

Deposition of nano and micron thick aligned fiber plasma polymerised coatings using an atmospheric plasma jet technique

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Abstract: This paper reports on the deposition of siloxane coatings exhibiting ‘aligned’ and ‘non-aligned’ fibrous structures using an atmospheric plasma jet system called PlasmaStream™. The coatings were deposited from both liquid HMDSO and TCFS (tetramethyl cyclotetrasiloxane / fluorosiloxane) precursors. These precursors were nebulized into a helium / nitrogen plasma and the coatings were deposited onto silicon wafer substrates. By controlling the deposition conditions superhydrophobic coatings exhibiting a needle-like coating morphology was obtained from both precursors. Initial fibre lengths were in the nm range but after longer deposition time’s coatings with micron long fibre lengths were obtained. In the case of the HMDSO precursor individual aligned fibres with diameters of up to 300 nm and lengths of up to 12 μm were observed. The TCFS coatings were structurally different as they exhibited a non-aligned, more densely packed, fibrous structures. For the same deposition time as used with HMDSO, the TCFS coatings exhibited fibre lengths of up to 10 microns. Coating morphology, water contact angle and functional chemistry were examined using optical profilometry, contact angle and FTIR techniques respectively. The micron thick fibrous coatings both exhibited superhydrophobic properties with contact angles of over 150°.

Keywords: *aligned fibre, superhydrophobic, siloxane coatings, atmospheric plasma*

1 Introduction

Atmospheric plasmas have been used to deposit a wide range of coatings from siloxanes to fluoropolymers [1]. Coating morphology has been found to be related to the plasma deposition conditions [2]. The plasma polymerization process can occur at the substrate surface or within the plasma. In the case of the latter a large number of particulates can be incorporated into the deposited coatings [2]. Coatings with hydrophilic to superhydrophobic properties are deposited. In the case of the latter the coatings exhibits a needle-like morphology, with typical fibre peak to trough heights of approximately 20 nm [3]. In this study the effect of longer deposition times on the morphology and structure of atmospheric plasma deposited superhydrophobic coatings is investigated.

2 Experimental details

The superhydrophobic coatings were deposited from both hexamethyldisiloxane (HMDSO) and

fluorinated siloxane (TCFS) precursors. The TCFS coatings were deposited from an equal volume mixture of tetramethylcyclotetrasiloxane (TC) (HSiCH₃O)₄ (Aldrich 99%) and perfluorooctyltriethoxysilane (FS) (C₁₄H₁₉F₁₃O₃Si) (Aldrich 98%). These coatings were deposited using the processing conditions described previously [3], onto 1-side polished p-type, boron doped silicon wafers (450 μm thick). The wafers were ultrasonically cleaned in methanol followed by acetone and dried prior to deposition. Coatings were deposited using a non-thermal atmospheric plasma jet system manufactured by Dow Corning Plasma Solutions, under the trade name PlasmaStream™. This system has been described previously in detail elsewhere [4]. The system was configured with a dielectric head housing two pin electrodes either side of a pneumatic nebuliser (Burgener Mira Mist nebuliser) through which the aerosol precursor was introduced. The plasma discharge was formed using a mixture of helium and nitrogen. This along with the aerosol exited the system through a 75 mm long

by 15 mm diameter Teflon tube. Very low frequency electrical power was delivered to both electrodes from a modified PTI 100W rf power supply at a frequency of approximately 15-25 kHz. While a current measurement system is not available on the PlasmaStreamTM source, voltage measurements were obtained using a custom-built HV probe. The deposition studies reported in this study were carried out at approximately 13.5 kV. The entire plasma device was moved over the surface of the substrate in a raster pattern (xy directional scan) using a CNC device with a line speed of 15 mm/second and a step interval of 2.5 mm, over the area of 100 x 100 mm. The substrate to source (tube orifice) distance was set at 2.5 mm. Coatings were deposited at a precursor flow rate of 3 $\mu\text{l}/\text{min}$.

Contact angle measurements were determined (24 hours after deposition), using the sessile drop technique at room temperature (OCA 20 from Dataphysics Instruments). Deionised water, diiodomethane and ethylene glycol were used for surface energy measurements. Contact angles were calculated at three different locations, averaged and the OWRK (Owens, Wendt, Rabel and Kaelbe) method was used to calculate the surface energy of the deposited coatings [5, 6].

Optical profilometry measurements were used to examine the morphology and to quantify the roughness values of the deposited coatings. These measurements were carried out using a Wyko NT1100 optical profilometer operating in vertical scanning interferometry (VSI) mode. Both the R_a (arithmetic average roughness) and R_q (root mean square roughness) were obtained. The thickness of superhydrophobic coatings was also determined using this technique, based on step height measurements. These measurements were facilitated by masking part of the wafer surface with scotch tape prior to deposition, to obtain a clean coating edge profile.

