Silicon Nanowires with Permanent Electrostatic Charges for Nanogenerators

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ABSTRACT: Electrets are dielectric materials possessing a quasi-permanent electric charge or dipole polarization. Frequently, the electrets are adversely affected by environmental temperature and humidity, leading to charge instability, which severely restricts applications. Here we show that silicon nanowires (SiNWs) via modified oxide-assisted growth can surprisingly serve as electrets with permanent electrostatic charges and surface potential up to 7.7 mV. Significantly, the extraordinary electret behavior of SiNWs is extremely robust, remaining stable against immersion in water for over 2 months. The SiNWs were utilized to fabricate a nanogenerator, which yielded an output electrical power of 2.19 × 10⁻¹¹ W with a conversion efficiency of 2.2%. The nanogenerator consists of only one movable part, giving highly sustainable and stable output signals, and thus holds promise for various self-powered applications. The permanent electrostatic charges on SiNWs are attributed to the formation of α-quartz in SiNWs.

KEYWORDS: Nanogenerators, silicon nanowires, electret, alpha quartz

Nanogenerators find applications in various self-powered nanosystems, such as sensors, robotics, electromechanics, electronics, and tumor therapy.¹,² Use of nanogenerators in nanosystems would circumvent the need of external power resources (e.g., batteries) and related accessories (e.g., wires and re-chargers). To date, numerous nanogenerators have been fabricated based on nanostructures, such as ZnO nanowires,³,⁴ InN nanowires,⁵ lead zirconate titanate nanowires,⁶ poly(vinylidene fluoride) nanowires,⁷ or CdS nanowire.⁸ For practical applications, Si-based nanogenerators are particularly desirable. Here, we report the fabrication of a novel nanogenerator based on the extraordinary electret properties of silicon nanowires (SiNWs), which are already commanding intense interest due to their distinctive semiconducting, mechanical, and optical properties. SiNWs are readily prepared via numerous ways, such as the laser ablation method,⁹ thermal-evaporation oxide-assisted growth,¹⁰⁻¹² supercritical fluid solution-phase approach,¹³ and electroless etching.¹⁴ Among these approaches, thermal evaporation oxide-assisted growth is uniquely attractive because it is simple, produces a high yield, is impurity free, is catalyst free, and can be produced on a large scale.¹⁰,¹¹ Although many electrets have been obtained,¹⁵⁻¹⁷ the charges in them either are difficult to be injected or disappear/decay in air easily. Further, there has been no report on the fabrication of Si electrets. For practical use, Si electrets possessing stable charges are desirable for various applications. In this work, we modify the oxide-assisted method to enable the synthesis of SiNWs with permanent electrostatic charges and thus excellent electret behavior. The as-prepared SiNWs are fabricated into a nanogenerator, yielding an output electrical power of 2.19 × 10⁻¹¹ W at a conversion efficiency of 2.2%.

The synthesis of SiNWs with permanent electrostatic charges was conducted as follows: briefly, SiO powder (Aldrich, 325mesh, 99.9%) in an alumina boat was placed at the center of a horizontal alumina tube mounted inside a high-temperature tube furnace. The system was evacuated to a base pressure of 100 Pa. The furnace was heated to 1300°C at a rate of 40°C/min, kept at this temperature for 4 h, then cooled to 600°C at a rate of −1°C/min, kept at this temperature for 0.5 h, and subsequently cooled down to room temperature naturally. During the half hour at 600°C, 50 sccm (standard cubic centimeter per minute) of air was allowed to flow continually through the furnace. The products were collected on the internal surface of the alumina tube. The morphology of the as-prepared SiNWs was characterized by scanning electron microscopy (SEM) and atomic force microscope (AFM). To measure the surface potential distribution, electrostatic force microscopy (EFM) was employed to monitor concurrently the surface topography and local charge distribution on the SiNWs at the same position.¹⁸
measurements, a two-pass lift mode was introduced. In the first scan, topographical data were recorded with the tapping mode. The cantilever was then raised to the force scan position with a constant tip–sample distance, and the second force scan was performed as a response to the local electric fields. The detailed parameters of the EFM experiment are listed in the Supporting Information.

