Nanotransplantation Printing of Crystallographic-Orientation-Controlled Single-Crystalline Nanowire Arrays on Diverse Surfaces

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Supporting Information

ABSTRACT: The fabrication of a highly ordered array of single-crystalline nanowire structures prepared from solution-phase or vapor-phase synthesis methods is extremely challenging due to multiple difficulties of spatial arrangement and control of crystallographic orientation. Herein, we introduce a nanotransplantation printing (NTPP) technique for the reliable fabrication, transfer, and arrangement of single-crystalline Si nanowires (NWs) on diverse substrates. NTPP entails (1) formation of nanoscale etch mask patterns on conventional low-cost Si via nanotransfer printing, (2) two-step combinatorial plasma etching for defining Si NWs, and (3) detachment and transfer of the NWs onto various receiver substrates using an infiltration-type polymeric transfer medium and a solvent-assisted adhesion switching mechanism. Using this approach, high-quality, highly ordered Si NWs can be formed on almost any type of surface including flexible plastic substrates, biological surfaces, and deep-trench structures. Moreover, NTPP provides controllability of the crystallographic orientation of NWs, which is confirmed by the successful generation of (100)- and (110)-oriented Si NWs with different properties. The outstanding electrical properties of the NWs were confirmed by fabricating and characterizing Schottky junction field-effect transistors. Furthermore, exploiting the highly flexible nature of the NWs, a high-performance piezoresistive strain sensor, with a high gauge factor over 200 was realized.

KEYWORDS: nanotransplantation printing, single-crystalline nanowires, orientation control, field-effect transistor, strain sensor

Recently, flexible and stretchable electronics have attracted significant interest due to their extensive usefulness in diverse applications where conventional hard-substrate-based device platforms cannot be applied.1,2 Flexible electronics/optoelectronics include an extensive range

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well-aligned Si nanowires were formed on the receiver substrate. Weaken the adhesion between the adhesive and NWs. (g) Detached NW/PMMA/adhesive film was placed in a chamber containing a solvent mixture of acetone and heptane to weaken the adhesion between the adhesive film and PMMA. (h) The sample was removed from the chamber and carefully contacted to a desired receiver substrate. Then, only the adhesive film was separated from the wafer. (i) After washing away the PMMA film with the solvent, well-aligned Si nanowires were formed on the receiver substrate.

Figure 1. Procedure of nanotransplantation printing (NTPP). (A) Printing of etch mask. (a, b) Macroscopic formation of aligned etch mask patterns on a single-crystal Si wafer through nanotransfer printing (nTP). Solvent-assisted nanotransfer printing (S-nTP) was used to form 25 nm metallic mask patterns. (B) Nanowire (NW) fabrication via reactive ion etching. (c) Two-step combinatory reactive ion etching (anisotropic vertical etching followed by isotropic etching) was performed to define Si NWs. (d) Fabrication of perfectly aligned Si nanowires, which are connected to the substrate via narrow bridges. (C) NW transplantation. (e) A PMMA film was spin-casted on the wafer as an infiltrated polymeric transfer medium to grasp the fabricated Si NWs. (f) PI adhesive film was attached for extracting the polymeric transfer medium and NWs. (g) Detached NW/PMMA/adhesive film was placed in a chamber containing a solvent mixture of acetone and heptane to weaken the adhesion between the adhesive film and PMMA. (h) The sample was removed from the chamber and carefully contacted to a desired receiver substrate. Then, only the adhesive film was separated from the wafer. (i) After washing away the PMMA film with the solvent, well-aligned Si nanowires were formed on the receiver substrate.

of devices such as displays, sensors, solar cells, and energy harvesters. In particular, flexible electronics combined with biomedical instruments can realize smart health-monitoring devices that are conformable to human skin and organs and can enable in situ monitoring of physical conditions of the human body and early detection of diseases based on collected information.

