A comparison of reactive plasma pre-treatments on PET substrates by Cu and Ti pulsed-DC and HIPIMS discharges

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Abstract

PET web samples have been treated by magnetically enhanced glow discharges powered using either medium frequency pulse direct current (p-DC) or low frequency high power pulse (HIPIMS) sources. The plasma pre-treatment processes were carried out in an Ar–O₂ atmosphere using either Cu or Ti sputter targets. XPS, AFM and sessile drop water contact angle measurements have been employed to examine changes in surface chemistry and morphology for different pre-treatment process parameters. Deposition of metal oxide onto the PET surface is observed as a result of the sputter magnetron-based glow discharge web treatment. Using the Cu target, both the p-DC and HIPIMS processes result in the formation of a thin CuO layer (with a thickness between 1 and 11 nm) being deposited onto the PET surface. Employing the Ti target, both p-DC and HIPIMS processes give rise to a much lower concentration of Ti (< 5 at.%), in the form of TiO₂ on the PET treated surface. The TiO₂ is probably distributed as an island-like distribution covering the PET surface. Presence of Cu and Ti oxide constituents on the treated PET plasma treatments is beneficial in aiding the adhesion but alone is not enough to provide very high levels of hydrophilicity as is clear from sessile drop water contact angle measurements on aged samples. Exposure to the plasma treatments also

leads to a small amount of roughening of the substrate surface, but the surface roughness in all cases is below 2.5 nm. The PET structure at the interface with a coating is mostly or wholly preserved. The oxygen plasma treatment, metal oxide deposition and surface roughening resulting from the HIPIMS and p-DC treatments will promote adhesion to any subsequent thin film that is deposited immediately following the plasma treatment.

Keywords: polyethylene terephthalate (PET), plasma pre-treatment, XPS, contact angle, HIPIMS, vacuum web coating.

1. Introduction

Vacuum web coating is an important manufacturing process that is used to produce technological thin films for a wide variety of applications [1]. Thin film adhesion to the polymer web is one of the most important quality characteristics of a coated product. It can be improved significantly by web plasma pre-treatment methods, which are now used routinely in roll-to-roll coating systems [2-11]. Magnetically enhanced glow discharges (e.g. using single/dual planar and/or rotatable magnetrons [6-8, 11, 12]) form a branch of relatively new [as opposed to more conventional radio frequency (RF) and/or microwave discharges] plasma treatment processes to enhance the quality and performance of plasma processed and/or vacuum coated web products. Despite the fact that magnetron based technologies have been used routinely in certain industries for some time now, little research work results concerning the effects of such treatments to substrates have been reported in the scientific and technical literature. However, dual rotatable magnetrons have recently been successfully applied for the high rate production of nanostructured functional polymeric web surfaces [12, 13]. Very little is known about the effects of various magnetron configurations and power supply technologies, which is why this topic has been studied in this work.

There are a vast number of application areas for vacuum web plasma pre-treated and coated materials [1, 4-12]. Examples are food packaging, electronics, thin film photovoltaics, touch panels, displays and lighting devices, optical devices, thin film batteries and so on.

Thermoplastic polymers, such as polyethylene terephthalate (PET), are widely used in vacuum web coating as substrates. However, they usually exhibit relatively poor surface properties. An increasing number of applications require high performance polymers, hence, plasma and/or ion treatments are often used to alter the PET surface properties and provide the required functionalisation. Activated surfaces form stronger chemical bonds with films deposited onto their surfaces, improving the adhesion by orders of magnitude. Some typical industrial application examples where plasma/ion treatments are employed are: moisture barrier films (e.g. SiO_2 ; plasma treatment is used to improve adhesion and barrier properties), light barrier films (e.g. Al; plasma treatment is used to improve adhesion and barrier properties), ITO coatings (plasma treatment is used to improve adhesion and uniformity of electrical properties), plastic optical devices (plasma treatment is used to provide anti-reflective surface), etc.

