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Large-scale ordered silicon microtube arrays fabricated by Poisson spot lithography

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Abstract
A novel approach based on the Poisson spot effect in a conventional optical lithography system is presented for fabricating large-scale ordered ring patterns at low cost, in which the pattern geometries are tuned by controlling the exposure dose and deliberate design of the mask patterns. Following this by cryogenic deep etching, the ring patterns are transferred into Si substrates, resulting in various vertical tubular Si array structures. Microscopic analysis indicates that the as-fabricated Si microtubes have smooth interior and exterior surfaces that are uniform in size, shape and wall-thickness, which exhibit potential applications as electronic, biological and medical devices.

1. Introduction

Lithography has been one of the key drivers for the semiconductor industry. Moore's law states that the number of devices on a chip doubles every 18 months. Roughly half of the density improvements have been derived from improvements in lithography. Current leading-edge production lithography systems employ very complicated illumination systems that operate at the conventional Rayleigh diffraction limit. The typical rule of thumb is that the smallest features that can be produced are about equal to the wavelength of the light used. However, those methods are rather costly due to the requirement of complicated and expensive high numerical aperture optics [1]. Meanwhile, interference lithography takes full advantage of the wave property of light and has been used to fabricate complicated 2D and 3D periodic nanostructures [2–5].

As one type of potential structure, periodic tubular structures have been reported with a broad range of applications, such as photonic devices [6, 7], sensors [8], and microelectromechanical systems (MEMS) [9, 10]. Quite a few techniques have been reported for the synthesis and fabrication of Si tubes [11–15]. One of these methods is chemical vapor deposition (CVD); such a technique is very cost-effective and microtubes can be synthesized in single crystalline phase over a hundred micrometers in length, though the shape, size and distribution of the grown tubes are not well controlled [11, 12]. Self-rolling is another kind of technique that utilizes the anisotropic strain of the substrate for Si tubular microstructure synthesis. Unfortunately, microtubes fabricated by this method are randomly distributed on the substrate and the technique has a lack of repeatability [13]. Template-based methods have also been explored to fabricated ordered microstructures, in which the uniformity of tube distribution, size and geometry can be improved and determined mainly by the properties of the templates [14]. Thermal oxidation [15] is a technique that could be used to grow tubular sub-micron structures based on a wide range of materials, though it may involve other wet chemical etching processes. Meanwhile, contact lithography, the most common and widely used method for fabrication of micro-size photoresist patterns, has the merits of low cost and high-efficiency, though it cannot be used to produce patterns with feature sizes down to sub-micron or a few tens of nanometers by applying a normal exposure dose [16]. Thus a feasible and controllable fabrication method for large-scale, ordered, small size and complicated Si tubular structures is still a challenge.

The Poisson spot, a bright point which appears due to Fresnel diffraction at the center of the wave shadow of a circular object, is a very well-known term in optics [17]. In