For the realization of high-performance flexible electronics, nanoscale device elements should be formed on nonconventional substrates. Among the diverse material components for these devices, organic semiconductors have been considered as active materials due to their innate mechanical flexibility. However, the relatively insufficient physical properties and instability of organic materials under ambient conditions limit both their functionality and reliability. Nanostructured inorganic semiconductors with superior electrical properties and physical/chemical robustness have thus been considered to be promising components for practical flexible electronic devices. In particular, semiconducting inorganic nanowires and nanoribbons are highly desired due to their device-oriented geometries. In addition, various nanowires with high functionalities can offer enhanced device performance.

Among diverse semiconducting nanowires, Si nanowires (Si NWs) are the most widely studied nanostructures, and their extensive usefulness in diverse applications has already been demonstrated. In general, high-quality Si NWs can be synthesized using vapor–liquid–solid growth (VLS growth). However, the difficulty of uniformly aligning synthesized nanowires on a macroscopic substrate area remains a critical challenge. Another method is to pattern Si microstructures from wafers through wet etching. Nevertheless, the printing of high-density nanoscale Si structures has not been demonstrated using this technique, and this method inevitably wastes the remaining portion of Si-on-insulator (SOI) wafers. Moreover, the use of photolithography or e-beam lithography involves at least one of the issues of limited resolution, fabrication cost, and scalability. Although nanotransfer printing (nTP) can be a cost-effective and scalable processing route, it can usually produce only polycrystalline or amorphous nanostructures.

Here, we introduce a nanotransplantation printing (NTPP) technique for uniform formation of single-crystalline Si NWs on diverse surfaces. Si NWs are fabricated from a low-cost bulk Si wafer using direction-controlled dry etching in the presence of nanotransfer-printed hard etch mask patterns with a lateral width ranging from 25 to 200 nm. The NWs can be subsequently transplanted on various unconventional substrates by the use of an infiltrated polymeric transfer medium and a solvent-assisted adhesion switching mechanism. This methodology provides several advantages over the above-mentioned conventional techniques. First, material and processing costs for the fabrication of ordered, high-quality Si NWs can be significantly reduced compared to the above-mentioned research because typical low-cost bulk Si wafers can be used instead of relatively expensive SOI wafers. Second, the geometrical parameters of the Si NWs can be extensively controlled by modulating transfer-printed etch-mask nanopatterns and controlling the dry etching parameters. Third, the Si NWs can be transplanted onto any desired surface including...
Flexible substrates, curved surfaces, and even biological surfaces. Moreover, three-dimensional geometries such as crossed-wire structures or suspended NWs can also be obtained. The Si NWs formed through NTPP are electrically active and can be used as crucial elements in diverse functional devices. The electrical characteristics of the nanowires were examined by fabricating a Schottky-barrier field-effect transistor (FET) device with a field-effect mobility of \( 71.2 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1} \). Furthermore, a high gauge factor of 205.2 was obtained from a flexible strain sensor, confirming the high quality and high performance of the Si NWs.

### RESULTS AND DISCUSSION

**Nanotransplantation Printing of Single-Crystal Nanowires.** Figure 1 presents a schematic illustration for the procedure of NTPP. An NTPP process comprises the following sequential substeps: (1) nanoscale etch mask formation using nanotransfer printing, (2) fabrication of the Si NWs through anisotropic and isotropic combinatorial dry etching, and (3) transfer printing of Si NWs on diverse receiver substrates based on an infiltration-type polymeric transfer medium and a solvent-assisted adhesion switching mechanism. First, metallic or polymeric etch mask patterns were formed on a single-crystal Si wafer (Figure 1A). We employed nanotransfer printing (nTP) as a reliable and uniform patterning methodology. The
nTP can generate well-defined nanopatterns on various substrates by coating resist materials on an elastomeric mold having surface nanopatterns followed by conformal contact of the mold with a desired receiver substrate. It is a simple, low-cost, and large-area patterning method without the need of any complicated equipment such as an optical stepper. In particular, we used solvent-assisted nTP (S-nTP), which we previously developed, as a universal pattern formation method that can also cover patterning resolution down to 10 nm (Figure 1b; see the Experimental Section for more details). Figure 2b and e show scanning electron microscopy (SEM) images of printed polymeric (poly(4-vinylpyridine); P4VP) patterns with a width of 200 nm and metallic (Cr) patterns with a width of 25 nm serving as etch masks, respectively.