Fourier transform infrared spectroscopy (FTIR) measurements were carried out using a Bruker Vertex-70 system, which has a spectral resolution of 4 cm^{-1} . The transmission spectra of the coated

silicon substrates were obtained by the overlay of 64 scans to increase the signal to noise ratio. Cross-sectional imaging of the plasma polymerized coatings were carried out on fractured samples using both an Hitachi TM-1000 scanning electron microscope and a Zeiss Orion Plus Helium-Ion Microscope.

3 Results and Discussion

3.1 Deposition of plasma polymerized coatings

Both HMDSO and TCFS monomers were nebulized into the plasmajet glow discharge. This jet plasma was formed from a mixture of helium and nitrogen gas at fixed flow rates of 5 l/min and 50 ml/min respectively. The plasmajet system was rastered in a repeated pattern (number of passes), over the silicon wafer substrates to increase coating thickness.

3.2 Coating characterisation

Table 1 presents the surface characterization results of the HMDSO and TCFS coated and uncoated silicon wafers deposited after 3 passes of the plasma jet over the wafer. Coating morphology was examined using optical profilometry. Both coatings exhibit a needle-like morphology as illustrated in Figure 1 for the TCFS coating.

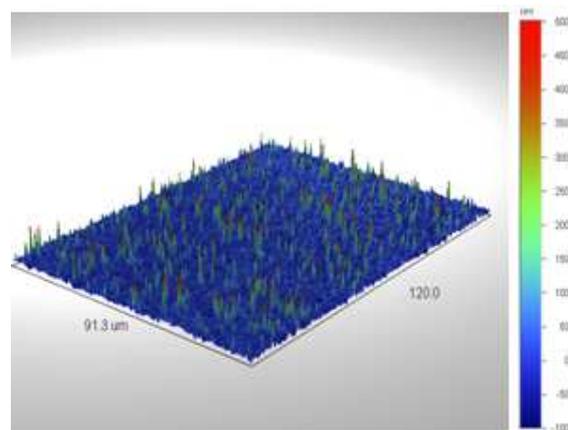


Figure 1: Optical profilometry image showing the surface morphology of the TCFS coating, deposited with 3 passes of the atmospheric plasma jet over the silicon wafer substrate

The nanoscale surface roughness values R_a and R_q were obtained using optical profilometry (Table 1). The marked difference between R_a and R_q for both

coating types, is indicative of their relatively inhomogeneous coating surface morphology.

Table 1: Properties of the siloxane coatings deposited on silicon wafer substrates

Measurement	Uncoated	TCFS	HMDSO
Water Contact Angle (°)	75	156	154
Surface Energy (mN/m)	31	0.80	1.2
Dispersive	19.6	0.79	1.2
Polar	11.2	0.02	0.03
Thickness (nm)	2*	250	285
Roughness (R_a) (nm)	2	28	27
Roughness (R_q) (nm)	3	47	34

*ellipsometry analysis measured a 2 nm native oxide layer thickness on the uncoated silicon wafer

3.3 Coating Chemistry

Analysis of the coating chemistry by FTIR analysis demonstrated the retention of the precursor functional groups chemistry as we have reported previously for both the HMDSO and TCFS coatings [3]. The two coating types exhibited relatively low surface energies as expected for superhydrophobic surfaces (Table 1). The dispersive and polar components of surface energy were determined and in particularly both coatings exhibited a very low polar component of surface energy.

3.4 Formation of Micron Thick Coatings

By increasing the duration of the deposition process from 3 passes of the jet up to 20 passes, micron thick superhydrophobic coatings were formed from both precursor monomers. This corresponded to a plasma exposure time of approximately 20 minutes at a given point on the substrate. Both coating types were examined in cross section at different stages in the deposition process (Figure 2). Using these cross-section images it was observed that for both precursors a smooth polymerized film was initially formed on the wafer substrate. Non-uniformities in the smooth surface morphology were then identified, from which a fibrous structures formed. Coating thickness was dependant on the number of passes of the plasma jet over the surface of the wafer. As illustrated in Figure 2, in the case of the HMDSO coatings after a 20 pass deposition, a fibrous structure was observed with fibre height of up to 12 μm . The individual fibre had diameters of

approximately 300 nm. In contrast to the deposition of aligned fibrous structures from the HMDSO monomer, coatings deposited using the fluorosiloxane TCFS precursor was structurally different. The latter exhibited a non-aligned, nano-fibrous matrix structure for which fibre lengths of up to 10 microns were obtained (Figure 3).

