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N-doped TiO₂ coatings grown by atmospheric pressure MOCVD for visible light-induced photocatalytic activity

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Abstract

N-doped TiO₂ films were deposited by atmospheric pressure CVD from titanium tetra-isopropoxide (TTIP) and N₂H₄ as reactive gas in the temperature range 400–500 °C on various substrates. The films grown at 400 °C are amorphous and exhibit a compact structure and a smooth surface morphology. Increasing the deposition temperature first leads to the crystallization in the anatase structure (temperature range 410–450 °C) and then to the formation of rutile, so that an anatase-rutile mixture is observed in the temperature range 450–500 °C. Correlation between the structure, the morphology, optical properties, hydrophilicity and photocatalytic activity of the thin films both under UV and VIS light are presented and discussed in relation with deposition conditions.

Keywords: AP-MOCVD; N-doped TiO₂; Supported photocatalyst; Visible photocatalysis

1. Introduction

Titanium dioxide (TiO₂) is an efficient and well studied semiconductor for various photodriven applications, as in photocatalysis [1] and photoelectrochemical cells [2]. Both nanoparticles powder and polycrystalline thin films of TiO₂ are easily and inexpensively produced by various processes and they show a good chemical stability under illumination in most environments. However, there are some drawbacks for useful applications. A major one for solar energy applications is that the band gap energy, 3.2 eV for anatase, only allows ultraviolet (UV) absorption. To improve the photoelectrochemical efficiency of this material it is desirable to red-shift the photoelectrochemical onset to also include the less energetic but more intense visible part of the solar spectrum. This can be achieved by doping the oxide semiconductor, which will generate new electronic states in the band gap.

Recently, nitrogen was used as anionic doping to create a visible light response in TiO₂ [3]. Theoretical modelling of the band structure of doped TiO₂ suggested that substitution doping by N is effective because its 2p states contribute to bandgap narrowing by mixing with the O 2p states [3,4]. Also, because of the comparable ion size of oxygen and nitrogen, the distortion of the crystal lattice should remain low, so that not a large numbers of recombination centres are generated. However, there still exists some controversy about the physical and electronic structure of visible light active nitrogen doped anatase [5–8].

Concerning N-doped TiO₂ films Yates et al. found no evidence for photocatalytic activity in the visible light range of films made by atmospheric pressure CVD using ammonia as reactive gas [9]. However, under low pressure, Maeda et al. reported visible light activity of N-doped TiO₂ films prepared by PECVD using titanium(IV) tetraisopropoxide (TTIP) and NH₃ [10].

This paper deals with the deposition of N-doped TiO₂ thin films by atmospheric pressure MOCVD using TTIP and hydrazine (N₂H₄) as N source on glass, Si(100) and stainless steel (SS 304) substrates. The physico-chemical, structural characteristics and photocatalytic activity of N-doped TiO₂ films are discussed in relation with the growth conditions.

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2. Experimental procedure

A cold-wall vertical CVD quartz reactor, 5 cm in diameter, was used for the deposition of the layers. The substrates were placed on a stainless steel sample holder (3.2 cm in diameter) heated by HF induction [11]. For the N doping, hydrazine was used because it allows the formation of reactive nitrogen in the gas phase at relatively low temperature (150 °C) [12] compared to NH_3 which requires temperature higher than 600 °C. The typical experimental procedure is described in a companion paper [13]. Here a second bubbler containing hydrazine was connected to the reactor. The substrates were glass, Si(100) wafers and stainless steel. Table 1 presents the MOCVD conditions used for the growth of N-doped TiO_2 layers.

The film microstructure was studied by X-ray diffraction (XRD) using grazing geometry ($\text{Cu K}\alpha$). The surface morphology was observed using a scanning electron microscope and the film thicknesses were determined on cross sections and by reflectometry. The film composition was analyzed by secondary ion mass spectroscopy (SIMS), electron micro-probe analysis and X-ray photoelectron spectroscopy (XPS). Optical properties were determined using a UV–VIS–NIR spectrophotometer equipped with an integrating sphere. The bandgap was determined by extrapolation of the absorption edge using Tauc's plot.