For the fabrication of Si NWs, the wafers were patterned through a reactive ion etching (RIE) process (Figure 1B). Two-step combinatorial dry etching was designed and performed (1) to precisely define the width and height of NW structures and (2) to facilitate the release of NWs from the substrate during the subsequent transfer printing process. For the anisotropic vertical etching, the so-called Bosch etching process (the successive treatment of SF₆ plasma followed by C₄F₈ plasma) was performed. SF₆ plasma vertically etches exposed Si, and C₄F₈ plasma forms a polymeric fluorocarbon protection layer on the sidewalls of NWs, suppressing lateral etching during the anisotropic etching step. Figure 2a-ii presents a cross-sectional SEM image of a vertically etched Si wafer. For facile separation of Si NWs from the substrate, final isotropic etching with low-power SF₆ plasma was performed. Because the sidewalls of Si NWs are passivated with fluorocarbon, etching of Si begins at the bottom part of line pillars and propagates to the center. Proper control of isotropic etching time can leave a narrow bridge with a smallest width of 10−30 nm between the NWs and the substrate, which should be maintained because the complete separation of the Si NWs from the substrate by the RIE process degrades the alignment of NWs during subsequent transfer. The SEM image of Figure 2a-iii shows defined Si NWs after the completion of the lateral etching process followed by removal of the P4VP etch mask. Also, Figure 2a-iv, c, and d exhibit low- and high-magnification SEM images of fabricated Si NWs, which were uniformly formed over a macroscopic (20 mm × 15 mm) area. The polymer etch mask was simply removed by a short oxygen plasma treatment or gentle washing with an organic solvent (isopropyl alcohol, IPA).

As we mentioned above, we could systematically control the width and height of the Si NWs by modulating the width of the transfer-printed etch mask nanopatterns and by adjusting the etch depth of the first anisotropic (vertical) etching process,
respectively. Although the ultimate minimum scale of printed etch mask patterns depends on the resolution of lithographic tools used for the patterning of its original master template, the width of the printed P4VP nanopatterns of 200 nm can additionally be reduced to 50 nm by oxygen plasma trimming, as demonstrated in Figures S1 and S2.

Additionally, narrower Si NWs were formed via NTPP (Figure 2e–g). We previously reported solvent-vapor-assisted nanotransfer printing, which can form ultrafine metallic nanopatterns with even sub-10 nm resolution.43 Using S-nTP, we formed 25 nm metallic etch mask patterns. Figure 2e and f depict SEM images of printed 25-nm-wide Cr NWs on a Si wafer and fabricated Si NWs with a width of 25 nm and height of 30 nm, respectively. By modulating the etch depth, Si NWs with a width of 25 nm and a height of up to 180 nm were fabricated (Figure S3). Figure 2g presents a corresponding high-magnification SEM image and a large-area photograph of fabricated NWs.

We also demonstrate how NTPPP provides the controllability of crystallographic orientation of the Si NWs, which influences their physical properties to a great extent.33,47,48 Si wafers with a specific crystallographic orientation were obtained using the process presented in Figures 2h–o. For example, we could form (100)-oriented and (110)-oriented Si NWs from the same (100) Si wafer by controlling the orientation of the long-axis direction of the printed etch mask. Figure 2h–o illustrate large-area formation of (100)- and (110)-oriented line patterns on a Si wafer and also provide corresponding cross-section SEM images and selected area electron diffraction (SAED) patterns of NWs after the RIE process, which clearly confirms the formation of (100)-oriented and (110)-oriented Si NWs, respectively. Cross-section transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of Si NW are shown in the insets of Figure 2k,o and Figure S4. The different physical properties of the NWs will be discussed in detail later in this paper.