Various power supply technologies have always played an important role in vacuum processing for both the substrate pre-treatment and subsequent coating deposition. Changing the power supply characteristics can lead to end product quality improvements (e.g. employing an arc free medium frequency AC power mode for the fabrication of insulating oxide films [14]). High Power Impulse Magnetron Sputtering (HIPIMS) [15] is one example of a recently developed power supply technology that holds promise to enhance the properties of certain coatings. HIPIMS processes are typically characterised by high voltage (e.g. 0.7–2 kV), high current and relatively low duty cycle (e.g. 0.5–10%) pulses, the peak power of which can be several megawatts (e.g. 1–6 MW), resulting in a very high level of metal vapour ionisation (up to ~90%). Various power supplies, plasma generators and processing systems that are either capable of producing HIPIMS discharges or make use of the generated plasma have been

developed and are available commercially. Although the target voltage and current waveforms exhibited by different plasma generators can be different, resulting in different plasma and sputtered flux properties, the common features of various HIPIMS power sources and/or processes are: relatively low pulse frequency (typically 50 to 1000 Hz), low duty cycle (typically 0.5 to 10%) and the pulse duration approximately in a range between 10 and 1000 μ s. So far, HIPIMS has mostly been used to produce metal and ceramic coatings or plasma etch alloy substrates for hard coating applications. The presence of a substantial metal ion content in HIPIMS discharges, the energy distribution of which range from 1-2 eV to few tens of eV [16-18], may present new polymeric web surface engineering opportunities – the area largely unexplored until now. An interesting example has been reported in reference [19] where ionised metal containing plasmas have been applied to produce buried conducting layers in polymers. Both, reactive and non-reactive processes may have a strong potential to improve important functional and mechanical properties.

In this paper, we present results on PET web pre-treatment by sputter magnetron-based glow discharges powered by either a) medium frequency (150 kHz) pulse direct current (p-DC) or b) low frequency (100 Hz) high power pulse (HIPIMS) sources. The plasma pre-treatment processes were carried out in an Ar–O₂ atmosphere. XPS, AFM and sessile drop contact angle measurements have been employed to examine changes in surface chemistry and morphology for different pre-treatment process parameters.

2. Experimental Procedure

A Gencoa Ltd GenLabTM coating deposition system has been used for the experiments. The system is shown schematically in reference [20]. A magnetron fitted with either Cu or Ti targets (both 99.5 % purity and 188 mm x 296 mm x 9.5 mm) was used as a plasma treatment and coating deposition source. Normal strength balanced/unbalanced and low strength (e.g. as used

for radio frequency magnetron sputtering) magnetic field configurations have been investigated. A base vacuum, better than 0.002 Pa, was attained prior to the plasma treatment. The working pressure was maintained at 2 Pa during all runs. A SpeedfloTM (Genco Ltd) process controller was used to supply both Ar and O₂ into the system. A 5 kW ENI RPG-50 pulsed-DC power supply and a 10 kW Chemfilt Ion sputtering AB Sinex-3 HIPIMS power supply were used as plasma generators. The power applied to the targets was ~500 W in all cases. In pulsed-DC mode the pulse frequency was 150 kHz and the reverse time was 2 micro seconds. In HIPIMS mode the plasma treatment trials were carried out at target pulsing frequency of 100 Hz; the pulse-on time was 50 micro seconds. DuPont Teijin ST504 125 micron thick PET samples were mounted on a 9.5e-2m diameter drum rotating at 1rpm (~0.3m/min tangential speed). The PET side containing no adhesion promoter was exposed to the plasma. Table 1 lists the samples produced in this study and describes the process configurations used.

XPS analyses were performed on a ThermoFisher Scientific (East Grinstead, UK) Theta Probe spectrometer. XPS spectra were acquired using a monochromated Al K α X-ray source ($h\nu = 1486.6$ eV). An X-ray spot of ~400 μ m radius was employed. Survey spectra were acquired employing a pass energy of 300 eV. High resolution, core level spectra for C1s, Ti 2p_{3/2}, Cu 2p_{3/2} and O 1s were acquired with a pass energy of 50 eV. All other high resolution core level spectra were acquired with a pass energy of 100 eV. All spectra were charge referenced against the C 1s peak at 285.0 eV to correct for charging effects during acquisition. Quantitative surface chemical analyses were calculated from the high resolution, core level spectra following the removal of a non-linear (Shirley) background. The ThermoFisher Scientific Advantage software was used which incorporates the appropriate sensitivity factors and corrects for the electron energy analyser transmission function. XPS depth profiles were acquired on a ThermoFisher Scientific (East Grinstead, UK) K-Alpha spectrometer. XPS spectral depth profile data was acquired using a monochromated Al K α X-ray source while sample etching was

achieved using a Ar ion gun operated at 100 eV and delivering $\sim 1\mu\text{A}$ of Ar^+ etch current. The sample was rotated during etching to minimise ion induced roughening. Conversion of etch time to thickness was performed by applying the 'Single Overlayer' calculation (in the Advantage software) to the recorded profile which enables the layer thickness at the metal oxide/PET interface to be determined (using the Beer-Lambert equation [21]) and the etch rate calculated.

