Sensors and Actuators B 187 (2013) 386–394

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

Gas sensing properties of pulsed laser deposited vanadium oxide thin films with various crystal structures

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ARTICLE INFO

Article history:
Available online 27 December 2012

Keywords:
Vanadium oxides
V_2O_5
V_7O_{16}
Thin film
Resistivity change
Gas sensing
NO_x
H_2

ABSTRACT

Vanadium oxide thin films were fabricated by pulsed laser deposition. The crystal structure and symmetry of the deposited films were studied with X-ray diffraction and Raman spectroscopy, respectively. The film microstructure was also studied with atomic force microscopy and scanning electron microscopy. The thin film crystal structures varied between almost pure V_2O_5 phase and another phase, suggested being V_7O_{16}, generally found in samples composed of nanotubes and identified as VO_x-NT. The measured optical transmission spectra of the films also supported the existence of two different phases. The electrical resistivity of the films as a function of temperature behaved like in a typical semiconductor. The gas sensing properties of the films were characterized for different NO_x, CO and H_2 concentrations. The results showed a response to NO_x and H_2, which varied from oxidative to reducing according to the film composition and gas background environment. Only very small response was seen towards CO. Gas response and resistivity measurements indicated that the VO_x-NT-type phase has both n-type and p-type conduction mechanisms.

1. Introduction

The concern about pollution increase around the globe causes the regulations towards different type of emission to get tighter by time. This also relates to atmospheric gas emissions. Novel gas sensor structures and materials are needed to meet these new demands and they are studied widely in the scientific community. Solid state semiconducting gas sensors are one of the most popular research topics in the gas sensing science. They are typically based on different types of metal oxides such as SnO_2, TiO_2, WO_3, etc. Vanadium oxides are considered as a new candidate for gas sensors and have been studied to some extent before. Different vanadium pentoxide (V_2O_5) structures have shown sensitivity towards NH_3 [1,2] and amines [3]. Vanadium dioxide (VO_2) nanowires have been investigated as a H_2 sensor by taking advantage of the metal–insulator transition phenomena of the material [4,5]. Polycrystalline vanadium oxide thin films have also demonstrated sensitivity towards NO [6] and NO_2 [7,8].

There are several methods for fabricating vanadium oxide thin films, e.g. sputtering methods [9,10], chemical vapor deposition [11], sol–gel method [12] and pulsed laser deposition [13–15]. Pulsed laser deposition has some advantages including good repetition of stoichiometry of the target in the films on the substrate and easily controllable film composition by deposition parameters. Vanadium oxide nanotubes (VO_x-NT) have been fabricated by chemical methods for some time [16–19]. The structure of the tube is composed of a wall with VO_x layers and a chemical amine in between the layers. The crystal structure of VO_x has been suggested to be composed of triclinic V_7O_{16} phase [16,17].

In this study, the possibility to use pulsed laser deposited polycrystalline vanadium oxide thin films as sensors for different gases was examined. The polycrystalline thin films are suggested to be composed of both the V_2O_5 phase and the phase similar to VO_x-NT in a heterojunction structure. According to literature this is the first time that this type of film composition has been fabricated by PLD and tested for gas sensing. Thus the observed crystalline phases are called V_2O_5 phase and VO_x-NT-type phase in this paper.

2. Materials and methods

Lambda Physik Compex 201 excimer laser operating at the wavelength of 308 nm was used to deposit vanadium oxide thin films on single crystalline c-plane Al_2O_3, i.e. sapphire, substrates with thickness of 500 μm. The pulse repetition rate was 5 Hz. The rotating target used was a pure ceramic V_2O_5 target (SCI Instruments) and the laser pulse energy densities were $I = 1.275\ J/cm^2$ and $I = 2.55\ J/cm^2$. The substrate temperatures of in situ PLD processes were $T = 400\ ^\circ C$ and $T = 500\ ^\circ C$. The deposition chamber was

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http://dx.doi.org/10.1016/j.snb.2012.12.067

Table 1
The pulsed laser deposition parameters for each vanadium oxide film type.

Thin film name/composition	Substrate temperature, T [°C]	Oxygen partial pressure, $p(O_2)$ [mbar]	Laser pulse energy density, I [J/cm^2]
V_2O_5[a]	400	1.0×10^{-2}	1.275
V_2O_5 + VO_x-NT	400	1.5×10^{-2}	2.55
VO_x-NT	500	1.5×10^{-2}	2.55

[a] The film was post-annealed at 400 °C for 1 h in air atmosphere.

first pumped to a base pressure of ~5×10^{-5} mbar and then oxygen partial pressure ($p(O_2)$) of 1×10^{-2} mbar or 1.5×10^{-2} mbar was added in the chamber. One of the samples was post annealed in an oven at 400 °C for 1 h in air atmosphere. The deposition parameters for each sample are described in Table 1.

Crystal structure of the films was studied using θ–2θ X-ray diffraction (XRD) by Philips PW1380 diffractometer, and HORIBA Jobin Yvon LabRAM HR800 Raman spectroscope with argon-ion laser with the wavelength of 488 nm. The surface morphology was studied using Veeco Dimension 3100 atomic force microscope (AFM). Scanning electron microscopy (SEM) studies were made by using Helios Dual-Beam FIB/FESEM device. Optical transmission spectra of the films were measured between wavelengths of 250–2250 nm by using Varian 5000 UV-vis-NIR spectrophotometer.

