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silicon nanowires by light**

Journal:	<i>Journal of Materials Chemistry C</i>
Manuscript ID:	TC-ART-07-2014-001431.R2
Article Type:	Paper
Date Submitted by the Author:	24-Sep-2014
Complete List of Authors:	liu, lin; North China Electric Power University,

Cite this: DOI: 10.1039/c0xx00000x

ARTICLE TYPE

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Regulation on the morphology and photoluminescence in silicon nanowires by light

Lin Liu^{a,b}*Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX*

DOI: 10.1039/b000000x

In this article, we synthesize porous silicon nanowires arrays with excellent photoluminescence properties successfully. It is found that light not only promotes the formation of silicon nanowires array, but also enhances its porosity. The porous silicon nanowire arrays illustrate excellent photoluminescence properties, silicon nanowire arrays on moderate-doped substrate display luminescence intensity increase by 11 times than that prepared in black on the same substrate, while high-doped substrate increase by 1.8 times than that prepared in black on the same substrate; moreover, the PL properties of as-prepared silicon nanowire arrays are stable. We suggest that the porous SiNWs have potential applications in gas sensors, photocatalysis, and solar cells.

Introduction

Silicon nanowires (SiNWs) have been attracting considerable attention over the past decade, partly due to their potential applications in modern industry. Up to now, silicon nanowires have been extensively investigated for transistors^{1,2}, sensors³, photovoltaic⁴⁻⁶, thermoelectric^{7,8}, and battery electrodes⁹. They exhibit superior electrical, optical, and thermal properties. SiNWs are expected to play a key role in technological applications in the future. Porous silicon (PS) is famous for their ability in emitting light in the visible range¹⁰. The luminescent property promotes silicon to an interesting material for photonic applications. The disordered web of pores on the PS could also permeate a variety of substances and support specific reactions. In the structure, quantum effects play a fundamental role. In the recent years, porous silicon nanowires which integrate the above two characteristics are proposed¹¹⁻¹³. It may open new opportunities for silicon as its potential applications in gas sensors, photocatalysis, and solar cells.

SiNWs synthesized by metal catalyzed electroless etching (MCEE) has attracted much attention in the recent years¹⁴. It is a simple and cost-effective technique. The MCEE process of silicon is a microscopic galvanic corrosion in nature, silicon beneath noble metal particles is etched away in aqueous HF solution containing oxidizing agents such as hydrogen peroxide or oxygen¹⁵. To understand the mechanism deeply, it is very important to know how the movement direction of electron and hole in the vicinity of metals. It is well known that silicon under light-irradiated will alter its properties and light may induce some wizardly phenomenon on silicon, however, the influence of light on SiNWs made by MCEE has never been reported yet.

In this paper, we achieve regulation of morphology and photoluminescence in silicon nanowires by light. We present a simple and economical method of fabricating porous SiNWs. We not only synthesize porous SiNWs by the method of MCEE, but also investigate the effect of light on the formation of SiNWs. The comparative morphologies of the SiNWs are present, and the etching mechanism is discussed. The effect of light is investigated with different parameters, including the doping concentration of the wafer, etching time and different power. The photoluminescence (PL) properties are also carried out on the porous SiNWs. Various analyses are carried out to reveal the possible origin of PL intensity enhancement.

^a Key Laboratory of Condition Monitoring and Control for Power Plant Equipment of Ministry of Education, North China Electric Power University, Beijing 102206, China

^b Beijing Key Laboratory of Energy Conversion and Storage Materials
Beijing Normal University, 100875 Beijing, P.R. China
Electronic mail: liulin2014@ncepu.edu.cn

Results and discussion

SEM and TEM images of the prepared SiNWs are summarized for 2h in Fig.1 and Fig.2. Samples made from moderate-doped are named as A (without light-irradiated) and B (with light-irradiated), high-doped are named as C (without light-irradiated) and D (with light-irradiated) respectively. From TEM results, we can observe that samples with light-irradiated had stronger porosity in the wires than those without regardless of the doping concentration. Length of sample A is about 20 μm , that of B is about 22 μm . We consider light promotes the formation of SiNWs array. Length of sample C is about 17 μm , however, that of D is about 10 μm . The average diameter of the SiNWs on moderate-doped substrates is about 180nm whether light-irradiated or not. But the change on high-doped substrates is apparent, the average diameter of SiNWs without light-irradiated is about 160nm, that is 80nm with light-irradiated, there are rather thin SiNWs as shown in Fig.2(d). The reasons will be explained in the following.

