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Cr-inserted TiO_2 thin films for chemical gas sensors

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Abstract

Cr–Ti oxide thin films were prepared by rf sputtering of Cr-inserted Ti targets. The roles played by Cr content and thermal treatments on both the structure and the electrical conductivity of thin films were investigated. Selected series of samples were tested as sensors for different gases like carbon monoxide and ethanol.

In both the cases, samples exhibiting the best sensing performances were determined and possible correlations between structure and electrical properties were evidenced.

Keywords: Cr-inserted TiO_2; Gas sensors; CO; Ethanol; XRF microanalysis; GIXRD

1. Introduction

TiO_2 thin films are extensively investigated in many fields of materials science because of their interesting chemical, electrical, and optical properties, which are mainly related to different crystallographic phases [1,2]. Anatase films are widely studied for photocatalytic applications: indeed, these materials could accomplish the photocatalytic degradation of organic compounds under UV irradiation. Thus, a large variety of applications for environmental protection are expected [3,4]. On the other hand, rutile thin films can be used in artificial heart valves in view of their good blood compatibility [5]. Other important applications of TiO_2 layers concern optical devices because they exhibit a high reflective index and are transparent over a wide spectral range [2]. Recently, these materials have been studied as gas sensors since they show a very good chemical stability at high temperatures and in harsh environments. Unfortunately, TiO_2 is a high resistive n-type semiconductor, so that it is scarcely sensitive to oxidative gases. Several efforts have been done to enhance the selectivity of these materials towards a specific gas. The conductivity of titanium dioxide can be improved through the introduction of proper dopants or by producing mechanical mixtures with different oxides. Particular doping metals offer the possibility to tune the selectivity of sensor devices: Pt is employed for oxygen detection [7,8], Nb for ethanol sensor [37], and Cu for CO sensing [9,10]. Addition of Cr can change the electronic conductivity of TiO_2 from n- to p-type: that has triggered a lot of interests towards the development of novel gas sensors [11–13,34]. Many techniques have been proposed to grow TiO_2 thin films [4–6]. Among them, radio frequency (rf) magnetron sputtering is one of the most suitable ones for the industrial scaling-up of the thin films deposition process, because it allows to synthesize high quality thin films onto large areas substrates. Recently, a novel deposition approach starting from a target with a controlled amount of dopant inserted into holes drilled into a target disc has been developed [19]. The possibility to carry out many syntheses in a cheap and carefully controlled way makes this technique very promising for an effective production of sensing devices. Several papers report the electrical characterization of Cr-doped TiO_2 films obtained by sol–gel technique [13,20] or by aerosol assisted chemical vapour deposition (AACVD) [39]. To our knowledge, this is the first time in which thin films of Cr-inserted TiO_2 have been

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deposited by rf magnetron sputtering, using a Ti target with a different numbers of Cr inserts. The influences of the Cr content and the annealing treatments on the structure and the electrical conductivity of thin films have been investigated. The sensing behavior of selected series of samples has been tested to different gases like CO and ethanol.

2. Experimental

Film deposition was carried out at an 8×10^{-3} mbar total pressure by rf-magnetron sputtering in a reactive Ar (50%)/O_2 (50%) atmosphere. The target (diameter: 101.6 mm) was made of titanium (certified at 99.99% purity) with the possibility to insert up to 12 cylinders (diameter: 5 mm, height: 4 mm) of either chromium or titanium. This option allowed to prepare thin films with different Cr contents. During deposition, the substrate temperature was kept at 300 °C. Three different series of Cr–Ti oxides were synthesized by using 4, 6 and 12 inserts of Cr. The thin films were characterized "as-grown" and after the oxidation cycle performed in a furnace at controlled flux (0.2 l/min) of humid synthetic air.

The oxidation cycle was performed in two steps: the first at 250 °C for 4 h and the second at 600 or 800 °C for 12 h. Temperature was changed slowly in order to avoid additional stresses or cracks in the thin layer. The thickness of the layers, measured with a profilometer after the deposition process, was 300 nm approximately.

For compositional, morphological, and structural analyses, thin films were deposited onto ultra-thin monocrystalline 1 0 0-oriented Si. For electrical characterization, films were deposited onto alumina 3×3 mm^2 substrates equipped with a platinum meander on the backside, acting as a heater and temperature sensor. Platinum interdigitated contacts were sputtered onto the layer after the annealing treatment.

