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VO_2 thin films deposited on silicon substrates from V_2O_5 target: Limits in optical switching properties and modeling

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Abstract

Thermochromic VO_2 thin films presenting a phase change at T_c=68 °C and having variable thickness were deposited on silicon substrates (Si-001) by radio-frequency sputtering. These thin films were obtained from optimized reduction of low cost V_2O_5 targets. Depending on deposition conditions, a non-thermochromic metastable VO_2 phase might also be obtained. The thermochromic thin films were characterized by X-ray diffraction, atomic force microscopy, ellipsometry techniques, Fourier transform infrared spectrometry and optical emissivity analyses. In the wavelength range 0.3 to 25 μm, the optical transmittance of the thermochromic films exhibited a large variation between 25 and 100 °C due to the phase transition at T_c: the contrast in transmittance (difference between the transmittance values to 25 °C and 100 °C) first increased with film thickness, then reached a maximum value. A model taking into account the optical properties of both types of VO_2 film fully justified such a maximum value. The n and k optical indexes were calculated from transmittance and reflectance spectra. A significant contrast in emissivity due to the phase transition was also observed between 25 and 100 °C.

Keywords: Oxides; Thin films; Optical materials; Sputtering; Optical properties

1. Introduction

Vanadium dioxide (VO_2) presents a reversible metal-insulator phase transition at T_c=68 °C [1–3]. Above T_c, it presents a tetragonal structure (noted as VO_2(R)) characterized by metallic conduction [4], with cell parameters a_r=455 pm, c_r=286 pm, and space group P4$_2$/mnm (no. 136) [5]. Below T_c, the VO_2 phase is monoclinic (noted as VO_2(M)) and behaves as a semiconductor with a narrow gap (0.7 eV for a single crystal); the rutile structure presents a distortion with cell parameters a_m=575 pm, b_m=452 pm, c_m=538 pm, β=122.6° and space group P2$_1$/c (no. 14) [5]. These structural modifications induce large changes in electrical and optical properties [6–8] and a lot of electrical and optical applications [9,10] might be envisaged: smart windows for thermal regulation using the transmittance contrast of VO_2 [11], accordable IR mirrors for LASER applications using the reflectance contrast of VO_2 [12] and uncooled micro-bolometers [13]. A large variety of methods was used to prepare VO_2 thin films, such as radio-frequency reactive sputtering [14–16], chemical vapor deposition [17], sol–gel process [18–20] and pulsed laser deposition [21,22]. In previous works, targets prepared from pure vanadium material were used to insure a high purity of final thin film [14,15]. In this case, vanadium metal was oxidized during deposition process. Recent studies showed that V_2O_5 targets might be used [23].

The present work describes the optimization of thin film deposition process from V_2O_5 targets, and establishes the relations between material thickness, nature of substrate and final switching optical properties. A modeling approach is proposed to interpret the data.

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2. Experimental details

2.1. Sample preparation

2.1.1. Target preparation

Thin films were deposited by radio-frequency reactive sputtering technique. Targets were prepared using V_2O_5 commercial powder (Acros Organics, 99.9%). The V_2O_5 powders were compacted in a stainless mould especially machined with the diameter of radio-frequency sputtering target (80 mm), then compressed under a pressure of 20×10^6 Pa. The target was then sintered at 400 °C, during 2 h, before being placed in the pulverization device. This low sintering temperature was selected because of low melting point of V_2O_5 (690 °C).

