Chapter 19
Synthesis, Characterization, and Ammonia Sensing Properties of Vanadium Pentoxide Nanocrystals

G. Rizzo, A. Bonavita, G. Neri, A. Arena and G. Saitta

Abstract The optical and electrical properties of vanadium pentoxide films simply prepared by direct deposition from stable ethanol suspensions of V_2O_5 nanoparticles, are found to change after exposure to ammonia. Aimed at developing solid state ammonia sensors able to work at room temperature, spectrophotometric investigations and electrical measurements are performed on vanadium pentoxide films deposited on glass, on V_2O_5 films deposited on flexible substrates, having nanosilver electrodes applied on the top, and on *n*-Si/V_2O_5 heterojunctions.

19.1 Introduction

Vanadium pentoxide is a versatile semiconductor, characterized by the property to change its optical and electronic behaviour reversibly, in response to a variety of stimuli including externally applied electric field [1], ultraviolet light irradiation [2], and thermal treatment [3]. In addition V_2O_5 is a promising candidate for gas sensing applications, because of its ability to change its electrical resistance when it is exposed to a variety of gas targets. In common with other transition metal oxides used in resistive sensors, the gas sensing performances of vanadium pentoxide in terms of sensitivity and response/recovery times, are found to

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improve by reducing the crystal size. V_2O_5 processed as nanotubes, nanowires, and nanobelts in order to maximize the surface area, has been used successfully to detect ethanol [4], ammonia [5], and ammines [6]. This paper reports on a simple synthesis to prepare nanostructured vanadium pentoxide having excellent film forming property, and low temperature sensitivity towards ammonia. The material, prepared using as starting reagent ammonium metavanadate (NH_4VO_3), and sintering the reaction product in air at 400°C, is found to consists of highly crystalline V_2O_5 nanoparticles.

19.2 Experimentals

The morphology and microstructural properties of the V_2O_5 nanoparticles are investigated by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements performed using an Ital Structure APD 2000 diffractometer and a JEOL 2010 EX instrument. Optical measurements were performed using a Perkin–Elmer Lambda 9/19 spectrophotometer and a Nicolet Avatar 360 spectrometer. Electrical characterization of thin V_2O_5 films deposited on *n*-Si wafer and on flexible substrates was performed using a Keithley 2004 sourcemeter, and an Agilent 34970A multimeter. A CMOS sensor (from Sensirion) was used to check the temperature and RH into the measurement chamber. Electrical measurements were performed at constant RH, and under exposure to calibrated NH_3 flux, inserting both the sensor based on V_2O_5 and the reference sensor into an aluminium measurement chamber. The relative humidity level inside the measurement chamber was settled and controlled by mixing steams of dry air and saturated air, using a number of digital mass flow meter controllers connected to dry air and to a bubbler held at constant temperature. NH_3 fluxes were generated by a permeation tube, calibrated to flux 14 ppm ammonia when kept at 50°C. The way V_2O_5 films coated on quartz crystals respond to RH at constant temperature was evaluated using an automated system purchased from BioAge, able to measure the resonance frequency shifts of a coated quartz crystal.

19.3 Results and Discussion

The analysis of XRD patterns (Fig. 19.1a) reveals that the material prepared starting from ammonium metavanadate consists of highly crystalline V_2O_5 nanoparticles, having few tens nanometers average size. High crystalline degree is confirmed by TEM measurements also (Fig. 19.1b).

In addition, TEM investigations reveal that the nanoparticles have a trend to organize aligning along the same preferential direction (Fig. 19.1c).

The film forming attitude shown by the nanoparticles allows compact films, highly adherent to the glass, plastic, and silicon substrates, to be obtained by direct

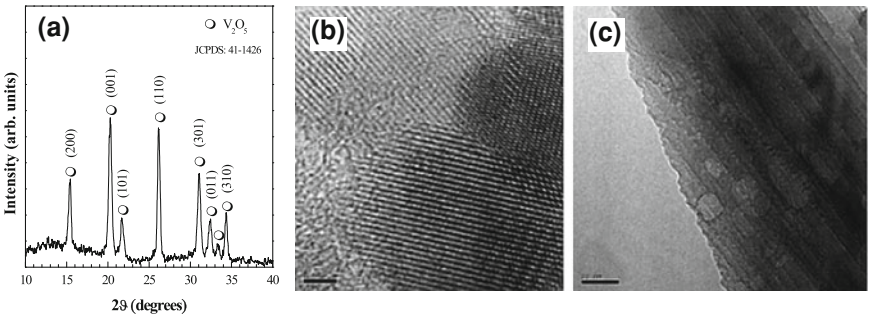

Fig. 19.1 **a** XRD spectrum and **b** TEM image of the V_2O_5 nanoparticles (the scale bar is 2 nm); **c** TEM image of V_2O_5 nanoparticles organized to form an agglomerate evidencing a certain degree of order (the scale bar is 20 nm)

