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Highly reflective polymeric substrates functionalized utilizing atomic layer deposition

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Reflective surfaces are one of the key elements of solar plants to concentrate energy in the receivers of solar thermal electricity plants. Polymeric substrates are being considered as an alternative to the widely used glass mirrors due to their intrinsic and processing advantages, but optimizing both the reflectance and the physical stability of polymeric mirrors still poses technological difficulties. In this work, polymeric surfaces have been functionalized with ceramic thin-films by atomic layer deposition. The characterization and optimization of the parameters involved in the process resulted in surfaces with a reflection index of 97%, turning polymers into a real alternative to glass substrates. The solution we present here can be easily applied in further technological areas where seemingly incompatible combinations of polymeric substrates and ceramic coatings occur. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4928375]

In solar thermal electricity plants, reflective surfaces are key elements for concentrating solar energy towards the receivers. Their reflexion index is proportional to the amount of solar energy that can be concentrated and thus converted. High transmittance glass mirrors with a reflecting coating are most commonly introduced in industrial plants due to their good performances. However, they have all the drawbacks glass brings about, primarily fragility and high weight both contributing to a high production and maintenance cost. The reduction of production cost is among the critical issues that have triggered the development towards more efficient and technologically improved materials and production strategies.

Synthetic polymers stand out as suitable alternatives for an implementation as high performance glass avoiding reflective mirrors. Among the wide range of thermoplasts, fluorinated ethylene propylene (FEP) Teflon has been identified as one suitable polymeric substrate for reflective mirrors for several reasons;[1] FEP is a polymer chemically very inert, it withstands both high and low temperatures, it is largely abrasion resistant and, of utmost importance, it has excellent optical properties.[2,3] FEP can also be further functionalized and modified in order to increase its abrasion resistance and improve its mechanical properties. One of the possible approaches towards enhancement of the physico-chemical properties is through coating of the polymer with functional thin films, which can be performed in various ways. However, a problematic issue resulting from current coating strategies is the poor adhesion of inorganic coatings on hydrophobic fluoropolymers, such as sputtered oxide or metal thin films on the surface of FEP.[4,5] Two approaches have been reported and commercialized in the field of reflective mirrors on polymeric substrates, provided by Refletech and NREL.[6,7] The mirror described by Refletech is based on a silver PVD (Physical Vapour Deposition) coating on PET (polyethylene terephthalate) protected by another polymeric film that shows a reflectance of 93%–94%. The reflector reported by Kennedy consists of a silver layer on top of Teflon and has a reflectance of around 90% together with a poor surface specularity.

A strategy for encountering the problem of poor adhesion may involve substitution of PVD as deposition technique with atomic layer deposition (ALD). ALD is a coating technique that enables deposition of thin inorganic films with sub-nanometre precision. This technique, developed in the 1970s, is based on sequential delivery of gaseous precursors to the substrate and their chemical interaction with the surface of the substrate.[8,9] The self-saturating reactions that take place at the gas-solid interphase lead to a perfectly controlled and conformal growth of the coating. ALD is considered to be the method-of-choice for material development in numerous emerging applications, including the fabrication of sensing devices, photonics, corrosion protection and sensitive material encapsulation, flexible electronics, etc.[10–14]

Optical devices, solar cells in particular, are one of the growing industries that took advantage of the unique benefits of ALD in order to improve properties and performance of some solar gadgets. However, most of the studies have been focused on the development of solar cells and on the implementation of good encapsulation strategies.[15–17] Only few investigations relate to the fabrication of reflective mirrors by means of ALD, and none of them is attributed to heliostats or solar reflective mirrors.[18,19]

In this work, a TiO_2 thin film deposited by ALD has been applied as an intermediate coating between the surface of FEP and the sputtered silver. TiO_2 has been widely used in industrial applications, mostly as white pigment, thanks to its outstanding physico-chemical features (thermal stability,

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chemical inertness to both organic and inorganic solvents, nontoxicity, biocompatibility, etc.).[20,21] The incorporation of the ceramic layer as bridge between the silver reflective layer and polymeric substrate enables the implementation of alternative routes for the fabrication of polymer-based mirrors for heliostats. This paper demonstrates that an optimized ALD deposition of TiO_2 on the surface of Teflon FEP allows the overcoming of the main drawbacks of the current approaches, primarily the insufficient adhesion and poor crack resistance of the coating layer. Eventually, highly reflective mirrors based on plastic substrates are fabricated.