2.1.2. Deposition conditions

Thin films were deposited on (001) oriented Si substrates, from radio-frequency reactive sputtering technique, using such vanadium pentoxide targets. The Si-(001) substrates were selected for their optical transparency in the infrared range. The variable deposition parameters were: gas flux, environmental enclosure pressure, substrate temperature, power applied to the target and deposition time. The distance between electrodes is 50 mm. Recently, Dillon et al. [24] prepared thin films from metal vanadium target and showed that the oxygen flow must be very low compared to the argon flow. To determine adequate reducing conditions, we tested variable oxygen and argon flows. Each film is noted V_N where N is a reference number. Each substrate was first cleaned with successively hot trichloro-ethylene, hot acetone and ethanol. After drying under nitrogen flow, the substrates were directly set up in the enclosure and a vacuum pumping was carried out until a pressure of 1 Pa; then, gas flows were introduced in the enclosure. Between two deposition cycles, a pre-pulverization under argon flow (8.45×10^{-2} Pa m^3 s^{-1}) was carried out during 1 h. The flow unit usually used is the “sccm” for standard cubic centimeter per minute. Its conversion in the international system is: 1 sccm$=1.69\times10^{-3}$ Pa m^3 s^{-1}. The experimental parameters are reported in Table 1.

2.2. Characterization methods

2.2.1. Structural properties

X-ray diffraction (XRD) patterns were recorded on Siemens-Brucker D5000 equipment, with copper X-ray source ($\lambda=154.06$ pm), Soller slides, a secondary monochromator and a rotating sample holder, working in a classical θ–2θ coupled mode. The patterns were recorded with a 2θ step of 0.04° and 25 s per step.

Atomic Force Microscopy (AFM) images were acquired by a Park Instruments system, and then analyzed from the standard Park software, in order to obtain topological information about the layers. The images were carried out using an Ultralever 06A tip and with a scan frequency of 1 Hz per line.

2.2.2. Optical properties

In the wavelength range 0.3 to 2.5 μm, transmittance and reflectance spectra were recorded on a Perkin Elmer Lambda 9 spectrometer, using the Winlab software. The VO_2 optical

Table 1
Experimental conditions for thin film deposition (power (P_w) fixed at 50 W for all samples)

Sample	Oxygen gas flow $F(O_2)$ (Pa m^3 s^{-1})	Argon gas flow F(Ar) (Pa m^3 s^{-1})	Tension U (V)	Substrate temperature T (°C)	Time of deposition t (min)	Objectives
V1	1.69×10^{-3}	8.45×10^{-2}	210	450	15	Evolution of oxygen gas flow at 450 °C
V2	5.07×10^{-3}	8.45×10^{-2}	210	450	15	
V3	1.52×10^{-2}	7.09×10^{-2}	210	450	15	
V4	1.18×10^{-3}	8.45×10^{-2}	160	450	30	
V5	5.07×10^{-4}	8.45×10^{-2}	165	450	30	
V6	1.18×10^{-3}	8.45×10^{-2}	210	450	30	
V7	5.07×10^{-4}	8.45×10^{-2}	160	450	45	
V8	8.45×10^{-4}	8.45×10^{-2}	160	450	45	
V9	1.18×10^{-3}	8.45×10^{-2}	160	450	45	
V10	–	8.45×10^{-2}	160	550	30	Evolution of oxygen gas flow at 550 °C
V11	8.45×10^{-4}	8.45×10^{-2}	208	550	30	
V12	6.76×10^{-4}	5.07×10^{-2}	165	550	30	
V13	–	8.45×10^{-2}	170	550	60	
V14	8.45×10^{-4}	8.45×10^{-2}	170	550	60	
V15	4.22×10^{-4}	8.45×10^{-2}	170	550	60	
V16	4.22×10^{-4}	8.45×10^{-2}	170	550	45	Evolution of deposition time (thin film thickness)
V17	4.22×10^{-4}	8.45×10^{-2}	170	550	30	
V18	4.22×10^{-4}	8.45×10^{-2}	170	550	15	
V19	4.22×10^{-4}	8.45×10^{-2}	170	550	45	
V20	4.22×10^{-4}	8.45×10^{-2}	170	550	45	
V21	4.22×10^{-4}	8.45×10^{-2}	170	550	5	
V22	4.22×10^{-4}	8.45×10^{-2}	170	550	40	
V23	4.22×10^{-4}	8.45×10^{-2}	170	550	20	
V24	4.22×10^{-4}	8.45×10^{-2}	170	550	45	
V25	4.22×10^{-4}	8.45×10^{-2}	170	550	45	
V26	4.22×10^{-4}	8.45×10^{-2}	170	550	45	