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Patterning of self-assembled monolayers by phase-shifting mask and its applications in large-scale assembly of nanowires

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A nonselective micropatterning method of self-assembled monolayers (SAMs) based on laser and phase-shifting mask (PSM) is demonstrated. Laser beam is spatially modulated by a PSM, and periodic SAM patterns are generated sequentially through thermal desorption. Patterned wettability is achieved with alternating hydrophilic/hydrophobic stripes on octadecyltrichlorosilane monolayers. The substrate is then used to assemble CdS semiconductor nanowires (NWs) from a solution, obtaining well-aligned NWs in one step. Our results show valuably the application potential of this technique in engineering SAMs for integration of functional devices. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4907042]

Self-assembled monolayers (SAMs) have drawn technological interests and been extensively used to modify the interfacial properties of surfaces.[1] Patterned SAMs, in which mixed components of SAMs are distributed spatially on a flat platform, provide an efficient solution for surface engineering and functionalization. Upon choosing different end groups of SAMs at predefined regions, patterned functionality (wettability, conductivity, adhesion, chemical reactivity, etc.) can be achieved on a planar surface.[2] By employing patterned SAMs as receiver substrates, nanowires (NWs),[3–6] nanoparticles,[7,8] cells,[9] or other biomolecules[10] could be easily assembled into well-ordered architectures. To meet the ongoing requirements of these applications like nanowire alignment, various methods have been developed to pattern SAMs, including microcontact printing,[11] UV lithography,[12] dip-pen nanolithography,[13] scanning probe lithography,[14] and direct laser patterning.[15] However, these methods have their inherent limitations like inaccessibility, particularity, time consuming, size limitation, etc. In this paper, we present a facile, scalable, and nonselective SAM patterning method, which is a significant contribution to the SAM patterning toolbox for its accessibility and generality. Furthermore, it was subsequently applied in large-scale assembly and alignment of nanowires.

Figure 1 is the schematic of the proposed SAM patterning method. Phase-shifting mask (PSM) is an extensively used diffractive optical element that can spatially modulate laser beams, forming a lateral interference pattern in the direction of the incident laser beam.[16] Laser irradiated through a 1D PSM is divided into two coherent beams of comparable intensities to create a 1D interference pattern. Specifically, a spatially modulated laser beam introduces heat distribution on SAMs, indicating more heat is generated at the coherent enhancement and less at the coherent attenuation. In Figure 1(b), high temperature caused by laser irradiation accelerate SAM desorption reaction;[17,18] consequently, organic molecules are desorbed where local temperature rises above the desorption threshold, leaving the surface exposed *in situ*. Striped patterns are then generated on SAMs because adsorbates in other regions are retained. In addition, binary-component SAMs can be fabricated upon backfilling the exposed regions with new adsorbates, as shown in Figure 1(c).

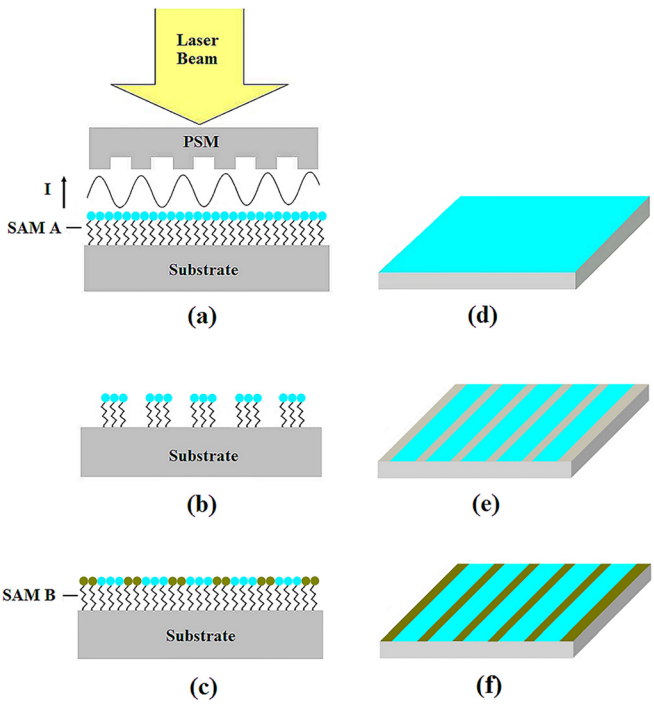

FIG. 1. Schematic of the laser-PSM patterning process. (a) A PSM is placed on top of the substrate with SAM A under laser. (b) Laser-induced pattern of alternating SAM A and exposed substrate. (c) Backfilling the exposed substrate with SAM B. (d), (e), and (f) are the top views of (a), (b), and (c), respectively.

