Decomposition of organic dyes with sputtered TiO_2 photocatalytic films

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This article reports on the photocatalytic activity of transparent crystalline TiO_2 films deposited on unheated glass substrates at low substrate surface temperature T_{surf}≈180°C using a dual magnetron operating in bipolar asymmetric mode in $Ar+O_2$ mixture and equipped with Ti(99.5) targets of 50 mm in diameter. The photocatalytic activity (PCA) of TiO_2 films was characterized by the photocatalytic decomposition rate of two organic dyes (Acid Orange 7 and Methylene Blue). It was found that the Acid Orange 7 is more convenient for the testing of PCA activity of TiO_2 films due to its higher stability. It was shown that (i) dual magnetron sputtering is suitable for a low temperature sputtering of thin TiO_2 photocatalysts, (ii) thin TiO_2 films sputtered at temperatures T_{surf}≈180°C exhibit high PCA which strongly increases with increasing film thickness, and (iii) TiO_2 films prepared at high values of p_T and p_{O2} have anatase structure and highest PCA.

1. Introduction

In recent years, a great attention has been devoted to the titanium dioxide (TiO_2) due to its excellent chemical stability, high refractive index, nontoxicity, and good mechanical hardness. Besides, the TiO_2 films can exhibit excellent photocatalytic and superhydrophilic properties after UV light irradiation. The UV light irradiation results in the formation of electron-hole pair that diffuses to the surface and due to its favourable chemical potential leads to the formation of highly reactive hydroxyl radicals (•OH) on the surface of TiO_2, see Fig. 1 and comparison of e-h pair potential vs. standard hydrogen electrode (SHE). The hydroxyl radicals (•OH) very quickly oxidize a wide range of organic pollutants. The formation of (•OH) and oxidation process is described by the following formulas and shown:

$$TiO_2+h\nu \rightarrow e^-_{vb}+h^+_{vb} \quad (1)$$

$$e^-_{surf}+O_{2(ads)} \rightarrow \bullet O^-_2 \quad (2)$$

$$h^+_{surf}+OH^-_{(ads)} \rightarrow \bullet OH_{(ads)} \quad (3)$$

$$\bullet OH_{(ads)}+dirt \rightarrow xCO_2+ yH_2O \quad (4)$$

Photoactivity of TiO_2 films can be used in many applications, e.g., in self-cleaning, antifogging and antibacterial self-sterilization processes and in a removal of organic pollutants from surfaces, dissociation of water or in the production of hydrogen [1-3].

However, there are several drawbacks of the TiO_2 photocatalysts preventing to their wider utilization. The first problem is connected with the activation of TiO_2 films by the UV light. It covers a small fraction of the total sun radiation only and it results in a very low efficiency of the sunlight activation. The second problem is the formation of the photoactive TiO_2 coatings on thermally sensitive substrates, e.g., polymer foils or polycarbonate, at T_{surf}<200°C. Among many preparation methods, the magnetron sputtering is very promising one for the large-area deposition of thin, high quality, photoactive, crystalline TiO_2 films at low values of T_{surf} [4-8]. However, the deposition of crystalline photoactive TiO_2 films without a preheating of the substrate or a post-deposition annealing has not been fully mastered yet [4,5,8].

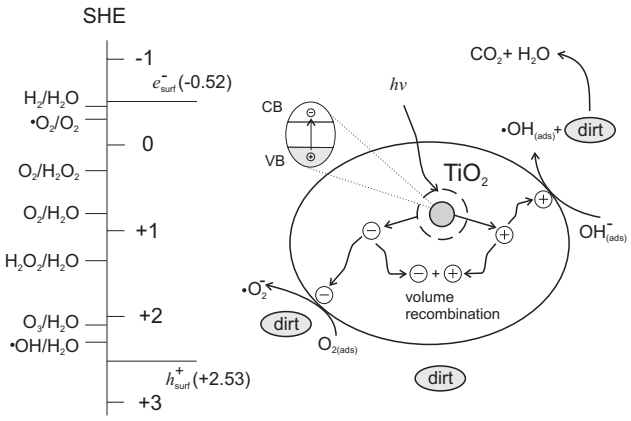

Fig. 1. Principle of photocatalytic processes on the surface of TiO_2 film [1,2].