The topography of the plasma treated samples was characterised by tapping mode AFM in air under ambient conditions using a Veeco Dimension 3100 Atomic Force Microscope. Commercial etched silicon micro-cantilever probes (Olympus OMCL-AC160TS) were used with a nominal spring constant of 42 N/m and a resonance frequency of approximately 300 kHz. The probe tip radius was specified by the manufacturer as less than 10 nm. The area analysed was $1 \times 1 \mu\text{m}^2$ with a z deflection scale of 100 nm for all samples.

Immediately after deposition, at Gencoa, the surface energies of the pre-treated samples were qualitatively examined through photographing the spreading of a distilled water drop. The results are shown in Figure 1. It can be seen that there is extensive spreading of the water drop contact angles for both of the Ti and Cu based pre-treatments, indicative of low contact angles ($< 30^\circ$) and hydrophilic surfaces in both cases. The samples were then sent from Gencoa's R&D facilities to Surrey University for contact angle analysis. Sessile drop water contact angles were measured at Surrey University on a Krüss EasyDrop DSA100 instrument using distilled water. The contact angles given are an average of 10 individual readings.

As the contact angle analysis was due to be undertaken some weeks after deposition, the samples were allowed to age or, in other words, to lose the effect of reactive plasma treatment [3], and develop adventitious hydrocarbon layer, both of which are known to increase the contact angle measured. The samples were first cleaned in acetone for 90 seconds and then immediately measured. To check the effect of the acetone clean, XPS was undertaken

before and after cleaning, and the acetone clean had resulted in a substantial reduction in the C 1s peak intensity. Nevertheless, it is clear that the quantified contact angle results given in Table 1 should not be taken as absolute values (the real contact angles of fresh surfaces being significantly lower than these measurements indicate as evidenced by preliminary qualitative wetting tests at Gencoa), but are given as they provide valuable comparative data that evaluates the contribution and effect of the deposit material formed on PET samples as well as surface morphology effects.

3. Results

3.1. XPS

The elemental compositions obtained from XPS for all 8 specimens are given in Table 1. The unmodified PET reference material is comprised of only carbon and oxygen as anticipated. Samples 1 to 4 (Cu target) show surface compositions of C (27 - 31 at.%), O (36 - 38 at.%) and Cu (31 - 35%) with traces of N. The C, O and Cu concentrations for samples 1 - 4 are similar (within +/- 2%). Samples 5 - 7 (Ti target) show higher C concentrations (59 – 64 at.%), similar O concentrations (33 – 35 at.%) and low Ti concentrations (1 - 4 at. %).

Figure 2 shows the XPS C 1s spectra for the samples deposited from the Cu target [Figure 2 (a)], the Ti target and PET reference [Figure 2 (b)]. It can be seen that the C 1s spectra for the samples deposited from the Ti target have a very similar C 1s peakshape to the PET, whereas the samples deposited from the Cu target show much lower intensities of the C-O and C=O components. It should be noted that the HIPIMS samples show smaller C-O and C=O components than the p-DC samples. The C 1s spectra from the Cu HIPIMS samples are typical of a surface exhibiting hydrocarbon contamination originating from atmospheric exposure. Figure 3 shows the Cu 2p_{3/2} and Ti 2p regions for the samples deposited from the Cu and Ti targets respectively. The Cu 2p_{3/2} peak has a binding energy of 934.1 eV, which is indicative of

Cu in the 2+ oxidation state, indicating the presence CuO. This assignment of CuO is further supported by the presence of a Cu 2p_{3/2} shake up satellite at 943 eV, diagnostic of Cu²⁺ species, and a stoichiometry CuO_{1.09} for this sample (Table 1). The Ti 2p_{3/2} peak has a binding energy of 458.8 eV, attributable to TiO₂.

