substrate by heating the Au/Si substrate at 1000 °C. On the other hand, the formation of Pd–Au nanoislands with a uniform size distribution (a diameter of around 100 nm) by heating the Pd–Au/Si substrate at 1000 °C was observed in the FE-SEM measurement (Fig. 1(b)). From the EDX analysis, it was found that the formed Pd–Au nanoislands have a dual structure consisting of Pd surrounded by Au. In addition, the EDX spectrum collected from the nanoislands showed the presence of Au, Pd, Si, and O elements. Interestingly, no nanowire growth was seen on the Au/Si substrate, while SiO_x nanowires were locally formed on the Pd–Au/Si substrates, as shown in Fig. 1(b), in spite of the same heating temperature of 1000 °C. This fact indicates that the dual structure consisting of Pd surrounded by Au facilitates the formation of nanowires.

Fig. 2 shows FE-SEM images revealing the general morphologies of SiO_x nanowires grown on Au/Si and Pd–Au/Si substrates at 1050 °C. As shown in the FE-SEM images, a large number of nanowires with lengths of tens of

micrometers and diameters around 100 nm were formed on the Pd–Au/Si substrate surface, while a small number of nanowires with lengths of a few micrometers were locally formed on the Au/Si substrate. EDX results in Fig. 3 show that our SiO_x nanowires grown on the Au/Si substrate have an atomic ratio of Si/O higher than the $\frac{1}{2}$ of SiO_2 . On the other hand, the atomic ratio of Si/O in the SiO_x nanowires formed on the Pd–Au/Si substrate is nearly consistent with the $\frac{1}{2}$ of SiO_2 , indicating the formation of SiO_2 nanowires on the Pd–Au/Si substrate at this growth temperature.

Since no source of Si vapor existed, and the process temperature was not high enough to evaporate Si atoms into the Si substrate, the formation mechanism is different from the well-known VLS process requiring source materials and an evaporation technique. In addition, Si substrates were covered by a thin layer of Pd–Au and Au. Thus, the possible source for formation of SiO_x nanowires comes from the Si substrate, indicating that the formation mechanism of the SiO_x nanowires relies on a solid–liquid–solid (SLS) process. The melting point (MP) of pure Au is 1063 °C. As shown in Fig. 1, no nanowires were observed on the Au/Si substrate heated at 1000 °C, while a small number of nanowires with lengths of a few micrometers were locally formed on the Au/Si substrate at 1050 °C. These results suggest that the formation of SiO_x nanowires on Si via a SLS process by introducing the Au catalyst is somewhat limited below the MP of pure Au, even though the Au–Si eutectic temperature of around 370 °C is much lower than the process temperature of 1000 °C. On the other hand, a large number of nanowires were uniformly formed on the Pd–Au/Si substrate surface in spite of using a heating temperature lower than the MP of both Au and Pd (1554 °C). This might be due to enhanced catalytic activities by Pd–Au alloying compared to pure Au.