As mentioned before, the key step for obtaining a reflective surface on top of a FEP substrate involves a stable and controllable coating of the polymer. The influence of the thickness of the deposited film in both the roughness and the finishing quality was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Samples with 50 nm and 100 nm thickness of TiO_2 were fabricated and characterized. The experimental process has been detailed in the supplementary material.[22] The characterization was done on at least 5 distinct areas of a minimum of 3 samples produced for each experiment. Figure 1 shows a schematic of the TiO_2 deposition ALD process and representative micrographs obtained from SEM. The corresponding AFM images are shown in supplementary Figure S1 (see supplementary material S1).[22] The schematic shows that for the initial step of the ALD growth presence of hydroxyl groups on the surface of the substrate is preferred. FEP Teflon by default has no such functional groups, but being a technical product, defects or impurities are present on or in the polymer that promote the initiation of the ALD coating. Initially, nucleation and island growth starts from such defects and impurities and proceeds towards compact coating of the whole substrate surface.[5,23]

The SEM micrographs of both samples show a serious crack density in the deposited TiO_2 layer. This cracking is mainly due to the difference in the thermal expansion coefficients of the two involved materials, the FEP polymer and the oxide coating, and the brittleness of the ceramic film that is mechanically stressed.[24] The characterization of the topography by AFM showed that both films are homogenously deposited and do not present obvious defects or pinholes besides the cracks mentioned. The calculated root mean squared roughness (RMS) of the samples is 13.07 ± 0.5 nm for the samples of 50 nm and 11.24 ± 0.8 nm for the ones of 100 nm.

It has been reported that the incorporation of an organic-inorganic hybrid interlayer (alucone) between the polymeric substrate and the ceramic coating in an ALD process minimizes the cracking of the deposited layer.[25,26] With this in mind, samples with 10 nm of alucone and 50 nm of TiO_2 were fabricated and analyzed. Supplementary Figures S2 and