This article is devoted to the preparation of TiO_2 films at low temperature (T_{surf}<180°C) using a dual magnetron and the evaluation of their PCA characterized by the decomposition of two organic dyes: Acid Orange 7 and Methylene Blue. TiO_2 films were reactively sputtered *in the oxide mode of sputtering*. The effect of a thickness h of the film sputtered at the same deposition conditions is discussed in detail.

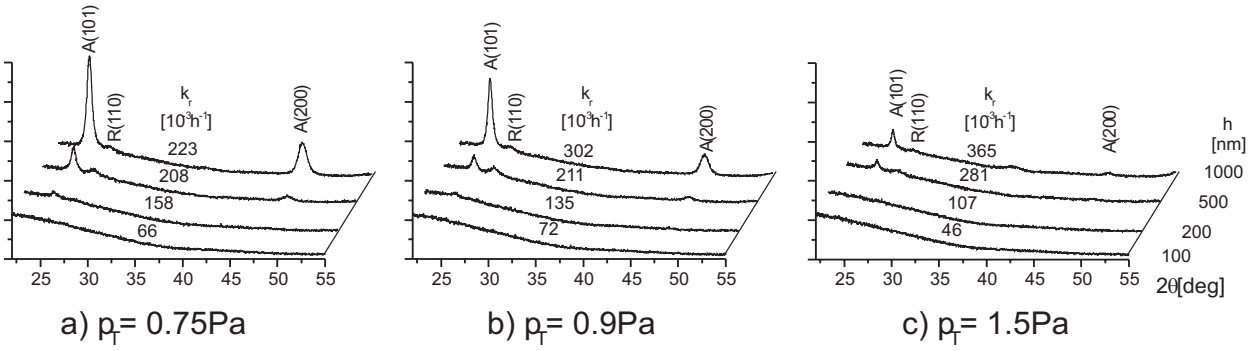

Fig. 2. The effect of film thickness h on XRD structure of the TiO_2 film prepared in the oxide mode of sputtering at total working pressure p_T= 0.75Pa (a), 0.9Pa (b) and 1.5Pa (c).

2. Experimental

DC pulsed dual magnetron operated in a closed field configuration equipped with Ti(99.5) targets (∅ 50 mm) was used to sputter transparent photocatalytic TiO_2 films on unheated microscope glass substrates (25x25x1mm^3) in a mixture of Ar+O_2. The target to substrate distance d_{s-t}= 100mm, repetition frequency of the pulses f_r= 350kHz, pulse discharge current $I_{da1,2}$=3A (pulse power densities about W_{da}≈60-70W/cm^{-2}). The substrate surface temperature during depositions T_{surf} was measured by the thermostrips (Kager GmbH, Germany) and was lower than T_{surf}≤180°C for all performed experiments. More details are given in reference [8]. The PCA was characterized by the decomposition of two organic dyes Acid Orange 7 (AO7) and Methylene Blue (MB) (Fluka Chemie GmbH) with initial concentration c_0=0.01 mmol/l in the deionized water. The TiO_2 films were immersed in the analyzed solution with volume V=10ml and UV light (Philips TL-DK 30W/05, W_{ir}=0.9mWcm^{-2}, λ=365nm) irradiated for six hours. The changes in the dye concentration were measured every hour by measuring the changes in magnitude of the dye absorption maxima (spectrometer SPECORD M400) at λ=485 and 665 nm (calibrated on the dye concentration) for AO7 and MB solution, respectively.

4. Results and discussion

The PCA of TiO_2 film was characterized by decomposition of the organic dye using the apparent first-order decomposition rate constant k_r defined by the following formula [9]:

$$c(t_{ir}) = c_0 e^{-k_r t_{ir}} \qquad (5)$$

Here c_0 and $c(t_{ir})$ are the initial concentration of the dye and its concentration after UV light irradiation for defined time interval t, respectively. A plot of $\ln(c_0/c)$ as a function of time t_{ir} represents a straight line with slope of k_r.

4.1. Structure of TiO_2 film

The structure of TiO_2 film strongly depends on its thickness h and total pressure p_T of Ar+O_2 mixture used in its sputtering, see Fig.2. From this figure it is clearly seen that (i) the film crystallinity improves with increasing h and decreasing p_T and (ii) the conversion of amorphous TiO_2 film h<200 nm to film with rutile and anatase structure h≈500nm to film with dominant anatase phase at h≈1000nm. This evolution of structure is in a good agreement with previous reported results [9, 10].

