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Chemical vapor deposition and characterization of nitrogen doped TiO_2 thin films on glass substrates

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ABSTRACT

Photocatalytically active, N-doped TiO_2 thin films were prepared by low pressure metalorganic chemical vapor deposition (MOCVD) using titanium tetra-iso-propoxide (TTIP) as a precursor and NH_3 as a reactive doping gas. We present the influence of the growth parameters (temperature, reactive gas phase composition) on the microstructural and physico-chemical characteristics of the films, as deduced from X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and ultra-violet and visible (UV/Vis) spectroscopy analysis. The N-doping level was controlled by the partial pressure ratio $R=[NH_3]/[TTIP]$ at the entrance of the reactor and by the substrate temperature. For $R=2200$, the N-doped TiO_2 layers are transparent and exhibit significant visible light photocatalytic activity (PA) in a narrow growth temperature range (375–400 °C). The optimum N-doping level is approximately 0.8 at.%. However, the PA activity of these N-doped films, under UV light radiation, is lower than that of undoped TiO_2 films of comparable thickness.

1. Introduction

Titanium dioxide (TiO_2) is extensively used in modern life applications, e.g. cosmetics, pigments, building materials, antibacterial surfaces, biocompatible material for prosthesis and solar cells [1–4]. Many research works of the past two decades focus on the photocatalytic properties of this semi-conducting transparent material. Under UV light (wavelength<387 nm) TiO_2-anatase leads to the degradation and total mineralization of a great number of pollutants dispersed in air or water [5]. Moreover, the photo-induced superhydrophilicity of TiO_2 films has also been achieved under UV light [6]. These two properties are very attractive: a thin film of TiO_2 can decompose atmospheric pollutants present on its surface and get self-cleaning from any dust and organic residues at the same time. Thus, the coating of large glass surfaces with TiO_2 (buildings, cars, etc.) is a smart way to decrease maintenance costs and contribute to the cleaning of urban air. Considering that the UV light is only 5% of the sun spectrum, real commercial applications will drastically develop if activation of these semi-conducting films by the visible light is enhanced.

A simple idea to activate the TiO_2 photocatalyst by the visible light is to reduce the band gap (initially 3.2 eV for TiO_2-anatase) by inserting intermediate electronic states in the band gap of the electronic structure. This can be achieved by creating defects, i.e. oxygen vacancies (TiO_{2-x}) or atoms in substitution or insertion (cationic and anionic doping). Oxygen deficient TiO_{2-x} films produced by MOCVD [7] and powders produced by TiC, TiN, TiO and Ti_2O_3 oxidation [8], gave positive results. Doping of TiO_2 anatase powders with Fe [9], Cr [10] and Ag [11] led to visible photocatalytic decomposition of oxalic acid, yellow XRG dye and rhodamine B, respectively. The optimum doping level reported so far is quite low (e.g. $Fe^{+3}=0.09\%$ or Fe/Ti = 0.05 [9]). TiO_{2-x} and cation-doped TiO_2 samples suffer from thermal stability and low photocatalytic activity because of the presence of uncontrolled structural defects which act as electron and hole traps [12].

Concerning anion doping, recently Asahi et al. [13] proposed an interesting approach for elaborating N-doped TiO_2 anatase films by substituting oxygen with nitrogen atoms. The small difference between nitrogen and oxygen ion radii facilitates nitrogen substitution and does not distort the crystal lattice much. Theoretical modeling was also used to demonstrate that the semiconductor band gap decreases when the N 2p states mix with the O 2p states, thus rendering the material active under visible light [13,14]. Still, the electronic structure of the efficient nitrogen doped anatase is under question [8,15,16]. Despite the great number of scientific reports about N-doped TiO_2 thin films, only few works mention successful results for supported thin layers. F.-D. Duminica et al. have proposed an atmospheric pressure CVD process (APCVD) for the growth of pure TiO_2 [17] and further, by using N_2H_4 as doping reactive gas, they have reported significant photocatalytic activity in the visible light range but for films deposited in narrow growth conditions [18]. Working with APCVD but using NH_3 as a reactive gas instead, Yates et al. found no evidence of photocatalytic activity [19]. However Maeda et al. [20]

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

Growth temperature (°C)	300–425
Pressure (Torr)	20
Carrier gas flow rate (N_2, sccm)	20
NH_3 gas flow rate (sccm)	25–100
NH_3/TTIP	555–2220
Total gas flow rate (sccm)	600
Bubbler temperature TTIP (°C)	25
TTIP molar fraction (10^{-6})	65
Deposition time (min)	180–360
Substrate	Borosilicate glass, Si(100)

reported visible light activity of films prepared by plasma enhanced CVD under low pressure and using NH_3 as reactive gas. Efficient photocatalysts under visible light were also produced using other deposition methods such as ion-assisted electron-beam evaporation [21] or magnetron sputtering [13,22].

This work reports the growth of photocatalytically active N-doped TiO_2 films by low pressure CVD on glass substrates, using titanium tetra-iso-propoxide (TTIP) as titanium and oxygen precursor and NH_3 as nitrogen source. The microstructural characteristics and the photocatalytic activity of the films are discussed in relation with the growth parameters.

