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Hydrophobic coating of surfaces by plasma polymerization in an RF plasma reactor with an outer planar electrode: synthesis, characterization and biocompatibility

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Abstract

This paper presents the plasma polymerization of poly(hexafluorobutyl acrylate) (PHFBA) thin films on different substrates in an RF plasma reactor with an outer planar electrode. This reactor configuration allows large area uniformity and fast processing times. Deposition rates of up to 60 nm min^{-1} were observed. The influence of plasma power and substrate temperature on the deposition rate, structure and wettability of the as-deposited films was investigated. It was observed that better hydrophobicity was obtained at high plasma power and in low temperature conditions. PHFBA thin films deposited on electrospun poly(acrylonitrile) fiber mats under such conditions resulted in superhydrophobic surfaces with contact angle values greater than 150°. *In vitro* cell studies using human epithelial cells demonstrated the non-toxic nature of the plasma-polymerized PHFBA films.

Keywords: plasma, hydrophobic, PECVD, polymer, biocompatible

(Some figures may appear in colour only in the online journal)

1. Introduction

The hydrophobic nature of surfaces with low surface energy is governed by the interaction of surface molecules with water droplets [1, 2]. If a water droplet is dropped on a low surface energy solid, thermodynamically it tends to minimize its contact with the surface. As a consequence of reducing the attraction between the solid and the liquid, the water droplets take the shape of a sphere and do not wet the surface [3–5]. Such hydrophobic surfaces are in great demand for fundamental research and some crucial industrial applications such as biomedical materials [6], textiles [7] and membranes [8], as well as anti-adhesion [9] and anti-icing systems [10]. Techniques to produce hydrophobic surfaces can be divided into two main groups: roughening the surface on a micro/nano scale, and decreasing the surface free energy by coating the surface with hydrophobic groups to render it more hydrophobic.

For coating applications, fluorinated polymers are widely used to make hydrophobic surfaces because of their very low surface energies. In addition, their low dielectric constant values and chemical inertness, when compared to hydrocarbon polymers, are other important features that make fluorocarbon polymers attractive [11, 12]. Polytetrafluoroethylene (PTFE) is by far the best known fluoropolymer and it has been extensively used in cookware applications for decades. However, the surface energies of polymers that have long fluorinated side groups are even lower than that of PTFE, hence it is advantageous to prepare

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hydrophobic finishes from precursors that contain long perfluoro alkyl end groups [13].

Fluorocarbon polymers are normally synthesized by various wet methods such as atom transfer radical polymerization (ATRP) [14], chemical modification [15], suspension polymerization [16] and direct fluorination techniques [17]. Chemical vapor deposition (CVD) is an all-dry method for preparing functional polymeric thin films [18, 19], and it can be optimized to functionalize fragile and geometrically complex substrates [20, 21]. So far, different CVD strategies, such as initiated CVD (iCVD) and plasma-enhanced CVD (PECVD), have been employed to synthesize fluoropolymers on various substrates [22, 23]. Magnetron sputtering is another dry alternative which has been used for the deposition of some fluoropolymers [24, 25]. In PECVD, reactions that yield a coating on the substrate surface occur after the creation of a plasma with reacting gases. In most conventional PECVD systems, radio frequency (RF) glow discharge is generated by inductive or capacitive coupling in terms of electrode position. The electrodes used in the inductively coupled plasma (ICP) systems are not in direct contact with the reactive plasma gases, hence ICP provides clean and reliable plasma conditions [26, 27]. Inductively coupled PECVD in a planar parallel-plate configuration enables high plasma density, consistent uniformity and reproducibility [28–30]. These features make planar systems very promising for meeting industrial requirements.

Previously, acrylates and methacrylates that have long perfluoro alkyl end groups have been used extensively to prepare hydrophobic surfaces [31, 32]. However, increasing concern exists over the adverse effects of long-chain fluorochemicals on human health and the environment [33, 34]. It has been revealed that the toxicity degree and bioaccumulative potential of fluorinated chemicals is directly proportional to the length of the fluoroalkyl chain [35]; therefore, using short-chain fluorinated chemicals in industry is becoming more important when taking environmental and health factors into account. Moreover, thin polymer films produced by PECVD are expected to exhibit good biocompatibility. In general, PECVD produces highly cross-linked polymer films which contain negligible amounts of chemicals with a low molecular weight that may be cytotoxic. Cytotoxicity is a good measure of biocompatibility, which is known to be the quality of a material being toxic to cells.

In this paper, the deposition of the PHFBA films from precursor hexafluorobutyl acrylate (HFBA) in an RF parallel plate reactor are reported. In this reactor, plasma power is applied to a spiral copper coil that has been placed on top of the reactor. This reactor type is preferred mostly within the microelectronics industry, in order to meet the requirements for large area uniformity and faster processing times [36]. The effects of deposition parameters that are important to the PECVD process, namely substrate temperature and plasma power, will be discussed. Silicon wafer and electrospun polyacrylonitrile (PAN) fiber mats were used as substrates. The electrospun fiber mats are good substrates for creating superhydrophobic surfaces because of their inherent roughness. In this study, PAN was selected to create fiber mats, because its behavior in electrospinning is well known. The fast deposition of uniform, nontoxic thin films on different surfaces, which was achieved through this process, may create new opportunities for hydrophobic thin film applications.