XPS depth profiles for samples deposited from the Cu and Ti targets are presented in Figures 4 and 5 respectively. Considering first the profiles for the samples deposited from the Cu target. In all cases, it is clear that a CuO layer has been deposited at the surface. The layer thickness varies from 1-2 nm for the p-DC unbalanced sample to 5-11 nm for the HIPIMS balanced sample. The HIPIMS samples show thicker CuO layers than the p-DC samples and the balanced configuration gives rise to thicker films than the unbalanced configuration. For the thicker HIPIMS CuO layers, the C concentration in the profile drops to very low levels (< 5 at.%). For the thinner p-DC layers, the C concentration at the surface initially drops, but then increases as the PET interface is approached. Consequently, it is the signal from the underlying PET which is causing the C intensity to increase in these very thin layers. Finally, it is interesting to note that the CuO/PET interface width appears to be larger for the p-DC samples compared to the HIPIMS samples, with Cu diffusing further into the PET from the interface region when processing using a p-DC supply.

Considering now the profiles for the samples produced with the Ti target (Figure 5). For these samples, in agreement with the elemental compositions in Table 1, there are low concentrations of Ti at the surface and the level of Ti decreases as a function of depth. Hence, it is clear from these profiles and the C 1s spectra for these samples, given in Figure 2 (b), that there is insufficient TiO₂ being deposited to form a continuous layer and that both PET and TiO₂ are present at the surface.

ToF-SIMS analysis of the samples deposited from the Cu and Ti targets [22] has shown the absence of any significant signals from diagnostic PET fragments on the surface of any of the Cu samples and the clear presence of PET fragments on the surface of all the 'Ti samples', confirming the growth of a CuO layer for the Cu samples and the most likely formation of an island-like TiO₂ distribution on the surface of the PET for the 'Ti samples'.

With regard to the CuO layer / PET interface, C 1s spectra are shown in Figure 6, taken from the interface region of the depth profiles for the p-DC unbalanced and HIPIMS unbalanced samples. Due to the low energy of the Ar⁺ ions (100 eV) used for the profiles, the C-O and C=O bonding of the underlying PET can still be observed. The amount of damage induced, even by these low energy ions, is not known, but it is clear that the PET structure at the interface is mostly or wholly preserved.

3.2. AFM

Figure 7 shows 3D AFM surface topography images for the untreated PET sample and plasma treated samples. The untreated PET exhibits a relatively smooth surface (roughness $R_a = 0.5$ nm). It can be seen from figure 7 that all the plasma treatment parameters investigated in this study resulted in a certain amount of surface roughening.

Employing a Cu target, the p-DC plasma treatment using a balanced array results in a roughened surface exhibiting surface feature sizes of a few nanometers ($R_a = 1.5$ nm). As expected, rougher surfaces with feature sizes clearly exceeding 10 nm are produced using the unbalanced array ($R_a = 2.2$ nm). A similar trend (i.e. balanced array resulting in finer features) can be observed for Cu HIPIMS plasma treated PET samples, but the roughness for these two samples is very similar ($R_a = 1.2 \pm 0.1$ nm). One obvious difference between the p-DC and HIPIMS treatments, despite the magnetic array configuration used, is that Cu HIPIMS glow discharges appear to produce coarser features compared to Cu p-DC.

For samples treated using a Ti target, p-DC plasma processing has again resulted in a surface with fine features and a higher roughness than the HIPIMS surface. The use of HIPIMS with a weaker magnetic array results in the presence of coarse features and low roughness, similar to those seen when employing the Cu target. However, the standard HIPIMS treatment in this case leads to a finer surface compared to that for the Cu target.

3.3. Contact Angle Measurements (acetone cleaned, aged surfaces)

The contact angle measurements for aged samples produced with Cu and Ti discharges are given in Table 1. A contact angle of 74.3° for PET is consistent with that found by other authors [23]. The presence of a more hydrophilic metal oxide at the surface would be expected to lower the contact angle, as is observed for all of the samples containing various amounts of either Ti or Cu oxides. The presence of a CuO layer by p-DC on to the PET surface has led to the contact angle dropping to 62° and employing HIPIMS power, a further drop in the contact angle is observed, to ~49° for both balanced and unbalanced magnetic array configurations. Using the Ti target, only a relatively small amount of TiO₂ is incorporated into the PET, but this still has the effect of increasing the hydrophilicity of the aged PET surface.

