Strain-Release Assembly of Nanowires on Stretchable Substrates

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ABSTRACT A simple yet effective method for assembly of highly aligned nanowires (NWs) on stretchable substrates is reported. In this method, NWs were first transferred to a strained stretchable substrate. After the strain was released, the NWs aligned in the transverse direction and the area coverage of the NWs on the substrate increased. This method can be applied to any NWs deposited on a stretchable film and can be repeated multiple times to increase the alignment and density of the NWs. For silver (Ag) and silicon (Si) NWs on poly(dimethylsiloxane) (PDMS) substrates, the probability of NW alignment increased from 29% to 90% for Ag NWs, and from 25% to 88% for Si NWs after two assembly steps; the density increased by 60% and 75% for the Ag and Si NWs, respectively. The large-strain elasticity of the substrate and the static friction between the NWs and the substrate play key roles in this assembly method. We find that a model that takes into account the volume incompressibility of PDMS reliably predicts the degree of NW alignment and NW density. The utility of this assembly method was demonstrated by fabricating a strain sensor array composed of aligned Si NWs on a PDMS substrate, with a device yield of 95%.

KEYWORDS: nanowire · assembly · alignment · strain · static friction

RESULTS AND DISCUSSION

Figure 1 shows schematically how a NW on strained PDMS moves when the PDMS is released. The NW motion is due to the geometric compatibility with the PDMS and the static friction between them. It is well-known that PDMS is an elastomeric material that can undergo large, nonlinear elastic deformation. For a NW with initial length \( L_0 \) and skew angle \( \theta_0 \), the width, height, and area of the rectangle bounding the NW are \( L_0 \sin \theta_0 \), \( L_0 \cos \theta_0 \), and \( A_0 = L_0^2 \sin \theta_0 \cos \theta_0 \), respectively (Figure 1a).

When the strain is released, assuming linear elasticity, the width, height, and area of the rectangle change to \( L_0 \sin \theta_0 / (1 + \varepsilon_{\text{pre}}) \), \( L_0 \cos \theta_0 / (1 + \varepsilon_{\text{pre}}) \), and \( A_1 = A_0 / (1 + \varepsilon_{\text{pre}}) \), respectively, where \( \varepsilon_{\text{pre}} \) is the strain and \( \nu \) is the Poisson’s ratio. Note that the Poisson’s ratio is defined in the linear elasticity model, which is only valid for a small deformation. The Poisson’s ratio of PDMS is approximately 0.5.
In the case of no static friction (i.e., no bonding) between the NW and the PDMS, the NW would not move at all (Figure 1b). In the case of static friction (i.e., no sliding) between the NW and the PDMS (Figure 1c), the new NW length and skew angle are

\[
L_1' = \frac{\sin \theta_0}{1 + \varepsilon_{\text{pre}}} L_0 \cos \theta_0 \lambda^{1/2}, \quad \theta_1 = \arctan\left(\frac{\lambda - \varepsilon_{\text{pre}}}{\tan \theta_0 \lambda^{1/2}}\right)
\]

respectively. The length ratio \((L_1'/L_0)\) and the new skew angle are plotted in Figure 2 panels a and b as functions of the strain and the initial skew angle. The NW density is inversely proportional to the associated area (i.e., the total number of NWs is equal to the NW density times the area). The density increase is given by

\[
\sigma(\varepsilon) = \frac{\tau w x}{A}
\]

where \(\tau\) is the shear strength (static friction per unit area), \(w\) is the contact width between the NW and the substrate, \(x\) is the Euler coordinate ranging from 0 to \(L_0\), and \(A\) is the NW cross-sectional area. The total length change of the NW is

\[
\Delta L = \int_0^{L_0} \sigma(\varepsilon) \frac{dx}{E} = \int_0^{L_0} \frac{\tau w x}{E A} dx = \frac{\tau w L_0^2}{2EA}
\]

where \(E\) is the Young’s modulus of the NW. The average axial strain of the NW is

\[
\varepsilon = \frac{\Delta L}{L_0} = \frac{\tau w L_0}{2EA}
\]

If the static friction is large, the NW could be stretched or compressed depending on the (substrate) strain and initial skew angle, as shown in Figure 2a. With the assumption of a uniformly distributed static friction, the axial stress on the NW due to the static friction is given by

\[
\sigma(\varepsilon) = \frac{\tau w x}{A}
\]

For a typical hexagonal Si NW with a length of 10 \(\mu\text{m}\), a diameter of 40 \(\text{nm}\) (contact width is 20 \(\text{nm}\)) and a Young’s modulus of 187 \(\text{GPa}\), a shear strength of 19.3 MPa is required in order to accomplish an axial strain (either tension or compression) of 1%. The real static friction is too small to accommodate this strain. The shear strengths of InAs NW on both silicon oxide and silicon nitride substrates ranged from 0.1 to 5 MPa. Various nanostructure/substrate systems also gave rise to shear strengths of 0.1–1 MPa. For the silicon nitride substrates, the shear strengths were found to be independent of the NW diameter and length. However, the shear strengths were found to be dependent on the NW diameter and length for the silicon oxide substrates. The shear strengths were found to be highest for the NW diameters of 20–40 \(\text{nm}\) and the NW lengths of 10–20 \(\mu\text{m}\). The shear strengths were found to decrease with increasing NW diameter and length. The shear strengths were found to be independent of the NW diameter and length for the silicon nitride substrates. The shear strengths were found to be highest for the NW diameters of 20–40 \(\text{nm}\) and the NW lengths of 10–20 \(\mu\text{m}\). The shear strengths were found to decrease with increasing NW diameter and length.
suggests this can be achieved by modifying the surfaces of the NWs or the PDMS in order to increase the static friction between them.

