



The influence of processing conditions on the morphology and thermochromic properties of vanadium oxide films



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ARTICLE INFO

Article history:

Received 14 May 2013

Received in revised form 11 February 2014

Accepted 11 February 2014

Available online 20 February 2014

Keywords:

Vanadium oxide
Solution deposition
Gel-aging
Nanostructured film
Morphology
Optical property
Thermochromism

ABSTRACT

Vanadium oxides belong to a class of multifunctional materials with a wide range of applications spanning catalysis to optical switches and smart windows for intelligent energy management. The most intriguing oxides of this family are VO₂ and V₂O₅ with peculiar optical properties that can be switched either by temperature variation (thermochromism) or electrical field (electrochromism). In this paper we address aspects of solution processing thin films that were until now ignored. We have established that the morphology of the films obtained depends on the drying temperature (Td) of the films after spin-coating. The resultant morphology is only revealed after final annealing at an optimum temperature of 560 °C. We show that the presence of polyethylene glycol as a film promoting agent, together with sample drying temperature after spin-coating result in drastic changes in film morphologies. When Td is <40 °C, mesoporous films with equiaxed VO₂ grains are observed, whereas for Td ≥ 55 °C self-organized hemispherical micro-discs of V₂O₅ are observed. This influence of Td is correlated with the ebullition temperature of the solvent used, in this case methanol. We also show that V₂O₅ can be reduced to VO₂, demonstrate how the starting morphology affects the final morphology of the product phase, after reduction, and discuss its formation mechanisms. Finally the optical and thermochromic properties are correlated to the different morphologies and structures, and are shown to reflect very well the effects thereof through absorption phenomena and thermochromic switching characteristics.

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1. Introduction

The recent drive for renewable and intelligent energy management for buildings and the need for efficient catalysts, sensors and many more applications are at the origin of tremendous research efforts towards the development and optimization of multifunctional materials. Although vanadium oxides belong to the most widely investigated materials for almost five decades now, they are still a source of original developments as attested by the soaring publication number in the last years. Oxides of vanadium have well known applications in the realms of heterogeneous catalysis, such as oxidative dehydrogenation of alkanes [1–4], thermo- and electrochromic devices [5–10], solar energy materials [11], electrical/optical switches [12–15], electrode materials in lithium ion batteries along with energy storage devices [16–20] and sensors [19,21,22].

VO₂ and V₂O₅ are probably most interesting insofar that their optical and electrical properties can be switched via temperature and/or electrical field changes, thus opening the possibility for a wide range of applications. All compounds above exhibit a semiconductor–metal transition (SMT) accompanied by electrical conductivity changes

of several orders of magnitude [23–25]. For the majority of applications vanadium oxides are applied as thin film coatings on glass and other substrates. Thin films and nanosized structures are more in the research focus because of their ability to better accommodate stresses and structure distortion upon multiple reversible phase transitions. In contrast, bulk materials are prone to fatigue and failure after few cycles [26]. A brief literature overview on vanadium oxide coatings reveals that processing conditions may dramatically affect structure and morphology of thin films and subsequently film properties. Annealing temperature and atmosphere, film thickness, grain size, and morphology have been investigated in detail, and conclusions as to structure–property relationship have been drawn [27–38]. The semiconductor–metal transition temperature (T_{SMT}) was shown to be inversely proportional to the square root of grain size and the width of the hysteresis loop decreased with increasing particle size as well [30,31].

The effect of VO₂ film texture on the hysteresis loop was addressed by Petit et al. [39] who had found that the [011] preferred crystal orientation promoted a narrow and symmetrical hysteresis loop while the randomly oriented crystals resulted in wider and asymmetric hysteresis loops. Annealing effects on the properties of sol–gel vanadium oxide films were recently studied by Zang et al. [37]. In particular it was suggested that annealing temperatures less than 450 °C could lead to residual pyrolysis products, mostly carbon, from the precursor solution that could create a reducing environment and partial reduction

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of V^{4+} to V^{3+} . The local non-stoichiometry could result in lower T_{SMT} . The results above attest to the complexity of SMT in vanadium oxides where obviously the nature and density of defects generated during specific processing routes play a prominent role in the thermodynamics and kinetics of transformation; defects present in the parent phase that are inherited by the product phase may affect fast-growing variants. Further the large volume change that accompanies SMT results in a high stored elastic energy which in case of constrained thin film–substrate interfaces may form complex stress patterns that in turn may affect transformation temperature to a variable degree (through the Clapeyron equation).

From the above, it appears that a multiplicity of factors can affect film (micro) structure, morphology and consequently film properties; all of them are essentially related to the multiplicity of vanadium oxidation states. However, rather than stressing on process control, we should emphasize more on the opportunity offered by the V–O-system to tune microstructure and functional properties. While work is still ongoing to trace the effects of different processing steps on vanadium oxide films and elucidate their mechanisms we show in the present paper that film morphology and properties may be decisively affected via a simple treatment step while the film is still in the gel state. We show that different film morphologies are obtained depending on the drying temperature of the gel film in air. For instance, it is possible to control the crystallite size to a high degree by just varying the drying conditions of the gel film. Further, drying temperatures higher than 40 °C result in locally ordered, self-organized V_2O_5 hemispheric discs interspersed with thin VO_2 film. Controlled reduction of these films yields monoclinic VO_2 that exhibits different optical properties in comparison to VO_2 from direct annealing.

