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Fabrication and characterization of the functional parylene-C film with micro/nano hierarchical structures

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ABSTRACT

Parylene has attracted significant research attention due to its attractive properties such as good mechanical performance, chemical inertness, and biocompatibility. The development of new methods for patterning the surface of parylene films is likely to lead to attractive new applications not only in the laboratory, but also for industrial products. In this work we present a universal single-step technique to replicate parylene-C films with micro/nano hierarchical structures from a silicon mold. By utilizing an improved deep reactive ion etching (DRIE) process, an ultra-low-surface-energy silicon mold is fabricated first. The parylene-C film is then peeled off from this reusable mold to replicate the micro/nano hierarchical structures directly. By this method, complex multi-scale patterns even on the inclined surfaces, including periodic microstructures and high-density nanostructures can be replicated on the parylene-C film. The parylene-C films presented in this work show enhanced hydrophobicity resulting from the combination of microstructures and nanostructures, achieving a maximum contact angle of 135°. Furthermore, parylene-C films with micro/nano hierarchical structures can be functionalized by design: for example, films with groove-shaped patterns show anisotropic wettability, which is very useful for directional droplet transportation. Additionally, the fabricated samples show remarkable surface-enhanced Raman scattering (SERS) properties, with a maximum enhancement factor of 2.3×10^4. This single-step fabrication process is low-cost, high yield, and suitable for mass production, and the parylene-C SERS material with enhanced hydrophobicity shows attractive potential for applications in areas such as microfluidics and biomedical microsystems.

1. Introduction

Both natural and artificial micro/nano hierarchical structures show several unique properties, such as anti-reflectance, super-hydrophobicity, and super-adhesion [1–5]. Thus, research into the fabrication and characterization of micro/nano hierarchical structures continuously increases, especially for polymer materials such as polydimethylsiloxane (PDMS), photoresist, and parylene-C [6–10]. Due to its mechanical properties, chemical inertness and remarkable bio-compatibility, parylene-C has attracted attention for many application fields, including wafer-level bonding, flexible microdevices, and microfluidics [11–14]. Patterning the surface is a useful method to functionalize parylene-C films, and is one of the most important research fields for parylene-C. There are two main technologies to pattern parylene-C films: photolithography and replication. A process of photolithography followed by plasma etching can be used to pattern a parylene-C film at the microscale level [15–17], but it is difficult to use this method for nanoscale patterns because of the minimum width limitation of photolithography.

The replication process is another common technology to pattern parylene-C films by copying patterns from a mold. This technology works well at both micro and nano scale [18–20]. However, in order to fabricate micro/nano hierarchical structures, the conventional replication process requires several steps. Previously, a two-step process including microscale replication and nanoscale plasma treatment of parylene-C was reported [8]. A further reduction in the number of fabrication steps can lead to reduced cost and complexity. Additionally, post treatment processes required in previous work, such as the removal of the mold by wet etching, may damage the surface texture of the parylene-C film [21], and therefore should ideally be made unnecessary.

In this paper we present a universal single-step technique to replicate parylene-C films with micro/nano hierarchical structures from an ultra-low-surface-energy silicon mold. An improved deep reactive ion etching (DRIE) process was used to fabricate a Si-based substrate with micro/nano hierarchical structures, which serves as the master for replication of parylene-C. The silicon molds have

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ultra-low surface energy resulting from both minimizing the solid–liquid interface area and the fluorocarbon layer deposited during the DRIE passivation steps. A parylene-C film with micro/nano hierarchical structures can be directly obtained from this master by a single-step replication process without any surfactant coating or post-treatment process. Two types of micro/nano dual-scale structures, pyramid arrays and V-shape grooves, have been designed with various dimensions (width, pitch and depth). The fabricated samples were systematically investigated and characterized, and show attractive properties such as enhanced hydrophobicity, anisotropic wettability and surface-enhance Raman scattering (SERS).

2. Experiments

The fabrication process for parylene-C films with micro/nano hierarchical structures consists of two main steps: the preparation of the silicon mold, and the pattern replication itself. Preparation of the silicon mold requires the fabrication of periodic microstructures and the subsequent formation of the highly-dense nanoforest. 4 inch (100) silicon wafers with thickness of 525 μm were used for the silicon mold. The periodic microstructures were formed by a potassium hydroxide (KOH) wet etching process. A 2000 Å Si_3N_4 layer was grown by low-pressure chemical vapor deposition (LPCVD) on the silicon surface to serve as a mask for KOH wet etching. After photolithography and reactive ion etching (i.e., RIE) process, the designed patterns from the mask were transferred to the Si_3N_4 layer. Then, the silicon wafers were etched in 30% KOH solution at 85 °C to produce periodic microstructures with triangle cross-section. Fig. 1(a) and (b) show the fabrication of microstructures.

