

HIGHLY ACTIVE PHOTOCATALYTIC COATINGS FOR TEMPERATURE SENSITIVE SUBSTRATES BASED ON TITANIUM OXIDE AND ZINC OXIDE PREPARED BY ATMOSPHERIC PRESSURE PECVD AND SOL-GEL DEPOSITION

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Abstract

In our investigations we prepared two different kinds of oxide coatings aiming for highly active photocatalytic properties and moreover deposition conditions, which could make them useful potentially also for temperature sensitive substrate materials. The first ones are titanium oxide thin films created by PECVD under atmospheric pressure conditions, Secondly, zinc oxide coatings were created by sol-gel technique via dip-coating. Investigations on the morphology (SEM), layer thickness (profilometry), and photocatalytic properties (decomposition of stearic acid after irradiation) were conducted. The results show the possibility to obtain layers with photocatalytic properties comparable with commercially available products even without any additional substrate heating during the plasma deposition or a thermal post treatment. However, thermal post annealing at 450 °C or flash lamp annealing can further improve this photocatalytic effect. Furthermore, first experiments showed that these coatings possess strong antimicrobial properties (towards bacteria and fungi).

Keywords: Atmospheric pressure PECVD, sol-gel deposition, photocatalytic thin films, antimicrobial properties, titanium oxide, zinc oxide, temperature sensitive materials

1. INTRODUCTION

Semiconductors, including TiO₂, ZnO, WO₃ and ZnS have been intensively investigated for solar applications [1]. Especially TiO₂ is of great interest due to many unique properties. The high refractive index of TiO₂ is suitable in optoelectronics for optical waveguides or antireflective coatings [2]. Other investigations were performed to optimize the high dielectric constant for e.g. memory cell capacitors [3] or linked to the high photocatalytic properties [4]. Zinc oxide (ZnO) is another available and inexpensive material of interest, because it shows also high photocatalytic and antimicrobial activity [5]. TiO_x or ZnO thin films can be deposited by a variety of methods including chemical vapor deposition [6], sputtering [7], sol-gel [8] and others. However, CVD processes usually operate at higher substrate temperatures (e.g. 250 °C [9]) to obtain films with photocatalytic activity. Applying sol-gel processes, a thermal curing step at elevated temperatures (~450 °C [10]) is often necessary. Therefore, film deposition on temperature sensitive materials such as plastics, wood or textiles is not possible.

In this work, films were created by use of a plasma jet (TiO_x) and sol-gel technology (ZnO) on glass without additional heating of the substrate during film deposition. To further improve the photocatalytic activity of the as-deposited films, on the one hand a thermal post-treatment (at ~450 °C) can be applied. However, this step is not suitable for temperature sensitive materials. On the other hand, film properties could be improved by flash lamp annealing, whereby this post-treatment method can be applied on temperature sensitive materials. Furthermore, another improvement of photocatalytic properties could be achieved by the incorporation of silver into the plasma-jet deposited TiO_x thin films [11]. This can lead to an increased activity even in the visible light spectral range. Moreover, silver shows high antimicrobial efficiency [12]. Hence, a combination of an improved photocatalytic activity and an improved antimicrobial effect could be achieved.

2. MATERIALS AND METHODS

2.1. Film deposition

Centrepiece of the used plasma deposition set-up is a blown arc device commercialized by Tigres GmbH (Marschacht, Germany) under its brand name CAT600. This device operates at power values from 50 to 600 W. For our investigations, this value was fixed at 600 W. In first experiments, we used air and nitrogen as working gases. However, the use of air leads to the formation of visual more powdery films with low mechanical resistance. This was determined by comparison of film thickness before and after abrasion resistance test. Hence, nitrogen was used for all film deposition procedures depicted in the following paragraphs. TIPO (titanium (IV) diisopropoxide bis(acetylacetonate), 75 wt.% in isopropanol, Sigma Aldrich) was used as titanium-organic starting precursor to form TiO_x films. Since this chemical compound is liquid at room temperature, the flow rate towards the plasma unit was controlled by a peristaltic pump and was set constant at a rate of 25 μl·min⁻¹. Additionally, silver nitrate Ag(NO₃)₂ solutions with 0.5 wt% Ag were introduced together with the TIPO using liquid flow rates of 0, 10, 20 or 40 μl·min⁻¹. The nebulization of the precursor took place by use of an atomizing system (patent EP2743373B1 [13]), which was also operating with nitrogen and furthermore, nitrogen was used as well as carrier gas to transport the aerosol to the plasma. Substrates were placed on a computer-controlled moving stage and were moved relatively to the plasma torch with a velocity of 250 mm·s⁻¹. In order to realize areal coatings this x-y-positioning system performed a meandering movement with a line distance of 1 mm. Overall 40 deposition runs were carried out to successively grow the thin layer.