Flow-through technique was used to test the gas-sensing properties of the thin film samples. A constant flux of synthetic air of 0.3 l/min was used as a gas carrier of the considered pollutant. All the measurements were carried out in a sealed chamber at 20 °C under controlled humidity. Electrical characterization was carried out by volt-amperometric technique; the sensor was biased by 1 V and film resistance was measured by a picoammeter.

X-ray fluorescence (XRF) microanalysis was carried out by means of a XMF-104 (Unisantis), equipped with a Si detector with a resolution of 200 eV. The radiation source was a Mo Kα and the beam size was about 100 μm. Measurements were performed at 12 kV/300 mA. Ten different points of each sample were analyzed and the average Cr/Ti ratio, based on the corrected value of the respective Kα of this elements, was reported.

Glancing incidence X-ray diffraction (GIXRD) measurements were collected with a Bruker "D8 Advance" diffractometer equipped with a Gobel mirror. The angular accuracy was 0.001°. The Cu Kα line of a conventional X-ray source powered at 40 kV and 40 mA was used.

MicroRaman spectra were collected by a Dilor Labram spectrograph. The exciting source was a HeNe laser (632.8 nm) with a power of less than 10 mW at the sample. The microscope was coupled confocally to the spectrograph. A 100× objective with a numerical aperture NA = 0.9 and a confocal hole opened at 200 μm were used. Suppression of the exciting line was obtained with a holographic notch filter.

3. Results and discussion

3.1. XRF microanalysis

The Cr/(Cr + Ti) ratio detected by XRF microanalysis ranges from 44% to about 75% on passing from the samples prepared with 4 (4A) to those prepared with 12 (12A) inserts, respectively. The trend of the Cr concentration agrees fairly well with the one reported by Bally et al. [19] for the system Fe_2O_3–TiO_2 synthesized with an analogous apparatus (see Fig. 1a). As in that case, the non-linearity of the monotonic increase of the Cr concentration with the number of Cr inserts can be explained by considering the difference in sputtering efficiency between Cr and Ti. Moreover, the Cr content noticeably changes as a result of the annealing procedure, as shown in Fig. 1b. The Cr content decreases as the annealing temperature increases, and the effect is more emphasized for the samples with lower initial Cr amounts. In particular, ranging from "as-grown" to 800 °C annealed samples, the Cr loss percentage is 42% in the case of the 4-insert series, whereas it is limited to 7% in the case of the 12-insert series. It is worth to note that the Cr loss becomes

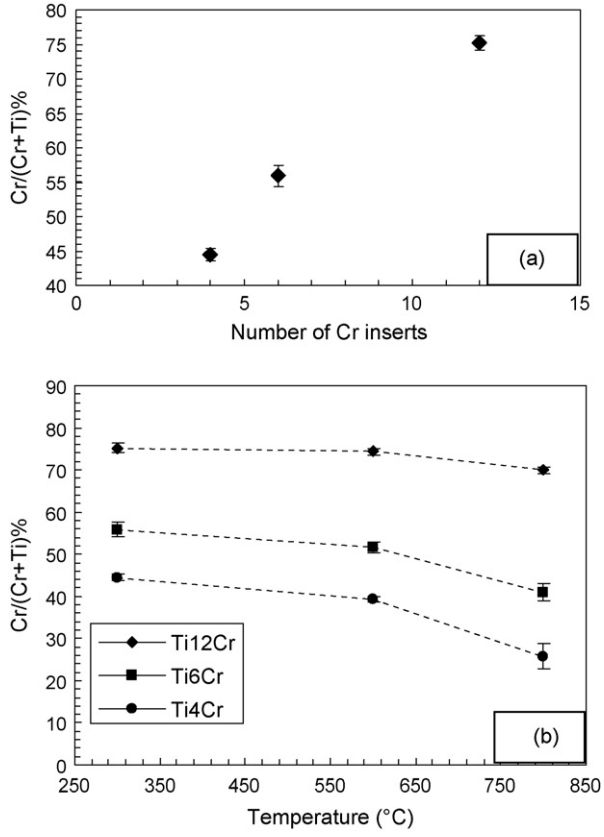

Fig. 1. XRF microanalysis results: Cr/(Cr + Ti) percentage ratio as a function of (a) the number of the Cr inserts inserted into the Ti target and (b) annealing treatment.