



One-step synthesis of lightly doped porous silicon nanowires in HF/AgNO₃/H₂O₂ solution at room temperature

Fan Bai^{a,b}, Meicheng Li^{b,c,*}, Dandan Song^b, Hang Yu^b, Bing Jiang^b, Yingfeng Li^b

^a School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 165001, China

^b State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University, Beijing 102206, China

^c Su Zhou Institute, North China Electric Power University, Suzhou 215123, China

ARTICLE INFO

Article history:

Received 11 May 2012

Received in revised form

11 July 2012

Accepted 13 July 2012

Available online 24 July 2012

Keywords:

Porous silicon nanowires

Lightly doped

Room temperature

One-step synthesis

Silver nanoparticles

ABSTRACT

One-step synthesis of lightly doped porous silicon nanowire arrays was achieved by etching the silicon wafer in HF/AgNO₃/H₂O₂ solution at room temperature. The lightly doped porous silicon nanowires (pNWs) have circular nanopores on the sidewall, which can emit strong green fluorescence. The surface morphologies of these nanowires could be controlled by simply adjusting the concentration of H₂O₂, which influences the distribution of silver nanoparticles (Ag NPs) along the nanowire axis. A mechanism based on Ag NPs-induced lateral etching of nanowires was proposed to explain the formation of pNWs. The controllable and widely applicable synthesis of pNWs will open their potential application to nanoscale photoluminescence devices.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

Silicon based nanostructures have attracted wide attentions due to their potential applications in photovoltaic, lithium battery, biomedicine, and optoelectronic devices [1–5]. Porous silicon and silicon nanowires have been particularly concerned and studied over the past decades because of their outstanding properties of antireflection and photoluminescence, respectively [6–12]. To combine these advantages, a novel composite nanostructure, porous silicon nanowires (pNWs), was proposed and has been applied in the fields of photocatalysts, gas-sensor, and Li-ion batteries in recent several years [13–18]. Generally, pNWs are fabricated by the metal-assisted chemical etching method, which mainly contains two procedures, i.e. the deposition of metal nanoparticles (NPs) or film on silicon substrate and the etching of silicon catalyzed by metal NPs in the etchant typically containing HF and H₂O₂ [19]. However, the controllable deposition of metal NPs on the starting silicon wafer makes this method complicated, and further hampers the massive application. Hence, a simplified method enabling simultaneous deposition of metal NPs and etching of silicon was proposed by dissolving AgNO₃ into HF etchant solution, and the highly doped pNWs with pores

approximately 10 nm in diameter were obtained [13]. Although this method was simple, it commonly has a significant drawback, i.e. the starting silicon wafer for fabricating pNWs can only be highly doped silicon wafer rather than lightly doped silicon wafer [13,20].

In this work, we report the one-step synthesis process of pNWs at room temperature, which is applicable even in the case of lightly doped silicon wafer. The H₂O₂ oxidant was introduced into the HF/AgNO₃ solution at an appropriate proportion, and lightly doped pNWs with a pore diameter around ~5 nm were obtained, which exhibited green fluorescence emission. Furthermore, the role of H₂O₂ on the formation of pNWs was analyzed and a novel mechanism based on Ag NPs-induced lateral etching of silicon nanowires (SiNWs) was proposed.

2. Experimental

Single-mirrored polished p-type Si(100) wafers (the resistivity of 7–13 Ω cm) were cut into 1 cm × 1 cm pieces and used for the experiment. The Si samples were cleaned using acetone, absolute ethyl alcohol and deionized water in the ultrasonic condition. And then the Si samples were dipped into dilute HF solution to remove native oxide. Following cleaning step, the Si samples were immediately placed into the etching solution. Here, the etching solution contained 4.6 M HF, 0.02 M AgNO₃, and H₂O₂ with variable concentrations (0, 0.005, and 0.05 M). After the etching process, the Si samples were rinsed with deionized water and then

* Corresponding author at: State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University, Beijing 102206, China. Fax: +86 10 86172951.

E-mail address: mcli@ncepu.edu.cn (M. Li).

immersed into concentrated HNO_3 to remove retaining silver. All treatments were performed in the dark at room temperature.

Surface morphologies of Si samples were observed by scanning electron microscope (SEM) with FEI Quanta 200F and transmission electron microscope (TEM) with Tecnai G² F20. The images of high resolution TEM (HRTEM), scanning transmission electron microscope (STEM) and selected area electron diffraction (SAED) were obtained on Tecnai G² F20 with an operation voltage of 200 kV. The luminescent property of the lightly doped pNWs was measured by confocal fluorescence microscope with Leica TCS SP5.