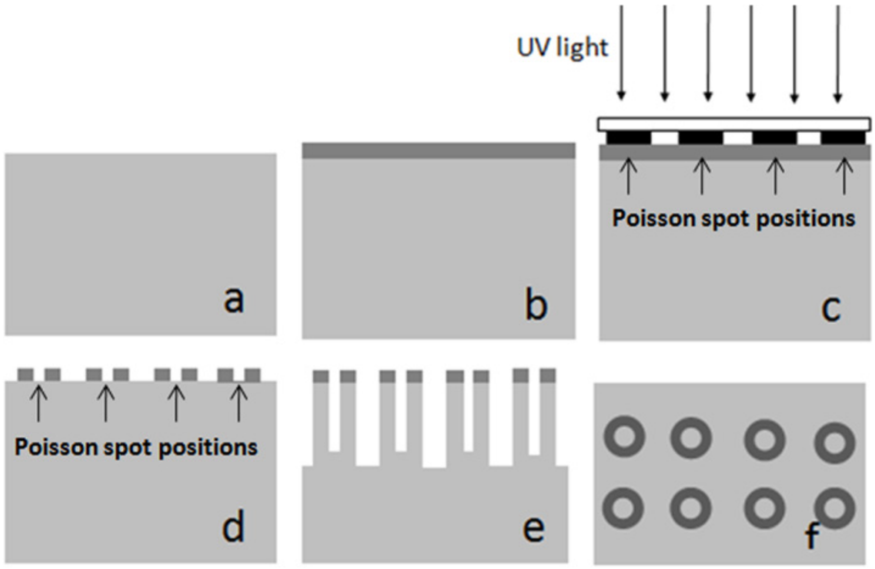

Figure 1. Schematic illustration of the Si tube array fabrication steps: (a) polished Si wafer; (b) Si wafer spin-coated with S1813; (c) UV light overexposure with an ordered circular pattern mask; (d) photoresist developing, showing the exposure resulting from the Poisson spot at the centers of the black circular areas; (e) pattern transfer, etching of the Si substrate to form Si tube arrays; (f) top-view of the Si tube array. The scale is not in proportion.

conventional optical lithography, it always exists though it is not welcomed since it can cause a distortion of the original mask patterns during exposure. This happens when light diffracts from black metal circular areas in the mask, it bends from all sides and adds up especially strongly in the middle as a bright spot [18]. In principle, this could also be used to expose the photoresist to fabricate complicated micro-/nanostructures.

Here, for the first time, we present a novel approach by utilizing the Poisson spot effect that always exists in conventional optical lithography. The process of fabricating the Si tubular arrays includes patterning of the Si substrate with photoresist rings using Poisson spot lithography followed by pattern transfer using cryogenic ICP etching. By doing this, perfectly ordered vertical Si microtube arrays were obtained in large scale. The wettability of the resulting structures was measured and the contact angle between the water droplet and these tubular structures is above 150°, indicating that such a tubular structure possesses the superhydrophobic property. In addition, other types of structures such as pillars and fins have also been obtained by controlling the parameters used for Poisson spot lithography and photoresist developing. For the first time, taking advantage of the Fresnel diffraction, we have developed a reliable and cost-effective method of fabricating ordered large-scale Si tubular structures with a classical optical lithography system.

2. Experimental details

The fabrication procedure of the Si microtube arrays is schematically illustrated in figure 1. The substrates used were n-type (100) Si wafers. The processing steps include the following. (i) Substrate cleaning: the Si wafers were ultrasonically cleaned in acetone, alcohol and deionized water in turn to eliminate surface contamination. (ii) Spin-coating: a UV sensitive positive photoresist layer, S1813, approximately 800 nm thick, was spin-coated on the substrates followed by pre-baking on a hot plate at 115 °C for 60 s. (iii) Exposure: the spin-coated substrates were exposed using an ultraviolet mask aligner (Karl Süss MA6). The employed exposure mode was hard contact and the light source was a mercury lamp with a light wavelength of 365 nm. The mask was about 3 mm thick in total and the mask patterns were periodic circles with a diameter of 5 μm and periodic distance of 10 μm. Overexposure was conducted with doses ranging from 150 to 350 mJ cm^{-2}. (iv) Developing: the exposed wafers were developed in MF-319 developer and rinsed with deionized water. It is also worth pointing out that by vibrating the wafer directionally during developing, different types of structures could be obtained. (v) Pattern transfer by cryogenic deep etching: the photoresist patterns were transferred into Si substrate by cryogenic ICP etching, which led to the formation of high verticality and low roughness Si microtube arrays as well as other nanoscale structures with different geometries.

The cryogenic etching was performed in an induction coupling plasma (ICP) system (PlasmaLab System 100, Oxford Instruments). SF_6 and O_2 were utilized as etching gases. The chamber pressure can be regulated over 1–70 mTorr. The system has a maximum ICP power of 3000 W and RIE power of 600 W at the substrate electrode. The substrate temperature can be controlled from −130 to 150 °C via liquid nitrogen cooling and a built-in resistance heater, the temperature used for our etching process was −110 °C. In the cryogenic etching process, fluorine-based etching is countered by the presence of O_2 and the formation of SiO_xF_y, which acts as a passivation layer to protect the sidewall during deep etching. The detailed etching parameters are listed in table 1.

The hydrophobic property of the Si microtube arrays was tested. The contact angles were measured using a KRUSS DSA

Table 1. Cryogenic etch process parameters.

Parameters	Value
Temperature (°C)	−110
SF_6 flow rate (SCCM)	40–50
O_2 flow rate (SCCM)	6–10
rf forward power (W)/dc-bias(V)	4/10
Chamber pressure (mTorr)	12
ICP power (W)	700

contact angle goniometer by injecting 5 μl of water onto the resulting Si tube structures. The value of the contact angle is the average of five measurements on the same sample.