The photocatalytic activity was evaluated by studying the initial rate of decomposition of aqueous Orange G solution (10 ppm) under UV and VIS irradiation. The concentration was determined by measuring the absorbance at 480 nm using UV–VIS spectrometry and plotted as a function of irradiation time. The decomposition rate (DR) was determined by the slope of the linear fitting over the first 150 min for UV exposures. For VIS tests, the fitting was made over the first 2800 min except for the most active samples for which the first 400 min were considered. For photocatalytic tests a UV lamp (365 nm) was used (HPLN Philips 125 W) and the sample was placed in a thermostated chamber in order to obtain a radiance of 1 mW/cm^2 . The surface area of the sample used for photocatalytic tests was 4 cm^2 . In order to determine the photocatalytic activity using visible light, two fluorescent lamps (FCE27 52 W) were used coupled with an UV cut filter (400 nm) providing a cumulative irradiance in the range 450–550 nm of 3 mW/cm^2 .

The hydrophilicity was evaluated by measuring the contact angle of a water droplet. Each value is an average of 3

Table 1
Typical MOCVD conditions used for the growth of N-doped TiO_2 layers

Growth temperature (°C)	400–500
Carrier gas flow rate (N_2 , sccm)	500
Pressure (torr)	760
Total gas flow rate (sccm)	5500
Carrier gas flow rate for N_2H_4 (N_2 , sccm)	300
Bubbler temperature N_2H_4 (°C)	40
Bubbler temperature TTIP (°C)	65
TTIP mole fraction	10^{-4}
$\text{N}_2\text{H}_4/\text{TTIP}$ ratio	5–25
Substrates	Si(100), glass, stainless steel
Deposition time (min)	15

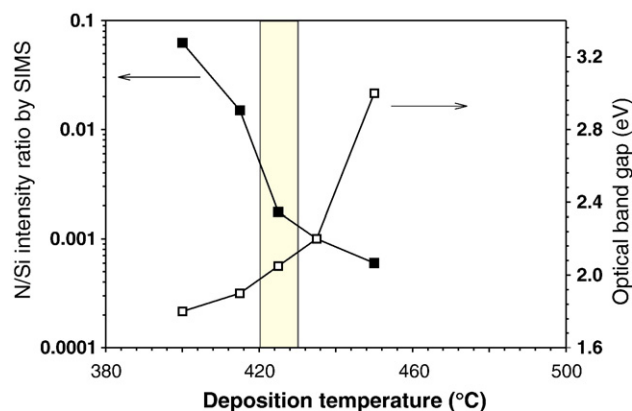


Fig. 1. Influence of the deposition temperature on the relative nitrogen content of N-doped TiO_2 films grown on Si(100), using a $\text{N}_2\text{H}_4/\text{TTIP}$ ratio $R=25$. The content is defined by the SIMS intensity ratio N/Si measured after Ar^+ sputtering of approximately 30 nm to avoid the surface contamination (film thickness $\sim 300 \text{ nm}$). The optical band gap of comparable films deposited on glass is also shown. Additionally, the region of maximum visible photocatalytic activity is marked (see following chapters for further details).

measurements on different areas of the sample surface. The measurements were realized on as-deposited sample stored in dark for a week and no illumination was performed on the sample before the test except the day light of the lab during few minutes.

All results in this paper refer to films deposited on stainless steel, except in the case of the SIMS measurement, where a silicon wafer was used as substrate for its low roughness, and in the case of the optical transmission measurements, where glass was chosen as substrate for obvious reasons.

3. Results and discussion

3.1. Composition, structure and morphology of N-doped TiO_2 films

SIMS measurements show that nitrogen is incorporated into the film. The N relative content decreases rapidly with the

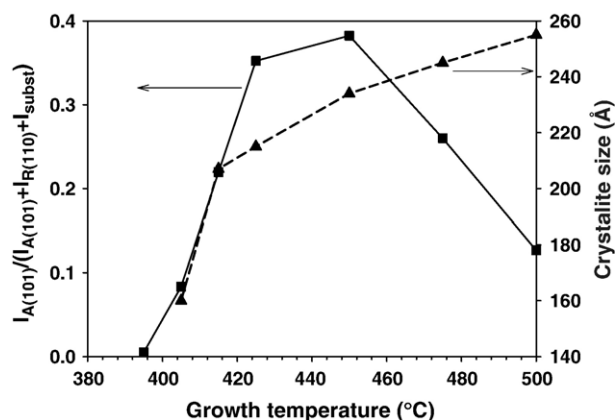


Fig. 2. Proportion of anatase given by the relative intensity ratio of XRD peaks of anatase (101), rutile (110) and substrate (stainless steel) and variation of the crystallite size of anatase (101) versus the growth temperature.

