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Low temperature sol-gel synthesis and humidity sensing properties of $Cr_{2-x}Ti_xO_3$

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Abstract

The low temperature sol-gel synthesis of chromium titanate (CTO) is reported. Crystalline CTO powders have been obtained at temperature as low as 400 °C. CTO thin films deposited by LPD on alumina substrates were tested regarding their humidity sensing properties. They were found sensitive to water vapor at room temperature showing fast response time. The humidity sensing mechanism on these thin films has been investigated and discussed on the basis of the film porosity and water–CTO surface interaction.

Keywords: CTO; Humidity sensor; Sol-gel

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1. Introduction

Semiconductor-based gas sensors include a wide class of devices which differ for configuration and principle of gas monitoring. On resistive-type gas sensors sensing mechanism arises from the variation in number of the charge carriers near to the semiconductor surface on changing the gas composition.

In virtue of the simplicity of principle, many oxides present a variation of conductivity at the interaction with various gases. The first commercial devices realized by Seiyama[1] and Taguchi [2] were based over ZnO and SnO_2 semiconductors, respectively. With the aim to promote gas sensors sensitivity, selectivity and stability, many studies have been carried out over innovative materials.

Chromium titanium oxide (CTO, $Cr_{2-x}Ti_xO_3$ with $x = 0.05–0.4$), is a new sensing materials commercialized by Capteur Sensors. CTO is currently prepared by solid state reaction between chromium and titanium oxide at temperatures >900 °C.[3] The disadvantage of this method is, in addition to high synthesis temperature, the poor chemical homogeneity of the material obtained and the components contamination, influencing negatively the sensing layer behavior. The sol-gel method should, in principle, allow the synthesis at lower temperature and provide a more uniform Ti distribution than the solid state chemical reaction and a better microstructural control.

In a recent paper the sol-gel synthesis of CTO has been reported.[4] The reported procedure is, however, rather complex and requires the use of surfactants. In this communication we report a simple one-step synthesis of CTO powders by a sol-gel route and subsequent thermal treatment at low temperature ($\leqslant 400$ °C). Moreover, CTO thin films obtained by LPD (Liquid Phase Deposition) have been prepared and tested for gas sensor applications. Here the humidity sensing properties of these films are presented and discussed.

2. Experimental

2.1. CTO preparation

CTO powders were prepared by a sol-gel synthesis as following. An ethanol solution of $CrCl_36H_2O$ in the opportune concentration was first prepared. Then anidrous titanium isopropoxide, $Ti(OC_3H_7)_4$ was added and the resulting solution maintained under stirring for 2 h at room temperature. The Cr/Ti atomic ratio was 9/1. The solution was then dried at 120 °C and precipitated powders successively calcined at 200, 400 and 900 °C for 3 h.

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2.2. Sensor configuration and electrical measurements

Gas sensing devices were prepared by using the above Cr–Ti precursors solution opportunely diluted and depositing a drop on alumina supports (3×3 mm^2) provided with gold interdigitated electrodes. The deposition was carried out into a LPD apparatus at 25 °C in air. The deposited film was then dried and annealed in air at the temperature of 200 and 400 °C. For sensing tests, sensors were mounted into a controlled flow chamber. Humidity sensing tests were carried out in the 0–100% RH range obtained by varying dry/wet air ratio. Measurements were carried out at 20 °C in ac by supplying a sinusoidal input of amplitude 1 V and 1000 Hz frequency, and acquiring the output signal by a lock-in amplifier Stanford mod. RS 830 DSP at fixed time intervals.

2.3. Microstructural characterization

With the aim of investigating the powders microstructure, XRD diffraction spectra were collected by a ItalStructures diffractometer mod. APD 2000. Diffraction peaks were compared with those reported in the JCPDS Data File. The grain size was derived by the Sherrer equation from the width at half the height of the diffraction peaks.

To study the powders and thin films morphology a scanning electron microscope, JEOL mod. JSM 5600LV, equipped with an Oxford EDX detector, was used.

3. Results and discussion

3.1. Microstructural characterization

The morphology of CTO powders obtained by sol-gel synthesis and annealed at different temperatures was investigated by SEM analysis. The formation of submicrometric spherical particles (see micrograph of the CTO900 sample in Fig. 1) has been highlighted. Smaller particles were observed on samples calcined at lower temperature.