Figure 1 presents the AFM images of the SiNW topography and corresponding electrostatic force measured at room temperature in air, revealing the surface morphology and the charge patterns on the SiNWs, respectively. The SiNWs are numbered 1–5 successively, and the bright regions correspond to the height of the SiNWs (Figure 1a). The topological features of SiNWs shown in Figure 1a are similar to those described in previous reports,11–13 and the diameters of the SiNWs are in the range of 1.1–3.7 nm (Figure S1, Supporting Information) with lengths of 1.4–3 μm.

Surface potential mapping of SiNWs by EFM image is shown in Figure 1b. Patterns of EFM signals in bright and dark segments can be observed, corresponding to the presence of positive and negative charges on SiNWs. Figure 1b shows all SiNWs are charged with positive and/or negative charges: SiNWs 1, 3, and 5 are mainly negatively charged with a few positive charges, while SiNW 2 is mainly positively charged. In particular, the largest potential difference is detected on SiNW 4, on which the maximal surface positive and negative potentials are +7.7 and −6.8 mV, respectively, according to the typical section analysis (in blue) of the EFM measurement shown in Figure S3 (Supporting Information). The potential analysis suggests that the distribution of space charge on SiNWs has no relationship with their morphology, and the large potential gap of 14.5 mV indicates different charged spots in the single SiNW 4. Remarkably, the electrostatic charges on the SiNWs remained stable after 1 year of storage under ambient conditions or 2 months of storage in water, which were certificated by the EFM images shown in Figure S4 (Supporting Information), signifying the superior stability of the electret behavior of the SiNWs.

The as-prepared SiNWs were fabricated into a nanogenerator with the experimental setup shown in Figure 2a. The SiNWs were fixed on an aluminum plate with diameter of 13.2 mm and thickness of 0.8 mm. An aluminum membrane with thickness of 5 μm was installed above the SiNWs. The distance between the SiNWs and the Al film was set to 5 μm using Teflon tape as the insulating spacer. Electrodes were connected to the aluminum film and plate, respectively. Then the assembled device was mounted 1.5 cm away from a metal sound fork with an operation frequency of 440 Hz. The output current as response to the vibration was collected by an external circuit at room temperature with a Keithley 4200-SCS semiconductor characterization system.

The equivalent circuit of the nanogenerator based on the as-prepared SiNWs is illustrated in panels b–d in Figure 2, in which the device can be regarded as a flat-panel capacitor with capacitance of \( C = \epsilon S/d \), where \( \epsilon \) is the spacer dielectric constant, \( S \) is the effective capacitor area, and \( d \) is the inter-spacing distance. As the charges in the SiNWs are fixed, a finite electrostatic potential \( (V_0) \) relative to the grounded Al membrane should be built up. When the sound fork is stationary, the Al membrane remains steady (Figure 2b), in which the induced counter charge quantity \( Q \) follows \( CV_0 = Q \). In this case, only the background noise current \( I \) (≈6 fA) can be detected. When the sound fork is vibrating, the Al membrane will be vibrating as well. As a consequence, \( d \) and hence \( C \) are changed alternately. Upon reduction of \( d \), more \( Q \) will be induced in the Al membrane, resulting in a transient current as schematically depicted in Figure 2c, and vice versa as depicted in Figure 2d. A continuous alternate current can therefore be generated in the circuit as shown in Figure 3. The average absolute current is about 2.8 nA with a large signal-to-noise ratio of about 40000. In contrast, no current response was observed in the reference device without SiNWs using the identical device structure (Figure S5, Supporting Information), indicating the charged SiNWs are responsible for the current generation in Figure 3. Therefore, this SiNW-based nanogenerator can be an excellent candidate for the applications involving vibrational to electrical energy conversion.

The efficiency of the electrical power generation by the SiNWs-based nanogenerator can be calculated as follows. The output electrical power is \( IV_0 = 2.19 \times 10^{-11} \) W, where \( I \) is the average absolute current in Figure 3 and \( V_0 = Q_0/C \) where \( Q_0 \) and \( C \) are determined by the simple plot in Figure S6 (Supporting Information). The vibrational energy of the sound generated by
the fork was measured by a sound level meter. Taking into account the device active area, the input sound power is $9.9 \times 10^{-10}$ W. Therefore, the efficiency of converting sound energy to electrical energy is $2.19 \times 10^{-11}/(9.9 \times 10^{-10}) = 2.2\%$ (Supporting Information). This efficiency could be further improved by the optimization of device structure, and the SiNWs-based nanogenerator is uniquely attractive in respect of its simplicity and robustness.