3. Results and discussion

Vertical lightly doped porous silicon nanowire arrays were obtained through one-step synthesis process with an appropriate H_2O_2 concentration (0.05 M) for 45 min at room temperature. The silicon nanowire arrays with a thickness of $\sim 20\ \mu\text{m}$ uniformly cover the silicon substrate, as shown in Fig. 1A. These nanowires are provided with the bundle-like structure obviously caused by Van der Waals force between the nanowires. From TEM image of the individual nanowire in Fig. 1B, it can be seen that dense and homogeneous pores distribute on the sidewalls of the nanowire. The corresponding HRTEM image (Fig. 1C) reveals that these pores are in circular-like shape with a mean diameter of 5 nm approximately, and the scale of remaining silicon scaffold is about 2 nm. Furthermore, selected areas SAED patterns (the inset in Fig. 1C) indicate the single-crystalline nature of pNWs, which is in consistent with the starting silicon wafer, suggesting that the integrity and continuity of the silicon lattice has not been destroyed in the etching process.

The luminescent property of the lightly doped pNWs has also been studied. To ensure photoluminescence (PL) from porous

nanowires, the pNWs were scratched from silicon substrate and the individual nanowire was measured; the result was shown in Fig. 2A. The lightly doped pNWs can emit strong green fluorescence under the excitation of 488 nm light, and a weak yellow fluorescence under the excitation of 514 nm wavelength light. As the average diameter of these nanowires is larger than the threshold value of the quantum confinement effect [21], the PL emission is considered to originate from the dense nanopores. In addition, the color of PL emission can also vary for different pNWs, for example, the highly doped pNWs can emit red fluorescence under the irradiation of 442 nm wavelength light, as shown in Fig. 2B [13]. The color differences are derived from several factors including the doping concentration of starting Si wafer, the pore density and the dangling bonds at the surface of pNWs [22].

The lightly doped pNWs are firstly obtained through chemical etching in $\text{HF}/\text{AgNO}_3/\text{H}_2\text{O}_2$ solution. As we know, the lightly doped pNWs are difficult to be produced through chemical etching in HF/AgNO_3 solution [13,23]. So the formation of pNWs here must have a certain relation with the presence of H_2O_2 .

Hence, the effect of H_2O_2 concentration in the etchant on the formation of pNWs was investigated. Vertically aligned silicon nanowire arrays were obtained in the condition of any H_2O_2 concentration used here, as shown in Fig. 3A and D. However, the surface morphologies of these nanowires were quite different. Without H_2O_2 , silicon crystalline nanograins (as proposed in the literature [21]) can be observed on the sidewalls of nanowires (Fig. 3B), the high resolution TEM image (Fig. 3C) of individual nanowire indicates that the nanowire surface is relatively smooth. In the case of low H_2O_2 concentration (e.g. 0.005 M), the nanowire surface is significantly rough, but no pores appear, as shown in Fig. 3E and F. When the H_2O_2 concentration reaches 0.05 M, the formation of pNWs can be achieved as given in Fig. 1. While the H_2O_2 concentration is further increased up to 0.5 M, porous structure has also been observed at the sidewalls of rare

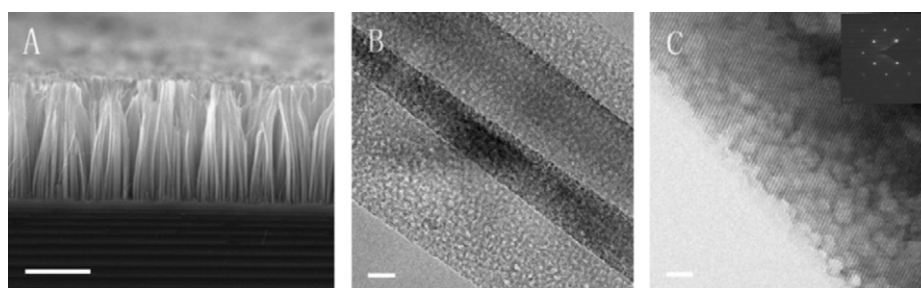


Fig. 1. SEM, TEM and HRTEM images with SAED patterns of pNWs. (A) SEM image of pNW arrays. (B) TEM image of individual nanowire. (C) HRTEM image corresponding to (B). The inset in (C) shows a selective areas SAED patterns of individual nanowire. The scale bars of SEM, TEM and HRTEM are 10 μm , 20 nm, and 10 nm, respectively.