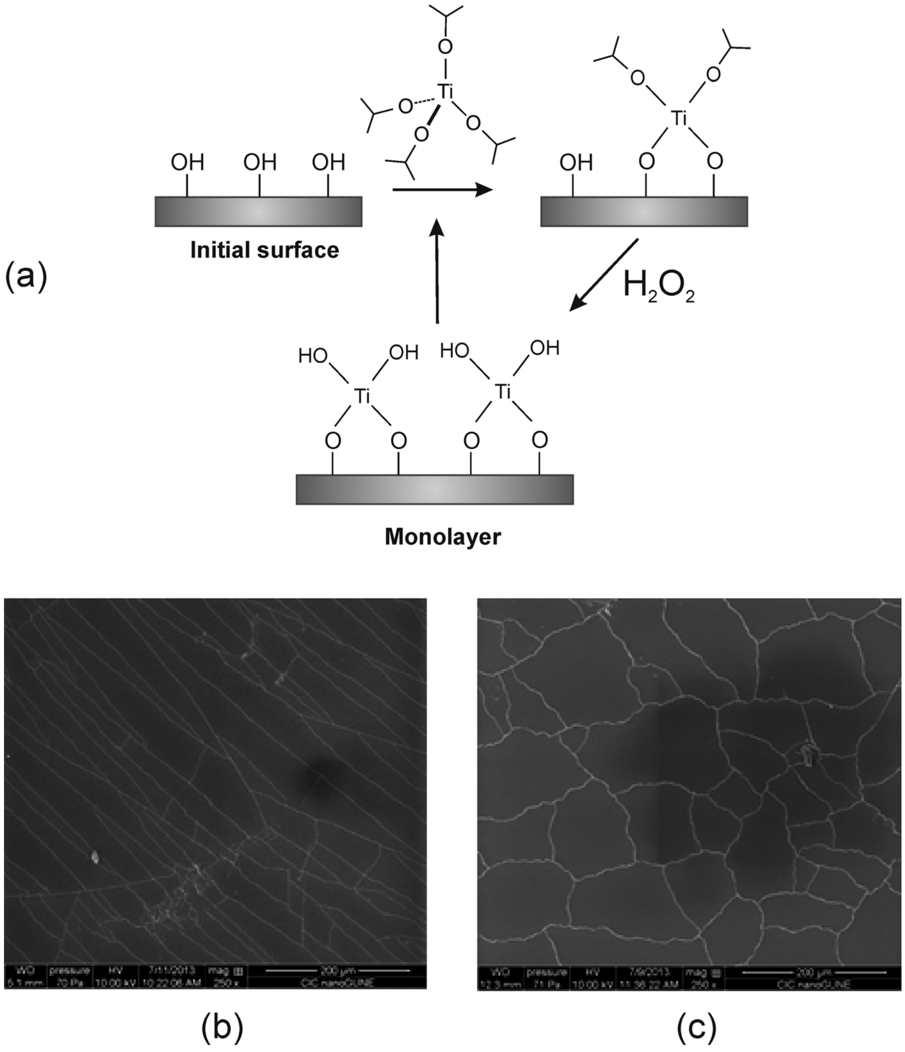

FIG. 1. (a) Schematic of the two-step deposition process for the growth of TiO_2 using TTIP (Titanium isopropoxide) and H_2O_2, (b) SEM micrograph of the FEP sample coated with 50 nm of TiO_2, and (c) SEM micrograph of the FEP sample coated with 100 nm of TiO_2.

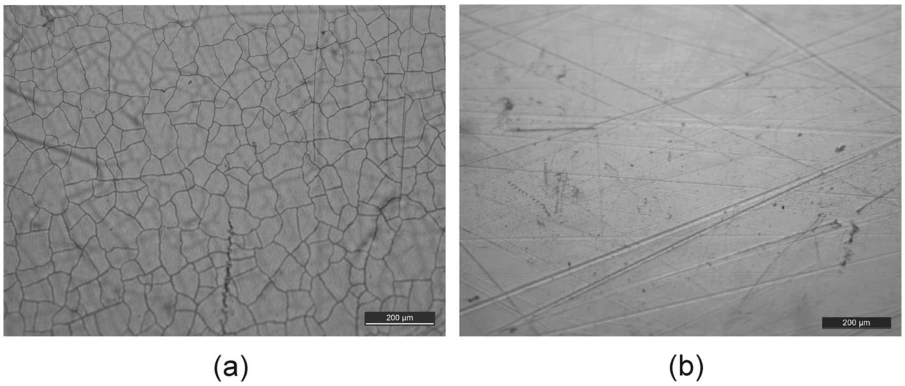

FIG. 2. Optical micrographs of 100 nm TiO_2 coatings on FEP teflon. (a) Upon regular post-processing and (b) upon gradual and controlled cooling after the deposition process.

S3 show the expected effect of the alucone, SEM and AFM images of the samples.[22] The SEM image in Figure S2(b) clearly shows that the alucone does not efficiently prevent the cracking of the TiO_2 coating. Therefore, the use of the organic interlayer as cracking prevention element appears not suitable for our purpose.

As an alternative attempt to minimize the cracking of the TiO_2 film after the ALD deposition, the impact of the temperature gradient upon cooling to ambient conditions after the deposition process was evaluated. Namely, the temperature was gradually decreased from the process temperature of 120 °C to 25 °C overnight. This approach was also expected to result in a lower crack density in the film.[27] An optical micrograph of a representative sample is shown in Figure 2(b).

