Physica B 405 (2010) 1176–1180

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Preparation of highly aligned silicon oxide nanowires with stable intensive photoluminescence

El-Shazly M. Duraia [a,b,c,*], Z.A. Mansurov [b], S. Tokmolden [c], Gary W. Beall [d]

[a] Suez Canal University, Faculty of Science, Physics Department, Ismailia, Egypt
[b] Al-Farabi Kazakh National University, Almaty, Kazakhstan
[c] Institute of Physics and Technology, 11 Ibragimov Street, 050032 Almaty, Kazakhstan
[d] Texas State University-San Marcos, Department of Chemistry and Biochemistry, 601 University Dr., San Marcos, TX 78666, USA

ARTICLE INFO

Article history:
Received 24 August 2009
Received in revised form
9 November 2009
Accepted 10 November 2009

Keywords:
Silicon oxide nanowires
Photoluminescence
FTIR

ABSTRACT

In this work we report the successful formation of highly aligned vertical silicon oxide nanowires. The source of silicon was from the substrate itself without any additional source of silicon. X-ray measurement demonstrated that our nanowires are amorphous. Photoluminescence measurements were conducted through 18 months and indicated that there is a very good intensive emission peaks near the violet regions. The FTIR measurements indicated the existence of peaks at 463, 604, 795 and a wide peak at 1111 cm^{-1} and this can be attributed to Si–O–Si and Si–O stretching vibrations. We also report the formation of the octopus-like silicon oxide nanowires and the growth mechanism of these structures was discussed.

1. Introduction

In the last years great attention has attached to the production of the one dimensional nanostructures such as nanowires, nanorods, nanotube, etc. These nanostructures have many useful applications on many fields such as nanoelectronics and optoelectronic devices [1,2]. The fundamental mechanism for the growth of 1D nanostructure is the vapor–liquid–solid (VLS) process [3,4]. There are several techniques that have already been used for the synthesis of silicon nanowires, such as vapor–liquid–solid growth (VLS) catalyzed by a gold layer on Si [5], laser ablation of targets which containing the metal catalyst [6], Ni-assisted solid–liquid–solid (SLS) process [7] and carbothermal reduction of Fe-catalyzed SiO_2 particles [8]. Some of the proposed growth models show that the formation of Si nanowires does not require the presence of a metal, because the top SiO_2 layer can play the role of a catalyst in the wire nucleation [9,10]. In this process a high melting point metal (such as Ni, Au, Fe, etc.) catalyst particles are used to control the 1D nanostructure's growth direction and defines the diameter of the 1D nanostructure [11,12]. One dimensional silicon oxide nanostructures, which considered as a good candidate for photoluminescence material, have been successfully synthesized, by using several methods [13,14]. Gallium droplets with low melting point have been used as an effective catalyst for the large-scale growth of highly aligned, closely packed silica nanowire bunches [15,16]. Silicon nanowires can be successfully synthesized without any metal catalysts by annealing the Si substrates at 1050 °C in the presence of active carbon nanoparticles [17]. Liang et al. [18] have been reported the formation of high yield of silicon nanowires by using the rapid thermal annealing of carbon film at temperature of 1100 °C for 60 s.

In this work, we report the formation of well aligned SiNWs without any additional source of silicon, and the effect of the annealing temperature and annealing time on the formation of SiNWs was studied and finally we hope to understand the growth mechanism deeply.

2. Experimental work

p-Type silicon wafers with resistivity 5.6 ohm m were cleaned with acetone ultrasonic bath for 30 min at room temperature and then these wafers were coated with 40 nm nickel (99.98%) by using ion beam evaporation. The ion beam evaporation parameters were as follows: current 20 mA, voltage 4 kV, Ar pressure 4×10^{-4} Torr and the substrate at room temperature. Then we made annealing at temperatures 1100, 1000 and 1200 °C in Ar (with about 3% oxygen) medium and on the air with varying time. After the furnace was slowly cooled to room temperature, with cooling rate of about 40 °C per minute, the Ar flow was turned off, and a white wool-like product was formed in high yield on the surface of the substrate. The furnace that we used consists of quartz tube of diameter (60 mm) and length (500 mm) and surrounded with heating material [19].

* Corresponding author at: Institute of Physics and Technology, 11 Ibragimov Street, 050032 Almaty, Kazakhstan. Tel.: +7 727 3865675.
E-mail address: duraia_physics@yahoo.com (E.M. Duraia).

