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Cr_2O_3, WO_3 single and Cr/W binary oxide prepared by physical methods for gas sensing applications

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Abstract

Thin films have been prepared by thermal evaporation of high purity Cr_2O_3, WO_3 powders in vacuum on Si/Si_3N_4 substrates provided with Pt interdigital electrodes and annealed between 300 and 600 °C for different times ranging from 1 to 24 h. Mixed oxides Cr/W films have been prepared by thermal evaporation of Cr_2WO_6 powders, previously synthesized by solid state reaction at 1200 °C from Cr_2O_3 and WO_3 precursor oxides. The electrical response has been measured exposing the films to sub-ppm NO_2 concentrations (100–300 ppb in dry air) at different operating temperatures ranging between 25 and 250 °C. The best response to NO_2 has been found to be at 150 °C. Cr/W mixed oxides films have shown enhanced gas sensitivity as respect to WO_3 and Cr_2O_3. Gas selectivity to NO_2 in NO_X mixtures (10 ppm NO and 0.7 ppm NO_2) were also improved by the presence of Cromium.

Keywords: Electrical conductivity; Films; Nanocomposites; Sensors; Transition metal oxides

1. Introduction

Transition metal oxides are catalytically active materials, which are finding a wide variety of uses including supports for heterogeneous catalysts, electrochromic devices and, more recently, as gas sensors.[1] These devices are crystalline and catalytically active, which change their resistance due to electron transfer between the measured gas and the sensing material, as a consequence of surface chemical reactions at operating temperatures ranging from 200 to 300 °C.[2]

The preparation of porous pellets or thick films by high temperature sintering of metal oxide powders, basically Pt-doped SnO_2 oxide, remains one of the most straightforward fabrication methods utilized in the fabrication of commercial devices.

Market needs have recently pushed sensors companies and the scientific community to explore for a new generation of sensors able to detect sub-ppm concentrations of oxidizing (i.e. O_3, NO_2 and Cl_2) and/or reducing (i.e. H_2 and CO) gases with improved selectivity and long term stability of the response. Considerable research has thus been addressed both to the validation of innovative preparations, based on thin film technology, and to the investigation of new materials.

Although sputtering[3] and vacuum thermal evaporation,[4] have been widely used and studied on metal oxide thin films, more recently, the sol-gel process has become popular for gas-sensing thin-film preparation.[5] If physical preparation routes show advantages in terms of reliability of the preparation and high compatibility with planar microelectronic processes, sol-gel technique, on the other hand, is superior considering that multicomponent systems can be prepared with a high degree of purity by mixing the molecular precursor solutions.

Regarding the investigation of novel materials, WO_3, Ga_2O_3, In_2O_3, Nb_2O_5, MoO_3, TiO_2, Cr_2O_3 single oxides have shown promising application for the selective detection of certain toxic gases.[6,7]

In this article, preliminary results of microstructural and electrical characterization of Cr/W binary oxides thin films for gas sensing applications are presented. The aim of this work is to compare the WO_3 and Cr_2O_3 single oxide responses to NO_2 with the gas response of Cr/W mixed oxides.

2. Experimental

Commercial WO_3 and Cr_2O_3 powders with 99.99% purity were electrically heated in a tungsten crucible at

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5×10^{-4} Pa. The vapour phase was condensed on Si/Si_3N_4 substrates with Pt interdigital electrodes. The film was deposited at 6 nm/min rate up to a thickness of 150 nm. Annealing was made in static air between 300 and 600 °C for different times ranging from 1 to 24 h. Cr_2WO_6 powder was synthesized by solid state reaction of Cr_2O_3 and WO_3 single oxides at 1200 °C for 24 h according to what previously reported.[8] Cr/W films were prepared by vacuum thermal evaporation of the Cr_2WO_6 powder under the same experimental conditions reported for the single oxides. Crystalline phases of the film were examined by grazing angle (GA) (2°) diffractometric conditions using an X-ray diffractometer (Siemens D5000) equipped with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) and 0.005° angular resolution. The surface topography was observed by a large sample probe microscope (NanoScope III, Digital Instrument Inc.). AFM equipped with a silicon tip of 15 nm radius was applied on the insulating substrate and semiconducting film.

