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Synthesis of V-doped TiO_2 films by chemical bath deposition and the effect of post-annealing on their properties

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ABSTRACT

Amorphous composite films, composed of a $Ti_{1-x}V_xO_2$ solid-solution phase and a V_2O_5 phase, were produced by chemical bath deposition and subsequently air-annealed at various temperatures up to 550 °C. The microstructure and chemical composition of the as-prepared and annealed films were investigated by a combinatorial experimental approach using Scanning electron microscopy, X-ray powder diffraction and X-ray photoelectron spectroscopy. Ultraviolet–Visible Spectrometry was applied to determine the optical band gap of the as-prepared and annealed films. It followed that the incorporation of vanadium in the as-deposited films reduces the optical band gap of TiO_2 from about 3.8 eV to 3.2 eV. Annealing of the films up to 350 °C leads to slight increase of band gap, as attributed to a reduction of the defect density in the initially amorphous oxide films due to the gradual development of long-range order and a concurrent reduction of the V^{4+}-dopant concentration in the $Ti_{1-x}V_xO_2$ solid-solution phase. The films crystallized upon annealing in air at 550 °C, which resulted in drastic changes of the phase constitution, optical absorbance and surface morphology. Due to the lower solubility of V^{4+} in crystalline TiO_2, V^{4+} segregates out of the crystallizing $Ti_{1-x}V_xO_2$ solid-solution phase, forming crystalline V_2O_5 at the film surface.

1. Introduction

Titanium oxide is one of the most widely used photocatalyst, because of its non-toxicity and chemical stability at high temperatures and in harsh environments [1]. The band gap of TiO_2 is about 3.5 eV, which is in the ultraviolet range. Doping of TiO_2 with certain transition metal ions reduces its band gap [2–4] and furthermore stabilizes the excited state, thus enhancing the photocatalytic efficiency by suppressing the recombination of electrons and holes.

The formation of a solid solution between the transition metal solute and the TiO_2 phase requires similar ionic radii for the transition metal dopant and Ti^{4+} (15% or less difference). In this regard, V^{4+} is considered as a suitable dopant for TiO_2, because the ionic radius of 0.72 Å for V^{4+} is very similar to that of Ti^{4+} (0.74 Å) [5]. The effects of surface and bulk doping on the photocatalytic activity of V-doped TiO_2 were examined on the basis of interfacial transfer and charge trapping [6]. An unwanted decrease of the efficiency of the photocatalyst by enhanced charge carrier recombination was reported above a certain V^{4+}-dopant threshold concentration [1,3,7]. Thus, typically the V^{4+}-dopant concentration should not exceed a certain optimum value.

V-doped TiO_2 has been synthesized with different particle sizes and phase compositions using various preparation methods and conditions [5,8–13]. For example, V-doped TiO_2 thin films were deposited by Radio frequency sputtering with V/Ti atomic ratios of 0.18; 0.25 and 0.82 [1]. Jiang and Chen [14] reported on the preparation of V-doped TiO_2 films by the sol–gel method. The chemical bath deposition (CBD) is an alternative route for the synthesis of V-doped TiO_2 films based on the thermohydrolysis of metal salts from aqueous solutions for the fabrication of oxidic films at near-ambient conditions and offers a gentle and inexpensive alternative to conventional routes for the deposition of thin oxide films [15–18].

In this work, Ti–(V)–O films were produced by chemical bath deposition and subsequently air-annealed at various temperatures up to 550 °C. The main focus of the present study was on detailed characterization of so formed films after annealing at various temperatures. First, the thermal stability of corresponding powders, as extracted from the precursor particles in the deposition solutions, was studied by thermogravimetry–differential scanning calorimetry–mass spectrometry (TG-DSC-MS) for optimizing the proper annealing temperatures. Next, the microstructure and chemical composition of the as-prepared and annealed films were investigated by a combinatorial experimental approach using scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Finally, Ultraviolet–visible spectrometry (UV–vis) was applied to determine the optical band gap of the as-prepared and annealed films.

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2. Experimental section

2.1. Preparation of the reaction solutions

Stock solutions of the titanium peroxo complex $[Ti(O_2)]^{2+}$ were prepared by the addition of titanium tetrachloride to an aqueous solution of hydrogen peroxide (35%, Merck) and then stored in a refrigerator. Stock solutions of ammonium metavanadate (p. a., Fluka) were prepared by dissolving the required amount in 1 M hydrochloric acid (Riedel-de-Haën, Fixanal) [17–19]. Next, four solutions of different vanadium concentrations were prepared for the film deposition step by adding specific volumes of the stock solutions to deionized water (preheated at 60 °C), as indicated in Table 1. Preliminary investigations of the CBD process showed that the precursor particles in solution nucleate and grow faster for higher vanadium concentrations in the reaction solution, whereas a higher concentration of hydrochloric acid (HCl) again reduces the nucleation and growth rate. Therefore the relative concentrations of vanadium ions and HCl (see Table 1), as well as the total reaction time, were adjusted such to control the deposition rate and thereby the thickness and surface morphology of the films (see Section 2.2). The corresponding solutions with increasing vanadium concentration (see Table 1) are further denoted as V0, V5, V10, V20.

