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ScienceDirect

Sensors and Actuators B 120 (2007) 560–567

SENSORS AND ACTUATORS B CHEMICAL

www.elsevier.com/locate/snb

Sol–gel derived polycrystalline $Cr_{1.8}Ti_{0.2}O_3$ thick films for alcohols sensing application

Suman Pokhrel, Lihua Huo *, Hui Zhao, Shan Gao

Laboratory of Functional Materials, School of Chemistry and Materials Science, Heilongjiang University, 150080 Harbin, PR China

Received 9 December 2005; received in revised form 12 March 2006; accepted 13 March 2006
Available online 2 May 2006

Abstract

The powder sample of $Cr_{1.8}Ti_{0.2}O_3$ (CTO) was obtained by a sol–gel method. The thick films were developed on identical ceramic tubes of 4 mm length comprising of two Au-electrodes and printing an eight-layer film prepared by mixing CTO with glass powder and α-terpinol as an organic vehicle. X-ray powder diffraction (XRD) patterns showed the formation of a single phase. The scanning electron microscope (SEM) images of the ceramic sensor treated at 850 °C revealed that the grain size was larger than 400 nm for the individual isolated grains on the surface, and the agglomerated dense spheroidal platelets had the size of 1–4 μm in diameter. The AC impedance measurement in ambient air showed that the resistance decreased nearly by two orders of magnitude with an increase in temperature in the range of 400–600 °C for both the powder sample and the thick film, and the activation energy E_a derived from the measurement was found to be 0.35 and 0.36 eV for the powder and the film, respectively. The films were exposed to various concentrations of alcohols (0.4–1.2 ppm of methanol and 1.0–5.0 ppm of ethanol), followed by determination of sensor response, sensitivity and reversibility and reproducibility. The origin of the gas response was attributed to the surface reaction of R-OH (R = methyl and ethyl group) with $O^-_{(ads)}$ to form adsorbed R-CHO, which was desorbed as a gas at 400 °C after the sensor departing from the gas.

Keywords: CTO thick film; Polycrystalline material; Alcohol sensing

1. Introduction

Solid-state sensors are among the most versatile of all sensors, as they detect a wide variety of gases, and can be used in many different applications. Different response characteristics are achieved by varying the semiconductor materials, processing techniques and sensor operating temperature. Among the unique attributes of the solid-state sensor are the abilities of the sensors to detect low ppm levels of gases as well as high combustible levels [1]. Solid-state oxide gas-sensing devices function by measuring the change in electrical resistance of an oxide film as a function of varying gas concentrations [2]. The adsorption (physisorption or chemisorption) of the gas species on the surface of the oxide results in the change in surface coverage which is responsible for the change in the surface electrical resistance [3]. Earlier reports [4,5] have shown the potential of several novel solid-state semiconducting materials as viable gas-sensing materials. Most of these materials are based on mixed metal oxides that change in electrical signal when the stoichiometric proportions of the metal centers are altered. When heated to elevated temperatures >200 °C, the mixed metal oxides exhibit extrinsic semiconducting behavior with either p- or n-type conduction [6]. In most cases the resistance change is observed when the oxidative or reductive nature of the gas is applied to these materials depending on the type of semiconductor used [7–9].

Titanium-substituted chromium oxide, $Cr_{1.8}Ti_{0.2}O_3$ (CTO) has all the properties of easy fabrication, chemical stability at operating temperature, resistance change of a measurable range and a sensitive gas response. It has a solid solution with the corundum crystal structure of the unsubstituted chromium oxide, with the charge balanced by chromium vacancies [8]. Recently these nonstoichiometric ternary oxides have been extensively used as solid-state sensors for relatively small concentrations of gases (e.g. NH_3, CO, H_2S and LPG) [10,11]. These $Cr_{2-x}Ti_xO_3$ (x = 0.1–0.5) are superior to traditional SnO_2 in many respects, e.g., they are stable, less sensitive to interference from water vapor and easy to control the grain size during preparation [12].

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* Corresponding author. Tel.: +86 451 86608737; fax: +86 451 86682541.
E-mail address: lhhuo68@yahoo.com (L. Huo).

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doi:10.1016/j.snb.2006.03.008

Alcohol vapor has been one of the most extensively studied [13–17] gases for metal oxide gas sensors, particularly due to the need for small practical devices to detect alcohol in human breath or even to detect leaks in industrial distribution lines. In the present work, we describe the preparation, characterization and sensing behavior of CTO thick films towards methanol and ethanol vapors.

2. Experimental

Analytical reagent (AR) grade chromium nitrate nonahydrate 99.99% $Cr(NO_3)_3{\cdot}9H_2O$, titanium(IV) *n*-butoxide 98% $[Ti(OCH(CH_3)_2)]_4$, triethylamine 99% $[(C_2H_5)_3N]$, were obtained from Huan Hua Chemical Co. LTD, China and they were used as received.

