Applied Surface Science 277 (2013) 218–222

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Preparation and investigation of sputtered vanadium dioxide films with large phase-transition hysteresis loops

Huafu Zhang [a,b,*], Zhiming Wu [a,*], Qiong He [a], Yadong Jiang [a]

[a] School of Optoelectronic Information, State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, PR China
[b] School of Science, Shandong University of Technology, ZiBo, Shandong 255049, PR China

ARTICLE INFO

Article history:
Received 31 January 2013
Received in revised form 1 April 2013
Accepted 10 April 2013
Available online 21 April 2013

Keywords:
Vanadium dioxide
Hysteresis width
Thin films
Reactive magnetron sputtering
Phase transition temperature

ABSTRACT

Vanadium dioxide (VO_2) films with large phase-transition hysteresis loops were fabricated on glass substrates by reactive direct current (DC) magnetron sputtering in Ar/O_2 atmosphere and subsequent in situ annealing process in pure oxygen. The crystal structure, chemical composition, morphology and metal-insulator transition (MIT) properties of the deposited films were investigated. The results reveal that the films show a polycrystalline nature with a (0 1 1) preferred orientation and consist of small spheroidal nanoparticles. All the deposited VO_2 films show large hysteresis loops due to the small density of nucleating defects and the large interfacial energies, which are determined by the characteristics of the particles in the films, namely the small transversal grain size and the spheroidal shape. The film comprising the smallest spheroidal nanoparticles not only shows a large hysteresis width of 36.3 °C but also shows a low transition temperature of 32.2 °C upon cooling. This experiment facilitates the civilian applications of the VO_2 films on glass substrates in optical storage-type devices.

1. Introduction

It is well known that vanadium dioxide (VO_2) thin films undergo a mental-insulator transition (MIT) which can be induced not only by temperature [1] but also by voltage [2] or light [3]. The MIT is characterized by significant changes in optical and electrical properties [4,5] as well as terahertz transmission [6,7], indicating a wide variety of potential applications such as storage devices [8–10], switching elements [11,12], smart windows [13] and terahertz modulators [6,7]. When VO_2 thin films are used as storage-type devices, a relatively large hysteresis width of 15–20 °C is required in order to operate the devices reliably [14,15]. As a matter of fact, the larger the hysteresis width of VO_2 film is, the more reliable the storage-type devices are. At the mean time, a lower transition temperature and sharper transition slope in cooling branch will lead to a higher stability, reliability and sensitivity at or near room temperature.

Up to now, pulsed laser deposition [16], ion implantation [17], laser ablation [18], polymer-assisted deposition [13] and complex process [1] have been applied to prepare VO_2 films or particles with large hysteresis width. In these methods mentioned above, however, high temperature (1000 °C [17], 850 K [18]) and relatively high-cost substrates (silicon [6], fused SiO_2 [17] or single-crystal sapphire [18]) are required. Although sputtering has been widely used to prepare VO_2 films, there are few reports on sputtered VO_2 films with large hysteresis width. As one of the most widely used deposition technique, magnetron sputtering possesses lots of advantages such as high growth rate, low deposition temperature and good adhension. Besides, magnetron sputtering can prepare large and uniform films more easily than pulsed laser deposition, and can prepare higher-quality films than polymer-assisted deposition or sol–gel method. Therefore, it is necessary to prepare VO_2 films with large hysteresis width on low-cost glass substrates at low temperature by magnetron sputtering.

In this work, nanostructured VO_2 films with large hysteresis width were deposited on glass substrates at low temperature by reactive direct current (DC) magnetron sputtering from pure vanadium target in Ar/O_2 atmosphere and subsequent in situ annealing process in pure oxygen. The crystal phase, chemical composition, morphology and MIT properties of the deposited films were investigated.

2. Experimental details

After being cleaned ultrasonically followed by drying in a high pressure N_2 gas, the K9 glass substrates were loaded into the

* Corresponding authors at: School of Optoelectronic Information, State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, PR China. Tel.: +86 15963310176.
E-mail addresses: huafuzhang@126.com (H. Zhang), zmwu@uestc.edu.cn (Z. Wu).

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http://dx.doi.org/10.1016/j.apsusc.2013.04.028

Table 1
The key preparation parameters and the designations of the corresponding films.

Sample	Reactive oxygen flow rates (SCCM)	Substrate temperature (°C)	Deposition time (min)	Annealing time (min)	Annealing temperature (°C)	Oxidation oxygen flow rates (SCCM)
I	1	100	25	30	350	5
II	1	100	50	30	350	5
III	1	100	100	30	350	5

reactive chamber. High-purity Ar gas as the working gas and O_2 gas as the reactive gas are introduced separately into the chamber by using two mass flow controllers after the chamber was evacuated to a base pressure of 2×10^{-3} Pa. The VO_2 films were fabricated by sputtering a pure vanadium target in Ar/O_2 atmosphere and subsequent in situ annealing process in pure oxygen. After the annealing, the films were cooled naturally down to room temperature. Prior to deposition, a 10 min pre-sputtering step is performed in order to get rid of any possible contaminations of the target surface. For convenience of discussion, the key preparation parameters and the designations of the corresponding films were listed in Table 1.

