Electronic Materials Letters, Vol. 6, No. 2 (2010), pp. 59-64
DOI: 10.3365/eml.2010.06.059 Published 30 June 2010

Strongly Superhydrophobic Silicon Nanowires by Supercritical CO_2 Drying

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This paper reports on the extremely superhydrophobic behavior of supercritical CO_2 processed silicon nanowires (SiNWs) with a contact angle in excess of ~177°. Vertically aligned silicon nanowires with 10 nm to 40 nm diameter and 1 mm to 3 mm in length were obtained by electroless etching (EE) technique. The as-fabricated SiNWs were superhydrophilic with no water droplet formation (zero contact angle), and were then completely transformed to an extreme superhydrophobic state when their nanoscale surface roughness is combined with trichlorosilane hydrophobic coating. The processed SiNW array was so hydrophobic that water droplets always bounced off the surface and did not allow contact angle measurements to be obtained unless the substrate was intentionally given a concave-curvature by vacuum suction. Utilization of a hydrophobically surface-treated micro-pipette syringe enabled the release of a water droplet onto this extremely superhydrophobic surface for contact angle measurement. To prevent severe nanowire agglomeration during the drying process of wet etched SiNWs, supercritical CO_2 drying was utilized, which process significantly improved the nano configuration and enhanced hydrophobicity.

Keywords: superhydrophobic surface, electroless etching, silicon nanowires, contact angle

The unique electrical, mechanical and optical properties of nanowires and nanotubes have made them extremely attractive for a variety of research and applications. Silicon nanowires (SiNWs) in particular are potentially very attractive, given the central role of Si in the semiconductor industry and considering the existing set of known fabrication technologies and established applications. Various alternative methods have been utilized for SiNW fabrication, such as the laser ablation, the metal-catalytic VLS (vapor-liquid-solid) method,[1-3] the oxide-assisted catalyst-free method,[4,5] and solution techniques.[6,7]

Among these methods, the electroless etching approach for obtaining oriented single crystalline SiNW arrays on silicon substrates using aqueous HF solution containing $AgNO_3$ has been proven to be a simple and efficient method to prepare large area samples.[7-9] These SiNWs are generally aligned parallel to one another and are held together in bundles. The length of the SiNWs could be controlled by adjusting the etching time and the concentration of $AgNO_3$ in the etching solution.

The realization of superhydrophobic surfaces[10-15] has become an exciting research topic in the nanotechnology and biotech fields. Superhydrophobic surfaces can be created by forming micro/nano-structures and surface coating. These superhydrophobic surfaces produce self-cleaning characteristics. Such unique characteristics obtained by the micro/nano-structures have been applied to many commercial products and have been widely studied in the scientific community.

In the present study, we have found an extremely superhydrophobic characteristic in vertically aligned SiNWs with a surface coating of the chemical compound trichlorosilane. The use of a hydrophobically-surface-coated small tip micro-pipette syringe enabled the release of a micrometer regime water droplet onto this extremely superhydrophobic surface to allow contact angle characterization. The problem of severe nanowire agglomeration during drying of wet etched SiNWs was mitigated by the use of supercritical CO_2 drying. The SiNW surface was so hydrophobic that water droplets always bounced off and did not allow contact angle measurements unless the substrate was intentionally given a concave curvatured of ~1-2 degrees by vacuum suction.

SiNW arrays were prepared using the electroless chemical etching method.[7-9] The samples were immersed in a solution composed of 4.6 M HF/0.02 M $AgNO_3$ for 20 min. The etching procedure was performed at 50°C. After the etching process, the samples were immersed in H_2SO_4/H_2O (1:1) to remove the silver dendrites formed during the etch process.

The samples were washed several times with distilled water and ethanol. During these steps, the samples were kept

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in the solution. The regular drying process for the wet etched SiNW samples was performed using a nitrogen gas environment. In order to reduce nanowire agglomeration, a supercritical CO_2 ($scCO_2$) drying process was also carried out and results were compared to those from the conventional drying method. For supercritical drying, the wet etched and washed samples were quickly transferred to a CO_2 pressure chamber. The chamber was pre-cooled to allow samples to be readily filled with liquid CO_2 from a gas cylinder and then heated to just above the critical temperature (+35°C) with subsequent critical pressure (1250 psi) applied. After that, CO_2 gas was vented slowly through a needle valve to avoid specimen distortion. The morphology of the dried SiNW sample was examined using an FEI field emission scanning electron microscope (SEM). Top view, tilted 45° view and cross-sectional view of the dried SiNWs were obtained.

A hydrophobic trichlorosilane coating was applied onto the SiNWs through a simple vaporization process in a vacuum. The measurement of the contact angle was carried out by a video contact angle measurement system Model No. VSA 2500 XE (by AST Products, Inc.). In addition to the VSA contact angle measurement system, the dynamic behavior of the bouncing water droplet on the surface of Trichlorosilane-coated SiNWs was captured by using a JIA CVM 4+CL high-speed camera.

A special micro-pipette was fabricated and utilized to reduce the adhesion force between the water and the syringe, and allow the release of a water droplet. A micropipette puller (Model P-2000, CO_2 laser-based, Sutter Instrument Company, Novato, CA, USA) was utilized for fabrication of micro-pipettes. Briefly, a CO_2 laser beam was projected onto the middle portion of a quartz capillary tube length (O.D. 1.0 mm, I.D. 0.70 mm, and 7.5 cm in length) by a reflective scanning mirror. The heat application to the quartz is achieved by repeatedly scanning the mirror. Micropipettes so fabricated can range in size from micrometers down to nanometers in diameter by changing process parameters.

Superhydrophobic surfaces[10-15] are useful for important technical applications including self-cleaning window glasses and fabrics, low-friction surfaces, and biomedical protection devices. There are two major types of mechanisms that explain the superhydrophobic phenomenon. In the Wenzel Model[10] (also called descriptively the total surface area model or the surface roughness model), it is assumed that the liquid wets all of the rough surfaces, and the increased total surface area geometrically enhances hydrophobicity, which can be expressed with the equation:

$$\cos\theta_c = r\cos\theta \quad (1)$$

where θ_c is the apparent contact angle of the liquid droplet on the macroscopically flat surface, with the overall surface area increased by a roughness factor r.

In the Cassie-Baxter Model[11] (which is also called in a descriptive way "the air pocket model), the presence of the two-phased surface is assumed, with one of the phases being air. This is like air trapped below the water drop, with the drop sitting mostly on air plus a small fraction of solid protrusion, leading to superhydrophobic behavior. The Cassie-Baxter Model is represented by the equation:

$$\cos\theta_c = f_1\cos\theta_1 + f_2\cos\theta_2 \quad (2)$$

where θ_c is the apparent contact angle of the liquid droplet, and f_1 and f_2 are the projected area fraction of phase 1 (e.g., water) and phase 2 (e.g., air), respectively. The angles q_1 and q_2 are the equilibrium contact angles of the droplet on the flat surface of phase 1 and phase 2 material, respectively. Since the water contact angle θ_2 in air is 180° (non-wetting), cos θ_2 = -1. Together with the relationship of $f_1 + f_2 = 1$, Eq. 2 becomes:

$$\cos\theta_c = f_1(\cos\theta_1 + 1) - 1 \quad (3)$$

If f_1 is very small, like a sharp needle array, there will be a lot of air under the water droplet, and $\cos\theta_c$ can approach -1 with the water droplet contact angle θ_c approaching 180°. It is well known that the contact angle of water on a typical hydrophobic surface is of the order of 100° to 120°, but surface microtexture can bring the value to as high as 160° to 175°.

