NANO EXPRESS

High-rate low-temperature dc pulsed magnetron sputtering of photocatalytic TiO$_2$ films: the effect of repetition frequency

**J. Šícha · D. Heřman · J. Musil · Z. Strýhal ·
J. Pavlík**

Abstract The article reports on low-temperature high-rate sputtering of hydrophilic transparent TiO$_2$ thin films using dc dual magnetron (DM) sputtering in Ar + O$_2$ mixture on unheated glass substrates. The DM was operated in a bipolar asymmetric mode and was equipped with Ti(99.5) targets of 50 mm in diameter. The substrate surface temperature T$_{surf}$ measured by a thermostrip was less than 180 °C for all experiments. The effect of the repetition frequency f$_r$ was investigated in detail. It was found that the increase of f$_r$ from 100 to 350 kHz leads to (a) an improvement of the efficiency of the deposition process that results in a significant increase of the deposition rate a$_D$ of sputtered TiO$_2$ films and (b) a decrease of peak pulse voltage and sustaining of the magnetron discharge at higher target power densities. It was demonstrated that several hundreds nm thick hydrophilic TiO$_2$ films can be sputtered on unheated glass substrates at a$_D$ = 80 nm/min, T$_{surf}$ < 180 °C when high value of f$_r$ = 350 kHz was used. Properties of a thin hydrophilic TiO$_2$ film deposited on a polycarbonate substrate are given.

Keywords TiO$_2$ film · Hydrophilicity · Deposition rate · Unheated substrate · Dual magnetron sputtering · Polycarbonate

J. Šícha · D. Heřman · J. Musil (✉)
Department of Physics, University of West Bohemia,
Univerzitní 22, Pilsen 306 14, Czech Republic
e-mail: musil@kfy.zcu.cz

Z. Strýhal · J. Pavlík
Department of Physics, J.E. Purkyně University, České
mládeže 8, Usti nad Labem 400 96, Czech Republic

Introduction

Titanium dioxide (TiO$_2$) is well known photocatalyst with good chemical stability, high refractive index, nontoxicity and good mechanical hardness. In recent years, photoinduced hydrophilicity characterized by the decrease of the water droplet contact angle (WDCA) to almost 0° on the TiO$_2$ films surface has been also reported. For these unique properties, TiO$_2$ can be used for the preparation of self-cleaning, antifogging and antibacterial self-sterilization coatings [1–3]. However, there are several problems which prevent a higher utilization of the TiO$_2$ photocalyst. A photoexcitation of an electron-hole pair by photons with wavelengths less than 385 nm (UV light region) is required due to an optical bandgap energy E$_g$ = 3.2 eV for the TiO$_2$ anatase phase [4]. The photoexcited electrons and holes play a crucial role in the photocatalytic and hydrophilic behaviour of the TiO$_2$ films. Therefore, the first problem is connected with the activation of the TiO$_2$ films because the UV light covers only a small fraction of the total sun radiation.

This article is devoted to the low-temperature (low-T) sputtering of the TiO$_2$ films with deposition rates sufficient for industrial production. Such a process is urgently needed for the preparation of films on heat sensitive substrates, such as polymer foils, polycarbonate (PC), etc., at low substrate surface temperatures T$_{surf}$, e.g. T$_{surf}$ < 130 °C in the case of the polycarbonate [5]. Recently, it has been shown that T$_{surf}$ can be much higher than that measured by a thermocouple incorporated in a substrate holder [6]. Among many preparation methods [7–12], the magnetron sputtering is a very promising technology for a low-temperature deposition of the high-quality crystalline hydrophilic

TiO$_2$ films. Several authors have reported on high-rate sputtering of the transparent amorphous TiO$_2$ films. The preparation of the crystalline hydrophilic TiO$_2$ films at a low-T without post-deposition thermal annealing, which can not be used, for instance, for the films sputtered on the PC substrate, remains an open problem [9, 11–19]. Therefore, this article is devoted to the optimization of the dual magnetron sputtering process for the low-T deposition of the TiO$_2$ films. The effect of the repetition frequency f$_r$ on the pulse waveforms, deposition rate a$_D$, substrate surface temperature T$_{surf}$, film structure and hydrophilic properties is discussed in detail. Trends of the next developement are also briefly outlined.

