



Synthesis of porous silicon nano-wires and the emission of red luminescence



Sun Congli^a, Hu Hao^b, Feng Huanhuan^a, Xu Jingjing^a, Chen Yu^a, Jin Yong^a, Jiao Zhifeng^a, Sun Xiaosong^{a,*}

^a School of Materials Science and Engineering, Sichuan University, PR China

^b National Engineering Research Center for Biomaterials, Sichuan University, Chengdu 610064, Sichuan, PR China

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ABSTRACT

This very paper is focusing on the characterization of porous silicon nano-wires prepared via a two-step route, the electroless chemical etching and the following post-treatment of HF/HNO₃ solution. Hence, scanning electron microscopy, transmission electron microscopy and confocal fluorescence microscopy are employed for this purpose. From the results of experiments, one can find that the as-prepared silicon nano-wire is of smooth surface and that no visible photo-luminescence emission could be seen. However, the porous structure can be found in the silicon nano-wire treated with HF/HNO₃ solution, and the clear photo-luminescence emission of 630 nm can be recorded with a confocal fluorescence microscope. The transmission electron microscopy test tells that the porous silicon nano-wire is made up of a porous crystalline silicon nano-core and a rough coating of silicon oxide. Besides, based on the post-HF- and -H₂O₂- treatments, the emission mechanism of the red luminescence has been discussed and could be attributed to the quantum confinement/luminescence center model which could be simply concluded as that the electron-hole pairs are mainly excited inside the porous silicon nano-core and then tunneling out and recombining at the silicon oxide coating.

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1. Introduction

Silicon nano-wires (SiNWs) have stimulated great interest over the past decade due to their paramount electrical, mechanical, and thermal properties [1,2]. Meanwhile it also presents good compatibility with the integrated circuits technology [3]. Their potential applications in nano-scaled electronics, thermoelectrics, battery electrodes, and electronic biosensors have been extensively investigated [4–7]. Yet, it has to be recognized that the indirect energy band-gap of bulk crystalline silicon would highly reduce the luminescence efficiency [8] due to the necessary participation of phonons in the electron transition process. Therefore, the application for optoelectronics is drastically restricted. On the other hand, it is also known that porous silicon (PS) could be an alternative for silicon based visible light emitter because of the strong quantum confinement effect, and thus far, both the opto- and electro-properties of PS have been intensively investigated for the last decade [9–12]. As such, it is rationally deduced that the porous silicon nano-wires (PSiNWs) would give rise to be a new building block for one dimensional silicon based nano-structure device

manufactory, and with their significantly high surface area [13] and optical activity [4], PSiNWs would have opportunities for the fabrication and application of high-efficient silicon-based optoelectronic devices.

PSiNWs have been increasingly investigated recently. The synthesis of PSiNWs is typically carried out via an electroless chemical etching route. As electroless chemical etching silicon wafers with high resistivity can only prepare SiNWs with both smooth surface and poor luminescent performance, silicon wafers with electrical resistivity about 0.001 Ω cm are, therefore, rationally required [13]. But highly-doped PSiNWs would limit their further applications in certain opto-electronic devices, such as solar cells [14]. In this case, the preparation of PSiNWs with slightly-doped silicon wafer is rather important. Besides, there are intense debates about the photoluminescence (PL) emission in PSiNWs. Lin [8,15] proposed that the PL emission of PSiNWs came from two elementary PL bands; one from the oxide layer formed on the surface of PSiNWs and the other one the H-terminated nano-structure. He [3] claimed that the localized state in PS might give rise to the PL emission of PSiNWs. Hochbaum [13] suggested that PL emission of PSiNWs came from quantum confinement of silicon nano-particles, and he also cited the possibility of emission from surface/defect states in the surface oxide. Qu [4] and Chen [16] believed that the visible light emission of PSiNWs came from the deep quantum confinement

* Corresponding author. Tel.: +86 28 85471569; fax: +86 28 85416050.

E-mail addresses: sunxs@scu.edu.cn, sunxs-scu@163.com (S. Xiaosong).

state in the porous structure. However, most previous studies dealt with the porous silicon nano-core, the surface state and the oxide layer separately and neglected their cooperation in the process of PL emission. The electron transfer between silicon core and its oxide coating, which gets possible when quantum effects of PS core become significant, is more or less overlooked. So, precise control of the post-treatments and analysis of the related luminescent spectra are necessary for us to understand their luminescent mechanism of PSiNWs.

In this paper, PSiNWs samples were prepared with *p*-silicon wafers ($\rho = 2\text{--}3 \Omega \text{ cm}$) via a two-step route, that is, the electroless chemical etching procedure was firstly carried out, and the following post-treatment procedure was, then, achieved by floating the as-etched silicon wafer on HNO_3/HF aqueous solution. The clear red luminescence of 630 nm can be seen with naked eyes under the excitation of mercury lamp of 350 nm. Confocal fluorescence microscopy test confirms that red luminescence comes from PSiNWs themselves. The tests of scanning electronic microscopy and transmission electronic microscopy have also been done. Together with the studies on the effects of post-HF- and H_2O_2 -treatments, as well as the change of luminescent spectra, the cooperative effects of porous silicon nano-core, the surface state and the oxide layer will be considered based on the quantum confinement/luminescence center model.