In order to create ZnO thin films on glass slides a sol-gel dip-coating method was used. Sols with different Zn²⁺ concentrations of 0.1 M, 0.3 M and 0.5 M were prepared by dissolving zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] into 100 ml of isopropanol (80 °C). After addition of zinc acetate to the isopropanol a white and murky dispersion was created. Monoethanolamine (molar ratio Zn²⁺ to monoethanolamine: 1:1) was added drop-wise to the sol and a clear and transparent solution was achieved. The sol was then stirred at 80 °C for about 2 h to accelerate the hydrolysis reaction. After this step the sol was allowed to cool down to room temperature and aged for at least 24 h. Dip-coating was performed at a withdrawal speed of 100 mm·min⁻¹ to create ZnO films on the substrate materials. In order to evaporate the solvent and cure the films substrates were stored at 80 °C for 24 h.

2.2. Characterization

Film thickness determination was carried out using a surface profilometer Alpha-Step D-600 (KLA Tencor, Milpitas, USA) with a scan length of 2000 μm. To get the step height, the substrates were prepared with a dissolving material. After deposition procedure this material could be easily dissolved in Isopropanol. Scanning electron microscopy (SEM) was performed with a Supra 55 VP (Carl Zeiss NTS GmbH, Oberkochen, Germany) using the inlense detector and an operating voltage of 5 kV in order to analyse the thin film morphology. Photocatalytic activities were evaluated by the observation of the degradation of stearic acid using FT-IR transmission spectra collected by a MB3000 FT-IR spectrometer (ABB, Zurich, Switzerland) in the spectral range of 2000 cm⁻¹ to 4000 cm⁻¹ with a resolution of 2 cm⁻¹. Stearic acid deposition on the films took place in a vacuum chamber by thermal evaporation. This preparation procedure has led to approximately 100 nm thick stearic acid films. After this, the samples were stored under dark conditions and then exposed to a daylight lamp (Ultra-VITALUX® sun lamp, OSRAM) placed 250 mm above for 3 hours. After 30, 60, 120 and 180 min of exposure FT-IR measurements of the CH₃ and CH₂ stretching mode peak areas were performed. The photocatalytic activity of TiO_x films deposited by use of the atmospheric plasma jet and ZnO sol-gel dip-coating was compared with the activity of commercially available photocatalytic glass. CFU microbial cell viability assay tests were performed to evaluate the antibacterial properties of coated glass surfaces. In these tests, the antibacterial effect of the coatings on the non-pathogenic gram-negative bacteria *Escherichia coli* HB 101 was determined. For the tests, glass discs (Ø = 14 mm) were immersed in 500 μl of a bacteria suspension (about 2 × 10⁶ cells·ml⁻¹) in physiological saline (0.9 % (w/v)) and incubated for 3 h. Subsequently,

volume parts of 100 μl of each tested suspension were diluted 10-fold, 100-fold, 1000-fold and 10000-fold and 30 μl of each dilution was inoculated on agar plates and cultivated for 18 h at 37 $^{\circ}\text{C}$. A more detailed description can be found elsewhere [12].

3. RESULTS

3.1. Layer properties

Film thicknesses of the TiO_x films deposited by atmospheric pressure PECVD were in the range of 118 ± 8 nm. ZnO films created by sol-gel dip-coating had thicknesses of 30 ± 3 nm, 68 ± 4 nm and 93 ± 6 nm using the 0.1 M, 0.3 M or 0.5 M Zn^{2+} sol concentrations, respectively. **Figure 1** shows the SEM images of TiO_x deposited by atmospheric plasma jet and ZnO films prepared by sol-gel dip-coating procedure (0.3 M Zn^{2+} concentration). The cross-sectional view of the TiO_x films is given and indicated by (a). TiO_x films appear porous and homogenous with a columnar-like structure. However, also larger particles and agglomerates can be seen. Agglomerate sizes can reach up to ~ 200 nm. Such a cauliflower-like structure is indicative of a mass-transport limited regime due to fast depletion of the precursor in the plasma. The fast depletion of the precursor led to the formation of clusters. These clusters can either form the thin film or agglomerate in the gas phase and form larger agglomerates, which were attached to the thin film surface. SEM cross-sectional images (b) suggest that ZnO films were formed by packing of ZnO granules. Furthermore, the films appear porous but very homogeneously without large particles or agglomerates on the surface.