The mechanism of energy conversion is attributed to the unique structure of the SiNWs, i.e., the presence of $\alpha$-quartz. A part of the SiNW core is converted to $\alpha$-quartz due to the reaction with oxygen during the annealing at 600 °C. The oxidized silicon is expanded 88% in volume in forming $\alpha$-quartz, while the outer amorphous silica layer remains unchanged or little changed. The expansion of the $\alpha$-quartz is thus restrained by the volume confinement, consequently leading to the local piezoelectric effect. Significantly, the amorphous silica shell is also a component of the electret because of its charge storage capability, as schematically shown in Figure 4a. As the $\alpha$-quartz is fully covered with the amorphous silicon oxide, the SiNWs with electrical charges could exhibit stable electret behavior. In the common oxide-assisted method, no air was introduced in the preparation; the obtained SiNWs, though covered by an oxide layer, did not exhibit electret behavior.

Raman spectroscopy, X-ray powder diffraction pattern (XRD), Fourier transform infrared (FTIR) spectroscopy, and high-resolution transmission electron microscopy (HRTEM) were performed to characterize the structure and components of the products. Curve 1 in Figure 4b is the Raman spectrum of the as-prepared SiNWs prepared by the conventional methods, showing the characteristic peaks of SiNWs (see detailed discussion in the Supporting Information). The Raman spectra of the as-prepared SiNWs (curves 2 and 3 in Figure 4b) show the distinct fingerprint peaks of $\alpha$-quartz at 1161, 795, 460, 395, 352, 254, 184, and 118 cm$^{-1}$, which are in excellent agreement with the previous report.$^{19}$

Quartz has been extensively investigated in the infrared due to its scientific and technological importance.$^{20}$ Figure 4c is the ATR-FTIR spectra of SiNWs, with the enlarged one shown in the inset part. From the spectrum of normal SiNWs (curve 1, Figure 4c), only two Si–O vibrations at $\sim$1050 and $\sim$800 cm$^{-1}$ were observed, which have been reported elsewhere.$^{21}$ The presence of $\alpha$-quartz is revealed through its characteristic IR peaks at 707, 1097, 1135, 1170, 1204, and 1630 cm$^{-1}$, which were assigned to the $A_2$ or $E$ modes, or vibrational modes of Si–O–Si, respectively (curve 2, Figure 4c).$^{20,22–25}$ In addition, the peak at $\sim$1420 cm$^{-1}$ could not be assigned to any Si–O mode, but it can be regarded as the characteristic band of $\alpha$-quartz.$^{23}$

The XRD pattern (Figure 4d) shows the characteristic diffraction peak of $\alpha$-quartz at 26.6°, indexed as (01–11) (JCPDS CARD 85-0798). The HRTEM image shows two sets of lattice fringes with a spacing of 0.33 nm (Figure S7, panels a and b, Supporting Information) indexed as (10–11) and (–1011) planes, and another set with a spacing of 0.25 nm (Figure S7, panels c and d, Supporting Information) corresponding to (11–20) crystal plane, and these lattice spacings are in close agreement with those of the quartz crystal (JCPDS CARD 85-0798). Taken together, the Raman, FTIR, XRD and HRTEM results convincingly confirm the existence of $\alpha$-quartz in the SiNWs.

In summary, SiNWs with permanent surface charges and electret behavior were synthesized, and the electret property arises from the formation of $\alpha$-quartz covered by the amorphous silica shell in the SiNWs. The SiNWs are fabricated into a nanogenerator yielding an energy conversion efficiency of 2.2%. The nanogenerator is simple with only one movable component, which ensures the robust sustainability and stability of the output electrical signals. Optimization of the nanogenerator via nanofabrication, such as patterning SiNWs with controlled spacing and alignment, is expected to yield significant performance improvement and promising applications.

ASSOCIATED CONTENT

Supporting Information. Description of the EFM experimental details, electrical capacitance, conversion efficiency, the response current without SiNWs, and HRTEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES


