RELATIONSHIP BETWEEN PHOTOCATALYTIC ACTIVITY, HYDROPHILICITY AND PHOTOELECTRIC PROPERTIES OF TiO_2 THIN FILMS

A. Kolouch[1], M. Horáková[1], P. Hájková[1], E. Heyduková[2], P. Exnar[1], P. Špatenka[1,3]

[1]Technical University of Liberec, Faculty of Mechanical Engineering, Department of Material Science, Hálkova 6, 461 17 Liberec, Czech Republic;
[2]Technical University of Liberec, Faculty of Education, Department of Chemistry, Hálkova 6, 461 17 Liberec, Czech Republic;
[3]University of South Bohemia, Pedagogical faculty, Jeronýmova 10, 371 15 České Budějovice, Czech Republic

TiO_2 thin films were prepared by PECVD technique from vapors of Titanium-IV iso-propoxide mixed with oxygen at different temperatures. The films were deposited on substrates with system of special platinum electrodes and on glass substrates. Photoconductivity and capacitance at different humidity, photocatalytic activity and photo-induced hydrophility 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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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 and humidity 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]. Very interesting property is photoinduced hydrophility. Wang et al. recently reported that ultraviolet illumination of TiO_2 surfaces could produce a highly hydrophilic surface, which was denoted as superhydrophilicity [4]. The originally less hydrophobic TiO_2 surface becomes highly hydrophilic (superhydrophilic) by its bandgap excitation via UV light irradiation and gradually reverts to originally less hydrophilic in the dark [5]. Among different methods of film deposition the sol-gel and plasma assisted deposition are the most frequently used.

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 [6]. Recently, a technique has been proposed for quality comparison of the thin film photocatalysts prepared by different methods, which uses the photocurrent images [7]. The photoconductivity and induced hydrophility 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 [8]. The aim of our paper is characterization of electrical and photocatalytic properties of thin films prepared by plasma enhanced chemical vapor deposition.

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 temperature was measured by thermocouple located on the inner side of the electrode and recalculated on the upper side of the electrode according to calibration curves. 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 showerhead upper 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 300°C, the 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.

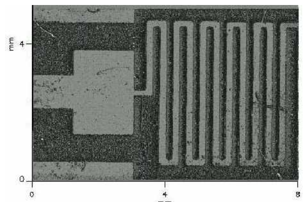

Fig. 1 Picture of special platinum electrode

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

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stray capacities, the apparatus was calibrated before measurement of particular samples. The photocatalytic activity was evaluated from decomposition speed of acid orange II aqueous solution (podium 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 decomposition speed (r), calculated from the slope of AOII concentration versus irradiation time curve in semilogaritmic coordinates and was normalized to the sample surface area, volume of the solution and UV intensity. The hydrophility of the TiO_2 thin films was evaluated from the contact angle of water droplet. The contact angle measurement was done by the home-made arrangement consisting of table with the micro-feed and CCD camera connected to the computer via a PCI card. For each samples the contact angle was measured before UV and after sample illumination by UV lights for 60 minutes. To eliminate film inhomogenity the contact angle was measured on five predefined position. The hydrophility of the sample was characterized by the average value and standard deviation calculated from these five values. The film thickness was measured by the optical profiler MicroProf® with CWL sensor from company FRT GmbH, surface morphology was evaluated by AFM.

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 average grain size increased from about 100 nm to 250nm with deposition temperature increased from 130°C to 280°C.

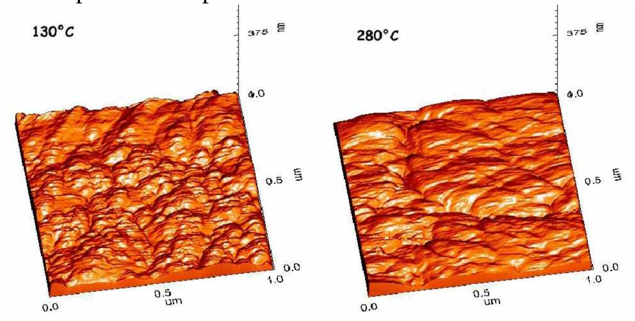

Fig.2. AFM pictures

The dependence of photocatalytic degradation speed on the deposition temperature is shown on fig. 3. The photocatalytic activity is low and very similar for all films deposited at temperature up to 230°C. Rapid increase of the photocatalytic activity has been observed for samples deposited at temperature higher than 255°C. The decomposition speed of AOII is approximately 4 times higher at deposition temperature 255°C that at 230°C.

Photoinduced hydrophility (hydrophobic to hydrophilic transition after UV irradiation) behaves very similar as photocatalytic decomposition speed, see fig. 4. The films deposited at temperature up to 200°C had all similar initial contact angle about 80 degrees which didn't change after UV irradiation. Films deposited at temperature 230°C and higher exhibited with lower initial contact angle which decreases considerably after UV irradiation. The transition between the hydrophobic and hydrophilic properties of the TiO_2 surfaces was attributed to the formation and extinction of a surface hydroxyl group.[9,10,11] UV irradiation caused reduction of Ti ions from Ti^{4+} to Ti^{3+} and the production of oxygen vacancies on TiO_2 surfaces. Succeeding dissociative adsorption of ambient water vapor at these oxygen vacancies resulted in the formation of a surface hydroxyl group [9,10].