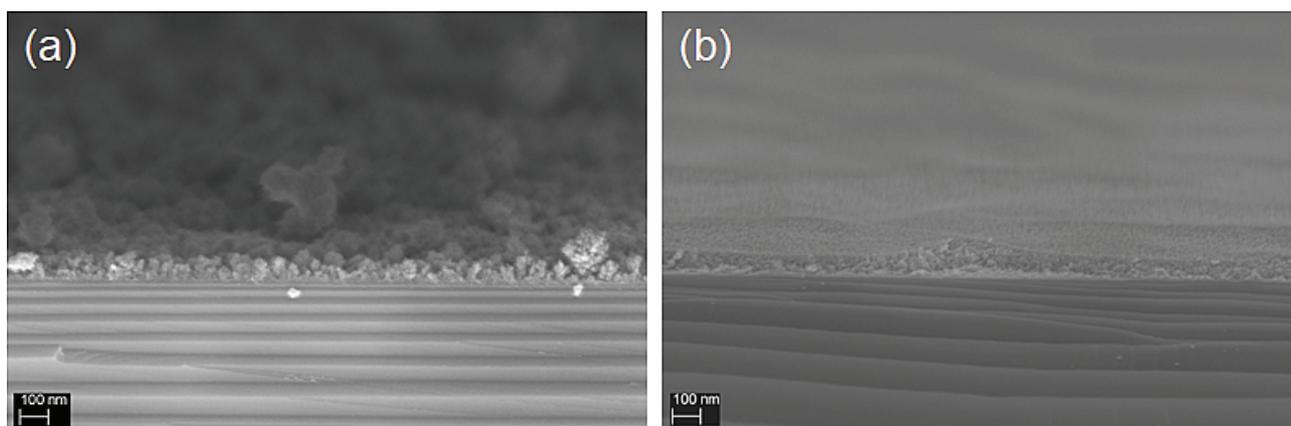


Figure 1 Cross-sectional SEM images of (a) TiO_x films deposited by atmospheric pressure PECVD and (b) ZnO films deposited by sol-gel dip-coating (0.3 M Zn^{2+} sol concentration)

3.2. Photocatalytic activity

The photocatalytic response of TiO_x and ZnO films were investigated by the photodegradation of stearic acid under daylight lamp irradiation. The photocatalytic effect was compared with the effect of a commercially available photoactive glass. From **Figure 2** it is obvious that no photodegradation of the stearic acid occurs on substrates without an active film (Glass (reference)). As-deposited films are depicted on the left-hand side (**Figure 2 (a)**). With increasing the Zn^{2+} of the sol from 0.1 M, to 0.3 M and 0.5 M and therewith the film thickness, the starting CH_3 and CH_2 peak area could be reduced to ~ 80 %, ~ 65 % and ~ 55 % after 3 h irradiation, respectively. One possible explanation for this behaviour could be an increasing total surface area of the porous film with increasing film thickness. A decrease of the stearic acid peak area to ~ 53 % was achieved by the photocatalytic glass and hence, the photodegradation effect is comparable with the effect of ZnO thin films created by sol-gel dip-coating using the 0.5 M concentration. Compared to this, the photocatalytic effect of the TiO_x films deposited by atmospheric pressure PECVD were in general higher with a stearic acid peak area reduction to ~ 30 % for undoped films. By doping of the TiO_x films with silver using

silver nitrate solution flow rates of 10, 20 and 40 $\mu\text{l}\cdot\text{min}^{-1}$ additional to the TIPO precursor the photocatalytic effect could be improved and peak area reductions to $\sim 19\%$, $\sim 3\%$ and $\sim 15\%$ could be achieved, respectively. The best effect could be obtained using a flow rate of 20 $\mu\text{l}\cdot\text{min}^{-1}$. Experiments showed that the addition of silver can help to increase the photocatalytic effect. From literature [11] it is known that the presence of Ag^+ ions can separate the electron hole pairs by attracting the conduction band electrons and recombination is avoided. Thus, the photogenerated holes in the valence band are free to react with electron acceptors such as oxygen creating oxygen radicals [15]. With increasing the silver loading of the TiO_x films by using flow rates of 40 $\mu\text{l}\cdot\text{min}^{-1}$ the photocatalytic effect became weaker compared to films created using flow rates of 10 or 20 $\mu\text{l}\cdot\text{min}^{-1}$. This could be caused by differences in the total surface area exposed to the irradiation. With increasing the silver content a partial occupancy of the reactive titanium oxide sides by silver could be possible. So, there could be a competition between the Ag^+ synergetic effect and the presence of Ag catalyst agglomerates on the titania surface. These agglomerates shouldn't have any degradation effect on the stearic acid and could act as a barrier.

