단일 Si 나노선 합성 및 광특성 연구

김경환, 김기현, 강정민, 윤창준, 정동영, 민병돈, 조경아, 김현석, 김상식
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Synthesis and photoresponse characteristics of single-crystalline Si nanowires

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Abstract

Photocurrent of a single-crystalline Si nanowire is investigated in this paper. Single-crystalline Si nanowires with amorphous SiO_2 shells were first synthesized from ball-milled SiO powders by thermal chemical vapor deposition, and then the amorphous SiO_2 shellswere etched out from the as-synthesized Si nanowires. For a single-crystalline Si nanowire, photocurrent-voltage curves taken in air at room temperature were non-linear, and rapid photoresponses were observed when the light was switched on and off. The photocurrent was not changed in intensity under the illumination. Photocurrent mechanism in the single-crystalline Si nanowire is discussed in this paper.

1. Introduction

The synthesis of nanostructured semiconducting materials has become one of important research issues since a notable discovery of carbon nanotubes [1]. Among the several issues, research of the one-dimensional Si nanowires has progress rapidly because Si nanowires are promising building blocks for electronic and optical devices. Recently, many researchers have studied the synthesis of Si nanowires with high crystal quality [2,3] and the fabrication of Si-based nanodevices with high performance such as field-effect transistors [4,5], integrated logic circuits [6], and biosensors [7]. Photoconduction has been investigated by many research groups for ZnO [8,9], InP [10], and SnO2 [11] nanowires. The investigation reveals the possibility that the semiconducting nanowires are very applicable to photodetectors. Moreover, the photoconduction for the semiconducting nanowires examines not only their purity and crystal quality [12,13]. However, photoconduction of Si nanowires has not been researched yet, to our knowledge, although photoconduction for other types of Si including amorphous [14], polycrystal [15], and porous Si [16] has been widely researched.

In this study, crystalline Si nanowires were first synthesized by thermal chemical vapor deposition (CVD), and then photocurrent-voltage characteristics and photoresponses of a single crystalline Si nanowire were investigated. Finally, the photoconduction mechanism is discussed in this letter.

2. Main Subject

2.1 Experimental

Silicon nanowires were grown on alumina substrates by thermal CVD using SiO powders under controlled conditions without any catalysts. High-purity SiO powders with a particle size of -325 mesh were employed as the starting material. Prior to thermal evaporation, the SiO powders were ground in a mechanical ball-mill system (SPEX 8000 M) for 20 h. The ball-milled SiO powders were placed at the center of an Al_2O_3 tube. The tube furnace system was heated at 1380 ℃ for 1h. During the synthesis of silicon nanowires, a mixture of Ar (95 %) and H_2 (5 %) was flowing with the rate of 500 sccm at a pressure of about 250 torr. The nanometer –scaled morphology and nanostructure of the as- synthesized Si nanowires were characterized by scanning electron microscopy (SEM, HITACHI S-4700) and high resolution transmission electron microscope (HRTEM, JEOL, JEM-2010).

The measurements of photocurrentvoltage curves and photoresponses were made in air at room temperature. The light sources for these measurements were the 325-nm wavelength line from a He-Cd laser and the 633-nm wavelength line from a He-Ne laser; the power density of the light was 10 mW/cm^2.

2.2 ResultandDiscussion

SEM image and X-ray diffraction spectra of Si nanowires synthesized by thermal CVD are presented in Fig. 1. The SEM image of Fig. 1(a) reveals that the synthesized Si nanowires are in the range of 50~100 nm in diameter and in the range of 10~50 μm in length and that their morphology is straight. The XRD pattern of Fig. 1(b) demonstrates typical lines of crystal Si overlapped with the lines (marked by asterisks) originating from the alumina substrate, illustrating that the synthesized nanowires are crystalline ones indeed.

TEM and HRTEM images of the Si nanowires shown in Figure 2 reveals that the Si nanowires were composed of crystalline silicon cores and amorphous SiO_2 shells; SAED pattern of a selected Si nanowire in the inset of Fig. 2(b) demonstrates that regularly arrayed spots originating from the crystalline Si core are overlapped with circular rings coming from the amorphous SiO_2 shell.
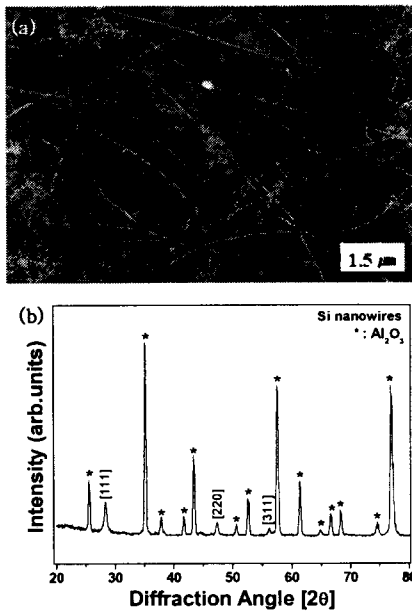
Figure 1. (a) SEM image and (b) X-ray diffraction spectra of the Si nanowires synthesized by thermal CVD.
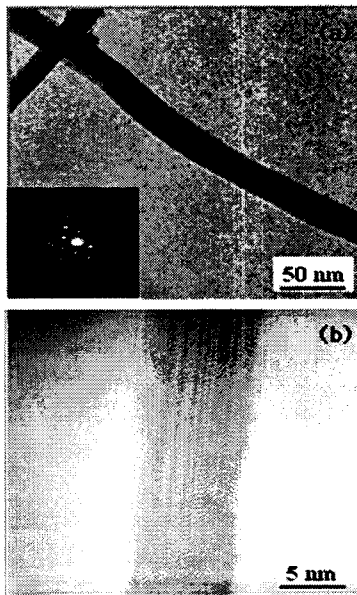