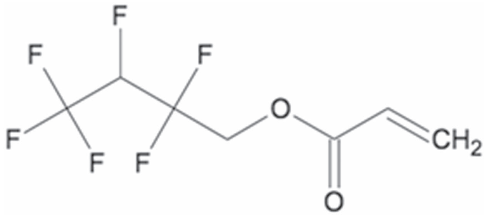

Figure 1. The chemical structure of an HFBA monomer.

2. Experimental

2.1. Materials

The monomer 2,2,3,4,4,4-hexafluorobutyl acrylate (95%) (figure 1) was obtained from Sigma-Aldrich, and used as received without any further modification or purification. Electrospun PAN (MW = 150 000, Sigma-Aldrich) fiber mats and silicon wafers (100, p-type) were used as substrates. N,N-dimethylformamide (99.8%, Sigma-Aldrich) was used as a solvent for PAN solution.

2.2. Electrospinning of PAN fibers

Electrospun PAN fiber mats were prepared using a laboratory scale electrospinning system (NE-100, Inovenso). First, 10 wt.% of the PAN solution was prepared in N,N-dimethylformamide, and then the solution was fed into a copper tip at a flow rate of 0.6 ml h^{-1}. An 18 kV electrical potential was applied between the tip and collector, where the aluminum foils were placed. The distance between the collector and the tip was 15 cm. After the spinning, PAN fibers with an average diameter of 170 nm were obtained.

2.3. Plasma polymerization

PHFBA thin films were deposited on different substrates by plasma polymerization in a custom built parallel plate reactor with an outer spiral electrode (figure 2). In this reactor, 13.56 MHz RF power is applied to a flat spiral copper electrode with an outer diameter of 10 cm on the upper surface of the reactor. The coil is separated from the plasma by a quartz plate which has a 20 cm thickness. The reactor is a cylindrical stainless steel vacuum chamber, which is 15 cm high and 16 cm in diameter.

An LC matching circuit was placed between the coil and the generator for impedance matching. The transparent quartz cover also allowed visual inspection and *in situ* monitoring of the deposition rates with laser interferometry (JDS Uniphase). The HFBA monomer was vaporized in a glass jar and fed into the reactor at a flow rate of 2 sccm using a needle valve. A capacitance-type pressure gauge (MKS, Baratron) was used to measure the pressure inside the reactor. During all the deposition experiments, the pressure in the reactor was kept

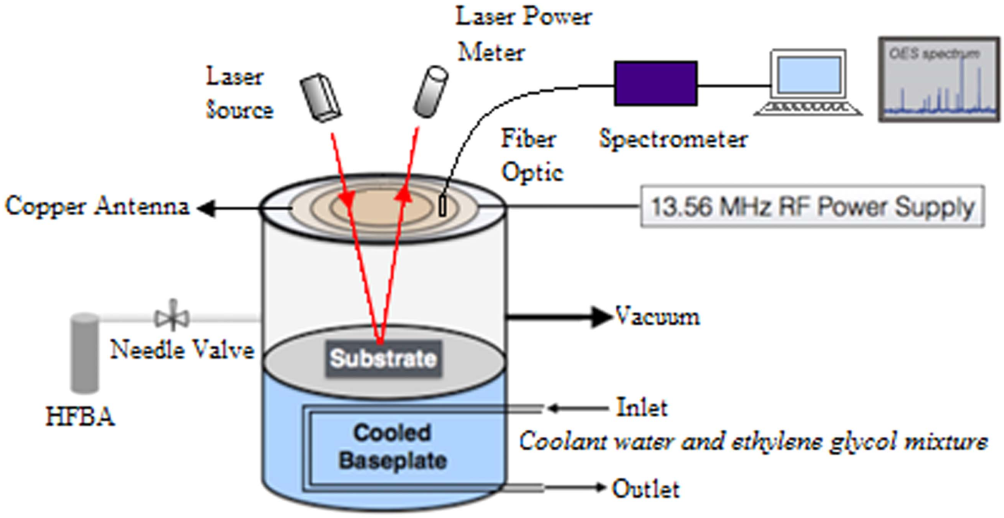

Figure 2. PECVD experimental system.

constant at 100 mTorr using a PID-controlled butterfly valve. The substrates were placed on a stage that was cooled on the back side using a water and ethylene glycol mixture from a recirculating chiller. The cooling stage is 10 cm below the quartz window. The effect of substrate temperature on the deposition rate and the structure of the as-deposited PHFBA films was investigated at different plasma powers. In order to evaluate the uniformity of the as-deposited PHFBA films, a whole 4 inch diameter Si wafer was placed in the reactor and coated with PHFBA at 50 W plasma power and 263 K substrate temperature. At the power levels applied in this study (up to 50 W), the plasma was generated in the so-called E-mode with prevailing capacitive coupling. Five locations (the center and four edges of the silicon wafer) were selected to measure the film thickness by using a profilometer.