For uniform and reliable transfer printing, the interfacial fracture energy between a nanostructure and transfer medium \( (G_{nm}) \) should be higher than that between the nanostructure and the donor substrate \( (G_{nd}) \) and should be lower than that between the nanostructure and the receiver substrate \( (G_{nr}) \). This constraint seriously limits the extent of applicable receiver substrates and necessitates additional surface treatments for substrates that do not meet the above conditions. Previous studies thus utilized a kinetically controlled transfer mechanism using polydimethylsiloxane (PDMS) with low surface energy, coating of an adhesive layer on receiver substrates, or water-assisted reduction of \( G_{nd} \).41,49,50 However, in this work, uprooting of the SiNWs makes the process challenging due to the physical connection of Si NWs to the receiver substrate via remaining bottom linkages. Also, it is difficult to maintain the alignment due to the shock from the neck being broken.

In the final step of the NTPP process, fabricated Si NWs were transplanted from the mother wafer onto desired substrates for various applications. We thus developed an upgraded transfer printing method based on extremely robust binding between a polymeric transfer medium and NWs and a solvent-assisted adhesion switching mechanism of polymeric transfer medium, as schematically presented in Figure 1C. First, we utilized the strategy of polymer penetration to the space between the NWs and the substrate. The spin-cast polymeric transfer medium (poly(methyl methacrylate); PMMA) deeply infiltrates even to the region below the NWs and strongly grasps the NWs to allow their uniform and reliable detachment from the Si wafer (Figure 3a).

Before detachment, we optimized the neck thickness by controlling the duration time of isotropic dry etching based on numerical modeling results because of the physical connection of Si NWs to the mother substrate. For physical analysis of the neck effect, von Mises stress and cross-sectional stress distribution simulations of the Si NWs were conducted for Si NWs with a width of 200 nm, a height of 80 nm, and a depth of 120 nm, where the NWs were trapped by PMMA (Figure S5). The maximum stress was applied on the neck when the PMMA moved upward by 12 nm (Figure Sb and Figure S5). A finite element method (FEM) simulation performed under these conditions showed that as the neck became thinner, the point of maximum stress moved from the contact point between PMMA and the Si NW to the narrow neck region of the Si NW. Moreover, the calculated stress applied at a neck thickness of <50 nm was higher than the fracture strength of Si (300 MPa).51 To investigate the effect of neck width on detachment yield, we fabricated Si nanowires with neck thicknesses of 150, 110, 70, and 30 nm by controlling the duration time of the isotropic dry etching process. Si NWs were not detached for neck thickness of ≥70 nm. However, a ~100% detachment yield was obtained for narrower necks of 30 nm. After optimization of the neck thickness, the polymer film and the nanowires were homogeneously released from the wafer by attaching a polyimide (PI) adhesive film (Figure 3c, d, e, f), which can be explained by the formation and propagation of cracks at the narrow bridges (neck).

Figures 1g–i depict the mechanism and the procedure of the solvent-assisted transfer onto the desired receiver substrates. The PI/PMMA/NWs was brought into a chamber containing a solvent mixture of acetone and heptane (5:5 volume ratio), and the evaporated solvent molecules penetrate the polymer film. The solvent molecules existing at the interface between the polymer film and the adhesive film weaken the adhesion between the polymer films due to a superlubrication effect via screening of interfacial adhesion.43,52,53 Even though the interfacial fracture energy (122.42 J/m²) at the interface between PMMA and the adhesive film was considerably high at a dry state, it was dramatically reduced to 0.208 J/m² when solvent vapor was applied (Table S2). (Fracture energy was calculated by measuring the peel strength, as shown in Figure S6.) Thus, the adhesive film can be selectively detached from the PMMA when the PI/PMMA/NWs was brought into contact with a receiver surface, leaving PMMA/NWs on the receiver substrate. Moreover, the considerably weakened adhesion induced by the solvent-assisted adhesion switching mechanism could overcome the limitation of the previous transfer-printing method, which could only transfer nanostructures with low interfacial fracture energy (~2 J/m²).41,50 Consequently, extremely low fracture energy at the solvent-vapor-treated PI/PMMA interface guarantees transfer printing of the nanowires onto nearly arbitrary surfaces without requiring an additional adhesive layer. After washing away the PMMA using an appropriate solvent, only the Si NWs were left behind on the substrate (Figure 1i).