2. Experimental

A horizontal hot-wall CVD quartz reactor 5 cm in diameter was used for the film deposition. Borosilicate flat glass and Si(100) wafers were placed on an inclined stainless steel sample holder at a distance 14 cm from the entrance. The main precursor decomposition zone, found from preliminary runs, is extended from 11 to 18 cm from the entrance of the reactor. The growth temperature was controlled by a thermocouple K plugged into the sample holder. Liquid TTIP was placed in a bubbler thermostated in a water bath at 298 K. Pure N_2 (99.9992%) was fed through two lines equipped with mass flow controllers, one to bubble through the TTIP precursor, the other to dilute it. The total pressure was maintained at 20 Torr. For the N-doping, NH_3 gas (99.999%) was fed through the reactor during the deposition. Table 1 presents the typical MOCVD conditions. The film microstructure was studied by X-ray diffraction (XRD) using θ-θ and grazing geometry (Cu Kα). The surface morphology was observed by scanning electron microscopy (SEM) and the film thickness was determined on cross sections and by optical methods [23]. The arithmetical average of the surface roughness profile (R_a) was measured using an optical interferometer. The film composition was analyzed by secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS). Optical properties were determined using a UV–Vis spectrophotometer equipped with an integrating sphere. The band gap (E_g) was determined by extrapolation of the absorption edge using Tauc's plot.

The photocatalytic activity of the one-side coated borosilicate flat glass (32×32 mm^2) was determined from the initial decomposition rate (r_0) of an aqueous Orange G solution (10^{-5} mol L^{-1}) under UV and visible irradiation. The sample immersed in 25.0 cm^3 of the dye solution was placed into a quartz vessel (28.8 cm^3) transparent to wavelengths >290 nm. All solutions were first agitated for 1 h in the dark in order to reach equilibrium with the photocatalyst. The concentration was determined by measuring the absorbance of Orange G at 480 nm and applying the Beer–Lambert law. The kinetic curves of Orange G decomposition were obtained by plotting the concentration as a function of irradiation time. The r_0 was determined by the slope of the linear fitting over the first 60 min for UV irradiation and over the first 360 min for the visible light irradiation. For UV tests the sample was irradiated with 1.05 mW cm^{-2} (365 nm) using a UV lamp (HPLN Philips 125 W). The tests under visible light were performed using two fluorescent lamps (FCE27 52 W) coupled with a UV cut filter (400 nm) providing a cumulative irradiance in the range 450–550 nm of 14.1 mW cm^{-2}. The results of the structural analysis (XRD), photocatalytic activity and optical properties refer to films deposited on borosilicate glass substrates while composition analysis (SIMS, XPS) and SEM observations were performed on films grown on Si (100) wafers.

3. Results and discussion

3.1. Growth rate

Fig. 1 shows the variation of the growth rate of undoped and N-doped TiO_2 films with the substrate temperature using a partial pressure ratio NH_3/TTIP of $R=2220$. Below 350 °C the growth rate is enhanced when NH_3 is added. Above 350 °C the growth rate increases slowly with the temperature both in presence of and without NH_3. Above this temperature threshold, the growth rate of undoped and N-doped films cannot be compared directly because the TTIP mole fraction is different. However, we observed that above 350 °C the growth rate of undoped-TiO_2 is approximately 4 times higher than that of N-doped TiO_2 (2 and 8 nm min^{-1}, respectively) which is certainly due to the fact that the TTIP mole fraction was 4 times higher for the growth of undoped layers. As a result, we assume the growth rate would be probably of the same order at high temperature if the same TTIP mole fraction had been used. By contrast, for deposition temperatures lower than 350 °C, the growth rate of N-doped TiO_2 is of the same order (or even higher at 300 °C) despite the higher TTIP mole fraction used for undoped TiO_2 films. In fact, the apparent activation energy for the deposition of N-doped TiO_2 films is very low (13 kJ mol^{-1}) comparatively to that of pure TiO_2 films (93 kJ mol^{-1}). This suggests that in the presence of NH_3 the process is not kinetically controlled as a result of fast reactions between NH_3 and TTIP. This is consistent with the observations of Jung et al. who considered that the decomposition of TTIP was catalyzed by NH_3 (direct interaction of NH_3 with electron deficient Ti in TTIP) leading to higher decomposition rates at temperatures lower than 330 °C [24].

3.2. Morphology, structure and composition

From X-ray diffraction patterns, the N–TiO_2 films grown above 350 °C using $R=2220$ are well crystallized while those prepared at temperatures equal to or lower than 350 °C contain a significant part of amorphous phase. All films exhibit the anatase structure and are constituted of nano-crystals of various sizes. For growth temperatures

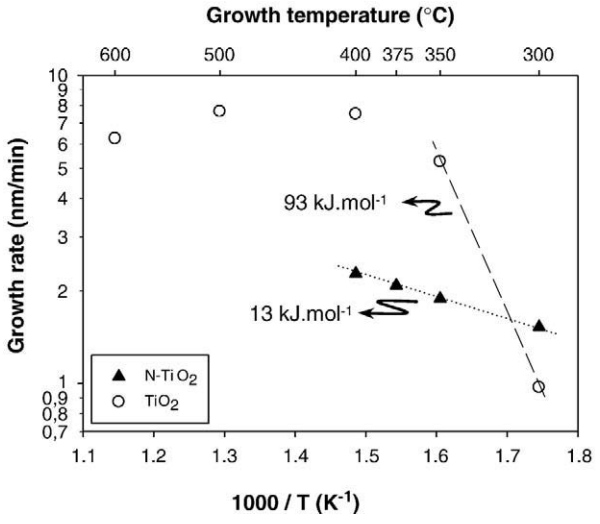

Fig. 1. Arrhenius plot of the growth rate of N-doped and pure TiO_2 films grown on Si(100) wafers using TTIP mole fractions of 65×10^{-6} (N–TiO_2) and 260×10^{-6} (TiO_2).