Effect of plasma conditions on growth of photocatalytic TiO_2 layers using pulse magnetron sputtering and plasma-activated evaporation

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Abstract
Crystalline TiO_2 thin films, especially layers with predominantly anatase phase, exhibit photocatalytic effects resulting in hydrophilic, self-cleaning and antifogging properties. In this paper, a comparison of the photocatalytic properties of layers deposited with two different PVD techniques is given: reactive pulse magnetron sputtering (dynamic deposition rate: 8…50 nm·m/min) and reactive electron beam evaporation (dynamic deposition rate: 500…1000 nm·m/min). Plasma impact was adjusted by changing pulse parameters and by applying an additional spotless arc discharge (Spotless arc Activated Deposition - SAD-process), respectively.

Characterization of layer properties
The structure of the films was characterized by X-ray diffraction using Cu Kα radiation and grazing angle of incidence of 1°. The photoinduced hydrophilicity of the films was investigated by measuring the contact angle of water after irradiation with ultraviolet light (P_{UV-A}=1 mW/cm^2). Photocatalytic decomposition of organic matter was evaluated by measuring decolouration of a solution containing methylene blue organic dye (MB). Bioactivity was examined by the example of algae and bacteria for an assortment of samples. Those results will be reported in a poster filed for presentation at this workshop [1].

Pulse Magnetron Sputtering (PMS)
A reactive PMS system allowing to change the pulse mode (unipolar, bipolar or pulse packet) and the duty cycle has been used for the sputter deposition of TiO_2 films [2…4]. This system consists of two flange mounted magnetrons (target: Ti), a switching unit (UBS-C2) to generate the pulse powering, gas control devices and a process management computer for complete automatic control. The reactive gas control loop using the optical emission of the Ti line (500 nm) allows to stabilize the sputtering process at a reactive working point in the transition mode between the metallic and the reactive sputter mode.
The total pressure had been kept constant at 0.7 Pa. Substrate material was float glass (thickness: 3 mm). The maximum temperatures of the substrates were between 130 °C and 240 °C for all the experiments, i.e. significantly below the annealing temperature necessary to obtain crystallization of amorphous TiO_2 films.
By changing the pulse mode the substrate bombardment by energetic plasma particles can be adjusted [5]. Based on layer thickness the unipolar pulse mode resulting in relatively low plasma impact whereas bipolar pulse mode and pulse packet mode resulting in a medium plasma impact (factor 2 in comparison to unipolar derived from thermal substrate load). Further investigations were carried out by choosing a more reactive working point. Thus, a very high plasma impact was achieved (factor 10 in comparison to unipolar in transition mode).

Plasma impact	Low: 1	Medium: 2	High: 10
Pulse mode	Unipolar	Bipolar / Pulse Packet	Pulse Packet
Dynamic deposition rate	51 nm*m/min	47 nm*m/min	8 nm*m/min
Layer thickness	500 nm	500 nm	47 nm, 85 nm and 170 nm

XRD investigation showed significant higher peak intensities of anatase and rutile phase for layers deposited in pulse packet mode and bipolar mode than for layers deposited in the unipolar pulse mode. This can be explained by higher crystallinity and lower defect densities.
The photoinduced decrease of water contact angle is shown in Figure 1. Layers deposited using medium plasma impact in the bipolar pulse mode and pulse packet mode show highest activity reaching super hydrophilic state (water contact angle <10°) after irradiation time of only 30 min. In contrast, unipolar deposited layers (low plasma impact) have a smaller activity, not reaching super hydrophilic state after 6 h irradiation. The MB decomposition behaves accordingly for these films. The lower activity corresponds to a lower crystallinity indicated by a significantly lower intensity of anatase and rutile XRD peaks.
All thin layers deposited using high plasma impact exhibit super hydrophilic behaviour after irradiation time of 5 h in maximum. Among these films highest activity was achieved for the 170 nm thick layer, which shows similar good performance than the 500 nm thick layers deposited using medium plasma density. One important result is that we observed super-wettability even for the thinnest layer although we could not prove crystallinity by XRD. We assume that a thin crystalline surface layer might be the cause for this behaviour. The maximum substrate temperature during deposition of this layer was 130 °C, only.
A further very interesting result was obtained by investigating the properties of post annealed amorphous layers that contain anatase only. Their crystallinity is higher than that of in situ crystalline deposited layers, indicated by higher peak intensity in XRD investigation. Nevertheless, these post annealed layers showed a considerably lower MB decomposition ability and slower decrease of water contact angle. This might be caused by the significantly lower roughness of the films. Further investigations are in progress.

