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Thermal reflow of plasma-polymerized fluorocarbon for nanochannels and particle encapsulation

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ABSTRACT

Thermal reflow is an important property for thermoplastic polymers, which has been studied extensively especially for photoreists and electron beam resists in semiconductor industries. While the surface smoothening effect is beneficial to reduce the roughness of micro- and nanostructures, the drastic morphology change has been tested to be efficient to fabricate optical devices like microlens arrays. Plasma-polymerized fluorocarbon (PPFC) is a feasible polymer material, which can be achieved conveniently with standard plasma etching systems, however, there have been limited studies regarding its properties and applications apart from its usage as a passivation layer during reactive ion etching. In this study, the thermal reflow behavior of PPFC on various substrates will be presented, including planar surfaces, gratings and trenches. Importantly, the formation of buried micro- and nanochannels has been demonstrated, when PPFC is heated above its glass transition temperature on trench structures. This encapsulation dynamics is analyzed with regard to various parameters like temperature and duration of thermal treatment, trench widths and initial thickness of PPFC film. As a proof of concept, silicon nanorods have been encapsulated in the microchannels by the reflowed PPFC. The results have demonstrated strong potentials of PPFC for applications like micro- and nanofluidics, microcontainers and drug delivery. Because of its good chemical stability and biocompatibility, PPFC can also be expected to be used for various biological devices like brain-machine interfaces, neural probes, epidermal devices and biological implants.

1. Introduction

Biocompatible polymers have been attracting considerable research interest due to their huge potential for applications like flexible electronics, biological implants and drug delivery systems. Specifically, the physical and chemical properties of polymers, e.g. Poly(methyl methacrylate) (PMMA) and SU-8, have been investigated extensively in previous studies and already employed successfully in devices like neural probes [1,2], artificial eyes [3] and microcontainers [4]. For thermoplastic polymers, a characteristic phenomenon is thermal reflow, which has been widely used in semiconductor industries and photonic engineering. Briefly speaking, when a thin layer of polymer is heated above its glass transition temperature by direct heating or irradiation with energetic particles, the stiff polymer will become viscoelastic and a morphological change will be driven by the surface tension [5]. This will lead to a rounded polymer surface, which represents a minimal surface energy, in the same time, the surface roughness of polymer film is also reduced significantly. This feasible technique has enabled fabrication of three dimensional (3D) structures [6], reducing the roughness of resist patterns [7], manufacturing of microlens arrays [8], etc.

Plasma-polymerized fluorocarbon (PPFC) grown by ionized gas species, like C₄F₈ (octafluorocyclobutane) or CF₄ (tetrafluoromethane), is an accessible fluoropolymer in semiconductor industries, however, it has been mostly used as passivation layers during plasma etching processes and recently as an etching reactant in atomic layer etching [9]. The chemical composition of PPFC is traditionally considered as polymerized CFₓ units (x = 1, 2, 3), resembling the structure of polytetrafluoroethylene (PTFE) [10–12], which has a long history of being employed in biotechnologies and surgeries, and has favorable physicochemical properties like lubricity, hydrophobicity, chemical inertness, etc. [13] Compared with other types of polymer materials, PPFC can be fabricated conveniently by gas precursors with standard techniques in semiconductor industries, thus is much easier to be integrated in complicated fabrication processes and device architectures, making it possible for manufacturing micro- and nanooptoelectromechanical systems (MOEMS/NOEMS) on a flexible substrate.
In this study, the thermal reflow of PPFC on micro- and nano-engineered substrates will be presented, which is enabled by the thermoplasticity of PPFC material deposited by a commercially available plasma etching system. The morphology evolution of PPFC on planar surfaces, gratings and trench structures are compared directly, besides, optical and chemical properties of PPFC are also investigated after thermal treatments. Importantly, an encapsulating dynamics has been demonstrated when heating PPFC-coated trench structures, during which viscoelastic PPFC on the top of the trenches will bridge and lead to formation of cavities. Various parameters have been studied to understand the dynamics of encapsulation, including the time and the temperature of thermal treatments, trench widths and the initial thickness of PPFC film. As a proof of concept, Si nanorods have been encapsulated inside cavities by the reflowed PPFC, implying capabilities for the applications like drug delivery and microcontainers. Besides, this method is also promising to fabricate micro- and nanochannels conveniently without wafer bonding, which can create a novel platform for the studies of microfluidics.

