NANO LETTERS
LETTER
pubs.acs.org/NanoLett

Fabrication of Nanowire Electronics on Nonconventional Substrates by Water-Assisted Transfer Printing Method

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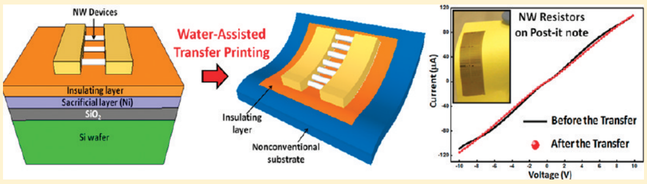
Supporting Information

ABSTRACT: We report a simple, versatile, and wafer-scale water-assisted transfer printing method (WTP) that enables the transfer of nanowire devices onto diverse nonconventional substrates that were not easily accessible before, such as paper, plastics, tapes, glass, polydimethylsiloxane (PDMS), aluminum foil, and ultrathin polymer substrates. The WTP method relies on the phenomenon of water penetrating into the interface between Ni and SiO_2. The transfer yield is nearly 100%, and the transferred devices, including NW resistors, diodes, and field effect transistors, maintain their original geometries and electronic properties with high fidelity.



KEYWORDS: Nanowire, transfer printing, nonconventional substrates, flexible electronics, transparent electronics

Nanowires (NWs), due to their unique mechanical and electrical properties,[1,2] have been widely proposed as building blocks for high-performance flexible/transparent electronics,[3−6] but other than on bulk wafers, their devices have been fabricated only on plastic, glass, and thick polyimide (PI, over 20 μm thick) layers.[5−8] Fabrication of NW electronic devices on nonconventional substrates will enable the utilization of many desired properties of the substrates, such as flexibility, transparency, biocompatibility, conductivity, and low cost, and hence benefit a range of technologies, such as flexible displays,[9] paper electronics,[10] solar cells,[11] conformal sensors,[12] and biointegrated electronics.[13] Toward this goal, traditional approaches directly conduct lithography on the desired substrates, so the choice of substrates is limited by the processing temperature, compatibility with chemicals, and handling requirements.[3−5] Another notable approach, the transfer printing method, uses elastomer to transfer materials from donor to receiver substrates using the fact that the transferred materials have the best adhesion to the receiver substrate, followed by the elastomer and then the donor substrate.[14,15] Nevertheless, the transfer of multiple layers with high fidelity using the transfer printing methods is still challenging due to difficulties in controlling the delicate adhesion differences between different layers and substrates. An alternative approach involves the lift-off of thin film devices prefabricated on bulk wafers using a sacrificial layer that is removed by either chemical etching assisted by etch holes or thermal melting, but this method requires the devices to tolerate harsh etchants and thermal stress.[12,16−20] To date, none of the existing methods can fabricate NW electronic devices on arbitrary nonconventional substrates at a wafer scale with high yield. Here, we present a simple, versatile, and wafer-scale water-assisted transfer printing method (WTP) that enables integration of NW devices onto diverse nonconventional substrates that were not easily accessible before, such as paper, plastics, tapes, glass, poly(dimethylsiloxane) (PDMS), Al foil, and ultrathin polymer substrates. The transfer yield is nearly 100%, and the transferred devices maintain their original geometries and electronic properties with high fidelity.

The WTP method relies on the phenomenon of water penetrating into the interface between nickel (Ni) and silicon dioxide (SiO_2), which leads to lift-off of a Ni layer from a SiO_2/Si donor substrate.[21] The WTP method is schematically illustrated in Figure 1. First, a thin Ni layer (300 nm thick) is deposited on a SiO_2/Si wafer and a thin layer of PI (800 nm) or silicon nitride (SiN, 300 nm) is deposited on top to function as an insulating and supporting layer for the NW devices. Subsequently, arrays of the NW devices are fabricated on top of the insulating layer by conventional photolithography. Thermal release tape (TRT) as a temporary holder is then attached to the top of the substrate with a layer of spin-casted poly(methylmethacrylate) (PMMA) in between to prevent the NW devices from polymer contamination by the tape (Figure 1a, (i)). Next, the whole structure is soaked in deionized water at room temperature, followed by the peel-off of an edge of the TRT to initiate the penetration of water. Within 3−4 s, the entire structure separates at the interface between Ni and SiO_2, and thereby the NW devices are separated from the Si wafer and sandwiched between the Ni layer and the TRT (Figure 1a, (ii)). The Ni layer is then etched away by Ni etchant (Figure 1a, (iii)). Finally, the TRT carrying the structure (PMMA/NW devices/insulating and supporting layer) is pasted onto any target substrates, for which nonadhesive target substrates are precoated with a thin adhesive layer, such as PDMS or poly(vinyl alcohol) (PVA), for the purpose of adhesion, planarization, and strain isolation.[22,23] Afterward, the TRT is released from the structure by heating at 90 °C for 5−6 s, followed by dissolution of the PMMA with acetone, leaving only the NW devices on the target substrate (Figure 1b). Alternatively, NW devices on ultrathin PI substrate are

