

Role of Ni doping in surface carbon removal and photocatalytic activity of nano-structured TiO₂ film

Marshal Dhayal*, S.D. Sharma, Chander Kant, K.K. Saini, S.C. Jain

National Physical Laboratory, Dr. K.S. Krishnan Road, New Delhi 110012, India

Received 21 August 2007; accepted for publication 27 December 2007

Available online 12 January 2008

Abstract

Nickel doped and undoped TiO₂ films have been coated on cleaned glass substrates by sol–gel dip coating technique. Coated films were characterized by XRD, XPS, AFM and photocatalytic measurements after annealing at 500 °C. XRD studies confirmed the formation of anatase phase in both the films and crystallites size decreased from 10 to 6 nm in doped films with porous structure. From XPS observations, prominent decrease in C/Ti, increase in O/Ti and an enhancement of Ti³⁺ states at the film surface has been observed after Ni doping. The increase in O/Ti was related to partial replacement of Ti by Ni atoms. The photo degradation studies indicated the pseudo-first-order kinetics and an increase in kinetic constant by factor of two have been obtained in 10 M Ni doped films. The enhancement of photoactivity after doping was attributed to removal of surface carbon and increase in Ti³⁺ concentration.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Nano-structures film; TiO₂; Surface states; Photo catalyst

1. Introduction

TiO₂ films with superhydrophilic and photocatalytic characteristics have attracted a great deal of attention in last decade. They have many advanced functions and features including antifouling, deodorizing, sterilizing and antifogging. When exposed to UV light TiO₂ film can breakdown organic molecules and enable water to spread evenly on the surface easily to realize self-cleaning effect. Titanium dioxide (TiO₂) films have been widely used for several industrial applications such as a photocatalyst for degradation of environmental pollutants [1,2] due to its non-toxic and stable properties at the normal pressure and temperature [3,4], eye-glasses, glass sheets for shop-window, coating on flat panel displays and different optical systems [5–8] and in solar cells [3].

However, it can be activated only under UV light (wavelengths <387 nm) irradiation due to its large band gap of 3.2 eV. The solar spectrum usually contains about 4% UV light. Owing to this inherent limitation, the solar energy cannot be utilized efficiently in the photocatalytic process [9–11]. There have been numerous research papers [12] reporting improvement in photocatalytic activity and super hydrophilicity of TiO₂ thin films prepared by various techniques. Recently, Fujishima et al. [13] have reviewed the progress in the area of TiO₂ photocatalysis and discussed its potential applications. Chang et al. [14] had studied photocatalytic performance of chromium or nitrogen doped arc ion plated-TiO₂ films and excess presence of Ni and Cr can reduce photoactivity and crystallinity. Higher photoactivity and phase stability of anatase-type TiO₂ observe after ZrO₂ doping even at higher temperature [15]. It can be concluded from these studies that photoactivity of crystalline TiO₂ increases with doping concentration, however if the film changes from crystalline to amorphous the photo catalytic activity reduces irrespective of presence of doping atoms.

* Corresponding author. Tel.: +91 11 2574 2610x2486; fax: +91 11 2572 6938.

E-mail address: marshaldhayal@yahoo.com (M. Dhayal).

The photocatalytic activity of TiO₂ usually depends on a competition between the following two processes, first the transfer rate of surface charge carriers from the interior to the surface and second the recombination rate of photo-generated electrons and holes. If the recombination of photo-generated electrons and holes occurs too fast (<0.1 ns), then there is not enough time for any other chemical reaction to occur. Compared with other semiconductor, the surface charge carriers of TiO₂ are relatively long-lived (around 250 ns), allowing the electrons or holes to travel to the crystallite surface. Therefore, different types of radicals are formed on TiO₂ surface and OH radical is the most common. These radicals are free to carry out other chemical reactions on the surface of TiO₂ [16,17].

In order to extend its light absorption efficiency and also to reduce the recombination of photo-generated electrons and holes, various metal and nonmetal ions have been incorporated into TiO₂ [18–23] during film formation. Surface modification by ion implantation, electron beam and plasma treatments can also enhance the photoactivity [24–27] of the film. Suggested mechanisms for improvement in photoactivity mainly include (i) efficient electron hole separation, (ii) band gap narrowing, due to which optical absorption edge shifts into the visible part of electromagnetic spectrum, and (iii) increasing surface area due to reduction of crystalline size. However, the clear understanding about viable mechanism is still lacking.