2.4. PHFBA film characterization

Fourier transform infrared (FTIR) spectra were obtained in a Bruker Vertex 70 FTIR spectrometer at wavenumbers between 400 and 4000 cm^{-1} and a resolution of 4 cm^{-1}. All the FTIR spectra were baseline-corrected and the thickness normalized. The thickness of the as-deposited PHFBA film on the silicon wafers was measured by both *in situ* (interferometer) and *ex situ* (AEP 500LS profilometer) methods; hence it was possible to calculate the deposition rate of the PHFBA. The emitted light from the plasma was collected by an optical fiber, which was placed above the quartz window and connected to a spectrophotometer (Ocean Optics QE65000) with a spectral range of 200–1100 nm. The spectrometer was equipped with a CCD image sensor (Hamamatsu S7031-1006) as a detector.

Water contact angle measurements were carried out to determine the wettability of the as-deposited PHFBA surfaces using a Kruss Easy Drop contact angle goniometer. SEM experiments were performed using a Zeiss LS-10 scanning electron microscope.

2.5. Toxicity test of PHFBA thin films

2.5.1. Cell line and culture conditions. The colonic epithelial cell line CCD 841 CoN (CRL-1790™), which is a model cell line for normal human epithelial tissue, was used for toxicological assessment. The cells were maintained as an attached type monolayer culture in Dulbecco's modified Eagle's medium (DMEM/Ham's F12) (Biochrom AG, Berlin) supplemented with 10% heat-inactivated fetal bovine serum (FBS) (Biochrom AG, Berlin) and 0.1 mg ml^{-1} gentamicin (Biological Industries, Israel). Incubation conditions of 37 °C in a humidified atmosphere of 5% CO_2 were maintained in a CO_2 incubator (Binder GmbH, Germany). The cultures were passaged by trypsinization when the cells reached 70% confluency under sterile conditions in a Class II Laminar Flow (Nuaire inc., Plymouth, USA). CoN cells were frozen in a freezing medium (10% DMSO+ 90% FBS) and stored in liquid nitrogen for long periods.

2.5.2. Toxicological assessment of PHFBA materials on human epithelial cell line. The effects of PHFBA materials deposited on a silicon wafer on the proliferation of normal human epithelial cells were evaluated by means of a cell proliferation kit (XXT, Biological Industries) in 24-well flat-bottomed micro titer plates. The cells were seeded into the plates (5×10^4 cells/well) and incubated for 24 h. The test materials were sterilized in an autoclave at 121 °C for 21 min and then put into the wells. The cells were incubated at 37 °C for 96 h. Finally, XTT reagent was applied to form soluble formazan crystals, which is an indicator of viability. After incubation at 37 °C for 4 h, formazan crystals were produced by the mitochondrial enzymes of the living cells and the optical density of the chromogenic product was measured at 490 nm with a 96-well plate reader (BioTek microplate reader). The effects of the materials on cell proliferation were determined, and the effects of the materials on the cell morphology and viability were also analyzed under microscope (Leica Microsystems, 10×).

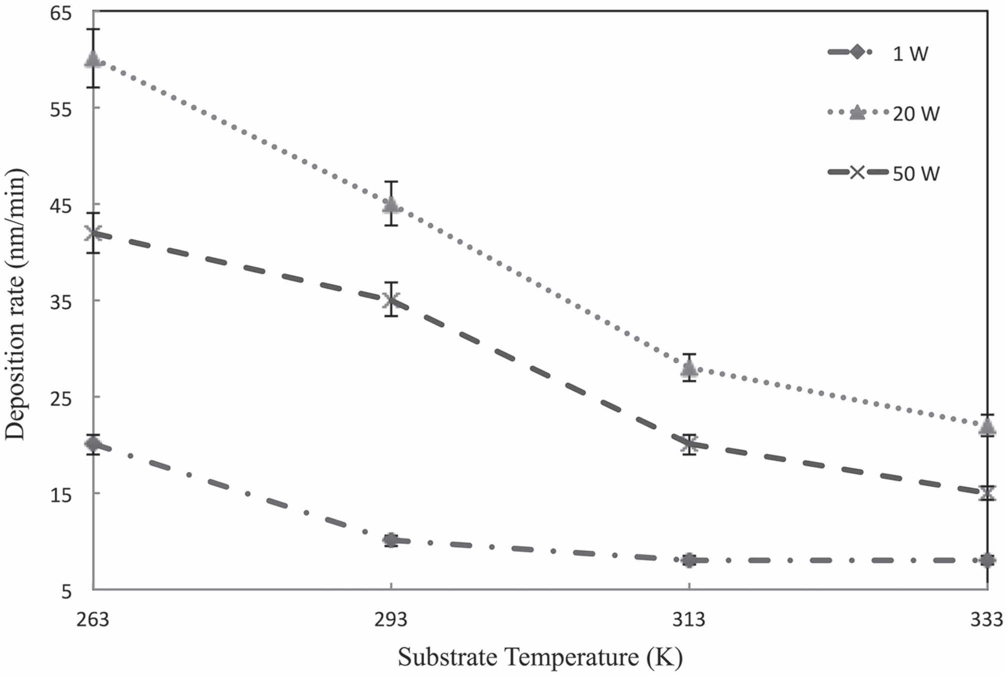

Figure 3. The effect of substrate temperature on PHFBA deposition rate at different plasma powers.