Received: June 4, 2011
Published: June 22, 2011

dx.doi.org/10.1021/nl201901z | *Nano Lett.* 2011, 11, 3435–3439

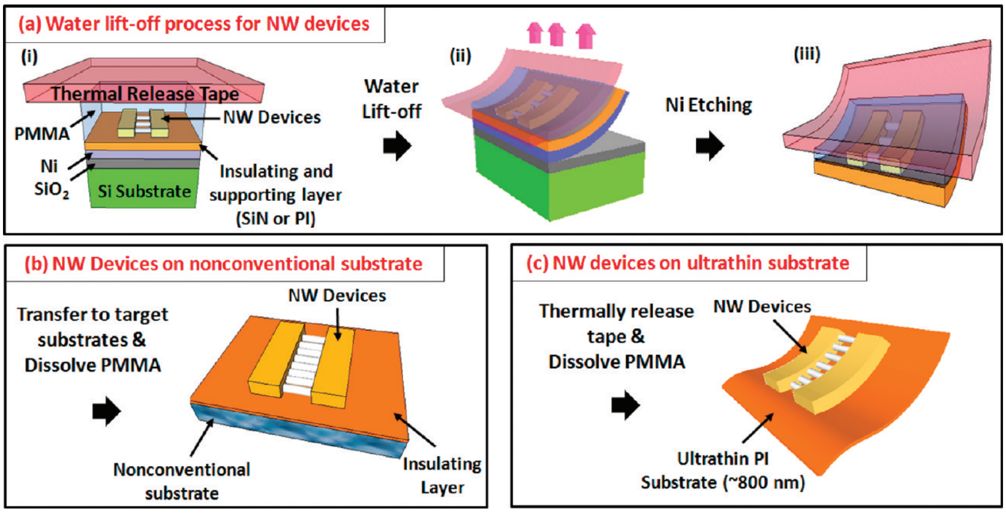


Figure 1. Illustration of the WTP steps for transferring the NW devices to nonconventional substrates: (a) (i) prefabricated NW devices on the donor substrate → (ii) peel-off in water → (iii) etch the Ni layer; (b) the transferred NW devices on a target substrate with an insulating layer in between; (c) the transferred NW devices on an ultrathin PI substrate (~800 nm).

achieved simply by releasing the TRT and dissolving the PMMA without any target substrates (Figure 1c).

The present WTP method offers several key advantages compared to previous methods. First, since the WTP process requires no harsh chemicals and applies negligible mechanical/thermal stresses on the target substrates, almost any substrate can be used as long as they can withstand the heating temperature (90 °C) for releasing the TRT and the acetone for dissolving the PMMA. Second, the WTP method is highly scalable and reliable. We successfully transferred 4 in. wafer-scale areas of microelectrodes to diverse nonconventional substrates with high fidelity to their original shapes (i.e., straight and round edges), thicknesses (80 to 250 nm), feature sizes (dimension from 30 μm to cm), and electrode gap distances (down to 3 μm, which is limited by the resolution of photolithographic equipment, not by the WTP method) (Figure S1, Supporting Information). Significantly, the transfer yield is nearly 100% regardless of feature geometries and materials. More importantly, when the WTP method is used to transfer NW devices, the electric properties of the NW devices are also preserved after the transfer. Last, the WTP method is very fast in that a 4 in. wafer of NW devices is separated from the donor substrate within 3−4 s in water at room temperature. In addition, the original donor SiO$_2$/Si wafer is clean and reusable after the transfer, which is a major cost-saving factor (Figure S2, Supporting Information).