Both the crystallinity and phase composition of TiO_2 film strongly influences its PCA.

4.2. Decomposition of organic dyes vs. film thickness

The dye concentration of AO7 and MB during UV light irradiation of TiO_2 film immersed in tested solution decreases with increasing time of irradiation t_{ir}, see Fig.3. The decrease of concentration increases with increasing thickness h of TiO_2 film. For comparison, a self decomposition of the dye solution was measured for glass reference without the TiO_2 film, see Fig.3. The self-decomposition is lower than the decomposition in presence of irradiated TiO_2 films.

The decomposition rate constant k_r was determined from dependences $\ln(c/c_0)=f(t_{ir})$ using Eq.(5). These dependencies exhibit almost linear increase with increasing t_{ir}. The values of k_r were determined as slopes of lines fitted to measured curves. Calculated values of k_r are summarized in Table 1.

As expected, the TiO_2 film thickness h plays a crucial role on its PCA, mainly due to the improvement of film crystallinity with increasing

film thickness h. Highly photoactive anatase phase dominates over the rutile phase with poor PCA if the thickness h of TiO_2 film is higher than 500 nm. Recent results have also shown that the increase in h leads to the increase of film surface roughness R_a what also improves the PCA [10].

Table 1: The decomposition rate constant k_r. and the concentration c/c_0 of AO7 and MB solution after 6 hours decomposition with TiO_2 film of different thickness h irradiated by UV light. h=0 is the bare glass substrate.

	Acid Orange 7		Methylene Blue	
h [nm]	c/c_0 [%]	k_r [$10^{-3}h^{-1}$]	c/c_0 [%]	k_r [$10^{-3}h^{-1}$]
0	14	24	47	107
100	33	66	59	149
200	61	158	78	252
500	71	208	86	329
1000	74	223	91	385

The photocatalytic decomposition rate constant k_r, of both AO7 and MB organic dyes exhibit a similar evolution with increasing film thickness h, see Fig 4. Higher values of k_r obtained for the MB solution can be explained by its worse stability against UV irradiation, see Table 1, and different dye composition. The self-decomposition of MB solution was almost 50% after 6 hours of UV irradiation compared to 15% for more stable AO7 solution. In summary we can conclude that the AO7 solution is, due to its higher stability against UV irradiation, i.e. the low self-decomposition, more suitable for the measurement of the PCA of TiO_2 films.

4.3. Effect of total pressure

The increase of total working pressure p_T results in a deterioration of the film crystallinity, see Fig. 2. It is due to the decrease of energy delivered to growing films by bombarding ions and condensing atoms in consequence of collisions between particles [11]. The increase in p_T shifts the start of crystallization to films with higher thickness h; h>200nm is needed for preparation of the crystalline TiO_2 films at p_T=1.5Pa. This means that a longer time is needed to deliver a minimum energy necessary for the film crystallization. It is also worthwhile to note that our films were sputtered with the deposition rate a_D=10 to 12 nm/min. Besides, it was found that a strong suppression of rutile phase exhibit 1000 nm thick TiO_2 films sputtered just at p_T=1.5 Pa.

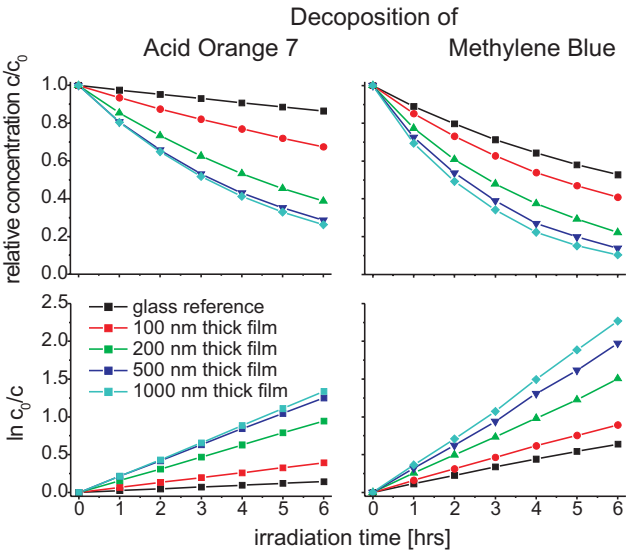

Fig. 3. Relative concentration c/c_0 and ln c/c_0 of AO7 and MB as a function of UV irradiation time for TiO_2 films with different h sputtered at p_T=0.75Pa and p_{O2}=0.3Pa.