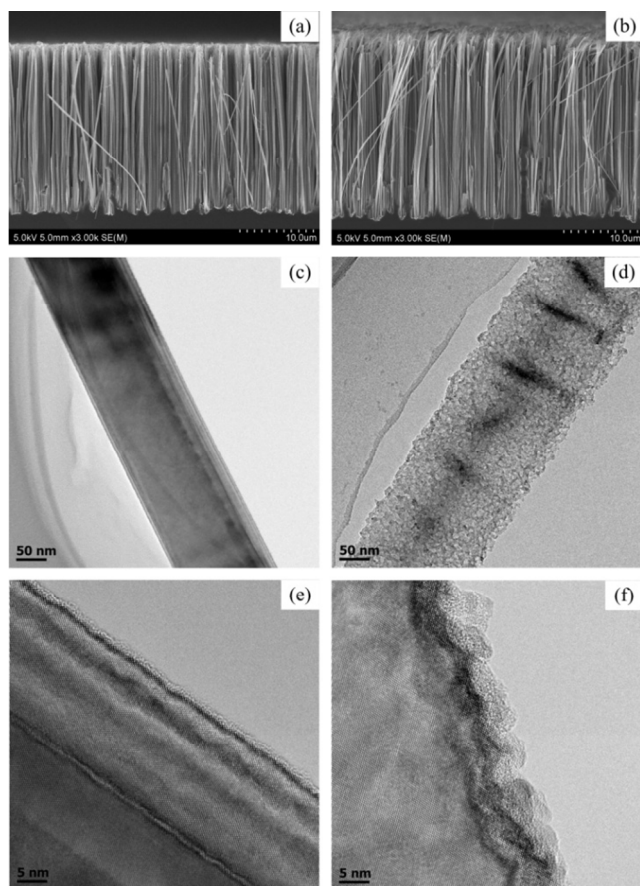


Fig.1 SEM and TEM images show the silicon nanowire morphology from substrates with 2-2.7 $\Omega\text{-cm}$ resistivity. (a, b) Cross-sectional SEM image of SiNWs for sample A and B respectively (c, d) Low-resolution TEM image of SiNWs for sample A and B respectively (e, f) High-resolution TEM image of SiNWs for sample A and B respectively.

Firstly, we discuss the effect of light on the morphology of silicon nanowires. A schematic diagram for porosity effect of light is given in Fig.3. The energy-band diagrams for n-type silicon with and without light-irradiated in HF/H₂O₂ are compared¹⁶⁻¹⁷. In our system, the formation of PS and SiNWs by MCEE happens simultaneously. Charge separation of the photo-