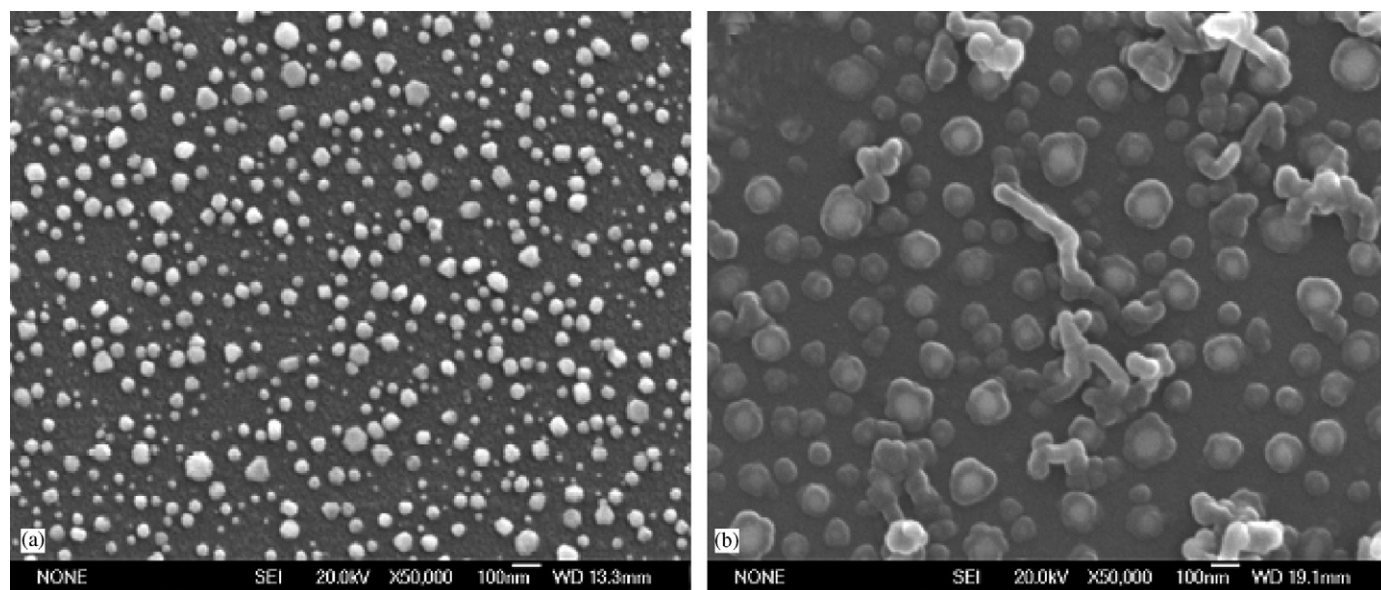


Fig. 1. FE-SEM images revealing general surface morphologies of (a) Au/Si and (b) Pd–Au/Si substrates treated by thermal processing at 1000 °C in an Ar ambient atmosphere in the tube furnace. The scale bar indicates 100 nm.