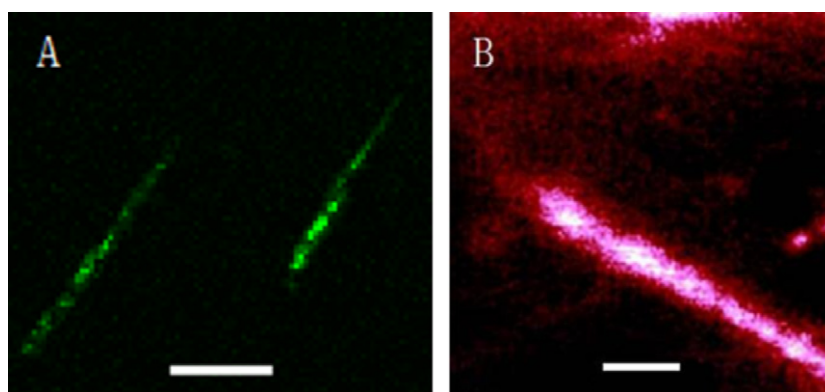


Fig. 2. The photoluminescence images of individual pNWs obtained from different doping level of the starting p-type silicon wafer. (A) Lightly doped pNWs. (B) Highly doped pNWs [13]. Scale bars are 1 μm and 2 μm , respectively.

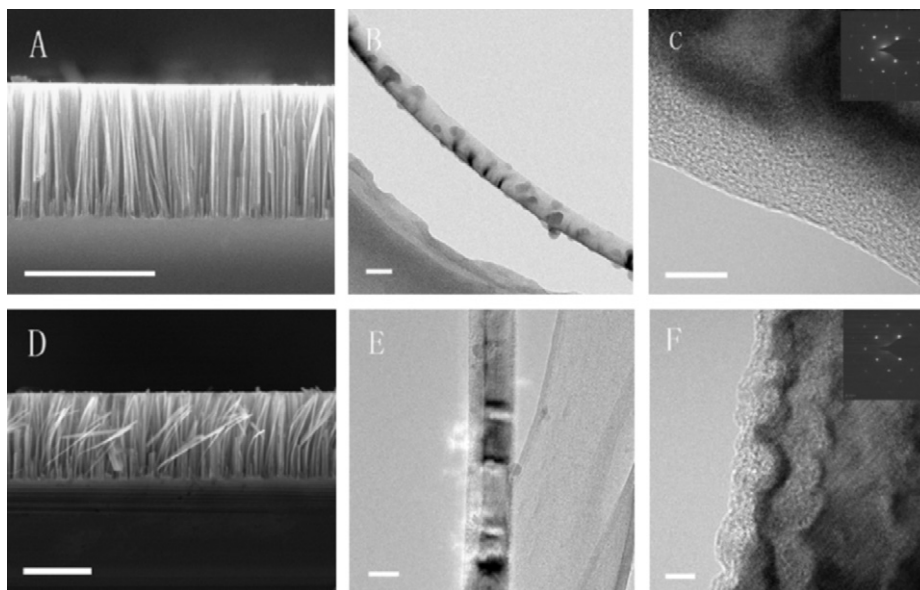


Fig. 3. SEM, TEM and HRTEM images of SiNWs etched using p-type Si(100) with 7–13 Ω cm resistivity in a solution containing 4.6 M HF, 0.02 M AgNO_3 and different concentrations of H_2O_2 for 45 min. (A–C) adding 0 M H_2O_2 . (D–F) adding 0.005 M H_2O_2 . The scale bars of SEM, TEM and HRTEM are 10 μm , 50 nm and 10 nm, respectively.