Experimental

The transparent TiO$_2$ films were prepared by reactive magnetron sputtering in a mixture of Ar + O$_2$ by dc pulsed dual magnetron equipped with Ti(99.5) targets of 50 mm in diameter. The magnetron was supplied by a dc pulsed Advanced Energy Pinnacle Plus + 5 kW power supply unit (PSU) operating in a bipolar asymmetric mode and duty cycle τ/T = 0.5; here τ and T are the length of pulse and the period of pulses, respectively. The PSU in bipolar asymmetric mode can be operated with a repetition frequency f$_r$ ranging from 100 to 350 kHz. Further details on the dual magnetron system are given elsewhere [20]. The films were deposited on unheated microscope glass slides (26 × 26 × 1 mm^3) and unheated polycarbonate (PC) substrates (26 × 26 × 3 mm^3). The TiO$_2$ films with a constant thickness h ≈ 1,000 nm were prepared in order to avoid a strong influence of the film thickness h on their properties [6, 21].

The thickness of the films was measured by a stylus profilometer DEKTAK 8 with the resolution of 1 nm. The structure of the films was determined by X-ray diffraction (XRD) analysis using a PANalytical X'Pert PRO diffractometer working in Bragg-Brentano geometry using a CuKα (40 kV, 40 mA) radiation. The water droplet contact angle (WDCA) α_{ir} on the surface of the TiO$_2$ films after their irradiation by the UV light (Philips TL-DK 30 W/05, W$_{ir}$ = 0.9 mW cm^{-2}, λ = 365 nm) was measured by a Surface Energy Evaluation System (Masaryk University in Brno, Czech Republic). The surface roughness R$_a$ was measured by atomic force microscopy (AFM) in non-contact mode using an AFM-Metris-2000. The measurements were performed in ambient atmosphere at room temperature. The substrate surface temperature

T$_{surf}$ was measured by the thermostrips (Kager GmbH, Germany). More details are given in Ref. [6].

Results and discussion

Recent results have shown that the low-T sputtering of the crystalline hydrophilic TiO$_2$ films with the anatase structure can be realized in the oxide mode [6, 21]. A systematic investigation of the correlations between the deposition process parameters and the properties of the TiO$_2$ films showed that an increase of repetition frequency f$_r$ from 100 to 350 kHz at constant values of p$_T$ = 0.9 Pa, I$_{da1,2}$ = 3 A and d$_{s-t}$ = 100 mm results in a significant increase of the film deposition rate a$_D$ in both the metallic (p$_{O2}$ = 0 Pa) and oxide mode (0.15 Pa) of sputtering, see Fig. 1. An improvement of the photoinduced hydrophilicity of the TiO$_2$ films with increased f$_r$ was observed as well. However, only a slight increase of maximum substrate surface temperature T$_{surf}$ from 160 to 180 °C was measured when f$_r$ increased from 100 to 350 kHz. These effects are further discussed in detail.

Time evolution of pulse waveforms

The time evolution of the pulse waveforms of current I$_d$ and voltage U$_d$ in the dual magnetron discharge generated in the oxide mode of sputtering (p$_{O2}$ = 0.15 Pa) at different values of the repetition frequency f$_r$, average discharge current I$_{da\ 1,2}$ = 3 A and p$_T$ = 0.9 Pa are displayed in Fig. 2. Here, the waveforms in one channel of the dual magnetron are given. The waveforms in the second channel are shifted by a half of the period T. This experiment shows that the time evolution of voltage at f$_r$ = 100 kHz can be