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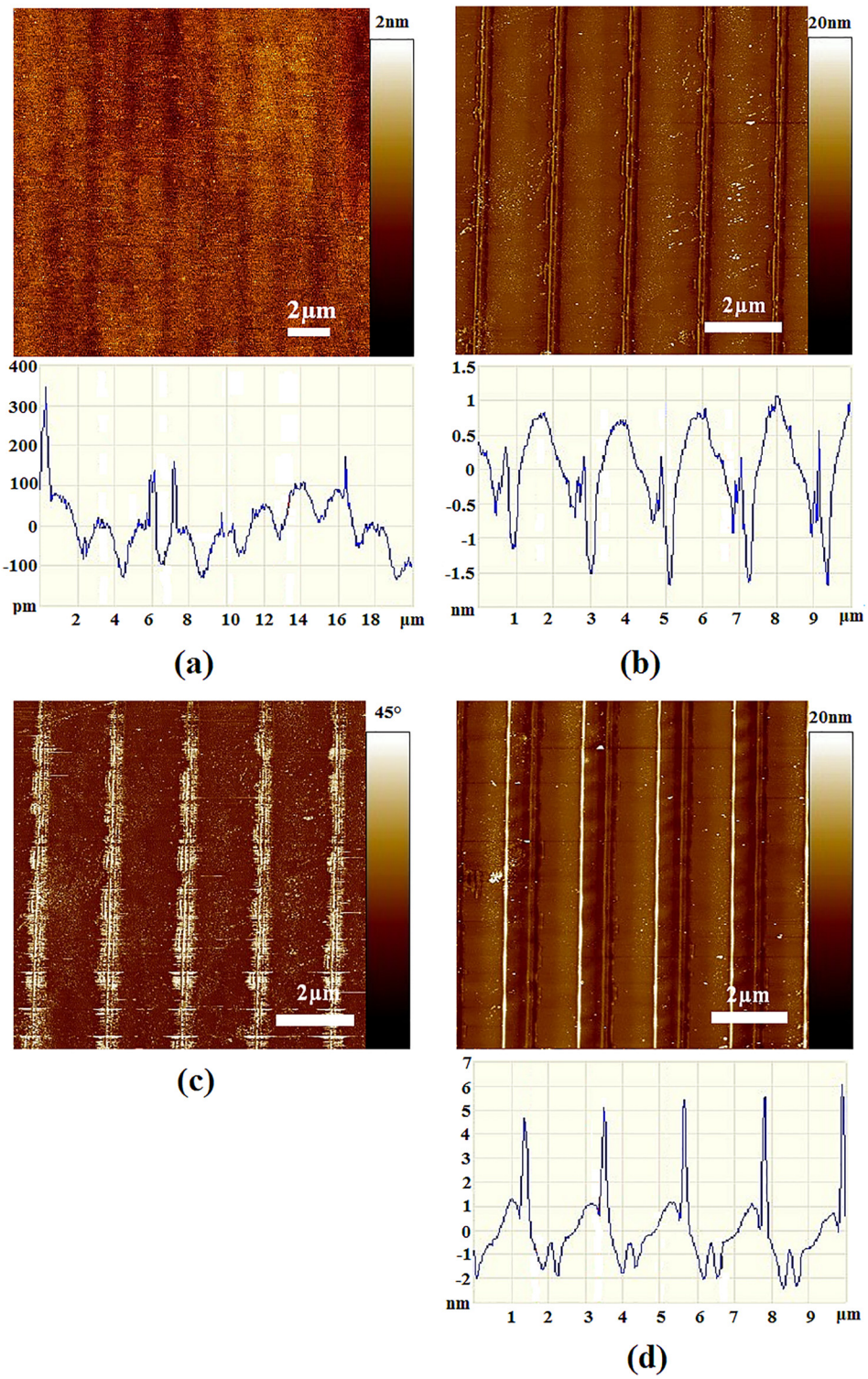

FIG. 2. Topography images and high profiles of samples fabricated at different laser powers. (a) 400 mJ·cm^{-2} for one pulse. (b) and (c) 400 mJ·cm^{-2} at 10 Hz for 2 s and the corresponding phase mode image. (d) 400 mJ·cm^{-2} at 10 Hz for 5 s.

