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General

Pulsed Laser Deposited Nanostructured Vanadium Oxide Thin Films Characterized as Ammonia Sensors

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ABSTRACT

Vanadium oxide thin films were fabricated by pulsed laser deposition. The microstructure and crystal symmetry of the deposited films were studied with X-ray diffraction, scanning electron microscopy (SEM), and Raman spectroscopy, respectively. The films surface morphology was examined by atomic force microscopy. Raman spectroscopy and XRD results showed that the thin film phase-structure was composed of pure orthorhombic V_2O_5 phase, or they had a mixed phase structure of orthorhombic V_2O_5 and triclinic V_7O_{16}. Surface morphology of the films consisted of nanosized particles, although in pure V_2O_5 films some bigger agglomerates and flakes were also seen. The conductivity based gas sensing measurements showed a clear response already at ppb-levels of NH_3 and strong selectivity to ammonia was found when compared to NO and CO gases. Also, the films showed promising gas sensing behavior in cross-sensitivity measurements between NO and NH_3, being able to sense ammonia even in the presence of NO. This is an important property when considering possible sensing applications to control Selective Catalytic Reduction processes, *e.g.* in diesel engine exhausts, where introduced ammonia, or urea, transforms nitrogen oxide gases in a catalytic converter to nitrogen and water.

1. Introduction

Nitrogen oxide gases like nitrogen dioxide, NO_2, and nitric oxide, NO, are formed in combustion processes where oxygen and nitrogen are present. These gases are toxic and dangerous for both human beings and the environment, and therefore the allowed emissions of these gases are almost down to zero today. The most efficient way to reduce NO and NO_2 (NO_x) from exhausts gases is to use Selective Catalytic Reduction (SCR). In the SCR process, ammonia NH_3, or urea (NH_2CONH_2), which together with water forms NH_3 and carbon dioxide CO_2 at temperatures above 150 °C, is injected in the exhausts of, *e.g.* diesel vehicles and stationary engines, and in the catalytic converter NH_3 reacts with NO_x and form harmless nitrogen and water. This process has to be controlled in order to be enough efficient to meet legislations, and this can be performed by either nitrogen oxide sensitive sensors or by an ammonia sensor [1,2]. The requirements on an ammonia sensor for the SCR process depend on the application, but for diesel exhausts, the demands set by the car industry for sensitivity to NH_3 are in the range 0 - 100 ppm with an accuracy of ± 5 ppm for new and aged sensors, and for response time 3 seconds from 10 - 90% of the full response, low cross sensitivity to other gases, temperature resistance between 20 °C–600 °C, high long-term stability, and resistivity to contaminants such as soot, sulphates, and phosphates [1–4].

Vanadium oxides form an interesting material group because of its varying oxidation states between V^{2+} and V^{5+}, the most famous compounds being V_2O_5 and VO_2. These different compounds have been studied also as a possible gas sensing materials, *e.g.* for NH_3. VO_2 has an interesting metal-insulator-transition (MIT) property where it changes its phase structure from low-temperature insulating state to high-temperature (T > 68 °C) metallic state. This property has been studied in the context of, *e.g.* hydrogen sensor [5]. Nanofibers of V_2O_5 have been studied as a ppb-level NH_3 sensor [6,7], and as a sensing material to amines [8]. Also, the remarkable catalytic properties of V_2O_5 have been reported in the case of sensing materials based on mixtures of V_2O_5, WO_3, and TiO_2 [9,10]. The sensitivity to ammonia increased with higher content of V_2O_5. Lately, a growing interest has been shown for chemically grown vanadium oxide nanotubes (VO_x-NT) whose wall are composed of triclinic V_7O_{16} layers [11,12] and they have been studied also as a possible ethanol sensor [13]. Some studies have also revealed the complex behavior of mixed-valence vanadium oxide thin films, when tested as conductometric gas sensors for different gases in various conditions [14]. It was concluded, that

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the gas sensing behaviour of vanadium oxide thin films is highly dependent of the measurement conditions, and that the presence of both V^{5+} in the *n*-type V_2O_5 material and V^{4+} ions in the *p*-type V_7O_{16} material, respectively, causes the sensor devices to even switch between *n*-type and *p*-type semiconducting behavior. This behaviour depends on measurement temperature and whether the surrounding gas atmosphere is oxidizing or reducing.