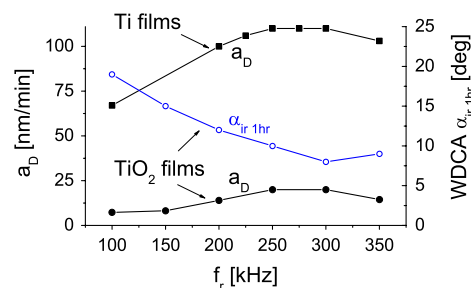**Fig. 1** The effect of the repetition frequency f$_r$ on (1) the deposition rate a$_D$ of (a) the Ti films sputtered in the metallic mode (p$_{O2}$ = 0 Pa) and (a) the TiO$_2$ films sputtered in the oxide mode (p$_{O2}$ = 0.15 Pa) at I$_{da1,2}$ = 3A, p$_T$ = 0.9 Pa, and d$_{s-t}$ = 100 mm and (2) the water droplet contact angle $\alpha_{ir\ 1hr}$ on the surface of the TiO$_2$ films after UV irradiation (0.9 mW cm^{-2}) for 1 h
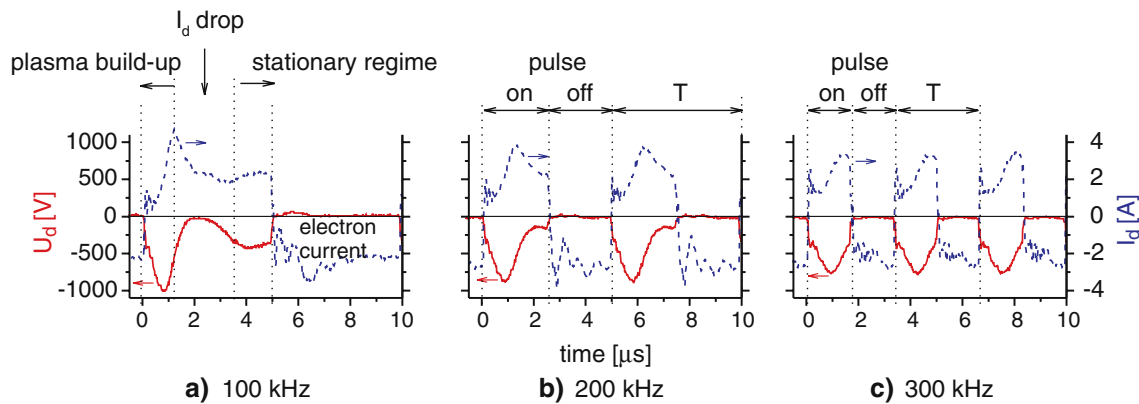
Fig. 2 The time evolution of discharge voltage U_d and current I_d in the dc pulsed discharge generated by the dual magnetron equipped with Ti targets at $I_{da1,2}$ = 3 A, p_{O2} = 0.15 Pa (oxide mode), p_T = 0.9 Pa and three values of f_r = 100, 200 and 300 kHz; $I_{da1,2}$ is the discharge current averaged over the pulse length τ

divided into three regimes: (1) a strong overshooting (up to –1,100 V) at the pulse beginning (t <1 μs) corresponding to the build-up of the discharge and accompanied by a strong sputtering with a maximum at t = 1 μs, (2) a subsequent voltage drop below –100 V ($1 \leq t \leq 2$ μs) when the discharge current approaches to a stationary value $I_d \approx 3$ A and (3) a very low-voltage (less than –100 V) regime with a very weak sputtering in the time interval from ~ 2 to ~ 3 μs followed by a stationary regime at $U_d \approx$ –400 V and the interval of sputtering from ~ 3 μs to the end of the pulse. The shape of the voltage pulse waveform strongly influences the utilization of the sputtering within the pulse-on time. No sputtering takes place during the pulse-off time. This means that the period T = 10 μs is very ineffectively used for sputtering. Similar results have been reported by Welzl et al. for pulsed magnetron sputtered the MgO films [22].

However, it is clearly seen from Fig. 2 that the utilization of the period T = 10 μs (f_r = 100 kHz) can be improved if f_r of the pulses is increased. Due to shortening of the pulses and cutting of the stationary regime only the first time interval with a strong sputtering is present and plasma build-up regime starts to dominate; see the time evolution of current at f_r = 200 and 300 kHz. Moreover, operating in the plasma build-up regime leads to an intensification of the ion bombardment and the increase of energy delivered to the surface of the growing film by ions given by $E_{bi}^* = E_i v_i \approx T_e^{3/2} n_e$ [23] where, E_i and v_i is the average energy of one bombarding ion and the flux of bombarding ions, respectively. Here the electron temperature T_e is significantly higher compared to the stationary regime, while the electron density n_e doesn't change remarkably, experimentally shown by Bradley et al. [24]. Shortening of the pulses also leads to a

higher preionization at the beginning of every pulse and thus the decrease of maximum overshooting voltage U_{max} and power loading $W_{d\ max}$ that can prevent the thermal overloading of the target. This fact simultaneously results in the increase of the deposition rate in the oxide mode of sputtering from 7.3 to 14.5 nm/min for TiO_2 films and 67 to 103 nm/min in the metallic mode for Ti films at f_r = 100 and 350 kHz, respectively. Obtained results are summarized in Table 1.