The images clearly evidence the hypothesis mentioned before, that a progressive and controlled decrease of the sample temperature will result in prevention of cracks in the deposited TiO_2 layer. The cracking virtually disappears resulting in a continuous and flat surface with few defects. The trade-off is, however, the increase of the processing time upon inclusion of the cooling step into the fabrication process.

Besides the cracking of the layer, the adhesion of the ceramic coating to the polymeric substrate is of paramount importance when functionalizing plastic materials such as PTFE (Polytetrafluoroethylene) or polycarbonate.[5,28–30] In order to study the adherence of the TiO_2 layer to the FEP, a mechanical test with an adhesive tape was carried out.[31] Figure 3(a) is a micrograph showing FEP coated with 100 nm TiO_2 after the tape test. It clearly shows that the adhesion of the TiO_2 is poor and the coating is easily mechanically removed. This is very likely due to the lack of active surface groups on the FEP and therefore weak chemical bonding of the coating to the substrate. This result is in agreement with the work of Kemell, claiming rather physical interactions between PTFE and TiO_2 than chemical ones.[32]

In the case of the implementation of the hybrid organic-inorganic coating of alucone and TiO_2 (Figure 3(b)), the adhesion subjectively appears even worse than in the previous case. This difference in the adhesion of the coating may be due to the mechanical weakness intrinsically imposed by the precursors used for the organic-inorganic interlayer. Figure 3(c) shows a micrograph of a tested sample coated with TiO_2 and gradually cooled after the deposition process. Although the final coating shows a slightly better adhesion than the previously mentioned samples, the adhesion of the coating to the substrate surface is still too weak, resulting in plenty defects after the tape test.

In an attempt to increase the adhesion of the TiO_2 to the FEP substrate, pre-treatment of the FEP substrate with an oxygen plasma was carried out. The plasma ashing process aims at activating the surface of the inert polymer by introducing oxygen and in this way promoting enhanced chemical bonding between the ceramic layer and the substrate.[28,33] Visual inspection of the coating after the plasma pre-treatment, ALD process, and progressive cooling shows an improved finishing of the coating, with no appreciable macroscopic defects or cracks. The corresponding micrograph is shown as supplementary Figure S4.[22] The RMS of the 100 nm TiO_2 coating after the plasma treatment is 10.81 ± 2.1 nm, which means that the plasma ashing does not influence the surface roughness of the consequent ALD layer. Figure 3(d) shows the sample surface after the tape test.

The comparison of the four images allows to conclude that the successive improvements included into the process, both for the pre-treatment and the post-treatment, enable the fabrication of a topographically homogenous, TiO_2-coated FEP Teflon with a minimum of superficial cracks and strongly anchored ceramic coating.

To further characterize the composite, the hardness of the coated and uncoated polymer was analyzed through nanoindentation. Nanoindentation or depth-sensing indentation (DSI) is becoming a routine technique for the characterization of some mechanical properties of polymers and polymer based nanocomposites, which can be derived from deformations of the material on the nanoscale upon external load.[34] Figure 4 shows the hardness of the bare FEP samples and samples upon various treatments as described before. The graphs with representative load values as a function of the indentation depth performed with the analytes as well as AFM images of the performed indents are shown in the supplemental Figures S5 and S6.[22]

Obviously, both the inorganic (TiO_2) and the hybrid (Alucone + TiO_2) coatings do not significantly alter the hardness of the FEP Teflon. The nanometric thickness of the coating and the brittleness and thus the susceptibility of the film to cracking induce no detectable variation in the mechanical resistance of the polymer. Besides, neither the pre-treatment with the oxygen plasma nor the gradual cooling of the samples after the deposition process seems to have any