3. Results and discussions

3.1. Deposition kinetics

Figure 3 shows the influence of plasma power and stage temperature on the PHFBA deposition rate. It must be noted that the deposition rate was observed to be stable with deposition time. The rate of deposition is observed to increase as the substrate temperature decreases at all applied plasma powers. This behavior can be attributed to an adsorption-limited regime, which is commonly observed in a low-temperature CVD of similar acrylate monomers [37]. The specific reaction rate on the surface depends highly on the temperature, and it usually increases as the temperature increases. On the other hand, the adsorption of a reactive species on the surface is always exothermic and the coverage of the surface by the species decreases with increasing temperature [38]. Thus, for this study, it can be concluded that the surface concentration of the adsorbed monomer decreases more quickly than their consumption through surface reaction, causing a decrease in the overall deposition rate with increasing temperature.

Applied plasma power is the other important parameter for the deposition rate. The deposition rates are dramatically increased when the plasma power is increased from 1 W to 20 W. However, a further increase of applied power up to 50 W causes a decrease in the deposition rate. The change of deposition rate with plasma power can be attributed to the competition of different mechanisms during film growth. During PECVD, deposition and plasma etching may proceed simultaneously. Going from 1 W to 20 W increases the deposition rate through the generation of more active gaseous species that take part in the deposition process. The optical emission spectra (OES) of an HFBA plasma discharge created under different applied RF powers are shown in figure 4. The dissociation of the monomer molecule and the formation of the reactive species are obvious from the spectra, which shows the signals of CO, H and F moieties at the wavelengths of 450–650 nm, 656.2 nm and 703.4 nm, respectively [39–41]. In particular, the detachments of hydrogen and fluorine may play a very important role in creating free radicals and some other active species [42, 43]. The change in plasma power results in a change in the relative intensity of hydrogen and fluorine moieties. It is well known that fluorine atoms and molecules that are present in the plasma are responsible for the process of etching [44–46], and the extensive creation of fluorine moieties at high applied plasma powers may result in the etching of the polymer surface during film growth. Besides, at higher powers, it is quite possible that the bombardment of the substrate surface with energetic ions will increase the ablation rate, which in turn decreases the overall deposition rate.

3.2. Film structure and uniformity

Figure 5 shows the FTIR spectra of the HFBA monomer together with the spectra of PHFBA thin films deposited at different temperatures and plasma powers. The FTIR spectra of all PHFBA thin films display the following peak assignments: 1756 $\mathrm{cm^{-1}}$ (stretching, C=O), 1500–1350 $\mathrm{cm^{-1}}$ (bending, C–H), 1250–1295 $\mathrm{cm^{-1}}$ (asymmetric $-CF_2-$), 1206 $\mathrm{cm^{-1}}$ (symmetric $-CF_2-$) and 1115 $\mathrm{cm^{-1}}$ ($-CFH-CF_3$). Different from the spectra of PHFBA, characteristic C=C bonds were observed at 1640, 1416, 1087 and 991 $\mathrm{cm^{-1}}$ in the spectrum of the HFBA monomer. The absence of these peaks in the polymer spectra implies that polymerization occurs through unsaturated double bonds. According to figure 5, the increase in plasma power accompanies an increase in the intensity of the asymmetric $-CF_2-$ peak at 1295 $\mathrm{cm^{-1}}$. Similar behavior is observed with a decrease in substrate temperature. Hence, it can be concluded from FTIR