2. Materials and methods

Silicon wafers (4 in., 〈100〉 orientation) were used as substrates for PPFC deposition and thermal reflow experiments. The grating and trench structures were fabricated by DREM processes [14,15] with a dual-source induced coupled plasma (ICP) etching system DRIE-Pegasus (SPTS Technologies Ltd). A relatively small coil generator power of 500 W was applied to reduce the scallop size, which can generate roughness on the structure sidewall and interfere with the PPFC reflow process. The PPFC was deposited by a C4F8-based plasma, with coil power of 1000 W, platen power of 20 W, C4F8 gas flow rate of 100 sccm, chiller temperature of 0 °C and processing pressure of 20 mTorr. The deposition rate is estimated to be around 400 nm/min, which is measured by a spectroscopic ellipsometry system (Ellipsometer VASE, J. A. Woolam), and the PPFC deposition mechanism has been discussed in detail in previous studies [16]. Thermal treatments were performed by a hotplate with various temperatures.

PTFC structures on a planar surface were created by standard lithographic techniques. Positive tone photoresist AZ 5214E (Micro-Chemicals GmbH) was spin-coated on wafer surfaces deposited by PPFC films, and ultraviolet (UV) exposure was performed with a maskless aligner system (Heidelberg Instruments Mikrotechnik GmbH). The photoresist was then used as a mask layer to etch the PTFC film by oxygen-based plasma, and the resist residues were removed by acetone solutions. Various techniques have been performed to characterize the samples. Optical profilometry (Sensofar) and scanning electron microscopy (SEM) was employed to study the morphology evolution of PPFC films (SEM Supra60VP, Carl Zeiss AG). Energy-dispersive X-ray (EDX) spectroscopy was used to characterize the elements of obtained PPFC material. The surface profiles of PPFC film was measured by an AFM ICON-PT atomic force microscope (AFM). To study the optical properties, PPFC films were deposited on planar glass wafers and measured by a microspectrophotometer (GRAIC Technologies, Inc).

3. Results and discussions

A schematic illustration (Fig. 1a) shows the morphology evolution of PPFC films on various substrates after thermal treatments, during which the whole sample is heated above the glass transition temperature \( T_g \) (for PTFE the \( T_g \) is estimated to be between 110 and 130 °C [17]). For a planar Si surface without geometrical boundaries, the thermal reflow of a box-type PPFC structures represents a classical reflow dynamics, where the surface tension will drive the viscoelastic polymer surface towards a minimized surface energy, giving a continuous curvature profile and an aspheric lens-like shape. For PPFC films deposited on...
grating and trench structures, the thickness of as-deposited PPFC is not uniform on the Si surface and follow the regime of plasma-enhanced chemical vapor deposition (PECVD) [18], which means that the thickness of PPFC on the top of Si structures is larger compared with the sidewalls and the bottom due to the ion shadowing effect and the depletion of FC species. For grating structures, the abundant PPFC on the top will reflow into a bulb-like structure covering the tip of gratings. While for trenches, the viscoelastic PPFC on the sidewall will bridge and merge together, leading to the formation of a void buried under the PPFC film. SEM images are presented in Fig. 1b to demonstrate the thermal reflow of PPFC on a planar surface, where the PPFC are patterned by standard UV lithography followed by O₂-based plasma etching, giving a linewidth of around 2 μm and a height of 1.7 μm ((1) in Fig. 1b). After thermal treatment at 200 °C for 5 min and 10 min, the rounded profiles can be clearly seen ((2) and (3) correspondingly in Fig. 1b). Optical profilometry has been performed to measure the PPFC structure in Fig. 1b (1) and (3), showing a rounded geometry upon thermal treatment (Fig. 1c). Besides, by integrating the measured profiles, the total cross-section area of the PPFC structures is calculated to be reduced by 20.95%, this can be attributed to the evaporation of primary polymer units and the crystallization-induced shrinkage [19, 20]. For thermal reflow of PPFC on grating and trench structures, the samples are heated to 200 °C for 10 min, and the morphology evolution is presented by SEM images in Fig. 1d and e correspondingly. Again, relocation of PPFC films on the structure surfaces can be observed, as the PPFC on the structure sidewalls is reduced significantly, while PPFC films on the top and bottom of the structures are rounded, giving a bulb-like profile on the top of the grating and a cavity in the trench structures.