In Fig. 2 the XRD spectra of these powders are reported. At the temperature of calcination of 200 °C the sample is amorphous. The development of a well crystalline structure was instead observed at 400 °C. Diffraction peaks match exactly with reflections of CTO powders previously reported in literature.[4,5] It can be noted however that Cr_2O_3 presents the same XRD pattern, so the direct identification of CTO phase was not possible. On the other hand, no TiO_2 peaks were formed also after annealing at 900 °C. Because titania is known to crystallize in the rutile structure during annealing in an oxidizing atmosphere at temperatures just above 600 °C, its absence strongly suggests that a solid solution of TiO_2 in Cr_2O_3 was formed on these samples. Furthermore, EDX elemental analysis has shown an homogeneous distribution of Ti and the expected Cr/Ti ratio in the prepared materials indicating the complete dissolution of titanium into the chromia lattice.

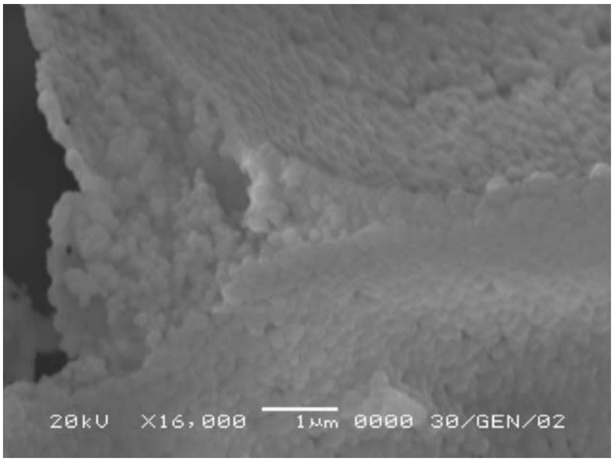

Fig. 1. SEM micrograph of CTO powders calcinated at 900 °C.

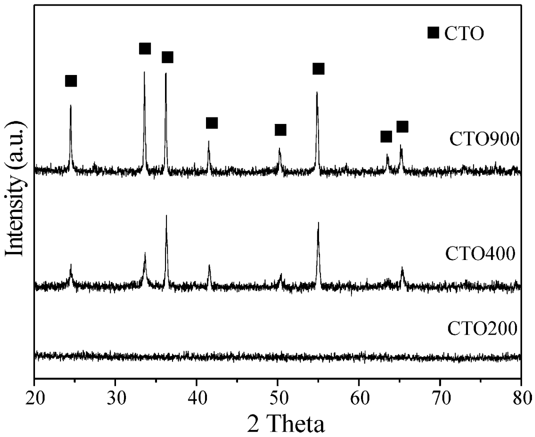

Fig. 2. XRD spectra of CTO powders calcinated at different temperatures.

Analysis of the diffraction peaks has confirmed that the particle size increases with the annealing temperature. On the sample calcined at 400 °C an average particle size of about 70 nm was calculated. The value calculated for the sample calcined at 900 °C (> 110 nm), indicates that the annealing process leads to a significant sinterization and growth of the particles size.

The morphology of CTO thin films on alumina substrates can be observed in Figs. 3a, b. The top view and cross-section of a film are presented, respectively, showing the smooth film surface and the presence of a few microcracks.

3.2. Gas sensing properties

CTO is known as a humidity insensitive material [3]. This is likely due to the high temperature

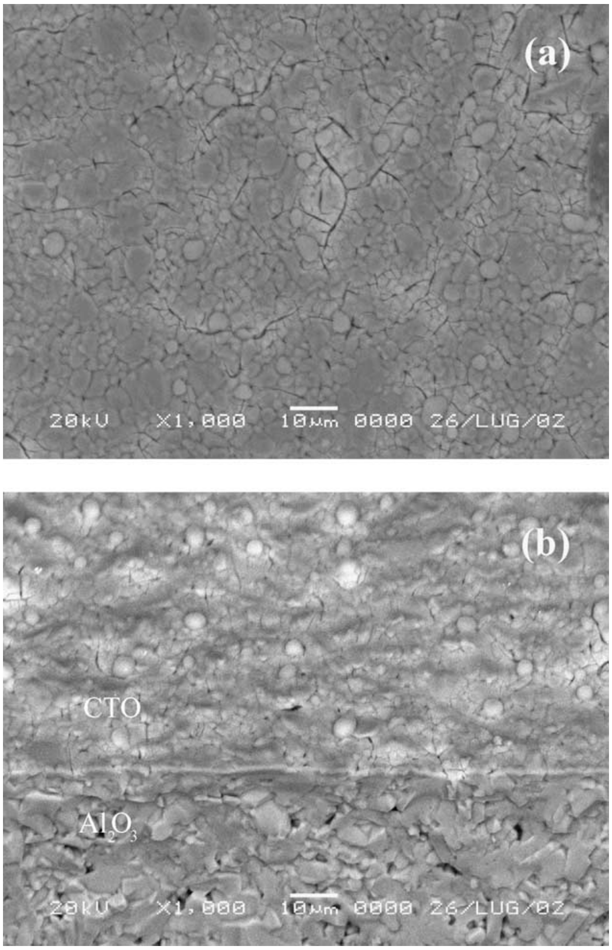

Fig. 3. SEM micrographs of CTO films: (a) top view; (b) cross section.

