Photocatalytic Coatings

Initial situation

Processing techniques for TiO₂ thin films have been developed at Fraunhofer ISC for optical applications. Starting from metal alkoxides large areas of glass can be coated with high optical qualities at moderate investment costs. Problems arising during this sol-gel procedure regarding the reproducibility and the stability of coating solutions have been overcome by using amorphous soluble precursor powders.

Development of highly active photocatalytic coatings

The structural features of TiO₂ surfaces are very important for the performance of the material. Sol-gel processing offers many possibilities of adjusting and optimizing the microstructure of thin films. For optical applications dense TiO₂ films with smooth surfaces were required, whereas for photocatalytic applications TiO₂ films with rough and high surface areas may be advantageous.

To evaluate the specific activity of different materials, a reactor for photochemical degradation reactions was fabricated at Fraunhofer ISC (Figure 1). The oxidation of dichloroacetic acid (a) to carbon dioxide and hydrogen chloride or the oxidation of methanol (b) to formaldehyde in the presence of photocatalytic TiO₂ coatings can be measured as a function of irradiation time:

\[ \text{a) } \text{Cl}_2\text{CH-COOH} + \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{HCl} \]
\[ \text{b) } 2 \text{CH}_3\text{OH} + \text{O}_2 \rightarrow 2 \text{CH}_2\text{O} + 2 \text{H}_2\text{O}. \]
The photocatalytic degradation of dichloroacetic acid can easily be monitored by measuring the amount of chloride ions formed during the photocatalytic experiments, whereas formaldehyde is detected by a specific color reaction and subsequent photometric measurements.

In figure 2 the photocatalytic activity of dense TiO$_2$ thin films prepared by the sol-gel processing is compared to a commercially available product developed for architectural applications. The degradation rates of both samples are similar indicating that already the dense TiO$_2$ films developed for optical applications can well compete with the commercial product manufactured by an APCVD (Atmospheric Pressure Chemical Vapour Deposition) method.

The addition of specific organic molecules to the coating solutions and the burn-out of these substances in a final curing step, thereby generating a defined porosity, increase the photocatalytic activity of the porous TiO$_2$ film (Figure 2). The electron and the atomic force micrograph (SEM, AFM) in figure 3 shows that the access of organic pollutants to lower parts of the TiO$_2$ film is facilitated by pores, which thereby enlarge the TiO$_2$ surface for photocatalytic reactions. The embossing of sol-gel films with a stamper, thus forming a periodic pattern, is another method of changing the microstructure of these inorganic surfaces. Such a periodic pattern of a TiO$_2$ thin film on glass is displayed in an atomic force microscopy profile (AFM) in figure 4.

Thin film analysis and perspectives

For the characterization and development of photocatalytic coatings there are, besides SEM and AFM, many analytical methods available at Fraunhofer ISC, e.g. FTIR, Raman, UVVIS and fluorescence spectroscopy as well as TEM, XPS and XRD. Besides the two constituting effects (photocatalytic activity, photoinduced hydrophilicity) of photocatalytic coatings, there are many other properties required for different applications: e.g. hardness, scratch resistance, transparency, weathering and long-term stability. These qualities can also be tested by diverse methods (taber abraser, sun and xeno test, QUV (abbreviation for Q Panel Company Ultraviolett) weathering).

The comparison of the photocatalytic performance of TiO$_2$ coatings by the evaluation of further test methods and the development of coatings that are active over a long period of time and activated in the visible light range ($\lambda > 400$ nm) is the key part of our ongoing research and development project in co-operation with other Fraunhofer institutes (IST, IFAM, FEP, ISE, IGB, IME). In this project photocatalytic coatings are prepared by various methods (e.g. sol-gel, magnetron sputtering, atmospheric plasma processing etc.). Additionally, analytical testing methods and devices will be developed, and biological and environmental aspects of photocatalysis will be investigated.