Atmospheric Pressure DBD plasma torch for area-selective coating – investigations of the deposition mechanisms through experimental and CFD simulation

K. Acharya[1], S. Bulou[1], T. Gaulain[1] and P. Choquet[1]

[1] *Luxembourg Institute of Science and Technology, MRT, 28, avenue des Hauts-Fourneaux, L-4365 Esch-sur-Alzette, Luxembourg*

Abstract: Hereafter we report the use of an in-lab developed Atmospheric Pressure DBD plasma torch for submillimetric area-selected PECVD. In particular, we explore the possibility of tuning the deposition size by varying the experimental parameters. Besides, we investigate the deposition mechanisms and the influence of vinyl and ethoxy groups groups in the monomer. Vinyl groups favours deposition in the centre, while ethoxy branches are linked with deposition on the periphery area.

Keywords: Atmospheric Pressure selected area PECVD, plasma printing, CFD,

1. Introduction

Additive manufacturing is identified as a key enabling technology for the development of future on-demand and low impact manufacturing industrial processes [1]. For the deposition of localised material at a submillimetric scale, Inkjet Printing (IP) which uses inkjet printers to deposit mixture of solvent and monomer is largely used up to date, due to its easiness and the wide-possibility offered by this technique [1]. IP presents nevertheless some drawbacks, mainly because of the drying steps, and the surface energies of substrates and solvants has in consequence to be well controlled. Localised atmospheric pressure plasma assisted chemical vapour deposition (AP-PACVD) appears as a promising alternative deposition process. Indeed, the main advantage of PACVD compared to IP is that the deposition of solid film occurs directly from vapour precursors, without the use of solvent. Plasma processes thus offer an interesting alternative as the deposition is possible on a wide range of substrate, do not need solvent nor drying steps.

In one of our previous work, we demonstrated the possibility of depositing plasma-polymerised Methylmethacrylate (ppMMA) coatings with a submillimetric resolution using an atmospheric pressure co-axial DBD plasma torch. This process is based on the interaction of 2 gas flows in the close vinicity of the substrate: the precursor vapours and the plasma post-discharge gaseous reactive species in the close vinicity of the substrate. The precursor vapour is introduced within the plasma flowing post-discharge, where it interacts with the flowing reactive species resulting in the deposition of plasma polymer dots. The introduction of the precursor in the post-discharge allows a “mild” polymerisation, and thus, MMA oligomers up to n=17 are detected. In addition, the size of the coating dot can be controlled by the plasma process tubes diameter and the different gas flow. Indeed, it appears that the ppMMA deposition kinetics and coating size strongly depends on the two gas flows involved: plasma gas flow and precursor carrier gas flow.

We propose here to study the influence of experimental parameters on deposition patterns of plasma polymers. The influence of various experimental deposition parameters on the as-grown coatings, in order to optimise the process as well as to study the deposition mechanisms at stake. Carefull choice of these parameters allow the deposition of a plasma-polymer dot equal to the size of the inner diameter capillary tube. Computational Fluid Dynamics simulation enlight the paramount role of gas mixing. In addition, comparison between 4 very similar organosilicon precursors: Triethylvinylsilane (VTES), Vinyltriethoxysilane(VTEOS), Tetraethoxysilane (TEOS) and Tetraethylsilane (TES). According to experimental evidences, it appears that vinyl groups favours the deposition of MMA plasma-polymer with oligomers up to n=17 [2].

2. Experimental

In-lab build coaxial shape plasma torch consisting of two tubes has been used throughout the experiments (Fig. 1). The central glass capillary is coated with Platinum to make it conductive and acts as the grounded electrode. Plasma is generated in Ar gas between the central capillary and cylindrical outer quartz tube by the application of a sinusoidal High Voltage generator (55 kHz, V_{P-P}=4 kV, 20 W, AFS®). A bubbler is used to inject the precursor vapours, with Ar as a carrier gas, into the central capillary tube. Precursor vapours mixes with plasma post-discharge in the close vinicity of the substrate and leads to a coating Different organic (methylmethacrylate, MMA) and organosilicon (Triethylvinylsilane (VTES), Vinyltriethoxysilane(VTEOS), Tetraethoxysilane (TEOS) and Tetraethylsilane (TES) precursors have been used.