required to obtain chromium titanate by solid state reaction which comports a low porosity of the material obtained. Low synthesis temperatures should favor the formation of a microporouse structure and hence increase the sensitivity. Fig. 4 shows the resistance of CTO thin films prepared by sol-gel route and successive annealing at low temperature (200 and 400 °C) as a function of the relative humidity. The CTO400 film, annealed at 400 °C, has shown no significant response to water vapor. On the contrary, the film treated at low temperature, CTO200, was found to be sensitive to humidity with a decrease of the resistance of about one order of magnitude in the 0–100% RH range.

To explain the humidity sensitivity of these films we first consider the interaction of water with CTO surface. The most active surface metal ion for water chemisorption in CTO might be assumed to be the chromium ion. The origin of charge carriers could be then related mainly to the interaction between the surface Cr^{+3} ions and the adsorbed water which provide mobile protons migrating by hopping from sites across the surface. Other possible adsorption sites for water might be oxygen vacancies. In both cases, this would lead to a significant decrease of resistance at low RH.

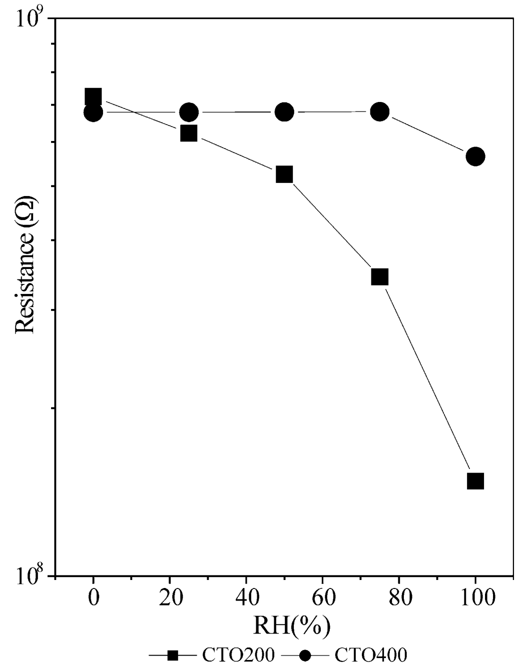

Fig. 4. Resistance variation of CTO-based sensors in the 0–100% RH range.

The shape of logR–RH characteristics strongly suggests instead that the sensitivity to humidity of the CTO200 film is mainly due to water condensed within the film porosity.[6,7] On porous materials the degree of pore filling depends on its radius and thickness of the physisorbed layer and hence RH. The increase in humidity provides more water molecules physisorbed to form multilayers reducing the barrier height at the grain boundaries and this leads to an exponential decrease in resistance at high RH as experimentally observed. Such hypothesis is in agreement with the dynamic adsorption–desorption curve reported in Fig. 5, showing as the adsorption process is slower than the desorption one.

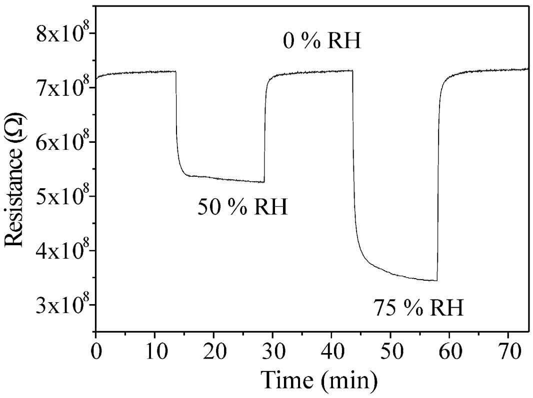

Fig. 5. Dynamic response of the CTO200 sensor for different humidity values.

4. Conclusions

The low temperature sol-gel synthesis allows to obtain CTO thin films for gas sensors applications. Films annealed at low temperature are sensitive and show fast response to water vapor. Future work will be focused on the doping of the base material in order to obtain CTO-based gas sensors with enhanced humidity and gas sensitivity.

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