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Applications of silicon nanowires functionalized with palladium nanoparticles in hydrogen sensors

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Abstract
Silicon nanowires (SiNWs) modified by palladium (Pd) nanoparticles were investigated for hydrogen detection. SiNWs were fabricated via a thermal evaporation method using tin (Sn) as the catalyst. The as-grown SiNWs were chemically treated to remove surface oxide and then coated with a thin layer of Pd nanoparticles. A gas sensor device was fabricated with the Pd-functionalized SiNWs. The sensor showed better sensitivity to hydrogen and faster responding time than the macroscopic Pd wire hydrogen sensor.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One-dimensional silicon nanowires (SiNWs) have been attracting much interest due to their potential applications in electronic devices (e.g. field effect transistors [1, 2]) and sensors (e.g. PH sensors [3] and biosensors [4–8]). Applications for gas sensing with nanoscaled materials is an important field due to anticipated high sensitivity resulting from large surface-to-volume ratio. TiO_2 nanoparticles [9], nanostructured WO_3 [10], nanograined ZnO [11], quasi-1D SnO_2 nanostructures functionalized with Pd particles [12], as well as Pd nanowires [13, 14], have been applied for sensing different kinds of gases. In this work, a hydrogen sensor was fabricated by functionalizing SiNWs with Pd nanoparticles. It was observed that, upon introducing 5% of hydrogen into an argon (Ar) environment, conductivity of Pd-coated SiNWs increased by twenty times with fast response. The sensing mechanism can be explained by the Fermi level modulation upon chemical absorption of hydrogen gas in Pd nanoparticles that leads to the band diagram change at the metal–semiconductor interface.

2. Experimental session

1D SiNWs were synthesized by thermal evaporation of high-purity SiO (99.9%) mixed with 1% Sn powder. The source power was loaded into an alumina boat put at the centre of an alumina tube. The alumina tube was then evacuated to 1×10^{-2} Torr with a mechanical pump. Ar gas pre-mixed with 5% H_2 was fed through the tube during the entire deposition process at a flow rate of 50 sccm, and a pressure of 300 Torr. The centre part of the alumina tube was kept at 1350 °C for 6 h. After cooling down, deposition products were collected from the inner wall of the tube. The oxide sheath on the as-grown SiNWs was removed by immersion in a 5% hydrofluoric acid (HF) aqueous solution for ten minutes. After cleaning with distilled water, the sample was immersed in a saturated palladium chloride ($PdCl_2$) solution for another ten minutes and Pd particles were deposited on the surface of SiNWs. The Pd-modified SiNWs were dispersed onto a silicon wafer with a 300 nm oxide layer. Gold electrodes were deposited onto the sample by thermal evaporation. I–V measurements were carried out with a two-probe measurement system.

3. Results and discussion

Figure 1(a) is the x-ray diffraction (XRD) spectrum of the as-grown SiNW sample which mainly contains cubic Si (JCPDS file: 27-1402) and a small amount quantity of Sn. Scanning electron microscopy (SEM) observation (figure 1(b)) shows a Sn droplet at the tip of a SiNW. The SEM image in figure 1(c) demonstrates each nanowire consists of a uniform Si core with a diameter of 80–200 nm and an oxide sheath with a structure

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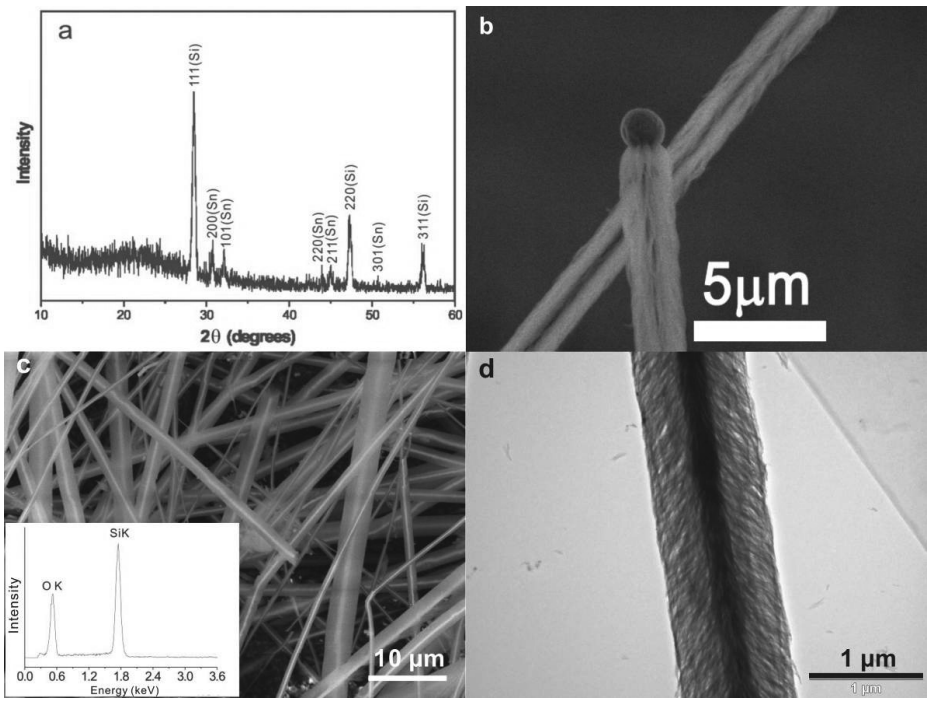