To demonstrate the general applicability of the proposed alignment method, Ag\textsuperscript{33} and Si\textsuperscript{25,34} NWs were selected as two model materials to represent

Figure 2. (a) The length ratio ($L_1/L_0$) (assuming a large static friction between NWs and PDMS) and (b) the new skew angle ($\theta_1$) as functions of the strain and initial skew angle. (c) The density increase as a function of the strain. In panels a–c, the dash lines represent the linear elastic analysis and the solid lines represent the nonlinear elastic analysis.
NWs grown in solution or on a substrate, respectively. Figure 3 is a schematic illustration showing the process of the alignment method. A mechanical testing stage (Ernest F. Fullam) was used to mechanically stretch the PDMS substrate to a desired level of strain, as shown in Figure 3a. Then, two different strategies based on contact line deposition and contact printing were adopted to transfer Ag and Si NWs, respectively, to the PDMS substrate. For Ag NWs, the NW solution was first dropped on the strained PDMS substrate, and a glass tube was brought into contact with the drop and the PDMS substrate. A contact line formed between the solvent and the substrate (Figure 3b); the capillary flow sorted the NWs along the contact line during the rolling process. Gradually rolling the tube moved the contact line across the PDMS substrate, and the NWs deposited along the contact line. As a result, a roughly aligned film of Ag NWs was obtained. For Si NWs, the growth substrate was placed upside down on top of the strained PDMS substrate. A gentle downward pressure was applied on the growth substrate, and it was moved perpendicular to the stretching direction (Figure 3c). After the growth substrate was removed, the PDMS was coated with a roughly aligned film of Si NWs. For both the contact printing and contact line deposition techniques, when the
PDMS substrate was released, the alignment and density of the NWs increased (Figure 3d).

Subsequent transfers of the NWs can be performed to further increase the alignment and density. Adhesion between NWs and PDMS is critical to the yield of NW transfer. To increase the adhesion, subsequent PDMS substrates were radiated under a UV lamp (BHK, Inc.) for ~5 min with the assistance of UV-generated ozone.36–38 As shown in Figure 3e, the first (released) PDMS sheet with NWs was then brought into contact with the second (strained) one that had been treated by UVO. After a short contact (e.g., a few minutes), the first PDMS was slowly peeled from the second one, and the NW film was left on the second PDMS substrate. Releasing the strain of the second PDMS substrate further increased the NW alignment and density (Figure 3f). These transfer/release steps can be repeated multiple times as needed to further improve NW alignment and density.

The alignment process of Ag NWs is shown in Figure 4. Initially, the NWs were roughly aligned on a strained PDMS substrate ($t_{pre} = 80\%$) by contact-line deposition35 (Figure 4a). NWs are considered to be aligned if the skew angle is less than 5° with respect to the transverse direction; 29% of Ag NWs were aligned in this initial step (similar to the reported one-step contact-line deposition).35 After the strain on the PDMS substrate was released, the alignment of NWs was improved to 56% and the NW density was increased by 33 ± 5% (theoretical value: (1.8)$_{1/2}$ − 1 = 34%) (Figure 4b). Figure 4c shows the NWs after they were transferred to the second PDMS substrate (also with a strain of 80%). By comparing Figure 4 panels b and c, we determined that 92% of the Ag NWs were transferred to the second PDMS substrate. The orientation of the NWs on the second substrate is the mirror image of those on the first. Releasing the second PDMS yielded a NW alignment of 90% NWs (Figure 4d). Meanwhile, the NW density increased by 60 ± 10% (theoretical value: $\lambda_1\lambda_2\xi - 1 = (1.8)^{1/2} \times (1.8)^{1/2} \times 92\% - 1 = 66\%$, where $\lambda_1$ and $\lambda_2$ are the respective stretches in two PDMS substrates and $\xi$ is the transfer rate of NWs from the first to the second PDMS) after the second transfer/release step, compared to the NW density before the first strain release. To account for the inhomogeneous distribution of NWs, five images of different locations were used to count the number of NWs per unit area before and after release of the PDMS substrate.

Figure 5 shows an optical image of the Si NWs transferred to a strained PDMS substrate using the contact printing method.19,20 Only a small percentage (25%) of NWs were straight and aligned initially, which was typically the case in our work when contact printing was used for the initial alignment step. Most others were either skewed with respect to the transverse direction or buckled (likely caused by the kinetic friction force during the sliding process). The alignment was improved to 53% and 88%, respectively, after the first release and second transfer/release; 99% of the Si NWs were transferred from the first to the second PDMS substrate. The NW density was increased by 33 ± 3% (theoretical value: 34%) and 75 ± 7% (theoretical value: 1.8 $\times$ 99% − 1 = 78%), respectively, after the first and second transfer/release step.