The solvent-assisted adhesion switching phenomena by the incorporated solvent molecules enable fast, uniform, and reliable transfer of NWs while maintaining their alignment direction over a large area. Figure 3e and h show photographs and SEM images of transfer-printed Si NWs on a Si substrate. The photograph in Figure S7 also represents the ultralong
connectivity and large-area arrangement of the printed nanowires on a bending substrate. Furthermore, NTPP using the infiltrated polymeric transfer medium showed a markedly improved transfer yield compared to the conventional PDMS contact transfer printing, as shown in Figure S8a. The evaluated transfer yield (printed area/original area of Si NWs (width = 200 nm)) of NTPP and contact printing was 98% and 34%, respectively (Figure S8b). Also, NTPP provides good alignment quality after transfer printing. The average misalignment angle of nanowires produced by NTPP was 1.2°, which is substantially smaller compared to that (19.6°) of PDMS-based transfer printing (Figure S8c). This can be attributed to the strong grasping capability of the infiltrated polymeric transfer medium. In addition, we also confirmed that the mother Si wafer can be recycled after using it for NTPP by surface polishing and cleaning processes (Figure S9), which can significantly reduce the material cost for the production of Si NWs.

In a similar way, 25 nm Si NWs also could be produced and transfer-printed onto diverse substrates through NTPP. Figure 3f and g present the mother wafer after the detachment of Si and the photograph of detached NWs on the polymer/adhesive film. Figure 3h and Figure S10a and b also show high- and low-magnification SEM images of transfer-printed Si NWs with a width of 25 nm onto a Si wafer and a PI flexible film, respectively. The single-crystalline nature of printed nanowires can be clearly recognized in the TEM image (Figure 2k and o and Figure S10c).

**NTPP of Single-Crystal Nanowires onto Diverse Surfaces.** One strong advantage of NTPP is that it does not require any adhesive layer or treatment on receiver substrates, and thus it allows printing on nearly arbitrary surfaces regardless of surface chemistry and topography. As an example, the formation of inorganic semiconductors on biological surfaces such as human skin can contribute to the realization of future biomedical electronics such as electronic skin and health-care monitoring devices. As schematically illustrated in Figure 4a, Si NWs were successfully printed on the surface of human skin (Figure 4b). These printed NWs on skin would be able to directly collect biosignals.

Additionally, the fabrication of three-dimensional (3D) complex structures was also realized by implementing NTPP multiple times on the same receiver substrates. As a demonstration of three-dimensional nanostructures, we fabricated simple crossed-wire structures through sequential printing of Si NW arrays (Figure 4c,d). First, we transfer-printed a first layer of Si NWs, and after removal of the PMMA transfer medium, a second layer of Si NWs was printed while arranging the angle between the upper and lower nanowires at 90°. The low- and high-magnification SEM images in Figure 4d...
were obtained after removal of the PMMA medium. Successive printing of Si NWs can generate even more complex 3D structures, and such three-dimensional periodic nanostructures can be useful for diverse applications including photonic crystals, metamaterials, and sensors.

