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Vanadium oxide nanostructured thin films prepared by Aerosol Spray Pyrolysis for gas sensing and thermochromic applications

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ABSTRACT

Vanadium oxide (V_xO_y) nanostructured films were prepared by Aerosol Spray Pyrolysis technique with different concentrations of precursor solution (0.005 M, 0.01 M, 0.02 M), using ammonium metavanadate (NH_4VO_3) as precursor. The deposition was carried out onto glass substrates (Corning glass) at two different substrate temperatures (300 °C and 400 °C). Furthermore, oxalic acid was added to the precursor solution in order to grow the thermochromic VO_2(M) monoclinic phase via reduction of the Vanadium oxides in which Vanadium is in a higher oxidizing state. All films were characterized by X-Ray Diffraction technique and UV/Vis/NIR spectroscopy to identify their structural and optical properties, respectively. V_2O_5 films were tested against ozone, having a sensitivity of 29% in ultra-low concentration of 5ppb ozone, at room temperature. Moreover, nanostructured VO_2 films appeared to be thermochromic, having an IR-switching of about 5% at λ = 2500 nm, upon heating.

1. Introduction

Transition metal oxide films have been investigated in recent years since they can be used in a variety of applications such as 'smart' windows, thin-film transistors, solar cells, gas sensing, catalysis, optical switching and electrochemical devices. Vanadium oxides are materials of great interest due to the different vanadium / oxygen stoichiometry (different oxidation states) leading to individual phases such as VO, V_2O_3, VO_2, V_6O_{13} and V_2O_5 with characteristic properties. Vanadium oxides are considered to be new candidates for gas sensing elements and have already been studied to some extent. More specific, Vanadium pentoxide (V_2O_5) has high electrochemical activity and stability, thus it is a promising material for gas sensing applications [1–4], while Vanadium dioxide (VO_2) is a well-known thermochromic material [3]. From the chemical point of view, the properties of V_2O_5 are due to its rich and diverse chemistry based on its oxidation states and the variability of oxygen coordination geometries. This structural richness is the source of the existence of differently coordinated oxygen ions, which provide an important ingredient for controlling the physical and chemical surface properties [5].

V_2O_5 thin films have been prepared on different substrates by various methods, such as electron beam evaporation [6], reactive sputtering [7,8], pulsed laser deposition (PLD) [9–12], chemical vapor deposition (CVD) [13], spray pyrolysis [14,15], solvothermal [16] and sol–gel [17,18]. In particular, V_2O_5 films prepared by spray pyrolysis technique at 300 °C were tested against 500ppb ethanol [19] having a response time of 17 s and a recovery time of 55 s. On the other hand, VO_2 belongs to the strongly correlated electron system materials and it undergoes a semiconductor-to-metal (SMT) first-order phase transition at a critical transition temperature (T_C) of about 68 °C, accompanied by an abrupt change in its resistivity and near-infrared transmission. Thus, below T_C it is a semiconductor with monoclinic structure and high IR transparency, while above T_C it shows a metallic behavior with a tetragonal rutile structure and high IR reflectivity. As a result, thermochromic VO_2 has received great attention for smart window applications because of its ability to control solar heat gain in response to the temperature variations [20]. It is also of great interest in condensed-matter physics because it is a classic strongly correlated electron system. However it is not clear yet if this semiconductor to metal transition is due to electron-electron correlation (Mott-Hubbard transition) or to electron-phonon interaction (Peierls transition) [21]. In general, vanadium oxide thin films grown at relatively low substrate

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temperature (< 300 °C) are amorphous while crystallization temperature depends on the growth technique as well as the structure (crystalline or amorphous) of the substrate material which are growing on [22].

In this work, we report on preparation of vanadium oxides (V_2O_5 and VO_2) grown by aerosol spray pyrolysis technique, using ammonium metavanadate (NH_4VO_3) as precursor with different concentrations (0.005 M, 0.01 M, 0.02 M) and additives (such as oxalic acid), on corning glass. V_2O_5 films were investigated as potential gas sensing elements exhibiting a sensitivity of 29% at 5ppb O_3, while VO_2 was examined as a thermochromic coating, exhibiting a IR-switching of 5% upon heating.

2. Experimental section

Aerosol Spray Pyrolysis technique was applied on a homemade system described with details in our previous work [23]. Vanadium oxide thin films have been deposited from aqueous solution of ammonium metavanadate (NH_4VO_3) in different concentrations, from 0.005 M to 0.02 M. The solution was sprayed onto pre-heated glass substrates (Corning 1737F), at two different temperatures, namely 300 °C and 400 °C, controlled by a thermocouple fed to a temperature controller, in order to be constant during deposition. The overall reaction process can be expressed as heat assisted decomposition of ammonium metavanadate solution to form clusters of Vanadium oxides on the heated substrate. Prior to deposition, the substrates were cleaned with acetone and isopropanol under ultrasonication. Compressed air at pressure of 0.1 bar was used as a carrier gas. The nozzle to substrate distance was 13 cm, while the deposition time was varied from 20 to 40 min.