To illustrate these features of the WTP method, we applied the WTP method to transfer a range of NW electronic devices, such as resistors, diodes, and field effect transistors (FETs), onto diverse nonconventional substrates with desired properties, such as flexibility (e.g., tapes and Post-it notes), transparency (e.g., glass and PDMS), and conductivity (e.g., Al foil and conductive tapes that can be used as back gate electrodes of the NW FETs). Figure 2a shows representative optical images and current−voltage ($I-V$) curves of NW electronic devices transferred to the Post-it notes, glass, and Al foil. Closer scanning electron microscopy (SEM) inspection (Figure 2b) shows that the WTP process produces no visible damage to the SiNWs and the metal electrodes. Furthermore, all the $I-V$ curves (Figure 2a), including those nonlinear ones (Figure S3, Supporting Information), remain almost the same after the transfer, suggesting that the WTP process generates negligible mechanical/thermal stresses to the NWs and the metal electrodes. More importantly, the transferred NW electronics clearly show linear, rectifying, and gate-modulated behaviors as expected for the NW resistors, diodes, and FETs, respectively (Figure 2a). The transconductance of the transferred SiNWs are 148 nS on Al foil and 74 nS on conductive carbon tape (Figure S4, Supporting Information), comparable to those observed in SiNW FETs fabricated on a planar SiO$_2$/Si wafer by electron beam (e-beam) lithography with a transconductance ranging from 45 to 800 nS.[24,25]

Next, the WTP method was applied to fabricate NW devices on an ultrathin sheet of PI, which was achieved by releasing the TRT and dissolving the PMMA without any target substrates (Figure 1c). The lifted ultrathin PI sheet (800 nm) with the NW devices on top can be mounted onto soft and curved surfaces, potentially such as biological tissues, and the highly conformal interface between the NW devices and the tissues is important for improving the signal-to-noise ratios for biosensing applications.[12] To demonstrate the conformal coating capability, the ultrathin PI sheet with the NW devices on top was wrapped around two finger tips (Figure 3a, left). Moreover, the PI sheet can be released from the finger tips by soaking in water and loaded repeatedly onto other surfaces such as a squeezed plastic bottle (Figure 3a, right), demonstrating the mechanical robustness and conformability of the ultrathin sheet. Representative SEM images (Figure 3b) clearly show that the metal electrodes are smoothly wrinkled following the deformation of the PI sheet, and the NWs bridged between the metal electrodes have no visible damage after the transfer. Moreover, the $I-V$ curves of the NW devices are almost identical before and after the transfer, confirming that the NW devices are intact during the WTP process. Given the conformability, robustness, and biocompatibility of the PI substrate, we believe that the ultrathin NW FETs can be applied as conformal ultrasensitive biosensors for biological tissues.[12]

Finally, we investigated the mechanism for the separation of the Ni layer from the SiO$_2$/Si wafer in the presence of water. We believe that Ni reacts with SiO$_2$ during the Ni deposition process by e-beam evaporation, forming Ni silicate or Ni oxide. When the Ni silicate or Ni oxide contacts water, Ni hydroxide (Ni(OH)$_2$) is