In this paper, we report that the SiNWs are superhydrophilic in the as-fabricated state, but their morphology, distributions, and surface state can be modified so as to exhibit extremely superhydrophobic behavior. The SiNWs fabricated by electroless chemical etching were coated with a hydrophobic monolayer of trichlorosilane, and the water droplet contact angle behavior was investigated.

In the electroless etched and dried state, the SiNW array was very hydrophilic, with a water droplet added becoming completely absorbed into the in-between nanowire pores, thus exhibiting $q_c = 0$, a state of zero contact angle (superhydrophilicity). However, this state is then completely transformed to one of extreme superhydrophobicity when the nanoscale surface roughness is combined with a trichlorosilane hydrophobic coating, as described below.

Because of the extreme superhydrophobic behavior of the trichlorosilane-coated and $scCO_2$ dried SiNWs (with contact angle > ~177°), the water droplet could not be supplied onto the SiNW sample surface through a syringe in the first place as the droplet usually prefers to stay within the syringe tip rather than detach for release onto the SiNW surface. Therefore, we devised a tool to release the water droplet --- a specially fabricated micropipette drawn by a laser heated pipette maker, the inside wall of which was also coated with

hydrophobic trichlorosilane to assist in the release of the water droplet from the tip of the micropipette. A regular micropipette with an inside diameter of ~175 μm (Fig. 1(a)) failed to release the water droplet onto the extremely superhydrophobic SiNW surface, even with the contact of the syringe-tip adhered water droplet touching the sample surface, while the small-diameter micropipette with an inside diameter of ~2 μm and outside diameter of ~4 μm (Fig. 1(b)) was now able to release a water droplet onto the SiNW sample surface. This is most likely due to the much smaller contact area of the water droplet with the micropipette tip. Such a micro-pipette release technique as devised here can be useful and convenient for future studies of wetting and contact angle behavior on a variety of materials with extremely superhydrophobic surfaces, such as nanowire or nanocone array structures.

Another problem encountered in the investigation of such an extremely superhydrophobic surface was the geometrical instability of the water droplet and the static placement on a flat surface. Once the water droplet was made to separate from the micropipette and was placed on the SiNW surface, the droplet never stayed in place. The surface always repelled the droplets and they would immediately be rolled away to the side, thus not allowing contact angle measurement to be preformed using the video camera and other characterization tools. In order to solve this problem, the Si substrate (containing the SiNW array on the surface) was vacuum suctioned from underneath to intentionally introduce a concave curvature (with a curve angle over the 0.5 cm distance, from the center of the contact point to the edge of the substrate sample dimension, estimated to be roughly ~1.5 degrees), which provided the droplet a sufficient geometrical (gravimetrical) stability to stay on the sample surface, as illustrated in Fig. 2. This technique allowed contact angle measurements of the extremely superhydrophobic surface to be obtained.

Shown in Fig. 3 are the SEM micrographs of the Si nanowires formed by wet chemical etching and contact angle measurements on the surface with a water droplet. The as-etched and N_2 gas dried SiNWs, shown in Fig. 3(a), show a relatively uniform nanowire distribution (typically in the range of 10 – 40 nm, with an estimated average diameter of ~20 nm). The SiNW geometry depends on the etching time, temperature, and etch solution concentration. The average height of the etched nanowires was ~2.4 μm. A considerable variations in the SiNW height was observed as the nanowires were remnants of Ag particle etching of the Si substrate for formation of vertical pores and their sideways merging. When the wet-etched SiNWs were dried by the nitrogen gas atmosphere, nanowire tangling/agglomeration was observed, as is evident in Fig. 3(a). When coated with trichlorosilane, the contact angle of the water droplet measured was $\theta_c \sim 155^\circ$, as shown in Fig. 3(b). As can be seen from Fig. 3(a), the N_2 gas dried SiNWs were locally