3. Results and analysis

3.1. Fabrication of Si tubular structure arrays with disc mask patterns

By performing optimized overexposure (in that the exposure dose is right to expose the positive photoresist at the Poison spot position, a place where the light would be completely blanked in a conventional optical lithography approach), extra light circles are generated at the center beneath the mask patterns, resulting in arrays of photoresist ring. In principle, the width of the ring is the mask pattern interspacing and is exposure dose dependent. Figure 2 shows the scanning electron microscopy (SEM) images corresponding to each fabrication procedure. Figure 2(a) displays the photoresist patterns fabricated by ultraviolet Poison spot lithography. It can be seen from the figure that rings 2.5 μm in inner diameter, 4 μm in outer diameter, 10 μm in periodical distance, and about 700 nm in thickness were formed. As expected, differently from the original patterns on the mask, the centers of the black areas were also exposed due to the Poisson spot effect. Figure 2(b) shows the SEM image of Si microtubes fabricated by cryogenic etching in an ICP apparatus. The tubes are about 30 μm in height with an aspect-ratio of about 30, a wall verticality of about 90° and very uniform in height. For comparison, a conventional photolithography routine with the same mask was used to form disc patterns, which were further transferred into Si pillars by ICP etching; this is shown in the inset of figure 2(b). The optimized exposure dose used for disc pattern formation was 100 mJ cm^{-2}, but using exposure doses in the range of 80–130 mJ cm^{-2}, solid disc photoresist patterns could also be obtained. Figure 2(c) displays the image of tubes being deliberately destroyed, it reveals that these tubes have ultra-smooth inner and outer side walls. It is interesting to note that the ratio of the depth of the inner hollow cavity to the tube height is about 5/6, which mainly caused by the aspect-ratio dependent etching (ASDE) effect [19]. This effect is well known in plasma etching and resulted from the reduced presence of reactive species at the bottom of the narrow cavity compared to the large open area. Figure 2(d) gives an SEM top-view image of a Si microtube array; we can see that the Si microtubes have a very good uniformity in size and wall-thickness, which basically follows the photoresist ring patterns as shown in figure 2(a), with an outer diameter of 4 μm, an inner diameter of 2.5 μm and a period of 10 μm.

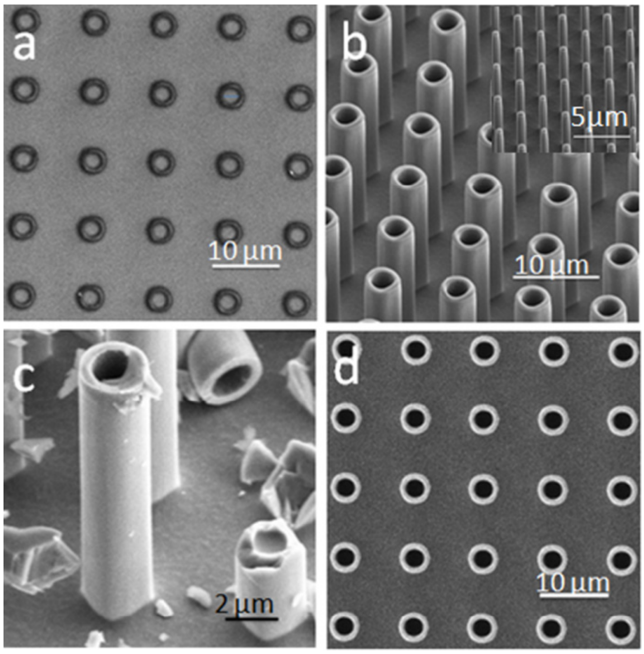

Figure 2. SEM images of (a) the top-view of a photoresist ring array fabricated by Poisson spot lithography; (b) a side-view of a Si microtube array obtained through cryogenic etching of the sample shown in (a), the inset shows the image of the Si pillars etched using disc photoresist as masks (obtained with in-dose exposure of solid circular patterns); (c) the side-view of tubes being deliberately destroyed; (d) the top-view of the Si microtube array.