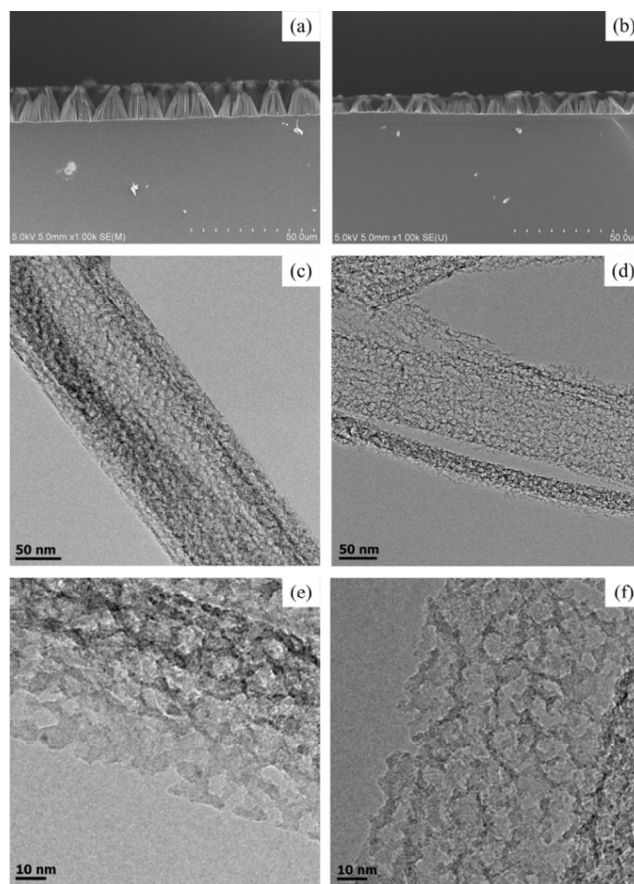


Fig.2 SEM and TEM images show the silicon nanowire morphology from substrates with 0.001-0.004 $\Omega\text{-cm}$ resistivity. (a, b) Cross-sectional SEM image of SiNWs for sample C and D respectively (c, d) Low-resolution TEM image of SiNWs for sample C and D respectively (e, f) High-resolution TEM image of SiNWs for sample C and D respectively.

generated electron-hole pairs happens due to the depletion region. Holes obtained with light-irradiated transport to the surface, and take part in the oxidation reaction with surface atoms. Electrons generated drift to the back side. The oxidation product will be decomposed. The reactions can be expressed as follows: (1) Cathode $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$, (2) Anode $\text{Si} + 4\text{h}^+ + 6\text{HF} = \text{SiF}_6^{2-} + 6\text{H}^+$. The peak of SiNWs is more easily dissolved than the root because of the depletion region. The regions where oxidation and dissolution happen are so random that the porous in SiNWs are also inhomogeneous. As the porosity is enhanced by light, the size of silicon crystallites on SiNWs becomes smaller while its number will increase.

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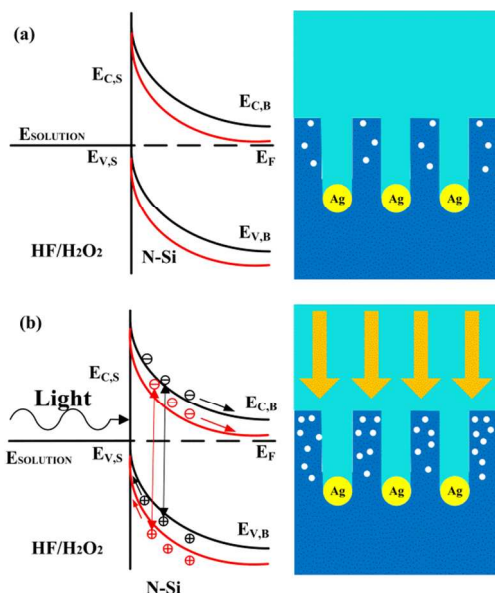


Fig.3 Energy-band diagrams for n-Si immersed in HF/H₂O₂ solution without light-irradiated (a) and with light-irradiated (b). Black bending lines represent the energy-band bends of n-type moderate-doped substrates. Red bending lines represent the energy-band bends of n-type high-doped substrates.

Light also has the promoted effect for MCEE SiNWs. Part of the electron-hole pairs generated by light will recombine in body, the electron-hole pairs near the interface will separate due to interface effect. Now we focus on the electron-hole pairs near the metal. As shown in Fig.4, the experimental conditions are the same as that in Fig. 1(b) except no hydrogen peroxide in etchant. As the silver metal has stronger electronegative^{14,18}, it will attract the surrounding electrons generated by light and transfer them to the solution for reacting with the oxidant outside. Such leaving holes around the silver metal will increase the valence of silicon, which will promote the dissolution of silicon under the metal. This effect will appear whatever the doping concentration of the substrate is. In our previous work, we have confirmed that light irradiation is an alternative means to speed up silicon nanowires etching when using macroscopic galvanic system¹⁵, and it is also confirmed in this system.