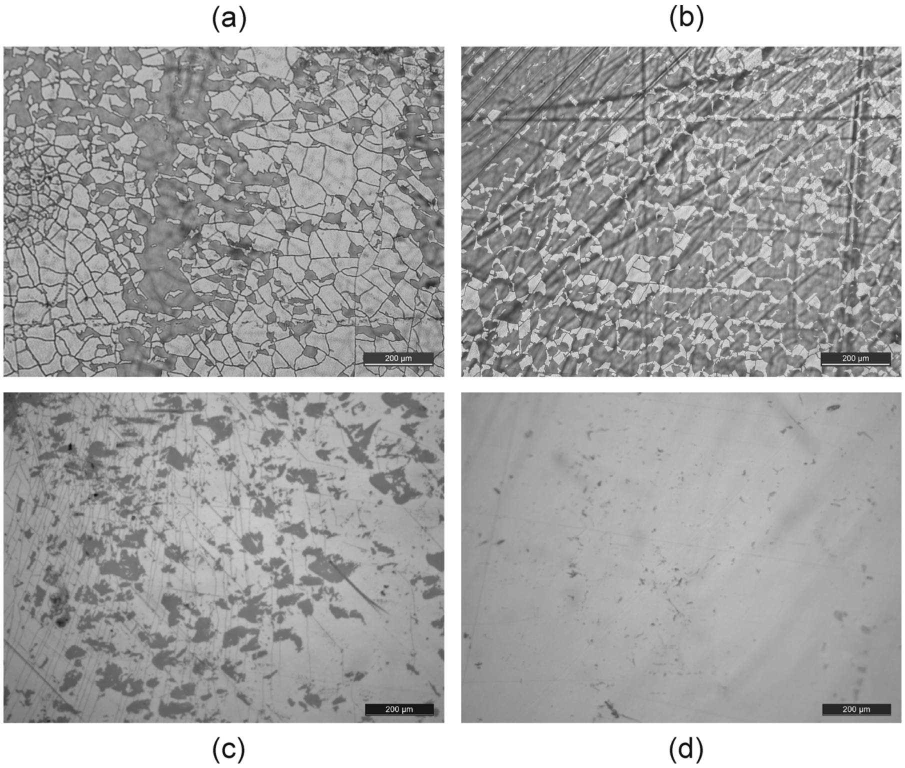

FIG. 3. Optical micrographs of FEP teflon coated with 100 nm TiO_2 after the tape test. Samples were prepared with (a) a regular TiO_2 coating process, (b) a hybrid alucone interlayer and subsequent TiO_2 coating, (c) a TiO_2 coating and subsequent gradual and controlled cooling, and (d) an O_2 plasma pre-treatment, TiO_2 coating and subsequent gradual cooling.

impact on the mechanical properties of the FEP. However, when the optimized coating process is applied, the hardness of the material clearly increases.

This increase can be associated with a structural change in the FEP surface after the plasma treatment. The AFM images of that sample (supplementary Figure S7) show that the polymeric surface undergoes morphological changes after the O_2 plasma treatment.[22] The roughness of the surface increases from RMS 10.02 ± 1.57 nm as measured from the neat FEP to 21.26 ± 1.74 nm in case of the plasma-treated sample. The increase in the roughness and its influence on the promotion of nucleation sites has been already studied for other ALD coatings and confirms the obtained results.[23] This roughening of the surface results in a corrugation of the subsequent coating and thus in a virtually thicker TiO_2 film that is reflected in an increase of the hardness of the coated polymer. This corrugation also increases the number of possible bonding sites of substrate and coating and in this way improves the adhesion of the ceramic layer to the FEP Teflon. However, this corrugation does not imply a roughening of the final surface as mentioned above.

Finally, a silver thin-film was deposited on top of the functionalized FEP by DC sputtering in order to fabricate the final reflective layer. As validation of the reflective polymeric mirrors, an optical characterization of the device was carried out in order to verify whether or not the proposed FEP/TiO_2/Ag is suitable for the targeted solar mirror application. Figure 5 shows the reflectance results obtained.