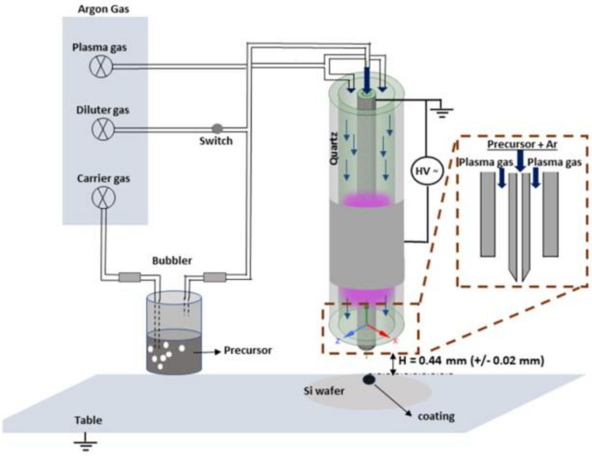

Fig. 1. Schematics of the AP-DBD plasma torch used for the area-selective deposition with precursor post-discharge injection.

The morphology and thickness of the deposited plasma polymer dots were characterized by optical microscope and profilometry (KAL-Tencor P-17 profiler, Milpitas, CA). The atomic and molecular composition of the deposited thin film patterns are characterised by FTIR (Bruker Hyperion 2000), XPS (Kratos Axis Ultra DLD) and ToF-SIMS (CAMECA SC-Ultra).

In order to get a detailed insight into the gas flow mixing and its interaction with the substrate, CFD calculations have been performed using Ansys Fluent software. The simulation domain is a 2-dimensional axisymmetric geometry of plasma torch comprising its working environment.

Experimental results and CFD simutlation results are compared to progress in the understanding of the deposition mechanisms at stake.

3. Results and Discussion

The coatings of ppMMA was obtained by carefully setting the two different gas flows: [Ar + MMA] in the central capillary and [Ar, 15 slm] in the plasma discharge tube [3]. In order to get a circular dot of plasma polymerised MMA, the precursor carrier gas flow has been varied from 30 to 60 sccm (Fig. 2). One can see that the coating pattern strongly depends on the capillary gas flow, and that a slight modification changes drastically the coating pattern. Depending on the central capillary flow, three distinctive deposition patterns are observed: ‘no deposition’, ‘circular dot deposition’ and ‘circular ring deposition’. In the ‘no deposition’ regime (capillary gas flows < 30 sccm) no measurable coating deposition can be measured. With higher capillary gas flow, i.e. 35 sccm < [Ar + MMA]< 50 sccm, ‘circular dots’ deposition of ppMMA are observed. In this ‘circular dot’ regime, the interactions between MMA molecules and plasma reactive species are limited to the area in front of the capillary tube nozzle.

At capillary gas flows higher than 50 sccm, annular deposition of ppMMA coatings is observed. In this ‘circular ring’ regime, there is no deposition right under the capillary outlet. This is much likely because the high capillary gas flow prevents plasma reactive species to mix with MMA molecules in the central zone.

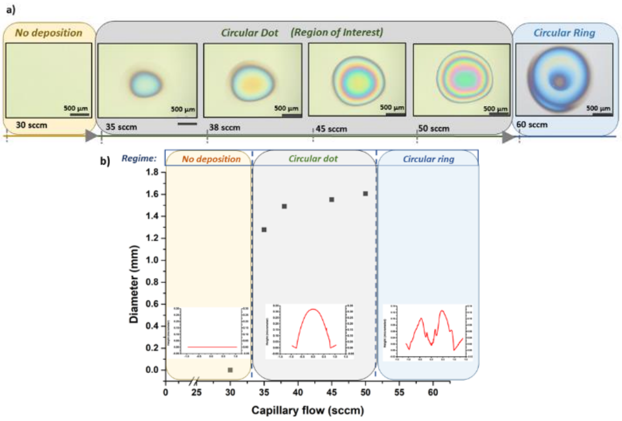

Fig. 1. (a) Evolution of the diameter of the (ppMMA) deposited dots when increasing the capillary gas flow from 30 sccm to 60 sccm. (b) Three regimes as “no deposition”, “circular dot deposition” and “circular ring deposition” has been identified.