From SEM results, we find that the length and diameter of the SiNWs prepared with light-irradiated is shorter than that prepared in dark when using high-doped substrate. It means that more quality of the SiNWs is dissolved by light. There may be two main factors¹⁹: the narrower depletion region (as shown in Fig.3)

and the smaller silicon crystallites. Due to the narrower depletion region, the dissolution of the SiNWs by light is much more likely to happen on high-doped substrate. The smaller silicon crystallites on the SiNWs could be obtained when using higher-doped substrate¹³. The shorten length and diameter of SiNWs on high-doped substrate could be explained as the dissolved effect of SiNWs by light is stronger than its enhanced effect.

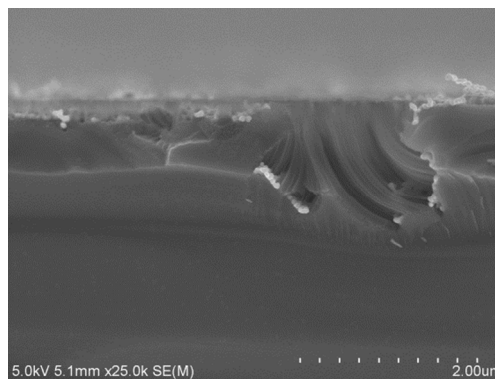


Fig.4 SEM image show the silicon morphology from substrates with 2-2.7Ω·cm resistivity with light-irradiated but without hydrogen peroxide in the etchant.

For a better quantitative interpretation of the light effects, the mass loss rate of the silicon substrate is measured in our experiment. m_1 represents the mass of silicon with silver film before etching, m_2 represents the mass of silicon with silver film after etching, ε represents the mass loss rate of the silicon substrate. We define ε as Eq.1. The measurements and calculated results are show in Table I. It is found that ε has a higher value when with light-irradiated than that without light-irradiated. It indicates that light assisted etching dissolved much more mass of silicon from quantitative point.

$$\varepsilon = \frac{m_1 - m_2}{m_1} \times 100\% \quad (1)$$

Fig.5 displays the PL spectrums taken from the as-prepared SiNWs arrays. It could be clearly observed that SiNWs arrays exhibited a broad emission peak in red-color region at room temperature, and it is consistent with the previous reports^{11,12}. The relative value of PL intensity peek of sample B is about 117.6, while that of sample A is about 9.8, so PL intensity increased by 11 times with light-irradiated, and PL wavelengths of sample A and B are both centered at about 650nm. The relative value of PL intensity peek of sample D is about 394.2,

while that of sample C is about 141.5, so PL intensity increases by 1.8 times with light-irradiated. The PL intensity of the samples with light-irradiated increases apparently compared with those without light-irradiated. Compared to sample C, we also find that the blue-shift of the PL spectrum on sample D. These differences are due to the change of the number and size of silicon crystallites and the diameter of SiNWs, which are caused by light.

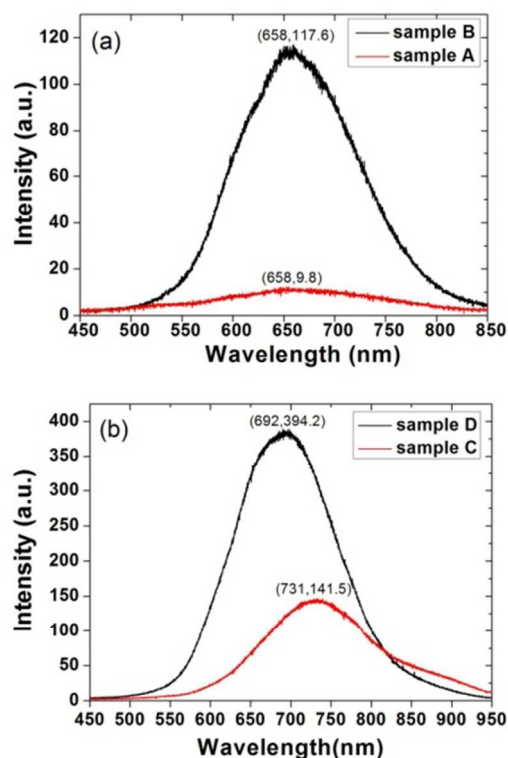


Fig.5 Photoluminescence spectrums of silicon nanowires. (a) Substrates with 2-2.7 Ω -cm for sample A (without light-irradiated) and sample B (with light-irradiated) (b) Substrates with 0.001-0.004 Ω -cm for sample C (without light-irradiated) and sample D (with light-irradiated).