The same time evolution of discharge current and voltage shown in Fig. 2 was measured for an arbitrary content of oxygen in the sputtering gas. It means that the results given above are valid for the transition, oxide and metallic mode of sputtering.

Effect of repetition frequency on XRD structure and hydrophilicity of TiO₂ films

The transparent TiO_2 films with thickness h ≈ 1,000 nm were reactively sputtered in the oxide mode of sputtering (p_{O2} = 0.15 Pa) on the glass substrates at $I_{da1,2}$ = 3 A, d_{s-t} = 100 mm, p_T = 0.9 Pa and different values of the repetition frequency f_r ranging from 100 to 350 kHz. Under these deposition conditions, the substrate surface temperature T_{surf} increases with the increasing deposition time t_d and saturates at maximum value $T_{surf\ max}$ after t_d > 20 min [6]. In all the experiments $T_{surf\ max} \leq 180$ °C. $T_{surf\ max}$ increases from 160 to 180 °C when f_r is increased above 200 kHz; caused by the increase of the pulse target power density W_{da} and the substrate ion bombardment discussed above.

The structure of a TiO_2 film also strongly influences the hydrophilicity of its surface. The evolution of the film structure with increasing f_r is displayed in Fig. 3. All the TiO_2 films contain the anatase structure. This

Table 1 The deposition rate a_D and average pulse magnetron voltage U_{da} in the metallic and a_D, U_{da}, the target power densities W, maximum discharge voltage U_{max} and the substrate surface temperature T_{surf} in the oxide mode for the Ti and TiO_2 films sputtered at $I_{da1,2}$ = 3 A, d_{s-t} = 100 mm, p_T = 0.9 Pa and different repetition frequency f_r using the dual magnetron

f_r [kHz]	metallic mode–p_{O2} = 0 Pa		oxide mode–p_{O2} = 0.15 Pa						
	a_{Dti} [nm/min]	U_{da} [V]	a_{DTiO2} [nm/min]	U_{da} [V]	W_{da} [Wcm^{-2}]	W_d [Wcm^{-2}]	$W_{d\ max}$ [Wcm^{-2}]	U_{max} [V]	T_{surf} [°C]
100	67	–310	7.3	–387	58	29	180	–1100	160
200	100	–415	14	–462	70	35	140	–890	180
300	110	–440	20	–488	73	36.5	100	–770	180
350	103	–430	14.5	–452	68	34	100	–733	180

W_{da}, average pulse power density; W_d, average period power density ($W_d = W_{da}*\tau/T$); $W_{d\ max}$, maximum target power density; U_{max}, maximum discharge voltage

Fig. 3 Development of the structure in the ~ 1,000 nm thick transparent TiO_2 films reactively sputtered on unheated glass substrates at $I_{da1,2}$ = 3 A, d_{s-t} = 100 mm and $T_{surf} \approx$ 160–180°C, p_T = 0.9 Pa and p_{O2} = 0.15 Pa with increasing f_r
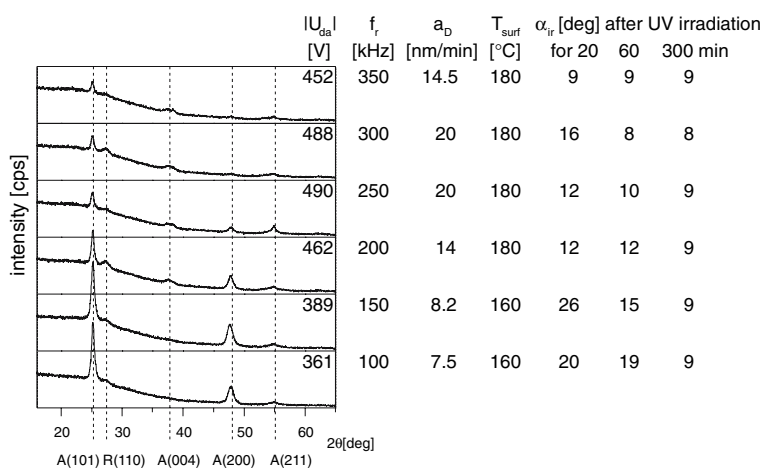

figure shows, that the increase of f_r leads to a partial suppression of the crystallinity characterized by the decrease of anatase (101) peak intensity. This phenomenon can be explained by a reduction of the energy delivered to the growing film by ions per deposited particle due to increasing deposition rate a_D ($E_{bi} \approx E_{bi}^*/a_D$) [23]. However, the intensification of the ion bombardment at f_r > 200 kHz discussed above ensures that the TiO_2 films remain crystalline even at significantly higher deposition rates.