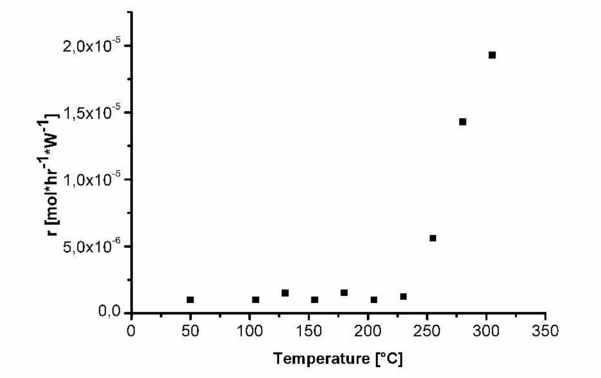

Fig. 3 Variation of photocatalytic decomposition speed with deposition temperature

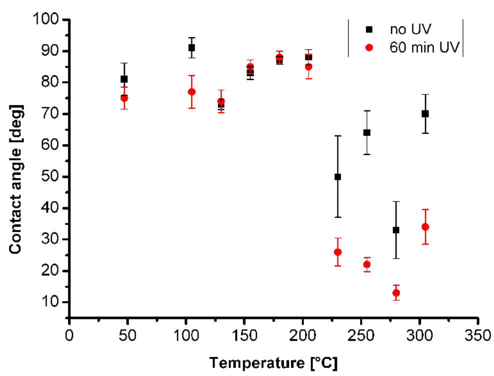

Fig. 4. Variation of contact angle with deposition temperature

The TiO_2 is known to posses occurs in two crystalline forms. It is known that the anatase crystalline structure features higher fotoactivity than rutile. The XRD measurements revealed first poor anatase structure at the deposition temperature 230°C but well developed anatase structure was found for the deposition temperature 280°C. Thus our experimental results intimate that both the enhancement in the photoactivity as well as in the hydrophility are connected with formation of anatase structure of the films deposited above 200°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 photoconductivity is not the same order as photocatalytic activity, see fig. 4, 5. The highest photoconductivity and capacity has the film deposited at 305°C, which is also the only the 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.

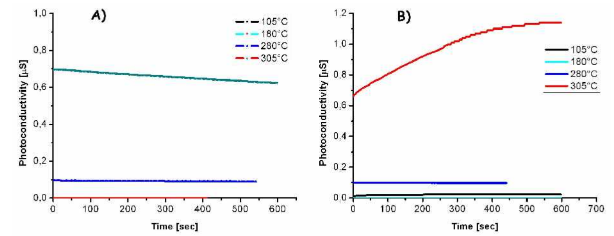

Fig. 5. Time dependence of photoconductivity for different humidity, A) humidity 0,13 %, B) humidity 75%

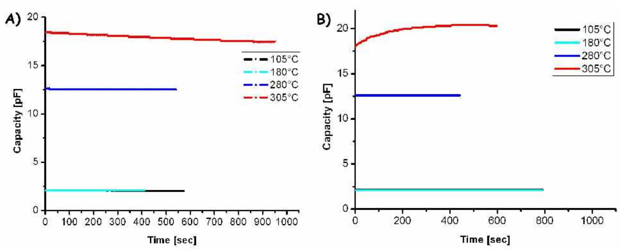

Fig. 6. Time dependence of capacity for different humidity, A) humidity 0,13 %, B) humidity 75%

CONCLUSIONS

- PECVD deposition method is convenient for low temperature deposition of photocatalytic TiO2 thin films;
- the photocatalytic activity and photoinduced hydrophility of PECVD TiO_2 films is related to its photoconductivity;
- photocatalytic activity, photoinduced hydrophility and photoelectric properties have been found to be connected with the formation of anatase structure.

ACKNOWLEDGEMENTS

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СВЯЗЬ МЕЖДУ ФОТОКАТАЛИТИЧЕСКОЙ АКТИВНОСТЬЮ, ГИДРОФИЛЬНОСТЬЮ И ФОТОЭЛЕКТРИЧЕСКИМИ СВОЙСТВАМИ ТОНКИХ ПЛЕНОК TiO_2

A. Kolouch, M. Horáková, P. Hájková, E. Heyduková, P. Exnar, P. Špatenka

Тонкие пленки TiO_2 были приготовлены методом PECVD из паров изо-пропилата титана (IV), смешанного с кислородом, при различных температурах. Пленки осаждались на подложки с системой специальных платиновых электродов и на стеклянные подложки. Оценивались фотопроводимость и емкостное сопротивление пленок при разной влажности, их фотокаталитическая активность и фотоиндуцированная гидрофильность при облучении ультрафиолетом, а также морфология поверхности. Из результатов следует, что фотопроводимость зависит от влажности и связана с фотокаталитической активностью.

ЗВ'ЯЗОК МІЖ ФОТОКАТАЛІТИЧНОЮ АКТИВНІСТЮ, ГІДРОФІЛЬНІСТЮ І ФОТОЕЛЕКТРИЧНИМИ ВЛАСТИВОСТЯМИ ТОНКИХ ПЛІВОК TiO_2

A. Kolouch, M. Horáková, P. Hájková, E. Heyduková, P. Exnar, P. Špatenka

Тонкі плівки TiO_2 було приготовлено методом PECVD із пару ізопропілату титана (IV), змішаного з киснем, при різних температурах. Плівки осаджувалися на підкладки із системою спеціальних платинових електродів і на скляні підкладки. Оцінювалися фотопровідність і ємнісний опір плівок при різній вологості, їхня фотокаталітична активність і фотоіндукована гідрофільність при опроміненні ультрафіолетом, а також морфологія поверхні. З результатів випливає, що фотопровідність залежить від вологості і зв'язана з фотокаталітичною активністю.