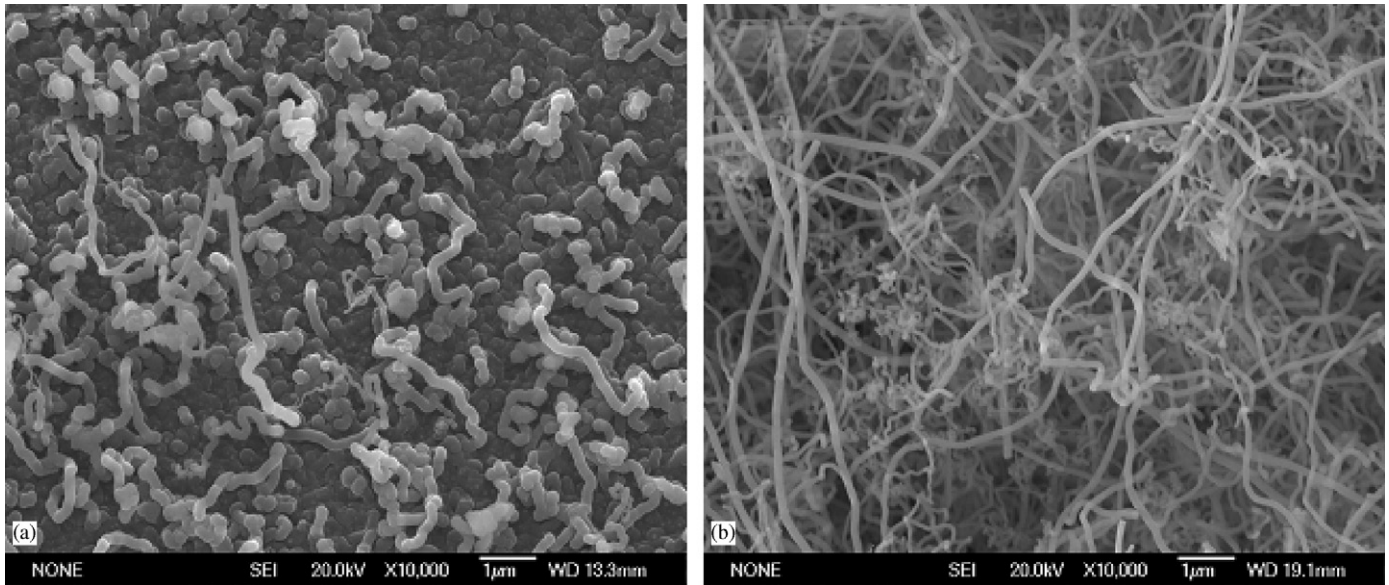


Fig. 2. FE-SEM images revealing general surface morphologies of SiO_x nanowires grown on (a) Au/Si and (b) Pd–Au/Si substrates at 1050°C in an Ar ambient atmosphere. The scale bar indicates $1\ \mu\text{m}$.

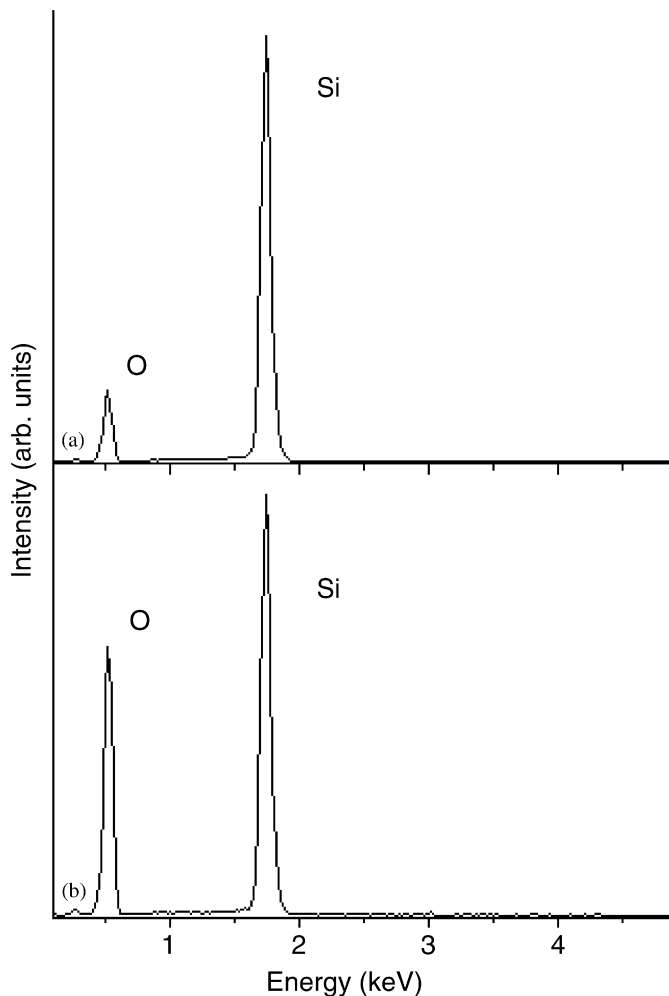


Fig. 3. (a) EDX spectrum from the sample presented in Fig. 2(a). The SiO_x nanowires on the Au/Si substrate have an atomic ratio of Si/O higher than the $\frac{1}{2}$ of SiO_2 . (b) EDX spectrum from the sample shown in Fig. 2(b). The atomic ratio of Si/O in the SiO_x nanowires on the Pd–Au/Si substrate is nearly consistent with the $\frac{1}{2}$ of SiO_2 .

An efficient diffusion path for Si in the Pd–Au alloy may result from the formation of many grain crystal boundaries allowing effective formation of liquid-phased PdSi silicides (PdSi MP: 972°C) at the process temperature of 1050°C [11–13].