The electrical properties of the films to NO_2 gas were measured by an automated system. Dry air was mixed by an MKS147 multi gas mass controller with diluted NO_2 mixtures (10 ppm in air) in order to have gas concentrations at the outlet in the range 100–1000 ppb. Electrical measurements were carried out selecting the operating temperature of the films in the temperature range 25–400 °C. The resistance of the films was measured by a volt-amperometric technique by a Keitley 2001 multimeter. The gas relative response here defined as R, represents the ratio of the measured film resistance in presence of gas R_{Gas}; and the resistance in presence of air R_{Air}, i.e. $R = R_{Gas}/R_{Air}$

3. Results and discussion

3.1. Structural characterization

Fig. 1(a)–(c) show the AFM overall morphology of the WO_3, Cr/W and Cr_2O_3 films respectively after annealing at 600 °C for 1 h. The WO_3 film shows small protrusions, which cover homogeneously the examined surface. These features may be identified as crystallites with vertical height of 2–5 nm and lateral width of 35–45 nm. The Cr/W film shows the on-set of large "domains" of typical width of 260 nm, which may be identified as grains. Inside each grain single crystallites can be clearly distinguished with lateral and vertical dimensions almost similar to the ones found for the WO_3 film. The AFM pictures of the Cr_2O_3 film reveals that the fine crystalline structure within each grain has disappeared, while is more evident grains separation along grain boundaries.

XRD analysis of the films highlighted the formation of triclinic WO_3 (JCPDS 20-1323) and rhombic Cr_2O_3

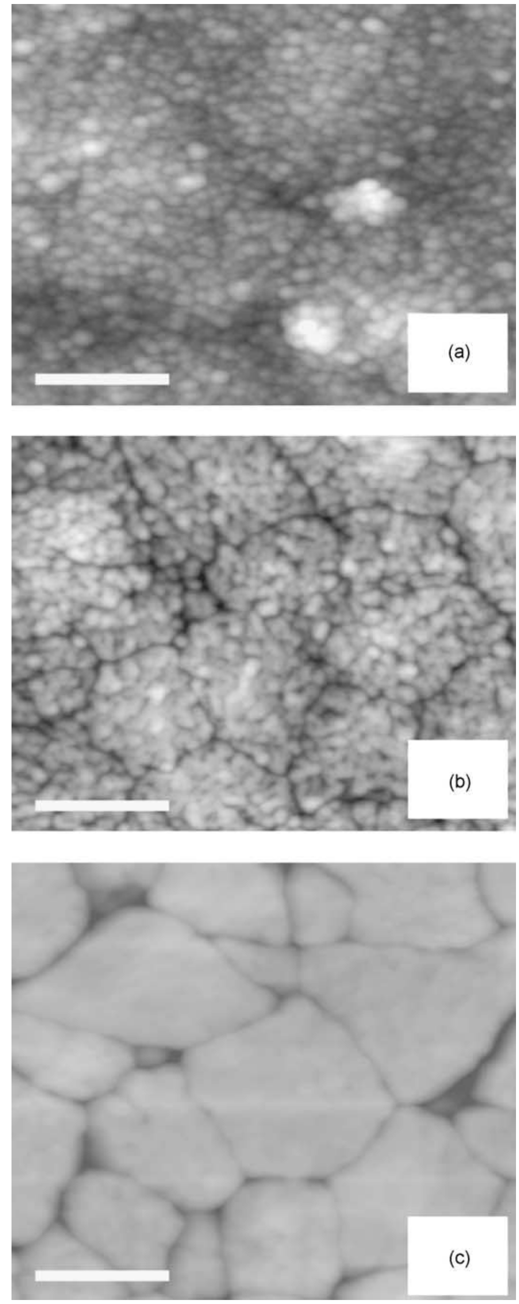

Fig. 1. AFM picture over (1×1 μm^2 area) after annealing the films at 600 °C for 1 h. (a) WO_3, (b) Cr/W, (c) Cr_2O_3 (white marker 250 nm).