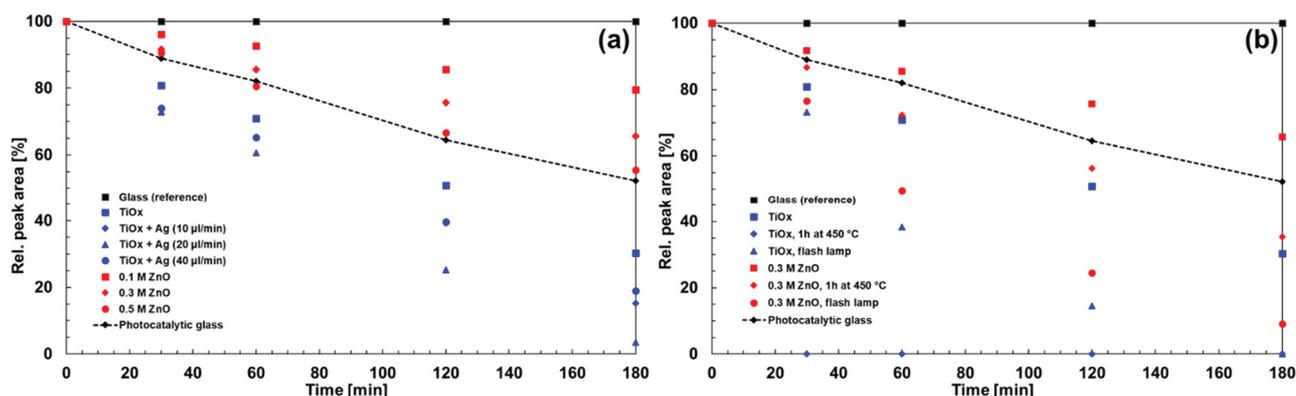


Figure 2 Stearic acid degradation: Relative band area (band area of CH_2 and CH_3 stretching vibrations from stearic acid) vs. irradiation time of as-deposited thin films (a) and post-treated thin films (b)

To improve the photocatalytic effects of TiO_x or ZnO thin films it is also possible to connect the film deposition procedure with a post-treatment step. Films were heat treated in a furnace for 1 h at 450 °C under ambient atmospheric conditions or by flash lamp annealing using a DTF-FLA-D100PA from DTF Technology Dresden (one pulse, millisecond duration) under nitrogen atmosphere. Results of stearic acid degradation tests are shown in **Figure 2 (b)**. After heat treatment the ZnO thin films showed a significantly increased photocatalytic effect and stearic acid band areas were reduced to 35 % after 3 h irradiation. An even better effect was achieved after flash lamp annealing and the stearic acid peak was reduced to 9 % after 3 h. The flash lamp annealing in terms of photocatalytic effect was also beneficial for TiO_x thin films deposited by use of the atmospheric pressure plasma jet. Whereas only a reduction to 30 % of the stearic acid band area was observable after 3 h irradiation for the as-deposited films, no stearic acid was detectable after 3 h for the flash lamp annealed films. The highest improvement of the photocatalytic effect was achieved by conventional heat treatment and no stearic acid could be detected already after 30 min irradiation. However, the conventional heat treatment is not suitable for temperature sensitive materials.

3.3. Antimicrobial properties

The antimicrobial test (CFU) results are shown in **Figure 3**. Among all tested films, the ZnO thin films deposited by sol-gel dip-coating showed the strongest antimicrobial effect, independent of the used Zn^{2+} sol concentration. No CFU could be found on the Agar plates after the 18 h cultivation step (exemplarily shown for ZnO film deposited by use of 0.3 M Zn^{2+} concentration), which means a reduction in bacterial growth of at least log 4 is achieved. The as-deposited TiO_x films showed an inhibitory effect towards the bacteria and the

total number of CFU was reduced to ~60 % with respect to uncoated glass. By addition of silver to the TiO_x films an increased bactericidal effect was achieved and CFU was reduced to ~52 %, ~43 % and ~1 % using Ag solution flow rates of 10, 20 and 40 µl·min⁻¹, respectively. So a clear increase of the antimicrobial behaviour with increasing silver concentration could be detected.

