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Plasma-enhanced atomic layer deposition: a gas-phase route to hydrophilic, glueable polytetrafluoroethylene†

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This communication reports an approach based on plasma-enhanced atomic layer deposition of aluminium oxide for the functionalization of polytetrafluoroethylene (PTFE or "Teflon") surfaces. Alternating exposure of PTFE to oxygen plasma and trimethylaluminium causes a permanent hydrophilic effect, and a more than 10-fold improvement of the "glueability" of PTFE to aluminium.

Polytetrafluoroethylene (PTFE) commercially known as "Teflon" has excellent properties such as chemical inertness, thermal stability, low dielectric constant, and low water absorption.[1] PTFE can sustain harsh environmental conditions. These properties render PTFE an interesting material for corrosion protective coatings, composite membranes in fuel cells, microelectronic packaging, and biomedicine and space applications.[2,3] In spite of this wide range of applications, the low surface energy of PTFE presents a technical challenge because it leads to poor adhesion with other materials (such as metals and ceramics, and other polymers).[1,4]

Plasma treatment is a well-known, relatively fast and easy, technology for modifying polymer surfaces, especially for inducing wetting transitions and improved adhesion.[1,5] A major drawback is however the aging effect.[5,6] The active polymer surface species created by the plasma often decompose or get removed over time during environmental exposure. As a consequence, plasma-treated polymers may return to their original state in terms of surface composition and wettability. Oxygen plasma generally induces hydrophilic effects on hydrophobic polymers. However, for PTFE, it can also increase the hydrophobicity.[2,7] Careful optimization of the oxygen plasma operating parameters is therefore essential for the realization of a hydrophilic effect on PTFE substrates.[8]

Kemell *et al.* reported surface modification of planar PTFE substrates *via* thermal atomic layer deposition (ALD) of metal oxides.[9] PTFE substrates were exposed to alternating pulses of a metalorganic precursor and water vapour resulting in Al_2O_3 or TiO_2 deposition. Unfortunately, the adhesion of the deposited metal oxides was poor on PTFE as the ALD layers were easily removed during a Scotch tape test. This poor adhesion might be due to the absence of covalent bonds between the deposited oxide and the PTFE substrate, as no active functional groups are available on the PTFE surface to initiate a ligand exchange type ALD process. In addition, it is impossible to cleave the covalent C–F bond during a thermal ALD process using water vapour. Therefore, thermal ALD is likely initiated by physical adsorption of precursor vapour and/or by anchoring at defect sites, leading to weak bonds at the oxide/PTFE interface.

This communication reports the successful synthesis of stable hydrophilic and glueable PTFE surfaces *via* plasma-enhanced (PE-)ALD of Al_2O_3. In this process, the PTFE substrate is sequentially exposed to oxygen plasma and trimethylaluminum (TMA) vapour. It is shown that the oxygen plasma breaks the C–F bond, thus making active surface species that can react with TMA during the subsequent precursor pulse. In this way a strong covalent bond is established between the Al_2O_3 coating and the PTFE substrate. Also, because Al_2O_3 is an inorganic material that is stable in air, the PE-ALD approach does not suffer from aging effects like the traditional plasma treatments.

Thermal and PE-ALD of Al_2O_3 on planar PTFE substrates were compared for different numbers of ALD cycles. The depositions were performed as explained in the ESI.† Energy dispersive X-ray (EDX) spectroscopy of the aluminium content revealed that the amount of Al_2O_3 deposited by PE-ALD was much higher than by thermal ALD (Fig. 1a). Possible explanations for this are a higher deposition rate on PTFE for PE-ALD compared to thermal ALD, as also observed on a Si reference wafer (0.13 *vs.* 0.10 nm per cycle), and/or a faster nucleation of the PE-ALD process on PTFE.

The native hydrophobic PTFE substrates had a water contact angle of 103° (Fig. 1b, 0 cycles). Treatment with oxygen plasma

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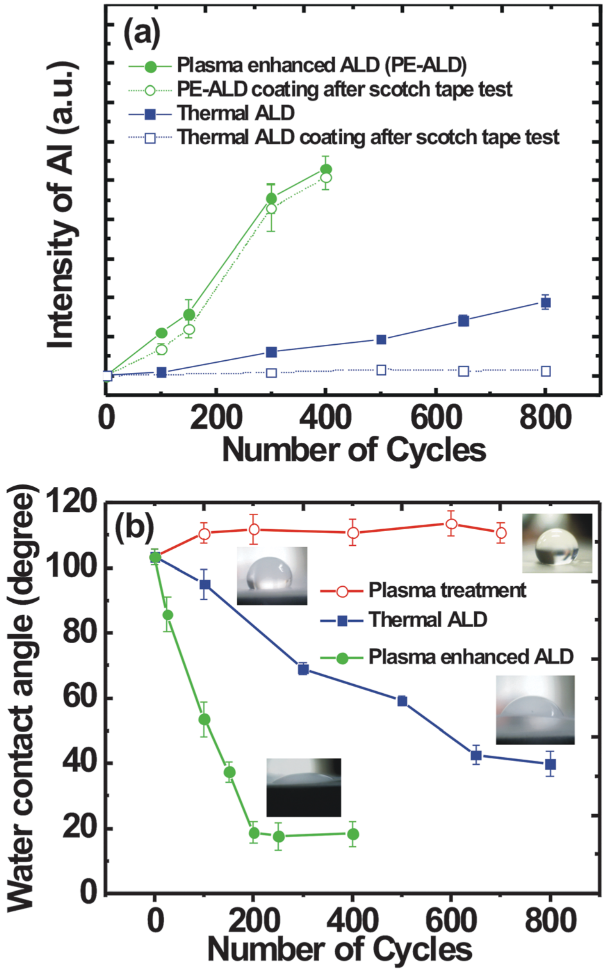