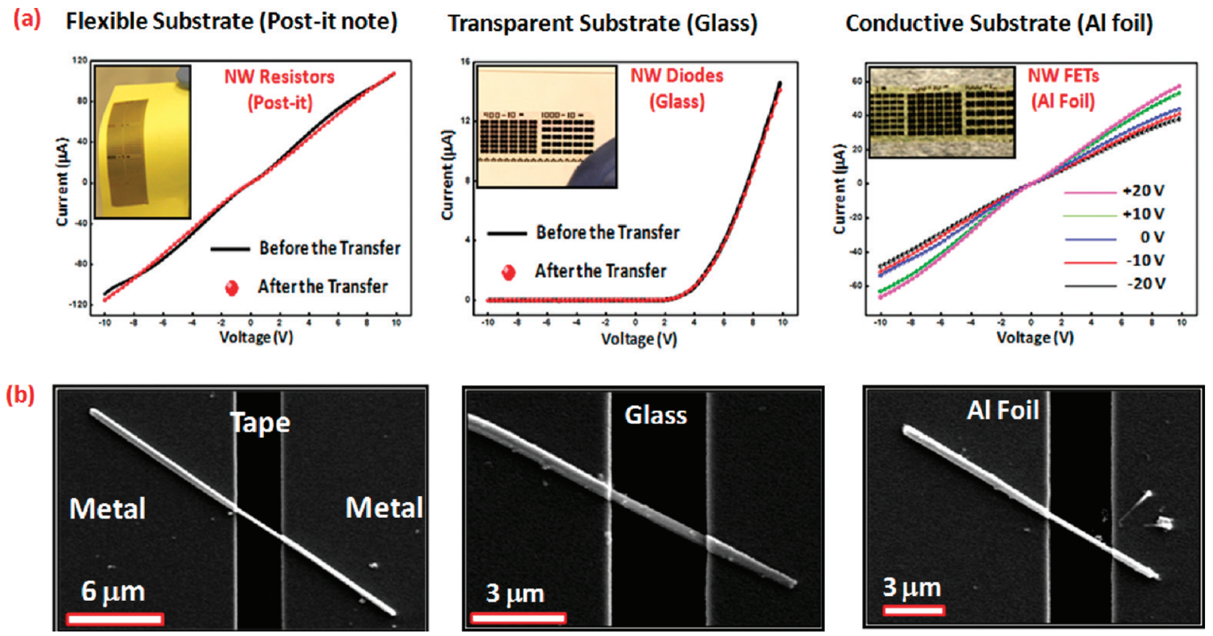


Figure 2. (a) Representative $I-V$ curves of NW resistors (left) and NW diodes (middle) before (black lines) and after (red dots) the transfer to Post-it note and glass. The transferred NW FETs onto the Al foil (right) are clearly modulated by the applied gate voltages ranging from −20 to +20 V. Insets provide photographs of the transferred NW devices. (b) SEM images of the transferred NW devices on tape, glass, and Al foil.

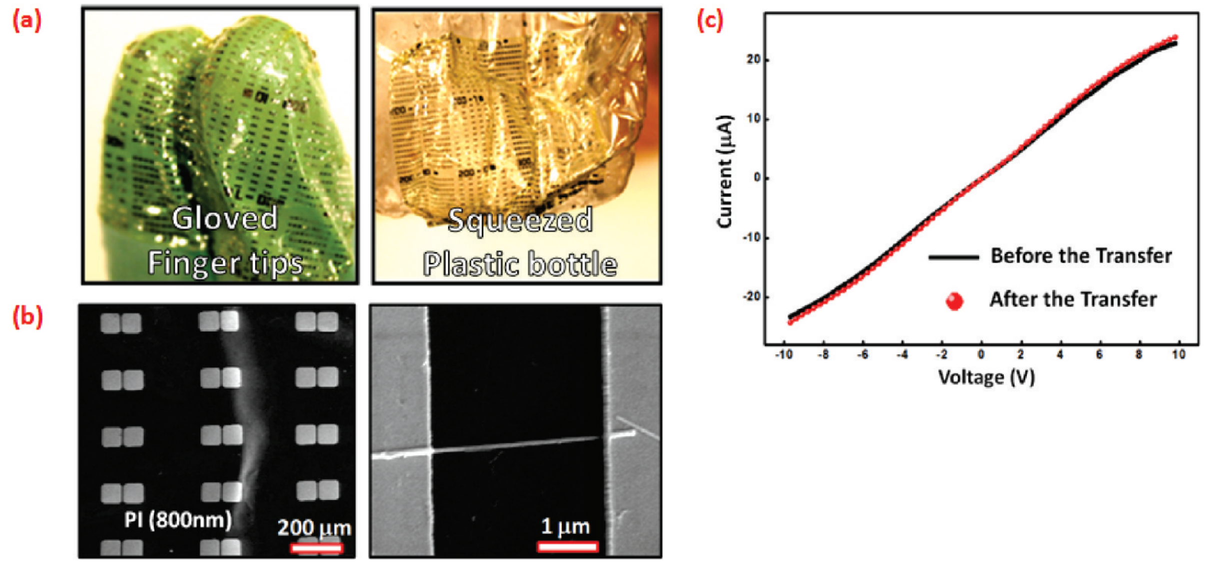


Figure 3. (a) Photographs of the transferred NW devices on top of an ultrathin PI sheet. The ultrathin PI sheet is wrapped around gloved finger tips (left) and a squeezed plastic bottle (right). (b) SEM images of the transferred NW devices on the ultrathin PI substrate. (c) Representative $I-V$ curve of the NW devices before (black lines) and after (red dots) the transfer to the ultrathin PI substrate.

formed, and thus its surface becomes hydrophilic. On the other side of the split interface, the SiO_2 surface is terminated with −H and/or −OH groups when in contact with water and becomes hydrophilic as well. Consequently, water can quickly penetrate into the interface between the two hydrophilic surfaces, leading to the separation of the Ni layer from the SiO_2/Si wafer. To further test this, we deposited an array of circular Ni patterns (3 μm in diameter) on a SiO_2/Si wafer by the e-beam evaporation, followed by the water soaking process (Figure 4a). The SEM (top) and atomic force microscopy (AFM) (bottom) images in Figure 4b clearly show that the water soaking process detaches the Ni circles from the donor substrate with some Ni residues left at the edges. Moreover, Figure 4c shows that the average height along the centerline on the donor substrate is lower inside than outside the circle (Figure S5 in the Supporting Information for statistical data). Further AFM measurements of 24 randomly chosen circles indicate that the average height inside the original Ni circle on the donor substrate is approximately 2.45 Å lower than that of the outside. These results confirm that the top surface of the SiO_2 layer is consumed by reacting with the Ni, supporting the above reaction mechanism.

