Photoconductivity of TiO_2 films deposited by PECVD

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TiO_2 thin films were prepared by PECVD technique from vapors of Titanium–IViso-propoxide mixed with oxygen at different temperatures. The films were deposited on substrates with system of special platinum electrodes and on glass substrates. Absorption spectra in the visible light region, photoconductivity and capacitance at different humidity, photocatalytic activity under UV irradiation and surface morphology were evaluated on the films. The results revealed that the photoconductivity is influenced by humidity and is connected to the photocatalytic activity.

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1 Introduction

Titanium oxide thin films attract considerable attention of many research teams due to their great variety of interesting properties resulting in numerous applications such as optical films, photoelectrochemical solar cell, photocatalyst, gas sensors etc. Titanium dioxide has been considered to be photoconductive material. It is one of the n–type semiconductors potentially applicable to photochemical electrodes for energy conversion from solar to other form such as electricity [1, 2, 3]. Among different methods of film deposition the sol–gel and plasma assisted deposition are the most frequently used.

Extensive research has been conducted on the development of a TiO_2 photocatalyst operating under visible light irradiation [4, 5, 6]. TiO_2 photocatalysts doped with transition metals such as Cr, Mn, Co, Fe, etc. have been found to absorb visible light [7–13]. Matsumoto et al. [7] have shown that Co–doped polycrystalline TiO_2 electrodes prepared at $673 \div 823$ K show an apparent visible light response $420 \div 550$ nm. They explained that the response is based on the newly formed

d–band by the interaction of the interstitial Co ion in the TiO_2 lattice. Ghosh and Maruska [9] have also found that the presence of Cr gives rise to optical absorption extending from the fundamental band edge of TiO_2 at 415 nm to well past 550 nm, a wavelength region containing a major portion of the solar radiation. However, in most cases, the primary ultraviolet activity of the TiO_2 photocatalyst tends to decrease because the doped metals act as an electron–hole recombination center [13, 14].

Usual method how to test the photocatalytic activity is decomposition of different organic compounds, but there is no common standard developed for comparison of photocatalytic activity [15]. Recently, a technique has been proposed for quality comparison of the thin film photocatalysts prepared by different methods, which uses the photocurrent images [16]. The photoconductivity is also crucial property for sensor applications. Indeed, a correlation between photoconductivity and photocatalytic activity had been demonstrated in certain cases; in some films, however, another author reported that an increase in photoconductivity is not accompanied by an increase in the contaminant degradation rate [17]. The aim of our paper is characterization of electrical and photocatalytic properties of thin films prepared by plasma enhanced chemical vapor deposition.

2 Experimental

The depositions were performed in the capacitive coupled homemade planar reactor. The bottom electrode (12 cm in diameter) was connected to the RF power generator with excitation frequency 13.56 MHz via the matching unit and could be resistively heated up to 500 °C. The electrode worked as substrate holder. The single molecular precursor titanium (IV) iso–propoxide ($Ti[OCH(CH_3)_2]_4$, 97 % purity, TTIP) was used as source of titanium. The precursor was evaporated in the liquid heated evaporator at temperature 50 °C and the vapors were transported through the shower head shaped gas inlet situated upon the electrode into the chamber. The mixture of TTIP vapors and oxygen was used as the working gas. The flow rate of TTIP vapors and oxygen was independently controlled by a needle valve and a mass flow controller, respectively. The working pressure was held constant at 8 Pa using a throttle valve controller. Based on other experiments we used very low RF power about 2 W which results in formation of a negative self bias as high as −50 V. The depositions were carried out with respect to the substrate temperature ranging between 20 °C and 500 °C, the typical deposition time was 2 hours. The films were deposited on glass and on special substrates with system of special platinum electrodes (Fig. 1.) on alumina plates. The electrodes used for measurements of photoconductivity and capacity were obtained from the Elceram company.