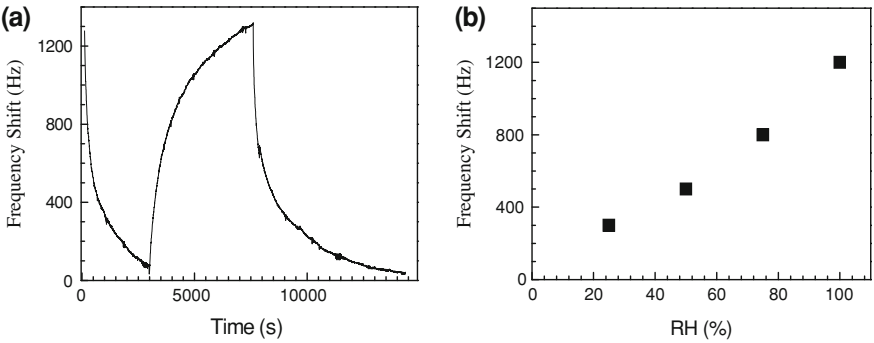

Fig. 19.2 **a** Frequency shift of a QCM coated with vanadium pentoxide, recorded as the RH level inside the measurement chamber changes between 0 and 100%; **b** relationship between the frequency shift and RH

deposition from ethanol nanoparticles suspensions, without the use of any binder, and without the need of any substrate surface treatment.

To investigate on the sensing properties of the nanostructured V_2O_5, thin films have been deposited onto AT-cut quartz crystals (10 MHz) having Al electrodes on the top. The resonance frequency of the coated quartzes changes reversibly as the RH level changes (Fig. 19.2a). The frequency shift is linearly related to the RH level in the range between 0 and 100% RH (Fig. 19.2b).

The absorption spectrum of pale yellow V_2O_5 films deposited on transparent substrates (Fig. 19.3a) is characterized by a band positioned between 350 and 400 nm. The films bleach when exposed in air to concentrated NH_3. Exposure to NH_3 has remarkable effects on the IR spectrum also (Fig. 19.3b).

Figure 19.3 shows that exposure to an elevated concentration of NH_3 at high RH, has remarkable effects in the UV–VIS–IR properties of the nanocrystalline V_2O_5 films under investigation. Such effects are found to be persistent, and likely originate from a reaction that occurs between ammonia and the V_2O_5 nanocrystals,

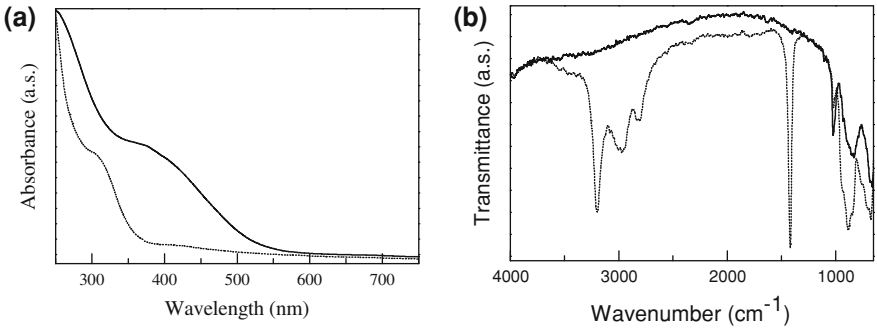

Fig. 19.3 **a** UV–VIS absorption spectrum and **b** FT–IR transmittance spectrum of a V_2O_5 film before (*solid*) and after exposure to highly concentrated ammonia in air, at 28°C, 65% relative humidity

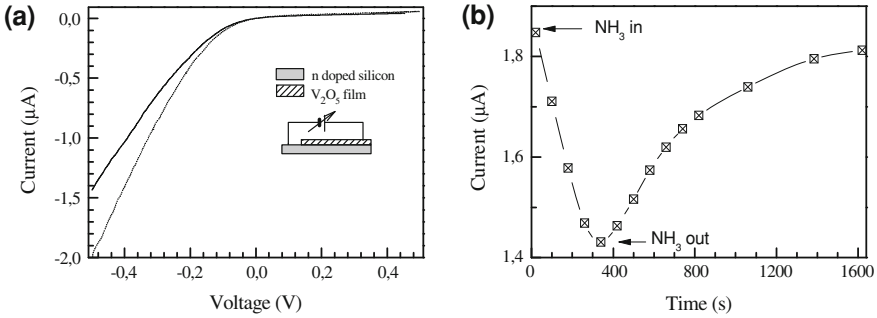

Fig. 19.4 **a** *I/V* plot measured at 28°C on a junction between V_2O_5 and *n*-doped silicon as deposited (*solid*) and after 350 s exposure to 7 ppm dry ammonia; **b** dynamic behaviour of the current through the V_2O_5/*n*-Si measured at $V = -0.5$ V, in response to a 350 s lasting pulse of 7 ppm dry ammonia