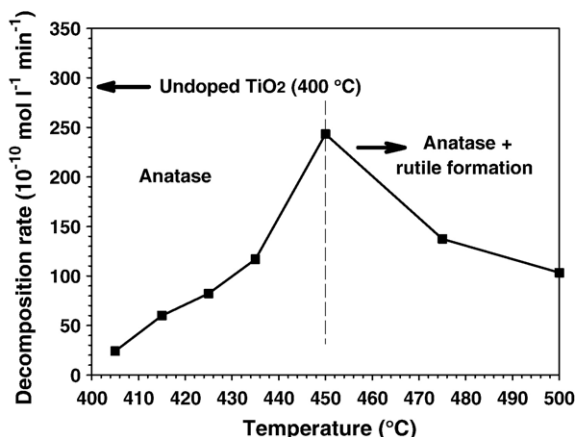


Fig. 3. Photocatalytic decomposition rate of Orange G solutions (10 ppm) under UV irradiation using N-doped TiO₂ layers (~300 nm thick) grown on stainless steel at various temperatures, using N₂H₄/TTIP mole ratio $R=25$. The TTIP mole fraction was 0.01%. The rate for undoped anatase ($R=0$) grown at 400 °C is given as reference.

increase of the deposition temperature in the range 400–425 °C. In the temperature range 425–450 °C, the N content has always a decreasing tendency, but with a smoother slope (Fig. 1).

The N1s XPS spectrum of film grown at 400 °C shows one peak with the binding energy at 396.4 eV, which indicates that the nitrogen incorporated in the N-doped TiO₂ films is a nitride form and not a molecular chemisorbed species. Asahi et al. proposed that the peak around 396.5 eV be assigned to substitutional N, which may be related to photocatalytic activity under VIS light. Increasing the temperature to 425 °C and above the nitrogen is not detectable by XPS.

As-deposited N doped TiO₂ films at 400 °C are amorphous, as can be concluded from XRD. At this temperature and without N₂H₄, anatase is normally formed [13], consequently the presence of nitrogen leads to the amorphization of the layers. The increase of the deposition temperature leads then to the crystallization of the films in anatase form in the temperature range 410–450 °C. Starting from 450 °C, an anatase/rutile

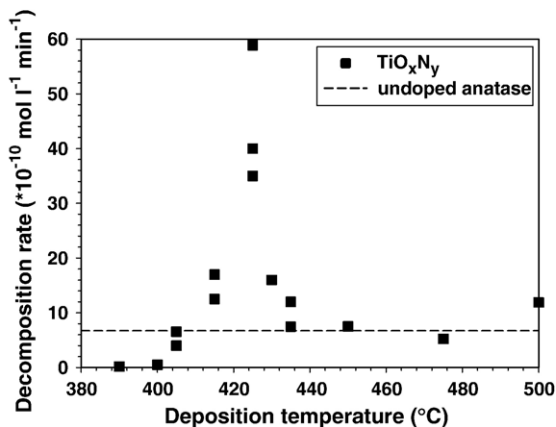


Fig. 4. Photocatalytic decomposition rate of Orange G solutions (10 ppm) under VIS irradiation (>400 nm) using N-doped TiO₂ layers (~300 nm thick) grown on stainless steel at various temperatures using N₂H₄/TTIP mole ratio $R=25$. The rate for undoped anatase ($R=0$) grown at 400 °C is given as reference.

mixture is formed with a rutile amount increasing with the temperature. The rutile proportion is approximately 5% at 450 °C and it reaches 30% at 500 °C. Fig. 2 shows the variation of relative intensity ratio of XRD peak of anatase (101), rutile (110) and the substrate in the temperature range 400–500 °C. The amount of anatase related to rutile and the film thickness increases with the temperature attaining a maximum at 450 °C followed by a decrease due to the formation of rutile. The crystallite size, determined using the Scherrer formula, increases continuously with the temperature to reach the typical value of 24 nm at 450 °C.