Pulsed laser deposition (PLD) has been used to manufacture vanadium oxide thin films for several applications [15], since the method has several advantages including easily controllable film composition by deposition parameters, and a good repetition of stoichiometry of the target material in the films deposited on the substrate. In our earlier studies, pure V_2O_5 thin films and films with mixed phases of V_2O_5 and V_7O_{16} were deposited by PLD and then tested as sensors for NO and H_2, for example [14]. Here we characterize these sensors for NH_3 sensing for the possible application to control the SCR process.

2. Experimental

Pulsed laser deposition (PLD) technique utilizing Lambda Physik Compex 201 excimer laser operating at a wavelength of 308 nm was used to deposit vanadium oxide thin films on oxidized silicon substrate with a pulse repetition rate of 5 Hz. A pure ceramic V_2O_5 disc was used as rotating target and the laser pulse energy density was I = 2.6 J/cm^2. Substrate temperatures of *in-situ* PLD processes were T = 400 °C or 500 °C. The deposition chamber was first pumped down to a base pressure of below 5×10^{-5} mbar and then an atmosphere of oxygen partial pressure $p(O_2) = 6 \times 10^{-2}$ mbar or 1.5×10^{-2} mbar was used for PLD.

The crystal structure of the films was studied using grazing incidence diffraction (GID) of X-ray diffraction (XRD) by utilizing Bruker D8 Discover diffraction device. Raman spectroscopy using argon-ion laser with a wavelength of 488 nm was used to study the crystal symmetry of the samples by utilizing HORIBA Jobin Yvon LabRAM HR800 device. Scanning electron microscopy (SEM) studies were carried out by using Helios Dual-Beam FIB/FESEM device. Thermo Fisher Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS) device was used to study the valence states of the thin-film surfaces. The surface morphology was studied using Veeco Dimension 3100 atomic force microscope (AFM).

Platinum (Pt) electrodes with thickness of 400 nm together with 10 nm-thick titanium (Ti) adhesion layers were sputtered on the surfaces of the thin films. Then the sensors were glued on alumina platforms with platinum thick-film heaters and Pt-100 temperature sensors. The resistance measurements were performed with a Keithley sourcemeter and Bronckhorst flow meters were used to control the gas pulses injected into a 1 cm^3-sized gas measurement chamber. The carrier gases used were 20% of O_2 in N_2, and 8% of O_2 in N_2 to simulate the conditions in diesel engine exhausts, and the measurement temperature was 350 °C, known to be a good measurement temperature for V_2O_5 sensors. In all gas measurements, the temperature was raised rapidly to 350 °C and then the sensors were kept at that temperature for several hours in order to get more stable resistance baseline. Before the ppb-level ammonia measurements, the plastic gas tubes were replaced with new ones in order to prevent the buildup of NH_3 in the gas line, and thus affecting the concentration of ammonia in the measurement chamber.

3. Results and discussion

3.1. Structural characterization of the thin films

Raman spectroscopy and XRD experiments confirmed pure vanadium oxide phases of the films. In Fig. 1 a), Raman spectra of

