

PLASMA OXIDATION OF PRINTED POLYSILOXANE LAYERS

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Abstract

Organosilica binders are a promising way to interconnect various nanoparticles in printed coatings for photovoltaic cells and other applications. Post-deposition treatment of printed nanoparticle films with organosilica binders is required to remove the organic moieties and thus achieve the optimal optoelectronic properties of the resulting film. As a result, the polysiloxane binder is converted to almost fully amorphous silica and this process is called mineralization. Atmospheric pressure plasma operating in open air has proven to be the most promising method, as the operating temperature can be kept below 70 °C and the overall treatment time required is in order of minutes. These are significant advantages compared to alternative approaches like thermal sintering, where temperatures required are around 450 °C, or chemical or UV light treatment, where the treatment times extend into the order of hours. To better understand the underlying chemistry in the interaction of the ambient air plasma and the organosilica binder we performed an X-ray photoelectron spectroscopy (XPS) study on the plasma-treated films of silica binder, regularly used with titania nanoparticles. The detailed analysis of core-level spectra of C 1s, O 1s and Si 2p were used to observe the removal of methyl groups from the film and gradual transformation into amorphous SiO₂. The scanning electron microscope revealed significant patterning of the surface by interaction with plasma after exposures longer than 16 seconds.

Keywords: Nanoparticle binder, organosilica, plasma mineralization, DCSBD, atmospheric pressure plasma

1. INTRODUCTION

Sol-gel processes are widely used to prepare various silica gels for different applications including protective hydrophobic coatings [1]. Recently a process involving methyltriethoxysilane (MTEOS) precursor was developed and used to prepare a matrix in which titania nanoparticles were dispersed to obtain porous and flexible photocatalytically active coating [2]. The organosilica matrix acted as a binder interconnecting the nanoparticles. This has substituted the connections between nanoparticles that form during traditional high-temperature sintering and are necessary for desired properties of the film. It has been shown that these new coatings can be used as photoanodes in photovoltaic devices such as perovskite solar cells, which is the most interesting application of the coating so far [4].

As-deposited coatings without any curing, however, don't display satisfactory performance. The methyl groups in the organosilica binder hinder the electrical properties of the films and cause poor wettability if any subsequent overprinting is desired for more complicated devices. Three approaches for post-printing curing were compared: thermal sintering, UV light treatment, and air plasma treatment [6]. It was shown that all three methods cause mineralization of the binder resulting in fully insoluble and stable coating with improved mechanical properties of the film. Out of the three, the plasma approach is extremely attractive as the treatment times necessary can be reduced to one minute, the temperature can be kept below 70 °C providing

compatibility with the temperature-sensitive flexible substrates, and the process is readily compatible with roll-to-roll processing for preparing large area coatings.

The mechanism of mineralization of the organosilica binder is believed to involve the cleavage of methyl groups bonded to silicon and transformation into amorphous SiO_x . The energetic nitrogen and oxygen species in plasma, specifically oxygen radicals, react with $\text{Si}-\text{CH}_3$ groups on the surface resulting in surface active sites [8]. We chose to study in the detail the chemical changes happening on the surface of polysiloxane coating. Up to now, all the studies reported the effect of curing on coatings of binder together with the nanoparticles. Elimination of the nanoparticles and analysing the polysiloxane coating by itself can give more detailed information about the mineralization process.

2. EXPERIMENTAL PROCEDURE

The preparation of recently developed organosilica binder, a hybrid silica sol based on MTEOS [2] was adopted without modification. The binder was diluted with isobutanol in ratio 1:20. The mixture was spin-coated onto a crystalline silicon wafer at 800 RPM for 10 s and then 3000 RPM for 30 s.

Plasma was generated in ambient air by diffuse coplanar surface barrier discharge (DCSBD) – a dielectric barrier discharge with a coplanar arrangement of electrodes; commercialized by Roplass s.r.o. (Czech Republic) [3]. DCSBD generates plasma of high uniformity and power density up to 100 W/cm^3 , while maintaining temperature below $70 \text{ }^\circ\text{C}$. The plasma region of the DCSBD unit was around 0.3 mm thick. To ensure a good contact of the sample surface with the plasma region the sample holder was distanced from the ceramics of the DCSBD unit by 0.3 mm of Kapton tape. The exposure time of the treated sample surface was varied from 0 s to 128 s.

The surface chemistry of the films was determined from X-ray photoelectron spectra (XPS) obtained by AXIS Supra spectrometer from *Kratos Analytical Ltd.* (United Kingdom). The instrument uses $\text{Al K}\alpha$ spectral line (1486.6 eV photon energy) and an electron flood gun was utilized for charge compensation. The acquisition of narrow regions of the spectrum was performed with the pass energy 20 eV. For analysis of the spectra CasaXPS software was used. The spectra were calibrated to C—C/C—H peak of C 1s at 285 eV binding energy.