3.2. The exposure dose effect in Poisson spot lithography

The above results indicate that the morphology of the Si microtube arrays is fully dependent on the photoresist pattern generated by Poisson spot lithography; thus it is very important to investigate the optimized Poisson spot lithography conditions. In general, by tuning the exposure dose, photoresist patterns with various sizes and geometries can be obtained. We found that for too much overdosed exposure, there would be no photoresist pattern left at all; though a lower dose suitable for classical photolithography would not be sufficient to expose the photoresist at the Poisson spot position. Figure 3 shows the mean width (outer radius minus inner radius), the inner diameter and the outer diameter of the photoresist rings as a function of exposure dose. These width values of the rings were derived from the SEM images, which are not shown here. For exposure dose in the region of 150 to 350 mJ cm^{-2}, the width decreases monotonically with increasing exposure dose. It is found that the width of the photoresist ring can be tuned from about 1200 to 300 nm. In addition, it can be seen that the changing rate of the inner diameter with exposure dose is faster than that of the outer diameter. This can be explained as being because when light which formed the Poisson spot is reflected back by the substrate or the photoresist it can be reflected forward again by the metal patterns above. So the metal mask can serve as a mirror and confines the incident light in the Poisson spot zone. As a result, the exposure dose in such an area is relatively larger compared with that for the light transparent zone without metal. For the particular mask

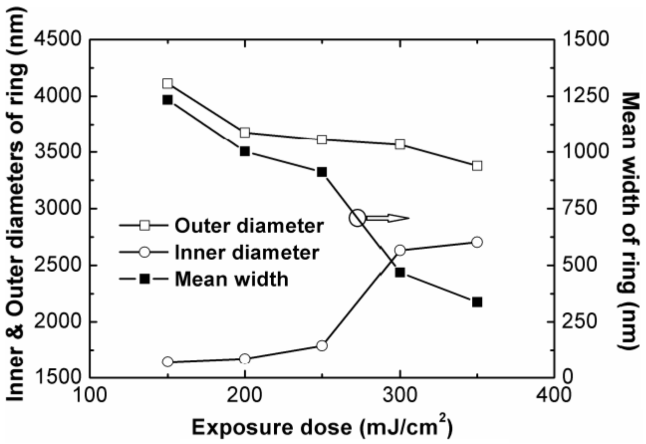

Figure 3. The width, the inner diameter and the outer diameter of the photoresist ring as a function of the exposure dose.

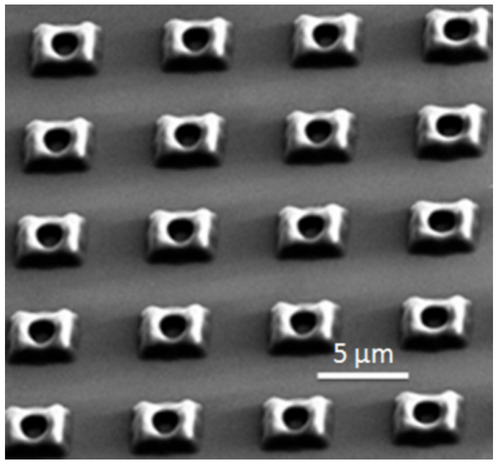

Figure 4. SEM image of hollow square photoresist patterns fabricated by Poisson spot lithography with square mask patterns.

pattern, photoresist type (S1813) and photoresist thickness (800 nm) we used in this experiment, the most suitable exposure dose that was required for ring pattern generation was about 300 mJ cm^{-2}, which could be used to produce a perfect photoresist ring patterns about 500 nm in width with very smooth and vertical inner and outer edges. We would also like to point out that for a certain designed mask pattern to be exposed with a certain mask aligner and light source, the dose required for other annuli in the Poisson diffraction to be transferred to the photoresist is photoresist thickness and sensitivity dependent, the higher the sensitivity, the lower the dose it requires; meanwhile, the thinner the photoresist is, the less exposure dose it demands. Thus to avoid extra ring formation by additional exposure by light from other annuli in the Poisson spot, photoresist with medium sensitivity and thickness is preferred.

Generally speaking, the parameters that should be satisfied to produce Poisson spots include the size of the mask pattern, the wavelength of the exposure light source, the thickness of the mask plate, the distance between the mask bottom surface and the top surface of the photoresist, and the characteristics of the photoresist (mainly its thickness and sensitivity). However, regarding whether this phenomenon can be quantified using the Fresnel number as a criterion, a more in-depth understanding and theoretical analysis are required and related experiment and simulation work are currently underway to address this issue.