The film photoconductivity and capacitance were measured on the apparatus built on Technical University of Liberec in dependence on ambient air humidity and deposition temperature. AC signal of 10 MHz and 1 V in the amplitude was used for our measurements. To eliminate stray capacitances, the apparatus was

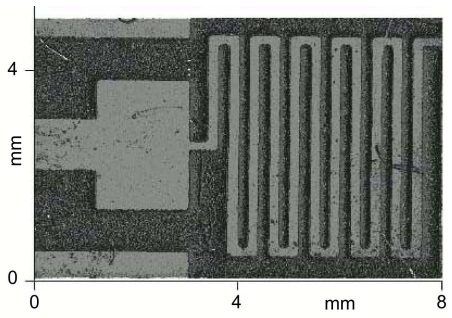

Fig. 1. Picture of special platinum electrode.

calibrated before measurement of particular samples. The photocatalytic activity was evaluated from decomposition speed of acid orange II aqueous solution (sodium salt of sulphonated azo dye, AOII), exposed to UV. Irradiation was provided by a fluoresced black light tube (Philips 60 cm, 20 W, 365 nm). Photocatalytic efficiency was expressed by Photocatalytic degradation speed (r), calculated from the slope of AOII concentration versus irradiation time curve and was normalized to the sample surface area, volume of the solution and UV intensity. The film thickness was measured by the optical profiler MicroProf with CWL sensor from company FRT GmbH, surface morphology was evaluated by AFM and the film transmittance was measured by UV–VIS spectrometer 916 GBC.

3 Results and discussion

The film thickness measured by optical profiler was about 600 nm and was similar for all films. The surface morphology investigated by AFM is shown on Fig. 2. The surface is quite rough and the average grain size is about 300 nm.

UV–VIS transmission spectra of the films are shown on Fig. 3. For the sample deposited at low temperature quite low absorption was observed above wavelength longer than 360 nm. The films deposited at higher temperature exhibited much higher absorption in the visible light region. The highest absorption have the films deposited at temperature higher that 400 °C. Light absorption is a necessary condition for high photocatalytic activity although it is not the sufficient condition. We can conclude that new absorption bands for visible light region are created in the films.

The dependence of photocatalytic degradation speed on the deposition temperature is shown on Fig. 4. The photocatalytic activity is low and very similar for all films deposited at temperature up to 350 °C. Rapid increase of the photocatalytic activity has been observed for samples deposited at temperature higher that 350 °C. This is in a good agreement with the results from measurements of transmission spectra. The decomposition speed of AOII is approximately 6 times higher at deposition temperature 400 °C that at 350 °C. The TiO_2 is known to occur in two base crystalline forms. It is known that the anatase crystalline structure features higher

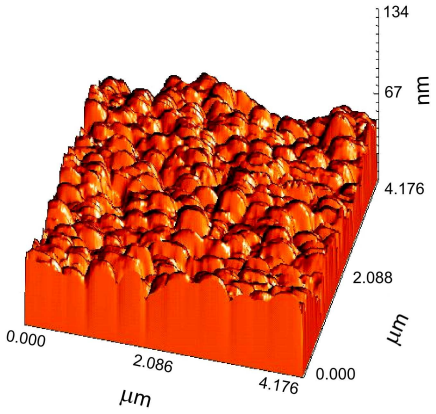

Fig. 2. AFM picture of the film deposited at 500°C.

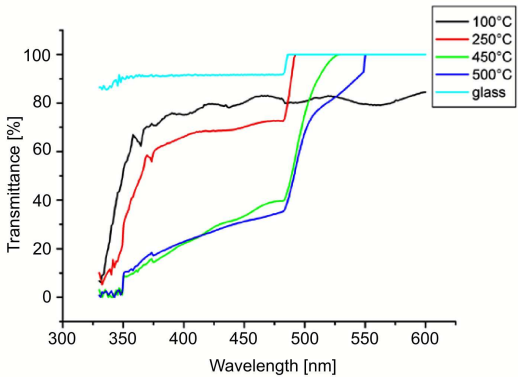

Fig. 3. Transmission spectra from UV–VIS measurements

fotoactivity than rutile. The XRD measurements revealed first poor anatase structure at the deposition temperature 350 °C but well developed anatase structure was found for the deposition temperature 400 °C. This is in quite good agreement with the literature according to which the transition from amorphous to anatase form started at temperature close to 300 °C. Thus our experimental results intimate that the enhancement both in the photoactivity as well as in the photoabsorption are connected with formation of anatase structure of the films deposited above 350 °C.