The adhesion switching effect makes it possible to print nanostructures on topographically modulated surfaces, where only a minimum contact area between donor and receiver substrates exists. We successfully fabricated suspended NW structures on a deep trench substrate, as shown in Figure 4e. To fabricate suspended nanowire structures, a PMMA/NWs was carefully laid on a supporting deep trench structure with a depth of 1 \( \mu \text{m} \) and a width of 50 \( \mu \text{m} \). Toluene vapor was then applied to the PMMA transfer medium by proximally approaching a toluene-saturated PDMS gel pad, which was prepared by dipping a dry PDMS pad in a toluene bath for 6 h. After removing the PMMA film by dipping the whole device into a solvent bath (toluene), suspended nanowire structures were successfully obtained (Figure 4f). These suspended nanowire structures can be particularly useful for high-performance nanosensors with a high sensitivity because all the surface areas can be exposed to analytes. In addition, suspended or free-standing semiconducting nanowires can be exploited to realize emerging biomedical applications such as intracellular recording and cell endoscopy based on free-standing nanowires attached to optical fibers.

Electrical Characterization and Demonstration of a Flexible Strain Sensor. For the electrical characterization of printed NWs, we fabricated a Schottky-barrier FET, where the NWs function as an active channel (Figure 5A). In a Schottky-barrier FET, junctions are formed between the semiconductor and the source/drain metal electrode. To prepare the FET device shown in Figure 5a, we transfer-printed Si NWs on a heavily doped p-type Si wafer with a thermally grown oxide layer (thickness = 300 nm). It is well known that the electrical response of the Schottky-barrier FET varies depending on the work functions of the electrode and the semiconductor. We formed a Ti/Au electrode on two sides of the Si NWs and annealed the sample at 600 \( ^\circ \text{C} \) for 5 min in a vacuum system using rapid thermal annealing equipment to form a Schottky junction. Figure S11a shows an SEM image captured from the central region of the fabricated device.

Electrical characterization of the 200-nm-wide p-type Si-NW FET device was then performed. Figure 5b (\( I_{d}\) vs \( V_{g} \)) clearly shows the switching of the device with an on-off current ratio of nearly 10^4 at a \( V_{ds} \) of 1 V, and the field-effect hole mobility was calculated to be 71.2 cm^2 v^-1 s^-1. The electrical performance of our device upon the application of gate bias is consistent with that of a previously reported FET device with a Ti/Au electrode and p-type Si NWs. Similarly, we also fabricated a FET device with 25-nm-wide NWs using an n-type Si wafer (resistivity = 1 \( \Omega \cdot \text{cm} \)). Figures 5c and S11b show the obtained \( I_{d} \) vs \( V_{g} \) curve and \( I_{d} \) vs \( V_{ds} \) curve of the device.

Figure 5. Device applications of Si NWs. (A) Electrical characterization of Si NWs. (a) Schematic showing the structure of a nanowire-based FET device. (b) Drain current (\( I_{d} \)) vs gate bias (\( V_{g} \)) characteristics for 200-nm-wide Si (p-type) nanowires. (c) \( I_{d} \) vs \( V_{ds} \) characteristics of 25-nm-wide Si (n-type) nanowires. (B) Demonstration of a flexible strain sensor. (d) Conceptual drawing of the strain sensor. (e) Change of \( \Delta R/R_{o} \) and gauge factor depending on strain. (f) Cycling test of the strain sensor device. (\( \Delta R/R_{o} \) was repeatedly measured for 50 strain cycles.)
and the field-effect mobility of electrons of 1.6 cm² V⁻¹ s⁻¹. The significantly reduced mobility of small-diameter nanowires can be attributed to the contribution of surface defects and trap sites from surface roughness.³⁰,⁵⁵ Because the mobility of a field-effect transistor highly depends on the fabrication conditions, we expect that the mobility can be even further enhanced through optimization of the fabrication process, for example, by decreasing the doping level or minimizing the trapping states on the nanowire surface.³⁰,⁵⁷

The possibility of an ultrasensitive piezoresistive strain sensor using Si NWs has been suggested.³³,³⁸,³⁹ For example, Yang et al. experimentally demonstrated giant piezoresistance of Si NWs with a diameter of 50–300 nm.³³ In addition, the highly flexible nature of Si NWs can be utilized to realize a high-performance strain sensor, which can be easily mounted onto diverse surfaces. However, as mentioned above, vapor- or solution-phase synthesis and rearrangement of NWs can accompany technical issues such as large variation of the physical response and reproducibility.