To illustrate the effect of light-irradiation for the PL enhancement deeply, we use tungsten lamps with three different powers conducting the experiment. The results are shown in Fig.6. The luminosity near the wafers is about 220lx, 120lx, 40lx respectively. According to the results, the PL intensity is stronger than that without light-irradiation. We could also find that the PL intensity is enhanced with the increase of the light energy.

Si, an indirect bandgap that makes it a poor light emitter, Canham is the first researcher to report PL from porous silicon¹⁰. Various mechanisms are proposed to explore the luminescence origins of PS and SiNCs. In our system, the size and number of silicon crystallites and the diameter of SiNWs change very remarkably.

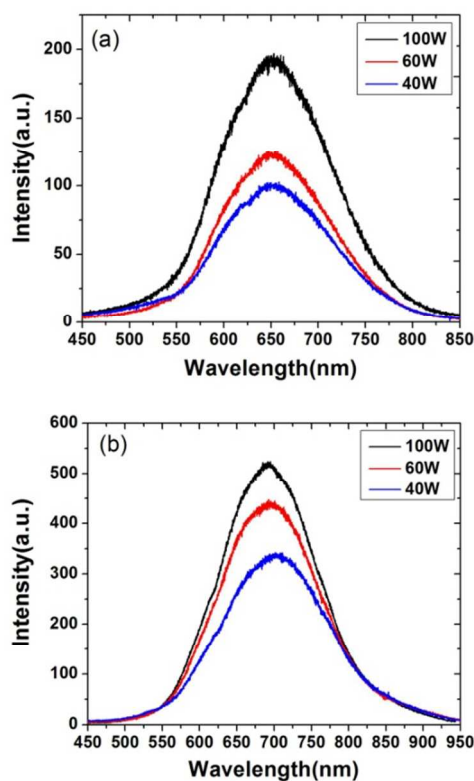


Fig.6 Photoluminescence spectrums of silicon nanowires. (a) Substrates with 2-2.7 Ω -cm for samples (b) Substrates with 0.001-0.004 Ω -cm for samples using different lamp powers.

According to the quantum confinement model¹⁰, if the size of silicon decreases enough, the bandgap will increase and conservation of momentum will break down, consequently, silicon will have emission properties and will behave as a semiconductor with a quasi-direct bandgap. So the smaller size of silicon in our experiments may become a semiconductor with a quasi-direct bandgap. Once this structure absorbs light with a wavelength shorter than the emission wavelength, electrons in the conduction band can annihilate holes in the valence band directly, and then PL can be observed. The enhanced PL intensity is caused by the increased number of the illuminated silicon. The reason for the blue-shift of the PL spectrum in Fig.6 (b) is: the size of silicon crystallites and SiNWs decreases and the bandgap will increase, so the optical emissions should move to higher energies. The bandgap become much narrower in heavily doped silicon than that in moderately one, which has been proved²⁰, therefore, the PL peak energy of sample B is larger than that of sample D.

Except for the quantum confinement model, bond structure on the surface of porous silicon is also a key influencing factor^{21,22}. To investigate the relationship between the enhanced PL intensity

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and bond structure on the surface of SiNWs arrays, FTIR measurements have been performed. The results are present in Fig. 7. It is clearly seen that the intensity of absorption bands at about 1070 cm^{-1} , which are attributed to Si–O–Si bonds. At the same time, the absorption bands at about 882 cm^{-1} , standing for Si–H bonds. The above two are similar in the spectrums using the same wafers. Therefore, it can be concluded that the improved PL intensity is not related to Si–H or Si–O–Si surface bonds. The enhanced PL intensity is due to the increased number of the illuminated silicon on SiNWs, which is manifested as enhanced porosity.