All of the plasma treated samples show low roughness values ($R_a < 2.5$ nm), hence it is unlikely that the roughness variation between the samples is having any significant effect on the contact angle measurements. Compared to the lower contact angles observed for the HIPIMS samples, the very thin CuO films deposited using p-DC power may have caused an increase in the contact angle, with the underlying hydrophobic PET still exerting some effect on the surface energy of these samples or there not being complete uniform coverage of the PET by the CuO layer. However, even when the Ti target is employed and TiO₂ is incorporated in the PET surface for the p-DC power sample, it is the HIPIMS samples which exhibit the lower contact angles. Consequently, these results indicate that use of HIPIMS power (for the processing

parameters investigated) has led to a more hydrophilic metal oxide surface being generated compared to p-DC power.

4. Discussion

The results have shown that under the process conditions employed, in a mixed Ar-O₂ atmosphere with fully poisoned Cu or Ti targets, CuO or TiO₂ is deposited in differing amounts onto the PET surface. When employing the Cu target, a CuO layer is deposited which gives full (or almost full) coverage of the PET substrate, whilst for the Ti target, a much smaller amount of TiO₂ is deposited, probably leading to a composite surface comprised of TiO₂ islands distributed over the PET substrate. In all cases, coating deposition with either major or full coverage leads to an increase in the hydrophilic nature of the surface, as evidenced by a reduction in the contact angle of aged samples. The outer surface of any exposed native PET has been modified by the O₂ plasma, resulting in some O containing functional groups being formed, which will act to increase its hydrophilic nature. Hence, the beneficial effect on the adhesive properties of the treated PET is expected due the presence of both metal oxide constituents and modified PET.

A much larger amount of CuO is deposited using the Cu target onto the PET surface than TiO₂, using the Ti target. This is not surprising, since the sputter yield of Cu is substantially higher than that of Ti under both non-reactive and reactive conditions [24]. Interestingly, HIPIMS appears to yield higher sputter rates than p-DC when employing the Cu target, but p-DC gives a higher sputter rate than HIPIMS for the Ti target.

The C 1s peaks given in Figures 2 and 6 indicate that these plasma process conditions give rise to the deposition of CuO and TiO₂ onto PET without any significant damage to the PET structure. From the depth profiles in Figures 4 and 5, use of p-DC power appears to result in a higher diffusion of Cu and Ti into the underlying PET compared to HIPIMS. This may be

explained by the substrate experiencing a higher thermal load under p-DC compared to HIPIMS power.

Surface roughness appears to be influenced mostly by the power mode employed, p-DC giving rise to rougher surfaces than HIPIMS. p-DC power appears to deliver the most aggressive treatment when used with the Ti target, which is due to differences in plasma composition and fluxes of charged species delivered to PET surface, with negative oxygen ions perhaps playing an important role. The use of HIPIMS power with the Cu target results in coarser but smoother surface morphologies and weakening the magnetic field reduces the plasma/PET interaction, yielding a smoother surface.

The contact angle results for aged samples have shown that: (i) thicker metal oxide films provide lower contact angles; (ii) CuO and TiO₂ surfaces treated by HIPIMS exhibit more hydrophilic surfaces than those deposited using p-DC power. The influence of film thickness may simply be a question of depositing a sufficiently thick metal oxide film to ensure uniform coverage of the PET surface. Clearly there may be other influencing factors such as surface/film morphology, grain structure and chemical composition. Such influences however cannot be individually discerned at the moment. We hypothesize that the reasons for the HIPIMS power giving rise to more hydrophilic surfaces is related to the fact that HIPIMS process gives a significant amount of ionized metal species and substantially different (i.e. higher average) energy distribution functions of both metal and gaseous species in the plasma, which yields metal oxide films with higher surface energies. All the surface modification processes (i.e. metal oxide deposition and surface roughening) are beneficial in terms of promoting adhesion to any subsequent thin film deposition that (in the vast majority of roll-to-roll coaters) is carried out immediately after plasma treatment without braking vacuum.

5. Conclusions

PET web samples have been treated in an Ar–O₂ atmosphere by magnetically enhanced glow discharges using either medium frequency pulse direct current (p-DC) or low frequency high power pulse (HIPIMS) power sources to sputter Cu or Ti targets. Employing the Cu target, both power modes result in the deposition of a thin film of CuO on the PET surface with thicknesses between 1 and 11 nm. The balanced p-DC and HIPIMS configurations give thicker films than the unbalanced configurations and HIPIMS gives thicker CuO films than p-DC. Utilising the Ti target, only a small amount of TiO₂ is deposited for both p-DC and HIPIMS power modes and this probably leads to a composite surface comprised of TiO₂ islands distributed over the PET substrate. It is also clear from the XPS analyses that the PET structure at the CuO/PET interface is mostly or wholly preserved.

