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Direct mechano-sliding transfer of chemical vapor deposition grown silicon nanowires for nanoscale electronic devices[†]

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Silicon nanowires (SiNWs) have been widely used in the new generation of nanocircuits. In order to establish efficient and reliable fabrication procedures of one-dimensional nanowire devices, controllable assembly of SiNWs is a key challenge. Although various methods have been reported to assemble SiNWs, they brought unexpected problems, such as low efficiency, chemical contamination or high-cost. Here, we demonstrate a mechano-sliding strategy to directly transfer chemical vapor deposition (CVD) grown SiNWs in a solvent-free, fluid-free, and lubricant-free manner with a highly simplified operation. The distribution density of the transferred SiNWs can be controlled by pressure, so that single- or multi-nanowire FET devices for high-sensitivity biological detection or high-density arrays can be obtained. The fabricated device exhibited excellent surface charge response characteristics and chemical modification versatility. These advances pave the way for a feasible, efficient and low-cost approach to fabricate SiNW-based biosensors as a general and powerful platform for chemical detection and biological detection.

Introduction

Semiconductor nanowire materials offer great application possibilities in electronic and optoelectronic circuits $^{1-3}$ and

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directed alignment and an appropriate density distribution of the nanowires for the further nanofabrication process.^{11,12} Considerable efforts have been devoted to improving the nanowire-transfer assembly, such as fluid assisted alignment of micro-channel fluidics assembly,13-15 Langmuir-Blodgett film,16-18 the blown bubble method,19 the electric/magnetic field induced alignment method,²⁰⁻²² mechanical printing²³ and nanoscale combing.²⁴ These methods, however, require large quantities of nanowires and are technically demanding. As for fluid assisted or electric/ magnetic field induced transfer, the nanowires are subjected to two transfer steps, from a grown substrate to a fluid and then from the fluid to a receptor substrate. The remaining problems in each transfer step, such as reunion and instability, make the transfer process less efficient. While most already existing direct contact transfer methods utilize chemically treated receptor substrates to enhance immobilization of the nanowires, or lubricants to assist the alignment, either of them has an unexpected effect of contaminants for further chemical and biological modification processes. Various types of patterning processes for nanowire assembly were recently introduced to obtain a specific assembled geometry or orientation.^{25,26} However, they need well-designed auxiliary means such as solution evaporation or stripping surface patterns, which have limited scalability as they require setting new experimental parameters such as the solution concentration or the surface coating thickness for different one-dimensional nanostructures. In addition, to obtain single-nanowire devices, electrode fabrication requires an elaborate electron beam lithography (EBL) process,^{14,24} which is more expensive and less effective than the conventional photolithographic writing process. Consequently,

biosensing.4-6 The controllable and scalable assembly of the nano-

wires has posed new challenges and opportunities in the develop-

ment and improvement of the nanodevice fabrication process. Most

fabrication procedures, except for a few cases of in situ grown^{7,8} or

etching-prepared^{9,10} nanowires, involve a transfer step to achieve

efforts are continuing to advance the nanowire transfer process. Our previous studies have achieved ultrasensitive detection of gas,²⁷ single influenza H1N1 viruses,²⁸ DNA hybridization

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dynamics,²⁹ and single nucleotide polymorphism genotyping³⁰ using single-nanowire-based field-effect transistors (FETs). However, these were fabricated using a complex and timeconsuming fluid assisted process for the nanowire transfer.¹⁵ In order to improve the transfer efficiency, overcome the contamination problem, and simplify the fabrication process, we demonstrated herein a highly simplified and effective method to directly transfer chemical vapor deposition grown silicon nanowires via a solvent-free, fluid-free, and lubricantfree mechano-sliding process. This process is based on direct physical interaction between nanowires and substrates without any auxiliary means and thus applicable to other onedimensional nanostructure assembly. The distribution density of the transferred nanowires can be controlled by applying an appropriate pressure on the grown substrates, so that we can obtain single- or multi-nanowire devices, which are expected to be applied in high-sensitivity biological detection²⁸⁻³² or highmultidensity application in thin-film transistors,³³ nanochannel FETs³⁴ and nanowire arrays.³⁵

