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Monolayer Resist for Patterned Contact Printing of Aligned Nanowire Arrays

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In recent years, single crystalline, semiconductor nanowires (NWs) have been widely explored as the potential building blocks for various technological applications, such as electronics,[1] photonics,[2] sensors,[3] and energy conversions.[4] To fully extend the potential, however, the development of generic assembly methods is required.[5] Recently, we demonstrated a simple contact printing approach for the large-scale assembly of parallel arrays of NWs on rigid and mechanically flexible substrates.[6] During this process, direct and aligned transfer of NWs from the growth (i.e., donor) substrate to the receiver substrate is attained. This highly versatile approach is attractive for large-area printable electronics with the printed NW parallel arrays being configured as the channel or active material for transistors and sensors. Previously, the NW patterning was achieved by photolithographically patterning a polymeric resist layer on the receiver substrate prior to the printing process.[6] Following the printing process, the resist layer covered with the printed NWs is dissolved in a solvent, leaving behind only the NWs assembled at predefined locations. To further demonstrate the versatility of the contact printing process, here, we report patterned printing of NWs by using fluorinated self-assembled monolayers (SAMs) as the resist layer. By projecting a light pattern on the surface of the SAM resist in an oxygen-rich environment, sticky and nonsticky regions on the surface are directly defined in a single-step process which then enables the highly specific and patterned transfer of the NWs by the printing process, without the need for a subsequent lift-off step. This work demonstrates a novel route toward scalable, patterned printing of NWs on substrates by utilizing very ultraviolet (VUV) tunable, nanoscale chemical interactions.

The process flow for the patterned NW printing with an SAM resist is illustrated in Figure 1. First, a Si/SiO_2 (50 nm, thermally grown) substrate is chemically reacted with (heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane (HDF) to form a highly stable, fluorinated SAM on the surface of the substrate. A light pattern is then projected on the SAM resist by using an excimer light source (172 nm, ~25 mW/cm^2) and a shadow mask (Figure 1a). The VUV light exposure in the presence of O_2 results in the chemical cleavage of the F−C bonds and the formation of −COOH and −CHO functional end groups (Figure 1b).[7] While the original fluorinated SAM is highly nonsticky to the NWs, the VUV-modified monolayer exhibits strong binding interactions with the NWs, most likely through H-bonding. Following the patterned exposure of the SAM resist, the NW printing is conducted by directionally sliding a growth substrate consisting of a dense forest of Ge or Si NWs (grown nonepitaxially by vapor−liquid−solid process) on top of the receiver substrate. A lubricant (octane: mineral oil, 2:1 v/v) is applied between the two substrates to minimize the mechanical interactions, enhancing the dominant role of the well-controlled chemical interactions in guiding the NW transfer process. During the printing process, NWs are dragged on the receiver substrate, resulting in their alignment in the direction of the shear force

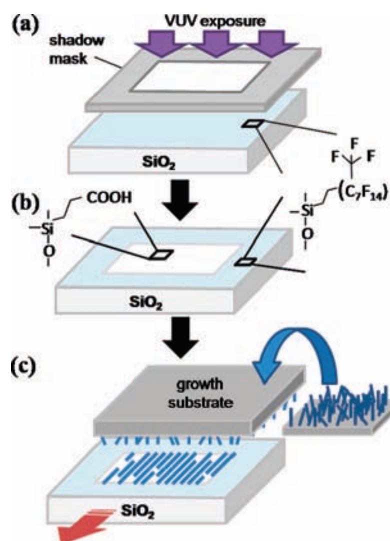

Figure 1. Schematic of the patterned contact printing process with monolayer resist. (a) Patterning of fluorinated SiO_2 surface is carried out by VUV irradiation in the presence of O_2. (b) C−F bonds in the exposed regions are cleaved and replaced with −COOH or −CHO functional groups. (c) Contact printing results in the aligned transfer of NWs on the VUV exposed regions.

(Supporting Information). Once anchored to the surface of the receiver substrate by chemical binding interactions, NWs are detached from the growth substrate. As a result, highly aligned NW arrays are assembled on the exposed SAM regions of the receiver substrate while no NWs are assembled on the unexposed, fluorinated SAM regions (Figure 1c).

To characterize the properties of the VUV exposed SAMs, contact angle, XPS, and ellipsometry measurements were performed as a function of the exposure time. As shown in Figure 2a, the contact angle of the HDF treated surface is ~100°, showing a highly hydrophobic surface property. As the monolayer is exposed to VUV, however, the contact angle decreases and the surface changes to possess a hydrophilic property. Specifically, the contact angle is reduced to ~10° after 60 min of exposure in 3 Pa O_2/N_2 (21, 79%) ambient. On the other hand, when irradiation is carried out at 10^5 Pa, it takes <20 min to achieve a similar contact angle. This accelerated chemical transformation of the monolayer by increasing the pressure depicts the important role of O_2 in the VUV enabled surface chemical modification.[7]

From XPS measurements (Figure 2b), the VUV-induced, chemical modification of the monolayer is directly confirmed. While the F 1s peak at 688 eV, originating from C−F bonds, is clearly observed for the unexposed SAM, it is completely diminished after the VUV irradiation. This is also seen from the C 1s spectrum, where the C−F peak at 292 eV disappears upon VUV irradiation.