It was found that the deterioration of the anatase film crystallinity and the conversion of the anatase structured films to the close X-ray amorphous films improves the hydrophilicity. This finding is in a good agreement with previous reported results [21, 25]. The TiO_2 films prepared at f_r = 350 kHz exhibited best hydrophilicity; the WDCA α on their surfaces decreases rapidly after 20 min of the UV irradiation to $\alpha_{ir\ 20min}$ = 9°. The surface roughness remains almost the same (R_a in the range from 9 to 10 nm) for all the TiO_2 films prepared at different values of f_r. It means that an influence of the film surface morphology on the improvement of hydrophilicity can be excluded. This experiment shows that the increase in f_r opens a new possibility of the preparation of hydrophilic

transparent TiO_2 films in the oxide mode of sputtering with significantly higher deposition rates compared to that of films produced at low f_r and even a better hydrophilicity.

The hydrophilicity improvement due to the increase of f_r is similar to the effect of the increased total working pressure p_T at f_r = 100 kHz in the oxide mode of sputtering reported in Ref. [6], where the increase in p_T also resulted in the conversion of the TiO_2 films with the anatase structure into the close to X-ray amorphous TiO_2 films with suppressed anatase crystallinity and enhanced surface hydrophilicity.

Effect of oxygen partial pressure p_{O2}

A higher a_D of the TiO_2 films can be achieved in the transition mode of sputtering (compared to the oxide mode). The operation in the transition mode was accompanied by the instabilities and the oscillations of the oxygen flow rates ϕ_{O2} at f_r > 200 kHz and p_T = 0.9 Pa when high values of $I_{da1,2} \geq$ 3 A are used. The deposition process was stable at f_r = 100 kHz, i.e. no oscillations occur. The cause of this phenomenon is a greater amount of Ti atoms sputtered at f_r > 200 kHz what requires a higher value of ϕ_{O2} to form $TiO_{x \approx 2}$

film together with desired oxygen partial pressure p_{O2}. In this case the total flow rate of sputtering gas mixture $\phi_T = \phi_{Ar} + \phi_{O2}$ exceeds a critical value given by the pumping speed of the system, which results in a slower system response leading to instabilities in a closed control circuit [26, 27]. The closed control loop is discussed in detail in Ref. [20]. While the total working pressure p_T in the system is controlled by the pumping speed, instabilities can be suppressed if operating at decreased p_T and thus higher pumping speed of the vacuum system.

Based on the process stability study discussed above the experiments were carried out at $f_r = 350$ kHz, $I_{da1,2} = 3$ A and $p_T = 0.75$ Pa. A series of the ~ 1,000 nm thick TiO_2 films at different p_{O2} were prepared. All the films were sputtered at $T_{surf} \leq 180$ °C. As expected, p_{O2} strongly influences the film structure, its hydrophilicity and the deposition rate a_D, see Fig. 4. The increase of the oxygen partial pressure p_{O2} leads to (i) a decrease of the deposition rate a_D of the transparent TiO_2 films from 80 nm/min in the transition mode to 15 nm/min in the oxide mode, (ii) a change in the film structure from a mixture of the rutile + anatase in the transition mode of sputtering ($p_{O2} < 0.15$ Pa) to the anatase film in the oxide mode ($p_{O2} \geq 0.20$ Pa).