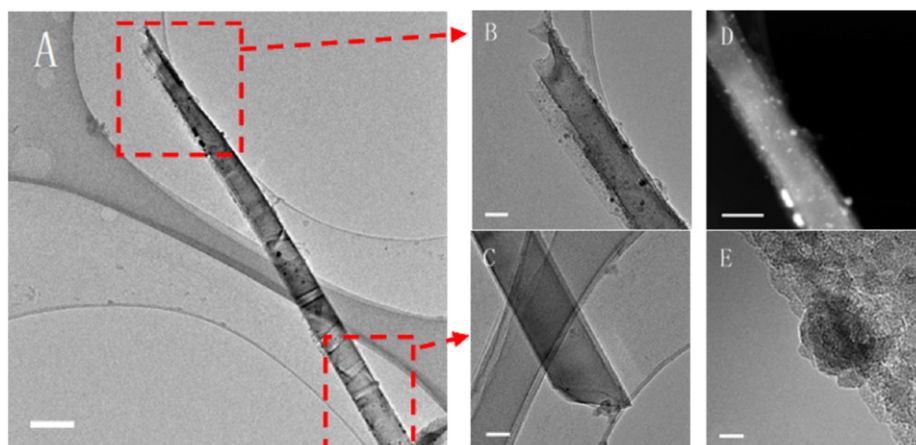


Fig. 4. Surface morphology of individual nanowire without HNO_3 treatment. (A) TEM image of individual nanowire. (B) The high magnification TEM image at the top site of this nanowire. (C) The high magnification TEM image at the root site of this nanowire. (D) STEM image of this nanowire corresponding to (B). (E) HRTEM image of individual Ag nanoparticle on the sidewall of this nanowire. The scale bars of TEM, the high magnification TEM, STEM, and HRTEM are 0.2 μm and 50 nm, 100 nm, and 5 nm, respectively.

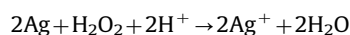
nanowires, but a quite large number of Si NWs were destroyed due to the excess etching.

The above results demonstrate that the presence of H_2O_2 significantly affects the surface morphologies of nanowires and the concentration of H_2O_2 has a certain range for the formation of pNWs. However, it is well known that H_2O_2 itself is not able to etch silicon [14]. Thus, the effects of H_2O_2 should be mediated by other factors, and Ag NPs-induced etching of Si NWs has the greatest possibility in this process.

Therefore, the Si NWs without HNO_3 treatment were characterized to learn the relation between H_2O_2 concentration and Ag NPs. When utilizing the etchant (HF/AgNO_3) without the presence of H_2O_2 , there were few Ag NPs on the sidewalls of the resultant nanowires, which is consistent with the previous report [23]. In the case of H_2O_2 added (e.g. 0.005 M) into the etchant, many NPs decorate on the sidewalls of the nanowires, especially at the top site of the nanowire, as shown in Fig. 4A. These NPs exhibit a wide distribution along the nanowire axis. According to the results from STEM image (Fig. 4D) and HRTEM image (Fig. 4E), it was

demonstrated that these NPs were composed of silver. As H_2O_2 concentration increased to 0.05 M, more Ag NPs were observed along the nanowires axis. These results reveal that H_2O_2 facilitates nucleation and growth of Ag NPs on the sidewalls of nanowires. And these Ag NPs induce the lateral etching of nanowires leading to the formation of the pNWs.

Based on the above analyses, a novel formation mechanism of the pNWs by chemical etching in $\text{HF}/\text{AgNO}_3/\text{H}_2\text{O}_2$ solution was proposed. When lightly doped silicon wafer was dipped into the etchant, Ag NPs were deposited on silicon surface, as depicted in Fig. 5A. And the silicon nanowire arrays were formed by the silicon etching catalyzed by small Ag NPs, whereas their surface was covered by the loose Ag dendrites layer, as depicted in Fig. 5B. As the standard reduction potential of H_2O_2 (1.77 eV) is larger than that of Ag (0.78 eV), the growing Ag dendritic layer can simultaneously be oxidized into Ag^+ ions by H_2O_2 , as depicted in Fig. 5C. The corresponding reaction equation is as following:



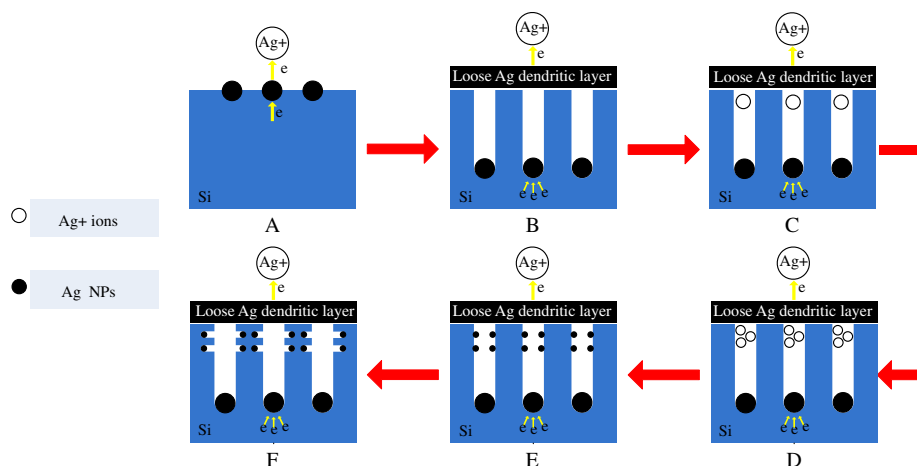


Fig. 5. Schematic illustration of the formation mechanism of Si pNWs arrays through one-step synthesis in HF/AgNO₃/H₂O₂ solution.

Since the growing and the dissolution of the Ag dendritic layer are in a state of dynamic equilibrium, as reaction time increases, a large number of Ag⁺ ions are generated near the Ag dendritic layer (Fig. 5D), and then these Ag⁺ ions trap electrons from the sidewalls of nanowires, re-nucleate and grow to Ag NPs. These grown Ag NPs have unique catalytic activity for etching silicon, meanwhile they are difficult to be oxidized by H₂O₂ [24]. Therefore, Ag NPs were decorated on the sidewalls of nanowires, as depicted in Fig. 5E. And these Ag NPs induce the lateral etching of nanowires leading to the formation of pNWs, as shown in Fig. 5F.

This mechanism can well explain the effect of H₂O₂ concentration on the surface morphologies of nanowires in our experiments. At a low concentration of H₂O₂, Ag nucleation on the sidewalls of nanowires is less possible due to the slight amount of Ag⁺ ions generated by dissolving the Ag dendritic layer, and smooth or rough Si NWs are formed. But at a high concentration of H₂O₂ (e.g. 0.05 M), the large number of the dissolved Ag⁺ ions produce plentiful Ag NPs, which catalyze the lateral etching of nanowires leading to the formation of pNWs. Therefore, the concentration of H₂O₂ has a limited range for the formation of pNWs.

The non-uniform distribution of Ag NPs and nanopores along the nanowire axis (as shown in Fig. 4B and C) can also be explained by this mechanism. Because Ag⁺ ions generated by dissolving Ag dendritic layer mainly distribute at the top surface of silicon nanowire arrays, these Ag⁺ ions has a non-uniform distribution along nanowire axis from bottom to top. Thus, Ag NPs and nanopores are preferable to form at the top of the nanowire.

From above results and discussions, it can be seen that the essential formation mechanism of pNWs is that Ag NPs-induced the lateral etching of nanowires. Hence, the porous structure on the sidewalls of nanowires can be modulated by adjusting the size, amount, and distribution of Ag NPs. In our work, the changing of H₂O₂ concentration has been proven to indeed influence the distribution of Ag NPs on the sidewalls of nanowires, resulting in different surface morphologies including smooth, rough and porous structures. In fact, H₂O₂ is not the only factor influencing the formation of pNWs. According to the proposed mechanism, other important factors such as the concentration of AgNO₃, the reaction temperature and the reaction time can also be deduced. Thus, modulating these technique parameters comprehensively will be an effective approach to fabricate pNWs with predictable and controllable porosity for different applications.

4. Conclusions

In conclusion, lightly doped pNWs has been successfully fabricated through one-step synthesis at room temperature. The lightly doped pNWs exhibit strong green fluorescence emission under the irradiation on 488 nm wavelength light. It is found that the concentration of H₂O₂ in the etchant plays a key role in the formation of pNWs. A novel mechanism is proposed to explain the formation of pNWs in HF/AgNO₃/H₂O₂ solution. The synthesis method is also able to produce highly doped pNWs. Furthermore, this controllable and widely applicable synthesis method of pNWs can further open their fresh application to photoelectric devices, energy harvesting and storage devices.

Acknowledgments

We acknowledge support by the National Natural Science Foundation of China (51172069), and Ph.D. Programs Foundation of Ministry of Education of China (20110036110006), and the Fundamental Research Funds for the Central Universities (Key Project 11ZG02).