Results and discussion

Direct mechano-sliding transfer of SiNWs

As shown in Fig. 1a, the substrate with vertically grown SiNWs (Fig. 1a-i; Fig. 1b) was put upside down on the marked region of a receptor substrate (Fig. 1a-ii). Without a vertical pressure, SiNWs under the grown substrates will not (or rarely) fracture under their negligible gravity, and there is an obvious adhesion force interaction between the grown substrate and the receptor substrate (the grown substrate will not slip even when vertically tilting the grown and receptor substrates close to 90°). Then, we gently pushed the grown substrate horizontally forward using a tweezer (Fig. 1c), and this could make the longer SiNW fracture and lay down on the receptor substrate along the sliding orientation (Fig. 1a-iii). Compared with a previous timeconsuming fluid assisted transfer process, the direct mechano-sliding transfer (DMST) can be completed in only a few seconds. Another significant advantage of DMST is that, for each time, only a fraction of SiNWs are subjected to be transferred, thereby allowing the reuse of the grown substrate. As CVD grown SiNWs are extremely energy- and timeconsuming, the reuse of them produces a significant improvement in the device fabrication efficiency and a reduction in cost.

Although the diameters of SiNWs (20–40 nm) we synthesized here were beyond the resolution limit of an optical microscope, a clear shadow of each SiNW could be resolved due to light scattering and absorption with tens of micrometers in axial length (Fig. 1d–f). This suggested an efficient and convenient approach to check the results of each DMST operation and assess the distribution density and orientation of the transferred SiNWs after each step. Generally, most of the SiNWs were distributed uniformly and aligned along the sliding orientation. Only a few distorted or fractured SiNWs were distributed disorderly, which may generate from the non-linear growth and

irregular fracture of SiNWs on the grown substrates. Also, the effect or interference of them can be minimized using the subsequent region-protecting technique and mature transfer operation. According to different applications of the devices fabricated by SiNWs, the transferring effect of SiNWs is able to be evaluated by their distribution. For distributions that do not meet the proposed requirements (e.g., too less dense or too short), the transferred SiNWs could be removed from the substrates by dust-free tape or ultrasonication so as to regenerate clean silicon wafers. In the case of fluid assisted transfer used in previously reported work, polydimethylsiloxane (PDMS)-based narrow channels were required to flow hundreds of microliters of ethanol suspension of SiNWs for about 30 min. Then, a receptor substrate with 3-aminopropyltriethoxysilane (APTES) surface functionalization was used to strengthen the adhesive interaction between SiNWs and the substrate to anchor them with an appropriate distribution.²⁸ This distribution effect could also be attained by DMST in a few seconds, and each grown substrate can be reused for three to five times without surface chemical treatments, thereby greatly improving the transferring efficiency, surface cleanliness and material utilization. Noteworthily, the transferred SiNWs on the receptor substrate by DMST the first time were significantly less than the second or third time (Fig. 1d-i-iii). The initial transferred SiNWs were relatively sparse but long, because these grown SiNWs initially contacting with the receptor substrate were the longest, which were relatively less and might slide and be transferred in priority. The number of fragmentized SiNWs increases with the transfer times (Fig. 1d-iii-v), and at the time of Fig. 1d-v, the grown substrate needs to be replaced with a new one for the next device fabrication. Fig. 1e-ii show that, after DMST, there remained considerable amounts of SiNWs on the grown substrate, which are distributed in accordance with the sliding orientation. For the receptor substrates with an optimal location of the transferred SiNWs, region-protecting photolithography was carried out (Fig. 1a-iv and 1f-i). The region where the source and drain electrodes are connected by SiNWs was protected by photoresist deposition, and the redundant SiNWs were removed by ultrasonication in deionized water (Fig. 1a-v and 1f-ii). After photoresist lift-off by rinsing with acetone, metal electrodes were fabricated by photolithographic writing and Cr/Au thermal deposition to obtain SiNW-FET devices (Fig. 1a-vi and Fig. S2, ESI⁺).