The anatase TiO_2 film prepared at high value of $p_{O2} = 0.20$ Pa exhibits a very good hydrophilicity and low WDCA $\alpha_{ir\ 1h} < 10°$ after the UV irradiation for one hour. The decrease of p_{O2} leads to a deterioration of film hydrophilicity, except the TiO_2 film sputtered with $a_D = 80$ nm/min in the deep transition mode at
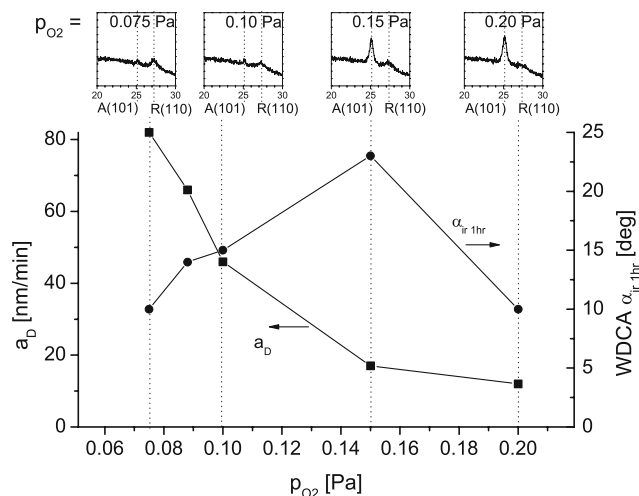

Fig. 4 The deposition rate a_D, UV induced hydrophilicity characterized by WDCA $\alpha_{ir\ 1hr}$ after 1 h of UV irradiation (0.9 mW cm^{-2}) and the X-ray structure of 1,000 nm thick transparent TiO_2 films prepared at $I_{da1,2} = 3$ A, $p_T = 0.75$ Pa, $d_{s-t} = 100$ mm, $f_r = 350$ kHz and $T_{surf} \approx 180$ °C as a function of p_{O2}
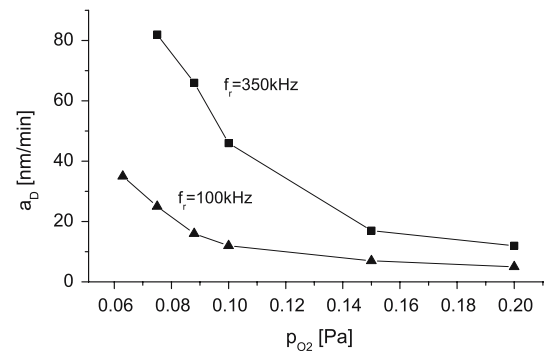

Fig. 5 The effect of the oxygen partial pressure p_{O2} on the deposition rate a_D of the TiO_2 films sputtered at $I_{da1,2} = 3$ A, $p_T = 0.75$ Pa, $d_{s-t} = 100$ mm and different repetition frequency (a) $f_r = 100$ kHz [6] and (b) $f_r = 350$ kHz

$p_{O2} = 0.075$ Pa, which also exhibited hydrophilic properties. This is in a good agreement with our previous reported results, where the same hydrophilicity was observed on the anatase films sputtered in the oxide mode and the anatase + rutile films sputtered at very low p_{O2} in the transition mode. The deterioration of the film hydrophilicity in the transition mode is explained the decrease of the highly photoactive anatase phase content in the films in favor of the rutile phase. The high photoactivity of the films sputtered at very low p_{O2} in the transition mode of sputtering is a result of their very high surface roughness that increases in the transition mode of sputtering with decreasing p_{O2}; for more details see Refs. [21, 28].

The effect of p_{O2} on the deposition rate of the TiO_2 films sputtered at above described deposition conditions and different repetition frequency $f_r = 100$ kHz [6] and 350 kHz is shown in Fig. 5. As expected, the pulse waveforms evolution and operating in the plasma build-up regime with more effectively used sputtering pulse at $f_r = 350$ kHz (discussed in section "Time evolution of pulse waveforms") leads to significantly higher deposition rates even in the transition mode of sputtering.

TiO_2 deposition on thermal sensitive substrate

At present, there is an urgent need to deposit thin films on thermal sensitive substrates, such as the polycarbonate (PC). However, that is a very difficult task. In this section we report on a successful deposition of the TiO_2 films on the PC at the substrate surface temperature $T_{surf} < 130$ °C. This experiment is based on our recent investigations that clearly show that T_{surf} can be effectively driven by the pulse target power density [6, 23].