0921-4526/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2009.11.031

The specimens were subjected to the study of the analytical scanning electron microscope JEOL JSM-6490LA with resolution (3 nm), and energy dispersed X-ray spectroscopy which is being attached to the SEM, X-ray diffraction, FTIR spectroscopy BRUKER IFS 66V/S in the range of 400–2300 cm^{-1}. All the measurements were carried out at room temperature, and photoluminescence excitation was performed by 325 nm-He–Cd laser at room temperature. The film structures were investigated by X-ray diffraction using photographic registration of X-ray reflections. The X-ray diffraction patterns were obtained with the help of a collimated ($0.05 \times 1.5\ mm^2$) monochromatic (Cu K_α) beam directed at an angle of 5° to sample surface.

3. Results and discussion

The typical scanning electron microscope of the silicon oxide nanowires is shown in Fig. 1. The effect of the annealing temperature on the formation of silicon nanowires was studied. Fig. 2 shows the formation of silicon oxide nanowires at Ni/Si substrate after annealing at temperatures 1000, 1100 and 1200 °C for annealing time of 1 h. From these figures we can see the effect of the growing temperature on the formation of silicon oxide nanowires, where at the temperature of 1000 °C there is no SiNWs; when the temperature changed to 1100 °C we find a good amount of SiNWs with a small amount of silicon nanoribbons. And when the temperature increased to 1200 °C we received only SiNWs with a very high yield and well aligned. So that, by changing the synthesis conditions, the growth of the nanowires may switch to a quasi-two-dimensional growth resulting in a ribbon or belt morphology. So we can say that the temperature 1100 °C may considered as a threshold temperature for the growth of the SiNWs in our case because the experiment was repeated many times below this temperature but the SiNWs has not been formed. Similar experiments were carried out in the air and the results were negative for the formation of SiNWs which indicates that the argon plays an important role in the formation of SiNWs, and a trace amount of oxygen is needed for the growth, whereas excess amount of oxygen is not a good condition for the growth of SiNWs and we work on this point at the present time.

The effect of the annealing time was also investigated. The carried experiments indicated that the annealing time has an effect on the yield of the silicon nanowires, whereas the annealing temperature is the most important factor in the formation and the morphology of the SiNWs. Fig. 3A and B shows the scanning electron microscope images of the producing silicon nanowires after annealing in argon atmosphere for 2 h and 30 min at 1200 °C.

As we can see that the amount of fiber is very high for longer time and slowly decreases as the annealing time decreased.

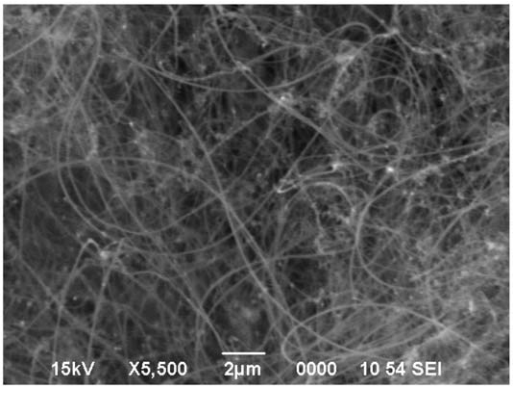

Fig. 1. Silicon nanowires formed by the annealing of silicon substrate in argon atmosphere.

Because there is no source for the silicon vapor and our growing temperatures are very low from the temperature required to evaporate the silicon atoms, we suggest that our growth mechanism is not the well-known vapor–liquid–solid mechanism in which the silicon vapor is needed. Moreover, from Fig. 3B, we note that the silicon nanowires are connected to each other like a network and also we note the formation of silicon–nickel alloy layer between the substrate and the SiNWs, and this supported our growth mechanism via solid–liquid–solid mechanism.

There was no additional source of silicon except the substrate, so we believe that the silicon used in the growth of SiNWs is supplied from the substrate itself and the SiNWs are grown without using any additional source of silicon. In our experiment we used two kinds of substrates on the same time and at the same conditions; the first consisted of Ni/Si substrate which is placed in the direction of the argon flow and then we placed Si substrate without any catalyst at the same horizontal line at a distance of about 0.8 cm. When we investigated these substrates by using the scanning electron microscope we find a dramatic difference between the two substrates. What we can see on Fig. 4C is looks like the back of the human head which indicates that there is a very large amount of well aligned vertically silicon nanowires.

