Features of fluoropolymer deposition on SWCNT by HWCVD

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Abstract. The fluoropolymer coatings with different structures on the layers of single-walled carbon nanotubes were deposited by the method of hot wire chemical vapor deposition. The layers of single-walled carbon nanotubes of different orientations were made by doctor blade method from an aqueous dispersion, containing 0.1\% Tuball\textsuperscript{TM}. The influence of the single-walled carbon nanotubes’ layers on the structure and growth rate of the deposition of the fluoropolymer coatings was investigated. It has been shown that fluoropolymer coatings deposited on differently orientated single-walled carbon nanotubes’ layers keep their hydrophobic and superhydrophobic properties, which are specific for them at depositing on a smooth silicon surface.

1. Introduction

Unique properties of single-walled carbon nanotubes (SWCNTs) are attractive for various applications, for example, in fillers of polymer nanocomposites to increase their strength and electrical conductivity, in manufacturing transistors, displays and LEDs, as well as in the production of high-performance batteries and others [1]. SWCNTs are used for production a superhydrophobic surface, for example, by combination with a thin fluoropolymer coating to obtain the lotus effect [2-4]. The nanotubes are known to be used for control the wettability by creating a coating with a one-sided orientation of the tubes [2]. However the method is complicated and not practical. This work shows the possibility of using differently orientated SWCNT layers to obtain superhydrophobic composite coatings by applying fluoropolymer having hydrophobic properties [5]. In such composites, the SWCNT layers provide the strength of the composite, and the fluoropolymer coating has stable hydrophobic and superhydrophobic properties. These composite coatings can be used as protective coatings, self-cleaning coatings, coatings for intensifying heat transfer [6], for separating liquids with different wetting properties in separator devices [7], etc.

2. Experimental details

2.1. Deposition SWCNT

SWCNTs Tuball\textsuperscript{TM} were produced by OCSiAl [8] and contain less than 1\% metallic impurities. The water based dispersion containing 0.1\% of SWCNT and 1\% of sodium dodecylbenzene sulfonate (SDBS) as surfactant was obtained by the use of sonication. The mild centrifugation at 10000 g was
used in order to remove residual aggregates. Doctor blade technique was used for obtaining of SWCNT layers of the different orientations. Si (100) was used as substrate for deposition of SWCNTs.

The silicon samples coated by SWCNT layers were annealed in vacuum during 2 hours at a temperature of 300 °C and a pressure of 1 Pa. Annealing was carried out to remove the surfactants from the SWCNT surface.

2.2. Deposition of fluoropolymer
The fluoropolymer coatings was deposited by Hot Wire Chemical Vapor Deposition (HW CVD) [2,5]. The method and experimental setup were described in [5]. The experimental parameters of deposition process are presented in table 1. The precursor gas hexafluoropropylene oxide (C₃F₆O) was fed at flow rate \( Q_{HFPO} \) to the “shower” located above the activator. The flow rate was regulated by MKS 1179BX mass flow controller. The NiCr 80/20 mesh with the wire diameter of 0.5 mm was used as a catalytic activator. The temperature \( T_f \) of the activating mesh wire was monitored by electrical resistivity measurements. The fluoropolymer coating was deposited on substrate, fixed on a holder (90 mm diameter) located at a distance \( D = 50 \) mm under the activator mesh. The substrates were 15 × 15 × 0.5 mm² silicon wafers (100). The substrate temperature \( T_S \) was varied from 30 to 100 °C by resistive heater. If necessary, the holder was cooled by additional water cooling system to prevent undesirable substrate heating by the hot catalyst mesh. Temperature \( T_S \) was measured by two chromel-alumel thermocouples with the measurement error ±10 °C. The precursor gas pressure \( P \) in the chamber during deposition was controlled by a bellows-operated valve and measured using a MKS Baratron 623B capacitance manometer with relative error 1%.

| Table 1. Experimental parameters of fluoropolymer coatings deposition process |
|---------------------------------------------------------------|
| Regimes           | \( T_f \) (°C) | \( P \) (Pa) | \( T_S \) (°C) | \( t \) (min) | \( D \) (mm) | \( Q_{HFPO} \) (sccm) |
| Regime 1          | 640           | 0.5          | 30            | 90            | 50           | 25                     |
| Regime 2          | 680           | 0.5          | 30            | 30            | 50           | 25                     |
| Regime 3          | 680           | 1            | 100           | 30            | 50           | 25                     |

2.3. Characterization technics
The surface morphology and elemental composition of SWCNT, fluoropolymer coatings and composites were examined using a JEOL JSM6700F scanning electron microscope (SEM) equipped with an Quantax 200 (Bruker, Germany) analyzer for element composition determination by energy dispersive X-ray spectrometer (SEM-EDS). The EDX spectra were recorded by a X-Flash 6 detector with energy resolution < 129 eV. The results were analyzed using the Esprit 2.1 software with P/B-ZAF correction.