Mira3 scanning electron microscope (SEM) from *Tescan* (Czech Republic) was employed for the analysis of the morphology of the coatings and the effect of plasma. Prior to analysis the films were coated with 10 nm of Au/Pd conductive film to reduce the charging of the surface by incident electrons. The images were captured at with 2000x and 5000x magnification, 10 kV accelerating voltage and at a working distance of 10 mm.

3. RESULTS AND DISCUSSION

We used X-ray photoelectron spectroscopy (XPS) was used to analyze the changes in the surface chemistry on the surface of the polysiloxane coatings. In **Table 1** the atomic concentrations of the elements detected on the surface are shown. Immediately after the exposure to plasma for just one second, we observe a significant increase in the oxygen concentration from the original 45 % to 61 % and a decrease of the carbon concentration from 32 % to 13 %. A small amount of nitrogen was introduced to the surface (below 1 %) during the ambient air plasma treatment. Prolonged plasma exposure did not cause any further changes in the surface elemental composition. After 128 seconds the surface contained 62 % of oxygen and 12 % of carbon. The silicon content remained relatively stable during the plasma treatment, 24 % on the original coating and 26% after 128 seconds of treatment. The removal of carbon and replacement by oxygen agrees with the results of previous studies [4].

Table 1 Atomic concentrations on the surface of polysiloxane film before and after plasma exposure, obtained from XPS

| Treatment time | Silicon [%] | Oxygen [%] | Carbon [%] | Nitrogen [%] |
|----------------|-------------|------------|------------|--------------|
| 0 s | 23.7 ± 0.1 | 44.8 ± 0.6 | 31.5 ± 0.6 | 0 |
| 1 s | 25.5 ± 0.6 | 61 ± 1 | 13.0 ± 0.7 | 0.51 ± 0.01 |
| 8 s | 25.4 ± 0.1 | 62 ± 1 | 12 ± 1 | 0.6 ± 0.3 |
| 16 s | 24.9 ± 0.2 | 62.8 ± 0.1 | 11.6 ± 0.1 | 0.8 ± 0.2 |
| 32 s | 25.2 ± 0.1 | 62.1 ± 0.7 | 12.0 ± 0.3 | 0.7 ± 0.5 |
| 64 s | 25.7 ± 0.1 | 61.6 ± 0.1 | 12.1 ± 0.4 | 0.7 ± 0.2 |
| 128 s | 25.8 ± 0.1 | 62.1 ± 0.2 | 11.7 ± 0.1 | 0.4 ± 0.1 |

The high-resolution core-level XPS spectra of the films are shown in **Figure 1**. **Figure 1a** compares the C 1s region of the untreated and plasma-treated film. The main peak at low binding energy is made up of two components corresponding to Si—CH₃ environment and the carbon in C—C—H hydrocarbon from some organic contamination on the surface at binding energies 284.5 eV and 285.0 eV, respectively. Furthermore, we observe contribution from C—OH at 286.5 eV and after plasma treatment contributions from O—C=O at 288 eV appear. This is a result of oxidation by plasma. We also observe significant shift of the main peak from 284.5 eV to 285.0 eV over the increasing plasma treatment times. This is a direct observation of the removal of methyl groups that are bound to silicon in the binder.

Figure 1b shows the high-resolution O 1s XPS spectrum. The reference sample of untreated displayed a single peak at 532.4 eV corresponding to a oxygen in the CH₃—Si—O_{3/2} [2, 5]. After the exposure to ambient air plasma for just one second a shift towards higher binding energies is observed. This shift is believed to be caused by a transformation of the surface of the coating into amorphous silica under the influence of oxygen species in plasma. After exposure to plasma the position of the peak is 532.9 eV corresponding to the oxygen in SiO₂. The Si 2p region of the XPS spectra is shown in **Figure 1c**. The contribution from the silicon atoms in CH₃—Si—O_{3/2} and SiO₂ are located at 102.5 eV and 103.7 eV [7]. Since the difference in binding energy is larger than in the O 1s spectrum, the changes in the chemistry can be observed more easily. After the plasma treatment we can see a shift from the original position 102.5 eV to higher binding energies. After short treatments the resulting peak is broader, indicating a combination of contribution from both environments. With prolonged treatment time the peak gets narrower and moves to higher binding energies, suggesting a complete transition to amorphous silica and an increased depth in the film where the plasma has an effect. This ultra-fast mineralization of the polysiloxane film offers the same result as a much slower mineralization under exposure to UV light presented in previous studies [2].