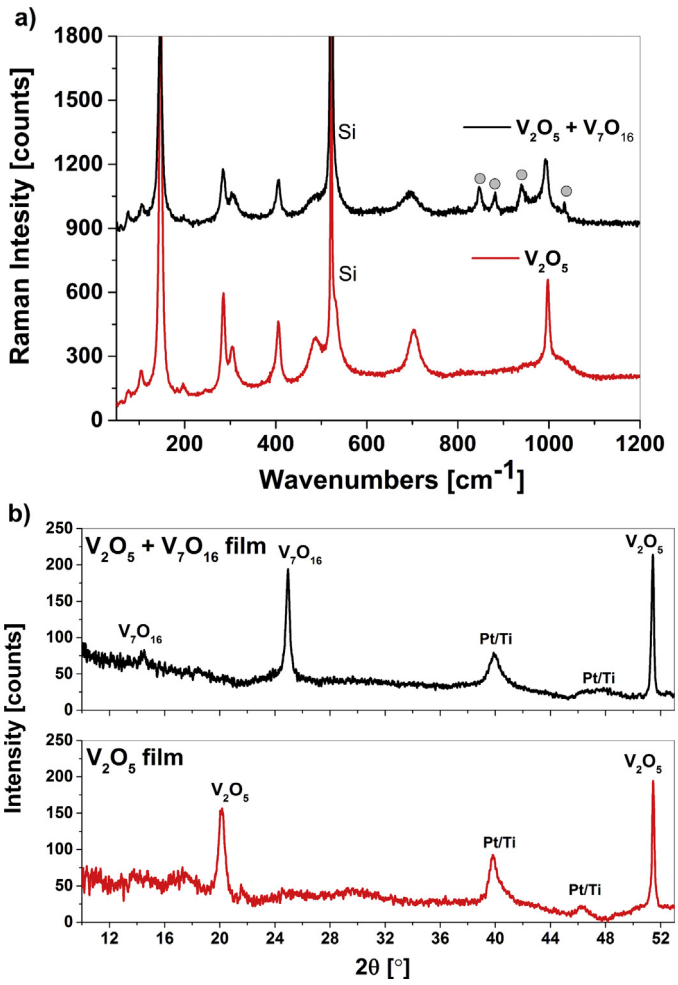

Fig. 1. a) Raman spectroscopy and b) the grazing incidence X-ray diffraction results of the vanadium oxide thin films. The films with only V_2O_5 phase were deposited at 400 °C and in $p(O_2) = 6 \times 10^{-2}$ mbar (red curves), and the films deposited at 500 °C and in $p(O_2) = 1.5 \times 10^{-2}$ mbar contained also V_7O_{16} phase (black curves). The gray circles in (a) present Raman modes originating from V_7O_{16} phase.

PLD deposited films are presented. According to the data, both films had pure V_2O_5 phase present [16] whereas the other film, deposited at 500 °C with O_2 partial pressure of 1.5×10^{-2} mbar, contained also another minority phase present, indicated by small peaks with wavenumbers 847, 882, 940, and 1034 cm^{-1} (grey circles). All the other Raman modes shown in Fig. 1 a) originate from orthorhombic V_2O_5 structure, or from silicon substrate. This other phase is identified as triclinic V_7O_{16} [14,17], the crystal structure typically found in the walls of vanadium oxide nanotubes (VO_x-NT) [18,19]. Grazing incidence diffraction (GID) X-Ray diffraction results support the findings of Raman spectroscopy, as shown in Fig. 1 b). It should be noted here that due to high noise and background level of GID data of nanostructures, the data has been smoothed and the high background was removed from the results. While the film deposited at 400 °C with O_2 partial pressure of 6×10^{-2} mbar, presented by red curves in Fig. 1, shows a clear diffraction pattern of pure orthorhombic V_2O_5 film, the other films had also the peaks corresponding to V_7O_{16} present at $2\theta \approx 24.95°$ and 14.45°. This particular phase structure is now shown to exist in a solid-state thin-film form and also tested as ammonia sensing material for the first time. From now on in this study, these films containing both V_2O_5 phase and V_7O_{16} phase will be denoted as mixed-phase films.

The oxidation state of the mixed-phase thin film was studied using X-ray photoelectron spectroscopy, and in Fig. 2 a), the Voigt

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