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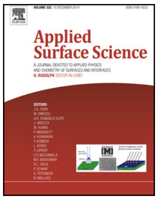

Reduction of V_2O_5 thin films deposited by aqueous sol–gel method to $VO_2(B)$ and investigation of its photocatalytic activity

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ABSTRACT

A way of preparation of $VO_2(B)$ thin films by reduction of V_2O_5 films synthesized from an aqueous sol–gel system has been developed and photocatalytic properties of the obtained films were studied. The reduction was performed by annealing of the V_2O_5 film in vacuum as well as in H_2/Ar atmosphere, which was followed by temperature dependent XRD. It has been shown that the reduction is influenced by the layered-structure of the vanadium oxides. It is a two-step process, where the mixed-valence vanadium oxide V_4O_9 is first formed before reaching the $VO_2(B)$ phase. The film microstructure was characterized by SEM and AFM and the valence states of vanadium in $VO_2(B)$ films were evaluated by XPS. The $VO_2(B)$ polymorph shows an energy band-gap around 2.8 eV and it exhibits photocatalytic properties. It was measured by following the degradation of rhodamine B under UVA as well as metalhalogenide lamp irradiation, which has similar spectral distribution as natural sunlight. The $VO_2(B)$ films show distinct photoactivities under both lamps, although they were found to be more active under the UVA irradiation. The film annealed under reducing hydrogen atmosphere, which exhibits higher granularity and surface roughness, shows higher photoactivity than the vacuum-annealed film.

1. Introduction

Vanadium oxide thin films are highly promising materials because of the wide range of their attractive properties [1,2]. A large variety of techniques can be used to prepare vanadium oxide films. Among others, pulsed laser deposition (PLD) [3], magnetron sputtering [4], chemical vapour deposition (CVD) [5], spray pyrolysis [6] and sol–gel method [1] are most commonly employed. The latter method is of great interest due to its low cost, while the quality of the obtained films is mostly comparable with those prepared by the other above-mentioned processes [1].

Vanadium pentoxide (V_2O_5) thin films have been widely studied due to their layered structure and semiconducting properties which allow them to be used for Li-intercalation in batteries as well as for gas sensing [7–10]. Under reducing conditions, V_2O_5 films can be reduced to various vanadium oxides such as mixed-valence phases (V_3O_7, V_4O_9, V_6O_{13}) as well as VO_2 and V_2O_3, where vanadium is in the +IV and +III oxidation state, respectively [11–13]. The VO_2 (M/R) phase is thermotropic and thus exhibits switching in optical, electrical, and magnetic properties at its critical temperature ($T_c = 68\,^\circ C$) [2,14]. This phase has been largely investigated for bolometer application as well as for thermal IR detectors and smart windows [5,15,16]. Another phase of vanadium dioxide, $VO_2(B)$, which can be synthesized by various methods such as sol–gel and hydrothermal techniques [12,17], is semiconducting. Deposited in the form of films it exhibits a layered-structure and has been studied for Li-intercalation [17,18]. These two allotropic phases of VO_2 show significant structural differences. The B-polymorph is considered to be a metastable phase since it can be converted irreversibly to the thermotropic phase, $VO_2(M/R)$ by annealing in inert atmosphere [12,18]. The $VO_2(M/R)$ phase exhibits a monoclinic (distorted rutile) structure at room temperature (reported as M) and a rutile structure when the critical temperature is reached (reported as R) [2]. The structural changes in the thermotropic VO_2 are responsible for switching of its properties, particularly for the metal-to-semiconductor transition (MST) [2].

It has been reported that some of the vanadium oxides exhibit photocatalytic properties [13]. Most of the interest has been devoted to the vanadium pentoxide such as flower-like V_2O_5 films grown by hydrothermal method which shows excellent photoactivity by degradation of more than 60% of methylene blue under UV and visible light irradiations [19]. In others works,

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hydrothermally grown V_2O_5 films exhibiting porous wall-like and amorphous structures were able to degrade around 60% of stearic acid, which is a result comparable to the activity of TiO_2 films [20,21]. For the hydrogen production from water splitting, powders containing different vanadium oxide phase such as VO_2(B), V_2O_5, or V_6O_{13} have been prepared by hydrothermal route [13]. It has been shown that all of these powders are able to produce hydrogen under visible light irradiation. The hydrogen production has been found to be the highest for V_6O_{13} and the lowest for VO_2(B). Depending on the way of synthesis and also on the resulting structure of the vanadium oxide thin films, their energy band gap can vary. However, it is mainly situated in the range between 2.1 eV and 3.1 eV for VO_2, V_6O_{13} and V_2O_5, respectively [13,17]. Near UV irradiation as well as part of the visible light spectrum can thus be used for photoexcitation of such films.

Usually VO_2(M/R) films, which find broad application for their thermotropic properties, are prepared by chemical alkoxide sol–gel process or physical methods [22,23]. So far, the formation of VO_2(B) from V_2O_5 films prepared by aqueous sol–gel route was far less investigated although it is a simple and promising process. The semiconducting VO_2(B) has been already studied in the form of nanorods and powders synthesized by thermal oxidation of vanadium and hydrothermal method, respectively [13,24].

Therefore in this work, the preparation of VO_2(B) thin films was performed by reduction of V_2O_5 films synthesized from an aqueous sol–gel system. To the best of our knowledge, it is the first time that such films were prepared by aqueous sol–gel method and that the B-polymorph of VO_2 was studied as photocatalyst. The mechanism of the reduction process from V_2O_5 to VO_2(B) films was investigated by temperature-dependent X-ray diffraction (XRD). The influence of the reduction conditions on the VO_2(B) film microstructure is shown. The obtained vanadium dioxide films were characterized by UV–vis and XPS spectroscopy. The results of scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies are also reported. Furthermore, the photoactivity of VO_2(B) films was tested under both UVA and visible light.