2. Materials and methods

2.1. Sample preparation

Vanadium oxyacetylacetonone (>97%, Fluka, Germany) was dissolved in methanol (CH_3OH , Fluka, Germany) to obtain 0.16 M solution. The mixture was stirred 20 min at room temperature. To promote film formation and avoid cracking 0.02 g of polyethylene glycol (PEG 400, ABCR, Germany) per 1 ml solution was added and stirred for a further 40 min. The solution obtained was then filtered through a 0.2 μm filter and subsequently aged for 5 days before further processing. The substrates consisted of 2×2 cm² quartz glass and oxidized (100) silicon. Before use the substrates were ultrasonically cleaned in a mixture of ethanol and acetone, and subsequently immersed in a hydrochloric acid solution in de-ionized water. Three layers were sequentially spin-coated at 1500 rpm for 20 s. After each layer, the samples were dried at temperatures from 40 °C to 70 °C in ambient atmosphere. Final annealing was conducted in a furnace at 450 °C or 560 °C for 30 min in flowing N_2 atmosphere to yield a thin film with nominal thickness of 250 nm. For V_2O_5 film preparation annealing was performed in air under the same conditions. For controlled reduction experiments of V_2O_5 films the samples were heated in 5% H_2 :95% N_2 atmosphere at 500 °C for 60 min with a heating rate of 5 °C/min.

2.2. Characterization of films

Structure was characterized using X-ray diffraction (XRD) (X'Pert Pro diffractometer PanAnalytical, Holland) in a grazing incidence

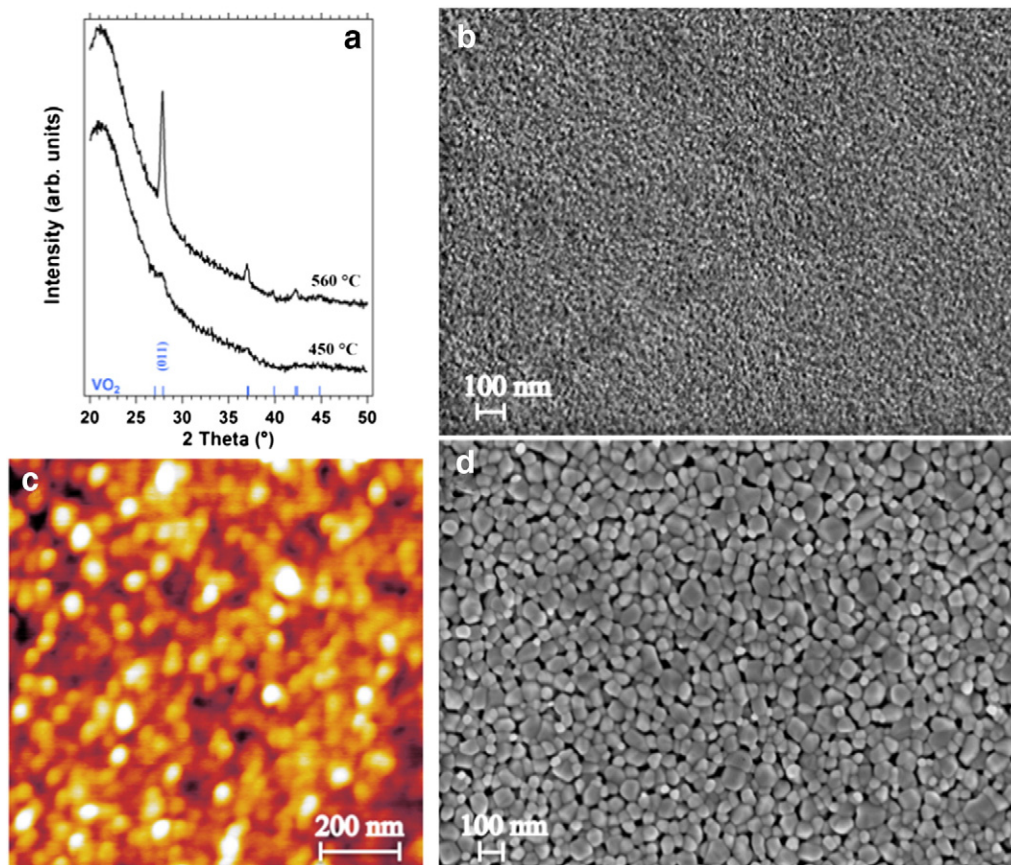


Fig. 1. (a) XRD patterns of VO_2 films annealed at 450 °C (sample A) and 560 °C (sample B). Patterns are shifted vertically for clarity. Tick marks denote the peak positions for the VO_2 ($P2_1/c$) phase. (b, d) Scanning electron microscopy (SEM) images of the VO_2 films A (b) and B (d) annealed in a N_2 flow. (c) AFM micrograph of sample A showing topography and particle morphology details. The height difference between the highest (white) and lowest features (dark) is 4.7 nm. The root mean square (rms) AFM roughness of this film is 0.88 nm. The film B exhibits an rms roughness of 3.93 nm.

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