PHOTOCATALYTICALLY ACTIVE TITANIA PRODUCED BY MOCVD PLASMA PROCESSES

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Abstract

The deposition of photocatalytically active titania layers at ambient temperature was developed using the plasma enhanced metal organic chemical vapour deposition (PE-MOCVD) method at low and atmospheric pressure. An increase of the photo-activity in the near ultraviolet (UV) and blue light irradiation was achieved by doping the titania layers using the elements nitrogen and/or carbon.

Investigation of the chemical and structural features of the titania layers was carried out by x-ray photoelectron spectroscopy, atomic force microscopy, and Raman. The optical energy bandgap and photocatalytic activity at 365/428 nm for various titania layers were analyzed using ellipsometry and the methylene blue dye bleaching according to ISO 10678:2010, respectively. The reduction of the aqueous methylene blue solution was similar for the two categories of titania layers. However, the photo-induced properties such as the mineralization of stearic acid for investigating anti-fingerprint effects evidenced a weaker interaction between the mostly hydrophobic PE-MOCVD titania surfaces than for the hydrophilic and rougher PVD produced titania layers when irradiated under UV light.

The observed differences were related to the chemical and structural features since the hydrophobic PE-MOCVD produced titania layers were amorphous and nitrogen and carbon incorporation into TiO_2 led to an enhanced photocatalytic ability by a factor of two regarding the dye tests, whereas the energy bandgap remained at about 3.2 eV. Substitutional and interstitial doping of nitrogen and/or carbon was evidenced by XPS. An additional benefit regarding the adhesion and abrasion resistance was observed for the tailored doping of titania layers.

Results and Discussion

For heat or plasma sensitive substrates the deposition by the PE-MOCVD technique is advantageous. In addition, the deposition rate is increased up to 300 nm/min and to more than 1000 nm/min for processes carried out at atmospheric pressure [1]. As far as the titania layers produced by PE-MOCVD are concerned, the illumination under near UV at 365 nm and blue light at 428 nm exhibits a remarkable increase in the photo-activity if carbon and nitrogen were incorporated into the amorphous TiO_2 lattice according to the dye tests. Surprisingly, the optical energy bandgap and the refractive index were not affected strongly and varied only by ± 0.1 eV. However, the absorbance in the UV vis spectra is clearly red-shifted for the nitrogen-doped PE-MOCVD-N and nitrogen/carbon-doped PE-MOCVD-N/C samples, being responsible for the yellowish tint of some layers which is due to N_s-doping [2]. In Tab. 1, the optical properties and photo-activities of the titania layers produced by PE-MOCVD are summarised.

For all coatings, XPS data revealed the incorporation of carbon and nitrogen by forming O-Ti-NC sites at a binding energy of 287 eV for the C (1s) core level and 398.7 eV for the corresponding N

(1s) core level. The clearly distinctive additional peak at 284.2 eV is observed just for the co-doped layer and is tentatively assigned to interstitially integrated carbon (C_i) since the binding energy of graphitic carbon is typically in this region.

Table 1: Photocatalytic activity and optical properties of selected titania layers produced by PE-MOCVD at reduced and atmospheric pressure compared to a PVD TiO_2 layer and a commercial Pilkington sample.

Titania layer on Si (100) and glass	Thick-ness (*nm*)	Rough-ness[a] (*nm*)	Refractive index[a] *(633 nm)*	E_{gap}[a] (*eV*)	Photo-activity[b] *(μmol/m^{2}h)*	CIF[c] (*365 nm*)	CIF[c] *(428 nm)*
PE-MOCVD	230	1.1	1.79	3.48	4.5	4.5	1.3
PE-MOCVD-N	339	0.5	1.71	3.27	3.9	3.4	1.7
PE-MOCVD-C	276	0.9	1.76	3.33	6.4	7.0	2.2
PE-MOCVD-N/C	237	1.0	1.79	3.39	6.6	7.3	3.1
PE-MOCVD-AP[d]	200	n.a	n.a.	n.a.	3.1	2.6	1.7
PVD	200	3.4	2.18	3.29	5.4	4.9	1.3
Pilkington	30	n.a.	n.a.	n.a.	1.3	1.5	-