2. Experimental

2.1. Synthesis of the $V_2O_5·nH_2O$ aqueous sol–gel and film deposition

Aqueous V_2O_5 solution was synthesized by dissolving 1 g of vanadium pentoxide powder, obtained by calcination of ammonium metavanadate (LaChema), in 100 mL of hydrogen peroxide 15% (Slavus). The reaction is exothermic so the addition of H_2O_2 is performed drop by drop. Once all the powder was dissolved, the clear orange solution containing oxo- and peroxo-vanadate was heated up to 70 °C and the solution turned progressively to a brown flocculate and finally to a dark red gel by polycondensation process. The synthesized $V_2O_5·nH_2O$ aqueous gel was deposited by spin-coating at 60 revolutions per second (rps) for 1 min on Si/SiO_2 and sapphire *c*-cut substrates (10 mm × 15 mm) with SCV-15 spin-coater (Novocontrol Tech.). The Si/SiO_2 substrate was prepared by heating of a pure Si substrate at 950 °C for 5 h in air to form a SiO_2 buffer layer on the surface of the silicon, which was necessary for the deposition of the aqueous gel. Without the SiO_2 buffer layer the deposition from aqueous gel on Si substrate proceeds only poorly. All the substrates were cleaned successively in detergent, acetone, ethanol, and distilled water using an ultrasonic cleaning bath (VWR) for 3 min and they were dried using hot-air gun at 80 °C. By this way, four-layer films were deposited from aqueous gel using intermediate annealing at 400 °C for 10 min to dehydrate the films. Subsequently, they were annealed in a tube-oven (MTI-GSL1600X) or in AntonPaar DHS1100 chamber for non-ambient in situ XRD (XPert Pro vs. 2.1E) using different parameters as shown in Table 1.

Table 1
Annealing parameters of the as-deposited films.

Sample	Substrate	Annealing conditions	Heating ramp
VO_{h2}	Si/SiO_2	500 °C – H_2/Ar – 30 min	2 °C/min
VO_{vac}	Si/SiO_2	625 °C – vacuum – 30 min	2 °C/min
VO_{aq}	Sapphire	500 °C – H_2/Ar – 60 min	4 °C/min

2.2. Characterization of the vanadium oxide thin films and photocatalytic measurements

The vanadium oxide coatings were characterized by X-ray diffraction (PANalytical XPert PRO MRD diffractometer equipped with AntonPaar DHS1100 chamber), scanning electron microscopy (Tescan Lyra III), atomic force microscopy (NT-MDT Solver P47 PRO), and X-ray photoelectron spectroscopy (Omicron multi-probe system). The XRD measurements have been performed in Bragg–Brentano parafocusing geometry using fixed divergence slit and PIXcel solid-state multichannel X-ray detector. The AFM surface analysis has been done in semicontact AFM mode using standard silicon AFM probes. The XPS method included etching of the films by Ar ion beam. The energy band gap of the vanadium oxide thin films was calculated from Tauc's curve from the transmittance UV–vis spectra of the films deposited on transparent sapphire, which were measured on Jasco V-530 device. The photocatalytic activity of the films was measured by following the degradation of the organic dye, rhodamine B (10^{-5} M), under both UVA irradiation (Philips HPA 400 W lamp; λ_{max} = 365 nm) and metal halogenide irradiation with broad spectral distribution characteristics comparable to visible light (HQI TS – OSRAM 400 W lamp; λ_{max} = 525 nm). The radiation intensity at 335–380 nm was determined to be 5.7 mW/cm^2 in the case of the UVA lamp and 2.1 mW/cm^2 for the metalhalogenide lamp by the UVX radiometer (UVX 36 Probe). In both cases, a pyrex glass filter was used in order to cut-off wavelength lower than 300 nm. The concentration of Rhodamine B was calculated by measuring the maximum absorbance at 554 nm of 1 mL solution taken-off every 30 min for 2.5 h with UV-visible spectrophotometer (Jasco V-530). The degradation of this organic dye was thus evaluated from its concentration as a function of time in order to estimate the photocatalytic activity of the thin multi-layer films.

3. Results and discussion

3.1. Reduction of V_2O_5 to VO_2(B) films

In the first experiments, we attempted to prepare reduced vanadium oxide films on lime-glass substrates. However, at temperatures above 340 °C, which was necessary for reduction of the V_2O_5, the substrate reacted with the film and calcium vanadates were formed. Silicon substrates were thus used. Prior to the deposition, the substrates were covered by silicon dioxide buffer layer by oxidation in air to lower its reactivity and hydrophobic behaviour. The deposition of the aqueous gel on Si/SiO_2 substrates led to yellow films in which V_2O_5 was identified by XRD measurements (ICDD # 00-009-0387). In order to understand the reduction process of V_2O_5 films to VO_2(B), the annealing process was followed by XRD in 5% H_2/Ar atmosphere and also in vacuum (10^{-1} Pa). The results of the temperature dependent XRD measurements are shown in Fig. 1. Fig. 1a shows that in the sample VO_{h2}, which was annealed in 5% hydrogen in argon with a heating ramp of 2 °C/min, the crystalline V_2O_5 film is progressively reduced as the temperature increases. As a result, the intensity of diffraction peaks belonging to the V_2O_5