3.3. The fabrication of Si tubular structure arrays with square mask patterns

To further explore the applicability of Poisson spot lithography, based on the aforementioned optimized parameters using the disc mask patterns, here square mask patterns were used to fabricate Si tubes with square outer surfaces but cylindrically shaped inner surfaces. Figure 4 shows the hollow tube patterns which are about 3.5 μm in length for a side for the outer edge and 1.5 μm in diameter for the inner cylinder. It can be seen that differently from the tubes obtained using circular patterns, the photoresist width is non-uniform for the tube structures achieved using the squares; it is relatively thicker at the corners than in the middles of the edges. This is because the light diffraction effect is not fully symmetric but reduces to four-fold self-symmetry for the mask patterns. However, using the same exposure dose, the shapes of the inner hollow areas are similar to those achieved using the disc patterns, demonstrating that such a technique has good repeatability and consistency.

It is most interesting that by varying the exposure dose, structures with various geometries can be obtained. Figure 5 shows the consequent shape evolution of vertical Si structures achieved using Poisson spot lithography and cryogenic etching related pattern transfer; the corresponding used exposure doses were 200, 250, 300, and 350 mJ cm^{-2} for the structures shown in figures 5(a)–(d), respectively. It can be seen that after ICP etching, the photoresist patterns still remained on the tops of the vertical structures which were about 20 μm in height, suggesting a very high etch selectivity of Si to photoresist when the pattern transfer was performed using a low rf power of 4 W for ICP etching. In other words, the as-formed photoresist could serve as a very solid and reliable mask for pattern transfer during ICP processing.

3.4. Rinsing effect related tubular structure evolution

To obtain more types of structures, a special developing style, vibrating the sample immersed in the developer with different vibrating frequencies along one side of the sample, was adopted. Thus, compared to the still immersing style, there is an additional rinsing effect in this kind of development, which makes the chemical reaction rate of the photoresist anisotropic. A typical image of the resulting photoresist pattern, pairs of wires about 500 nm in width and 2 μm apart, is shown in the inset of figure 6(a). We would like to point out that only two edges of the square remained compared to the original mask patterns, the other two edges vanished due to this rinsing action. By increasing the rinsing intensity from 30 Hz to a higher frequency, the photoresist patterns can be modified. Figures 6(a) and (b) demonstrate the transferred pairs of vertical Si slabs and fins, respectively. These two types

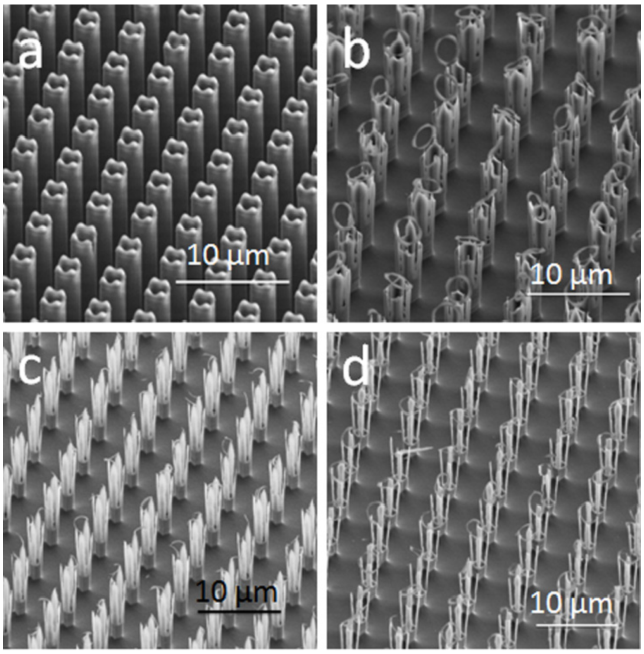

Figure 5. SEM images of Si structures fabricated with photoresist mask patterns obtained by increasing the exposure dose: (a) square Si tube; (b) the square Si tube partially etched on the top; (c) Si trumpet with thinned sidewall; (d) four needles on a cup chunk.

