

Suppression of the NO₂ interference by Chromium Addition in WO₃-Based Ammonia Sensors. Investigation of the Structural Properties and of the Related Sensing Pathways

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Abstract

WO₃ and Cr-WO₃ powders were prepared by sol-gel process, with Cr:W atomic concentration ranging from 2% to 8.8%. WCl₆ was used as W precursor and reacted with methanol in presence of acetylacetone as stabilizer. The required amount of Cr 2-ethylhexanoate was then added to the resulting solution, which was then dried. The resulting powder was heat-treated at temperatures ranging from 200 to 700 °C. With increasing the Cr concentration, the samples heat-treated at 500 °C contained an increasing amount of the additional phase Cr₂WO₆. The analysis of the X-ray diffraction and Transmission Electron Microscopy data showed that the use of the Cr 2-ethylhexanoate precursor seemed to favor Cr incorporation in interstitial position in the WO₃ lattice. The sensing tests towards ammonia gas, from 50 to 500 ppm, showed that, up to 5% concentration, Cr addition lowered the best operating temperatures and/or enhanced the response with respect to pure WO₃, then the response remarkably decayed. Detailed structural and electrical investigation showed that interstitial Cr controlled the concentration of the oxygen vacancies. The decrease of the latter hampered the parasitic response to NO₂. Beyond 5% Cr concentration, Cr₂WO₆ extracts Cr from the WO₃ structure, so restoring the oxygen vacancies and again increasing the parasitic NO₂ response.

Key words: WO₃, ammonia, doping, sensing mechanisms.

Introduction

Tungsten trioxide is known as ammonia sensing material, but its response is characterized by signal instabilities due to the production of NO₂ and NO during the sensing reaction. The use of additives for signal quality of WO₃ sensors has been reported: in particular, chromium could eliminate the known instabilities of pure WO₃ [1]. In a recent work [2], we have investigated the wet chemical synthesis of WO₃ and the related sensing performances, showing that it is possible to prepare stable and reliable sensors toward both reducing and oxidizing gases. It then seemed of interest to exploit the synthesis procedure for adding Cr dopant, in order to carry out a more

detailed investigation of the Cr effect on ammonia sensing. This task was made complex by the peculiar structural modification induced by Cr, which favored the formation of additional Cr₂WO₆ phase beyond the WO₃ host. The aim of the present work was the analysis of structural data depending on the Cr concentration and the investigation of their relationship with the sensing properties. In particular, it will be enlightened the influence of the Cr incorporation on the concentration of oxygen vacancies of WO₃ and the consequent modulation of the parasitic NO_x reactions during the ammonia sensing tests.

Experimental

WCl_6 (1 g) was reacted with a solution of acetylacetone (molar ratio to W was 3) in 10 ml of methanol. After a fast color change, from yellow to orange, a deep blue solution was finally obtained. Chromium addition, with a Cr : W nominal atomic concentration ranging from 2 to 8.8%, was carried out by adding to the solutions the required amount of Cr 2-ethylhexanoate. Powders were prepared from the solutions by evaporation in a rotary evaporator at pressure decreased from 10 kPa to 4 kPa in 30 min and with the bath temperature raised from RT to 80 °C in 1 h. The resulting product was a deep blue, redispersible powder. The evaporation product was heat-treated at various temperatures. After heat-treatment at temperatures higher than 300 °C, a bright yellow or brick-red powder for pure and Cr-modified WO_3 , respectively. The materials were characterized by X-ray diffraction and Transmission electron microscopy. Sensors were prepared by depositing a mixture of the WO_3 powder with 1,2-propanediol onto interdigitated electrodes, and subsequently annealing at 400 °C for 1 h. The ammonia sensing tests were carried out using a standard configuration for resistive sensor measurement, with Pt-interdigitated electrodes and a Pt-resistive-type heater printed onto an alumina substrate.