In order to enlighten the fluid kinetic mechanisms at stake, a CFD simulation was executed for the experimental gas flow velocities. It points out the existence of several circulary vortice (Fig. 3). In the ‘circular dot regime’ conditions, velocity vector plots evidenced two main turbulent areas.A small vortex originating from central capillary flow and circulating from outward to inward is stated as a capillary vortex (Fig 3(a)). Big vortex originating from plasma postdischarge annular gas flow, and circulating inward to outward, is stated as annular vortex (Fig 3(a)). The annular vortex surrounds and confines the central capillary flow to a specific region as a result of which the capillary vortex appears.

An MMA mass fraction plot superimposed on the velocity vector plot (Fig. 3(c)) evidences the high concentration of MMA species in a confinement region below the exit of the capillary tube delimited by the annular vortex. This vortex thus limits the precursor diffusion out from this zone. In addition, this annular vortex is also responsible for the transportation of plasma-produced reactive species from the annular post-discharge flow, which are crucial for the initiation of the plasma polymerization.

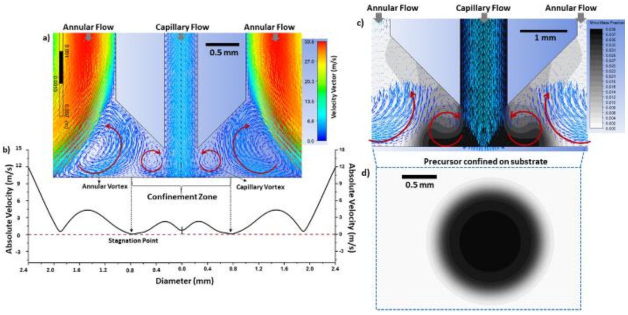

Fig. 3. (a) Velocity vector plot of plasma torch focused at the central capillary nozzle and substrate with the appearance of confinement zone as a result of interaction of central capillary flow to annular gas flow. (b) Absolute gas velocity vs radial distance next to the substrate (0.33 mm above) providing the precise confinement zone diameter. (c) MMA mass fraction plot adjoint on top of velocity vector plot, illustrating the retention of MMA species (black colour) in the confinement zone. (d) Precursor (MMA) mass fraction on the substrates without reaction (top view representation)

In a second step, we focused on the role of different chemical moieties of the precursor used on the deposition process. Indeed, former observations show the importance of vinyl bond on the deposition process kinetics. To do so, deposition of 4 very similar precursor in identical deposition conditions were done [4]. The 4 organosilicon precursor chosen, Triethylvinylsilane (VTES), Vinyltriethoxysilane(VTEOS), Tetraethoxysilane (TEOS) and Tetraethylsilane (TES), differs by the presence and/or absence of vinyl and/or ethoxy groups.

As it can be seen in Fig. 4, patterns of the coating drastically change depending on the precursor used. Linear profile measured by profilometry are also presented.

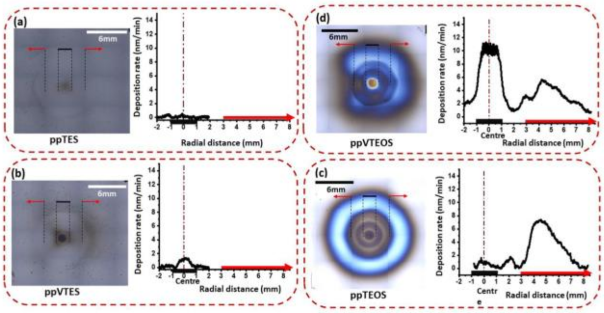

Fig. 4. (a) Plasma polymerised Tetraethylsilane (ppTES) (b) and plasma polymerised Triethylvinylsilane (ppVTES) after 24 min deposition duration. (c) plasma polymerised Tetraethoxysilane (ppTEOS) (d) plasma polymerised Triethoxyvinylsilane (ppVTEOS) after 12 min deposition duration

As shown in Fig. 4, the deposition profile for ppTES was below the profilometry noise level. No significant deposition able to be measured by the profilometry can be observed (<20 nm). One can clearly see that ppTEOS thickness is higher in the periphery area (Fig. 4c) whereas ppVTES is only deposited in the central region, with no deposition in the periphery region (Fig. 4b). Nevertheless, the thickness is quite low (< 40nm) and does not allow a reliable chemical analysis. This ppVTES is thus excluded from analysis. Interestingly, ppVTEOS coating profile presents deposition in both areas, i.e., in the central and periphery region.