2.1. Preparation of CTO powder

$Cr(NO_3)_3{\cdot}9H_2O$ (160 g, 0.4 mol) was dissolved in H_2O (400 mL), and the resulting solution was stirred for 10 min with triethylamine (29.7 mL) and 1,1,1-trichloroethane (40 mL, AR grade). The heavier organic layer was separated from the aqueous Cr^{3+} layer, resulting in the de-anionisation of the salt solution [18]. The extraction procedure was performed at least thrice to produce a lower NO_3^-/Cr^{3+} ratio. It was noted that the de-anionisation more than four times led to the quick gel formation and as a result we restricted the extraction procedure only for three cycles. The chromia sol can be prepared by removing anions from aqueous solutions of metal salts. As the anions are removed, the metal ions form oligomeric cations containing Cr–O–Cr linkage. Further de-anionisation produces a polymeric sol and eventually a polymeric gel depending on the anion to cation ratio.

TiO_2 sol was prepared by mixing $Ti(n\text{-}OBu)_4$ dropwise into a solution of *n*-BuOH, H_2O and acetylacetone (acac, AR grade) with simultaneously stirring. The resulting solution $Ti(n\text{-}OBu)_4$:*n*-BuOH:H_2O:acac was maintained at the ratio of 12.2:1.4:1.1:2.4 by volume. The solution was stirred for 15 min to obtain a clear yellowish creamy colored mixture. The chromia and TiO_2 sols separately prepared were mixed with the stoichiometric amount to get the nominal composition of $Cr_{1.8}Ti_{0.2}O_3$. The resulting clear mixture was then stirred for 30 min by a mechanical stirrer (CJJ-931 Model, China) at a rate of 2500 rpm and kept in dark overnight. The sol was then heated in an oven (Yiheng, DHG-9145A Model, China) at 100 °C to obtain gel particles. This fine gel powder was then dried in a muffle furnace (TDW SX-2.5-10 Model, China) at 150 °C, followed by elevating the temperature to 400 °C and finally at 1000 °C in a programmed furnace to obtain dark green homogeneous powder. The schematic representation of the sol–gel method for preparing CTO powder is shown in Fig. 1.

2.2. Sensor fabrication

The sensor used for sensitivity measurements comprised of a commercially available cylindrical Al_2O_3 Taguchi Gas Sensor (TGS) tube of 4 mm length with two permanent gold coatings spaced 1 mm around it. Each gold coating consisted of two probes connected by very thin platinum wires along with a coiled platinum wire inserted through the tube for the optimum performance at the working temperature. The ingredients of the paste were weighed together (90% CTO + 5% glass powder + 5% α-terpinol as an organic vehicle) in a container and then vigorously mixed to form a uniform blend and applied over the gold electrodes on the sensor material. Eight coatings were performed on the material and subsequently three sets (having three sensors each) of sensors were sintered at 850, 750 and 650 °C for 5 h in

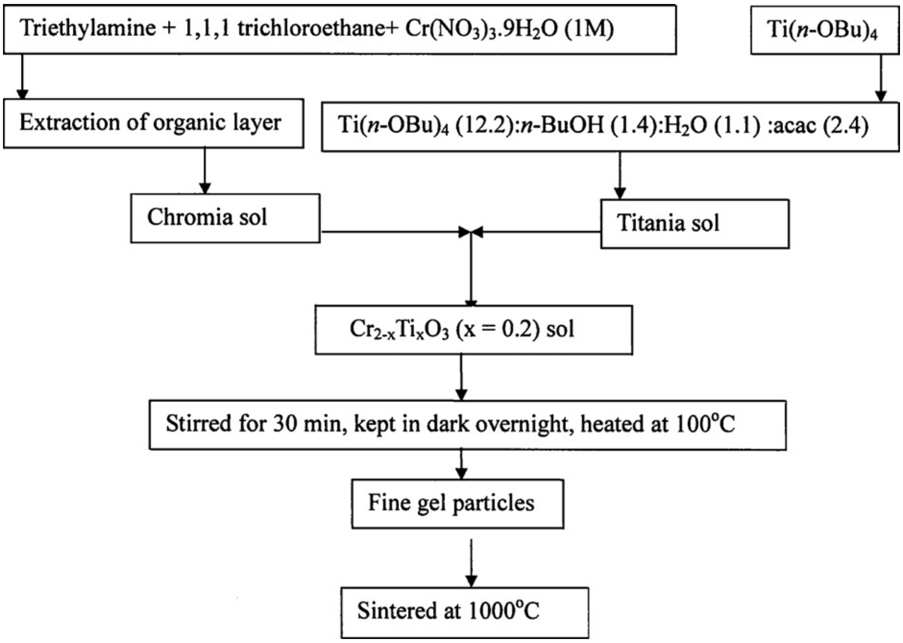

Fig. 1. Sol–gel method for preparation of CTO powder.