The different fibrous structures formed from the two precursors are most likely due to the variation in their reactivity. The HMDSO precursor has a much lower molecular weight and boiling point than the TCFS precursor. The higher volatility of HMDSO may thus facilitate the vaporization and polymerization of this precursor in the plasma.

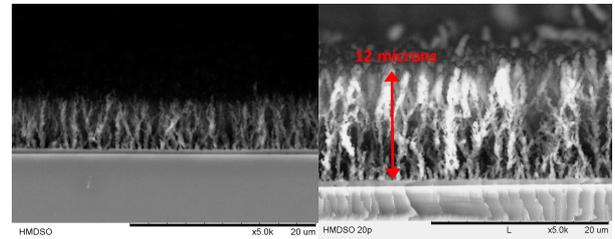


Figure 2: SEM cross-section image of HMDSO aligned fibres after 15 minutes plasma deposition – approx 8 μm thick (left) and after 20 minutes exposure - approx 12 μm thick (right).

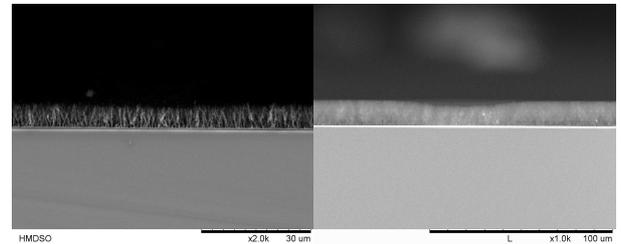


Figure 3: SEM cross-section image of HMDSO aligned fibres 6 μm (left) and TCFS nano-fibrous matrix structure 10 μm (right)

As outlined earlier at the base of both the HMDSO and TCFS coatings a dense polymerized film is formed between the silicon wafer substrate and the fibrous structure. This layer is observed in Figure 2 for HMDSO between the wafer substrate and the point where the dense fibre growth is observed. The thickness of this layer was observed to increase from approximately 470 to 550 nm, for the 15 and 20 pass deposition experiments respectively. In order to obtain a better understanding of the coating growth mechanism a He-Ion Microscope was used to obtain higher resolution images of the HMDSO

coating structure. As demonstrated in Figure 4 these images revealed the relatively dense but uneven coating layer at the base of the fibrous structure.

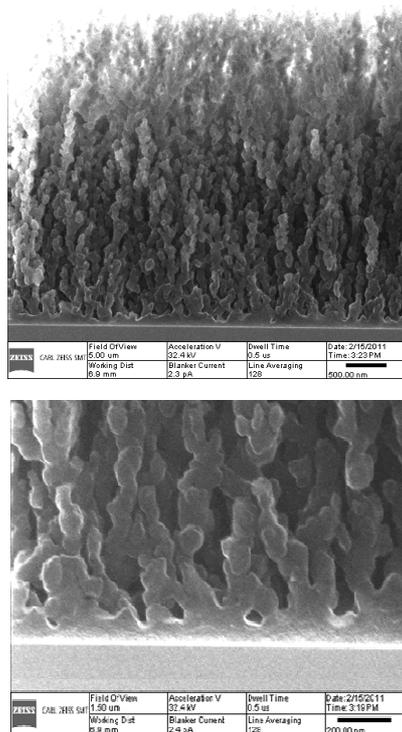


Figure 4: Helium-Ion cross-section images of HMDSO aligned fibres obtained for a 12 µm thick coating. Image scale bars are 500 nm (top) and 200 nm (bottom).

The formation of these fibrous structures is associated with the plasma processing conditions. It has previously been reported that coatings exhibiting a dense amorphous structure or with a large number of particulates is linked to the energy density in the plasma discharge and the number of fragmentation reactions which take place within the gas phase [7]. The explanation for the growth of the fibrous structure under the PlasmaStream deposition conditions used would appear to be related to the adsorption of the precursor monomer on the growing substrate layer. Using comparatively low precursor flow rates, significant gas phase reaction will occur resulting in the formation of small particulates in the plasma [7]. Coupled with a surface roughness and free energy effect, subsequent particle bonding/deposition occurs at peaks rather than troughs on the surface of the growing film. The further addition of the plasma activation of the surface during deposition results in columnar

growth. This may explain the plant like appearance of the fibrous coating shown in Figure 4.

4 Conclusions

This study investigated the growth of ‘aligned’ and ‘non-aligned’ micron thick fibrous coatings deposited from both HMDSO and TCFS siloxane precursors. Under the low precursor flow rates used, significant gas phase reactions are likely to occur in the jet plasma, facilitating the adsorption of the precursor monomer on the growing substrate layer resulting in fibrous coatings. To our knowledge this is the first time that micron thick fibrous coatings have been deposited using a PECVD process.

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5 References

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