Figure 2. TEM (a) and HRTEM (b) images of Si nanowires. The inset of Fig. (a) shows their SAED pattern.

Figure 3 shows the optical microscope image of a single-crystalline Si nanowire between two Au/Ti electrodes on a SiO₂/Si substrate (the separation between these electrodes is 3 μ) and I-V curves of dark current and photocurrent excited by the 325-nm wavelength light form a He-Cd laser or 633-nm wavelength light from a He-Ne laser for the single Si nanowire at applied voltages from 0 to 3 V. This Single Si nanowire has a length of about 7μ and a

diameter of about 80 nm. In order to make contacts, the oxide sheath was etched out by the 4 % Hydro Fluoric (HF) for 90 sec. The Au/Ti electrode pattern was made by photolithography. The I-V curves taken for the single-crystalline in darkness and under the illumination are non-linear, indicating an existence of Schottky barriers between the nanowire and the Ti contacts. The current flowing the Si nanowire is enhanced significantly under the illumination of the light, compared with that in darkness, indicating the presence of the photocurrent in the nanowire. The photocurrent excited by the 633-nm wavelength light is larger in intensity that excited by the 325-nm wavelength light.
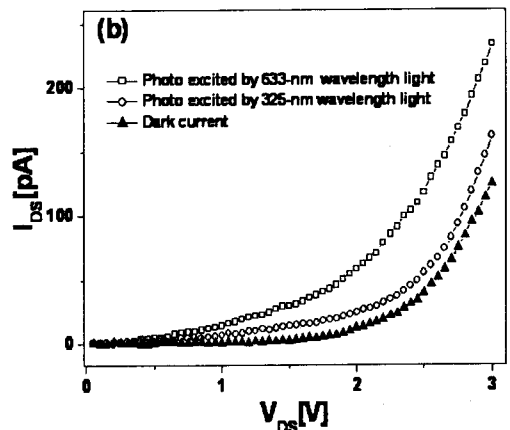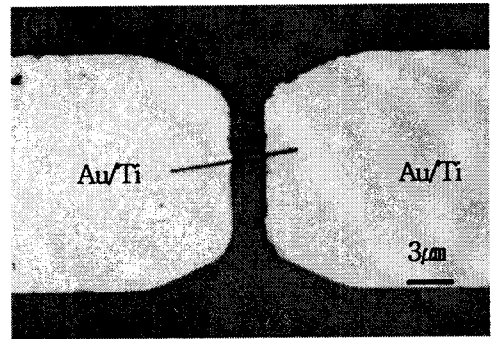

Figure 3. Optical microscope image (a) of a single-crystalline Si nanowire between two Ti/Au electrodes on a SiO₂/Si substrate, and current-voltage (I-V) curves (b) for the single-crystalline Si nanowire indark and under the illumination of 325-nm and 633-nm wavelength light.

Photoresponses of the single Si nanowire under modulated illumination of the 325- and 633-nm wavelength light are presented in Figure 4. The light was switched on and off per 100 sec in air at room temperature at a bias voltage of 3 V. The photocurrent is not changed in intensity under the illumination. The rise and decay times of the photoresponses are too short to be measurable in our system; these times should be shorter than 1 sec.
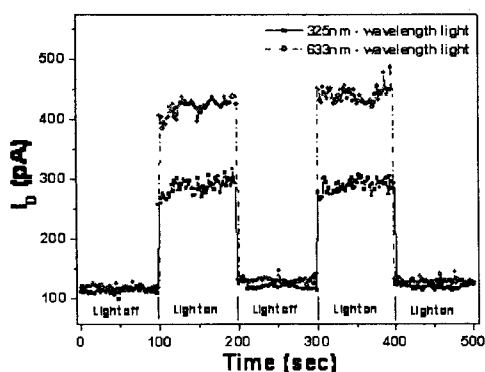
Figure 4. Time-dependent photocurrents under the illuminations of the 325-nm wavelength light and the 633-nm wavelength light.