The films grown at 400 °C using a N₂H₄/TTIP ratio $R=25$ have a very smooth surface morphology with a roughness (RMS) around 10 nm for a thickness of 300 nm. Increasing the temperature elongated and pointed crystallites grow perpendicular to the surface of the substrate leading to a columnar growth very similar to the one of TiO₂ films obtained without doping [11].

3.2. Optical properties

The film grown at 400 °C using $R=25$ has a low transparency (20% at 550 nm). It exhibits a green colour in the early stages and becomes metallic for thicknesses higher than 500 nm. Increasing the temperature, the transparency at the same wavelength is improved (55% at 425 °C and 70% at 450 °C) and the films exhibit a green-yellow colour. For all spectra, the fundamental absorption edge shifts towards the high wavelength, *i.e.* the low energy side, by decreasing the deposition temperature. This is shown in Fig. 1 where clearly the optical band gap of N-doped TiO₂ films grown in the temperature range 400–450 °C using $R=25$ decreases with decreasing temperature/increasing nitrogen content. Indeed, the absorption of the films grown at 400 °C shifts to the visible light due to a narrowing of the band gap to around 1.8 eV. Then, increasing the temperature the band gap increases to around 2.2 eV at 425 °C and to 3.0 eV at 450 °C, a value slightly lower than the one of pure anatase. Concerning the effect of the N₂H₄/

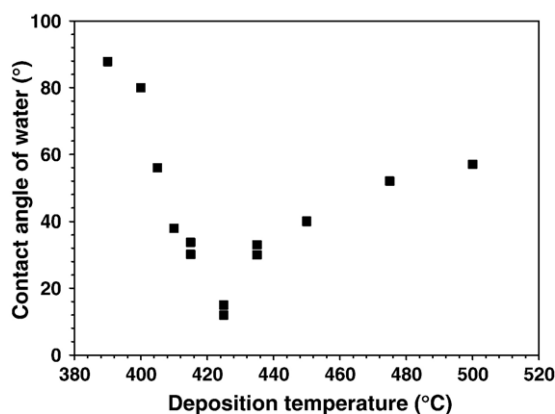


Fig. 5. Variation of the contact angle of water for various N-doped TiO₂ films grown on stainless steel at various temperature using TTIP conc.=0.01% and N₂H₄/TTIP=25. The film thickness was approximately 275 nm. Measurements were made under the day light of the lab without additional UV or Vis irradiation.

TTIP mole ratio, a decrease of the bandgap with increasing ratio is seen at 400 °C.

3.3. Photocatalytic activity

Fig. 3 shows the evolution of photocatalytic activity under UV light of N-doped TiO₂ films in the temperature range 400–500 °C using TTIP/hydrazine ratio=25. As reference a pure anatase TiO₂ film (300 nm thick) grown at 400 °C is represented on the graph. All photocatalytic tests were realized using samples with comparable surface area and film thickness. The UV activity of N-doped TiO₂ films increases with the deposition temperature and reaches a maximum at 450 °C. This increase of UV activity is likely due to the increase of crystallinity of the anatase phase. The maximum UV photocatalytic activity is obtained at 450 °C where also the maximum amount of anatase in the N-doped TiO₂ film is found (Fig. 2). Higher temperatures lead to rutile growth and a decrease of UV photocatalytic activity as found for undoped TiO₂ layers [13].

Concerning the effect of the N₂H₄/TTIP mole ratio, an increase of this ratio leads to a decrease in the UV photocatalytic activity of films grown at 400 °C until it becomes negligible for samples made using R=10 or more. This behaviour is also correlated with the decrease of crystallinity of the film.

