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Switchable wetting and flexible SiC thin film with nanostructures for microfluidic surface-enhanced Raman scattering sensors☆

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ABSTRACT

In this paper, we present the fabrication of the flexible surface-nanostructured silicon carbide (SiC) membrane, whose wettability can be simply tuned from super-hydrophobicity to super-hydrophilicity via the combination of an improved deep reactive ion etching (DRIE) process and the KOH wet etching process. The thermal annealing is utilized to reduce the stress of SiC membrane produced by the plasma enhanced chemical vapor deposition (PECVD) process. High-dense SiC nano-balls are fabricated by the improved DRIE process via the self-mask effect of the enhanced passivation step. Resulting from both the minimized liquid–solid contact area and the fluorocarbon layer atop deposited during the DRIE process, the SiC film with nano-balls shows an outstanding superhydrophobicity. Then, after the removal of silicon substrate by KOH wet etching, the flexible SiC membrane with nano-tips is realized, and the wetting behavior switches to superhydrophilicity. Correspondingly, the static contact angle (CA) remarkably achieves more than 160° and less than 1°, respectively. The wetting stabilities of these super-hydrophobic and super-hydrophilic samples have been demonstrated by the impact tests. The water droplet bounced 14 times on the super-hydrophobic SiC nano-ball surface, while it spread completely within 8 s on the super-hydrophilic SiC nano-tip surface. This switchable wetting behavior of SiC film was systematically investigated from both physical and chemical mechanisms by using SEM, AFM, EDX and FTIR. Furthermore, this novel surface-nanostructured SiC material shows the considerable surface-enhanced Raman scattering (i.e., SERS) property. The Raman spectrum of Rhodamine B (RhB) is significantly enhanced by a factor of 3.4×10^4, which is the first experimental demonstration of SiC-based SERS materials. In the meantime, the effects of the nanostructure morphology on both of the wetting behavior and the Raman scattering enhancement have been investigated by using the atomic force microscope (AFM). This flexible SiC SERS material with tunable wetting behavior has attractive application potential in micro/nano systems, especially in bio-medical fields.

1. Introduction

In the last decades, silicon carbide (SiC) has attracted much attention due to its unique properties, such as wide bandgap, outstanding electronic features, high Young's modulus and hardness, excellent oxidation and corrosion durability, and excellent chemical and physical stability [1–6]. The SiC material has been widely used both in scientific researches and in industrial fields, such as stencil lithography, anodic bonding, anti-high-temperature package, sensors and actuators working in the complex and harsh environment, and so on [7–12]. However, the wider and further application of SiC is limited by its intrinsic wettability, i.e., weak hydrophilicity with CA of ~75°. At micro/nano-scale level, the liquid flow resistance becomes huge and unacceptable due to the intrinsic wettability of SiC.

Super-hydrophobic and super-hydrophilic materials show wide applications in fields of various coatings, microfluidic systems, self-cleaning surface, etc. Additionally, tunable wettability is significant for microfluidic systems, especially for bio-medical MEMS and NEMS [13,14]. Super-hydrophobic SiC materials have been extensively investigated in the previous work [15]. Several techniques have been proposed to improve the hydrophobicity of SiC material, such as chemical coating [16], roughening [17], and nanostructuring [18]. However, there is still lack of knowledge about super-hydrophilic SiC. Besides, the switchable wetting behavior of SiC material has yet to be studied. Here, we present a single-step wafer-level process to fabricate super-hydrophobic SiC film based on an improved deep reactive ion etching (DRIE) process. Subsequently, the wetting behavior of SiC changes to be superhydrophilic after the KOH wet etching.

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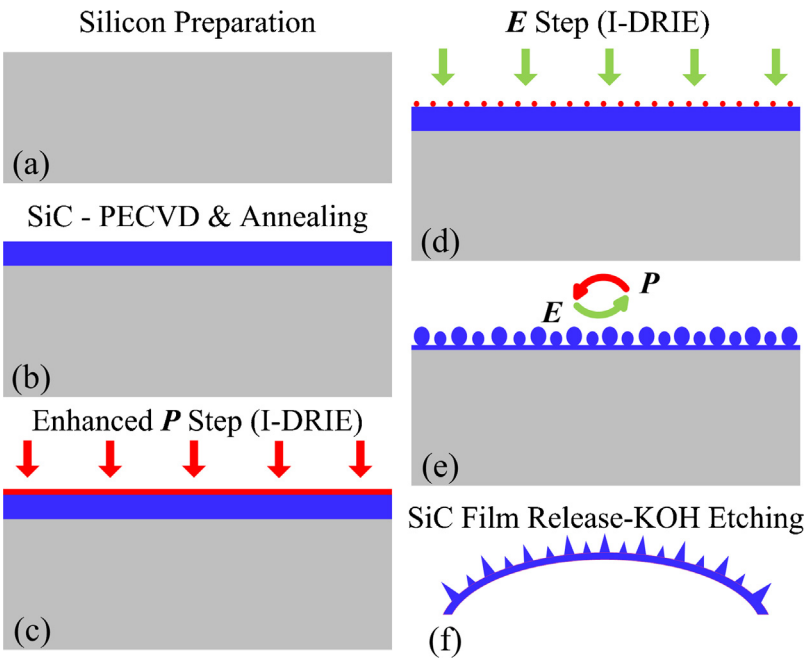