The presence of photocurrent in the Si nanowire indicates that the concentration of unintentionally doped impurites or defects in our synthesized Si nanowires are quite low. If significant concentrations of unwant impurities or defects were present in the nanowires, the photocurrent would be not detectable because of thermally recombing processes of photo-excited charge carriers at centers created by impurities or defects [17]. Moreover, the observed short rise and decay times indicate the highly purity and nearly perfect crystal of our synthesized Si nanowires. Notice that long rise and decay times observed in other semiconducting nanowires including ZnO and GaN nanowires are due to the trapping and detrapping of photoexcited charge carriers in the localized bands in the mid-gap created by unintentionally doped impurities or by defects including vacancies or dislocation [9,12,18]. These suggest that photocurrent is a valuable tool to evaluate the purity of Si nanowires.

Our observation on the photoresponse measured in air for the Si nanowire illustrates that photocurrent mechanism for the Si nanowire is different from those of ZnO and GaN nanowires. For ZnO and GaN nanowires, photocurrent rises and decays for longer times than 1 s, when exciting light is switched on and off in air at room temperature [9,18]. The reason for this is that the creation of holes by the light leads to chemidesorption of oxygens on the nanowires, causing the widening of the channel for charge carriers, and that the attachment of oxygens makes the narrowing of the channel; photoexcited holes may not participate in photocurrent efficiently [13]. However, the photoresponse measured in air for the Si nanowire does not show the rising and decaying, indicating that the creation of holes by the light may not allow chemidesorption of oxygens on the nanowire to happen and that oxygen ions do not affects the width of the channel. Therefore, we suggest that both electrons and holes excited by light may participate efficiently in photocurrent for the Si nanowire, independent of the existence of oxygen ions on its surface.

3. Conclusion

Si nanowires were grown by thermal CVD using the Si monoxide powders under controlled conditions without the catalyst. The synthesized Si nanowires were composed of crystalline silicon cores and amorphous SiO_2 shells. For a single-crystalline Si nanowire, photocurrent-voltage curves taken in air after etching out of the SiO_2 shell were non-linear, and rapid photoresponses were observed when the light was switched on and off. The observed short rise and decay times indicate the highly purity and nearly perfect crystal of our synthesized Si nanowires, suggesting also that photocurrent is a valuable tool to evaluate the purity and crystal quality of Si nanowires. Photocurrent mechanism for the Si nanowire is different from those of ZnO and GaN nanowires in that it is independent of the existence of oxygen ions on its surface.

[References]

[1] N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. 68, p. 1579, 1992.
[2] S. T. Lee, Y. F. Zhng, N. Wang, Y. H. Tang, I. Bello, and C.S. Lee. J. Mater. Res. 14, p. 4503, 1999.
[3] O. H. Elibol, D. Morisette, D. Akin, J. P. Denton, and R. Bashir, Appl. Phys. Latt. 83, p. 4613, 2003.
[4] Y. Cui, and C. M. Lieber, Science 291, p. 851, 2001.
[5] G. Zheng, W. Lu, S. Jin, and C. M. Lieber, Adv. Mater. 16, p. 1890, 2004.
[6] Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K. H. Kim, and C. M. Lieber, Science 294, p. 1313, 2001.
[7] J. Hahm, and C. M. Lieber, Nano Lett. 4, 51, 2004.
[8] H. Kind, H. Yan, B. Messer, M. Law, and P. Yang, Adv. Mater. 14, p.158, 2002.
[9] K. Keem, H. Kim, G. T. Kim, J. S. Lee, B. Min, K. Cho, M. Y, Sung, and S. Kim, Appl. Phys. Lett. 84, p. 4376, 2004.
[10] J. Wang, M. S. Gudiksen, X. Duan, Y. Cui, and C. M. Lieber, Science 293, p. 1455, 2001.
[11] J. -S. Lee, S. K. Sim, B. Min, K. Cho, S. W. Kim, and S. Kim, J. Cryst. Growth 267, p. 145, 2004.
[12] M. C. Jeong, B. Y. Oh, W. Lee, and J. M. Myoung, Appl. Phys. Lett. 86, p. 103105, 2005.
[13] Q. H. Li, T. Gao, Y. G. Wang, and T. H. Wang, Appl. Phys. Lett. 86, p. 123117, 2005.
[14] R. Schwarz, S. Grebner, P. Popovic, and F. Wang, J. Non-Cryst. Solids 198-200, p. 234, 1996.
[15] R. Pandya, and B. A. Khan, J. Appl. Phys. 62, p. 3244, 1987.
[16] H. Shi, Y. Zheng, Y. Wang, and R. Yuan, Appl. Phys. Lett. 63, p. 770, 1993.
[17] R. H. Bube, Photoconductivity of solids (John Wiley & Sons, Inc., New York, 1967).
[18] M. Kang, J. S. Lee, S. K. Sim, H. Kim, B. Min, K. Cho, G. T. Kim, M. Y. Sung, S. Kim, and H. S. Han, Jpn. J. Appl. Phys. 43, p. 6868, 2004.