Subsequently, the nano-scale structures were formed on top of the periodic microstructures. The silicon wafer with microstructures formed in the previous step was placed in an inductively coupled plasma etcher (Surfacing Technology Systems plc, Multiplex ICP 48443). The highly-dense nanoforest was formed atop the periodic microstructures by an improved deep reactive ion etching (i.e., DRIE) process [22–24]. The key change in the improved DRIE process is enhancing the passivation steps, such as increasing the passivation gas flow, so the polymer deposited on the horizontal surface during the passivation step cannot be removed completely by the next etching step. The polymeric residues therefore serve as the nanoscale self-mask and protect the silicon substrate. After several cycles of etching/passivation steps, a nanoforest forms atop the microstructures and the micro/nano hierarchical structures (alternatively named micro/nano dual-scale structures) are complete. Obviously, this improved DRIE process is a single-step wafer-level technique to fabricate Si-based micro/nano hierarchical structures without the mask. Figs. 1(c) and 2(a) show the formation of Si-based micro/nano hierarchical structures. The detailed process parameters for the improved DRIE process are given in Table 1.

Once the silicon mold is complete, the patterned parylene film can be produced by a simple process of parylene deposition and peeling off. And more importantly, this silicon mold is reusable. A 13 μm parylene-C film was deposited to cover the surface-textured silicon mold by using a parylene deposition system (PDS 2010, Specialty Coating Systems). The parylene-C thin film is formed by vapor deposition briefly including three main steps. Firstly, the parylene-C precursor (i.e., dimer) in the form of small pellets is placed into the vaporizer, then it will be vaporized and heated to form the dimeric gas (i.e., dimer molecule) under vacuum. Secondly, this dimeric gas is heated in the pyrolysis furnace, and then pyrolized to cleave the dimer into its monomeric form. Finally, this monomer polymerizes and forms a thin film atop the substrate placed in the coating chamber. Fig. 2(b) shows the deposition process of parylene-C membrane [25,26]. The process parameters of parylene-C deposition are as follows, the pyrolysis furnace temperature of 690 °C, the vaporizer temperature of

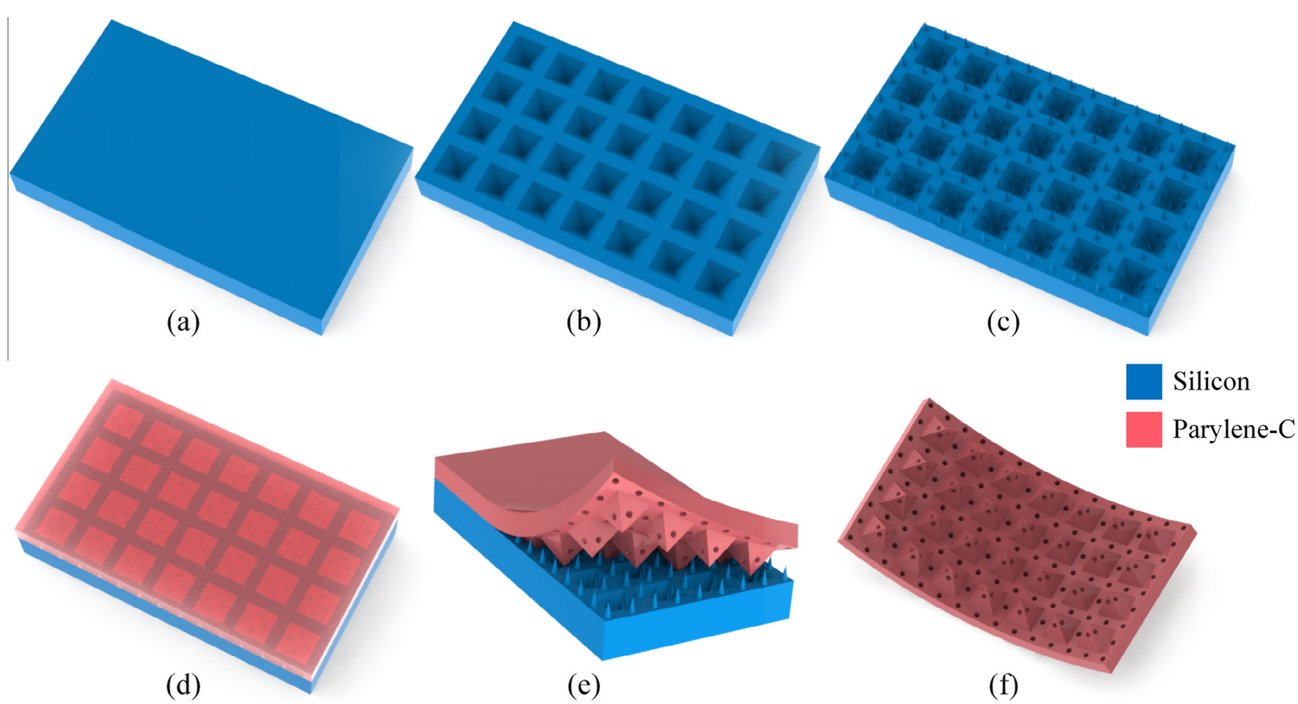

Fig. 1. The schematic view of the fabrication process flow to realize the parylene-C film with micro/nano hierarchical structures. (a and b) Si-based microstructures fabricated by using photolithography and KOH wet etching; (c) Si-based micro/nano hierarchical structures fabricated by using the improved DRIE process; (d–f) parylene-C film with micro/nano hierarchical structures replicated by peeling off from the silicon mold.