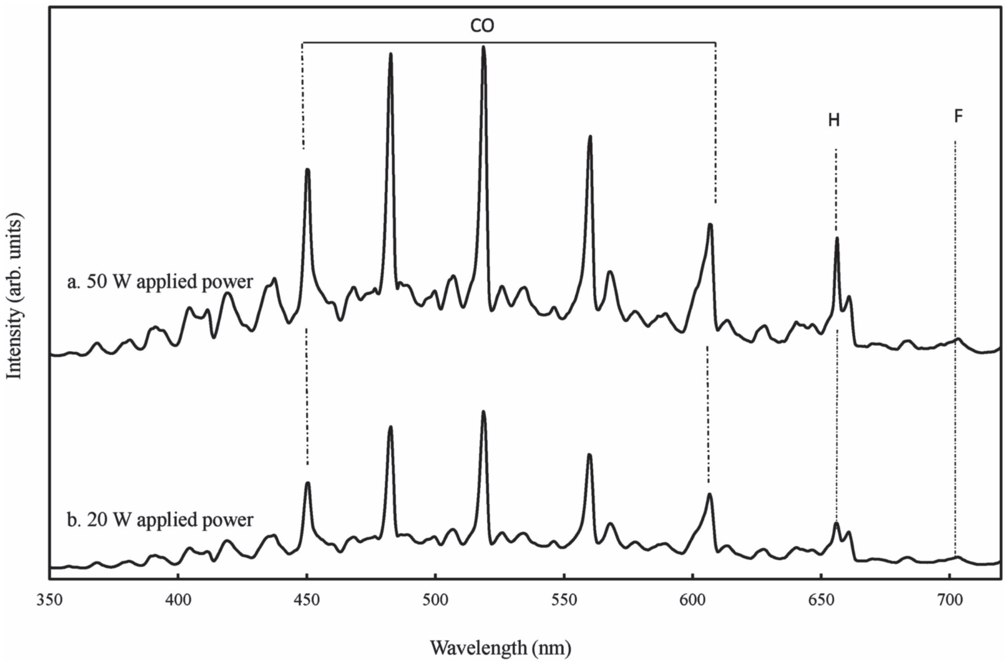

Figure 4. The OES spectra of the HFBA plasma discharge created under different applied RF powers.

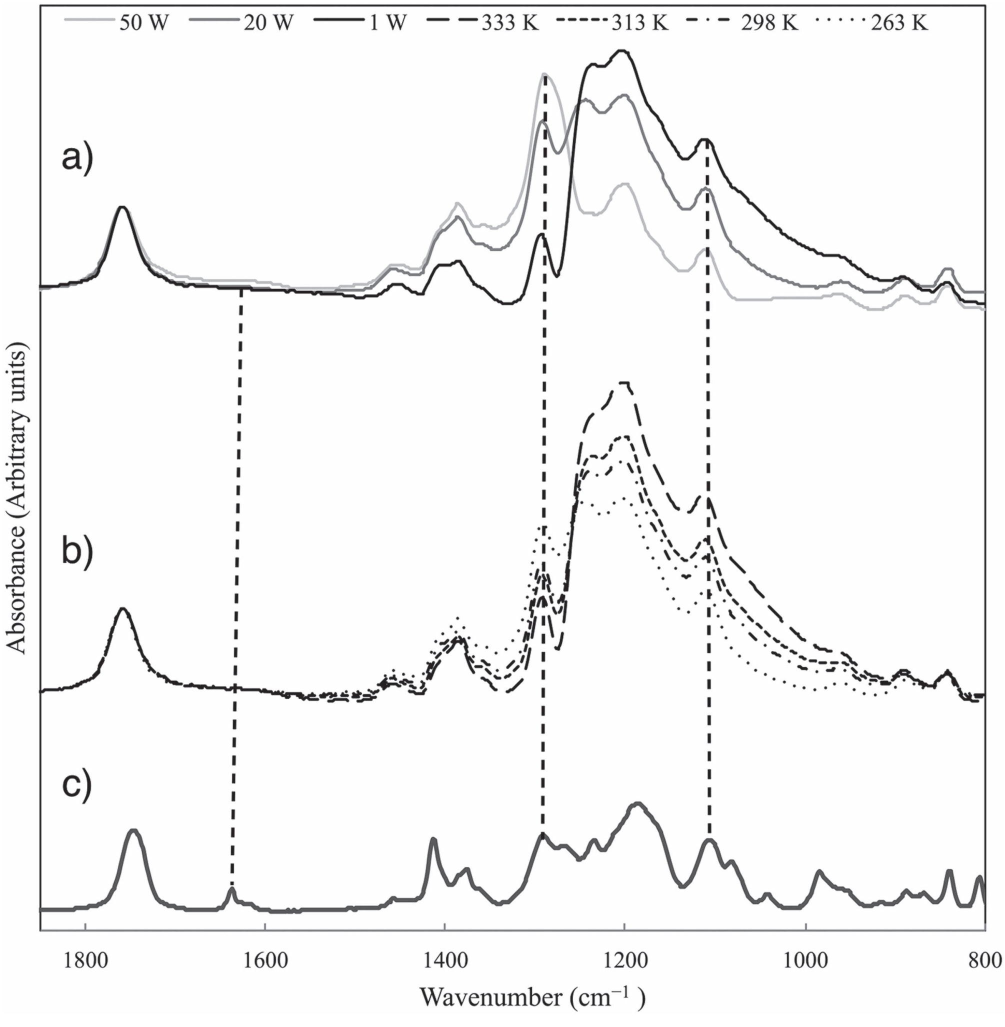

Figure 5. (a) The FTIR spectra of PHFBA thin films at different plasma powers, (b) the FTIR spectra of PHFBA thin films at different substrate temperatures, (c) the FTIR spectrum of the HFBA monomer.