In summary, we developed a water-assisted transfer printing method to integrate NW electronic devices on diverse

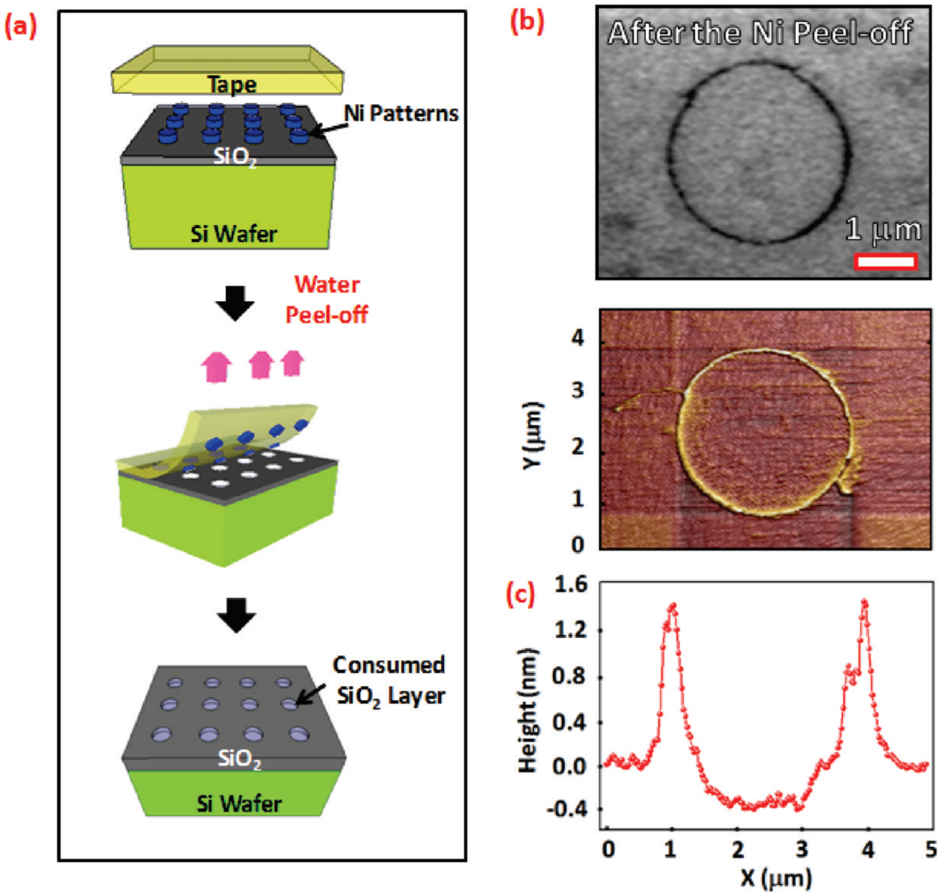


Figure 4. Mechanism study of the WTP method: (a) illustration of the WTP process for detaching the patterned Ni circles; (b) representative SEM (top) and AFM (bottom) images of the Ni circles after the WTP process; (c) the AFM measurement showing that the averaged height is lower inside than outside of the Ni circle. The height peaks at edges of the Ni circle denote Ni residues after the WTP process, and they were used to locate the Ni circles during the AFM measurements.

nonconventional substrates. The WTP method requires no harsh fabrication processes on the target substrates, enabling the use of many nonconventional substrates that were not accessible before. The WTP method has the advantages of simplicity, low cost, nearly 100% transfer yield regardless of the transferred materials and feature geometries, and high fidelity to the original devices after the transfer. The WTP method will endow electronic devices with desirable properties through their nonconventional substrates, such as flexibility, conformability, transparency, adhesion, conductivity, and biocompatibility, and thereby impact a range of applications, such as biosensing, flexible displays, robotics, and energy conversion systems. We believe that the WTP method can also be used to transfer electronic devices based on other nanomaterials (e.g., carbon nanotubes and graphene), thin film devices (e.g., thin film transistors, thin film solar cells), and vertical devices (e.g., vertical NW FETs) to nonconventional substrates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional figures showing transferred microelectrode arrays, reusable donor Si wafer and wafer-scale transferred microelectrode arrays on adhesive tape, nonlinear *I*—*V* curves, and statistical data of the AFM measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

X.L.Z. sincerely thanks NSF (Award Number 0826003) and Center for Integrated Systems of Stanford University for support of this work. D.R.K. acknowledges support from the Link Foundation Energy Fellowship. The authors also thank Pratap M. Rao for proofreading the manuscript.

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