Various techniques have been performed to characterize the PPFC film after thermal treatment for a better understanding of its material properties. Firstly, 2.5 μm thick PPFC was deposited on a pristine Si surface, and EDX analysis was performed on the surface of the film, showing significant signals from C and F with a weight percentage F/C = 2.17 (Fig. 2a). The result suggests an atomic F/C ratio of 1.45 thus a relatively high degree of polymerization [21, 22]. EDX analysis was also performed along the yellow axis as shown in Fig. 2b, both before and after thermal reflow, and the signals from C, F and Si are compared in Fig. 2c. While the intensities of C and Si signals are almost not influenced by the thermal treatment, F signal intensity is reduced, giving a weight percentage F/C of 1.69 and an atomic F/C ratio of 1.13. This is supposed to be caused by an increasing molecule size and thus less fluorine atoms. A reduction of surface roughness can also be observed with AFM measurements (Fig. 2d), which is supposed to be caused by reflow and merging of smaller PPFC grains. The root-mean-square roughness is measured to be 8.44 nm for as-deposited PPFC film with a thickness of around 1 μm, after thermal treatment of 200 °C for 10 min, the grain size is increased with a reduced surface roughness of 6.54 nm. The optical absorbance of PPFC films on a glass substrate is also characterized as shown in Fig. 2e. The absorbance is mostly in the UV-region at a wavelength of around 350 nm with a tail extending to the visible wavelengths, corresponding to the electronic transitional absorption. A larger UV absorbance is observed for thicker PPFC films, and thermal treatments can reduce the absorbance significantly, this is supposed to be caused by the reduced Rayleigh scattering, when the polymer structure become less amorphous after thermal treatments [23]. The low optical absorbance and the stable chemical properties make PPFC promising to fabricate optical devices as a replacement of transparent silicon oxide, which will be interesting to be investigated in the future.

Below the discussion will be focused on the thermal reflow dynamics
of PPFC-coated trench structures. Fig. 3a shows trench structures with width of 750 nm, which are deposited with 500 nm PPFC. Thermal treatments are then performed in 10 min with different temperatures of 100 °C, 125 °C, 150 °C, 175 °C and 200 °C on 5 different samples. For temperature of 100 °C, it is difficult to see significant morphological changes, and the roughness of deposited PPFC can still be observed on the sidewall. When the temperature is increased to 125 °C, reflow can be observed on the sidewall, where the roughness of as-deposited PPFC coalesce into larger grains. When the temperature is increased further, the PPFC on the sidewall is reduced, while the PPFC on the top and the bottom of trenches start to get rounded, giving a smooth void with rounded geometries. It can be noticed that the curvature of the PPFC structures on the top of trenches decreases with a higher temperature (illustrated by the yellow dash circles in Fig. 3a), which is plotted directly in Fig. 3b. This is understandable, since the viscosity of polymers decreases with a higher temperature due to the smaller intermolecular interactions, the surface tension will be able to drive the PPFC surface to reduce the local curvatures. To have a theoretical description of the dynamics, one might need to study from the perspective of capillary tubes, which however is not in the scope of this study. It should be mentioned that the thermal reflow happens in a relatively short time scale. Fig. 3c show trench structures with width of 1 μm and coated with around 500 nm of PPFC, the structures were then heated to 200 °C with different duration from 5 s, 1 min to 8 min. Migration of PPFC materials can already be observed after 5 s of thermal treatment. When the time increases, PPFC on top of the trench openings will start to reach to each other (1 min) and merge eventually (8 min), giving buried cavity structures. This type of encapsulation dynamics has been reported in electron beam resist structures [24], however, the thermal reflow of PPFC hasn’t been studied before according to the author’s knowledge.

