Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 516 (2008) 1484 – 1488
www.elsevier.com/locate/tsf

Thermochromic properties of vanadium oxide films prepared by dc reactive magnetron sputtering

Hai-Ning Cui [a,b,*], Vasco Teixeira [b], Li-Jian Meng [b,c], Rong Wang [a], Jin-Yue Gao [a], Elvira Fortunato [d]

[a] College of Physics, JiLin University, 2519 JieFangDaLu Road, 130021 ChangChun, PR China
[b] Centro de Física e Departamento de Física, Universidade do Minho, 4710 Braga, Portugal
[c] Departamento de Física, Instituto Superior de Engenharia do Porto, Rua de São Tomé, 4200 Porto, Portugal
[d] Dept. Ciência dos Materiais, CENIMAT, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, PT-2829-516 Caparica, Portugal

Available online 1 April 2007

Abstract

A transparent vanadium oxide film has been one of the most studied electrochromic (EC) and Thermochromic (TC) materials. Vanadium oxide films were deposited at different substrate temperatures up to 400 °C and different ratios of the oxygen partial pressure (P_{O2}). SEM, AFM and X-ray diffraction's results show detail structure data of the films. IR mode assignments of the films measured by IR reflection–absorbance in NGIA (near grazing incidence angle) are given. It is found that the film has V_2O_5 and VO_2 combined structures. The films exhibit clear changes in transmittance when the environment temperature (T_e) is varied, especially in the 3600–4000 cm^{-1} range. Applying a T_e that is higher than a critical temperature (T_c) to the samples, the as-RT (room temperature) deposited film with 9% P_{O2} has a transmittance variation of 30%, but the films that were deposited on a heated substrate of 400 °C have little variation. There is tendency of bigger variation in transmittance for the sample deposited at a larger P_{O2}, when it is applied by 200 °C T_e.

Keywords: Vanadium oxide films; Thermochromic property; XRD; IR; dc magnetron sputtering

1. Introduction

A vanadium oxide film has been one of the most studied electrochromic (EC) and Thermochromic (TC) materials [1,2]. TC materials change reversibly color with changes in an environment temperature (T_e). They can be semi-conductor compounds, liquid crystals or metal compounds. TC materials change color by a process that is involved a chemical reaction of thermally inducement or a phase transformation. The change in color happens at a determined temperature, is called a critical temperature (T_c), which can be varied by doping materials. Thermochromism is seen in a large number of organic and certain inorganic compounds. Some of these compounds are Fe_3O_4, NbO_2, NiS, Ti_2O_3, VO_2 and V_2O_5 [2]. Such material can be used to control transmittance and infrared emissivity of a glazing, and also as thermotropic (TT) material which can cause a significant change in its electronic properties from an insulator to semiconductor transition or from a semiconductor to metallic state when the T_e exceeds the material's T_c.

Vanadium has various valence states and results in a number of oxide forms of vanadium oxides. V_2O_3, VO_2 and V_2O_5 films have been widely studied for optical, electrical, electrochemical,

Table 1
Deposition conditions, parameters and thermochromic properties of vanadium oxide films

Sample	P_{O2}(%)	T_s (°C)	T_a (°C)	$IR_{at\ RT}$ T_{ts} (%)	$IR_{at\ 200\ °C}$ T_{ts} (%)	ΔIR T_{ts} (%)
V1	9	RT	–	79.0	49.0	30.0
V2	15	400	–	26.0	22.5	3.5
V3	20	RT	–	83.0	66.0	17.0
V1a	9	RT	400	27.5	16.0	11.5
V3a	20	RT	400	32	5	15.0
V4a	20	RT	200	53.0	14.0	39.0

ΔIR: transmittance different at the 4000 cm^{-1} (2.5 μm) before and after the sample is put, into 200 °C temperature environment, $\Delta IR = IR_{at\ 200\ °C} - IR_{at\ RT}$.

* Corresponding author. College of Physics, JiLin University, 2519 JieFangDaLu Road, 130021 ChangChun, PR China. Fax: +86 431 8498071 or 5650478.
E-mail address: hncui@yahoo.co (H.-N. Cui).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.03.131

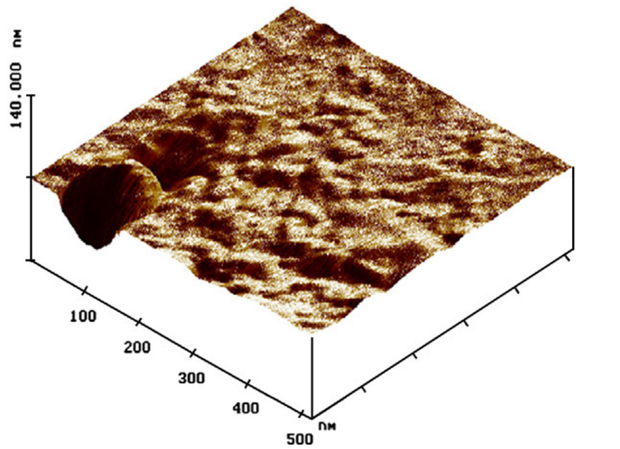

Fig. 1. Three dimensions (3D) AFM image of vanadium oxide film deposited with 9% oxygen partial pressure (P_{O2}) at room temperature.

thermo-chromic and thermal switching materials. VO_2 and V_2O_5 have been considered for window applications [3–6]. The interest in these materials has been increased in the last few years due to their potential applications in a wide variety of optical modulation devices.