Figure 1. (a) An XRD spectrum of as-grown SiNWs. (b) A SEM image taken at the tip of a SiNW. (c) A SEM image of as-grown SiNWs. The inset is an EDX spectrum of SiNWs. (d) A TEM image of an as-grown SiNW.

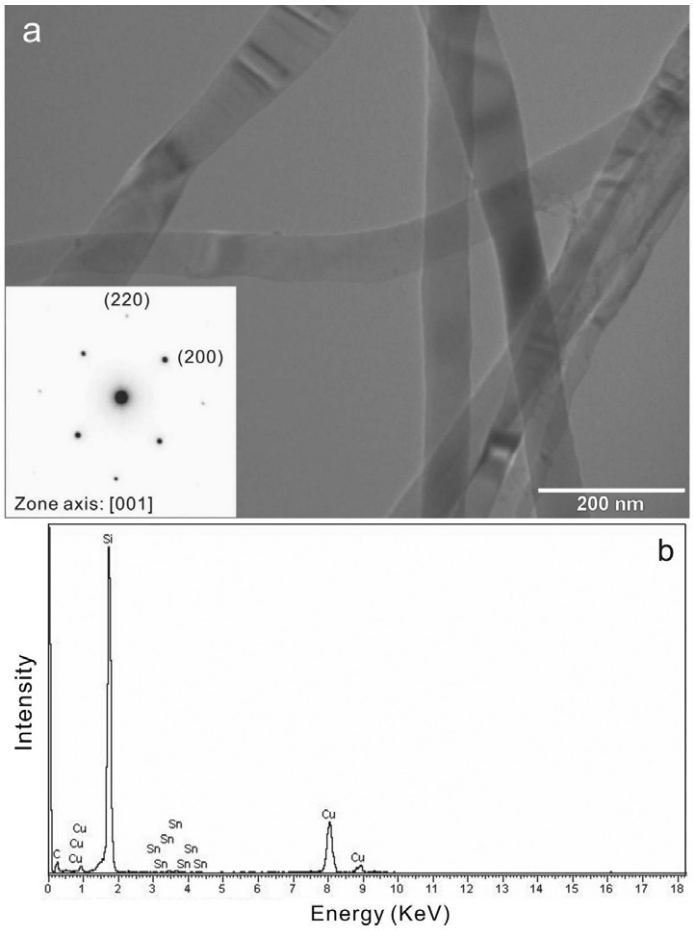

Figure 2. (a) A TEM image of the oxide-removed SiNWs. The inset is a SAED pattern of a SiNW. (b) An EDX spectrum of a typical SiNW.

