Photoinduced superhydrophilicity of amorphous TiO$_x$-like thin films by a simple room temperature sol-gel deposition and atmospheric plasma jet treatment.

V E Vrakatseli, E Pagonis, E Amanatides and D Mataras
University of Patras, Dept. of Chemical Engineering, Laboratory of Plasma Technology
E-mail: lefi@plasmatech.gr (Dr E. Amanatides)

Abstract. A room temperature sol gel process of TTIP / iPrOH / H$_2$O /HNO$_3$ sol was applied for the deposition of functional Ti alkoxide thin films on glass and polymeric substrates (PEEK). The unheated - amorphous films become superhydrophilic after 7 minutes of UV exposure which deteriorates after one day of storage in dark, exhibiting stable amphiphilic behavior. Superhydrophilicity is also obtained after 5 min of atmospheric pressure Ar - O$_2$ plasma jet treatment. As the plasma power and the oxygen content of the mixture of the treatment increase (70W, 3.2-5% O$_2$) the films high hydrophilicity is maintained for many days even in dark atmospheric conditions providing long term hydrophilic coatings.

1. Introduction
Titania (TiO$_2$) thin films have been extensively studied because of the unique properties of TiO$_2$ such as its photocatalytic activity and the photoinduced hydrophilicity. Since 1997 Wang et al.[1] discovered the ability of TiO$_2$ surfaces to alternate their wetting characteristics from hydrophobic or relatively hydrophilic to super hydrophilic under UV irradiation. Most of the research focused on the deposition of superhydrophilic TiO$_2$ thin films because of the great prospects for many new applications such as self-cleaning, antifogging and anti-ice surfaces. These applications are limited by the fact that TiO$_2$ hydrophilicity is not persistent in dark or under visible light illumination. An interesting related state of the art application for TiO$_2$ thin films is their use in microfluidic devices on polymeric substrates, where they could control fluid delivery without the need of external pumps or valves due to their amphiphilicity [2], [3] or simply act as hydrophilic fluid delivery channels [4] depending on the stability of hydrophilic films.

Much effort has been done on the in situ formation of the anatase structure since it is believed that the anatase crystal form is dominating in TiO$_2$ films exhibiting the best photocatalytic and hydrophilic functionality [5],[6]. However, anatase deposition and/or densification processes demand high
temperatures (> 300°C) [7], thus restricting their application to high temperature stable substrates. Plasma sputtering has been reported as a method for depositing TiO₂ thin films having high crystallinity in the anatase form also at low temperatures. [8], [9]. Nevertheless, plasma sputtering is an equipment demanding process with usually low deposition rates. On the other hand sol gel processes may be a cost effective tool for metal oxides thin film deposition at low temperatures although the as prepared films are amorphous and therefore a post deposition sintering process is needed to form anatase [10]. Yet another approach for the low temperature crystallization of amorphous TiO₂ is plasma treatment [11]. In this approach, Ar, N₂ and O₂ plasma treatments can be applied aiming to the enhancement of photocatalytic or hydrophilic properties of TiO₂ films [12]

Taking into account the limitations and opportunities described above, this work aims on room temperature deposition of TiOₓ-like thin films for application on glass and polymeric substrates, using a simple sol gel process, with no post deposition thermal annealing of the films. The thin films thus obtained are examined in terms of their photo induced hydrophilicity and stability before and after atmospheric Ar – O₂ plasma treatment, while the persistency of their wetting characteristics as they age in the dark is also recorded.

