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Nanostructured Fe_2O_3/TiO_2 thick films: Analysis of structural and electronic properties

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Abstract

Thick films using starting nanopowders of TiO_2 (anatase 99.7%) and α-Fe_2O_3 (hematite) mixed in the weight ratios 60:40 and 40:60 for thick film paste were fabricated by screen printing technology on an alumina substrate. Samples were sintered at temperatures of 800–950 °C for 60 min. Structural and electronic properties were analyzed by XRD and SEM analysis, UV/vis spectroscopy and current–voltage analysis in view of potential application as gas sensors and anodes in photoelectrochemical cells for hydrogen generation and water splitting. XRD analysis showed that at 800 °C monoclinic pseudobrookite formed and anatase had transformed into rutile. Increase in sintering temperature lead to a gradual transformation of monoclinic pseudobrookite into the orthorhombic phase. SEM analysis showed that a homogenous small grain structure was obtained especially in the case of thick film samples with the 40:60 ratio of starting anatase and hematite sintered at 850 °C.

Keywords: A. Films; A. Sintering; C: Optical properties; Pseudobrookite

1. Introduction

Interest in the preparation of nanocomposites based on semiconducting oxides has increased in view of improved functional performance in advanced fields such as opto-electronics, sensing and catalysts and also novel technological applications [1]. High performance devices can be produced at a very low cost using thick film technology [2,3]. Thick films of nanostructured pure and doped titania have been fabricated and characterized as gas sensors [3]. Titanium oxide is a low cost, non-toxic, environmentally clean material. Applications of nanostructured titania films include the field of optics, electrical insulation, photovoltaic solar cells, electrochromic displays, antibacterial coatings, photocatalytic reactors, anodes in ion batteries and gas sensing [2]. However, the band gap of anatase and rutile is large (3.2 eV and 3.03 eV, respectively), limiting its gas sensing ability. TiO_2 absorbs only the ultraviolet part of the solar emission resulting in low conversion efficiency for water photolysis [4]. Modification of both the optical and photo-electrochemical properties of TiO_2 by elemental doping has been investigated extensively, including transition metals, especially Fe [5]. Hematite is a stable, low cost material with a relatively narrow band gap (2.2 eV) that has been widely applied [6]. Gas sensing properties of titanium and iron oxide nanosized thin films [7] and iron titanium solid solutions [8] have been investigated. Nanocomposite iron titanium oxide thin films have been investigated in view of applications as humidity and gas sensors [1]. Fe_2O_3/TiO_2 tube-like nanostructures have been synthesized [9]. At higher temperatures they transform into Fe_2TiO_5 (pseudobrookite) nanostructures that exhibit enhanced sensing properties.

Pseudobrookite, a rare mineral present in ingenous and metamorphic rocks, has a short range antiferromagnetic order partly broken by Ti layers and anisotropic spin-glass behavior below 55 K [10,11]. Electrically it is an "n" type semiconductor [12]. Pseudobrookite has a band gap of about 2.0 eV, and thus

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good solar spectrum absorbing qualities so it has potential to be applied as a photoanode in photoelectrochemical cells [13]. Pseudobrookite with an orthorhombic structure was first described by Pauling [14]. It has been synthesized in bulk and thin film form through solid-state reactions between Fe_2O_3 and TiO_2, sol–gel methods or by ball milling and hydrothermal processes followed by thermal calcination [15–19]. Pseudobrookite in monoclinic form was described by Drofenik et al. [20] and investigated by XRD analysis, electron microscopy, Mossbauer spectroscopy and magnetic susceptibility [21,22].

The aim of this work was to perform a detailed study of structural and electronic properties of thick films fabricated, using thick film pastes composed of two mixtures of starting nanostructured TiO_2 (anatase) and α-Fe_2O_3 (hematite) oxide powders, by screen printing on an alumina substrate and sintered at 800–950 °C in view of possible applications as photoanodes and gas sensors.

2. Experimental

Homogenization of the starting TiO_2 (Alfa Aesar, 99.7% anatase, grain size 15 nm) and α-Fe_2O_3 (Alfa Aesar, 99%, grain size 20–60 nm) nanopowders in the 60:40 and 40:60 wt% ratio was performed in a planetary ball mill (Fritsch Pulversisette 5) in stainless steel bowls with stainless steel balls for 60 min. Two weight ratios with a small and larger amount of excess TiO_2 in regard to the ideal molar ratio 1:1 for the formation of pseudobrookite were chosen. According to Dondi et al. [15] one of the problems of solid state reactions between anatase and hematite was to achieve a complete reaction of iron oxide, so hematite-free pseudobrookite is usually obtained by adding a significant excess of titania in respect to Fe_2TiO_5 stoichiometry. Thick film paste was made my mixing the homogenized starting oxide powder mixture with an organic vehicle (butyl cellulose) and a small amount of binding lead boron silicone oxide glass frit. The two obtained pastes (6F4T and 4F6T denoting 60 wt%Fe_2O_3:40 wt% TiO_2 and 40 wt% Fe_2O_3:60 wt% TiO_2 mixtures, respectively) were screen printed on alumina substrate. Samples were sintered in a hybrid conveyor furnace at temperatures of 800, 850, 900 and 950 °C for 60 min. An example of a thick film sample is shown on Fig. 1a.