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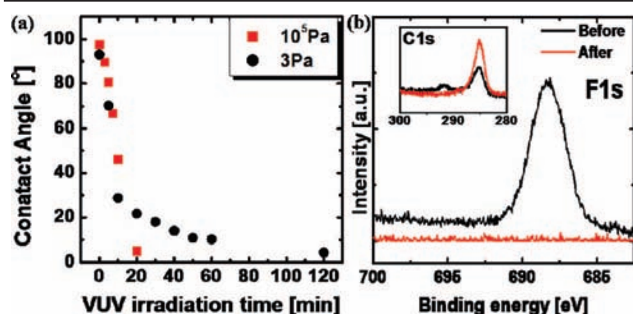

Figure 2. (a) Water contact angle as a function of VUV irradiation time. Irradiation is carried out at 10^5 Pa and 3 Pa, corresponding to 2×10^4 Pa and 0.6 Pa of oxygen partial pressure, respectively. (b) F1s and C1s (inset) XPS spectra of fluorinated surfaces before (black curve) and after (red curve) VUV irradiation for 30 min at 10^5 Pa.

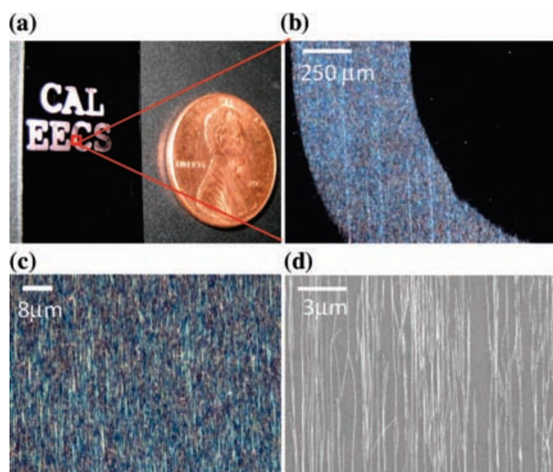

Figure 3. (a) Optical bright field, (b−c) optical dark field, and (**d**) SEM images of Ge NWs (d ∼30 nm) printed on the VUV patterned SAM-resist.

On the hand, the C 1s peak at ∼285 eV which corresponds to the C−C bond remains intact, even after the VUV exposure. The results suggest that the alkyl backbone of the monolayer remains intact with only the C−F bonds being oxidized upon VUV irradiation and replaced with polar −COOH and −CHO species. This is also confirmed from ellipsometry measurements where SAM thicknesses of ∼1.1 and 0.9 nm are observed for the unexposed and exposed SAMs, respectively. The observed results are consistent with the previously reported VUV modification of fluorinated SAMs on SiO_2 surfaces in the presence of O_2.[7] In those studies, it was proposed that O_2 forms highly active species upon VUV irradiation which then readily oxidize and cleave the C−F bonds. A similar surface chemical reaction is expected in our fluorinated SAMs.

Optical and scanning electron microscopy images of printed Ge NWs (d ∼30 nm) on the VUV-patterned fluorinated SiO_2/Si substrate are shown in Figure 3. Fluorinated regions possess highly nonsticky surface properties; therefore, preventing NW transfer during the contact printing process. On the other hand, NW parallel arrays are readily assembled on the hydrophilic regions, enabled by the VUV exposure. The transferred NWs are found to be relatively dense (2−5 NW/μm) and well aligned (Figure 3d). The density may be further enhanced in the future by using complementary surface modification of VUV-irradiated regions, which was not incorporated in this work. As clearly evident, this simple process enables a high degree of selectivity in the assembly of the NWs in well-defined locations on surfaces, especially for applications that do not require nm-scale positioning, such as for large-area electronics with the device dimensions on the order of tens of microns. In our current setup, a resolution limit of ∼5 μm is obtained which is limited by the nonideal contact between the shadow mask and the substrate.

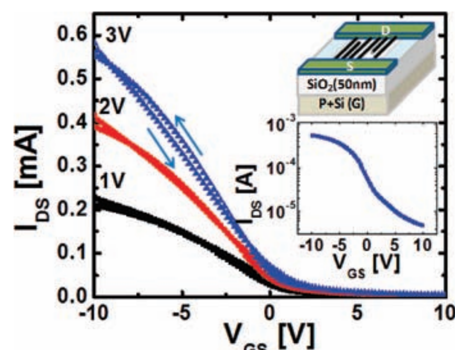

Figure 4. Transfer characteristics of a parallel-array Si NW FET with W ∼200 μm and L ∼3 μm (Insert shows log scale, $V_{ds} = 3$ V).

To further investigate the feasibility of this printing approach for electronic applications, we fabricated back-gated (gate oxide thickness ∼50 nm SiO_2), field-effect transistors (FETs) with channel width ∼200 μm and source/drain (S/D) spacing ∼3 μm by using p-type Si NWs (d ∼30 nm, B doped). Notably, the assembled NWs do not detach from the substrate during the standard microfabrication processing steps used here (Supporting Information). Figure 4 shows a representative transfer characteristic of such a proof-of-concept device structure. The transistor delivers a modest ON current of ∼0.6 mA at $V_{DS} = 3$ V with $I_{ON}/I_{OFF} > 100$. This ON current corresponds to ∼1 μA/NW assuming a NW density of 3 NW/μm, which is consistent with the observed I_{ON} for a typical single Si NW FET configured in a similar device geometry.

In summary, well-defined and highly specific NW assembly is achieved by combining contact printing with direct SAM patterning on SiO_2 surfaces. Here, the SAM is effectively used as the resist for the NW transfer process, enabling a highly versatile, one-step process for achieving a patterned assembly of parallel arrays of NWs on substrates.

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Supporting Information Available: Nanowire synthesis details, surface modification, and contact printing procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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