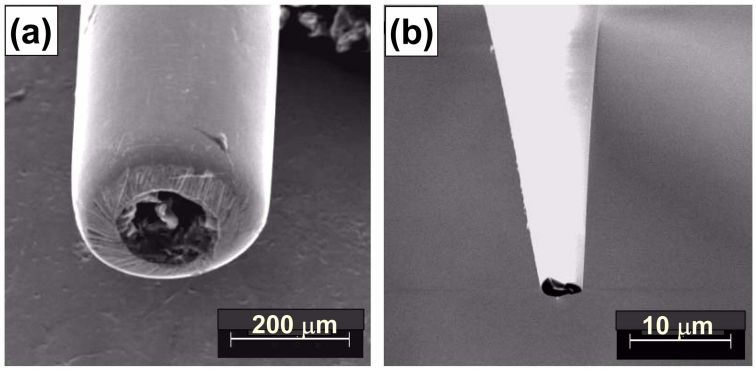

Fig. 1. SEM image of (a) conventional syringe, with which a release of a small water droplet is difficult, and (b) hydrophobic-surface-treated, small diameter micro-pipette prepared for release of a water droplet on superhydrophobic surface for contact angle measurement.

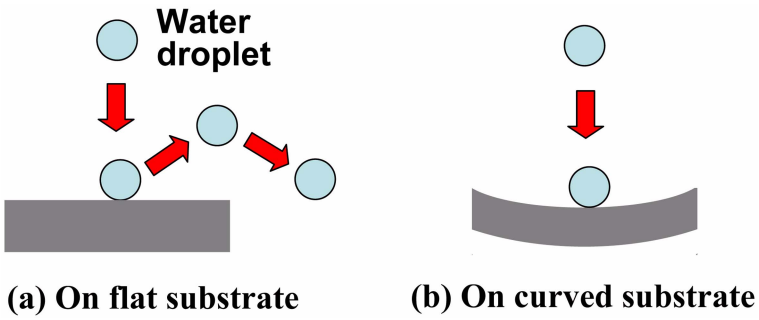

Fig. 2. Schematic illustration of superhydrophobic water droplet stability enhanced by intentionally introduced concave curvature in Si substrate.

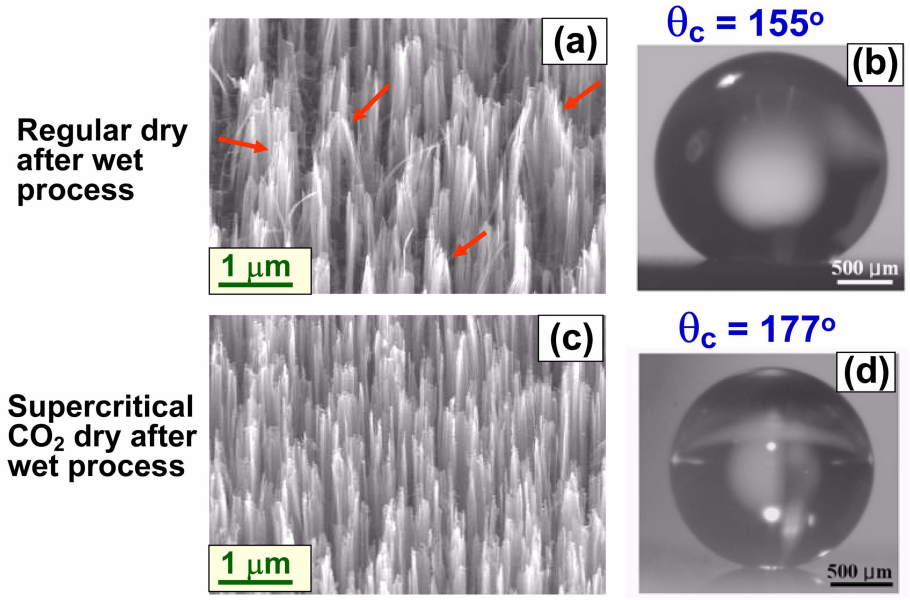

Fig. 3. (a) 45 degree tilted SEM image of electroless etched and nitrogen gas dried SiNWs, (b) water droplet contact angle image of the sample (a) after trichlorosilane coating, (c) SEM image of electroless etched and $scCO_2$ dried SiNWs, (d) water droplet contact angle image of the sample (c) after trichlorosilane coating and intentional curving of the substrate to hold the placed water droplet in position.