Fig. 1. Process flow to fabricate the tunable wetting and flexible SiC thin film (E: etching, P: passivation, I-DRIE: improved DRIE).

The Raman spectroscopy as a common tool is used to identify the type and the amount of the test material by the characteristic absorption peak and the corresponding signal intensity, which has attracted so much attention in biomedical fields due to the unique properties of fast response, simple and non-destructive [19]. Unfortunately, the intrinsic feature of high-concentration detection threshold (i.e., low sensitivity) limits the wide application of Raman spectroscopy. However, the surface-enhanced Raman scattering (SERS) technique offers an effective approach for the low-concentration detection even at molecular level [20–22]. There is no related report about the SiC SERS material with nanostructures, which possesses the ability of online monitoring chemical materials in harsh environments due to the inherent feature of super stability of SiC.

2. Experimental details

The polished (100) silicon substrate was treated by HF solution to remove the native silicon dioxide layer. Then, a SiC membrane with the thickness of 2 μm was grown on Si substrate by PECVD at 300 °C. The reaction gases contained SiH_4, CH_4 and Ar, with the gas flow rates of 20 sccm, 400 sccm and 400 sccm, respectively. The internal stress of SiC film was reduced to below 10 MPa by the thermal annealing at 450 °C for 50 min, as is shown in Fig. 1(a) and (b). The SEM images of as-prepared flat SiC film are shown in Figure S1 in the Supporting Information file.

Then an improved DRIE process with passivation enhancement was utilized to fabricate high-dense SiC nanostructure surface. Compared with the standard Bosch DRIE process, the passivation step of the improved DRIE process we presented is enhanced by increasing the passivation gas flow and the time of passivation step [23–26]. Therefore, the polymer deposited on the horizontal surface by the passivation step cannot be removed completely by the next etching step, and the nanoscale polymer residues will form and protect the substrate as the self-mask. As the cycle of etching and passivation increases, high-dense nanostructured SiC surface is obtained. The formation of SiC nanostructures is illustrated in Fig. 1(c)–(e). At this stage, the profile of the SiC nanostructure is ball-like (i.e., SiC nano-ball surface). An inductively coupled plasma (ICP) etcher (Surfacing Technology Systems plc, Multiplex ICP 48443) was used to realize the improved DRIE process. The optimized process parameters include gas flow, platen power, time ratio of etching/passivation, cycle and so on. The detailed information has been given in Table 1.

Finally, the sample was dipped into 30% KOH solution at 85 °C to remove the silicon substrate, and then the flexible SiC film with high-dense nano-tip forest ((i.e., SiC nano-tip surface)) was fabricated. Fig. 2 shows the flexibility of SiC film covered by a 10 μm parylene-C layer.

The static contact angle of samples and the impact test were measured by OCA 20 video-based contact angle meter (DataPhysics Instruments GmbH). The morphology effect of the surface-nanostructured SiC film was analyzed using the atomic force microscope (Dimension ICON, Bruker Corporation) and the scanning electron microscope (Quanta 600F, FEI Company). The chemical analysis of SiC film was carried out by using the Fourier transform infrared spectroscopy (Excalibur 3100, Varian, Inc.) and the scanning electron microscope with energy dispersive X-ray (EDX) analyzer (S-4800, Hitachi, Ltd.).

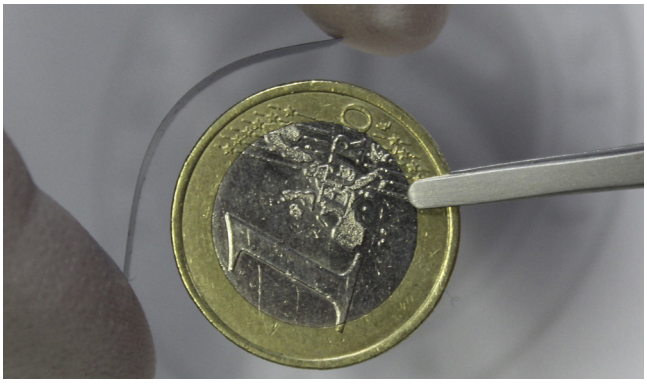

Fig. 2. Photograph of the flexible SiC membrane.