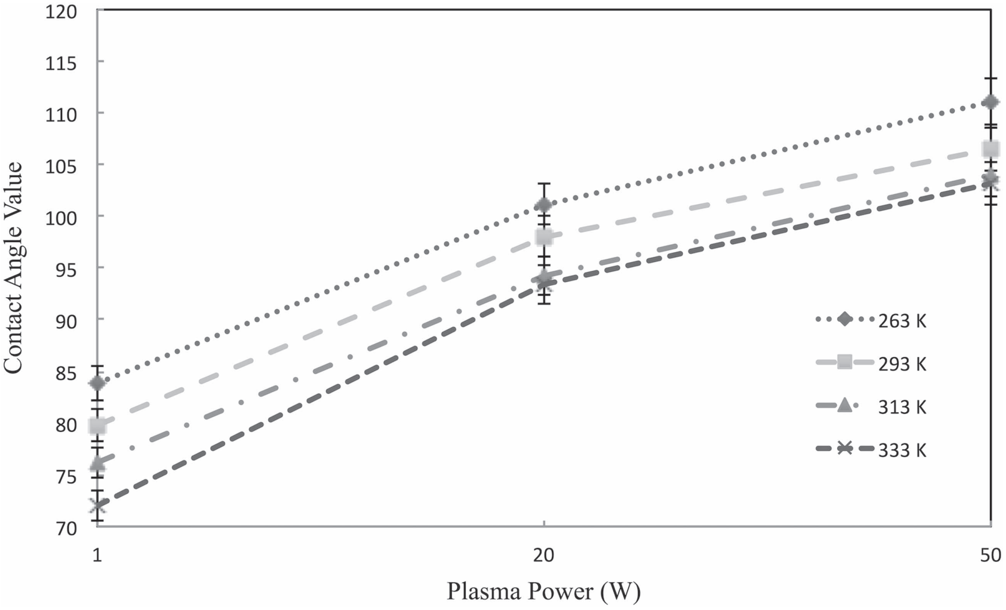

Figure 6. The static contact angle values of PHFBA surfaces at different plasma powers for different substrate temperatures.

Table 1. Water contact angle measurements on silicon wafers coated in different plasma conditions.

	Contact angle					
	1 Watt		20 Watt		50 Watt	
Substrate temperature	Advancing	Receding	Advancing	Receding	Advancing	Receding
263 K	88.2 ± 1.4	65.4 ± 1.5	105.2 ± 1.2	86 ± 1.2	114 ± 1.0	101.1 ± 1.2
293 K	84.5 ± 1.9	62.1 ± 1.4	100.4 ± 1.6	80.1 ± 1.5	109.9 ± 1.1	94.5 ± 1.7
313 K	82.0 ± 1.5	60.0 ± 1.7	98.2 ± 1.8	79.8 ± 2.0	107.6 ± 1.5	91.4 ± 1.4
333 K	76.3 ± 2.3	57.4 ± 1.2	98.5 ± 1.8	81 ± 1.7	107.9 ± 1.1	93 ± 1.9

Table 2. The PHFBA film thickness at five different locations.

Location	PHFBA thin film thickness (nm)
Center	422
Edge 1	416
Edge 2	403
Edge 3	397
Edge 4	427
Average	413

analysis that the amount of fluorine moieties, which are responsible for the low surface energy property, is high at a high applied plasma power and low substrate temperature. This observation is also consistent with the change of water contact angle by changing the plasma power and substrate temperatures. According to figure 6, the static water contact angle of the PHFBA film on a flat silicon wafer surface increases with decreasing substrate temperature and increasing plasma power. The observed significant changes in the contact angles can be attributed to the differences regarding the chemical properties of the as-deposited PHFBA films. The highest contact angle seen on the flat silicon surface is observed to be 110° in this study. Contact angles higher than that can only be achieved through the addition of surface roughness. In addition to static contact angle measurements, advancing and receding contact angles were also measured to evaluate the non-wetting performance of the as-produced coatings (see table 1). Besides this, in order to assess the stability of the coatings in time, the contact angle values were measured again six months after the initial ones, and there was no significant difference observed in the water contact angles.

It was postulated in the introduction that the planar system used in this study would produce highly uniform polymeric films. In order to evaluate the film uniformity, the film thicknesses were measured at different locations over a whole silicon wafer that had been used as the substrate in a typical run. The film thicknesses were measured by a profilometer and the results are shown in table 2.

Then, using equation (1), the non-uniformity of PHFBA was found to be 3.64%. This very low non-uniformity value can be attributed to the uniform coating ability of the planar