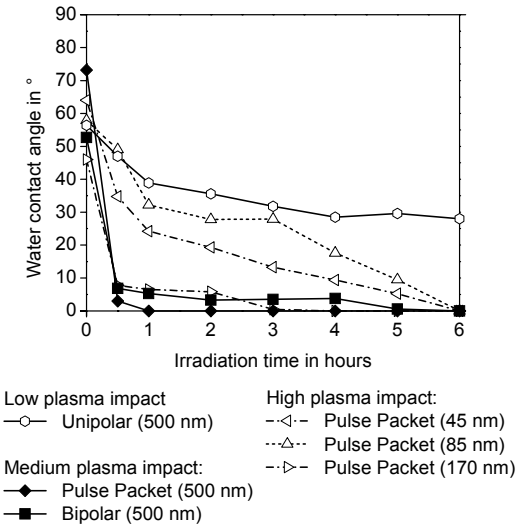

Figure 1: Decrease of the water contact angle for pulse magnetron sputtered TiO_2 layers

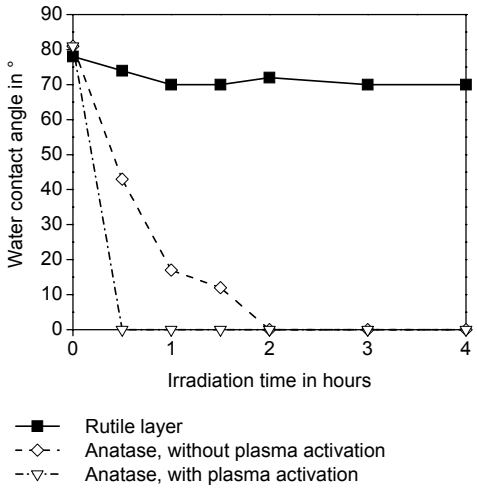

Figure 2: Decrease of water contact angle for layers deposited by evaporation with and without plasma activation

Plasma activated electron beam deposition (SAD)

Pure titanium was evaporated by a high voltage electron beam using an axial electron gun. Oxygen was introduced near to the substrate. Plasma activation was done by a spotless cathodic arc (Spotless arc Activated Deposition – SAD). Details to the SAD process can be found in previous publications [6, 7].

TiO_2 layers with thickness between 350 and 500 nm were deposited with a deposition rate in the range of 40 to 70 nm/s (dynamic deposition rate: 500…1000 nm·m/min). The layers were deposited on stainless steel sheets of grade X5CrNi18.10 (sheet 500 mm x 620 mm, thickness 1 mm). The maximum substrate temperatures were between 200 °C and 400 °C for all substrates.

With plasma activation the oxygen pressure influences the formation of anatase or rutile phase. At low oxygen pressure of 0.06 Pa layers contains only the thermodynamic stable rutile phase. By increasing the oxygen pressure the anatase proportion is raised and at oxygen pressure of 0.12 Pa the layer practically completely consists of anatase phase.

Layers with rutile phase maintains under UV irradiation a contact angle of about 70° and exhibited no decomposition of MB. Anatase and anatase-rutile layers show also a contact angle of 70° after storage in darkness, which is decreased <10° (super wettability), if the sample were irradiated by UV for a short time of 30 to 120 min (Figure 2). Layers, which consist completely of anatase phase, show a faster drop of the contact angle and faster decomposition of MB than anatase-rutile layers.

Films deposited with plasma activation exhibit faster UV-activation and longer sustainment in darkness of photo-induced superhydrophilicity. Moreover the MB decomposition occurred faster for these films. The observed larger TiO_2 grain size compared to films deposited without plasma activation might be the reason for this behavior.

Conclusions

In the present work the effect of plasma conditions on the photocatalytic properties of TiO_2 layers was investigated for pulse magnetron sputtering and plasma activated evaporation. Crystalline layers with anatase or rutile phase could be obtained at substrate temperatures significantly below the annealing temperature necessary for crystallisation of amorphous TiO_2 layers. Layers which contain a significant amount of the anatase phase show better photoinduced superhydrophilicity than layers containing the rutile phase, only. PMS and plasma activated evaporation allow to deposit layers with similar photocatalytic properties.

PMS technique allows to achieve very uniform layer thickness across extended substrates at high deposition rate (dynamic: 8…50 nm·m/min per double magnetron system or stationary: 0.3…3 nm/s). With this technique in situ crystalline deposited layers could be obtained that show a considerably higher photocatalytic activity and stronger decrease of water contact angle compared to post annealed amorphous layers. By adjusting the process parameters at high plasma impact it is possible to achieve thin films (<50 nm) with sufficient photocatalytic activity for various applications. Due to the low substrate temperature (<130 °C) the coating of plastic materials like polycarbonate (PC) and polyethylene terephthalate (PET) is now possible.

With plasma activated reactive evaporation crystalline TiO_2 layers could be deposited with extreme high deposition rates between 40 and 70 nm/s. The anatase layers show promising photoinduced superhydrophilicity and MB decomposition. Therefore the SAD process enables the coating of large areas well suited for applications as self-cleaning or antifogging coatings.

References

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