2. Experimental

TiO₂ films were prepared on clean glass substrates (sample size was 1 × 3 cm²) by sol–gel dip coating process. Ti sol (0.5 M) was prepared from titanium tetrabutoxide with isopropyl alcohol as solvent. The sol was partially hydrolyzed using DI water in presence of HNO₃ (46%) catalyst. The mixture was stirred vigorously with magnetic stirrer for 1 h under controlled humidity conditions. The solution was kept overnight in vacuum system (at 10 m Torr) and films of uniform thickness (160 nm) were obtained on glass substrates by dip coating technique at pulling speed of 12 cm min⁻¹. The film deposited substrates were dried at 100 °C for 30 min and subsequently annealed at 500 °C for 1 h in normal atmospheric conditions. To obtain Ni doping, calculated amount of Ni was added to the sol solution and above procedure was followed. Nickel doped films were obtained by taking nickel acetylacetonate which contains one Ni atom per formal unit therefore; atomic concentration is same as molar concentration because titanium butoxide, which was taken for the titanium precursor also contains one Ti atoms per formula unit. However, the wt.% is different because of different molecular wt.s of the two compounds.

Surface morphology of the films was obtained using Nanoscope IIIa Atomic Force Microscope (AFM). XRD was used to determine the change in surface structure of the films. XRD spectra of the samples were recorded using SIEMENS D-500 diffractometer with monochromatized

Cu K α radiation ($\lambda = 1.541 \text{ \AA}$). To determine the particle size slow XRD scans were repeated at selected peak positions to obtain accurate values of FWHM. The surface chemical states of the films were analyzed using X-ray photoelectron spectroscopy (XPS) with Al K α on a Perkin–Elmer ϕ model with hemispherical analyzer. Transmission and absorption spectra were recorded from 300 to 800 nm range with SHIMADZU UV-3101 PC UV–vis spectrophotometer at normal incidence. Surface energy (or hydrophilic nature) of the films was studied in terms of contact angle measurement. The contact angle was measured with water droplet using sessile drop method in KRUSS DSA10 system.

In order to have an insight into photo catalytic activity, the TiO₂ films were settled in aqueous eosine solution with a constant concentration in a quartz cell (1 × 1 × 3 cm³). High-pressure mercury lamp (125 W) was used as a source of exiting UV radiation and was exposed to one face (10 × 30 mm) of TiO₂ thin films along the normal direction. UV irradiance meter (Model UV-A) was used to measure the averaged intensity of UV irradiance and for all the experiment it was kept at 0.5 m W cm⁻² on the film surface. Dry air stream was bubbled to the solution during irradiation to maintain uniform degradation. The concentration of aqueous eosine was determined with a UV–vis spectrophotometer by measuring the absorbance at 490 nm.

3. Results and discussion

The surface morphology of doped and undoped films, recorded by AFM in tapping mode, is also shown in Fig. 1. The TiO₂ crystals of doped and undoped films exhibit similar shape and the crystal of the pure TiO₂ films has crystal size between 6 and 8 nm. AFM observations showed porous structure of both the films and reduction in particle size was also indicated by Ni doping. Non-uniform distribution in the crystal size has been observed at some locations in both the film surfaces.

The XRD patterns of undoped and Ni doped TiO₂ film annealed at 500 °C is shown in Fig. 1. Both types of TiO₂ films have only anatase TiO₂ phase and there was no indication about formation of rutile phase in TiO₂ films upto the sintering temperature of 500 °C. Three diffraction peaks at 2θ values of 25.3, 38.1 and 55.0 have been observed in the XRD patterns which are assigned to reflections from (101), (112), and (211) crystal planes, respectively. In both the cases similar XRD patterns were observed but significant change in the peak broadening has been observed in case of doped films. However, the dopant concentration has marginal effect on peak broadening. Crystalline phases of Ni metal on these films have not been detected in the XRD pattern of doped film up to 10 mol% concentration. The average particles size of TiO₂ particles was estimated by Debye–Scherer equation ($D = (\alpha \lambda) / (\beta \cos \theta)$), where D is mean particle size, α geometric factor is a constant (0.89), λ is X-ray wavelength (1.541 Å) and β is half width

Download English Version:

<https://daneshyari.com/en/article/5424962>

Download Persian Version:

<https://daneshyari.com/article/5424962>

[Daneshyari.com](https://daneshyari.com)