Air-Bridged Ohmic Contact on Vertically Aligned Si Nanowire Arrays: Application to Molecule Sensors

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For the last few years, nanowires have attracted enormous attention due to fundamental scientific importance\[^1-3\] and also to promising technological potential.\[^4-8\] Vertically aligned nanowires over an extended area have been considered as ideal platform for developing the advanced devices for energy harvesting and storage, molecule sensing, and information storage, because vertical configuration of nanowires offers distinct merits over lateral one in terms of the utilization of surface area and the integration density of individual active nano-components (i.e., nanowires).\[^9\] However, to date, the commercialization of such devices has been very limited due to the difficulties involved in integration of vertical nanowires into electrically conducting parts over technologically relevant scale. A number of approaches have been explored over the years to develop a method of construction for mechanically stable and electrically reliable top electrical contact to the vertically aligned nanowires. As one of the most frequently employed method, top electrical contacts on vertical nanowire arrays were formed by sputter deposition of metal on partially exposed tips of nanowires that were embedded in a polymer matrix, in which an insulating polymer prevents possible short-circuiting between the substrate and the top metal electrode.\[^10-13\] However, this approach has a drawback in terms of utilization of the large surface area of nanowires and the air gap formed by densely aligned nanowires, since the entire surfaces of nanowires are completely covered by a polymeric material. In an attempt to overcome this issue, fabrication methods for air-bridged electrical contacts (i.e., suspended metal interconnection) to vertically aligned nanowires have been recently explored.\[^14-16\] However, most methods reported in recent literatures also have inherent problems associated with the complete molding of aligned nanowires with photoresist (PR) material prior to a series of lithography processes. Moreover it is rather difficult to adopt the reported methods, especially when the diameter of nanowires is far smaller than 100 nm and/or the density of nanowires is considerably high. Herein, we report a general approach to an air-bridged Ohmic contact on extended arrays of vertically aligned silicon nanowires (SiNWs) without any assistance of time-intensive and serial lithographic processes. The key of our approach is to form a thin suspended polymer layer on the uppermost part of vertical SiNWs. We utilized the resulting suspended polymer layer as a deposition barrier for realizing a stable air-bridged top metal contact by sputter deposition of metal. We showed that our approach can be successfully implemented to fabricate nanowire-based molecule sensors.

Single crystalline [100] SiNWs used in the present work were prepared by wet chemical etching of (100)-oriented p-Si wafers (B-doped, \(\rho = 1 - 10 \, \Omega \text{cm}\)) using 25 nm-thick gold mesh with ordered arrays of nanoholes as etching catalyst (see Experimental Section).\[^17-19\] In general, vertically aligned SiNWs formed by metal-assisted chemical etching (MaCE) of silicon undergo a significant bundling upon drying in air due to strong surface tension exerted on the solid nanowires during the evaporation of liquid medium (i.e., \(\text{H}_2\text{O}\)) (see Figure S1 in Supporting Information). Degree of nanowire bundling increases as the aspect ratio (i.e., the length divided by the diameter) of SiNWs increases. This would greatly limit the practical applications of SiNWs to the development of the advanced devices that are based on vertically aligned nanowires. We could overcome this problem by employing supercritical point drying technique, which has been widely used in preparation of aerogel, aligned nanowires, and biological specimens for electron microscopy as well as in microelectromechanical system (MEMS) technology.\[^20-23\] By eliminating surface tension by means of supercritical fluid of \(\text{CO}_2\), we were able to obtain vertically aligned [100] SiNWs over the entire sample area. Figure 1 shows typical scanning electron microscopy (SEM) images of a SiNW sample after the supercritical \(\text{CO}_2\) drying process. The density of SiNWs of the present sample was estimated to be \(\sim 10^{10} / \text{cm}^2\). It is apparent from Figure 1a,b that all the SiNWs (diameter \(\sim 40 \, \text{nm}\)) are vertically aligned without any appreciable formation of nanowire bundles in spite of high aspect ratio (ca. 120) of nanowires. In fact, we found that supercritical \(\text{CO}_2\) drying process can be successfully applied for the vertical alignment of ca. 100 \(\mu\text{m}\)-long SiNWs (aspect ratio \(\sim 2500\)) (see Figure S2). Cross-sectional SEM images of the sample indicate that individual nanowires have well-defined tips, smooth surfaces, and uniform diameters along their axes without showing tapered morphology (Figure 1c,d).