The film thickness \( h \) was measured by SEM of samples cross-section. This allowed us to determine coatings growth rate \( G \) by the relation 1, where \( h \) is coatings thickness and \( t \) is deposition process time:

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G = \frac{h}{t}.
\]

3. Result and discussion
The morphology and cross-section of deposited SWCNT layers are shown in figure 1. Nanotubes are formed as chaotically oriented bundles with a diameter of 20-30 nm. The length of the bundles is 2-3 μm. The measurement of the cross section showed that the thickness of the SWCNT layer is about 270 nm.

The results of elemental composition measurements of the deposited layers before and after annealing in vacuum are presented in table 2. The elemental composition of SWCNT layers has carbon and oxygen as well as sodium, sulfur, phosphorus, etc. The presence of sodium, sulfur, and phosphorus indicates an incomplete removal of surfactants during long-term and high-temperature annealing. At the same time, the absence of iron indicates an effective cleaning of the obtained SWCNTs at synthesis.
Figure 1. Surface morphology (a) and cross-section (b) of the SWCNT layer on smooth silicon. The inset shows a photograph of the water droplet on the surface of the SWCNT layers.

Figure 2. Surface morphology of deposited fluoropolymer coatings on smooth silicon (a, c, e) and SWCNT layer (b, d, f). The insets show a photograph of the water droplet on the surface of the obtained coatings and composites.
Table 2. Elemental composition of SWCNT layers before and after annealing

| Samples         | C (%) | O (%) | Na (%) | S (%) | P (%) | Total (%) |
|-----------------|-------|-------|--------|-------|-------|-----------|
| before annealing| 69.66 | 24.71 | 3.07   | 2.45  | 0.11  | 100.00    |
| after annealing | 70.13 | 24.67 | 2.40   | 2.55  | 0.25  | 100.00    |

Fluoropolymer coatings (FPC) with different structure and wetting properties were deposited on the SWCNT layer. The thickness of the polymer coating was about 300 nm. FPC thickness was controlled by the growth rate and deposition time. These parameters were determined earlier in our paper [5] and have been verified in a lot of experiments. Figure 2 shows the surface morphology of the coatings obtained. The FPC deposition on clean silicon samples and silicon with SWCNT layers was occurred simultaneously. It can be noted that the morphologies of fluoropolymer coatings on a surface of smooth silicon (figure 2 (a, c, e)) and on the SWCNT layer (figure 2 (b, d, f)) are different. Figure 2 (a,b) shows a fluoropolymer coating deposited in Regime 1 (Table 1). On the silicon substrate this coating has a smooth structure (figure 2 (a)). The deposition of fluoropolymer coating on SWCNT with the same parameters (Regime 1) leads to the formation of FPC with a fine-grained structure (grain size 50-100 nm, see figure 2 (b)). For deposition in Regime 2 (Table 1), the coating structure changes from a fine-grained surface on smooth silicon (grain size 50 nm, see figure 2 (c)) to a coarse-grained (grain size of 0.5 – 1.5 μm, see figure 2 (d)) on the SWCNT layer. For deposition in Regime 3, FPCs have needle structures on a smooth surface of silicon (figure 2e), while on the SWCNT layer these structures are combined into dendrites of 0.5 – 2.5 μm in size (figure 2 (f)). A possible explanation of all the above FPC morphology changes is that the SWCNT layers are seemingly the source of a lot of additional polymer nucleation centers.

At low deposition rates, the growth rates on smooth silicon and on the SWCNT layers correspond to each other ($G = 0.1$ nm/s, figure 2 (a) and figure 2 (b)). At the same time, change of deposition parameters induces a significant increase in the FPC growth rate on the SWCNT layers. For FPCs with structure presented in figure 2 (c) and figure 2 (d) the growth rate increased from 0.3 nm/s to 3.1 nm/s. For FPCs with structure presented in figure 2 (e) and figure 2 (f), the growth rate increased from 0.3 nm/s to 2.5 nm/s. This may also indicate that the SWCNT layers are the source of a lot of additional nucleation centers.

Measurement of wetting properties of obtained samples has shown that coated SWCNT layers silicon by doctor blade technique is hydrophilic. Contact angle with water is less than 55° (figure 1(a)). This can be explained by the fact that SWCNPs have parallel orientation relative to the silicon surface. Similar wetting properties of SWCNT are observed in [9]. After deposition FPCs on the differently oriented SWCNT layers it was shown that the FPCs keep the hydrophobic and superhydrophobic properties typical of deposition on a smooth silicon surface.

4. Summary
As a result of the present work, the composite coatings consisting of differently orientated SWCNT layers coated by fluoropolymer with different structures were obtained. It was found that the presence of SWCNT layers significantly influences the structure of the FPCs and significantly increases its growth rate when deposited by the HW CVD method.

The obtained composites have hydrophobic and superhydrophobic properties. It is shown that fluoropolymer coatings deposited on differently orientated single-walled carbon nanotubes layers keep their hydrophobic and superhydrophobic properties, which are characteristic of them at depositing on a smooth silicon surface.

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