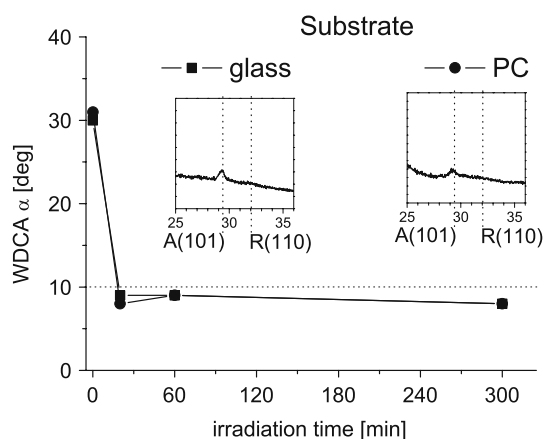The well hydrophilic ~ 1,000 nm thick transparent TiO_2 films were sputtered with $a_D = 5.2$ nm/min on the

Fig. 6 The X-ray structure of the 1,000 nm thick transparent TiO$_2$ films sputtered on glass and polycarbonate substrates at f_r = 350 kHz, $I_{da1,2}$ = 2 A, p_T = 0.9 Pa, p_{O2} = 0.2 Pa, d_{s-t} = 100 mm, T_{surf} ≈ 120 °C and a_D = 5.2 nm/min and their hydrophilicity as a function of time of UV irradiation

PC and glass substrates at $I_{da1,2}$ = 2 A, U_{da} = –400 V, f_r = 350 kHz, p_T = 0.9 Pa, d_{s-t} = 100 mm, oxide mode of sputtering at p_{O2} = 0.15 Pa and T_{surf} ≈ 120 °C. The XRD structure and hydrophilicity of these films is displayed in Fig. 6. The XRD patterns with broad low-intensity anatase (101) peaks confirm the nanocrystalline structure of the sputtered films and no difference in the photoinduced hydrophilicity characterized by the WDCA α after the UV irradiation show that the substrate has no effect on the TiO$_2$ film properties. Both films exhibit an excellent photoinduced hydrophilicity with a very fast decrease of the WDCA with increasing the UV light irradiation time ($\alpha_{irr20min}$ = 9° already after t = 20 min). Already very short UV irradiation converts the surface of the sputtered TiO$_2$ film into superhydrophilic one. The change in wettability of the surface of the TiO$_2$ film sputtered on the PC substrate after its UV irradiation for 20 min is shown in Fig. 7.

Obtained results clearly show that reactive pulsed dual magnetron sputtering is a one-step process suitable for the low-T preparation of the hydrophilic crystalline TiO$_2$ films on heat sensitive substrates.
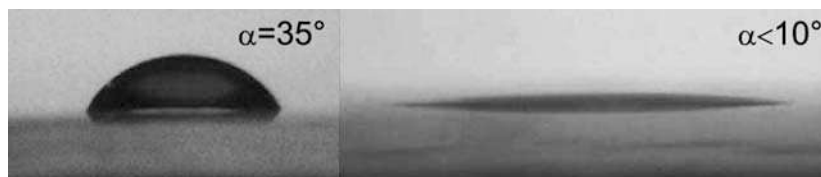
However, the coating of very heat sensitive substrates such as PC (T_{max} = 130 °C) has to be performed at decreased average pulse target power densities (≤40 W/cm^2) and low (≤5 nm/min) deposition rates.

Conclusions

Experiments described above clearly demonstrate that (i) dc pulsed reactive magnetron sputtering is a very perspective method for the low-T preparation of the crystalline hydrophilic TiO$_2$ films and (ii) the deposition process strongly depends on the pulse repetition frequency f_r. It was found that

1. The increase in f_r from 100 to 350 kHz and operating in plasma build-up regime results in (a) a strong increase of the deposition rate a_D of both Ti films sputtered at p_{O2} = 0 Pa (1.7×) and of TiO$_2$ films sputtered in the oxide mode at p_{O2} = 0.15 Pa (2×) while T_{surf} increases only slightly from 160 to 180 °C, (b) a decrease of peak discharge voltage which makes possible to sustain the magnetron discharge at high values of pulse target power densities achieving up to 240 W/cm^2 in our case.
2. The transparent hydrophilic TiO$_2$ film composed of a mixture of the anatase + rutile phase can be sputtered in the transition mode of sputtering at high deposition rate a_D = 80 nm/min on glass substrate located at the substrate-to-target distance d_{s-t} = 100 mm and T_{surf} ≈ 180 °C. The TiO$_2$ film with the excellent hydrophilic properties was successfully sputtered in the oxide mode at T_{surf} ≈ 120 °C, a_D = 5.2 nm/min and f_r = 350 kHz on a polycarbonate substrate without its thermal destruction.
3. The low-T deposition of the well hydrophilic TiO$_2$ films can be realized in a one-step process using the dc pulse reactive magnetron sputtering without a subsequent post-deposition thermal annealing.