Fig. 1 (a) EDX intensity of aluminium against the number of (PE-)ALD cycles before and after Scotch tape adhesion test. (b) Water contact angle against the number of (PE-)ALD cycles or plasma exposures.

pulses (without intermediate TMA pulses) increased the contact angle to 111° due to an even stronger hydrophobic behaviour. In contrast, when the oxygen plasma pulses were alternated with TMA exposures in PE-ALD, the water contact angle decreased and a steady value of 19° was reached after 200 PE-ALD cycles, proving that the PTFE surface became hydrophilic. After 800 cycles of thermal ALD, the water contact angle was only reduced to 40°, indicating that PE-ALD is more effective to induce a hydrophilic effect on PTFE. The hydrophilic thermal and PE-ALD samples were stable upon storage for 6 months in ambient air.

The adhesion of the Al_2O_3 coatings to the PTFE surface was evaluated by the Scotch tape test. The thermal ALD layers did not pass the test as most of the aluminium content was removed (Fig. 1a). This result is in agreement with the previous work by Kemell *et al.*[9] In contrast, the PE-ALD deposited Al_2O_3 coatings remained intact after removal of the Scotch tape, allowing us to conclude that the coating/substrate adhesion was significantly improved by using a plasma-activated process.

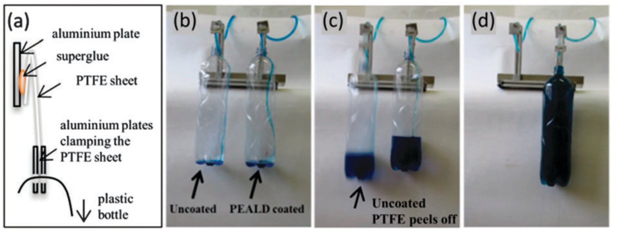

Fig. 2 Demonstration experiment on the ''glueability'' of uncoated and PE-ALD coated PTFE sheets. (a) Schematic representation of the experiment geometry. (b–d) The uncoated PTFE sheet peels off during filling of the plastic bottles with blue-coloured water, while the strong adhesion between the PE-ALD modified PTFE sheet and the aluminium plate allows complete filling of the bottle.

The ability for gluing of native PTFE and PE-ALD modified PTFE was compared in a demonstration experiment. Both PTFE sheets were glued on an aluminium plate using a commercial adhesive (Loctite 401 from Henkel) as indicated in Fig. 2a. Empty 1.5 liter plastic bottles were fixed to the PTFE sheets and slowly filled with coloured water. While the uncoated PTFE sheet peeled off from the aluminium plate when approximately 1/4 of the bottle was filled with water (Fig. 2c), the adhesion between the PE-ALD modified PTFE sheet and the aluminium plate was strong enough to allow the complete filling of the plastic bottle (Fig. 2d). This experiment illustrates the significant improvement in ''glueability'' of the PTFE substrate induced by the PE-ALD treatment.

To quantify the adhesion strength, peeling tests were carried out using an Instron 5565 set up, and the obtained peeling forces are presented in Fig. 3. PTFE samples of 20 × 20 mm^2 were glued to an aluminium block using the above-mentioned commercial adhesive. The peeling tests were performed at an angle of 180° using a speed of 0.5 mm s^{-1}. As reference, a Scotch tape was attached to the aluminium plate and the peel-off force was determined using the same peeling angle and speed. The peel-off force for the uncoated PTFE sheets was 0.90 ± 0.40 N whereas for Scotch tape a value of 3.75 ± 0.55 N was measured. For the thermal and PE-ALD treated PTFE sheets,

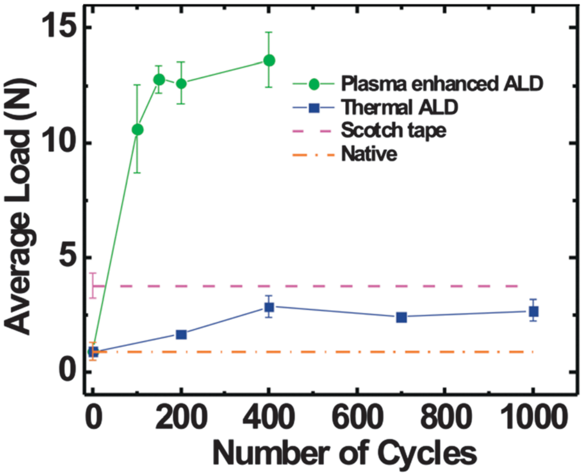

Fig. 3 Average maximum load in peeling tests against the number of (PE-)ALD cycles. The values obtained for uncoated PTFE and Scotch tape as reference are also indicated.