In order to investigate the formation behavior of SiO_x nanowires on Au/Si and Pd–Au/Si substrates at a temperature above the pure Au MP of 1063°C , we carried out thermal heating of Au/Si and Pd–Au/Si substrates at 1100°C . Fig. 4 shows FE-SEM images of SiO_x nanowires grown on Au/Si and Pd–Au/Si substrates, as well as an EDX spectrum of SiO_x nanowires grown on the Au/Si substrate at 1100°C . At this temperature, twisted SiO_x nanowires were uniformly formed on both sample surfaces, although the diameters of SiO_x nanowires (below $400\ \text{nm}$) on the Au/Si substrate were larger than those of SiO_x nanowires (below $200\ \text{nm}$) on the Pd–Au/Si substrate. In addition, it was found that the SiO_x nanowires formed on both substrates at the growth temperature of 1100°C had a sharp 1:2 Si to O atomic ratio, which is inconsistent with the EDX results of the samples grown at 1050°C . These facts suggest that Au may play a key role in the formation of SiO_2 nanowires which form irrespective of introducing Au or Pd–Au catalyst at a process temperature above the MP of Au. A more detailed investigation on the catalytic behavior of Pd for the formation of SiO_x nanowires will be reported in the near future.

The formation of the SiO_x nanowires with such large diameters might be due to the high process temperature above the MP of Au. The TEM image (Fig. 5(a)) shows that the grown SiO_x nanowires are of an amorphous state. The highly diffusive ring pattern in the selected-area electron diffraction (SAED) of the nanowires (Fig. 5(b)) also confirms that they have an amorphous crystal structure.