Also, as we can see from Fig 4A and B, there are a lot of spheres distributed on the surface of the substrate and surrounded by a very large amount of silicon nanowires. From the scanning electron microscope measurements we found that the radius of this spheres is around 8–12 μm.

Yan et al. [7] reported that the deposited Ni film can react with the Si substrate at a temperature above 930 °C, and forms Si_2Ni eutectic liquid alloy droplets, and due to the high solubility of silicon atoms on this alloy more and more atoms will diffuse to this liquid layer and at super saturation silicon nanowires begin to grow. Moreover Zhang et al. [20] reported the formation of SiNWs of prickly sphere white wool-like ball by using the bimetal Ga–Sn as a catalyst. The authors explain the formation of this structure when the Si wafer was dissolved in a molten bimetal Ga–Sn ball at an elevated temperature. So that in our situation, in order to understand the mechanism of the microsphere formation we suppose that at high temperature there was a formation of nickel liquid drops on the silicon substrate; this is the first step. On the second step silicon will start to diffuse in the formed nickel drop as shown in Fig. 5. Then silicon seeds will be formed on the surface of the drop. In the last step a lot of silicon atoms will be diffused and reach to the saturation which will lead in turn to the formation of these microwires. It was very interesting that wires are very straight for a dozen of micrometer and then suddenly change their direction and become again straight in spite of the high temperature. To understand the reason of this phenomenon we suppose that the reason is due to the missing of the catalyst particle at the top of the wires and the catalyst only exist at the bottom. So we have observed a lot needle shaped wires as we can see from the figure.

With respect to the FTIR measurements, we made all the measurements at room temperature in the range of 400–2300 cm^{-1}; we note that there are many peaks at 463, 604, 795 and a wide peak at 1111 cm^{-1} and this can be attributed to Si–O–Si and Si–O stretching vibrations [21]. Fig. 6A demonstrates the FTIR for the sample on Fig. 4C.

Fig. 6B represents the X-ray diffraction of the silicon nanowires. We can see only one wide peak at angle of 21.6° which indicates that our sample is amorphous silicon oxide [22].

With respect to the photoluminescence measurements, all the measurements were performed at room temperature under the excitation of a laser with wavelength of 325 nm in the range 340–1000 nm. The laser beam was focused onto the sample a very small spot size (of about 1 mm in diameter), and this in order to