The crystal structure, chemical composition and morphology of the deposited films were characterized by X-ray diffraction (XRD, Shimadzu XRD-7000), X-ray photoelectron spectroscopy (XPS, XSAM 800) and field emission scanning electron microscope (SEM, Hitachi S4800), respectively. The optical transmittance-temperature curves were monitored on a Shimadzu Spec-1700 UV–visible spectrophotometer equipped with a heating plate at a fixed wavelength of 1100 nm.

3. Results and discussions

3.1. XRD analysis

Fig. 1 shows the XRD pattern of the sample I. The strong peak at $2\theta = 27.89°$ is indexed to the diffraction from the VO_2 (0 1 1) phase. It can be found that a peak at $2\theta = 39.95°$ is also detected due to the reflection of the VO_2 (0 2 0) plan whose intensity is much smaller than that of the VO_2 (0 1 1) peak, revealing a polycrystalline nature with a (0 1 1) preferred orientation. The VO_2 (0 1 1) peak shows a narrow full width at half maximum with a value of 0.238°, suggesting that the deposited film shows a slightly better crystallinity than the usually reported VO_2 films [7,19]. According to the Scherrer's formula, the average crystallite size along VO_2 (0 1 1) peak is estimated to be ∼38 nm, indicating the deposited VO_2 film belongs to nanostructured crystal.

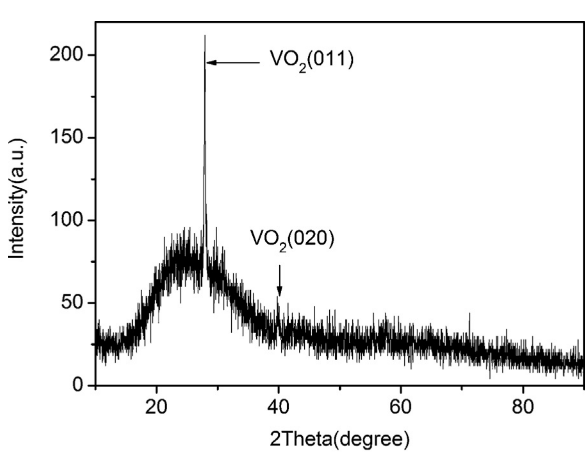

Fig. 1. XRD pattern of the sample I.

3.2. XPS analysis

Fig. 2(a) shows the wide range XPS spectrum of the sample I. We can see that besides vanadium and oxygen, other contamination elements were also detected, where sodium and silicon come from the glass substrate, carbon originates from the surface contamination and nitrogen arises from the air. Fig. 2(b) shows the high resolution scans of the $V2p_{3/2}$ core levels and its peak was fitted by applying a Shirley function with software XPS peak 4.1. It is obvious that the vanadium exists in two valence states, namely +4 and +5 valences whose binding energies are 516.0 and 517.3 eV, respectively. The phenomenon that there is V^{5+} in XPS while in XRD there is no indication of V^{+5} could be attributed to the fact that the V_2O_5 in the deposited films is not crystalline. According to the corresponding areas and sensitivity factors, the atom concentrations of +4 and +5 valences were evaluated as 66.5 and 33.5%, respectively.

3.3. SEM morphology analyses

Fig. 3 shows the SEM surface morphologies for the sample I(a), II(b) and III(c). In addition to a few pores or cracks, the sample I consists of relatively homogeneous and continuous nanoparticles

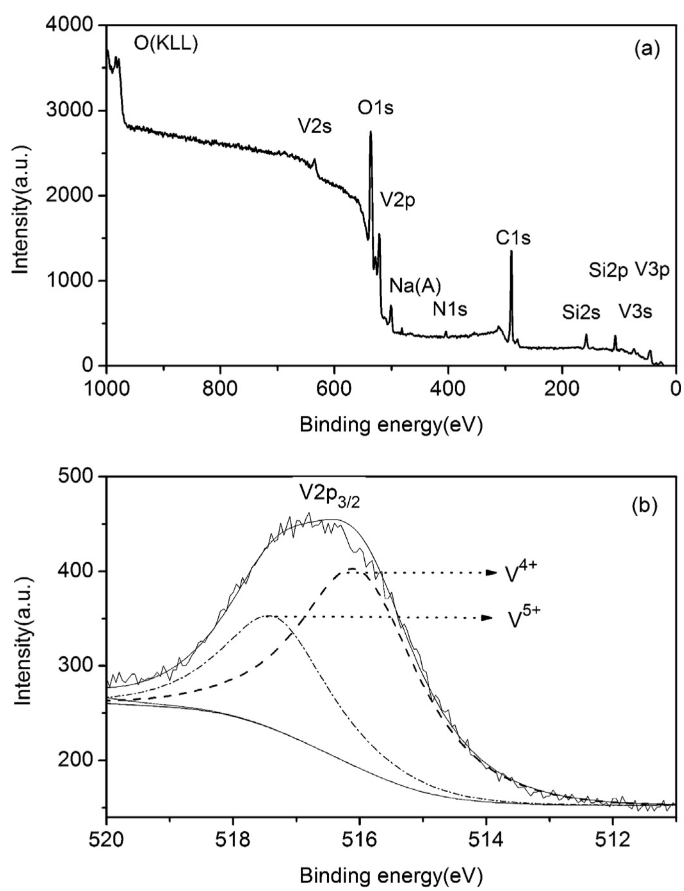

Fig. 2. XPS spectrum of the sample I: (a) wide range survey of binding energy in XPS; (b) high-resolution scans of the $V2p_{3/2}$.