References

- [1] E. Garnett, P.D. Yang, *Nano Lett.* 10 (3) (2010) 1082–1087.
- [2] K.Q. Peng, X. Wang, S.T. Lee, *Appl. Phys. Lett.* 92 (16) (2008) 163103.
- [3] S.K. Srivastava, D. Kumar, P.K. Singh, M. Kar, V. Kumar, M. Husain, *Sol. Energy Mater. Sol. Cells* 94 (9) (2010) 1506–1511.
- [4] Y.F. Huang, S. Chattopadhyay, Y.J. Jen, C.Y. Peng, T.A. Liu, Y.K. Hsu, C.L. Pan, C.H. Lo, Y.H. Chang, C.S. Lee, K.H. Chen, L.C. Chen, *Nat. Nanotechnol.* 2 (2007) 770–774.
- [5] C.K. Chan, H.L. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R.A. Huggins, Y. Cui, *Nat. Nanotechnol.* 3 (2008) 31–35.
- [6] A.I. Hochbaum, R. Chen, R.D. Delgado, W.J. Liang, E.C. Garnett, M. Najarian, A. Majumdar, P.D. Yang, *Nature* 451 (10) (2008) 163–167.
- [7] D.D.D. Ma, C.S. Lee, F.C.K. Au, S.Y. Tong, *Science* 299 (5614) (2003) 1874–1877.
- [8] K.Q. Peng, H. Fang, J.J. Hu, Yin. Wu, J. Zhu, Y.J. Yan, S.T. Lee, *Chem. Eur. J.* 12 (30) (2006) 7942–7947.
- [9] J. Zhu, Z.F. Yu, G.F. Burkhard, C.M. Hsu, S.T. Connor, Y.Q. Xu, Q. Wang, M. McGehee, S.H. Fan, Y. Cui, *Nano Lett.* 9 (1) (2009) 279–282.
- [10] X. Li, P.W. Bohn, *Appl. Phys. Lett.* 77 (16) (2000) 2572–2574.
- [11] M. Lipiński, S. Bastide, P. Panek, C. Lévy-Clément, *Phys. Status Solidi* 197 (2) (2003) 512–517.
- [12] J.Y. Lee, W.K. Han, J.H. Lee, *Sol. Energy Mater. Sol. Cells* 95 (1) (2011) 77–80.
- [13] A.I. Hochbaum, D. Gargas, Y.J. Hwang, P.D. Yang, *Nano Lett.* 9 (10) (2009) 3550–3554.
- [14] Y.Q. Qu, L. Liao, Y.J. Li, H. Zhang, Y. Huang, X.F. Duan, *Nano Lett.* 9 (12) (2009) 4539–4543.

- [15] C. Chiappini, X.W. Liu, J.R. Fakhoury, Mauro Ferrari, *Adv. Funct. Mater.* 20 (14) (2010) 2231–22339.
- [16] Y.Q. Qu, X. Zhong, Y.J. Li, L. Liao, Y. Huang, X.F. Duan, *J. Mater. Chem.* 20 (18) (2010) 3590–3594.
- [17] K.Q. Peng, X. Wang, S.T. Lee, *Appl. Phys. Lett.* 95 (24) (2009) 243112.
- [18] M. Xue, X. Zhong, Z. Shaposhnik, Y.Q. Qu, F. Tamanoi, X.F. Duan, *J. Am. Chem. Soc.* 133 (23) (2011) 8798–8801.
- [19] X. Zhong, Y.Q. Qu, Y.C. Lin, L. Liao, X.F. Duan, *ACS Appl. Mater. Interfaces* 3 (2) (2011) 261–270.
- [20] M.L. Zhang, K.Q. Peng, X. Fan, J.S. Jie, R.Q. Zhang, S.T. Lee, N.B. Wong, *J. Phys. Chem. C* 112 (12) (2008) 4444–4450.
- [21] M.G. Zhu, X.J. Chen, Z.L. Wang, Y. Chen, D.F. Ma, H. Peng, J. Zhang, *Chem. Phys. Lett.* 511 (1–3) (2011) 106–109.
- [22] L.H. Lin, X.Z. Sun, R. Tao, J.Y. Feng, Z.J. Zhang, *Nanotechnology* 22 (7) (2011) 075203.
- [23] K.Q. Peng, Y.J. Yan, S.P. Gao, J. Zhu, *Adv. Mater.* 14 (16) (2002) 1164–1167.
- [24] C.L. Lee, K.T. Sujino, Y.J. Kanda, S. Ikeda, M. Matsumura, *J. Mater. Chem* 18 (9) (2008) 1015–1020.