Photolithography process and RF-sputtering was used to manufacture 300 nm thick platinum interdigital electrodes (IDE) with 20 μm finger gap on the thin films. First 30 nm of titanium was sputtered between the platinum and vanadium oxide thin film to serve as adhesion layer. The electrical resistivity as a function of temperature, and the gas responses was measured using a probe station together with temperature controlled Linkam THMSE600 heating stage connected to Keithley 2636A sourcemeter and to Agilent 3458A multimeter. The probe station had a closed volume of ~100 ml and gas inlet and outlet. Signal Series 850 gas blender was used to mix the measured gas with a background gas of synthetic air or argon in a mixing chamber before the inlet to the probe station. All the gases used, including the background gases, were injected to the blender from commercial gas bottles. The samples were heated in the carrier gas atmosphere to the measurement temperature and the measurements were controlled by a LabVIEW software.

3. Results and discussion

3.1. Structural characterization

In Fig. 1(a), the Raman spectra of the deposited films are presented. According to the data, the post annealed film on the bottom curve had co-existent phases of a major V_2O_5 phase [15] and another minority phase. In the other two films, the presence of this other phase, identified as a structure found in VO_x nanotubes (VO_x-NT) [18–20], was clearly stronger. These nanotubes are usually fabricated by a chemical process and are formed as rolls of V_7O_{16} structure with layered walls and a chemical amine in between the layers [16,17]. This crystal phase V_7O_{16}, similar to VO_x-NT tube walls, was present in the films, but not as nanotube structure, as is also supported by AFM and SEM results below. The middle curve in Fig. 1(a) shows that the V_2O_5 phase of the film was nearly equally strong as the VO_x-NT-type phase, but in the top curve it is seen that the V_2O_5 phase of the film had almost disappeared and the VO_x-NT-type phase was dominating. The X-ray diffraction curves of three different types of vanadium oxide thin films are shown in Fig. 1(b). The results show that the post-annealed film on the bottom curve had a polycrystalline V_2O_5 structure with a strong orthorhombic (0 0 1) orientation, but in the other two films the V_2O_5 phase was weaker. The VO_x-NT-type phase could not be identified from these curves, but it has to be kept in mind that if the other phase was a triclinic phase as V_7O_{16}, the conventional θ–2θ set-up might have been insufficient for identifying this type of phase. If samples would contain tubular form of VO_x-NT phase, they should give an extra peak in XRD response at 2θ angles around 3° due to periodicity of tube structure. Since this reflection was not observed in XRD data, tubular structure is absent from these thin films [16,17]. However, the Raman spectra in Fig. 1(a) clearly identifies only two phases, namely the V_2O_5 and VO_x-NT-type phases, in the films studied here [15,18–20]. So, the VO_x-NT-type phase containing samples have the same crystalline structure as VO_x nanotubes, only without tubular shape. Nevertheless, the crystalline structure is the most important factor determining electrical and optical properties.

The AFM images of the three films can be seen in Fig. 2. They all showed a polycrystalline surface morphology, and in Fig. 2(b), with co-existing V_2O_5 phase and VO_x-NT-type phase, the largest variation in the surface height profile was obtained. Films with dominating V_2O_5 or VO_x-NT-type phases, had quite smooth surfaces, as shown in Fig. 2(a) and (c), respectively. Also, some particulates formed in the PLD process and deposited on the film surfaces were noticed, seen as bright white spots in the AFM images.

In Fig. 3(a) and (b), the SEM images of the thin films with two co-existing phases and dominating VO_x-NT-type phase are shown, respectively. The surface quality of the films supported the results gained from AFM measurements. From the cross-section micrographs, a clear porosity, seen as black holes, in the film with the co-existing phases of V_2O_5 and VO_x-NT-type phase could be noticed, as shown in Fig. 3(a). The film in Fig. 3(b), on the other hand, showed a very dense and smooth structure of dominating VO_x-NT-type phase. As anticipated from XRD results, no tubular structure was observed. PLD process generated particulate droplets are also seen as bright white spots in right hand surface SEM image in Fig. 3(b).

3.2. Optical and electrical characterization

The optical transmittance spectra of the three films and single crystalline c-plane Al_2O_3, i.e. sapphire, substrate are shown in Fig. 4. Film with a dominating V_2O_5 phase, showed a typical spectrum of V_2O_5 with absorption edge around 625 nm. In the film with the two co-existing phases, the VO_x-NT-type phase clearly shifted the transmittance to smaller values at lower wavelengths and when the VO_x-NT-type phase was dominant, the transmittance value dropped even more. This is due to another absorption edge at around 1000 nm originating from VO_x-NT-type phase in films with co-existing phases. The roughly estimated values E_{abs} for different absorption edges of the films were calculated with the following Planck's relation formula: $E_{abs}=hc/\lambda$, where E_{abs} = estimated absorption edge, h = Planck's constant, c = speed of light, and λ = wavelength value of the absorption edge. The estimated absorption edges are pointed out by arrows in Fig. 4. This type of estimation gives the range for the band gap values for the different thin films. However, modeling and calculating the exact band gap values for the films is beyond the scope of this manuscript. The calculated energy values for the two different absorption edges of the films were: E_{abs} ~2.43 eV and E_{abs} ~1.16 eV. The value of E_{abs}