2. Experimental

2.1 Preparation of the solution and thin film deposition.

Titanium alkoxide thin films were deposited using the sol–gel spin coating technique at room temperature on microscope glass slides and on PEEK substrates (Goodfellow 0.038mm), using a Laurell WS-650S spin coater. Before the deposition process all the substrates were ultrasonically cleaned, then rinsed with distilled water and ethanol and dried with N₂ gas. Ti-alkoxide solutions were prepared by hydrolysis and condensation of Titanium tetraisopropoxide, Ti(OiPr)₄, (Sigma Aldrich 99.999%) while isopropanol (PENTA, 99.8%) was used as the solvent. Titanium isopropoxide is a highly reactive precursor thus it was first diluted in isopropanol while a second solution of 0.5 ml of 3d water and isopropanol was added rapidly to TTIP/iPrOH solution. After 10 min of magnetically stirring, 0.25 ml HNO₃ (Fisher Scientific, 70%) was added to the solution thus reaching a pH = 1 and then the solution was covered and magnetically stirred at 300 rpm for 1h at room temperature. Another 3 ml of H₂O was then added to the solution which was stirred for 10 minutes before deposition. The volume ratio of the final solution is iPrOH : TTIP : H₂O : HNO₃ = 140/9/3.5/0.25

The deposition of the films was performed using the prepared Ti- alkoxide transparent sol before complete gelation occurred, by applying 1 ml of the solution for every deposited layer for a total of 10 layers, with a two-step spinning at 400 rpm followed by 900 rpm. All the films were left to dry at atmospheric conditions at least for 24h and stored in dark until examined. No heat treatment was applied on the films.

2.2 Thin film characterization.

In order to evaluate photo induced hydrophilicity of the films, water contact angle measurements were taken as the samples were exposed to UV irradiation (Puritec UVC lamp G8T5/OF) with a wavelength centered at 254 nm and 0.2 W/m² (@1 m). The samples were placed 5 cm under the UV source, so the corresponding intensity of the UV irradiance which is calculated by Newton’s inverse square law equals 8 mW/cm². Water contact angle measurements were carried out using the Kruss DSA 100 goniometer with 2μl drops of 2D water carefully placed on the sample. WCA measurements were performed 24 h hours after the deposition, after the UV or plasma treatments and as the films were aging in the dark both for the
as deposited and treated films. Ambient temperature and humidity may affect the hydrophilicity and the contact angle conversion rate of the films [13]. The storage conditions remained stable during the experiments and aging with a mean temperature $T_{\text{a}}=25^\circ \text{C}$ and relative humidity $R_{\text{H}}=55\%$, so that the results can be comparable. The XRD spectra of as deposited and aged films were recorded using a Bruker, D8 Advance X-ray diffractometer, in the range of 20° to 70°. SEM images and EDX analysis were taken using a JEOL JSM-6300 microscope.

2.3 Plasma Treatment
All plasma treatments of the coatings were performed at atmospheric pressure using an RF plasma jet source of 1 mm in diameter operating at 13.56 MHz provided by the Low Temperature Plasma Laboratory, National Institute for Laser, Bucharest, Romania [14]. Atmospheric plasma treatments were applied for 5 minutes with a distance between plasma jet source to the sample of 2.2 cm and the Ar gas flow at 8.5 slm. The parameters examined were the oxygen content of the Ar-O$_2$ mixture and the plasma generator power (40, 50 and 70W).

3. Results
As confirmed by the X-ray diffraction pattern (fig. 1), the as deposited films are as it is expected, in an amorphous state since no thermal treatment was used. The sample was stored in dark atmospheric conditions ($T_{\text{a}} =25^\circ \text{C}, R_{\text{H}}=55\%$) for 4 months before the XRD spectra measurement and this ensures that possible hydrolysis due to the atmosphere’s water and/or solvent evaporation has been completed.

![Figure 1. XRD spectra of 4 months aged Ti alkoxide film](image1.png)

3.1 Surface morphology
Macroscopically, the as prepared films show good adherence and transparency, they are smooth and crack free, however SEM images revealed a few cracks on the films at the scale of some $\mu$m (Figure 2a). Figure 2b shows that some aggregates are entrapped in or refrained from the network of the TiOx film. These solid particles can be attributed to the vigorous hydrolysis of Ti(iOR)$_4$ and formation of amorphous TiO$_2$ or Ti(OH)$_4$ despite the low pH value of the solution [15-17]. The EDX analysis indicates a high concentration of Ti and O on the agglomerates and a lower concentration of Ti and O in the bulk of the film with a corresponding higher concentration in carbon. The presence of carbon is attributed to the
terminal –OR groups of the Ti alkoxide network. Even though, the results of the present work indicate that the films performance and durability is not influenced neither by the carbon content nor by the aggregates formed on the surface.