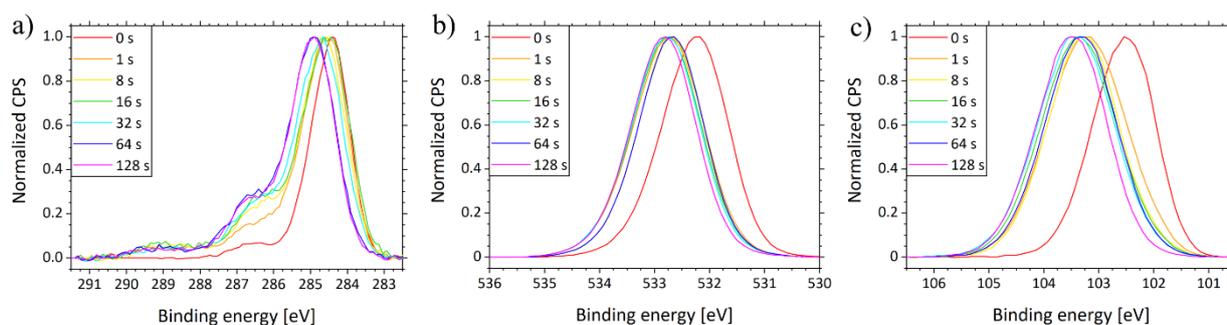


Figure 1 Comparison of a) C 1s, b) O 1s and c) Si 2p high-resolution core-level X-ray photoelectron spectra of untreated and plasma treated films

Figure 2 shows SEM images of untreated and plasma-treated coatings. The 16 s plasma-treated sample in **Figure 2c** begins to show patterning of the surface because of the interactions with the plasma. This patterning becomes more pronounced as the plasma exposure is prolonged. **Figure 2f** shows the sample treated for 128 s. The SEM image shows very sharp features of hills and valleys presumably caused by the etching of some areas on the surface of the film by plasma.

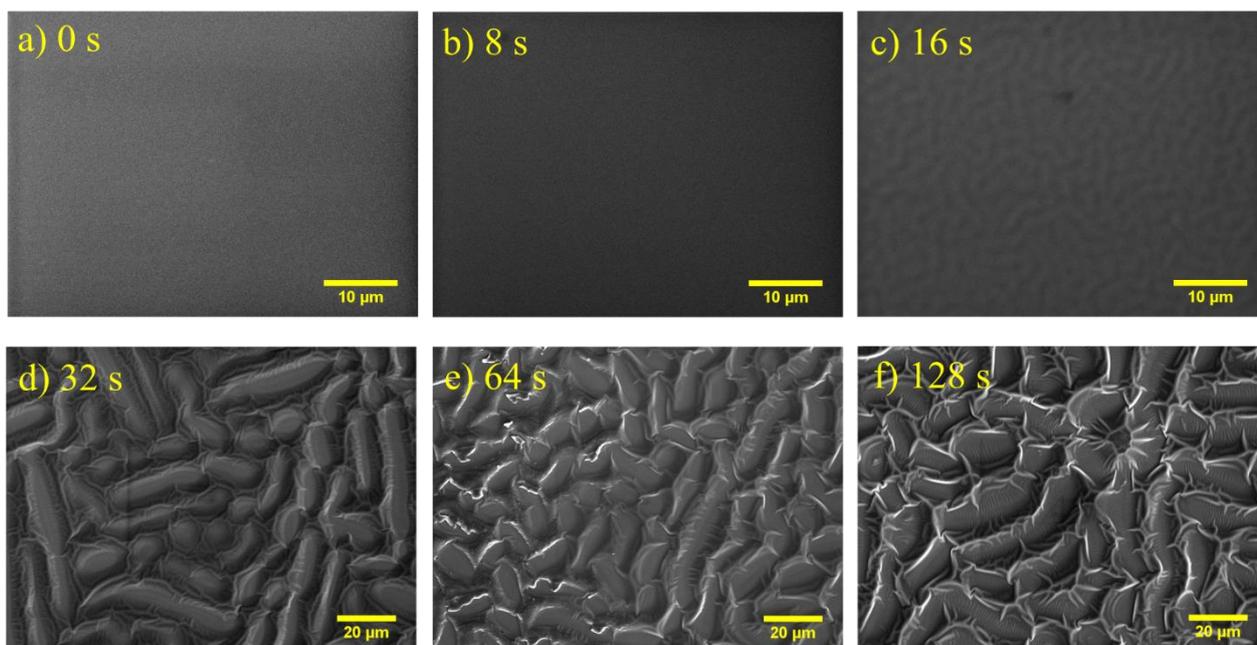


Figure 2 Images from scanning electron microscope of **a)** untreated and **b)-f)** plasma treated for 8-128 s. The **a)** untreated, **b)** 8 s and **c)** 16 s treated samples are magnified 5000 times. The **d)** 32 s, **e)** 64 s and **f)** 128 s treated samples are shown magnified 2000 times.

4. CONCLUSION

In this paper we report a detailed XPS study of an ultra-fast mineralization of polysiloxane coating by atmospheric pressure ambient air plasma. Energetic species from plasma react with the Si—CH₃ bonds on the surface transforming them into amorphous silica. The whole surface is converted after just one second of treatment. Prolonged exposure to plasma causes the mineralization to occur deeper in the film. It also causes etching resulting in patterning of the surface.

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