To create a stable and reliable air-bridged top electrical contact to the vertical nanowires, we developed a generic approach that involves the formation of a thin suspended layer of polymer on the upper most part of vertical nanowires and the subsequent utilization of the polymer layer as a deposition barrier.

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Figure 2. Fabrication process of air-bridged top metal contact on vertically aligned SiNWs; (a) formation of thin suspended layer of polystyrene (PS) on the uppermost part of vertical SiNWs, (b) partial removal of PS layer by oxygen plasma etching to expose the tips of SiNWs, and (d) sputter deposition of gold for electrical contact. SEM images of the corresponding sample structure are presented on the right side.

Figure 1. SEM images of extended arrays of vertically aligned [100] SiNWs obtained by metal-assisted chemical etching (MaCE) of Si(100) wafer by using a gold mesh as an etching catalyst; (a) plan-view and (b) cross-section view. (c,d) Magnified cross-sectional SEM images of SiNWs taken near the tips and the bottoms of vertical nanowires, respectively.

for sputter deposition of electrode materials. Figure 2 shows a schematic outline of the experimental procedure for construction of air-bridged Ohmic contact on vertically aligned SiNWs (left column) and SEM images of the corresponding sample structures (right column). About 1.3 μm-thick polystyrene (PS) (M. W. = 3.5 × 10^4 g/mol) film was spin-coated on a mirror-finished aluminum foil and then brought into contact with the surface of the nanowire sample that was preheated to the glass transition temperature (T_g = 101 °C) of PS. Subsequently, a pressure (∼10 N/cm^2) was applied for 10 s in order to allow the polymer in a high-elastic state to be slightly impregnated into the free-space formed by the tips of vertically aligned SiNWs. Typical depth of PS impregnation under the present condition was estimated to be ca. 800 nm. It should be mentioned here that the temperature of nanowire sample needs to be maintained at or just slightly above T_g of PS during the impregnation process. PS impregnation performed at temperatures well above T_g of PS, where the polymer chains become sufficiently mobile, resulted in complete bottom-up filling of the interspaces between vertical SiNWs by polymer (see Figure S3). This phenomenon can be attributed to spontaneous spreading of organic polymer with a low surface energy over an inorganic solid material with a high surface energy in order to minimize the associated total free energy, as it typically occurs in capillary force lithograph (CFL) or wetting of nanoporous templates by melt-processible polymers (i.e., thermoplastics). After partial impregnation of PS film, the sample was immersed into a mixture solution of CuCl_2 and HCl to remove the aluminum foil. The tips of SiNWs of the resulting sample were tightly fixed by the suspended PS film to maintain the vertical alignment of nanowires, ensuring large fraction of air-gap (i.e., free-space) between individual SiNWs (Figure 2a). Suspended PS film was etched from its surface by performing oxygen plasma treatment until individual tips of SiNWs were partially exposed (Figure 2b). Subsequently, 200 nm-thick gold layer was sputter-deposited on the surface of the resulting nanowire sample (Figure 2c). In this process step, the suspended PS film plays an important role in preventing undesired contamination of the nanowire surfaces by sputter-deposited metal. In other words, the polymer layer acts as a deposition barrier. When we directly deposited metal either on an aligned nanowire sample without PS deposition barrier or on a bundled nanowire sample, we were not able to obtain a reliable air-bridged top metal contact. The entire surface of SiNWs along their axial directions was found to be heavily contaminated with sputter-deposited material (see Figure S4).