Many research works have been focused on electrochromic coloration of this material, few works can be found on the study of the structure characterizations and thermochromic behaviours of vanadium oxide films. Different techniques have been used to synthesize vanadium oxide films, such as sputtering [7], thermal evaporation [4,5], pulse laser deposition [6], sol–gel [8] etc. Depending on the deposition conditions and techniques, films may present considerably different structural, optical and electrical character, and consequently different electrochromic and thermotropic behaviour. The sputtering is the most widely investigated and large-scale deposition set is available. With direct-current (dc) sputtering from a target Vanadium, thin film properties can be improved by controlling the reactive gas atmosphere and substrate temperature (T_s).

In this work, vanadium oxide films have been deposited onto glass substrates by dc reactive magnetron sputtering at different T_s and ratio of oxygen partial pressure (P_{O2}). The structural and thermochromic properties of these films are studied.

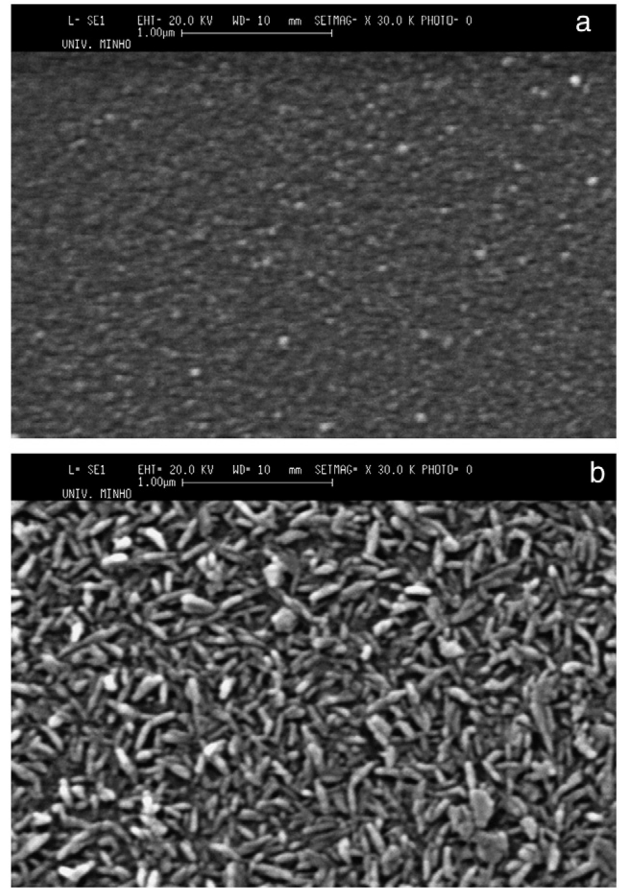

Fig. 3. SEM images of vanadium oxide films prepared at different depositing T_s (a) 100 °C and (b) 200 °C; scale is 1 μm.

2. Experimental details

Vanadium oxide films were deposited by using a home-made dc magnetron sputtering system. The target is a vanadium metal

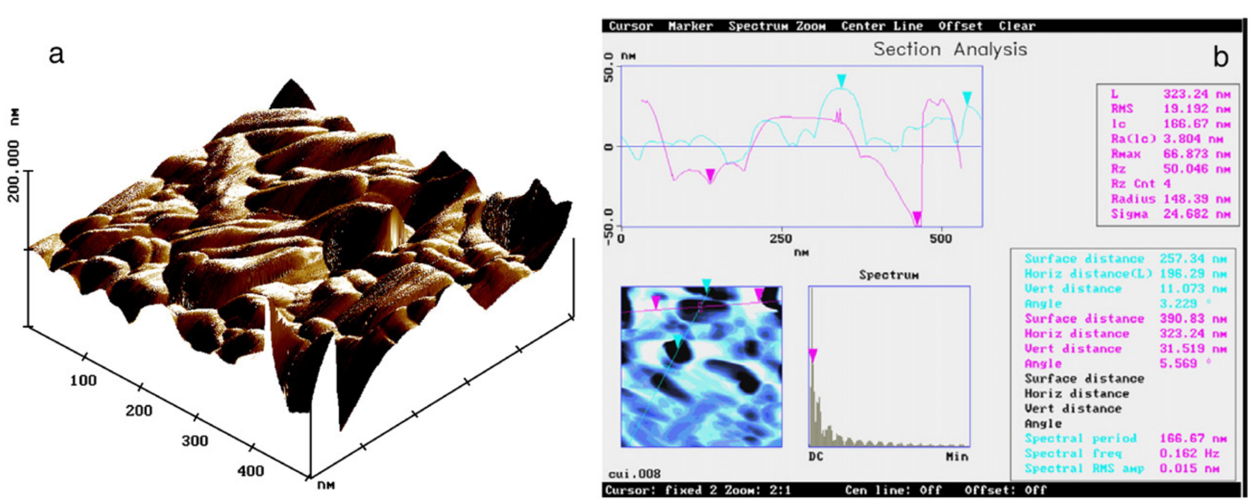

Fig. 2. AFM image (a) and section analysis (b) of vanadium oxide film deposited with 15% P_{O2} and at 400 °C depositing T_s for 20 min.