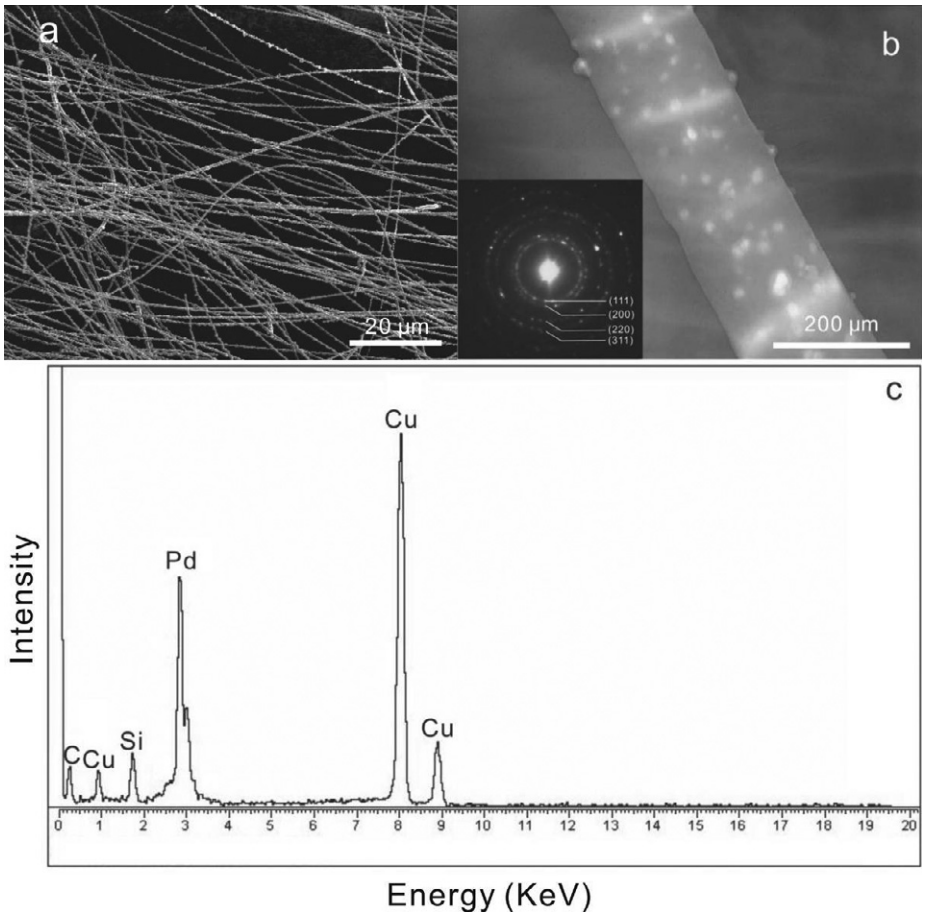

Figure 3. (a) A SEM image of Pd-functionalized SiNWs. (b) A TEM image of a Pd-coated SiNW. The inset is a SAED pattern of Pd nanoparticles on the surface of a SiNW. (c) An EDX spectrum taken from the nanoparticles in TEM.

similar to that reported by Wang *et al* [15]. The lengths of the SiNWs range from several tens to several hundreds of micrometres. A corresponding energy dispersive x-ray (EDX) spectrum in the inset confirms that the sample consists mostly of Si and oxygen. The transmission electron microscopy (TEM) images in figure 1(d) further confirm the structure of as-grown SiNWs are core-sheath.

The growth mechanism of synthesized SiNWs is considered as a combination of vapour–liquid–solid (VLS) and oxide-assisted growth (OAG). The Sn droplet at the tip shown in figure 1(b) is the evidence of VLS growth, while the silicon oxide sheath favours the OAG mechanism. Compared with traditional OAG-grown SiNWs, the length of these SiNWs can reach several hundred micrometres, and they are not easy to damage with HF treatment when removing the oxide sheath, which is a better choice for device fabrication.

After removing the oxide sheath with HF treatment, the SiNWs were observed with TEM. It can be seen from figure 2(a) that the oxide-removed SiNWs have uniform diameters. The inset in figure 2(a) is a selected-area electron diffraction (SAED) pattern of a typical SiNW, which confirms the single-crystal cubic silicon structure of the SiNW. EDX done in the TEM (figure 2(b)) shows that the composition of the nanowires is mainly silicon, with a trace amount of Sn and little O, which confirms the effective removal of the oxide sheath of SiNWs.

Pd-coated SiNWs were prepared by immersing the HF-treated SiNWs into a saturated $PdCl_2$ solution at room temperature. Pd^{2+} ions were reduced and Pd metal particles deposited onto the surface of SiNWs following the chemical reaction of $Pd^{2+} + 2Si{-}H \rightarrow Pd + H_2 + 2Si$. Figure 3(a) shows the SEM images of Pd-functionalized SiNWs. The TEM image in figure 3(b) is a high-magnification image showing a SiNW coated with Pd particles. The inset shows a SAED pattern of a Pd-functionalized wire which matches well with that of a face centred cubic (FCC) polycrystalline Pd structure. Figure 3(c) shows the corresponding EDX spectrum, which confirms the particles are Pd (Cu signals are due to the copper sample grid).