We demonstrate how the NTTP process can be used for the fabrication of high-performance NW strain sensors in a simple and reliable way (Figure 5B). First, using NTTP, well-defined Si NWs were formed on a flat PDMS pad as a stretchable substrate. The longitudinal crystallographic orientation of the nanowires was carefully controlled to be (100) or (110), where the (110) orientation was reported to have a stronger piezoresistive effect.³⁵ A metal electrode was then defined through thermal evaporation of Ag in the presence of a shadow mask (Figure S12a). For characterization, the strain sensor was mounted on a measurement device, as shown in Figures 5d and S12b. The resistance of the device was monitored with varying unidirectional tensile strain. The graph in Figures 5e depicts the change of the relative resistance (ΔR/R₀) as a function of the applied tensile strain (ε).

The gauge factor (GF), which is defined as (ΔR/R₀)/ε, was used as a measure of sensitivity. The (110)-oriented Si NW sensor recorded a GF of 205.2 (±7.4) in the applied strain range of 0–5%. The measured GF of our device was 30 times higher than the previously reported gauge factor of a strain sensor made of transfer-printed Si NWs.³⁸ In contrast, the device with (100)-oriented Si NWs shows a GF of 14.9 (±2.3) in the strain range of 0–5%, which is consistent with previous reports,³⁸ suggesting the importance of orientation controllability for maximizing the piezoresistive effect. The abrupt increase of resistance over 5% of strain can be attributed to the partial breakage of Si NWs.³⁸ However, it is worthwhile to note that even a large strain of 12% did not completely break the NWs, as shown in Figure S12c, implying the outstanding flexibility of our NWs. We also performed a cycling test (at a strain of 1.5%) to investigate whether the piezoresistive effect of (110)-oriented Si NWs is reversible. With repeated application and removal of strain, ΔR/R₀ changed reversibly and reliably over 50 times, as shown in Figure 5f. The standard deviation of ΔR/R₀ at the 1.5% strained state was approximately 10%.

CONCLUSION

In summary, we introduced a highly facile and reliable strategy of nanotransplantation printing to form high-quality, long-range-ordered single-crystalline nanostructures on arbitrary substrates. After printing nanoscale etch mask patterns with a width of 25–200 nm on a single-crystal Si wafer, a combinatorial reactive ion etching process composed of anisotropic and isotropic etching generates Si NWs connected to the substrate via narrow bridges with extensive control of the geometrical parameters of the NWs. A polymeric transfer medium infiltrated the nanoscale gap between defined NWs and the mother Si substrate leads to tight binding of the NWs in the polymer transfer medium, which enables uniform detachment of an array of the NWs from the substrate via homogeneous breakage of the narrow bridges. Dynamic adhesion switching by solvent vapor exposure facilitates rapid and efficient transfer printing of the single-crystalline NWs onto diverse substrates including flexible and biological surfaces without the need of any surface treatment, leading to an extremely high transfer yield of 96%. The electrical characteristics (field effect mobility of 71.2 cm² V⁻¹ s⁻¹) of the nanowires were confirmed by fabricating and characterizing a high-performance Schottky-barrier field-effect transistor and piezoresistive strain sensor devices. In particular, the controllability of crystallographic orientation results in a large gauge factor of over 205.2 for the (110) orientation. This concept of the NTTP process can be applied not only for Si NWs but also for various high-quality single-crystal semiconductor nanowires, and we expect that these nanostructures can be highly useful for various high-performance future nanodevices formed on arbitrary surfaces.