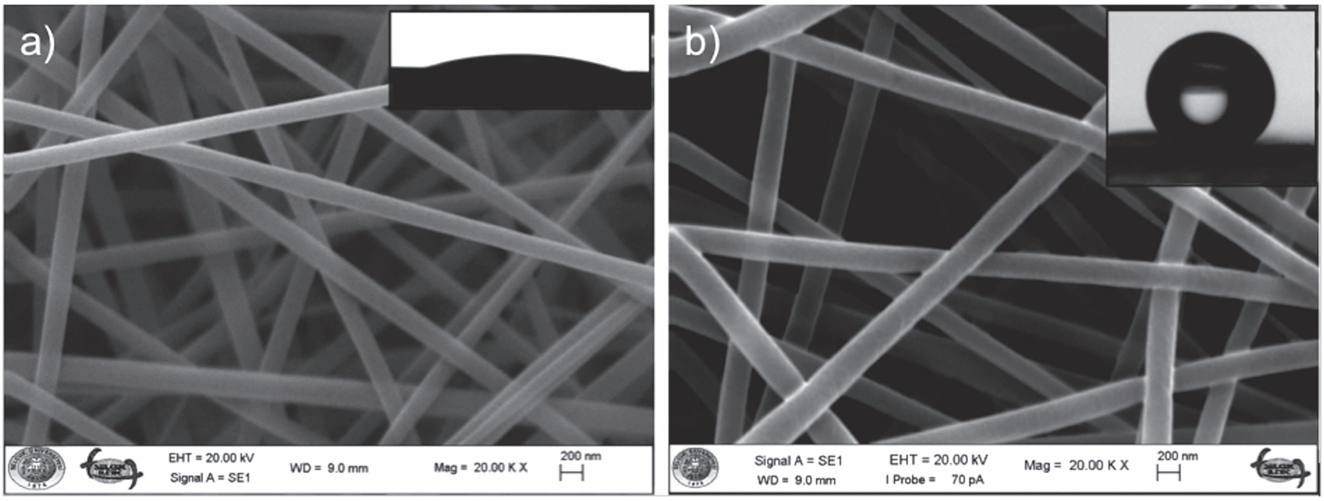

Figure 7. (a) An SEM image of PAN fibers without a coating, (b) an SEM image of the as-deposited PAN fibers (depositions were carried out at 100 mTorr plasma power, 263 K substrate temperature, and 1 W applied plasma power. The film thickness deposited on the reference silicon wafer was 100 nm).

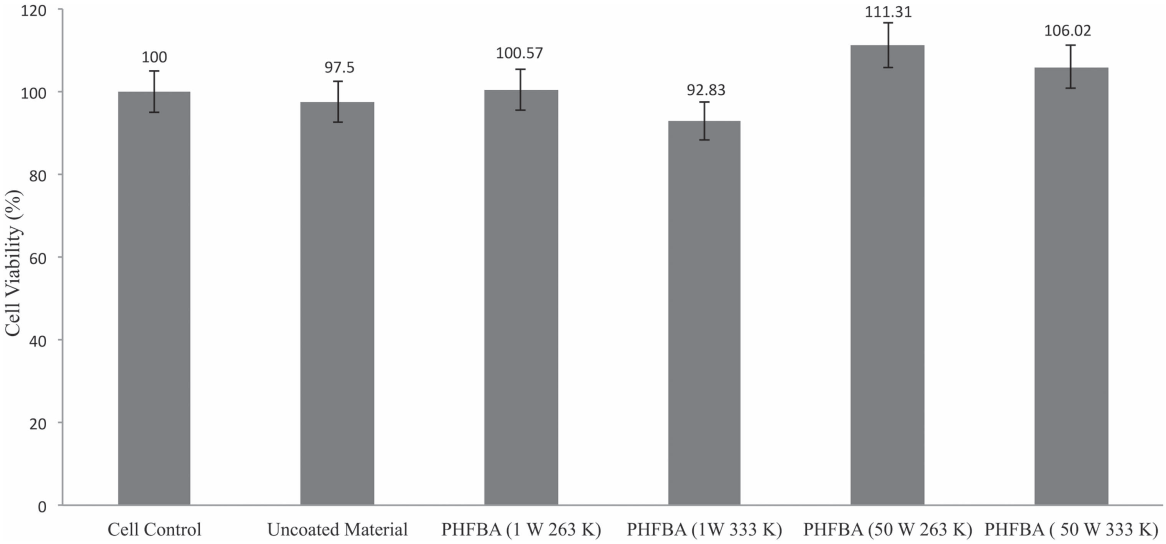

Figure 8. The effects of PHFBA materials on the proliferation of CCD 841 CoN cells after 96 h treatment.

system with the outer electrode used in this study

$$\text{Nonuniformity (\%)} = \frac{\text{Maximum value} - \text{Minimum value}}{\text{Maximum value} + \text{Minimum value}} \times 100. \quad (1)$$

The ability to deposit functional polymers at low temperatures and plasma powers allows fragile substrates, such as electrospun PAN fiber mats, to be coated. Electrospun fiber mat surfaces are good candidates for creating superhydrophobic surfaces because of their inherent roughness. When wet chemical coating techniques such as impregnation are used to coat the fiber mats with polymer, the fibers can bind together and block the porous fiber mat. However, preserving porosity in fiber mats is essential for porous material applications including hydrophobic breathable mesh fabrics. It is very difficult to keep the porosity in substrates using traditional liquid-based methods. On the other hand, inherent vapor-based coating methods provide an excellent conformal coating without agglomeration [20]. In this study, PAN fiber mat surfaces were successfully coated with fluoropolymer and the porosity of the fiber mat was preserved. The appearance of the PAN fiber before and after plasma polymerization are demonstrated in figures 7(a) and (b), respectively. As can be seen in the figure, fluorinated PECVD polymer coating is conformal. After the coating, the average contact angle increased from 10° to 156° for the PAN fibers. While the as-spun PAN fiber mat easily swallows water in a few seconds, the PHFBA-deposited PAN fibers can never be wetted under ambient conditions.