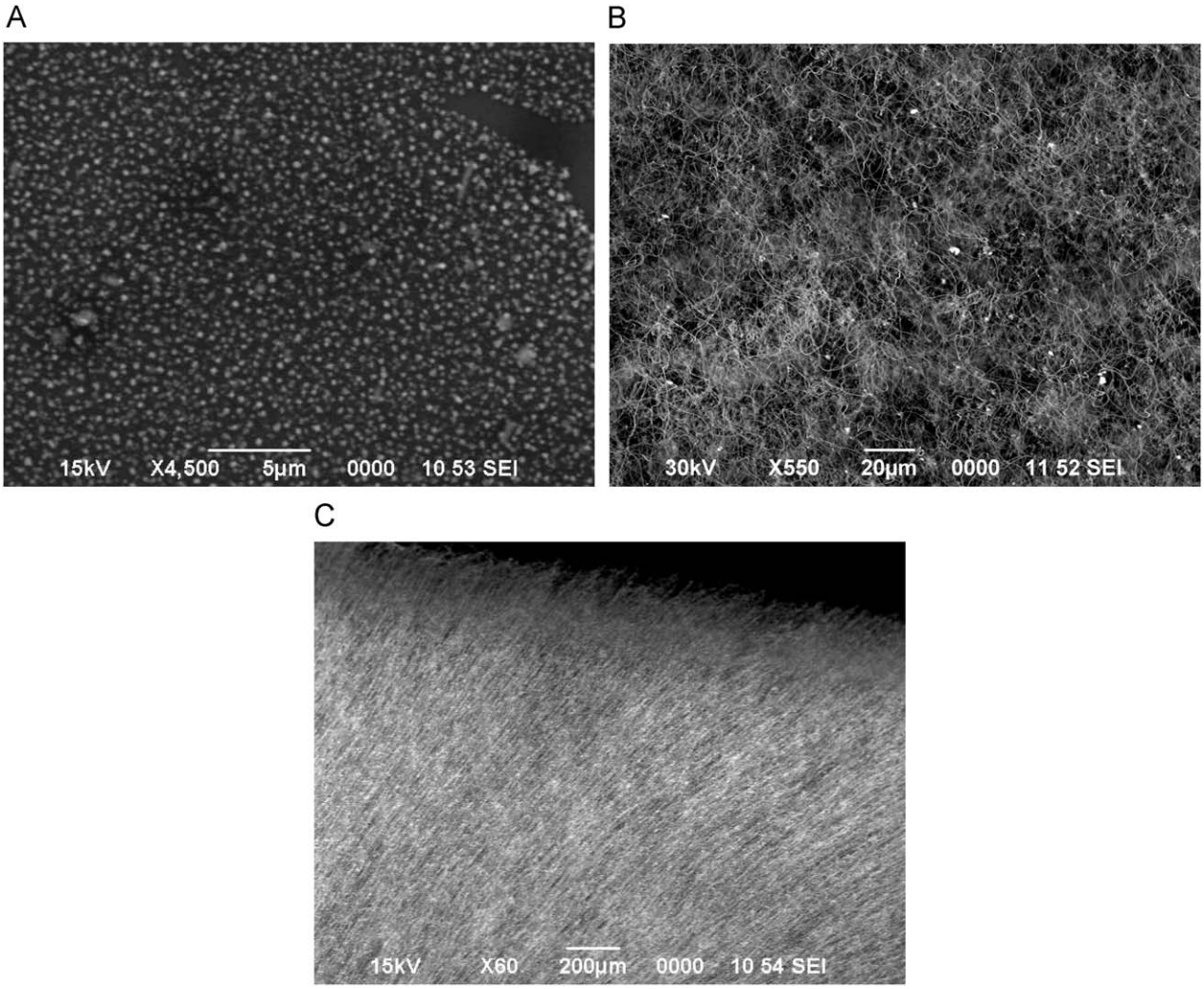

Fig. 2. Formation of silicon oxide nanowires at Si Ni C substrate at temperatures 1000, 1100 and 1200 °C, for 1 h.

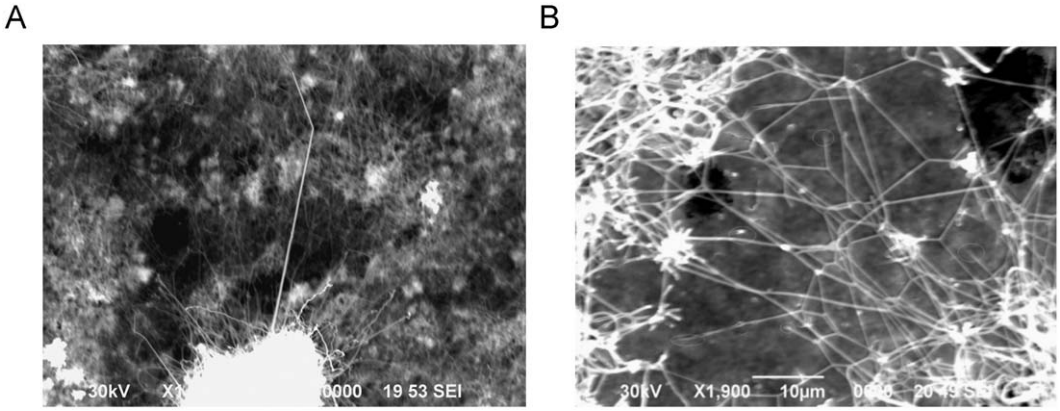

Fig. 3. Silicon nanowires network: (A) 1 h, 1200 °C and (B) 30 min, 1200 °C.

avoid local oxidation of the sample. The photoluminescence from the sample was very strong and easily visible to the eye. Fig. 7 shows the photoluminescence PL for the samples in the Fig. 4C. We can see from figure that there are very good photoluminescence in the visible range with two maximums, one peak at wavelength about 412 nm (or 3 eV) [23] and the other at wavelength about 438 nm (about 2.7 eV) [24]. These two peaks are too narrow and overlapping to give one strong peak with full width at half maximum FWHM of about 64 nm which is narrower than that of Lee et al. [25]. Our results are very close to that of Lee. However Lee said that when the SiNWs was annealed at 800 °C in air, the PL peak shifted to the red side; in our case the PL of the SiNWs was completely disappeared by annealing at 800 °C for 10 min in air, and it was very interesting when this PL was recovered by annealing in hydrogen at the same temperature and at the same time. The reason of the PL recovery after annealing in