2.2. Film deposition from the reaction solutions

Silicon wafers and quartz slides (Herasil 102) 10 × 10 mm² were cleaned by consecutive ultrasonification in chloroform and 2-propanol and subsequently washed abundantly with distilled water. Film deposition was performed in four successive steps as follows [20]. In the first deposition step, the substrate was immersed in a 10 ml aliquot of the reaction solution, sealed in a 20 ml glass flask and then placed in a furnace at 60 °C for 135 min, 110 min, 75 min and 60 min for solutions V0, V5, V10 and V20, respectively. Next, the substrates were removed from the aged containers, ultrasonically cleaned in distilled water and then immersed in a new aliquot of the freshly prepared reaction solution. In the successive (three) deposition steps (analogous to the first deposition step; see above), constant reaction times of 80 min, 50 min, 40 min and 40 min were applied for solutions V0, V5, V10 and V20, respectively.

Cross-sectional SEM analysis (not shown here) indicated that the thicknesses of the deposited films are in the range of 200–500 nm. A selection of as-deposited specimens was annealed in air for 10 h at various temperatures between room temperature and 550 °C at a heating rate of 10 °C/min.

2.3. Extraction of powders from the reaction solutions

Ti–(V)–O powders were extracted from the precursor particles in the reaction solutions V0 and V10 (see Table 1) by centrifugation of the corresponding reaction solution after a total reaction time of 180 min.

3. Analysis

The weight loss and phase transformations of the deposited Ti–(V)–O films and powders upon annealing were investigated by TG, DSC and quadrupole MS using a TG-DSC thermo balance (Netzsch STA Jupiter 449 C) equipped with a MS (GAM 200, InProcess Instruments) with the samples placed in a Pt crucible and heated in air at a rate of 10 °C/min.

Diffraction patterns of the as-deposited and annealed Ti–(V)–O films were recorded with a Philips MRD diffractometer employing Co-Kα radiation. A parallel beam path with an X-ray lens in the incident beam and a 0.18° parallel plate collimator in the diffracted beam was used. The average grain size of every crystalline phase was derived from the integral breadth of the Cauchy-component of a selected diffraction peak of the respective phase using the single-line method [20,21]. Measurements on a LaB_6 powder specimen (NIST standard reference material 660a) were made to determine the instrumental broadening of the diffractometer.

The morphology and thickness of the films were characterized using SEM (Zeiss DSM 982). Cross-sectional specimens were obtained by breaking Si or glass substrates bearing the film. Using a pair of pliers, a small notch was made on the substrate edge to control the position of the crack.

XPS analysis was performed with a Thermo VG Thetaprobe system employing monochromatic incident Al Kα radiation ($h\nu = 1486.68$ eV; spot size 400 μm, base pressure $< 5 \times 10^{-8}$ Pa). Survey spectra of the as-deposited and heat-treated oxide films were measured over a binding energy (BE) range from 0 to 1200 eV at constant pass energy of 200 eV with a step size of 0.2 eV. Detailed spectra of the Ti 2p, V 2p, O 1s, C 1s, N 1s and C 1s photoelectron lines were recorded at a constant pass energy of 50 eV with a step size of 0.05 eV. Spectral reconstruction was performed by constrained peak fitting of each background-corrected spectrum (as obtained after subtraction of a Shirley-type background) with one or more symmetrical, mixed Gaussian–Lorentzian line shape functions (adopting the same full-with-at-half-maximum and Gauss fraction for each fitted main peak). A constrained area ratio of 2:1 was employed in the fitting of the Ti $2p^3/_2$–$2p^1/_2$ spin-orbit doublet. To resolve the various oxidation states of vanadium in the surface region of the as-deposited and heat-treated V-doped oxide films, first the BE scale of the measured V 2p–O1s spectrum (see earlier discussion) was referenced to the BE position of the O 1s main peak at the lower-BE side of the O 1s peak envelop, taking at 530.0 eV [22,23]. Next, a constrained peak fitting of the thus obtained V $2p^3/_2$ main peak of the spin-orbit doublet was performed with the BE positions of the fitted V^{5+}, V^{4+} and V^{3+} $2p^3/_2$ main peaks constrained within the BE range of 517.2 ± 0.2, 515.84 ± 0.2 and 515.29 ± 0.2 eV, respectively [22,23].

Finally, UV–vis absorbance spectroscopy measurements were performed using a Varian Cary 5000 spectrophotometer. Values for the optical band gap of the as-prepared and post-annealed Ti–(V)–O films were estimated by fitting a straight line to a respective plot of $(\alpha \cdot h\upsilon)^n$ versus $h\upsilon$ and then determining the intersection of the fitted line with the abscissa $(\alpha \cdot h\nu)^n = 0$ (where α and hν denote the absorption coefficient and the photon energy, respectively).

Table 1
Concentrations of the reagents in the deposition solutions.

Solution	Ti [mM]	H_2O_2 [mM]	V [mM]	HCl [mM]
V0	15	30	0	50
V5	15	30	5	80
V10	15	30	10	100
V20	15	30	20	130

4. Results and discussion

4.1. Thermal stability of the powders by TG-DSC-MS

Prior to the investigations of the Ti–(V)–O films grown from the reaction solutions, a preliminary study was performed on the thermal stability of the corresponding powders, as extracted from the precursor particles in reaction solutions V0 and V10. TG–DSC–MS measurements of the extracted Ti–O powder (i.e. from solution V0; see Fig. 1a) upon annealing indicate a considerable weight loss at about 100 °C due to the release of water and oxygen, in accordance with the decomposition of peroxo species [24]. An exothermic peak without an associated weight loss is detected at about 437 °C, as attributed to the crystallization of TiO_2 (in accordance with the XRD investigations of the films; see later).