Electrical properties and photo-responses of SiNWs with selective anchored gold nanoparticles by using scanning probe bond breaking nanolithography

Chia-Hao Wu^{*1}, Jeng-Tzong Sheu², and Tieng-Sheng Chao³

¹Computer Science and Information Engineering, MingDao University 369 Wen-Hwa Road, Peetow, ChangHua 52345, Taiwan Phone: +886-4-8876660-ext.8125 *E-mail: <u>chiahao@mdu.edu.tw</u> ² Institute of Nanotechnology, National Chiao Tung University ³Institute and Department of Electrophysics, National Chiao Tung University 1001 Ta Hsueh Road, Hsinchu 30050, Taiwan

1. Introduction

Bridging the bottom-up and the top-down nanofabrication techniques for nano-electronic and nano-biosensing applications are the main subjects of current research. Scanning probe lithography (SPL) has been demonstrated as a powerful tool in nanofabrications [1-7]. The novel approach is introduced for selective deposition of colloidal gold nanoparticles (AuNPs) onto the nanowire surface of an unpatterned self-assembled monolayer. Filed-induced SPL bond breaking, as the electrochemical mechanism suggested [8-10], the water-meniscus between the tip and the substrate surface could work as an electrochemical nano-cell and could provide hydroxyl ions, hydrogen radicals, and oxygen species for decomposing among N-H, C-N and Si-O bonds of N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS) SAMs patterns at random under ambient. In this research, gold nanoparticles selective anchored onto the desired surface of silicon nanowires (SiNWs) were successfully dominated by the additional SPL electrical-field-induced chemical bond decomposing. After SPL selective decomposition of AEAPTMS SAMs, negative-charged gold nanoparticles were selectively anchored on the unexposured area of SiNWs via electrostatic force. Electrical properties and photo-responses of SiNWs with selective binding of AuNPs were demonstrated. It is believed that this novel technique can be widely applied in nanoelectronics and chemical biosensors.

2. Experimental details

In the experiments, the silicon nanowires devices with 100 nm wide and 10 µm long on the p-type (100)-oriented SOI substrate were fabricated by E-beam nano-lithography with an anisotropic RIE dry etching process. The silicon nanowires (SiNWs) were modified by silanization procedure with N-(2-Aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPTMS) so that self-assembly monolayer formed on the surface of SiNWs. Then, scanning probe lithography (SPL) was adopted to decompose the AEAPTMS SAMs on SiO₂ surfaces of SiNWs selectively. After the SPL chemical bonds decomposition procedure, negative charged gold nanoparticles (AuNPs) were selectively anchored on the unexposured area of SiNWs via electrostatic force. X-ray photoelectron spectroscopy spectra (spatial resolution 100 nm) were used to demonstrate the selectivity of deposition of gold nanoparticles. Scanning electron microscopy (SEM) was used to observe the selective deposition of gold nanoparticles on the patterned region. The Agilent 4156 semiconductor parameter analyzer was used to measuring the photoconductivity characteristics of p-type silicon nanowire devices with selective anchored AuNPs.

3. Results and Discussions

Figure 1 shows both the x-ray photoelectron microscopy (XPS) survey analysis at region of SPL bond breaking patterns on the SiO₂ surface and at region outside the SPL bond breaking patterns after self-assembly of AuNPs. The tip/sample bias of SPL bond breaking is 6 volts. The Au4f peaks corresponding to the gold nanoparticles on the region outside the SPL bond breaking patterns on the SiO₂ surface are clearly observed. And, no Au 4f signal is observed at the SPL bonds breaking patterns on the SiO₂ surface showing that AuNPs selectively deposited only on the SPL unexposed patterns. Figure 1 also shows the SEM image of 15-nm AuNPs selective anchored on the SPL unexposured AEAPTMS regions after immersion the samples in the AuNPs solution for 1.5 h. This proposed technique provides a simple process and a very reliable selectivity on anchoring AuNPs in nanometer scale resolution.



Fig. 1. Spectra from scanning x-ray photoelectron spectroscopy on the areas of SPL bond breaking patterns and outside the SPL bond breaking patterns to evaluate the selectivity of gold nanoparticles. Au4f signal was observed clearly outside the SPL exposed pattern area, and no Au4f signal was observed inside the SPL exposed pattern area.

It was clearly observed that the small amount of 15nm-gold nanoparticles were successfully controlled and selectively anchored on the desired SPL undecomposed region of SiO₂ surfaces of p-channel of SiNWs devices as shown in Figure 2. And, no gold nanoparticles is found at the remainder SPL bonds breaking patterns on the p-channel surface showing that gold nanoparticles selectively deposited only on the SPL undecomposed patterning region. Electrical properties (I_{ds} - V_{ds}) of a SiNW with different surface modifications at 300K are shown in Figure 3. After various chemical modification processes, a significant change in electrical conductance of the p-type Si nanowires

devices can be determined. The voltage of the d.c. source was maintained at 10 mV and the current was measured by a Agilent 4155 semiconductor parameter analyzer. The conductance of the SiNW has been strongly modulated by the surface modifications on the p-type SiNWs.