Density control of the transferred SiNWs

This DMST strategy could also realize density control of the transferred SiNWs on the receptor substrates by applied pressure (Fig. 2a and b). The extra pressure can be provided from different weights, which are anchored on the grown substrates with a hauling string between them. Then, the hauling string was pulled to hold a constant speed ($\sim 1 \text{ cm s}^{-1}$) of sliding the grown substrates for the transfer process. Different pressures applied on the grown substrates could adjust the density of SiNWs on the receptor substrates and change the number of SiNWs connected between each drain-source electrode gap (Fig. 2c). When the pressure originated from the self-gravity

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Fig. 1 Schematic of DMST of CVD grown SiNWs and fabrication of SiNW-FET devices. (a-i and b) Grown substrates of SiNWs. (a-ii and c) DMST of the SiNWs from a grown substrate to a receptor substrate. (a-ii) Transferred SiNWs aligning along the sliding orientation on the receptor substrate. (a-iv and f-i) Region-protecting photolithography of SiNWs *via* covering the electrode region by a photoresist. (a-v and f-ii) Removal of the redundant SiNWs out of the photoresist region by ultrasonication. (a-vi) Electrode fabrication on the SiNWs. (d) Optical images of SiNWs on receptor substrates after DMST five times, respectively. (e) Optical images of SiNWs on a grown substrate before (i) and after (ii) DMST.

of the grown substrate (5 Pa), the single-nanowire connection can attain an overall rate of $\sim 80\%$ from the statistics of the 50 devices (Fig. 2d), which also indicates that the optimal lower density of SiNWs matched to the electrode spacing is important for achieving a high yield of single-nanowire devices. When a higher pressure was applied, the density of SiNWs on the receptor substrates was gradually improved so as to fabricate density-controllable SiNW-FET devices (Fig. 2e). Likewise, with a constant density of SiNWs, the improvement of the connection number could also be achieved through fabricating wider electrodes. The width of the electrodes is able to broaden at the centimeter scale until attaining the distribution width of the transferred SiNWs, that is, the width of the grown substrates. Although these multi-nanowire devices enhance the background current and generates multiple sites for binding molecules, which are not of benefit to the sensitivity and reliability for single-molecule real-time detection, they are expected to exhibit excellent performance and low fabrication cost for the application of energy storage or sensing in ensemble measurements.

Electrical characteristics and detection

The basic electrical properties of these SiNW-FET devices with single- or multi-nanowires were characterized (Fig. 3). The drain–source current ($I_{\rm DS}$) versus voltage ($V_{\rm DS}$) for several gate voltages ($V_{\rm GS}$) exhibited a linear behaviour in output curves for the single-nanowire devices, which indicated that metal electrodes make a good ohmic contact with the nanowires. A high ratio of $I_{\rm on}/I_{\rm off}$ of ~ 10^3 – 10^4 in transfer characteristic curves confirms the excellent current regulation capacity and high gating sensitivity. It is in these single-nanowire devices that we have established covalent modification on their surfaces with receptors to realize a series of real-time and ultrasensitive biological detections at the single-molecule level.^{28–30} For the

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Fig. 2 Transfer of SiNWs with controlled density by pressure adjustment. (a and b) Schematic of the pressure adjustment by setting different weights on grown substrates. The grown substrates under various weights were pulled using a hauling string. The weight, grown substrate and hauling string were pasted by adhesive tapes. (c) Density of SiNWs between each column of the electrode and the number of SiNWs between each drain–source electrode under different pressures. Five devices were fabricated by DMST. (d) Statistics of total and single-nanowire connection after DMST with the self-gravity of the grown substrate. (e) SiNW-FET arrays with different densities of SiNWs obtained by the pressure adjustment in DMST.

multi-nanowire devices, the typical gate-dependent currentvoltage curves are nearly linear but tend to exhibit the electrical properties of the cumulative conductance effect according to the connection numbers of SiNWs (Fig. 3b). The $I_{\rm on}/I_{\rm off}$ ratio of these multi-nanowire devices remains at ~10³-10⁴ while $I_{\rm on}$ becomes larger with the increase of the connection number (Fig. 3c). These results demonstrated high quality reservation of each SiNW without electrodes fabrication interference generated in the DMST process.