Figure 2. SEM images of the as deposited film a) 20μm, b) 10μm and c) Ar-O₂ plasma treated film(10μm)

3.2 UV induced superhydrophilicity.

Figure 3. Contact angles of Ti alkoxide films deposited on PEEK and glass substrates after multiple UV exposures and aging in dark and atmospheric conditions (25°C, RH=55%). First UV exposure referred as day 0, 2nd is 12 days later and 3rd is 20 days after the first one.

Thus, figure 3 show the dependence of the contact angle on UV irradiation time as well as the recovery of the contact angle when the untreated samples are stored in the dark in atmospheric conditions. In order to evaluate the stability of the films, we repeated the exposures on the same sample during 20 days. After every UV exposure the sample was stored in the dark and the recovery of the contact angle was measured.
Before the first UV exposure the contact angle of the films were 70° to 80° depending on the type of the substrate and the ageing of the materials (days after deposition). All TiOx films, both on glass or on PEEK substrates become superhydrophillic when exposed to UV irradiance, reaching a 0° contact angle within 7 minutes of exposure, no matter what was their initial CA. The superhydrophilicity is lost if the films are stored in dark and the water contact angle almost reaches its initial value 24h after the UV exposure. It is then shown that the photo induced hydrophilicity is not a property of crystalline TiO$_2$ exclusively, but UV induced changes occur on the amorphous TiOx network as well. Gao et al. [18] claimed that the photoinduced hydrophilicity of the amorphous TiO$_2$ is associated with the shift of Ti-OH bonds to Ti=O dangling bonds on the surface resulting in chemisorption of H$_2$O molecules. Other authors attribute the good UV hydrophilicity of amorphous porous TiO$_2$ in the higher specific area compared to the crystalline, resulting in a high density of oxygen bridging sites on the surface [19].

In our case, the unheated Ti alkoxide films were deposited from the Ti alkoxide sol in which the molecular hydrolysis ratio is H$_2$O/TTIP = 6.3. The network formed derives from hydrolytic and poly-condensation reactions:

$$\equiv \text{Ti} - \text{OR} + \text{H}_2\text{O} \rightarrow \equiv \text{Ti} - \text{OH} + \text{ROH} \quad (1)$$

$$\equiv \text{Ti} - \text{OH} + \text{RO} - \text{Ti} \equiv \rightarrow \equiv \text{Ti} - \text{O} - \text{Ti} \equiv + \text{ROH} \quad (2)$$

The hydrolysis ratio in this experiment does not permit the formation of a very high percentage of the oxide network. The terminating bonds of this expanding oxide polymer contain -OH and -OR groups. [20]. On the other hand, the morphology of the material (fig. 2 a,b) does not imply a porous structure. Therefore, the mechanism proposed by Gao et al. may be valid for this case as well. The photogenerated electrons break the O-H bond of the terminal Ti-OH groups resulting in the formation of Ti=O bonds which is unstable and is more likely to accept the H$_2$O molecules.

### 3.3 Atmospheric Pressure Plasma Treatments.

Furthermore, a superhydrophilic surface can also be obtained after the application of 5 min Ar–O$_2$ atmospheric plasma treatment on the films. All the treated films obtain a zero contact angle after the treatment at any plasma power level. Figure 4 shows the measured contact angles as the films are aging in dark after the treatments at different plasma power levels. All the films were treated with 3.2 % volume fraction O$_2$ in Ar for 5 min at a distance of 2.2 cm from the plasma source. Moderate plasma power of 40 and 50 W does not severely influence the films aging. When higher plasma power (70 W) is applied the hydrophilic character of the films is prolonged reaching a 42° contact angle only, after 35 days stored in the dark.