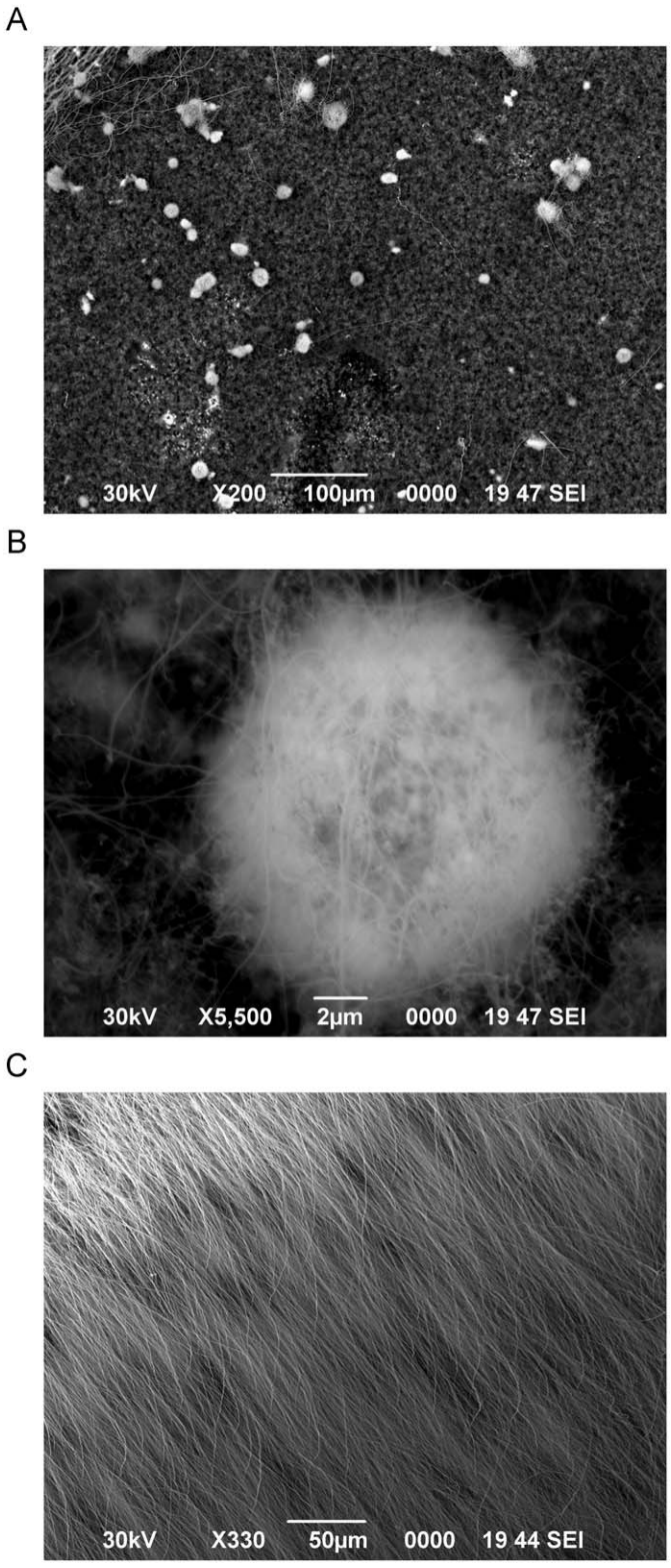

Fig. 4. (A) Formation of the microspheres (3 h, 1200 °C Si Ni C). (B) Magnification of A. (C) Just silicon 40 nm nickel as a catalyst.