The initial step using the contact printing method19 yielded a degree of alignment less than that which was previously reported. Possible reasons for this include (1) the substrate used here is PDMS instead of silicon or a different plastic.19 As the NW-substrate interaction (adhesion and friction) plays an important role in the NW alignment, the different interaction with the soft PDMS substrate could be responsible for the poor alignment.18 (2) Some parameters in the contact printing, such as the contact pressure and sliding force, might have not been optimized. (3) A lubricant, which was found to improve the alignment considerably in previous work,19 was not used in our process. Nevertheless, even though we did not optimize the contact printing process, we could apply strain-release assembly
alignment, the present method can further improve the alignment quality, for example, as shown in Figure 7a.

The new skew angles from a number of Ag and Si NWs after the release of a strain of 80% were measured and plotted in Figure 6 together with the nonlinear elastic analysis. It is seen that the nonlinear elastic predictions agreed with the experimental results remarkably well. Referring to Figure 2b, the linear elastic analysis overestimated the degree of NW alignment.

A two-terminal piezoresistive sensor array was fabricated using the aligned Si NWs on a PDMS substrate to demonstrate how the strain-release assembly technique can be incorporated into a fabrication process to produce a functional device. Thin layers of Ni (20 nm)/Au (80 nm) were evaporated through a shadow mask onto the aligned NWs to serve as electrodes. To improve the electric contact, the devices on PDMS were annealed at 280 °C for 3 min.39,40 Figure 7 panels a and b show the optical images of the Si NWs before and after the electrode deposition, respectively. Owing to their high-degree of alignment, a large percentage of the NWs bridged the 6 μm gap between the electrodes, even though the length of the NWs was only ∼40% greater than the gap.

Tensile and compressive strains were applied to the PDMS in the direction parallel to the aligned NWs by the Fullam mechanical testing stage loaded in a probe station (Micromanipulator). The current–voltage (I–V) response of a Si NW device was measured simultaneously using tungsten probe tips. Figure 7c shows the I–V response as a function of the applied strain (±3%).
Importantly, the conductance of the Si NWs returned to its original value once the applied strain (up to $\pm 3\%$) was released, confirming the robustness of the NW devices. The high-degree of alignment and high density of NWs on the substrate guaranteed that nearly every electrode was connected to neighboring electrodes by multiple NWs, ensuring that this process produced a high yield (95\%) of working devices. Here we define working devices as those with repeatable, measurable $I$–$V$ response within the strain of $\pm 3\%$. A common challenge of NW devices on polymer substrates is the contact between the NW and the evaporated electrodes; the contact resistance can change under stretching or bending. Indeed, if a tensile or compressive strain greater than 3\% was applied to the sensors, the $I$–$V$ curve did not return to its original state, likely due to change in the contact resistance at the NW-electrode interface.

**CONCLUSIONS**

We have demonstrated strain-release as a simple yet effective strategy for production of aligned NWs on stretchable substrates. This method can be applied to NWs synthesized by different methods or processed in different conditions (e.g., wet or dry methods). For instance, the alignment of Ag and Si NWs on PDMS substrates increased from less than 30\% to $\sim 90\%$, and the density increased by 60–75\%, after two assembly steps when the substrates were relaxed from a strain of 80\%. The success of this method relies on the large-strain elasticity of the substrates and the static friction between the NWs and the substrate. This method, combined with other alignment techniques, can be applied to a wide variety of nanostructures, and the aligned nanostructures can be transferred to other rigid or flexible substrates with the PDMS as a stamp to fabricate multilayered NW devices. The highly aligned NWs were instrumental in producing a strain-sensor array with a device yield of 95\%. This assembly method can be integrated in the fabrication of NW-based flexible devices (e.g., biosensors and thin-film solar cells), stretchable devices, transparent electronics and electrodes for organic electronics. Furthermore, the fundamental mechanics learned from this work might provide valuable guidelines for other applications involving NW/substrate interfaces.

**METHODS**

Preparation of NWs and PDMS. Ag NW ink was prepared following the procedure developed by Wiley et al. The obtained solution is then diluted with water in the ratio of 1:10 in volume. Boron-doped (p-type) Si NWs were synthesized on Si substrates by chemical vapor deposition (CVD) using gold nanoclusters as catalysts and silane (SiH4) as a vapor-phase reactant, following the method reported by Wu et al. PDMS substrates with thickness of 2 mm were prepared using “Sylgard 184” (Dow Corning) by mixing the base and the curing agent with a ratio of 10:1. The mixture was first placed in a vacuum oven to remove air bubbles and then thermally cured at 65 °C for 12 h. Rectangular slabs of suitable sizes were cut from the cured piece.

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Supporting Information Available: Alignment experiments at the microscope. This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES AND NOTES**