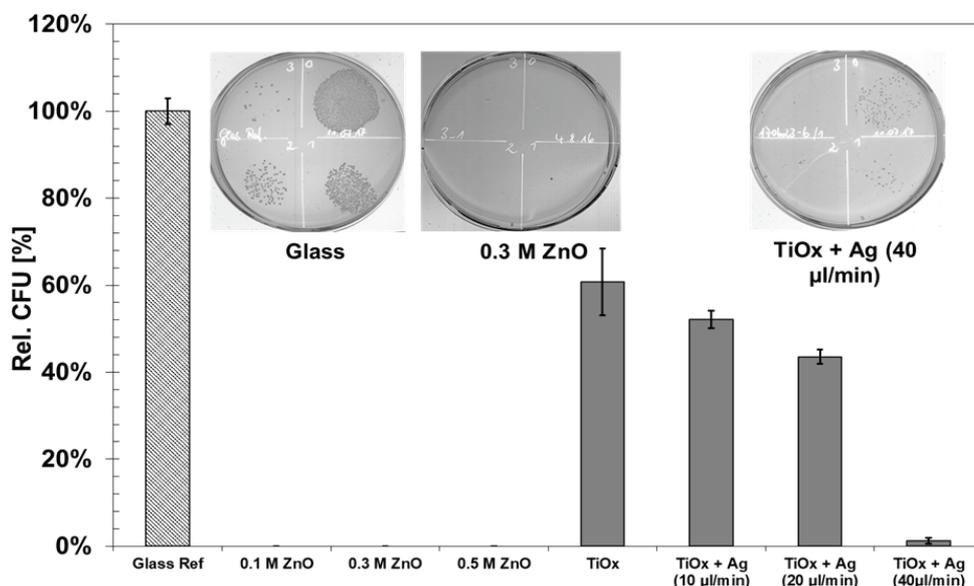


Figure 3 Colony-forming unit (CFU) test results including agar plates for uncoated, ZnO film sol-gel dip-coated and TiO_x films containing silver deposited by plasma jet on glass

In first experiments on temperature sensitive wood materials these ZnO coatings showed also improved resistance of the substrates towards mould fungi (*Aspergillus niger*, *Paecilomyces variotii*, *Penicillium funiculosum*, *Trichoderma viride*). This will be investigated in more detail by further experiments.

4. CONCLUSION

Aim of this study was to create thin films with beneficial photocatalytic and antimicrobial properties under atmospheric pressure and at low (< 100 °C) temperatures. Undoped TiO_x and ZnO films could be successfully deposited by an atmospheric pressure PECVD process using a plasma jet and a sol-gel dip-coating method on glass slides, respectively. Additionally, TiO_x could be doped with silver to further improve these properties. The as-deposited films were also post-treated either by a conventional furnace annealing at 450 °C or - with view on temperature sensitive substrates - by flash lamp annealing. SEM investigations exhibit a columnar-like growth structure of the plasma jet deposited TiO_x films. Contrary, the ZnO films were more flat and composed of a package of ZnO granules. Both films appear porous whereby this characteristic is desired for photocatalytic applications. Stearic acid degradation tests showed the possibility to create films with favourable photodegradation properties even in the as-deposited condition. With increasing the Zn²⁺ concentration of the ZnO sol the film thickness and photocatalytic effect increased. The TiO_x thin films showed in general higher photocatalytic degradation than the ZnO films. This strong effect could be further improved by Ag-doping, whereby the highest effect was achieved using Ag solution flow rates of 20 µl·min⁻¹. Photodegradation properties of ZnO were also improved by heat treatment at 450 °C and flash lamp annealing, whereby the improvement was higher using flash lamp annealing. An improvement by flash lamp annealing could also be achieved for TiO_x films, however for these films the conventional heat treatment was superior. Among the deposited films, ZnO sol-gel films showed the strongest antimicrobial effect and no CFU could be found on agar plates. The TiO_x films itself showed a small inhibitory effect towards bacteria, which could be further improved by Ag-doping. A clear decrease of the number of CFU was achieved by increasing the Ag-content of the films. These film deposition processes may provide a valuable alternative to modify temperature

sensitive materials in comparison to more commonly used technologies operating under vacuum conditions or using high substrate temperatures. Moreover, flash lamp annealing seems to be a beneficial method to post-treat such films, since this process is in general in-line capable, fast and even suitable for temperature sensitive materials.

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