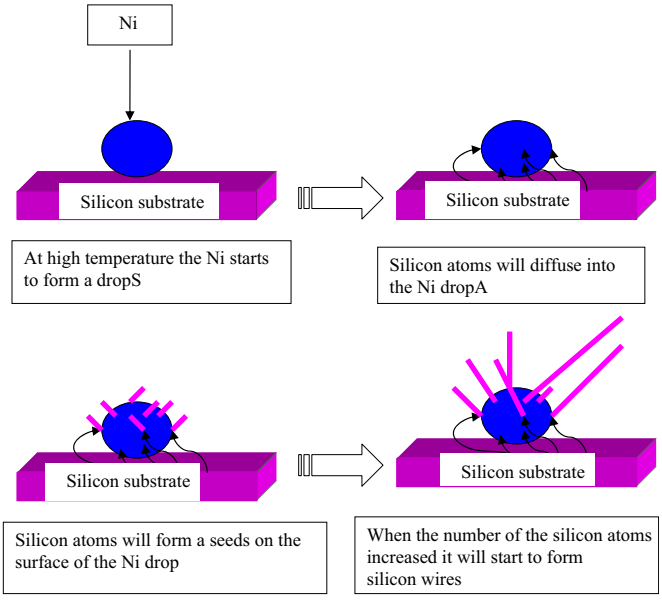

Fig. 5. Growth mechanism of the octopus-like silicon oxide nanowires.

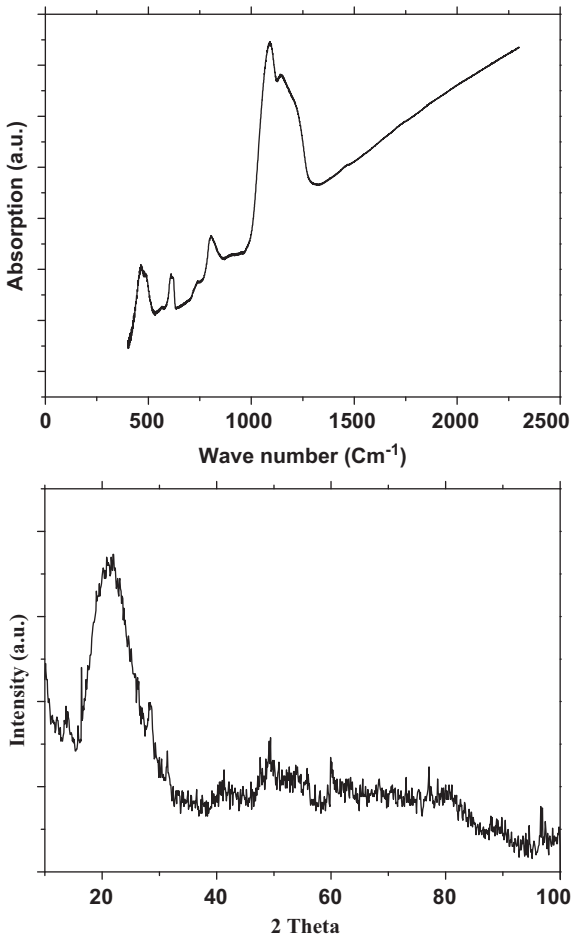

Fig. 6. FTIR spectrum and X-ray diffraction pattern for the sample on Fig. 4C.

hydrogen is under study at the present time. Recently similar peaks were observed by Duraia et al. for the amorphous carbon nanotubes grown on diatomite [26]. During the experiments we noticed that the intensity of this PL depends on the angle between the laser ray and the sample. The maximum PL was observed when the laser ray parallel to the surface of the sample and gradually decreased and reach the minimum value when the laser ray perpendicular to the sample. The photoluminescence of our samples was measured uniformly through 18 months, which indicates that the PL is stable.

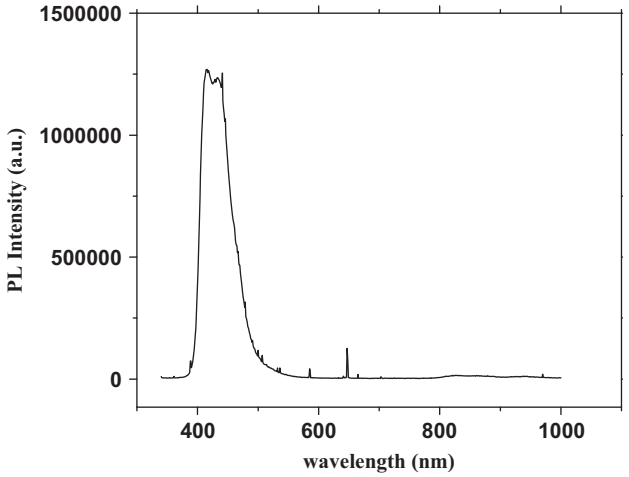

Fig. 7. Typical PL from the silicon oxide nanowires.