Results and Discussion

Figure 1 shows the XRD patterns measured on Cr- WO_3 powders with 8.8% Cr atomic concentration. The patterns are characterized by the reflection of the triclinic and monoclinic crystallographic phases of WO_3 , which cannot be unambiguously distinguished by XRD due to their crystallographic similarity and are usually found simultaneously in the same sample. Moreover, additional reflections, indicated by a star, were found in the patterns. They were identified as belonging to the Cr_2WO_6 . These peaks appear after heating at 300 °C, but can be found even for 5% Cr concentration after heat-treatment at 500 °C. The presence of Cr_2WO_6 phase was further confirmed by Transmission Electron Microscopy. The sequences of XRD patterns at various Cr concentrations were analyzed in detail. The influence of Cr on the structural properties emerges in Figure 3, where the results for the 500 °C samples are reported. Up to 5% Cr, the peaks shift to higher angles, then the reflection angle shifts back. Since at 5% Cr the Cr_2WO_6 formation takes place, these data were interpreted as follows. Initially Cr is incorporated in such a way to compress the WO_3 lattice,

resulting in the observed peak shift to higher angles.

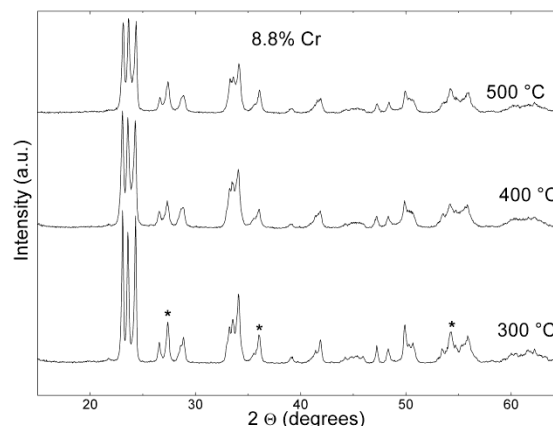


Fig. 1. XRD patterns of Cr- WO_3 powders heat-treated at the indicated temperatures. Cr:W atomic ratio was 0.088. The black stars indicate the Cr_2WO_6 phase in addition to the other peaks which all belong to the WO_3 phase.

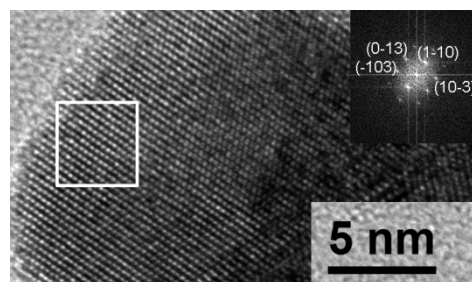


Fig. 2 High-resolution transmission electron microscopy images of the Cr- WO_3 powders (Cr/W atomic ratio was 0.05) heat-treated at 500 °C, showing the Cr_2WO_6 phase.

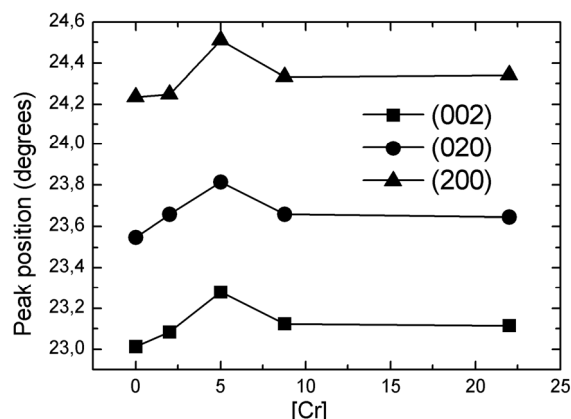


Fig. 3 Trend of the indicated WO_3 reflection positions depending on Cr concentration, for samples heat-treated at 500 °C.