The 1D-patterned Trichloro(octadecyl)silane (OTS) monolayer is fabricated on a SiO_2 substrate by procedures (a) and (b) in Figure 1. To prepare the substrate, a Si (100) wafer was soaked in piranha solution (concentrated sulfuric acid and 30% hydrogen peroxide mixed in the volume ratio of 7:3) for 1 h to regrow an oxide layer. SAMs were prepared on the SiO_2 by immersing substrates into a 3 mM n-heptane solution of OTS for 8 h. Subsequently, a KrF excimer laser (COMPex Pro 201F, Coherent, Inc.) at 248 nm was used to pattern the OTS SAMs on SiO_2 in the subsequent step. Quartz 1D PSM with a surface-relief structure of 2 μm periodicity and 260 nm depth was placed in contact with the substrate. Figures 2(a), 2(b), and 2(d) are the Atomic Force Microscope (AFM) topography images and height profiles of samples fabricated with increasing laser power. Periodic parallel stripes with a period of 2 μm are observed in the three figures and the height differences are around 0.2 nm, 2.5 nm, and 7 nm, respectively. The increasing laser power results in increasing height difference and decreasing width of the retained region. Because the length of OTS molecule is about 2 nm, Figure 2(b) is believed to have the molecules completely removed at coherent enhancement region whereas SiO_2 ablation may occur in

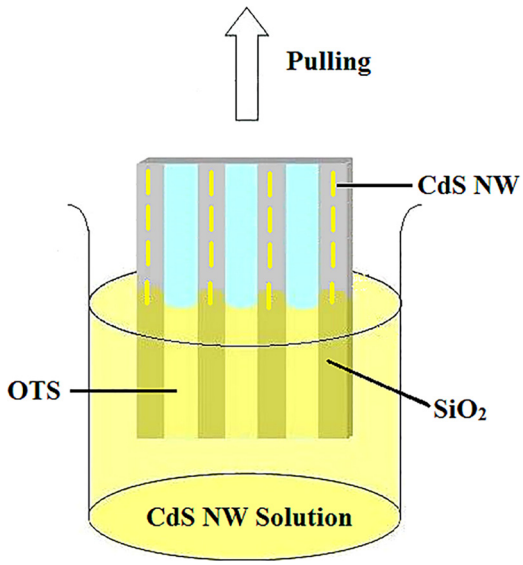

FIG. 3. Schematic of the pulling process. Patterned substrate is dipped into a CdS NW solution and then pulled up at a constant speed by a stepper motor. NWs are assembled in a repeating stick–slip motion during dip coating.

Figure 2(d) at maximum interference intensity. Figure 2(c) is the phase image of Figure 2(b), which reveals more clearly the difference in the chemical and the mechanical properties between the exposed SiO_2 surface (with a width of about 500 nm) and those of the remaining OTS monolayer. These AFM images reveal that by adjusting the irradiation conditions (laser power and irradiation time), partially or completely removed SAM patterns can be fabricated to obtain controllable structures. When the SAM is completely removed, a second adsorbate can be chosen to backfill the exposed substrate for surface engineering and further functionalization.

The photothermal excitation mechanism is widely available for SAMs. Related processing has been found not only on silane-based SAMs[19,20] but also on organo/silicon interfaces[21] and thiol-based SAMs[22,23] as well. Therefore, the present patterning method is able to efficiently generate patterns on different kinds of SAMs.

The stripe-patterned wettability is readily obtained as alternating hydrophobic areas on the OTS monolayer and hydrophilic areas on the SiO_2. To show the great potential of this technique in assembling nanostructures for device applications, the patterned substrate is used to assemble CdS NWs from solution. The CdS NWs were synthesized by the hydrothermal method[24] and measured ~26 nm in diameter on the average and several micrometers in length. To reduce surface tension and form a homogeneous thin film of an NW solution on substrates, 1 wt. % sodium dodecyl sulfate (SDS) was used as surfactant for a 0.05 wt. % CdS NW suspension. As shown in Figure 3, the patterned substrate is dipped into the solution and then pulled up at a constant speed by a stepper motor, which performs a repeating stick–slip motion while pulling up the substrate.[25] Hydrophilic SiO_2 stripes also function as microfluidic channels[26,27] during the process. This evaporation system allows the interaction of the downward shear force and the capillary force in microfluidic channels. Both forces effectively induce the assembly and alignment of the NWs.