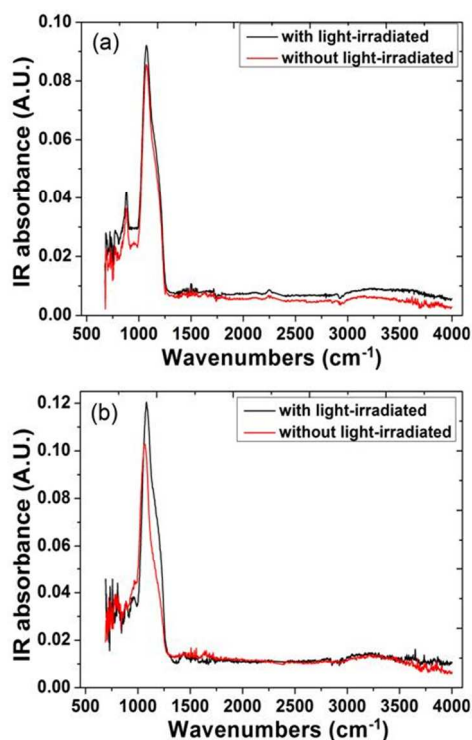


Fig.7 FTIR spectrums of the samples on moderately doped substrate (a) and on high-doped substrate (b).

The problems of low intensity²³ and degradation²¹ of the PL restrict the development of Si-based light-emitting devices. The relationship between PL intensity and etching time (in the range 0.5 to 4 hours) for different substrates is also analyzed, as is shown in Table II. Compared to those without light-irradiated, PL intensity of those with light-irradiated are enhanced dramatically. It is clearly seen that intensity is enhanced along with time prolonged. Long time light-irradiated and prolonged bathing time in HF/H₂O₂ all increase number of illuminated silicon on SiNWs.

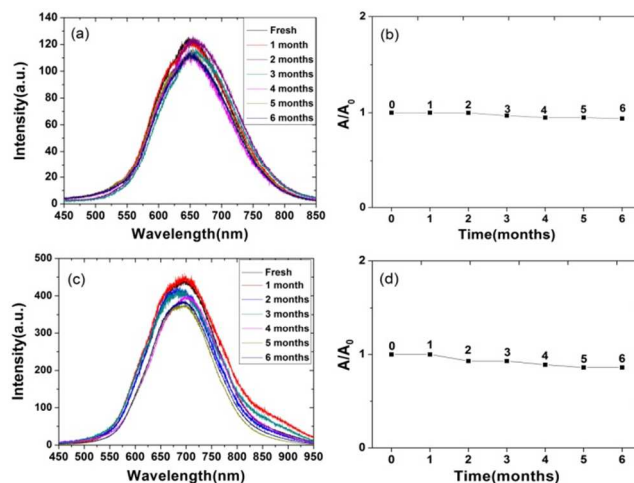


Fig.8 PL spectrums from prepared SiNWs array following storage in air for every month interval. Figureures represent the number of storage time (month). (a, b) moderate-doped samples. (c, d) high-doped samples. The evolution of the PL peak intensity ratio A/A_0 (the PL intensity for the storage sample to that for the freshly prepared sample) with storage time.

Stability of PL in SiNWs is investigated in our experiment. As shown in Fig.8, the intensity and wavelength change in tiny range. The moderate-doped sample showed its especial phenomenon in Fig.8 (a, b), the intensity almost doesn't degrade with time and the peak position remains unchanged. For high-doped substrate, there are much more defects in itself than moderate one. The unstable of PL in silicon has been investigated for several years; the most acceptable reason is the instability of surface conditions²⁴⁻²⁶. Many methods, such as thermal oxidation and treated by N or C for surface passivation were conducted for realizing its stability²⁴⁻²⁶. It has been proved that Ag plays an important role in the photoluminescence. The stable surface is formed²¹ during the movement of the silver; hence excellent stability of PL properties in silicon is achieved.