The reflectance of the polymeric mirrors reaches 97% over a very broad wavelength range, as it can be observed in Figure 5. For comparison, the two commercial approaches from Refletech and NREL mentioned before show a

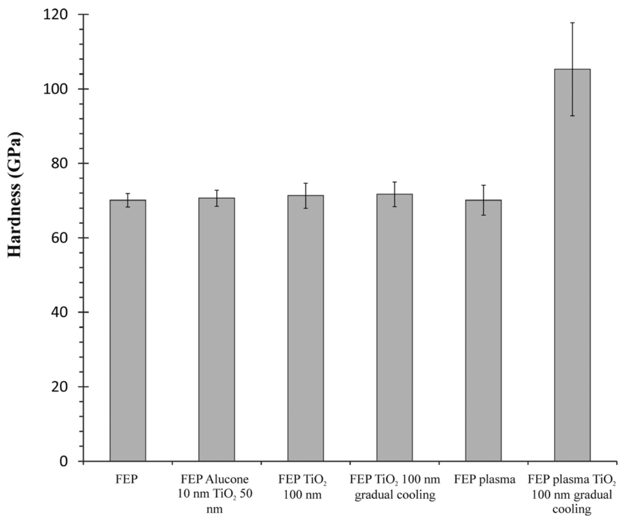

FIG. 4. Hardness values measured from neat FEP samples and FEP samples with different pre- and post-treatments.

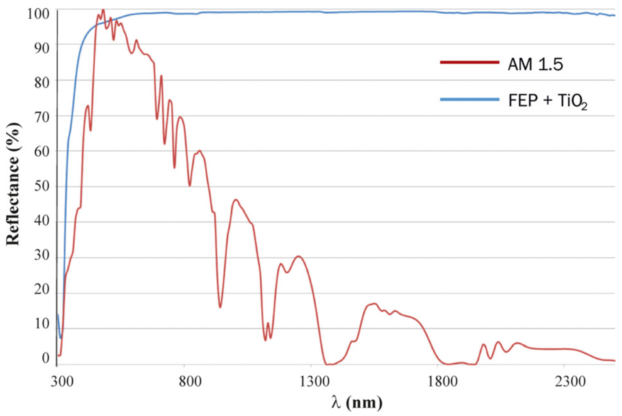

FIG. 5. Reflectance of the fabricated O_2-plasma pre-treated, TiO_2-coated and gradually cooled samples after Ag sputtering (blue line). The solar spectrum AM 1.5 (red line) is included as reference.

reflection index of 93%–94% and 90%, respectively.[6,7] Thus, the solution proposed here is a real alternative to glass based mirrors as the required optical features for this kind of device are well fulfilled, and a high level of physicochemical stability is achieved.

In summary, a nanoscale inorganic layer of TiO_2 deposited on top of FEP Teflon results in a structurally, mechanically, and optically suitable polymer-based alternative for the commonly used glass-based reflective mirrors in solar energy concentrators. The mismatch in the thermal expansion coefficients between the ceramic and the polymeric materials and the subsequent cracking of the coating can efficiently be solved through an optimization of the deposition process. Specifically, introducing of a gradual cooling step after the deposition process greatly minimizes the cracking of the film induced by mechanical stress. An additional pretreatment of the FEP surface with an oxygen plasma further stabilizes the composite by significantly enhancing the adhesion of the thin film to the polymer surface. The increased hardness of more than 100 GPa of the resulting coated surface provides further mechanical stability and opts for higher abrasion resistance. The high reflectance of 97% of the produced mirrors confirms the suitability of the fabricated material as effective and reliable component for heliostats. The approach clearly shows that the combination of thin films and polymeric substrates are promising for the development of new fabrication strategies and functional materials that may eventually contribute to lowering the cost for energy conversion.

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