(JCPDS 85-0869) after thermal evaporation and annealing at 500 °C for 1 h of the single WO_3 and Cr_2O_3 oxides respectively. Fig. 2 shows the XRD spectra of the films after evaporation of the Cr_2WO_6 powder and subsequent annealing of the deposited films between 300 and 600 °C for 1 h. In the figure the spectrum of triclinic WO_3 is also reported for comparison. No peaks corresponding to pure Cr_2O_3 or any kind of binary Cr/W oxide were detected after annealing. Crystalline [200] oriented triclinic WO_3 (JCPDS 20-1323) is the only clearly observable phase. Possible explanations could be tentatively given suggesting that Cr_2WO_6 when heated

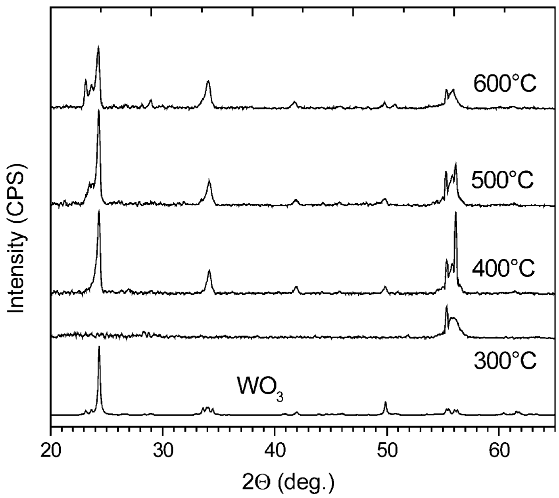

Fig. 2. Grazing angle (GA 2°) XRD patterns of the films evaporated from Cr_2WO_6 powder and annealed at different temperatures for 1 h.

in vacuum, decomposes and that WO_3 is the prevailing evaporating oxide which condenses on the substrate. This hypothesis is supported by the XRD analysis on the Cr_2WO_6 powder remaining in the crucible after thermal evaporation. The evidence that Cr_2O_3 and metallic W are the only species left in the crucible after evaporation, might confirm the hypothesis that WO_3 is the evaporating phase, which eventually crystallize into triclinic WO_3 at temperatures between 300 and 600 °C.

Further investigation of the XRD spectra near the 2Θ region at 23.72°, revealed also the formation of a distorted WO_3 triclinic phase. Cell parameters were found to be more displaced from the characteristic one of triclinic WO_3 the higher the annealing temperature of the films. The presence of strong Cr $_{2p}$ signals on all the annealed films, as revealed by XPS analysis, may suggest the occurrence of a partial solubility of cromium in WO_3 triclinic lattice and the formation of a substitutional solid solution. XPS quantitative chemical analysis of the films as calculated by computing the weighted area of each element, indicates that the atomic content of cromium yields approximately 5% for all the annealed films.

3.2. Gas sensing characterisation

Gas sensing characterization has been carried out at different operating temperatures between 25 and 400 °C, exposing the films to different NO_2 concentrations ranging from 100 to 300 ppb in dry air carrier gas. The electrical resistance of all the investigated films is found to increase upon exposure to NO_2 gas. The operating temperature of the oxide has been identified to be 150 °C as a trade off between high relative response [$R = R_{Gas}/R_{Air}$] and fast and reproducible base line recovery (i.e. ripetibility of the electrical resistance in air). This temperature is found to be not influenced by the chemical composition of the interacting material, but eventually mainly dependent on the prevailing nature of the ionosorbed surface reactive oxygen species like O_2^-, O^-, which the NO_2 gas seems to react with.[9]

Fig. 3 compares the electrical response of the WO_3, Cr_2O_3 and Cr/W films, annealed at 500 °C for 1 h, in dry air carrier and 150 °C operating temperature when the NO_2 concentration is varied from 100 to 300 ppb. When nitrogen dioxide concentration is increased and decreased stepwise in this range of concentration, sensor response is reproducible and stable. The baseline is recovered after NO_2 removal. Cr/W film yields at 100 ppb NO_2 a relative response $R = 42$ as compared to $R = 22$ and $R = 8$ of the Cr_2O_3 and WO_3 films respectively. The base line resistance (i.e. the resistance in dry air) is the highest for the WO_3 film, while is at its minimum for the Cr_2O_3 film.