Native PET has a contact angle of 74.3°. Deposits generated on PET samples during reactive oxygen containing sputter-based plasma treatments result in the following effects: deposition of a CuO thin film onto the surface leads to a decrease in the contact angle for both p-DC and HIPIMS power modes in balanced and unbalanced configurations; the lowest contact angle (measured on aged samples) of ~49° was recorded for the 5-11 nm thick CuO films deposited with the HIPIMS power supply; deposition of a small amount of TiO₂ onto the PET surface also decreases the contact angle; for Cu and Ti sputter sources, use of the HIPIMS power mode (in both magnetic configurations) at the conditions investigated in this study leads to more hydrophilic surfaces than p-DC.

All of the plasma treated samples show higher roughness values than the native PET, but the roughness was still very low ($R_a < 2.5$ nm). The unbalanced magnetic array resulted in a greater degree of plasma-PET interaction and, thus, a more aggressive treatment that is then manifested by rougher surfaces. The use of HIPIMS power, depending on the target material, allowed production of both rough and smooth surfaces. The degree to which the HIPIMS glow

discharge affected PET surface could be controlled further by changing the strength of the magnetic array.

Presence of Cu and Ti oxide constituents on the treated PET plasma treatments is beneficial in aiding the adhesion but alone is not enough to provide very high levels of hydrophilicity, which is clear from sessile drop water contact angle measurements on aged samples. The plasma surface modification methods that involve oxygen plasma treatment, metal oxide deposition and surface roughening (such as used in this study) will be most effective promoting adhesion to any subsequent thin film that is deposited immediately after treatment.

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Tables

Table 1. Table showing the process variables used for production of plasma treated PET samples; XPS determined elemental composition; AFM determined average roughness and water contact angles.

Sample	Sputter target	Magnetic array	Power technology	XPS composition (at.%)				Roughness R _a (nm)	Contact angle (°)
				C	O	Cu	Ti		
PET				67.0	33.0			0.5	74.3
1	Cu	Balanced	p-DC	28.9	37.5	33.0		1.5	62.0
2	Cu	Unbalanced	p-DC	31.0	37.9	30.8		2.2	62.3
3	Cu	Balanced	HIPIMS	27.1	37.6	34.9		1.3	48.8
4	Cu	Unbalanced	HIPIMS	30.2	36.2	33.3		1.1	49.5
5	Ti	Balanced	p-DC	59.2	35.2	-	4.0	2.3	64.7
6	Ti	Balanced	HIPIMS	59.8	35.4	-	1.9	1.5	58.2
7	Ti	low strength	HIPIMS	64.4	33.1	-	0.9	0.9	50.4

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Figure 1. Photographs showing wetting test results for a) untreated PET, b) PET treated using Ti sputter target and c) PET treated using Cu sputter target. The tests were performed immediately after the plasma treatment runs.

Figure 2. XPS C 1s spectra for the PET substrates after plasma treatment using the Cu (a) and Ti (b) sputter targets.

Figure 3. (a) XPS Cu $2p_{3/2}$ region for the PET substrates after plasma treatment using the Cu target; (b) XPS Ti 2p region for the PET substrates after plasma treatment using the Ti target.

Figure 4. XPS 100 eV Ar^+ depth profiles for the PET substrates after plasma treatment using the Cu target with (a-b) p-DC power and (c-d) HIPIMS power.

Figure 5. XPS 100 eV Ar^+ depth profiles for the PET substrates after plasma treatment using the Ti target with a) p-DC power and b) HIPIMS power.

Figure 6. XPS C 1s spectra taken from the CuO/PET interface region of the depth profiles for the a) p-DC unbalanced and b) HIPIMS unbalanced samples employing the Cu target.

Figure 7. 3D AFM surface topography images for the native PET (a) and the plasma treated samples (b-h). The area analysed was $1 \times 1 \mu m^2$, z deflection scale 100 nm.

PET

a)

'Ti' process

Water drops

b)

'Cu' process

c)

PET

Cu pDC bal

Cu pDC unbal

Cu HIPIMS bal

Cu HIPIMS unbal

Ti pDC bal

Ti HIPIMS bal

Ti HIPIMS low strength