Remarks: [a] Roughness, refractive index and optical energy gap (E_{gap}) were analysed by ellipsometry; [b] photo-activity was measured according to ISO 10678:2010; [c] CIF (catalytic improvement factor); [d] PE-MOCVD-AP was produced at atmospheric pressure

For all deposition processes, nitrogen was entering the partly or completely amorphous TiO_2 lattice and substituting an oxygen site (N_s at 396 eV) or stationing itself interstitially (N_i at 400 eV) [2]. Nitrogen was substituting the oxygen site in the TiO_2 network to a larger extend than carbon did. As a result, the N_s concentration reached up to 9.6 at% and nitrogen reacted also with carbon and formed Ti-NC sites.

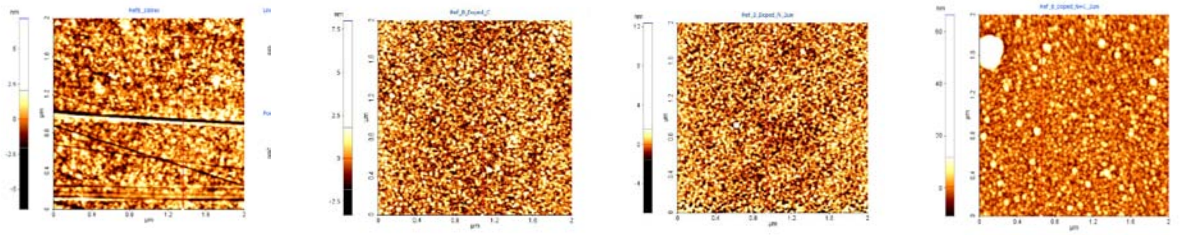
Despite the fact that predominant N_s incorporation is observed for all produced titania thin films, the different insertion of the doping elements, their combination possibilities, and the resulting formation of oxygen vacancies contributes in a complex way to the observed photo-induced properties. However, a higher concentration of N_i and N_s seems to be necessary to affect the functional properties of our amorphous titania layers than the concentration of 0.1 at% for N_i in anatase TiO_2 as explored by Dunnill [3].

Table 2: Photo mineralization of stearic acid (UV and blue light), roughness, water contact angle, surface energy, the inactivation and attachment of E. coli of selected PVD and PE-MOCVD produced titania layers.

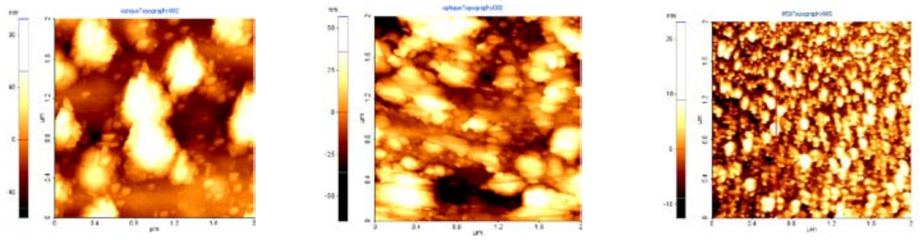
Titania layer on Si(100) / glass	Stearic acid *(mmol/h @ 365 nm)*	Stearic acid *(mmol/h @ 428 nm)*	WCA[a] *(°)*	Surface energy[b] *(mN/m)*	Ra[c] *(nm)*	Antibacterial[d] *(inactivation/ removal)*	Color[e] *(visual)*
PE-MOCVD	0.1	0.03	62	47.4	0.6	good	yellowish tint
PE-MOCVD-N	0.1	n.a.	60	40.8	0.6	excellent	yellowish tint
PE-MOCVD-C	0.1	n.a.	63	40.7	0.8	excellent	yellowish
PE-MOCVD-N/C	0.5	0.02	86	36.5	1.9	excellent	transparent
PE-MOCVD-AP	2.9/0.1	n.a.	48/66	50/43	28/12	n.a.	transparent
PVD	4.8	0.08	4	76.0	3.6	good	transparent