bent and severely agglomerated after the electroless etching process and subsequent drying, which is most likely due to the surface tension force of the advancing water-gas interface during the drying of the high-aspect-ratio SiNWs. A general trend observed was that the degree of Si nanowire agglomeration increased when a higher evaporation rate (drying rate) of the liquid was employed. Such nanowire agglomeration is highly undesirable for many potential uses of SiNWs including the superhydrophobic-related applications.

As the Si nanowire agglomeration was anticipated to reduce the contact angle, a supercritical CO_2 ($scCO_2$) drying process was introduced to avoid or minimize Si nanowire agglomeration and collapse in a similar method as demonstrated for wet-processed aligned carbon nanotube arrays.[16] Such an improvement in the nano configuration is beneficial for enhancing the superhydrophobicity. As shown in Fig. 3(c), the $scCO_2$ drying process resulted in SiNWs that are laterally well separated with minimal agglomeration. The resultant water droplet contact angle increased to $\theta_c \sim 177^\circ$ (after trichlorosilane coating) as shown in Fig. 3(d). A crude calculation of the f_1 value from the Cassie-Baxter Model Eq. 3 using $\theta_c \sim 177^\circ$ and $\theta_1 = 93^\circ$ (the measured wetting angle of trichlorosilane hydrophobic coating on flat Si surface), yielded $f_1 \sim 0.0015$, which agrees roughly with the calculated f_1 value assuming the presence of ~ten average Si nanowires per 1 mm^2 sample area, with the nanowire tip contact surface area of 20 nm diameter circle, and assuming that approximately one-half of the Si nanowires are too short to touch the liquid droplet bottom surface and contribute to the Cassie-Baxter Model wetting. The actual contact angle is expected to be higher than the 177° value indicated by the VSA contact angle measurement apparatus because the concave curvature of the substrate was intentionally introduced to hold the water droplet in place. Additional studies are needed to understand the quantitative effect of such substrate curving on contact angle evaluations.

To further evaluate the extreme superhydrophobicity behavior under a dynamic environment, the water droplet movement was traced using a JIA CVM 4+CL high-speed camera at 102 Hz frame rate. The sideview image frames shown in Fig. 4 show a time-sequence movement of the free falling water droplet on the SiNWs (without surface hydrophobic coating with trichlorosilane). As can be seen in Panel 4 of the figure, the dropped water droplet immediately wetted on the surface during its first impact on the SiNWs and became completely soaked in, exhibiting a superhydrophilic behavior with zero contact angle.

However, a significantly different dynamic behavior of the water droplet was observed on the surface with trichlorosilane coating (i.e., superhydrophobic SiNWs of Fig. 3(c) and (d)) as shown in Fig. 5. On these very superhydrophobic SiNWs, the water droplet kept bouncing on and off the sample surface without resting until finally it bounced away to the side.

The results described here indicate that the surface hydrophobicity of Si can be dramatically altered by control of the nanostructure configurations and the surface states. The flat Si substrate exhibits a typical water droplet contact angle of $\theta_c \sim 42^\circ$ as characterized by the VCA (video contact angle) measurement system. When this surface is coated

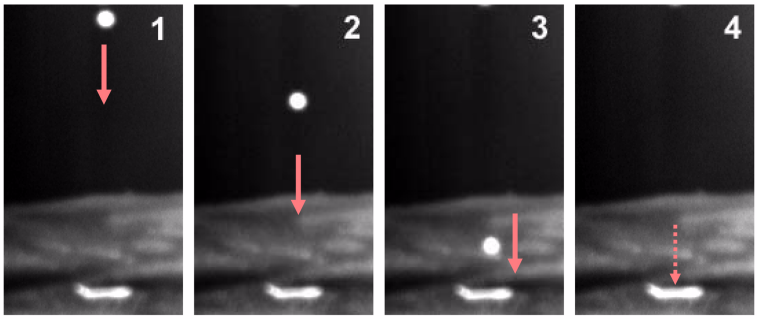

Fig. 4. Time sequence images of a water droplet free falling onto superhydrophilic SiNWs.