4. Conclusions

In summary, we successfully synthesized a large quantity of uniform, vertically and well aligned SiNWs on silicon wafers without any additional source of silicon at a temperature of 1200 °C. X-ray diffraction reveals that our silicon nanowires are amorphous and the energy-dispersive X-ray spectroscopy (EDS) analysis indicates that the nanowires have the composition of Si and O elements. The silicon substrate itself is considered to be used as a Si sources to produce SiNWs. We conclude that the growth mechanism is closely related to SLS growth model. Photoluminescence measurements indicated that there are two good emission peaks at 412 and 438 nm (about 3 and 2.7 eV, respectively). In the FTIR measurements there are many peaks at 463, 604, 795 and a wide peak at 1111 cm^{-1} and this can be attributed to Si–O–Si and Si–O stretching vibrations.

Acknowledgements

El-Shazly M. Duraia would like to acknowledge the Egyptian and Kazakhstan governments for the financial support. Prof. N. Besenkhanov and Prof. K. Chokin are acknowledged for giving an opportunity to make XRD and SEM-EDAX measurements.

References

[1] X.F. Duan, Y. Huang, Y. Cui, J.F. Wang, C.M. Lieber, Nature 409 (2001) 66.
[2] Y. Cui, C.M. Lieber, Science 291 (2001) 851.
[3] R.S. Wagner, in: A.P. Levitt (Ed.), Whisker Technology, Wiley, New York, 1970, pp. 47–119.
[4] R.S. Wagner, W.C. Ellis, Appl. Phys. Lett. 4 (1964) 89.
[5] J.D. Holmes, K.P. Johnston, R.C. Doty, B.A. Korgel, Science 287 (2000) 1871.
[6] Y.F. Zhang, Y.H. Tang, N. Wang, et al., Appl. Phys. Lett. 72 (1998) 1835.
[7] H.F. Yan, Y.J. Xing, Q.L. Hang, D.P. Yu, et al., Chem. Phys. Lett. 323 (2000) 224.
[8] X.C. Wu, W.H. Song, K.Y. Wang, T. Hu, et al., Chem. Phys. Lett. 336 (2001) 53.
[9] N. Wang, Y.H. Tang, Y.F. Zhang, et al., Chem. Phys. Lett. 299 (1999) 237.
[10] Z. Zhang, X.H. Fan, L. Xu, C.S. Lee, S.T. Lee, Chem. Phys. Lett. 337 (2001) 18.
[11] Z.W. Pan, S.S. Xie, B.H. Chang, et al., Nature 394 (1998) 631.
[12] P.D. Yang, C.M. Lieber, J. Mater. Res. 12 (1997) 298l.
[13] C.H. Liang, L.D. Zhang, G.W. Meng, et al., J. Non-Cryst. Solids 277 (2000) 63.
[14] Y.Q. Zhu, W.K. Hsu, M. Terrones, et al., J. Mater. Chem. 8 (1998) 1859.
[15] Z.W. Pan, Z.R. Dai, C. Ma, Z.L. Wang, J. Amer. Chem. Soc. 124 (2002) 1817.
[16] B. Zheng, Y. Wu, P. Yang, J. Liu, Adv. Mater. 14 (2002) 122.
[17] S. Botti, R. Ciardi, R. Larciprete, et al., Chem. Phys. Lett. 371 (2003) 394.
[18] X. Liang, L. Wang, X. Li, D. Yang, Thin Solid Films 515 (2007) 6707.
[19] E.M.A. Duraia, Z.A. Mansorov, S. Tokmolden, Phys. B Condensed Matter 404 (2009) 3952.
[20] J. Zhang, Y. Yang, S. Ding, J. Li, X. Wang, Mater. Sci. Eng. B 150 (2008) 180.
[21] K. Liu, et al., J. Non-Crystalline Solids 353 (2007) 1534.
[22] M. Shao, H. Hu, H. Ban, M. Li, H. Gao, J. Crystal Growth 303 (2007) 391.
[23] R. Tohmon, H. Mizuno, Y. Ohki, K. Sasagane, K. Nagasawa, Y. Hama, Phys. Rev. B 39 (1989) 1337.
[24] H. Nishikwa, T. Shiroyama, R. Nakamura, Y. Ohki, Phys. Rev. B 45 (1992) 586.
[25] K. Lee, C. Lofton, K. Kim, W. Seo, Y. Lee, M. Lee, et al., Solid State Communications 131 (2004) 687.
[26] E.M. Duraia, M. Burkitbaev, H. Mohamedbakr, Z. Mansurov, S. Tokmolden, G.W. Beall, Vacuum 84 (2009) 464.