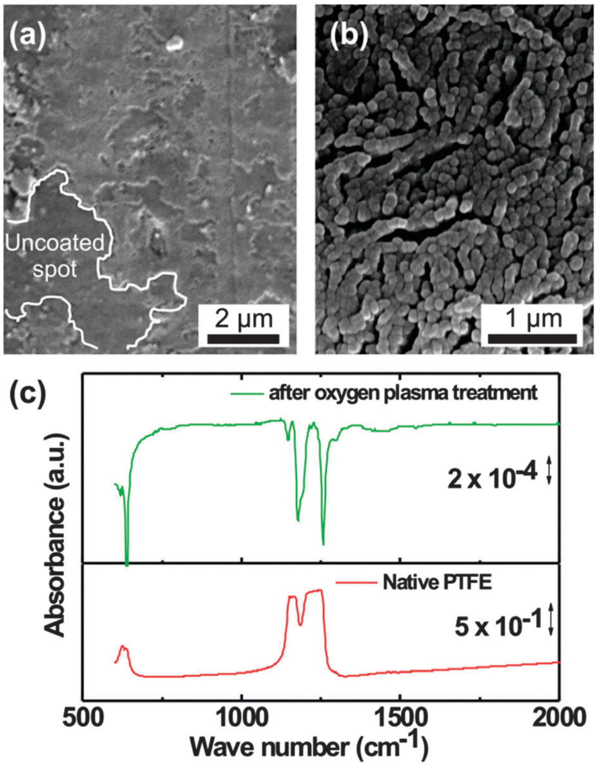

Fig. 4 (a) SEM image of an Al_2O_3 layer deposited on PTFE using 400 thermal ALD cycles. An uncoated region is indicated. (b) SEM image of an Al_2O_3 layer deposited on PTFE using 300 PE-ALD cycles. (c) FTIR spectrum for native PTFE (bottom) and difference spectrum after oxygen plasma treatment (top).

we obtained values of 1.66 ± 0.51 N and 12.60 ± 0.91 N, respectively. The PE-ALD treatment thus resulted in a significant, *ca.* 14-fold, increase of the PTFE/superglue/Al adhesion strength.

Scanning electron microscopy (SEM) images of the thermal and PE-ALD coated PTFE substrates are presented in Fig. 4a and b, respectively. The Al_2O_3 layer obtained *via* the PE-ALD process had a granular structure suggesting island type growth (Fig. 4b). During this process, nucleation likely started on various spots of the substrate due to the random activation of the PTFE surface by the oxygen plasma radicals. The thermally deposited Al_2O_3 layer appeared smooth in SEM, although large uncovered parts, as confirmed by local EDX measurements, were also observed (Fig. 4a). These uncoated regions possibly originated from damage of the coating during sample handling after deposition (given the poor adhesion of the Al_2O_3 layer for the thermal ALD process).

In situ FTIR spectroscopy was carried out to elucidate the faster nucleation and improved adhesion strength of the PE-ALD modified PTFE sheets. Spectra were recorded on 60 µm thick porous PTFE substrates in transmission mode using a Vertex 70v set up from Bruker. For native PTFE, two typical strong peaks were observed around 1155 and 1215 cm^{-1} (bottom Fig. 4c). The relatively sharp peak around 1155 cm^{-1} can be ascribed to CF_2 symmetric stretching, while the broad peak around 1215 cm^{-1} is due to asymmetric stretching.[10] The weak peak at 637 cm^{-1} is related to the wagging vibration mode of C–F bonds. The effect of an oxygen plasma pulse on the PTFE surface was evaluated by subtracting the FTIR spectrum of the native PTFE sample from the spectrum measured on the treated surface. This so-called difference spectrum showed negative absorbance for both the positions of stretching and wagging vibration modes (top Fig. 4c). This result indicates the dissociation of C–F bonds during the oxygen plasma pulse and explains the superior properties of the PE-ALD treated PTFE samples.

In conclusion, this work reported PE-ALD as an easy and elegant method to functionalize PTFE substrates. While oxygen plasma pulses resulted in an increased hydrophobic behaviour, alternating pulses of oxygen plasma and TMA resulted in an Al_2O_3 coating firmly attached to the PTFE substrate, inducing a stable hydrophilic effect. Because the degree of hydrophilicity increased with the number of deposited cycles, the presented PE-ALD approach allows for the controlled tuning of this surface property. Furthermore, an average peeling strength higher than 600 N m^{-1} was measured between aluminium and PE-ALD modified PTFE, using a commercial adhesive. This represents a more than 10-fold increase compared to native PTFE samples.

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