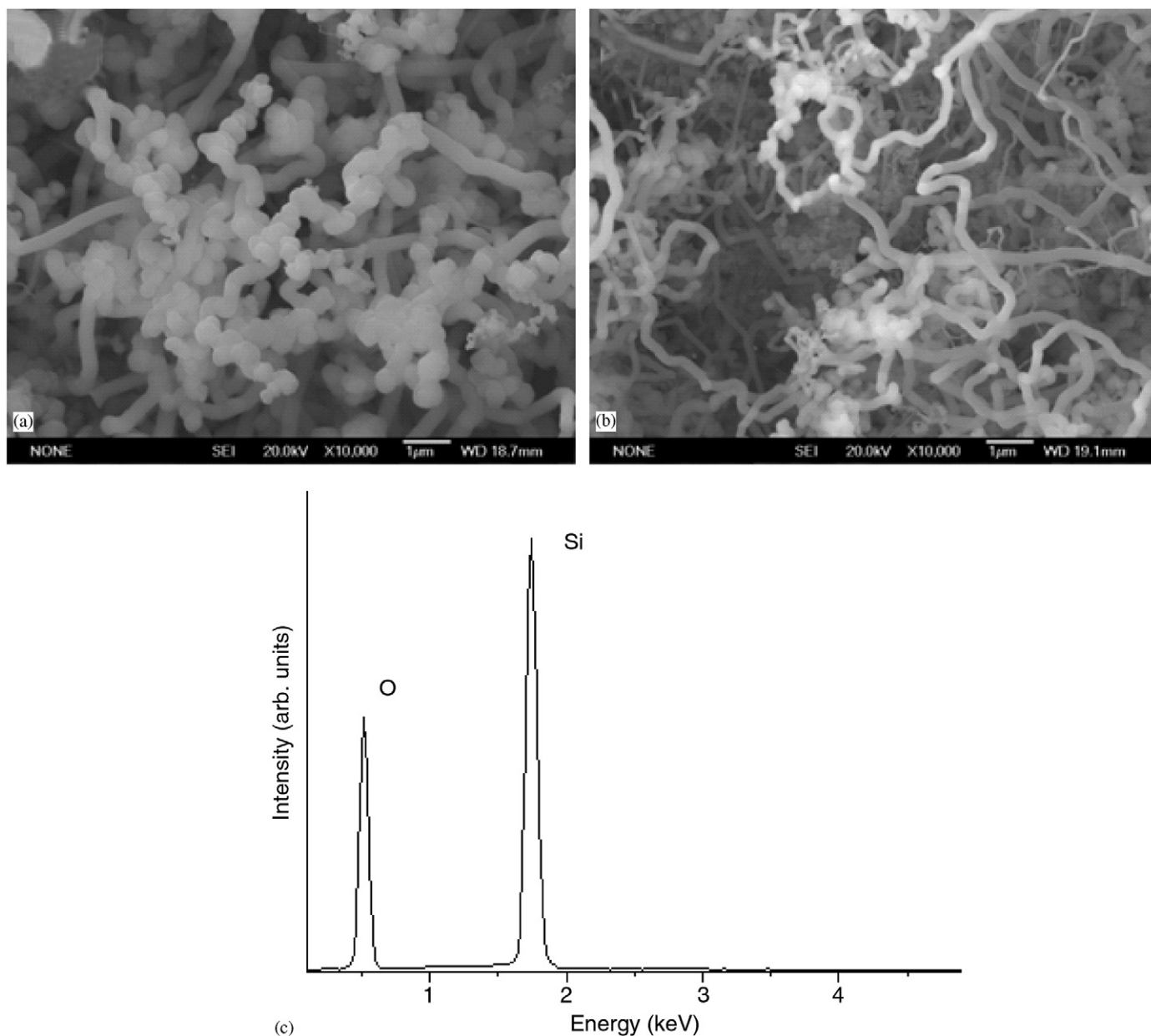


Fig. 4. FE-SEM images of nanowires on (a) Au/Si and on (b) Pd–Au/Si, and (c) an EDX spectrum of the SiO_x nanowires (sample shown in (a)) grown at 1100°C in an Ar ambient atmosphere. The scale bar indicates $1\ \mu\text{m}$.

The deposited Au thin film can effectively react with the Si substrate at a temperature above the MP of pure Au, resulting in the formation of Au–Si eutectic liquid alloy droplets. Due to the high solubility of Si atoms in the liquid phase of Au–Si eutectic droplets, a great number of Si atoms diffuse into the liquid phase via the interface between the substrate and the liquid-phased Au–Si droplets. Compositional supersaturation of the liquid Au–Si eutectic droplets by the continuous supply of Si atoms from the substrate results in the formation of SiO_x nanowires, instead of Si nanowires, due to the lack of vacuum during the heating process. From the results in this study, we could conclude that the formation mechanism of our SiO_x nanowires is explained by the SLS process.

4. Conclusion

In summary, we have reported amorphous SiO_x nanowires directly grown on Si substrates via the SLS process in this study. High-yield synthesis of SiO_x nanowires was realized by thermal processing of the Au and Pd–Au coated Si (001) substrates at 1000 – 1150°C in an Ar ambient atmosphere with no additional Si source materials. The grown SiO_x nanowires with diameters ranging from 50 to $400\ \text{nm}$ and lengths of a few tens of micrometers had an amorphous crystal structure. At temperatures below the MP of pure Au, the catalytic behavior of the Pd–Au alloying system for growing SiO_x nanowires was more active than the Au system. On the other hand, Au played