To examine the structure of the films, a RIGAKU X-Ray Diffractometer (model RINT 2000) using Cu Kα radiation (40 kV/82 mA) (λ_{Ka} = 0.154056 nm), was employed. Continuous scanning was applied with a slow scanning speed (0.02°/sec). A range of (2θ) from 10° to 65° was scanned, so that all possible diffraction peaks could be detected. The crystallite size was determined using Scherrer's equation. The films' thickness was determined by using a profilometer (Veeco Dektak 150). Optical transmittance measurements of thin films sprayed on glass substrates were carried out using a Perkin Elmer Lambda 950 spectrophotometer at wavelength range of λ = 250–2500 nm. The sensing properties of the films were identified by monitoring electrical current variations, upon exposure to Ozone, at room temperature. Specifically, the conductometric measurements were carried out in a home-made system described elsewhere utilizing a consecutive photoreduction and oxidation process [24]. Initially, the film was irradiated by UV lamp (mercury pencil lamp with an average intensity of 4 mW/cm^2 at a wavelength of 254 nm, placed at a distance of approximately 3 cm from the surface of the film) for 5 min leading to an increase of conductivity. As it is already known [25] Oxygen bonds are breaking upon UV illumination (photoreduction process) releasing two electrons per missing Oxygen atom. As a result free electron concentration is increased leading to an increase of film's conductivity. On the contrast, during oxidation process (where film is exposed to ozone) the adsorbed Oxygen atoms fulfill the Oxygen vacancies reducing the free electron concentration so as film's conductivity. For the subsequent oxidation process ozone was produced by an ozone analyzer (Thermo Electron Corporation, model 49i) at different concentrations ranging between 5 and 2600ppb and the chamber was backfilled with ozone at a pressure of 100mbar, for 5 min. In order to measure the induced electrical changes on the films during the photoreduction-oxidation procedure, a constant voltage was applied during the whole cycling procedure and the electric current variations were measured by a Keithley 6517A electrometer. The thermochromic properties of films were also investigated by receiving the transmittance spectrum from room temperature (RT) to elevated temperature. For this, a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer, operating at λ = 250–2500 nm,

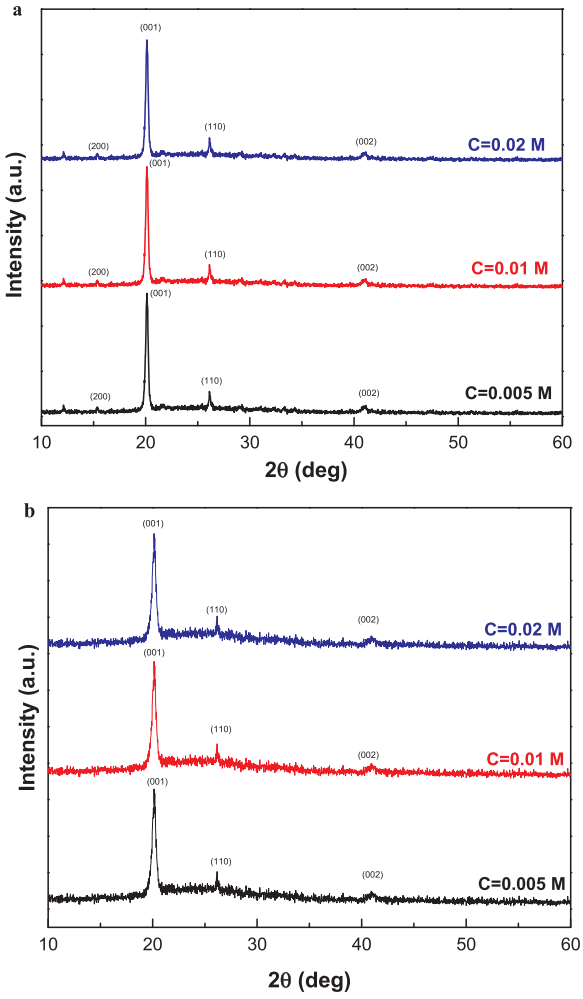

Fig. 1. X-ray diffraction pattern of aerosol spray pyrolysis V_2O_5 samples prepared from different solution concentrations of precursor at 400 °C (a) and 300 °C (b) deposition temperature.

with a homemade heating stage attached, was used. Temperature was controlled by a temperature controller, while a thermocouple on contact with film surface was used to control the temperature. Transmittance spectrum was recorded at 25 °C (RT) and 90 °C, that were well below and above the usual critical transition temperature (T_C = 68 °C) for bulk VO_2. At these two temperatures, the IR transmittance variation, namely IR-switching, (ΔTr_{IR}) at λ = 2500 nm defined as the difference of transmittance between RT and 90 °C, $\Delta Tr_{IR}(\%) = Tr_{IR}(25\,°C)(\%) - Tr_{IR}(90\,°C)(\%)$.

3. Results and discussion

3.1. Structural and optical characterization

Vanadium pentoxide films displayed a uniform yellow color similar to those prepared by other techniques. Such yellow color is an indication that vanadium is incorporated as V^{5+} in the VO_x lattice, in contrast to a blue color displayed when V^{4+} is present. Fig. 1 shows the XRD patterns of vanadium oxide nanostructured films prepared with different precursor concentrations (from 0.005 M to 0.020 M) on glass substrates at 400 °C, for deposition time D_t = 40 min, confirming the V_2O_5 phase formation. The intense of Miller plane (001) was observed at 2θ = 20.14° for all samples. The peaks were indexed by comparing our experimental data with the JCPDS card No 00-041-1426 for V_2O_5. Fig. 1b, shows the XRD patterns of vanadium oxide nanostructured films prepared with the same precursor concentrations on glass