yielding ammonium metavanadate as reaction product. NH_4VO_3 converts back to vanadium pentoxide and the optical spectra recover their original shape, by heating the exposed films in air, at about 400°C.

Current–voltage measurements carried out in dry condition on *n*-Si/V_2O_5 heterojunctions show that exposure to calibrated amounts of ammonia in the ppm range results in a decrease of the metal oxide conductivity. This finding is evidenced by comparing the current–voltage plots of a typical *n*-Si/V_2O_5 junction before and after exposure to 7 ppm dry ammonia (Fig. 19.4a). The resistivity changes arising from the interaction between the nanocrystalline V_2O_5 films and NH_3 in dry condition show a partial reversibility, as it is suggested by the evolution of the current measured through the junction at constant voltage, in response to a 350 s lasting pulse of 7 ppm dry ammonia (Fig. 19.4b).

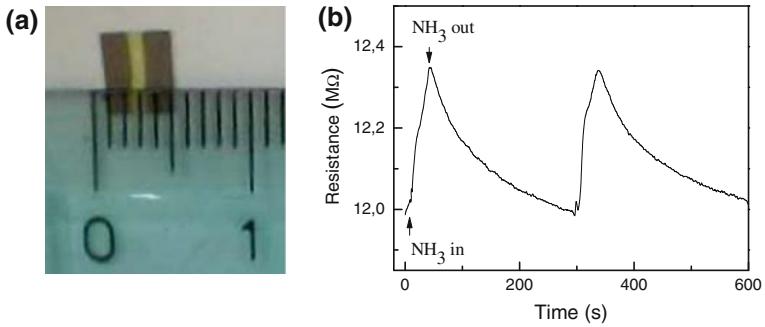

Fig. 19.5 **a** Typical flexible ammonia sensor based on V_2O_5; **b** response of the sensor measured at 28°C, 20% RH, by exposing the sample to a 4 ppm of ammonia

Figure 19.5a shows a typical sensor based on V_2O_5, deposited on a transparency sheet without the need of any post-processing, by direct deposition from stable dispersions of V_2O_5 nanoparticles. Linearly shaped electrodes are applied on the top of the semiconducting film by using standard refillable pens, charged with water dispersions of silver nanoparticles. Figure 19.5b shows the results of electrical measurements performed on the sensor of Fig 19.5a. It can be noticed that the resistance of the device increases with exposure to ammonia.

This latter finding is in disagreement with that commonly reported in literature, according to which V_2O_5 behaves as *n*-type semiconducting oxide, having an electrical conductivity that increases when it is exposed to ammonia [5]. Such a behaviour is commonly ascribed to interaction between the metal oxide and the gas target, resulting in formation of oxygen vacancies, associated to the reduction of vanadium ions from V^{5+} species to V^{4+}. This latter kind of response mechanism is that usually observed at high temperature. The response toward NH_3 observed by us at low temperature, as it is described in Fig. 19.4b, shows a different trend. A possible explanation, may be that the interaction between the oxide films and ammonia is mediated by the presence of thin water layers coating the semiconducting oxide, into which NH_3 dissolves, and dissociates. In such an hypothesis the metal oxide would behave as a pH sensor [7]. It is also noticed that the response of V_2O_5 based sensors is only partially reversible, as a certain uptake of NH_3 is not released during the sensor recovery. This behaviour is ascribable to the irreversible reaction that occurs between vanadium pentoxide nanocrystals and ammonia, resulting in the formation of NH_4VO_3 as reaction product [8].

19.4 Conclusion

Nanocrystalline V_2O_5 films developed by direct deposition from ethanol suspensions are found to have optical and electrical properties that change after exposure to ammonia. In particular while optical changes are ascribable to NH_4VO_3

formation, made reversible only by heating at 400°C, sensitive electrical changes, reversible to a certain extent, are observed at low temperature, in dry conditions, by exposing the V_2O_5 films to few ppm ammonia. These results can be promising in view of applications of the developed material in low temperature ammonia sensing applications.

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