Large-scale NW arrays are obtained at different pulling conditions (speed and direction), as shown in Figure 4. In Figure 4(a), the pulling speed is 0.05 $mm \cdot s^{-1}$ and the direction is parallel to the stripes. Precisely aligned CdS NW arrays form at the center of the SiO_2 stripes and more than 93% of the nanowires are within $\pm 10^{\circ}$ of the pulling direction from the angular distribution result in Figure 4(d),

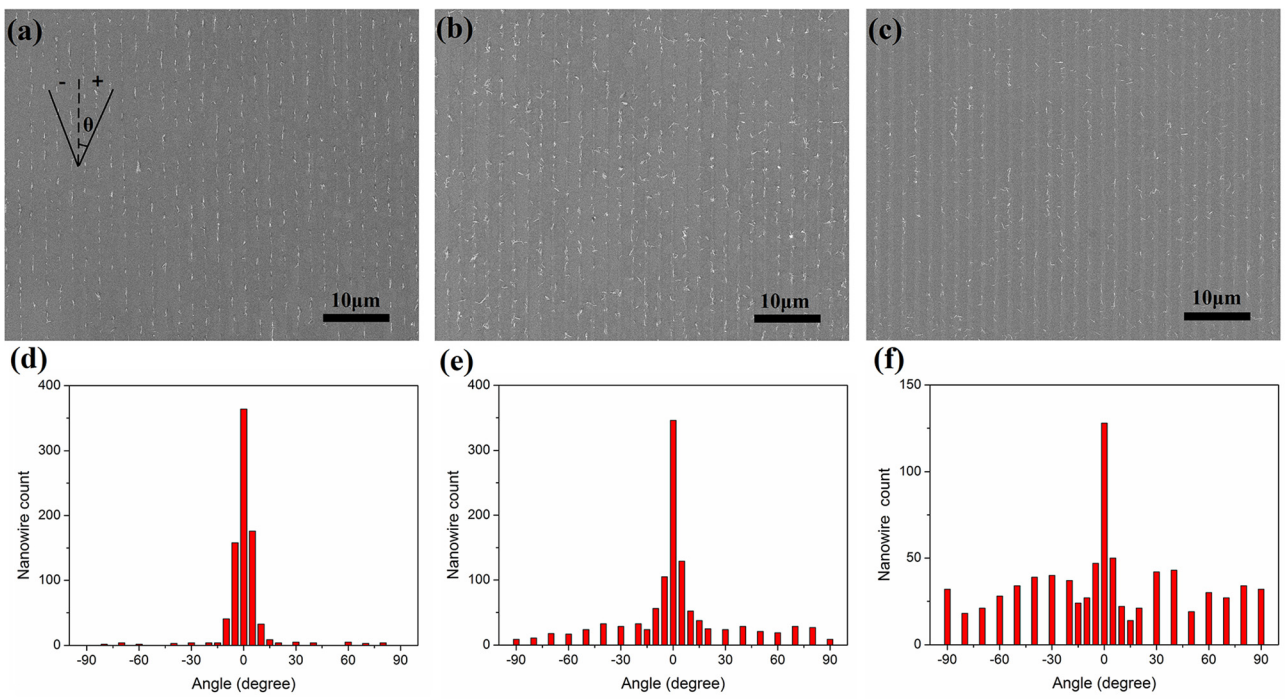

FIG. 4. SEM images and angular distribution results achieved at different pulling conditions. (a) Pulling at 0.05 $mm \cdot s^{-1}$ parallel to the stripe. (b) Pulling at 0.01 $mm \cdot s^{-1}$ parallel to the stripe. (c) Pulling at 0.05 $mm \cdot s^{-1}$ perpendicular to the stripe. (d), (e), and (f) are the angular distribution results of the nanowires in (a), (b), and (c), respectively.