Figures 5a and 5b present the influence of the oxygen content of the Ar-O$_2$ mixture of plasma treatments at 70 W on the persistence of the hydrophilicity of TiOx films deposited on glass or on peek substrates. For this evaluation, mixtures with 1%, 3.2% and 5% O$_2$ were tested. When a higher content of oxygen (3.2%) and a relatively high plasma power (70 W) is applied, the films exhibit a considerably prolonged hydrophilicity under atmospheric dark conditions. Increase of oxygen content to 5% does not induce any further changes. The Ar treatment (fig. 5a) affects also the persistence of the films hydrophilicity. Ar ion bombardment may induce a higher roughness on the surface which could lead to an enhancement of the hydrophilicity according to wenzel’s law [21] and it will induce changes on the crosslinks of the polymeric part of the material. On the other hand atmospheric plasma contains highly reactive species of atmosphere’s oxygen which could partially oxidize the surface. The SEM image of 3.2% O$_2$ in Ar plasma treated surface (fig.2c) reveals also a significant change in the film morphology.
and more precisely an increase of roughness and the formation of grains. The formation of grains on the film surface may have a strong effect on the film surface properties, due to the larger real area and the density of defects than on the smooth surface [22].

**Figure 4.** Change of the contact angle of atmospheric Ar – 3.2% O₂ plasma treated (5 min, @ 22 mm) Ti alkoxide films on PEEK substrate with different plasma power (40 W -70 W), as they age in dark atmospheric conditions of the laboratory.

**Figure 5.** Change of water contact angles of untreated and atmospheric Ar - (0% -5%) O₂ plasma treated films at 70 W on a) glass and b) PEEK substrates as they age in dark atmospheric conditions.

On the other hand, in oxygen containing plasmas, the mixture of ions, oxygen atoms, oxygen metastables and ozone that reach the surface have higher probability to stick and cause further material oxidation [23]. Furthermore, oxygen plasma treatment is also an effective method for removal of organic moieties from metal oxide/polymer films [24] and thus an enhancement of the content of the amorphous metal oxide phase may be obtained. According to our results, activation of the surface’s superhydrophilicity by the atmospheric Ar – O₂ plasma can be attributed to the plasma produced UV irradiance, oxidation of the surface along with the removal of organic contaminants and creation of organic polar groups on the terminating -OR groups of the Ti alkoxide network. The stability of hydrophilicity in the dark may be a result of the synergistic effects of the Ar – O₂ plasma treatment attributed to oxidization on the films surface along with an increase of surface roughness. The formation
of oxygen adatoms will decompose H₂O molecules into two –OH groups more easily, and can result to resistance of the surface to further oxidation from the atmosphere [25]. Additionally, the higher surface roughness will also have a permanent effect on surface hydrophilicity.

3.4 Comparison of UV treatment versus atmospheric plasma treatment effect.

![Figure 6](image.png)

**Figure 6.** Ratio of the contact angle of UV treated (7 min) and Ar - 3.2% O₂ atmospheric plasma treated (5 min) TiOx films on PEEK substrate as they age in dark atmospheric conditions to their initial contact angle (CA₀) before the treatments. As DCA is defined the difference between the absolute values of the contact angles after a week and 11 days.

Figure 6 shows the difference of the persistence of TiOx films hydrophilicity under dark conditions of a sample that was exposed to UV irradiance for 7 min and a sample that was plasma treated (3.2% O₂ in Ar) for 5 min. The superhydrophilicity obtained due to atmospheric plasma treatment in less time than the UV treatment could be attributed either to an effect of increased UV intensity produced in plasma (>8 mW/cm²) or Nevertheless - as already shown in fig.3 - the UV exposed films regain almost their initial contact angle after some hours of storage in dark, exhibiting an amphiphilic behavior, while the plasma treated films maintain a high hydrophilicity for many days. This difference in the contact angle conversion rates of the two cases indicates that plasma oxygen species affect the films more permanently than the UV irradiation.

4. Conclusions

Transparent amorphous TiOx-like films were prepared via a simple sol gel process at room temperature allowing for the deposition on temperature sensitive substrates. The deposited films become super hydrophilic after a few minutes of UV irradiation exhibiting a similar behavior as that of the anatase TiO₂ and a reasonable recovery of the contact angle in dark. The coatings exhibit amphiphilicity which makes them suitable for many applications such as sensors or microfluidic valves. Atmospheric pressure plasma treatment of Ar-O₂ can be used on such surfaces not only for the hydrophilicity activation but it can also prolong the hydrophilicity of the coatings depending on the plasma parameters. Relatively high oxygen percentage in the plasma Ar – O₂ gas mixture and a moderate plasma power may activate the photo induced hydrophilicity phenomenon in a short time but also induces a more permanent modification of
the surface which prolongs the hydrophilic properties of the material even in the dark thus expanding its applicability.