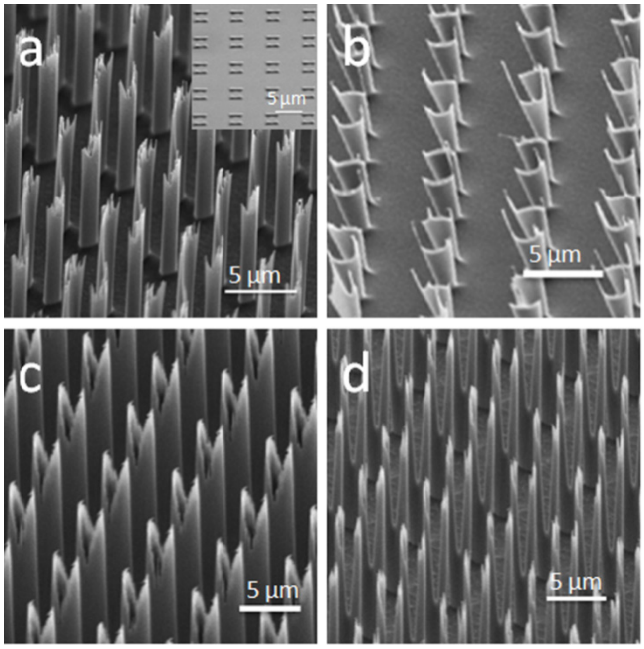

Figure 6. SEM images of Si structures showing the rinsing effect: (a) vertical slab pairs (the inset in (a) is the top-view image of pairs of photoresist wires developed with intense rinsing); (b) fin structures; (c) tubes with pointed cuts on top; and (d) slab pairs on a tube chunk.

of structures as evolutions from hollow square patterns clearly reflect the effect of rinsing intensity. With the same tendency, circular ring patterns also evolved to gapped rings then to arcs, which can be seen from the tubes with pointed mouths and curved slabs as shown in figures 6(c) and (d). These structures are of greatest potential application as emitters for displays.

3.5. Water wettability characterization

The hydrophobic property of the Si microtube arrays was investigated by measuring the static contact angle. Figure 7 shows a photograph of the water droplet shape on the fabricated Si microtube structures and that for a polished Si wafer. We obtained a contact angle of about 154° for the Si microtube structures and that of the polished Si surface was 95°. Obviously this tubular structure displays superhydrophobility comparable to reported nanostructures though our Si microtube structures have a relatively bigger size. These results are consistent with a theoretical prediction proposed by Bhushan [20, 21], in which the superhydrophobic property displayed in a hierarchical structure can be explained by high asperities resisting capillary waves, while nanobumps prevent nanodroplets from filling the valleys between asperities and pin the triple line in the case of a hydrophilic spot. In other words, when air pockets exist between the water droplet and the substrate, the larger the air pockets, the better the hydrophobility. Therefore, it is the hollow nature of the high-aspect-ratio Si microtubes that enhanced their hydrophobility since air pockets can be more easily formed and more stably fixed in the hollow parts of such tubular structures than in other types of structures.

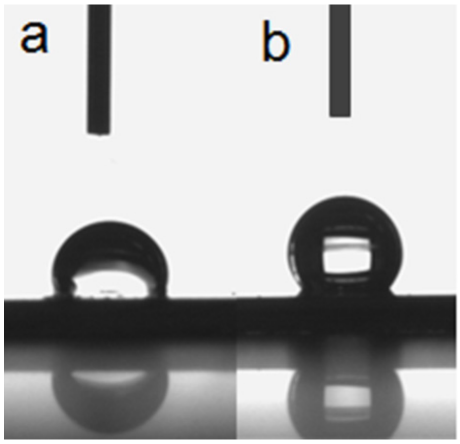

Figure 7. Photographs of a 5 μl water droplet on (a) polished Si wafer, (b) a Si surface that contains tubular structures.

4. Conclusion

We explored and proposed a new concept of Poisson spot lithography technology, which combines the mechanism of optical lithography with that of maskless interference lithography. By this method, ring-shaped patterns were cost-effectively fabricated. Following this by a cryogenic etching process, large-scale, ordered, vertical Si microtube arrays with sub-micron thick tube-walls were achieved. Such tubular structure displays a superhydrophobic property that could be very useful in biology and medicine. In addition, we have also obtained vertical Si structures with other cross-sectional profiles by controlling the lithography process and etching parameters, which could potentially be used as candidates for field emitters.

Acknowledgments

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