In the present work, we chose gold as an electrical contact material, because gold is known to form small energy barrier for charge carrier diffusion with p-type silicon, thus make an effectively Ohmic contact. In order to verify the reliable electrical contact between the sputter-deposited metal and the tips of individual SiNWs, we measured current (I) - voltage (V) characteristic of the nanowire samples. Figure 3 presents I–V characteristics measured from a single [100] p-SiNW (Figure 3a), arrays of vertically aligned [100] p-SiNWs with an air-bridged top metal contact (red dot trace in Figure 3b), and a bulk p-Si(100) wafer (black square trace in Figure 3b) for comparison. The linear I–V curves shown in the figures clearly manifest the
defined gold electrodes (inset of Figure 4a). Figure 4 presents typical electrical responses of (a) a single SiNW-based sensor and (b) vertical SiNW array-based sensor to periodic switches of O$_2$ gas at room temperature; O$_2$ exposure interval = 2 min. for (a) and 1 min for (b). False colored SEM images of the corresponding sensor are shown as respective insets.

Figure 3. (a) I–V curve of a single [100] $p$-SiNW, together with an SEM image of the corresponding nanodevices as an inset. (b) I–V curves of arrays of vertically aligned [100] $p$-SiNWs with an air-bridged top Au contact (red dot trace) and a bulk $p$-Si(100) wafer (black square trace). The inset in (b) presents a schematic illustration of measurement configuration.

Ohmic nature of the electrical contacts between the metal and silicon in all of our samples. The resistivity of a single SiNW was estimated to be $\rho = 15.6$ $\Omega$ cm, which is comparable to that of the starting silicon wafer used for SiNW preparation, indicating high quality of nanowire. Note also that our vertical SiNW array sample exhibited almost a comparable electrical conduction to that of a bulk silicon wafer (Figure 3b), manifesting that the tips of individual SiNWs form a good electrical contact with the air-bridging gold layer and thus each nanowire acts as a well-defined channel for carrier transport. The present experimental results indicate undoubtedly that various types of nanowire-based devices with technologically relevant scales can be effectively realized by our approach.

In order to demonstrate practical application of our method, we fabricated chemical sensors by using extended arrays of vertical SiNWs with air-bridged top metal contact and theirs gas sensing properties were investigated. To facilitate easy access of analyte gas molecules to the surfaces of SiNWs, air-bridging top metal electrode was patterned with arrays of 100 $\mu$m-sized holes by performing Ar-plasma etching through Cu-grid (see inset of Figure 4b). For comparative investigation, we also prepared a single SiNW-based chemical sensor with lithographically patterned Au top electrode (1 $\mu$m). Figure 4 presents typical electrical responses of (a) a single SiNW-based sensor and (b) vertical SiNW array-based sensor to periodic switches of O$_2$ gas at room temperature; O$_2$ exposure interval = 2 min. for (a) and 1 min for (b). The sensors responded sensitively to the cyclic changes of oxygen atmosphere. As seen in Figure 4, the resistance of both sensors decreased by 35–40% upon exposure to oxygen gas molecules. The observed electrical response can be attributed to the surface-transfer doping, in which the modifications of electrical transport by chemisorbed molecules can be qualitatively assessed by nonequilibrium Green’s function.

In which the modifications of electrical transport by chemisorbed molecules can be qualitatively assessed by nonequilibrium Green’s function. It is assumed that oxygen gas molecules adsorbed on $p$-type SiNWs extract electrons from silicon (i.e., injection of positive hole ($h^+$)) into the valence band of silicon). The consequence of such charge transfer is the accumulation of the majority charge carrier (i.e., $h^+$), leading to the enhancement of $p$-type conductance. We were able to corroborate this argument by performing control experiments using hydrogen as analyte gas molecules. It is well known that hydrogen molecules adsorbed on $p$-type nanowires take positive holes ($h^+$) from them (i.e., surface depletion of majority carriers, $h^+$), thus leading to decrease in $p$-type conductance. In fact, hydrogen...
exposure led to increase in the resistance by about 20% for vertical SiNWs array sensor (see Figure S5).