3.3. Cell viability analysis

For most potential applications, non-toxicity is a required property for a polymer. The effects of deposited PHFBA films on human cell viability were assessed. According to the

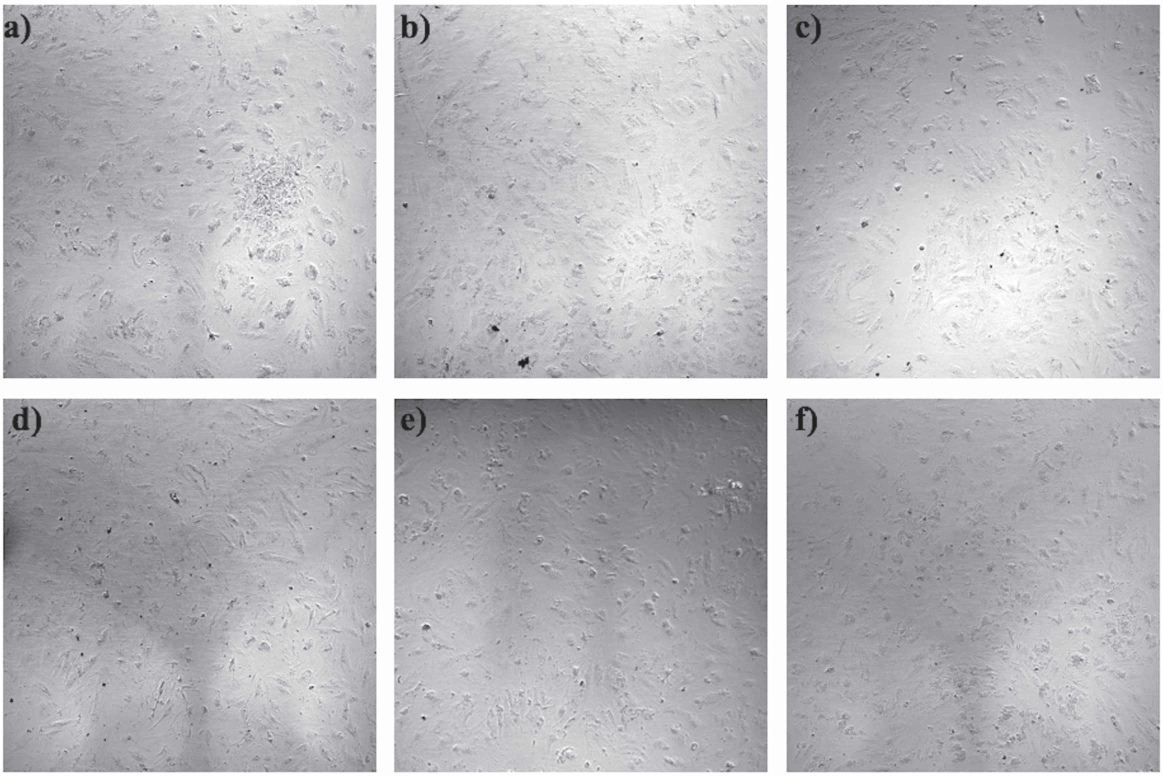

Figure 9. The cell images after 96 h incubation with and without materials: (a) cell control, (b) with uncoated material, (c) with PECVD-PHFBA (1 W, 263 K), (d) with PECVD-PHFBA (1 W, 333 K), (e) PECVD-PHFBA (50 W, 263 K), (f) PECVD-PHFBA (50 W, 333 K).

viability tests, PHFBA thin films were found to be non-toxic to human epithelial cells, showing good survival over a four-day period. Figure 8 demonstrates that cell proliferation after application of the materials is very close to 100% viability, like the proliferation the control cells exhibit. Microscopic images in figure 9 also clearly demonstrate that the materials do not inhibit cell viability after 96 h treatment. The non-toxicity of the PECVD-grown polymers can be attributed to the absence of solvents and the lack of the entrained monomer during the depositions, together with the short perfluoroalkyl chain of the polymer.

4. Conclusions

This work shows that PHFBA films can be successfully deposited in an RF plasma reactor with an outer spiral electrode from the vapors of the HFBA monomer on silicon and electrospun PAN fiber substrates. FTIR analysis of the as-deposited polymer film showed the complete disappearance of the vinyl bonds. The narrow FTIR peaks indicate high structural retention of the HFBA monomer during the polymer growth. Both the chemical structure and the wetting behavior of the as-deposited films were affected by the plasma power and substrate temperature. The low-temperature and solvent-free deposition with PECVD allowed conformal coatings on the fragile and rough electrospun fiber mats, which resulted in a superhydrophobic surface with a water contact angle of 156°. Importantly, the as-deposited PHFBA films were found to be non-toxic on human epithelial cells. Therefore, this work demonstrated that planar parallel plate configuration can produce superhydrophobic surfaces, which may potentially be used as a biomaterial.

Acknowledgments

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