The present oxide-removed SiNWs show n-type properties due to point defects and surface states in Si surfaces, which lead to an accumulation of electrons in nanowires and thus enhances n-type conductivity. I–V characteristics based on a single SiNW and a Pd-coated SiNW are shown in figure 4(a). The conductance of the Pd-coated SiNW is smaller than that of the pure SiNW due to electron depletion at the Pd and silicon interface. The inset is a SEM image of an electrode of the device based on a single SiNW.

Figure 4(b) confirms the main transport channel in the present SiNWs are n-type. The inset image in figure 4(b) shows the transconductance measurement of the SiNW. The drain-source current increases with increases of positive

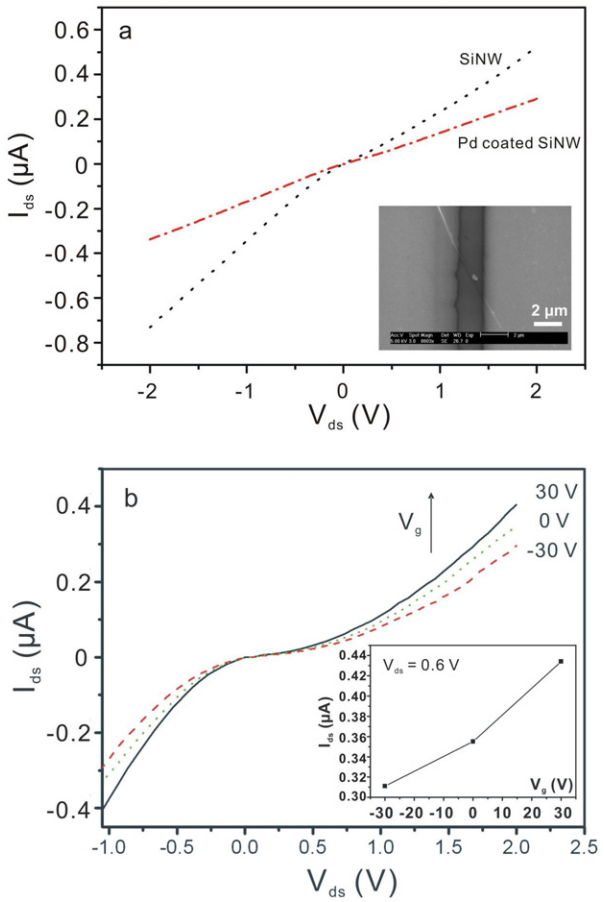

Figure 4. (a) I–V measurement for a single SiNW and a Pd-coated SiNW. The inset is the SEM image of a fabricated electrode device based on a single SiNW. (b) I–V measurement with different back gate voltages. The inset is the transconductance measurement of a single SiNW at 0.6 V of drain–source voltage.

gate voltage. The measurement demonstrates weak n-type properties because the thick silicon oxide layer (300 nm) may lower the effect of the back gate to the SiNW, leading to unobvious FET characteristics.

The Pd-functionalized SiNWs were dispersed onto a SiO_2/Si substrate to form a uniform thin layer of SiNWs (the inset of figure 5(c)). The sensor devices were fabricated by depositing gold electrodes through a shadow mask onto the sample. The device was put inside a chamber, which was then pumped to 10^{-2} Torr. The inset image in figure 5(a) shows the schematic diagram of the device and the chamber used in experiments. A direct current (DC) voltage of 2 V was applied across the two gold electrodes. A steady current of 1.7 μA was recorded. As Ar gas pre-mixed with 5% H_2 flowed in, the current increased abruptly from 1.7 to 40 μA, as marked by the arrow in figure 5(c). The effect of hydrogen on the conductivity was reversible. When hydrogen was replaced with pure Ar gas, the current sharply decreased to the background value. Pure SiNWs and SiNWs modified with Au nanoparticles showed no sharp current increase when 5% H_2 flowed in (figures 5(a) and (b)). No obvious signal change can be observed when 5% NH_3 or N_2O was fed onto the Pd-modified SiNWs device (figure 5(b)). This indicated that Pd-functionalized SiNWs had a selective sensing response to hydrogen. As shown in the