Overall, the deposition in the central region appears closely related to the use of precursors with a vinyl group. On the other hand, only ethoxy-containing precursors exhibit significative coating thickness on the periphery, i.e., at distances corresponding to the area outside the plasma post-discharge direct impact. Thus, deposition on the periphery appears closely linked to the use of precursors with ethoxy groups

Detailed chemical analysis of the central and periphery region point out the different composition of the coating on the central and periphery area for ppVTEOS (Fig. 5).

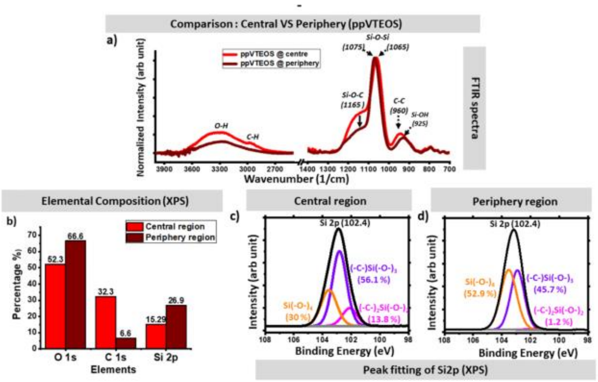

Fig. 5. Chemical characterization comparison between the central and periphery regions of ppVTEOS coating. (a) FTIR spectra of coating as obtained from the central region (red colour) and periphery region (wine colour). (b) XPS elemental compositional analysis. Peak fitting of Si2p high resolution spectra from (c) central region and (d) periphery region of ppVTEOS coating.

XPS elemental compositional analysis (Fig 5(b)) shows the strong decrease in C at. % from 32.3 % to 6.6 % with a subsequent increase in O from 52.3 % to 66.6 % while moving from the central region to periphery region. The peak fitting of Si2p shows that the component with a high amount of carbon (i.e., C2-Si-O2) almost vanishes compared to that of the central region (Fig. 5c & d). The main differences observed in FTIR spectra are presented

Fig 5(a) and confirms XPS results. The distinctive CHx group (2900 cm^{-1}) vanishes are only detected in central region. The shoulder at 1165 cm^{-1} is attributed to the bond vibration of Si-O-C structure; thus, its diminishing nature signifies the removal of carbon atoms from its network. The band at 960–965 cm^{-1} is a convolution of spectra arising from the C–C and Si–O vibration of the Si-O-C2H5 and Si-OH group, respectively. The shifting of broad band from 960 to 925 cm^{-1} is likely due to the less contribution from C–C bond, also a result of diminishing carbon atom in the coating.

The experimental results showed that the deposition of vinyl containing precursor was confined to the central location (i.e., VTES). In contrast, the deposition of the precursor with ethoxy groups was prominent in the periphery region, around the plasma torch (i.e., TEOS). Remarkably, the deposition of vinyltriethoxysilane, precursor containing both vinyl and ethoxy groups showed prominent deposition at both the central and periphery regions. The central region deposition appears to contain relatively high C content and CHx groups, thus presenting a certain organic character. The coating structure was identified to be silicon oxycarbide-like (SiOxCyH). Whereas the periphery region presents more silica-like (SiOx) coating, with low C content and no CHx evidence.

4. Conclusions

We report here the use of an in-lab plasma torch for the localised deposition of organic and metalorganic precursor. Ths process is based on the interaction in a localised area of precursor vapour, plasma post-discharge gas and substrate. The deposition patterns, composition and speed have been shown to be strongly dependent on the experimental deposition parameters. Hence, by carefully tuning the gas flow rates, a coating of the size of the capillary inner diameter can be obtained. CFD simulation results show that the confinement of the precursor by the outer plasma gas is a paramount mechanism that defines the diameter of the as-grown coating dot. Besides, in order to have a better understanding of the deposition mechanism at stake, comparison between similar organosilicon precursor have been done.

The results have indicated that the SiOxCyH deposition at central region from vinyl containing precursors (VTES & VTEOS) are strongly correlated with the higher concentration of precursor. Whereas SiOx deposition at the periphery region for ethoxy containing precursors (TEOS & VTEOS) is related to the intermixing area between plasma species and open air. These different results demonstrate the versatility of the AP-DBD plasma torch for the localised PECVD of different precursors.

5. Aknowledgments

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