The evolution of photocatalytic activity under visible irradiation ($\lambda > 400$ nm) for N-doped TiO₂ films grown in the temperature range 390–500 °C using N₂H₄/TTIP mole ratio=25 is shown in Fig. 4. As reference the activity of a pure anatase TiO₂ film (300 nm thick) grown at 400 °C was represented on the graph. Clearly, films with sensitivity to visible light are obtained within a small process window (415–435 °C). Several experiments confirm that the best temperature for the visible photocatalytic activity is 425 °C. The composition and morphology data of the films suggest that the narrow process window is caused by the temperature dependence of the nitrogen incorporation and its effect on crystallinity (as was shown nitrogen leads to amorphization of the films). Generally, increasing the temperature reduces the nitrogen incorporation (leading presumably to less activity), but consequently increases the crystallinity (leading to higher activity).

The film grown at 500 °C seems to exhibit a higher activity than those grown at 450 and 475 °C. Maybe this is not significant, but this slight increase could be due to the formation of rutile, which has a lower band gap than the anatase and subsequently a better efficiency to absorb visible light.

Interestingly, a nice correlation is observed between the influence of the deposition temperature on the wettability under the visible light of the laboratory (Fig. 5) and the photocatalytic activity under visible irradiation (Fig. 4). The wettability varies like the photocatalytic activity. These properties are related and frequently investigated in parallel. Thus the results concerning the wettability support the activity in the visible light range.

Fig. 6 shows the influence of the N₂H₄/TTIP mole ratio on the photocatalytic properties under UV and VIS light of N-doped TiO₂ film grown at 425 °C. The visible activity increases progressively with the increase of N₂H₄/TTIP mole ratio (for R=25 the activity is 5 times higher than that of the undoped

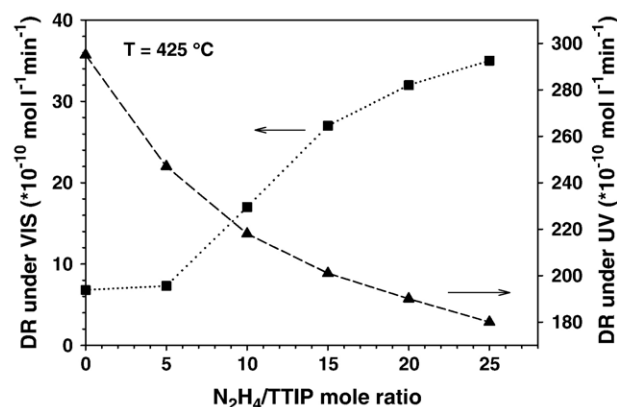


Fig. 6. Photocatalytic decomposition rate of Orange G solutions (10 ppm) using UV and VIS (>400 nm) light by N-doped TiO₂ (~300 nm) layers grown on stainless steel at 425 °C, using various N₂H₄/TTIP mole ratios.

anatase), while the UV activity decreases (for R=25 the activity is 40% lower than the anatase). The UV efficiency for N-doped TiO₂ films decays compared to undoped TiO₂. This is consistent with the behaviour of films with states in the band gap. They act as recombination centres for light-induced charge carriers, which lower the photoresponse in the UV region. The N-doped films show a considerable increase in their activity under visible light irradiation, compared to the situation for undoped TiO₂. The light absorption for N-doped TiO₂ films is shifted to around 550 nm, *i.e.* well into the visible region of the spectrum. This corresponds to a material with a band gap energy close to 2.3 eV, which is significantly lower in energy than for undoped anatase.

4. Summary and conclusion

N-doped TiO₂ films with a significant photocatalytic activity in the visible light range were deposited on various substrates by atmospheric pressure CVD using TTIP and N₂H₄ as reactive gas mixture. The process window to obtain visible light activity was found to be very narrow. The data suggest that this is due to the fact that the incorporation of nitrogen reduces the crystallinity of the films. Consequently, a compromise must be found between the amount of incorporated nitrogen, influencing the bandgap, and the anatase fraction in the film.

The films showing photocatalytic activity in the visible light were also very hydrophilic under ambient light in the laboratory.

While nitrogen doping lead to enhanced photocatalytic activity in the visible light region, the activity in the UV region was reduced. It is believed that the incorporation of nitrogen leads to states in the band gap that act as recombination centres.

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