Fig. 4 compares the WO_3, Cr_2O_3 and Cr/W films responses to NO_X mixtures (0.7 ppm NO_2 and 10 ppm NO) and to NO_2 (0.7 ppm). The test has been carried out in order to have the same NO_2 concentrations during the first and the second exposure (0.7 ppm), while changing the NO concentration. The aim of the test is to evaluate how the relative response to NO_2 may change due to the presence of NO interfering gas. The test has been carried out at 300 °C operating temperature, since 300 °C was found to be the operating temperature at which minor cross sensitivity effects take place. If we define as Δ the ratio of the resistance in NO_X gas [Ω_{NOX}] and the resistance in NO_2 [Ω_{NO}]: i.e. $\Delta = [\Omega_{NOX}] / [\Omega_{NO}]$, it turns out that Cr/W film yields $\Delta = 1.9$ while

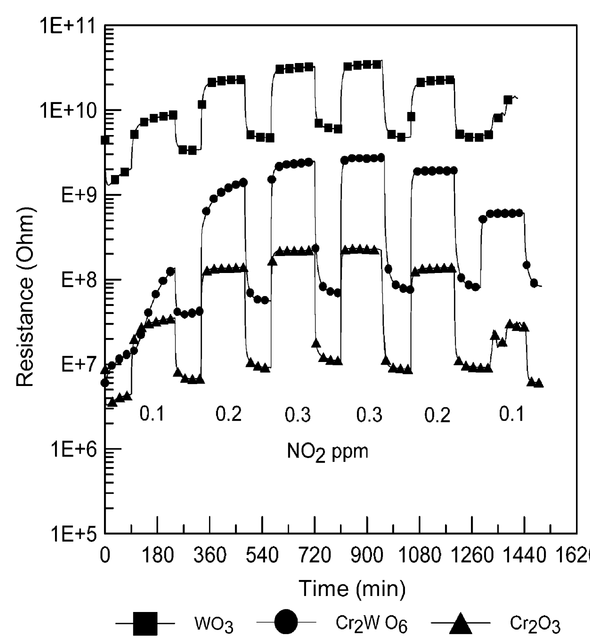

Fig. 3. Dynamic sensor responses of the WO_3, Cr_2O_3 and Cr/W films at 150 °C operating temperature and NO_2 concentrations ranging from 0.1 to 0.3 ppm.

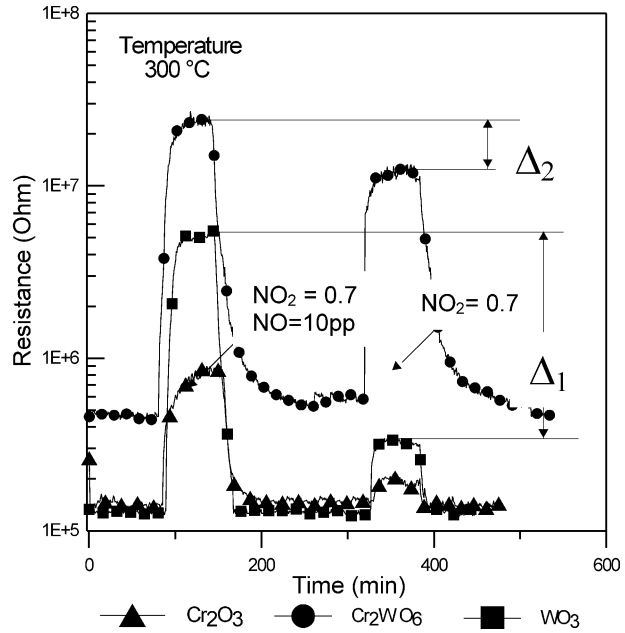

Fig. 4. Dynamic response of the WO_3, Cr_2O_3 and Cr/W films to NO_X (0.7 ppm NO_2 and 10 ppm NO) and NO_2 0.7 ppm.

Cr_2O_3 and WO_3 films yield $\Delta = 16.2$ and $\Delta = 3.0$ respectively. It turns out that Cr/W film is less affected by the presence of NO interfering gas as compared to the others.

4. Conclusions

Sensitive thin films based on single WO_3, Cr_2O_3 and binary Cr/W oxides have been prepared by physical thermal evaporation method. Annealing between 400 and 600 °C triclinic WO_3 and rhombic Cr_2O_3 phases are formed after evaporation of WO_3 and Cr_2O_3 single oxide powders respectively. Substitutional solid solutions of Cr in triclinic WO_3 lattice are likely formed after the annealing the evaporated Cr_2WO_6 binary oxides powders. The Cr/W film exhibited improved relative response to NO_2 gas as respect to WO_3 and Cr_2O_3 films, respectively. A cross sensitivity test, carried out in NO_x rich atmospheres highlighted a better selectivity of the Cr/W film. All the investigated oxides can be proposed as practical gas sensing materials for NO_2 monitoring in environmental applications.

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