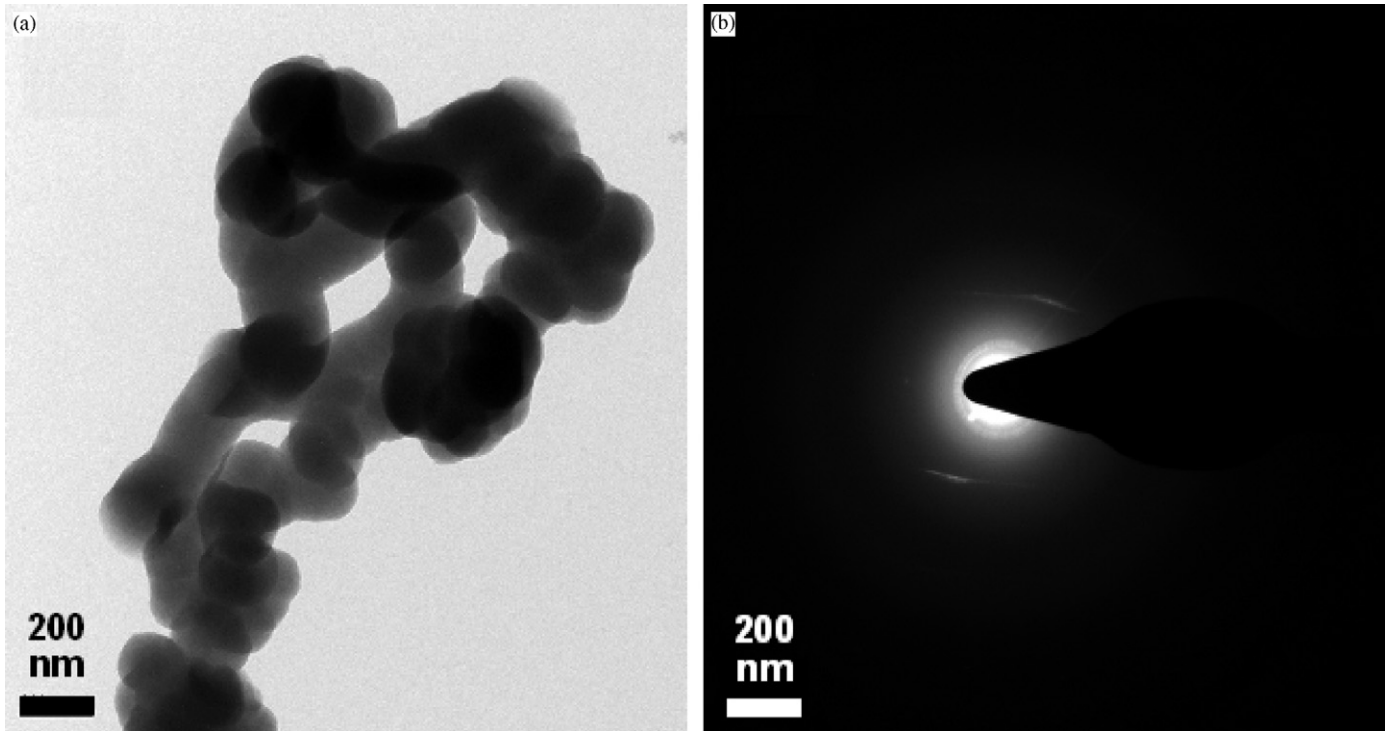


Fig. 5. (a) TEM image of a single amorphous SiO_x nanowire grown on the Pd–Au/Si substrate (Fig. 4(b)). (b) SAED pattern revealing the amorphous nature of the SiO_x nanowires.

an important role in the formation of SiO_x nanowires at process temperatures above the MP of Au, indicating the comparatively weakened catalytic behavior of Pd.

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References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* 292 (2001) 1897.
- [3] Y. Cui, Z. Zhong, D. Wang, W.U. Wang, C.M. Lieber, *Nano Lett.* 3 (2003) 149.
- [4] X. Duan, C. Niu, V. Sahl, J. Chen, J.W. Parce, S. Empedocles, J.L. Goldman, *Nature* 425 (2003) 274.
- [5] Y.X. Liang, Y.J. Chen, T.H. Wang, *Appl. Phys. Lett.* 85 (2004) 666.
- [6] D.P. Yu, Q.L. Hang, H.Z. Zhang, Z.G. Bai, J.J. Wang, Y.H. Zou, W. Qian, G.C. Xiong, S.Q. Feng, *Appl. Phys. Lett.* 73 (1998) 3076.
- [7] L. Tong, J. Lou, R.R. Gattas, S. He, X. Chen, L. Liu, E. Mazur, *Nano Lett.* 5 (2005) 259.
- [8] A.M. Morales, C.M. Lieber, *Science* 279 (1998) 208.
- [9] Z.Q. Liu, S.S. Xie, L.F. Sun, D.S. Tang, W.Y. Zhou, C.Y. Wang, W. Liu, Y.B. Li, X.P. Zou, G. Wang, *J. Mater. Res.* 16 (2001) 683.
- [10] N. Wang, Y.H. Tang, Y.F. Zhang, C.S. Lee, S.T. Lee, *Phys. Rev. B* 58 (1998) R16024.
- [11] Z.Q. Liu, Z.W. Pan, L.F. Sun, D.S. Tang, W.Y. Zhou, G. Wang, L.X. Qian, S.S. Xie, *J. Phys. Chem. Solids* 61 (2000) 1171.
- [12] J.L. Elechiguerra, J.A. Manriquez, M.J. Yacamán, *Appl. Phys. A: Mater. Sci. Process.* 79 (2004) 461.
- [13] D.K. Sood, P.K. Sekhar, S. Bhansali, *Appl. Phys. Lett.* 88 (2006) 143110.