Another important parameter, which has a straightforward impact on the encapsulation dynamics, is the size of trench opening D. For a specific initial thickness of deposited PPFC, smaller D will obviously give a higher throughput of channel encapsulations. To demonstrate this, trenches with various opening sizes (from 200 nm to 2 μm) are deposited with 500 nm PPFC, and were then processed by thermal treatment at 200 °C for 10 min. The results (Fig. 4a) illustrate complete encapsulation for trenches with D smaller than 1 μm, while for larger trench openings, reflowed PPFC is unable to encapsulate the channels. It should be noticed that due to the ion shadowing effect and the depletion of FC species, the deposition rate of PPFC on the top of trench structures is larger compared with the sidewall and the bottom, which means that for small trench openings, the PPFC on the top of the trenches will quickly grow and close the channels, thus blocking the transport of FC species inside the trenches. During thermal treatment, the PPFC layer on the top of trench structures will start to infiltrate the channels, which is caused by the difference of Laplace pressure on the PPFC surfaces and therefore a different thermal reflow regime compared with the situation with larger trench openings. An illustration is drawn in Fig. 4b, with a SEM image demonstrating arrays of nanochannels with PPFC infiltrated upon thermal treatments, the channels have a width of around 368 nm and a height of around 884 nm. Here the temperature was set to 200 °C to have a controllable and efficient reflow process. This method doesn’t require wafer bonding to enclose the trench openings, which is otherwise a standard process for fabricating microfluidic channels [25]. Besides, the reflowed PPFC is chemically stable and has a very small optical absorbance in the visible wavelength (below 0.03 at wavelength of 600 nm), making it a feasible and effective method to fabricate micro- and nanofluidic channels. To ensure a complete encapsulation of the trenches, there should also be sufficient PPFC deposited on the structures. Fig. 4c shows thermal reflow of PPFC with various initial thickness t0 of 188 nm, 282 nm and 500 nm. For the trench structures with same D and the same parameters during thermal treatment, a larger t0 will directly lead to a higher throughput of channel encapsulation. It should be mentioned that the critical dimension (CD) of the fabricated nanochannels is mostly limited by the size of the trenches on Si substrate. By using lithography tools with a higher resolution limit, like electron beam lithography, smaller Si trenches can be manufactured giving even smaller CD of nanochannels.

As a proof of concept, I will show how nanoparticles can be encapsulated by the thermal reflow of PPFC on trench structures. A schematic illustration is shown in Fig. 5a, nanoparticles are firstly assembled inside PPFC-coated trench structures, afterwards thermal treatment is performed, the nanoparticles in the bottom of the trenches will be trapped, while the reflowed PPFC will merge on the top of trenches and close the openings, thus the nanoparticles can be encapsulated conveniently. It should be mentioned that the assembly process of nanoparticles can be technically difficult itself, and a widely used method is to employ the capillary force to assemble nanoparticles from liquid solution to structures on the substrate [26]. In this study, freestanding Si nanorods are

![Fig. 3. Morphology of PPFC-coated trench structures after thermal treatments: (a) SEM images showing the cavity geometry with different temperatures during the thermal treatment, from left to right: 100 °C, 125 °C, 150 °C, 175 °C and 200 °C on 5 different samples; (b) Measured curvature of the top of cavities as a function of temperature for thermal treatments; (c) SEM images showing the morphology evolution of PPFC with increased time of thermal treatment.](image-url)
generated by mechanically scratching a wafer surface patterned with Si nanopillar arrays, then the wafer surface with detached Si nanorods was rubbed on the sample with PPFC-coated trench structure, thus part of the Si nanorods can be directly transferred into the trenches. The Si nanorods have a diameter of around 200 nm and length of 1 μm, and the trenches have a width of around 1 μm coated by 400 nm thick PPFC film. After a thermal treatment of 10 min at 200 °C, the Si nanorods are encapsulated by the reflowed PPFC, which can be seen in the SEM image in Fig. 5b. Zoomed-in images (Fig. 5c) show the details of the structures, where the Si nanorods are labeled by yellow colour. Since PPFC is chemically stable (similar to PTFE, which has excellent resistance to most of the solvents, acids and alkalis), the encapsulated nanoparticles can be well protected. However, it has been observed that acetone can reduce the adhesion between PPFC and Si substrate, making it possible to release the encapsulated nanoparticles.

4. Conclusions

In conclusion, I have experimentally demonstrated thermal reflow of PPFC on various types of micro- and nanostructures. The morphology evolution of PPFC beyond its glass transition temperature is studied with respect to various parameters, like temperature and time of thermal
Credit author statement

B. Chang: Conceptualization, Data curation, Investigation, Methodology, Funding acquisition, Writing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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