Remarks: a : Water contact angles (WCA) were after exposure to UV radiation for 24 hours
b: The surface energy was analysed after radiation with UV light at 365 nm for 24 hours
c: The roughness Ra was investigated using atomic force microscopy Park System XE-100 in non contacting mode
d: The inactivation and attachment of E. coli were analysed by applying several methods
e: The colour of the titania layers were compared by visual inspection

The surface topography of the TiO_2-layers was investigated using atomic force microscopy AFM in the non contacting mode and is presented in Figure 1. An area of 2 μm x 2 μm was scanned for all titania layers in order to compare the grain sizes and roughnesses (Tab. 2). Titania coatings produced at atmospheric pressure and PVD-TiO_2 are rougher and show a more open surface than PE-MOCVD TiO_2 layers whose roughness is typically < 1 nm.



a) PE-MOCVD b) PE-MOCVD-N c) PE-MOCVD-C d) PE-MOCVD-N/C



e) PE-MOCVD-AP f) PE-MOCVD-AP’ g) PVD

Fig. 1: AFM images (2 μm x 2 μm) of the titania layers with a thickness of about 200 nm; e) thickness of 100 nm; f) thickness of 200 nm

Conclusions

Collectively, the PE-MOCVD thin films are Raman amorphous, hydrophobic, and show smooth and closed surface topographies. All PE-MOCVD titania coatings deposited at ambient temperature exhibit a high photocatalytic activity in bleaching the aqueous methylene blue solution when irradiated under near UV (365 nm) and blue light (428 nm). The response to the UV/vis irradiation is improved by incorporation the non-metallic elements nitrogen and/or carbon into the titania lattice. The most photo-active titania layer for reducing methylene blue is the transparent co-doped PE-MOCVD-N/C layer.

The mechanical removal of the deposited stearic acid was straight forward for the hydrophobic and smooth PE-MOCVD surfaces. The reaction of the hydrophobic PE-MOCVD produced TiO_2 layers with the stearic acid is weaker than for the PVS-layer when irradiated under UV light. However, the PE-MOCVD and PVD titania layer showed similar reaction ability towards stearic acid when irradiated with blue light, while the characteristic attachment of the stearic acid is independent of the illumination. Furthermore, E. coli inactivation and/or removal is more efficient for the PE-MOCVD than for the rougher and hydrophilic PVD titania surface.

For the amorphous PE-MOCVD-N/C titania layer, XPS data reveal concentrations of 6.1 at% and 2.1 at% for substitutional N_s and C_s, respectively and 1.4 at% and 2.1 at% for interstitial N_i and C_i, respectively. The substitution of oxygen sites due to the formation of Ti-NC-like species (1.9 at%) is also observed. The non-doped titania PVD layer consists of > 50 % anatase grains embedded in the amorphous matrix and is superhydrophilic.

PE-MOCVD-AP titania layers produced at atmospheric pressure show a slightly reduced photo-activity compared to the coatings deposited at reduced pressure. However, their functional features combine nicely the advantages of the above described hydrophilic PVD TiO_2 layer and the PE-MOCVD titania thin films produced at low pressure.

It can be concluded that TiO_2 layers produced by plasma deposition techniques at ambient temperature operate as a photocatalyst and respond to the illumination under near UV and visible light which proves them to be a potential candidate for a wider application field since many white/visible light sources do have a minimal UV component. The observed different photo-induced features such as antimicrobial, anti-fingerprint, easy-to-clean, and self-cleaning effects enable to tailoring the manufacture of the titania layers towards the demanded specifications of the product.

References

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