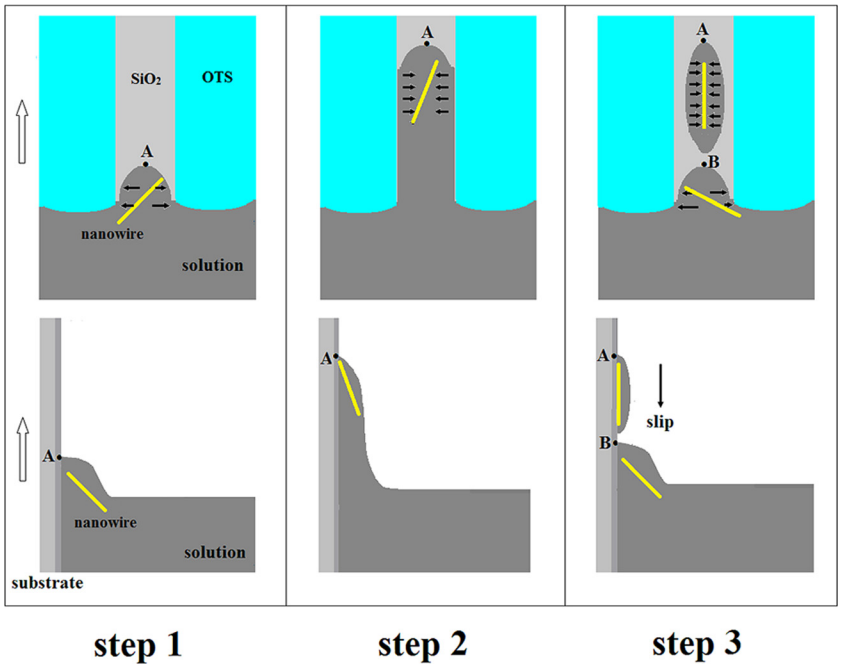

FIG. 5. Schematic of the NW assembly process. There are three steps in one stick-slip motion: (1) pinned contact, (2) before depinning, and (3) depinned contact. The top and bottom diagrams in each step are the front and side views, respectively.

exhibiting high alignment accuracy. Different pulling conditions are applied as a reference. Figure 4(b) shows the alignment achieved at a lower speed of 0.01 mm·s^{-1}. The NW arrays are denser and less ordered and about 62% of the nanowires are within $\pm 10^{\circ}$of the pulling direction from the statistics result in Figure 4(e), which is due to the weaken shear force from the lower pulling speed. The sample in Figure 4(c) is pulled at a perpendicular direction; some of the NWs are deposited at predefined region, whereas others have an average angular distribution in the substrate.

To illustrate the evaporation process and the alignment results, an evaporation model is established, as shown in Figure 5. The differential wettability of the substrate is believed to be vital for NW assembly in the present work. When the substrate is dipped into the CdS NW solution, hydrophilic SiO_2 stripes serve as cylindrical microfluidic channels which the solution is preferentially attached to. The contact line of the liquid repeats stick–slip motion when pulling the substrate with a constant speed and there are three steps in one motion.[25] In step 1, the contact line is pinned by the liquid surface tension together with frictional force at point A. The top and bottom diagrams are the front and side views, respectively. As pulling up the substrate with a constant speed, the contact line is stretched to its limit and diagrams in step 2 depict the moment before depinning occurs.[26–28] When the surface tension exceeds the pinning force in step 3, the contact line slips and reaches another equilibrium position (point B), leaving discrete cylindrical droplets of the NW solution above the new contact line. The capillary flow inside the droplet also reverses from edge-directed to centerline-directed according to the theory of Sharma.[28,29] In the, thereafter, evaporation process, the centerline-directed capillary flow assembles NWs in the droplets to the center of SiO_2 stripes and parallel to the boundary. In addition, the shear force between the solution and the substrate reorientates NWs to minimize the fluid drag force while pulling up. Thus, discrete NWs are assembled and aligned at predefined regions, as shown in Figure 4(a). Lower pulling speed in Figure 4(b) results in weaker shear force and the internal capillary force becomes insufficient, leading to less aligned nanowires. Thus, both capillary force and shear force play an important role in the nanowire alignment process.

Semiconductor NWs are difficult to organize in large scale because they are relatively heavier and more mechanically stable than lighter nanostructures such as nanoparticles and nanotubes. The proposed procedure applies substrate with alternating wettability to form cylindrical microchannels, in which the internal capillary force interacts with the shear force to organize heavy NWs from solution. Thereby, one-step precise assembly and alignment of CdS NWs is achieved in large scale.

In conclusion, a general SAM micropatterning method has been developed in this work. The technique is based on a PSM that modulates laser spatially, thereby generating interference patterns on SAMs in one step. A different adsorbate can be chosen to backfill the exposed regions for binary-component SAMs. Most advantage of this method is facile, scalable, and nonselective, exhibiting significant application potential in surface engineering and functionalization. Patterned OTS/SiO_2 substrate with alternating wettability has been fabricated to demonstrate the method, and it is then used to assemble CdS NWs from solution. The precisely assembled and aligned NWs evidently show the efficiency of the proposed patterning method as well as the assemble process. The application potentials of this technique for fabricating nanoscale functional devices are going to be further developed.

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