In summary, we can say that a higher total pressure p_T is needed to form the crystalline TiO_2 films with a high content of strongly photoactive anatase phase. Also, high partial pressure of oxygen p_{O2} is beneficial for the formation of TiO_2 film with dominated anatase phase, while recent results show that the rutile phase easily grows if films are sputtered in the transition mode at low oxygen partial pressures p_{O2}<0.1Pa [11]. The rutile phase, with lower PCA compared to the anatase phase, should be avoided in the TiO_2 films.

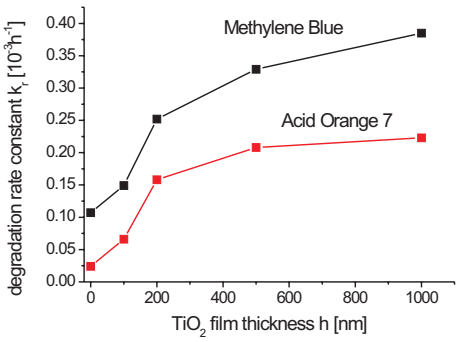

Fig. 4. Decomposition rate constant k_r of AO7 and MB solutions with UV light induced photoactive TiO_2 thin film as a function of film thickness h.

4.4. Decomposition of organic dyes vs. total pressure used in sputtering of TiO_2 films

The decomposition rate constant k_r of AO7 solution with photoactive TiO_2 films sputtered at different p_T and as a function of film thickness h is

given in Fig 5. As expected, k_r increases with increasing h and p_T. Since k_r is a measure of the PCA of TiO_2 film the highest PCA exhibits 1000nm thick TiO_2 film sputtered at p_T=1.5Pa. It is due to the lowest content of rutile phase in this film compared with other films in Fig.5.

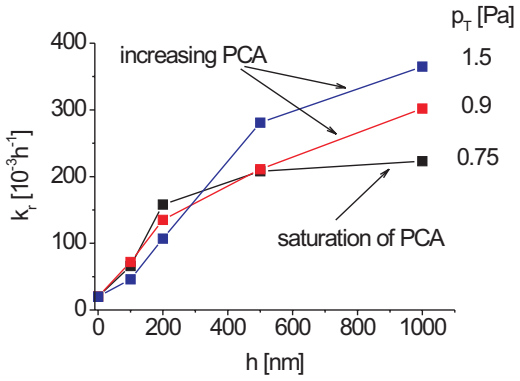

Fig. 5: The effect of total working pressure p_T and TiO_2 film thickness h on the PCA characterized by the decomposition rate constant k_r of AO7 during UV light induced photocatalytic decomposition.

The highest PCA of 200 nm thick TiO_2 film exhibit that sputtered at p_T=0.75Pa. However, PCA of films sputtered at p_T=0.75Pa saturates already at h≈200 nm. The saturation disappears if p_T increases. This behavior is connected with different phase composition and crystallinity of films sputtered at low and high values of p_T discussed above. For more details, see reference [12].

5. Conclusions

The efficient photocatalytic decomposition of AO7 and MB organic dyes solutions on the transparent, highly photoactive TiO_2 film with thickness h≤1000nm, sputtered using the dual magnetron at substrate surface temperatures T_{surf}≤180°C, was experimentally demonstrated. It was found that

1. AO7 organic dye solution is due to a good stability against UV irradiation more suitable compared with MB organic dye solution for the evaluation of the PCA of TiO_2 thin film photocatalysts.
2. The PCA of TiO_2 film strongly depends on phase composition and its crystallinity. The crystallinity improves with the energy delivered to the growing film and thus is not surprising that PCA of TiO_2 improves with increasing film thickness h.
3. Anatase TiO_2 films sputtered in the oxide mode at total pressure p_T=1.5 Pa exhibit the highest PCA. This is due to the fact that the formation of rutile phase with low PCA is strongly suppressed at p_T≥1 Pa.
4. DC pulsed dual magnetron is a very efficient tool to sputter photoactive TiO_2 films at low substrate surface temperatures T_{surf}<200°C.

Acknowledgements

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