The results from measurements of photoconductivity and capacity are summarized in the Fig. 5, 6. The photoconductivity was measured on selected samples and for two values of humidity, very low humidity 0,13 % and high humidity 75 %. The films with low photocatalytic have very low photoconductivity and capacity and have no sensitivity on the humidity. The films exhibited high photocatalytic activity exhibited also higher photoconductivity. The increasing of the photocon-

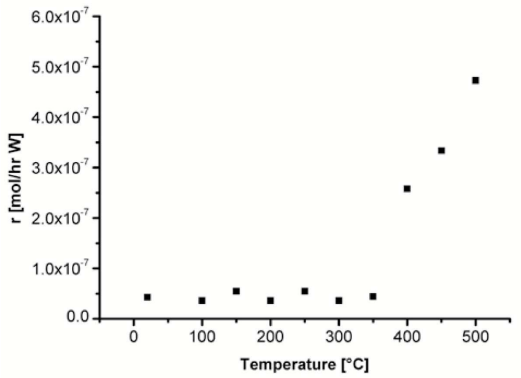

Fig. 4. Variation of photocatalytic degradation speed with deposition temperature

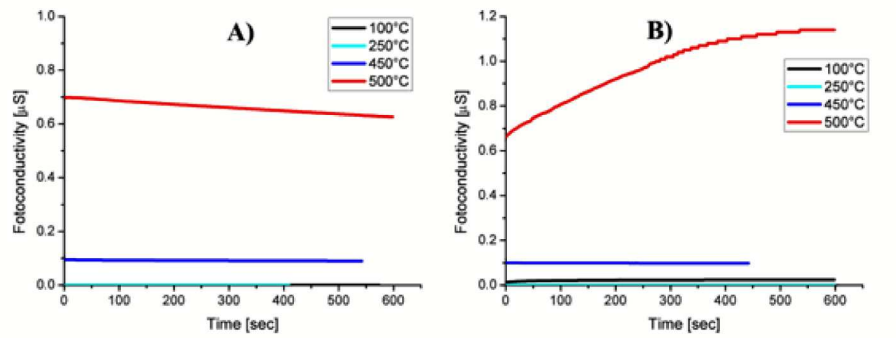

Fig. 5. Time dependence of photoconductivity for different humidity. A) humidity 0,13 %, B) humidity 75 %

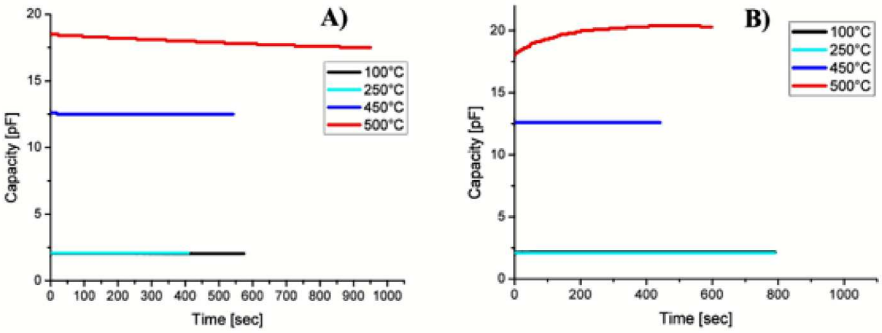

Fig. 6. Time dependence of capacity for different humidity. A) humidity 0,13 %, B) humidity 75 %

ductivity is not the same order as photocatalytic activity, see Fig. 4, 5. The highest

photoconductivity and capacity has the film deposited at 500 °C, which is also the only one with appreciable sensitivity to the humidity. When this film is placed in the environment with high humidity the water molecules are absorbed on the surface and increased the photoconductivity. Thus it can be concluded that photoconductivity is related to the photocatalytic activity although there is no direct relationship between these two properties.

4 Conclusion

- PECVD deposition method is convenient for low temperature deposition of photocatalytic TiO_2 thin films...
- The photocatalytic activity of PECVD TiO_2 films is related to its photoconductivity
- Both the properties has been found to be connected with the formation of anatase structure

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