EXPERIMENTAL SECTION

Fabrication of 200 nm Scale Master Mold. The Si master template was fabricated using KrF photolithography followed by reactive ion etching. A positive photore sist (PR, Dongjin Semichem Co. Ltd.) with a thickness of 400 nm was spin-coated and then exposed using a KrF scanner (Nikon, NSR-5203B), followed by developing using a developer solution (tetramethylammonium hydroxide, Dongjin Semichem Co.Ltd.). The PR patterns were used as an etch mask to pattern the Si surface by reactive ion etching (gas: CF₄, working pressure: 7 mTorr, plasma power: 2W). The Si master templates were 200 nm in width and 350 nm in height with a 1.2 μm period.

Fabrication of 25 nm Scale Master Mold. Directed self-assembly of polystyrene-b-polydimethylsiloxane (PS-b-PDMS) block copolymer (BCP) has been previously studied to create ordered patterns⁵¹,⁶¹ and various applications.⁶³–⁶⁶ We thus employed this technique for large-area preparation of a high-resolution master mold.⁶⁷–⁶⁹ PS-b-PDMS BCP with a MW of 48 kg mol⁻¹ (SD48), which forms 25-nm-wide lines, respectively, was purchased from Polymer Source Inc. and used without purification. SD48 BCP was dissolved in a mixed solvent of toluene, heptane, and propylene glycol monomethyl ether acetate (1:1:1 by volume), yielding a 1.0 wt % polymer solution. Surface-patterned Si substrates with a width of 1 μm, a depth of 40 nm, and a period of 1.25 μm were used as guiding templates. The substrate was treated with a PDMS brush (5 kg mol⁻¹, Polymer Source Inc.) at 150 °C using a vacuum oven. A solution of SD48 was spin-cast onto the template and annealed for 6 h in the chamber at room temperature using toluene vapor. In order to remove the top-segregated PDMS layer and organic block (PS), the samples were etched by CF₄ plasma (etching time 20 s, gas flow rate 30 sccm, working pressure 15 mTorr, and plasma source power 50 W) followed by O₂ plasma (etching time 30 s, gas flow rate 30 sccm, working pressure 15 mTorr, and plasma source power 60 W).

Formation of Polymeric Etch Mask Patterns on a Si Wafer. Surface patterns of the Si master template were 200 nm in width and 350 nm in height with a 1.2 μm period. Prior to the replication, the surface of the master template was treated with an OH-terminated PDMS brush (molecular weight (MW) = 5 kg mol⁻¹, Polymer Source Inc.). By rebreaking the cured PDMS from the template, surface patterns of the template were securely replicated on the mold. Poly(4-vinylpyridine) (MW = 60 kg mol⁻¹, Sigma-Aldrich Inc.) was dissolved in a mixture of IPA and acetonit (1:1 by weight), to yield a 4 wt % solution. P4VP thin film was then spin-casted on the elastomeric PDMS stamp to replicate the surface patterns of the mold.
the conformal contact of the PDMS stamp with a single-crystal Si wafer, the patterned P4VP film was securely transferred on the wafer. After short treatment of oxygen plasma (gas flow rate = 30 sccm, working pressure = 15 mTorr, plasma source power = 100 W, and bias power 60 W), the residual bottom polymer layers were removed, and 200-nm-wide nanopatterns with a 1.2 μm period were formed with a high uniformity over a large area (20 mm × 15 mm).

**Formation of 25 nm Metallic Etch Mask Patterns on a Si Wafer.** Prior to the replication, the surface of the master mold was treated with a PDMS brush (Polymer Source Inc.). PMMA (MW = 100 kg/mol, Sigma-Aldrich Inc.) was dissolved in a mixture of acetone, toluene, and heptane (4.5:4.5:1), yielding 4 wt % solutions. PMMA was deposited by electron beam evaporation followed by a lift-off process using a Keithley 4200-SCS and a probe station in ambient conditions. Electrical characterization of Si NW FETs was carried out using a Keithley 6487 and a probe station in ambient conditions. The authors declare no competing financial interest.

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