It is worth noting that our vertical SiNW array-based sensor exhibited very fast responses to analyte gas molecules compared to single SiNW-based one. When vertical SiNW array-based sensor was exposed to oxygen gas molecules, the resistance of vertical nanowires promptly decreased and then reached a relatively stable value. When oxygen exposure was terminated, the resistance abruptly increased and rapidly reached a relatively stable value. The response time and recovery time (defined as the time required to reach 90% of the final equilibrium value) were about 5 s (Figure 4b). The sensor responses were stable and reproducible for repeated testing cycles. To the best of our knowledge, the observed sensing performance is among the best ever reported for SiNW-based sensors. These excellent sensing properties of our SiNW array-based sensor may be attributed to the vertical configuration of sensing elements (i.e., SiNWs), which allows efficient utilization of the entire surface area of individual SiNWs compared to conventional nanowire sensors with lateral configurations. In addition, ultra-high integration density (typically ~ 10^10/cm^2) of sensing elements in our sensor is believed to maximize effectively signal-to-noise ratios. One may expect that sensing performance of SiNW array-based devices can be further improved by deliberately adopting analyte-specific surface modification techniques that are currently available for SiNWs.\[14,29-31]\n
In summary, we have developed a generic approach for constructing an air-bridged top electrical contact on extended arrays of vertically aligned nanowires. A suspended polymer layer was first formed on the arrays of vertical SiNWs by performing partial impregnation of polystyrene (PS) at its glass transition temperature and then utilized as a deposition barrier for selective sputter deposition of metal on the tips of nanowires. According to our electrical measurements, the air-bridging top metal layer forms an Ohmic contact with the tips of individual SiNWs. Our approach provides a simple, cost-effective, and highly reliable pathway for constructing an air-bridged electrical contact on large arrays of vertically aligned nanowires and thus will find practical applications in many fields, especially those that are developing advanced nanowire-based devices for energy harvest and storage, power generation, and sensing applications.

**Experimental Section**

**Pretreatment of Si Wafers:** (100)-oriented p-Si wafers (B-doped, ρ = 1–10 Ωcm) were cleaned by using either a RCA solution (NH\(_3\)/H\(_2\)O/H\(_2\)O\(_2\)/H\(_2\)O, v/v = 1/1/5) or a Piranha solution (98% H\(_2\)SO\(_4\)/30% H\(_2\)O\(_2\), v/v = 4/1) and then thoroughly rinsed by copious amounts of de-ionized (DI) water prior to use.

**Fabrication of Gold Mesh:** Thin gold meshes with ordered arrays of nanoholes, which were used as silicon etching catalyst in the present work, were conveniently replicated from nanoporous anodic aluminum oxide (AAO) as follows.\[18]\ A 25 nm-thick gold film was deposited onto the surface of AAO membrane in a sputter coater (208HR, Cressington, U. K.), equipped with a high resolution thickness monitor (MTM-20, Cressington, U. K.). Deposition of gold was carried out with a rotating sample stage (rpm = 100) that was oriented at an angle of ca. 45° with respect to the sputter source in order to minimize the deposition of Au on the pore wall surface of AAO. The resulting gold-coated AAO membrane was floated on the surface of 1 M NaOH solution to remove the oxide membrane. After that, the oxide etching solution was replaced with DI water. Subsequently, the resulting free-standing gold mesh (typical diameter = 1.6 cm) was placed on the surface of a diluted nitrohydrochloric acid (i.e., H\(_2\)N/\(_2\)HCl/H\(_2\)O, v/v = 1/3/2) solution for 3 s in order to remove gold nanoparticles from the edges of nanoholes at the bottom side of gold mesh. After solution neutralization with a copious amount of DI water, the resulting gold mesh was transferred on the polished surface of silicon wafer for metal-assisted chemical etching (MaCE). The structure of gold mesh is characterized by a hexagonal arrangement of nanoholes, of which pitch distance corresponds to the interpore distance (D\(_{\text{int}}\) = 100 nm) of AAO membrane.

**Preparation of SiNW Arrays:** Extended arrays of vertically aligned [100] SiNWs were prepared by metal-assisted chemical etching (MaCE) of p-Si(100) wafer using 25 nm-thick gold mesh with ordered arrays of nanoholes as etching catalyst. Gold mesh-loaded silicon wafer was immersed into an etchant solution comprised of 24.2 M HF and 1.06 M H\(_2\)O\(_2\) for a desired period of time. The resulting nanowire sample were thoroughly rinsed by using absolute ethanol. Subsequently, supercritical CO\(_2\) drying of the sample was carried out in a Tousimis AutoSamDri PVT-3D Critical Point Drier.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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