Fig. 2. SEM images of gold nanoparticles selectively deposited on the SPL undecomposed silanation-modified regions of (100) p-type silicon nanowire (SiNW) devices. Nanowire is about 110 nm wide and 10 μ m long. Bottom SEM image shows the details of nanowire device with AuNPs on defined area of the SiO₂ surface of SiNWs.



Fig. 3. Electrical properties of silicon nanowire devices with different chemical modifications at room temperature. Due to the changes of chemical potential after modifications, the electrical conductance of p-type SiNW devices have clearly modulated with the chemical modifications on the channel surface of p-type SiNWs.

Surface state potential of p-channel of SiNWs device was altered by chemicals with different types of electric charge polarity. Electrical conductance measurements also demonstrated expressly that the silicon nanowires can be detected with a very high sensitivity. In this study, the tuning wavelength of photoresponse measurements from the visible regions (420 nm) to near-infrared regions (820 nm) by using the monochromator, and the p-channel surface of SiNWs devices with few AuNPs were conducted under alternate light illumination (light on-state) of different wavelengths and under dark conditions (light off-state). Figure 4 demonstrates the electrical properties (I_{ds} - V_{ds}) of a SiNW with AuNPs after illumination with five different wavelengths at 300 K. It was found that there are noticeable responses at wavelength of 520 nm and wavelength of 720 nm, respectively. We suggested that the conductance of SiNW was enhanced by surface plasmon resonance (SPR) at 520 nm. Moreover, there is another enhancement of conductance for SiNW at 720 nm by SPR effect. It is believed that the second enhancement is resulted from of SPR effect from clustering of AuNPs. We believed that the proposed novel surface modifications of channel of silicon nanowires devices can be widely applied in chemical bio-sensors and nanoelectronics.



Fig. 4. Optical response measurements. Electrical properties of SiNWs capped with AuNPs at irradiation of five different light wavelengths at 300K with source-drain bias of 10 mV. Noticeable SPR enhancement on conductivity (circled in red) at wavelength of 520 nm and wavelength of 720 nm were observed, respectively.

4. Conclusions

A new approach has successfully demonstrated for the patternwise deposition of AuNPs onto the SiO₂ surface with nanometer-scale resolution by SPL field-induced decomposition of AEAPTMS SAMs. XPS spectra shows the cleanness of the selectivity of deposition of AuNPs. Surface potential of p-channel of SiNW device was modulated by chemical modifications. And, with only few AuNPs selective deposition, it was found clearly that the photoconductivity was enhanced at a surface plasmon resonance (SPR) wavelength of 520 nm and 720 nm at room-temperature. The enhancement of pohtoconductivity at 720 nm is believed to be the SPR effect of AuNP clusters. Based on the study, it is believed that this novel technique can be widely applied in chemical bio-sensors and nanoelectronics.

References

- R. Piner, J. Zhu, F. Xu, S. Hong, and C. A. Mirkin, *Science* 283, (1999) 661.
- [2] F. S.-S. Chien, C-L Wu, Y.-C. Chou, T. T. Chen, S. Gwo, and W.-F. Hsieh, Appl. Phys. Lett. **75**(16), (1999)2429.
- [3] G.-Y. Liu, S. Xu, and Y. Qian, Acc. Chem. Res. 33 (7), (2000)457.
- [4] Hun Zhang, Ki-Bum Lee, Zhi Li and Chad A Mirkin, Nanotechnology, 14, (2003)1113.
- [5] K. Matsumoto, S. Takahashi, M. Ishii, M. Hoshi, A. Kurokawa, S. Ichimura, A. Ando, Jpn. J. Appl. Phys. 34, (1995)1387
- [6] T. Yoshinobu, J. Suzuki, H. Kurooka, W.C. Moon, H. Iwasaki, Electrochimica Acta 48, (2003)3131.
- [7] S. Liu, R. Maoz, J. Sagiv, Nano Lett. 4 (5), (2004) 845.
- [8] H. Sugimura, N. Nakagiri, J. Am. Chem. Soc. 119 (39), (1997)9226.
- [9] Q. Li, J. Zheng, Z. Liu, Langmuir 19 (1), 166 (2003).
- [10] X. Ling, X. Zhu, J. Zhang, T. Zhu, M. Liu, L. Tong, Z. Liu, J. Phys. Chem. B 109 (7), (2005)2657.