Fig. 7 Photos of the water droplet profile on the surface of the TiO$_2$ film sputtered on polycarbonate substrate at T_{surf} < 120 °C (a) before and (b) after UV light irradiation for 20 min

References

1. A. Fujishima, K. Honda, Nature **238**, 37 (1972)
2. N. Sakai, A. Fujishima, T. Watanable, K. Hashimoto, J. Phys. Chem. B **107**, 1028 (2003)
3. A. Fujishima, X. Zhang, C.R. Chimie **9**, 750 (2006)
4. L. Miao, S. Tanemura, Y. Kondo, M. Iwata, S. Toh et al., Appl. Surf. Sci. **238**, 125 (2004)
5. O.H. Fenner, in *Handbook of Plastics and Elastomers,* ed. By C. A. Harper (McGraw-Hill, New York USA 1975)
6. J. Musil, D. Herman, J. Sicha, J. Vac. Sci. Technol. A **24**(3), 521 (2006)
7. P. Zeman, S. Takabayashi, J. Vac. Sci. Technol. A **20**(2), 1 (2001)
8. G. Zhao, Q. Tian, Q. Liu, G. Han, Surf. Coat. Technol. **198**, 55 (2005)
9. T. Modes., B. Scheffel, Chr. Meetzner, O. Zywitzki, E. Reinhold, Surf. Coat. Technol. **200**, 306 (2005)
10. W. Ho, J.C. Yu, S. Lee, Appl. Catal. B: Environ. DOI:10.1016/j.apcatb.2006.06.019 (2006)
11. S. Mathur, P. Kuhn, Surf. Coat. Technol. **201**, 807 (2006)
12. P. Frach, D. Gloss, Chr. Metzner, T. Modes, B. Scheffel, O. Zywitzki, Vacuum **80**, 679 (2006)
13. S.B. Amor, L. Guedri, G. Baud, M. Jacquet, M. Ghedira, Mater. Chem. Phys. **77**, 903 (2002)
14. Y.-Q. Hou, D.-M. Zhuang, G. Zhang, M. Zhao, M.-S. Wu, App. Surf. Sci. **218**, 97 (2003)
15. P. Frach, D. Gloss, K. Goedicke, M. Fahland, W.-M. Gnehr, Thin Solid Films **445**, 251 (2003)
16. O. Zywitzki, T. Modes, H. Sahm, P. Frach, K. Goedicke, D. Gloss, Surf. Coat. Technol. **180–181**, 538 (2004)
17. C. Barnes, S. Kumar, L. Green, N.-M. Hwang, A.R. Gerson, Surf. Coat. Technol. **190**, 321 (2005)
18. S. Ohno, T. Takasawa, Y. Sato, M. Yoshikawa, K. Suzuki, P. Frach, Y. Shigesato, Thin Solid Films **496**, 126 (2006)
19. F. Lapostolle, F. Perry, A. Billard, Surf. Coat. Technol. **201**, 2633 (2006)
20. P. Baroch, J. Musil, J. Vlcek, K.H. Nam, J.G. Han, Surf. Coat. Technol. **193**, 107 (2005)
21. D. Herman, J. Musil, J. Sicha, Photoactivated properties of TiO$_2$ films prepared by magnetron sputtering, *Proceedings of the PSE 2006 in Plasma Processes & Polymers*, accepted for publication, November 2006
22. Th. Welzel, Th. Dunger, F. Richter, Surf. Coat. Technol. **201**, 3959 (2006)
23. J. Musil, P. Baroch, J. Vlček, K.H. Nam, J.G. Han, Thin Solid Films **475**, 208 (2005)
24. J.W. Bradley, H. Bäcker, P.J. Kelly, R.D. Arnell, Surf. Coat. Technol. **142**, 337 (2001)
25. S.K. Zheng, T.M. Wang, G. Xiang, C. Wang, Vacuum **62**, 361 (2001)
26. I. Safi, Surf. Coat. Technol. **127**, 203 (2000)
27. S. Berg, T. Nyberg, Thin Solid Films **476**, 215 (2005)
28. J. Sicha, J. Musil, D. Herman, Z. Stryhal, J. Pavlik, Surface morphology of magnetron sputtered TiO$_2$ films, *Proceedings of the PSE 2006 in Plasma Processes & Polymers*, accepted for publication, November 2006