Then, when a critical concentration is reached, ranging around 5%, Cr is expelled from the WO_3 lattice, forming the Cr_2WO_6 phase, which partially restores the WO_3 lattice parameters to the pristine values. In Figure 4 and Figure 5 representative ammonia sensing results are

shown. The sensor response is completely recovered after exposure to each ammonia concentration, and there are no signal instabilities observed in any of the tests carried out. The following results are noteworthy: at 225 °C, the addition of Cr up to 5% increases the response with respect to the pure sample, while at 300 °C (not shown) the response of the Cr-modified samples is lower than the pure one. In all cases, the addition of Cr concentrations *higher than 5%* systematically results in the lowest response.

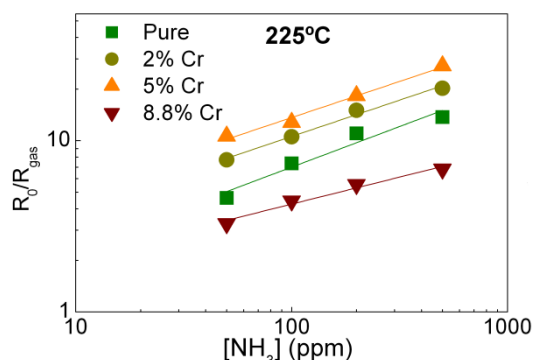


Fig. 4. Calibration of the indicated sensors to ammonia concentrations ranging from 50 to 500 ppm at 225 °C.

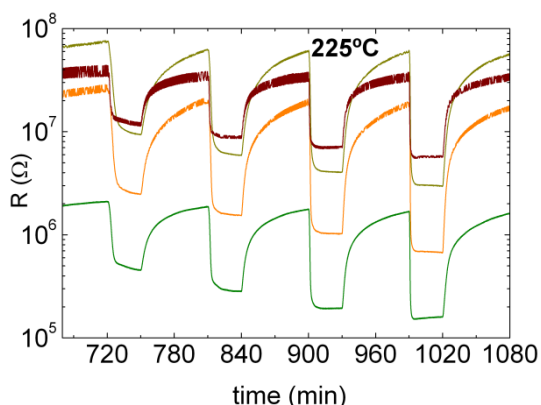
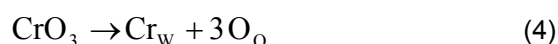


Fig. 5 Dynamic response curves at 225 °C of the sensors described in the previous figure.

From the dynamic curves in Figure 5, it is also seen that the electrical resistance is minimum for the pure WO_3 sample. For relating the presence of Cr to the sensing performances, the first step was the study of the Cr incorporation pathways. The sample color and the formation of Cr_2WO_6 suggested the simultaneous presence of Cr(III) and Cr(VI). The related incorporation equations for Cr(III) are:



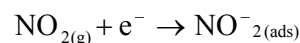
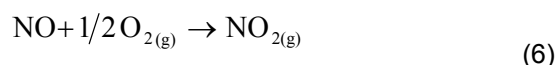
while, for Cr(VI):



The shift observed in the XRD patterns is compatible with interstitial Cr(III) and both species of Cr(VI), but it is seen that substitutional Cr(VI) does not affect the electrical properties of WO_3 . Interstitial Cr(III) and Cr(VI), instead, can trap electronic charges, explaining the increase of the electrical resistance with respect to pure WO_3 . The newly generated oxygen sites can annihilate pristine oxygen vacancies. This feature is essential for explaining the dependence of the ammonia sensing properties on Cr concentration. If we refer to one of the main ammonia sensing reactions:



then the generated NO molecule easily undergoes further reactions:



The adsorbed NO_2 species deplete the electron concentration, so producing a counter-effect to that of ammonia reaction, which explains the source of the parasitic reactions. The presence of Cr, decreasing the concentration of oxygen vacancies, hinders the parasitic effect of NO_2 adsorption (which is effective just on oxygen vacancy sites) and ultimately improves the ammonia response. When Cr concentration exceeds the threshold for Cr_2WO_6 formation, the expulsion of Cr from the WO_3 lattice decreases its beneficial effect against NO_2 adsorption. The high electrical resistance of the samples with 8.8% Cr show that, despite the newly increased oxygen vacancy concentration, a peculiar effect of Cr_2WO_6 itself, which is electrically insulating, should also be taken into account.

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