Conclusions

In conclusion, light in MCEE promotes the formation of silicon nanowires array and enhances its porosity. The porous silicon nanowires arrays we obtained show excellent PL properties. This silicon-based luminescent material is at its potential application in developing photoelectronic integration. As this kind of silicon nanowires has large specific surface area and apparent quantum confinement effect, therefore, it may be useful for application as sensors, solar cells or photocatalytic substrates.

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Table I Mass loss rate of the silicon substrate

Wafer Type	Experimental conditions	$m_1(\text{g})$	$m_2(\text{g})$	ϵ
N(100) 2.0~2.7 $\Omega\cdot\text{cm}$	without light	0.2366	0.2262	4.39%
	with light	0.2360	0.2215	6.14%
N(100) 0.001~0.004 $\Omega\cdot\text{cm}$	without light	0.2413	0.2282	5.42%
	with light	0.2420	0.2214	8.51%

Table II The relationship between PL intensity and etching time

Wafer Type		Etching time (h)							
		0.5	1	1.5	2	2.5	3	3.5	4
N(100) 2.0~2.7 $\Omega\cdot\text{cm}$	without light	3.2	6.3	6.9	9.8	14.6	19.5	26.2	35.1
	with light	10.1	20.2	52.4	117.6	142.8	169.6	184.8	195.2
	Growth rate	2.1	2.2	6.6	11	8.7	7.7	6.1	4.6
N(100) 0.001~0.004 $\Omega\cdot\text{cm}$	without light	9.6	49.3	63.5	141.5	210.4	300.6	420.1	560.7
	with light	120.2	150.6	330.7	394.2	520.2	730.4	899.6	1050.5
	Growth rate	11.5	2	4.2	1.8	1.4	1.4	1.1	0.8

Sample and experimental set-up

In our experiments, (100) oriented n-type single crystal Si wafers with resistivity of 2-2.7 $\Omega\cdot\text{cm}$ and 0.001-0.004 $\Omega\cdot\text{cm}$ were used as the starting materials. The experimental process was as follows: 1) cleaning the wafers with acetone, ethanol and deionized water via ultrasonic cleaning in turn and immersed into the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (3:1) boiling solution for 15 minutes, then dipping the wafers into 5% HF aqueous solution for tens of seconds; 2) placing the clean wafers into the solution contains 10% hydrofluoric acid (HF) and 0.02M AgNO_3 for 1 minutes to form a Ag nanoparticles film; 3) immediately throwing the prepared silicon wafers with Ag nanoparticles film into the etchant contains 10% HF and 0.6% H_2O_2 solution for chemical etching at room temperature. A Tungsten lamp with 60W was employed, and it was placed one meter above the wafer. After chemical etching, the surface fashioned silicon was rinsed with deionized water for several times in order to wash up fluorine (F) ions, afterwards it was dried in the dark.

Surface morphologies and microstructures of the as-prepared SiNWs were examined by field emission scanning electron microscopy (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100), the reflectance spectrums were measured by the UV-VIS system with integrating sphere (SPECORD 200). Bond structure was investigated using a

Nicolet Nexus 670 Fourier transform infrared (FTIR) spectrometer, PL spectrums and imagings were recorded by using confocal laser raman spectrometer (Horiba Jobin Yvon-LabRAM Aramis) with a He-Cd laser of wavelength of 325 nm as an excitation source at room temperature.

Acknowledgment This research was supported by National Basic Research Program of China (2012CB932400) and China Postdoctoral Science Foundation (2014M560934).