The rich diversity of the chemical/biological surface modification and the ultra-sensitivity of the surface charge enables SiNW-FETs to be constructed as sensors with molecular receptors and be regulated through accumulation or depletion of carriers in entire nanostructures, which can be electrically real-time monitored by conductance changes. To assess the sensing properties of SiNW-FETs fabricated by DMST, we modified the single-nanowire devices with APTES (Fig. S3a, ESI†), which can introduce a protonation or deprotonation process on the SiNW surface to chemically gate the conductance, in acidic and alkaline conditions, respectively.³⁴ Solutions of varying pH are sequentially drawn through a PDMS based microfluidic channel using a syringe pump while monitoring the conductance of the modified SiNW-FETs (Fig. 4a and Fig. S4, ESI†). The transfer characteristic curves exhibited a well-defined deviation to the left with a change in pH from 8.0 to 6.0 (Fig. 4b), indicating an electric field shift from negative to positive resulting from a more intense protonation process on the SiNW surface. Real-time current recording of the



Fig. 3 Electrical measurements of SiNW-FET devices with single- or multi-nanowires. (a) Scanning electron microscopy images of the single- or multi-nanowire device, respectively. (b) Family of source-drain current (I_{DS}) versus source-drain voltage (V_{DS}) plots at different gate voltages (V_{GS}) of -10 V to 10 V at an interval of 2 V (as follow the direction of arrow) for single- or multi-nanowire devices, respectively. (c) I_{DS} versus V_{GS} plotted on linear (black) and logarithmic (blue) scale at a V_{DS} of 0.3 V for the single- or multi-nanowire devices, respectively.

SiNW-FETs also exhibited a stepwise decline with a pH decrease in linear dependence (Fig. 4c), suggesting a feasible pH sensor constructed from the APTES-modified nanowire. The horizontal deviation of the transfer characteristic curves and long-duration real-time current recording under different pH conditions indicated the excellent sensing sensitivity and working endurance of these fabricated sensing devices. In addition, biological modification was conducted on these single-nanowire devices to realize surface functionalization and assess the biological sensing properties. The hairpin DNA terminated with an amine group was incorporated into the surface of the APTES-modified device using glutaraldehyde as a linker (Fig. S3c, ESI⁺). The transfer characteristic curve shows a welldefined deviation to the right, indicating that a negative electric field originated from the electronegative DNA was applied on the SiNW. This DNA-functionalized device can provide a platform with the opportunity to confront challenges in DNA hybridization²⁹ and genotyping.³⁰ These results demonstrated the excellent surface charge response characteristics and surface modification versatility of SiNW-FETs fabricated by the DMST, with the superiority of costefficiency and high productivity in comparison with the previous work.36

Conclusions

In summary, we have proposed an elegant strategy based on DMST for transferring CVD grown SiNWs to receptor substrates. This DMST strategy enables the transferred SiNWs to disperse uniformly in an appropriate region of the substrate and avoids direct contact contamination between in situ grown SiNWs and chemical reagents. Therefore, it guarantees the cleanliness of the SiNW surface so as to prevent subsequent surface functionalization from chemical inferences. In addition, this novel strategy improves the single-nanowire connection with a remarkable overall rate of $\sim 80\%$ by applying optimal pressure in DMST and allows the density control of SiNW-FET devices. In particular, photolithographic writing, rather than EBL techniques, was applied to fabricate electrode patterns, which permits immense simplification and costsaving of the device fabrication process. Convenient optical microscope imaging could as well allow the evaluation of the result of each transfer operation. Finally, considering the convenience and practicability of DMST, this advanced nanofabrication strategy opens up a promising avenue for both



Fig. 4 pH detection and DNA functionalization of a single-nanowire device. (a) Schematic of the PDMS microfluidic channel on the single-nanowire device for solution loading. (b) Transfer characteristic curves of APTES-modified devices at different pH values ($V_{DS} = 0.3 \text{ V}$). (c) Real-time current detection of APTES-modified devices at different pH values ($V_{DS} = 0.3 \text{ V}$). (c) Real-time current which exhibits a linear dependence with a sensing sensitivity of 57.8 mV/pH. (d) Transfer characteristic curves of the devices before (black)/after (blue) DNA modification, respectively.

academic research and industrial manufacturing, including exploration of the physical properties of new one-dimensional materials or large-scale application of industrially relevant materials.

Author contributions

X. G. and L. L. conceived, designed and supervised the work. D. Y. and J. L. fabricated the devices and performed the device measurements, with contributions from W. L., Z. Y., S. L. and M. L. J. L., D. Y., J. F. and X. G. analysed the data and wrote the manuscript. All the authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts of interest to declare.

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