Acknowledgements

Part of this work was co-financed by Hellenic Funds and by the European Regional Development Fund (ERDF) under the Hellenic National Strategic Reference Framework (NSRF) 2007-2013, of the Project “THALIS” DESIgn and fabrication of Robust supErhyDROPhobic/philic surfaces and their application in the realization of “smart” microfluidic valves”. The authors would like to gratefully acknowledge Prof. G. Dinescu and the group of Low Temperature Plasma Laboratory, National Institute for Laser, Bucharest, Romania for the Atmospheric Pressure Plasma Jet used in this study.

[1] Wang R, Hashimoto K, Fujishima A, Chikuni M, Kojima E, Kitamura A, Shimohigoshi M and Watanabe T 1997 Nature 388 431-433.
[2] Meng Z, Zhang X and Qin J 2013 Nanoscale 5 4687-4690
[3] Park H J, Kim I T, Park S H and Kim S K 2011 J. Micromech. Microeng. 21 095030
[4] Liu N, Li H, Wang H, Chena T, Wang J and Chang L 2012 Mat.Letter, 89 247–250
[5] Fujishima A, Rao T N and Tryk D A 2000 J. Photochem. Photobiol. C 1 1-21
[6] Liu Q J, Wu X H, and Wang B 2002 Mater Res Bul.l 37 2255-2262
[7] Ye Q., Liu P Y , Tang Z F and Zhai L 2007 Vacuum 81 Issue 5 627–63
[8] Musil J, Heřman D and Šícha J 2006 J. Vac. Sci. Technol. A 24 521
[9] Barnes M C, Kumar S, Green L., Hwang N M and Gerson A R 2005 Surf. Coat. Tech. 190 321–330
[10] Yu J, Zhao X and Zhao Q 2001 Mater. Chem. Phys. 69 25-29
[11] Ohsaki H, Shibayama Y, Suzuki M, Kinbara A, Yashiro H and Watanabe T 2008 Thin Solid Films 516 4490–4494
[12] Zhang K X, Wang W, Hou J L, Zhao J H, Zhang Y, Fang Y C 2011 Vacuum 85 990-993
[13] Simonsen M E, Li Z, Søgaard E G 2009 Appl. Surf. Sci. 255 8054–8062
[14] Ionita E R, Ionita M D, Stancu E C, Teodorescu M, Dinescu G 2009 Applied Surface Science 255 5448-5452
[15] Oskam G, Nellore A, R. Lee Penn, and Searson P C 2003 J.Phys.Chem. 107 (8).
[16] Vorkapic D and Matsoukas T, 1999, J. Colloid Interface Sci. 214 no. 2 283–291
[17] Galkina O L, Vinogradov V V, Agafonov A V and Vinogradov A V 2011 Int. J. Inorg. Chem. (8)
[18] GaO Y, Masuda Y and Kumoto K 2004 Langmuir 20 No. 8 3188-3194
[19] Sirghi L, Aoki T and Hatanaka Y 2002 Thin Solid Films 422 55-61
[20] Yoldas B E 1986 J. Materials sci. 21 1087-1092
[21] Wenzel R N 1949 J. Phys. Chem. 53 (9) 1466–1467
[22] L.Sirghi and Y.Hatanaka 2003 Surface Science 30 L323-L327
[23] Kim Y, Yoon C H, Kim K J, Lee Y 2007 J. Vac. Sci. Technol. A 25 1219
[24] Huang J, Ichinose I, Kunitake T and Nakao A 2002 Langmuir 18, No. 23
[25] Zhang K X, Wang W, Zhao J H, Hou J L, Zhang Y, Fang Y C 2012 Phys. Procedia 32 356 – 362