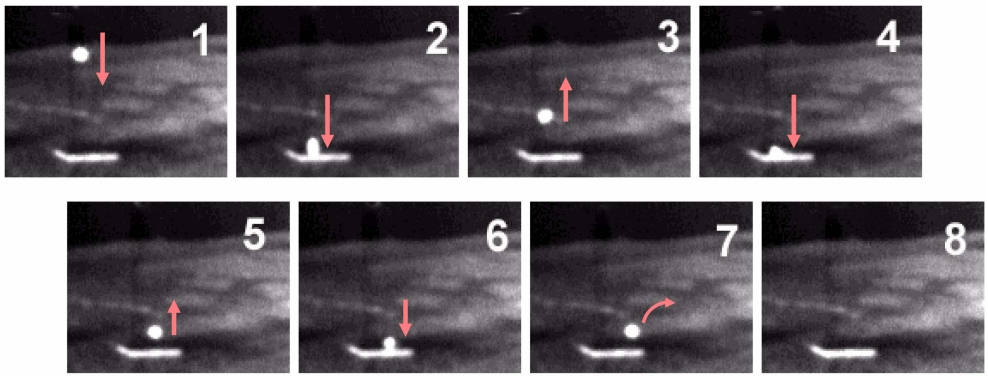

Fig. 5. Time sequence images of a water droplet on superhydrophobic SiNW surface (with trichlorosilane coating) showing bouncing and side roll-away of the droplet.

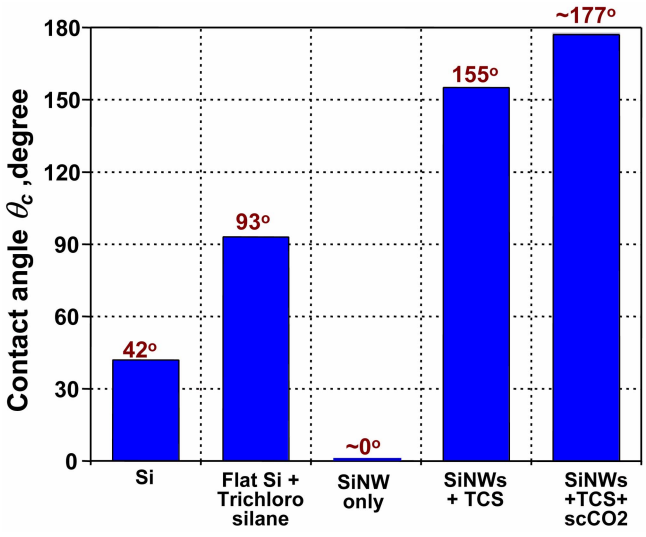

Fig. 6. Evolution of contact angle behavior with modification of nano configuration and surface state on Si surface.

with trichlorosilane hydrophobic coating, the contact angle increases to $\theta_c \sim 93^\circ$. If we take the as-fabricated superhydrophilic SiNW sample ($\theta_c = 0$), and apply the trichlorosilane hydrophobic coating, the SiNW surface state completely transforms to a superhydrophobic state ($q_c \sim 155^\circ$) because of the combined effect of nanoscale surface roughness and hydrophobic coating. Removal of the entanglement of nanowires using $scCO_2$ drying of wet-etch formed SiNWs further increased the contact angle to extremely superhydrophilic $\theta_c \sim 177^\circ$. The evolution of contact angle behavior with modification of microstructure and surface state is summarized in Fig. 6.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of this work from Iwama endowed fund at UC San Diego.

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