Notes and references

- 1 Y. Cui and C.M. Lieber, *Science*, 2001, 291, 851-853.
- 2 E. Stern, J.F. Klemic, R.A. Routenberg, P.N. Wyrembak, D.N.B. Turner-Evans, A.D. Hamilton, D.A. LaVan, T.M. Fahmy and M.A. Reed, *Nature*, 2007, 445, 519-522.
- 3 G.F. Zheng, F. Patolsky, Y. Cui, W.U. Wang and C.M. Lieber, *Nat. Biotech.*, 2005, 23, 1294-1301.
- 4 B.Z. Tian, X.L. Zheng, T.J. Kempa, Y. Fang, N.F. Yu, G.H. Yu, J.L. Huang and C.M. Lieber, *Nature*, 2007, 449, 885-888.
- 5 E.C. Garnett and P.D. Yang, *J. Am. Chem. Soc.*, 2008, 130, 9224-9225.
- 6 M.D. Kelzenberg, S.W. Boettcher, J.A. Petykiewicz, D.B. Turner-Evans, M.C. Putnam, E.L. Warren, J.M. Spurgeon, R.M. Briggs, N.S. Lewis and H.A. Atwater, *Nat. Mater.*, 2010, 9, 239-244.
- 7 A.I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J.K. Yu, W.A. Goddard and J.R. Heath, *Nature*, 2008, 451, 168-171.
- 8 A.I. Hochbaum, R. Chen, R.D. Delgado, W. Liang, E.C. Garnett, M. Najarian, A. Majumdar and P. Yang, *Nature*, 2008, 451, 163-167.
- 9 C.K. Chan, H.L. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R.A. Huggins and Y. Cui, *Nat. Nanotechnol.*, 2008, 3, 31-35.
- 10 L.T. Canham, *Appl. Phys. Lett.*, 1990, 5, 1046-1048.
- 11 A.I. Hochbaum, D. Gargas, Y.J. Hwang and P.D. Yang, *Nano. Lett.*, 2009, 9, 3550-3554.
- 12 Y.Q. Qu, L. Liao, Y.J. Li, H. Zhang, Y. Huang and X.F. Duan, *Nano. Lett.*, 2009, 9, 4539.
- 13 L. Gan, L.W. Sun, H.P. He and Z.Z. Ye, *J. Mater. Chem. C*, 2011, 3, 4060-4068.

-
- 14 K.Q.Peng, Y.Wu, H.Fang, X.Y.Zhong, Y.Xu and J.Zhu,
Angew.Chem.Int.Ed., 2005, 44, 2737-2742.
- 15 L.Liu, K.Q.Peng, Y.Hu, X.L.Wu and S.T.Lee, Adv. Mater., 2014, 26,
1410-1413.
- 5 16 N.Noguchi and I.Suemune, Appl. Phys. Lett., 1993, 62, 1429-1431.
- 17 S.Tomioka, T.Miyazaki and S.Adachi, Jpn. J. Appl. Phys., 2007, 46,
5021-5024.
- 18 J.S.Jie, W.J.Zhang, K.Q.Peng, G.D.Yuan, C.S.Lee and S.T.Lee, Adv.
Funct. Mater., 2008, 18, 1-7.
- 10 19 W.K.To, C.H.Tsang, H.H.Li and Z.F.Huang, Nano. Lett., 2014, 2,
2668-2673.
- 20 J. Wagner and J.A.Alamo, J. Appl. Phys., 1988, 63, 425-429.
- 21 M.A.Tischler, R.T.Collins, J.H.Stathis and J.C.Tsang, Appl. Phys.
Lett., 1992, 60, 639-641.
- 15 22 J.Y.Sun, W.L and X.W.Du, Appl. Phys. Lett., 2005, 86, 171509.
- 23 H.Koyama, T.Nakagawa, T.Ozaki and N.Koshida, Appl. Phys. Lett.,
1994, 65, 1656-1658.
- 24 V.Petrova-Koch, T.Muschik, A.Kux, B.K.Meyer, F.Koch and
Lehmann.V. Appl. Phys. Lett., 1992, 61, 943-945.
- 20 25 R.Boukherroub, D.D.M.Wayner, G.I.Sproule, D.J.Lockwood and
L.T.Canham. Nano. Lett., 2001, 1, 713-717.
- 26 X.J.Li, D.L.Zhu, Q.W.Chen and Y.H.Zhang, Appl. Phys. Lett., 1999,
74, 389-391.