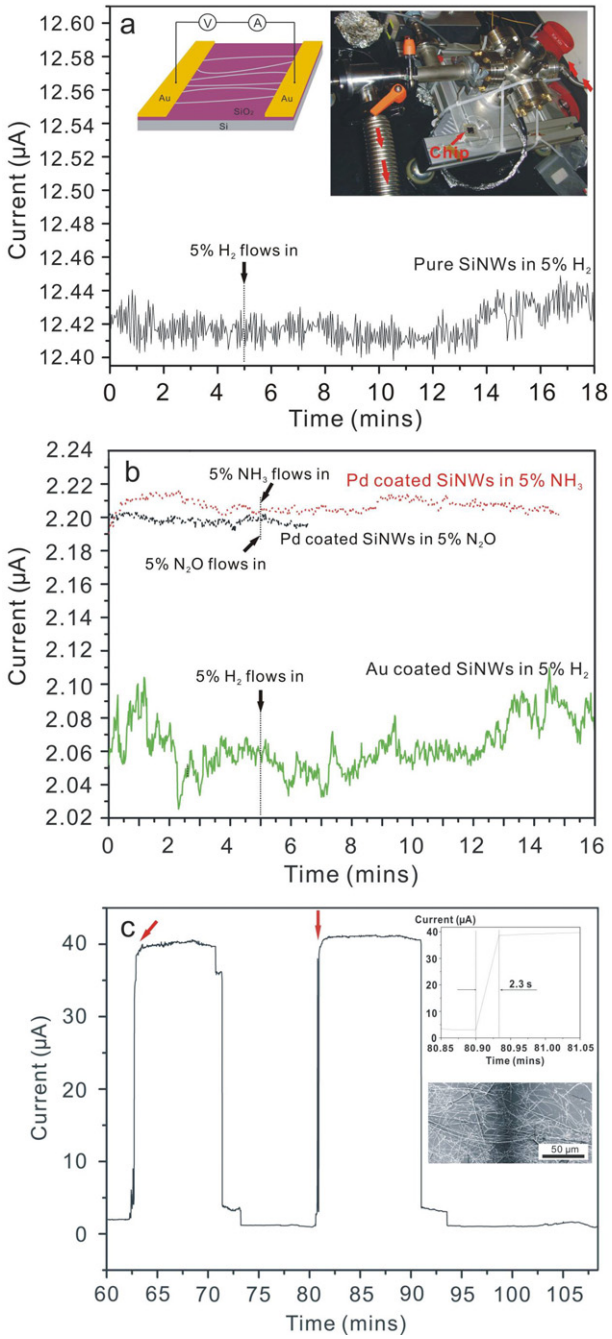

Figure 5. (a) Real time current response of pure SiNWs in 5% H_2. The inset shows a schematic diagram of the device and the chamber used in the experiments. (b) Current response of Au coated SiNWs in 5% H_2 and Pd coated SiNWs in 5% NH_3 and N_2O. (c) Real time current response of Pd coated SiNWs in 5% H_2. The inset images show the enlarged current response (upper) and a SEM image (below) of the device.

inset of figure 5(c), the rise time for signal saturation is only 2.3 s, which is much faster than a typical macroscopic Pd wire sensor [16], whose rise time is longer than 10 s.

The mechanism of the gas sensor can be explained by electron depletion (or even inversion) at the Pd/Si interface and consequently reducing electrical conductivity. At room temperature and atmospheric pressure, palladium can absorb up to 900 times of its own volume of hydrogen [17, 18].

Upon exposure to hydrogen, Pd will react with hydrogen to form hydride (PdH_x) rapidly. The Fermi level of PdH_x moves to a higher energy which is above the dense region of the d bands [19], which can bring up the Fermi level at the interface and result in the transition of electrons from Pd to SiNWs, returning it to more n-type behaviour. So depletion width is a critical parameter that controls how significant the Pd Fermi level shift can modulate the nanowire conductance. Due to the reversible reaction between Pd and hydrogen, PdH_x will release hydrogen quickly and lead to a decrease in conductance again. Compared with the back gate modulation in FET with a partition of thick silicon oxide layer, the coated Pd nanoparticles can modulate the conductance of SiNWs directly and more effectively.

4. Conclusion

SiNWs have been synthesized via thermal evaporation of SiO powder using Sn as the catalyst. The SiNWs were functionalized by metal Pd nanoparticles and fabricated into a hydrogen sensor. Upon exposure to 5% hydrogen, the current signal of the sensor increased by about 20 times. The response time was three seconds only, which is much faster than that of the macroscopic Pd wire sensor. Pd-functionalized SiNWs were shown to be a sensitive hydrogen sensor with a fast response time.

Acknowledgments

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