2. Experiment

2.1. Synthesis of SiNWs arrays

In the very experiment, mirror polished *p*-silicon (100) wafers ($\rho = 2\text{--}3 \Omega \text{ cm}$, $10 \times 10 \text{ mm}^2$) were used. Before electroless etching process, silicon wafers were cleaned by standard RCA method [17]. The AgNO_3/HF etchant was prepared with 0.02 M AgNO_3 and 4.8 M HF aqueous solutions by the volume ratio of 1:1. Cleaned silicon wafers were left to soak in the etchant for 3 h at 2°C in dark. During the etching procedure, a loose film of dendritic Ag formed on the top of SiNWs arrays. In order to remove the loose Ag film, the as-etched silicon wafers were ultrasonically cleaned in de-ionized water for 15 min and then immersed in 0.02 M HNO_3 for 20 min. At last, as-etched SiNWs wafers were washed with de-ionized water, and dried in nitrogen for further characterization.

2.2. Synthesis of PSiNWs arrays

The mixed HF/ HNO_3 aqueous solution was prepared with HF (40%)/ HNO_3 (65%)/ H_2O by the volume ratio of 1:1:5. Before this process, SiNWs were etched by HF (2%) for 30 min to remove their oxide coating. Then, the wafer of as-prepared SiNWs arrays was carefully floated on the mixed HF/ HNO_3 aqueous solution, during which the SiNWs arrays faced upward. After 10 h, the floating silicon wafer was washed with de-ionized water, dried in nitrogen and then collected for further characterization.

2.3. Characterization

Scanning electron microscope (SEM, HITACHI 4800) and transmission electron microscope (TEM, TECNAI G2F20) were employed for the morphology study. Luminescence performance was tested with fluorescence spectrophotometer (HITACHI F7000) and confocal fluorescence microscope (CLSM, Leica TCP SP5). The fast Fourier transformation infrared spectroscopy test (FT-IR) was carried out with Fourier transformation infrared spectroscopy (Nicolet iS10). For TEM and luminescence test, both the SiNWs and PSiNWs were, respectively, scratched out from the silicon wafer, where upon the resulting powder was then dispersed in ethanol by sonication for

several hours until no obvious precipitation could be observed and then dropped onto the copper grids.

3. Results and discussion

Fig. 1a–c are the cross-sectional SEM images of as-prepared SiNWs. It could be seen that the SiNWs are vertical to the surface of the silicon substrate. The length of SiNWs is approximately $15 \mu\text{m}$. And the diameter of nano-wires is in the range of 30 nm to 200 nm. Fig. 1d is the TEM image of SiNWs, in which smooth surface of as-prepared SiNWs is shown.

It is well recognized that the formation of SiNWs is a localized microscopic electrochemical cell process. As it is previously described [18], at the beginning, Ag atoms deposit on Si surface, forming nano nuclei on the surface of Si wafer. Then these Ag nuclei and the silicon next to these Ag nuclei could act as local cathodes and anodes. With the progress of Ag deposition, Ag nuclei acting as the cathodes are preserved, while the surrounding Si acting as anodes is etched away. At last, SiNWs arrays are formed. The equation is listed as follows:

Cathode:

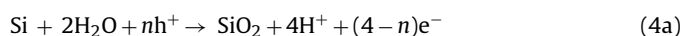
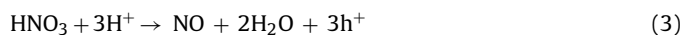


Anode:



Fig. 2a–c, are the cross-sectional SEM images of the SiNWs wafer after the treatment of floating etching procedure with HNO_3/HF aqueous solution. It could be seen that the diameter and length of SiNWs barely changed comparing with that of the SiNWs shown in Fig. 1. But the surface of SiNWs is rough and some pores can be seen. In order to clearly reveal the core structure of SiNWs and its surface oxide coating, TEM test was done, and corresponding image is illustrated in Fig. 2d, in which four nano-wires, whose diameter varies from 30 nm to 100 nm, stand side by side. The rough and porous surface of silicon nano-wire could be clearly seen and are coated by a rough layer of silicon oxide. The bottom-left-insert of Fig. 2d shows a single PSiNWs with the silicon core and silicon oxide coating as well. The selected area diffraction (SAED) pattern, the top-right-inset of Fig. 2d, demonstrates that the PSiNWs retain single crystalline structure, which indicates that pre-electroless chemical etching and post-HF/ HNO_3 treatment do not destroy the crystalline integrity of the starting silicon wafer.

The formation of PSiNWs via electroless chemical etching process has been investigated to some extent. Nowadays, the mechanism is understood more or less and discussed in the literature. Hereby, we would like to give a brief discussion about the formation of PSiNWs. When silicon wafer with SiNWs floats on HF/ HNO_3 solution, typical stain-etching process would take place on its solution-contacted surface. It is well recognized [19] that stain-etching procedure is an electrochemical process. Hence, both the anodic reaction and the cathodic one ought to occur on the solution-contacted surface of Si wafer, which could be listed in the following equations:



HNO_3 will oxidize silicon and the formed silicon oxide will be removed by HF. This process is actually that, firstly, HNO_3 decomposes and releases holes into silicon, Eq. (3). Then, holes and H_2O turn Si atoms into SiO_2 which would be etched by HF, Eqs. (4a) and (4b). Besides, unconsumed holes could drift upward into SiNWs,

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