XRD analysis of the thick film samples was performed on a Philips PW1050 diffactometer with CuKα radiation, step 0.02 s and hold time 10 s, 2θ 10–110°. Structural refinement was carried out by the Rietveld method using the GSAS package [23] with the EXPGUI graphical user interface [24]. Samples were analyzed for the presence of TiO_2 (anatase – space group $I4_1/amd$ and rutile – space group $P4_2/mnm$), α-Fe_2O_3 and pseudobrookite (orthorhombic and monoclinic). Starting values for monoclinic pseudobrookite (space group $C2/c$) were taken from Drofenik et al. [19]. Starting values for orthorhombic pseudobrookite (space group $Cmcm$) were taken from Tiedemann et al. [25]. Peaks originating from the alumina substrate were also expected and taken into account. SEM analysis was performed on a TESCAN Electron Microscope VEGA TS 5130 MM device.

Diffuse reflectance spectra of the thick film samples were measured on an UV/vis Shimadzu UV-2600 with an ISR2600-Plus Integrating sphere attachment in the measuring range 220–1000 nm.

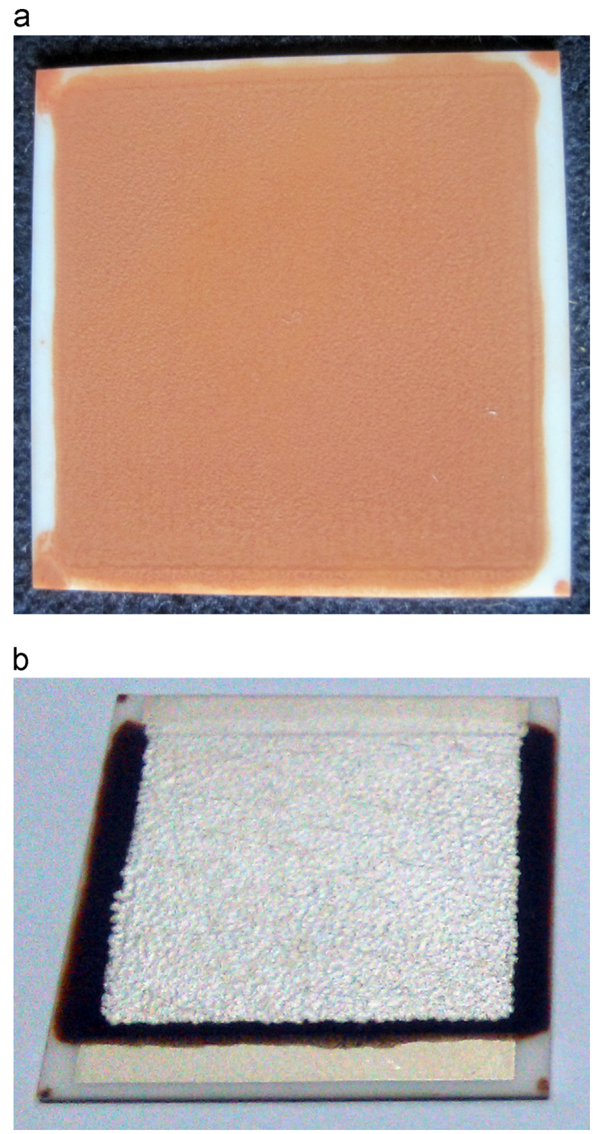

Fig. 1. Thick film samples (a) printed on alumina substrate and (b) prepared in sandwich form for current voltage measurements.

Samples for current voltage measurements were prepared in a sandwich form. First an electrode 6–8 μm thick using Pd–Ag paste was screen printed on alumina substrate, followed by a thick film layer around 25 μm thick (6F4T and 4F6T pastes), followed by a second electrode (as shown in Fig. 1b). The thick film layer was sintered at 850 °C. Current–voltage measurements were performed using a Keithley 237 Sourcemeter. The voltage was set as a linear stair in the range 0–500 V, with a step of 10 V and the current was measured. An Osram 120 V/300 W ELH halogen lamp was used as the light source with radiation intensity of 100 mW cm^{-2}.

3. Results and discussion

3.1. Structural characterization

XRD analysis showed that, besides noticeable peaks of alumina originating from the substrate, 4F6T samples contai ned: at 800 °C monoclinic pseudobrookite and rutile, at 850 °C