Journal of Non-Crystalline Solids 354 (2008) 4654–4660

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Phase transformation and crystal growth behaviors of La^{3+}/Ce^{3+}-doped TiO_2–20 wt% SnO_2 gels

Z.M. Shi [a,*], L. Yan [b]

[a] School of Materials Science and Engineering, Inner Mongolia University of Technology, Hohhot 010051, China
[b] School of Chemistry and Chemical Engineering, Yulin College, Yulin 719000, China

ARTICLE INFO

Article history:
Received 25 November 2007
Received in revised form 22 March 2008
Available online 4 July 2008

PACS:
81.07.Bc
81.16.Be
61.10.Nz

Keywords:
Amorphous semiconductors
III–V semiconductors
Ceramics
Crystal growth
Titanate
Nanocrystals
Sensors
Thin film transistors
X-ray diffraction
Transport properties gel
Conductivity
Fast ion conduction
Defects
Powders
Nano-composites
Nanoparticles
Sintering
Rare-earths in glasses
Sol–gels (xerogels)
Tin oxides
Thermodynamics

ABSTRACT

The transformation behaviors of La^{3+}/Ce^{3+}-doped TiO_2–SnO_2 gels were studied by using differential thermal analysis and X-ray diffraction methods so as to improve the phase transformation and decrease the granularity of crystals. Experimental results show that, anatase, rutile and SnO_2 nanocrystals can exist in the sintering products by varying La^{3+}/Ce^{3+} contents and sintering temperatures. 0.8–1.1 wt% of La_2O_3 or CeO_2 doping greatly depresses the growth of anatase and rutile crystals, obtaining nanosized crystals when sintered up to 600 °C for 2 h. With La^{3+}/Ce^{3+}-doping and increasing their contents, the transformations of gel to anatase and anatase to rutile, as well as the growth of anatase and rutile crystals can be depressed, while the transformation temperature of anatase to rutile receives much less affect. Moreover, the La^{3+}-doping has stronger effects on them than Ce^{3+} doping, but has a weaker inhibiting effect on precipitation and growth of SnO_2 crystals.

1. Introduction

Recently years, the monitoring and controlling of local environment become an important topic in fields of industry, agriculture and military. It is necessary to develop environmental sensing devices with high accuracy and high reliability to meet the requirements. Due to their special semiconductive properties, titania porous ceramics and films have been widely used for preparing chemical gas sensors (H_2, O_2, CO, NO_X, alcohol, ammonia, etc.) [1–11] and humidity sensors [12–19], which are working at ambient and elevated temperatures.

Generally, the sensing behaviors for chemical gases and humidity are greatly dependent on the adsorption and ionization of outer molecular as well as the ionic transport on the surface of sensing materials [2,4,14,19]. Therefore, phase composition, granularity and the crystal defects of the materials play an important part in these actions. Fortunately, these requirements can be tailored by means of ion-doping, nanostructure and composite in the preparation to improve the sensing properties of ceramic bulks and films.

* Corresponding author.
E-mail address: shizm@imut.edu.cn (Z.M. Shi).

0022-3093/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2008.05.039

Hazra and Basu [1] prepared Al^{3+}-doped porous titania films by the thermal oxidation of Titanium substrates, the sensor shows appreciably high sensitivity and fast response to hydrogen. Sotter et al. [2] found that the film with an anatase phase has a better effect on detecting trace oxygen than with a rutile phase. Sun, et. al [3] noticed that the nanosized titania thin film has a good sensing property to alcohol gas. Ferroni et al. [4] prepared thick films based on nanosized anatase powders doped with Ta and Nb for CO detection; the average granularity is respectively reduced from 110 nm to 35 nm and 45 nm for Ta and Nb doping. Dutta et al. [5] prepared the dense rutile films with a granularity of less than 20 nm as a high-temperature carbon monoxide sensor by the sputtering method. Nikolić et al. [6] prepared nanostructured titania coatings with a granularity up to 50 nm and a thickness less than 1 μm by the sol–gel method for gas sensing application. Gao et al. [7] evaluated the oxygen sensitivity of nano-scale rutile thick films calcinated at 800 °C; the improvement of oxygen sensitivity of films profits from their large surface area. Mohammadi and Fray [8] found that, the nanostructured and mesoporous TiO_2–Ga_2O_3 thin films exhibit a remarkable response to low concentrations of CO and NO_2 gases at low operating temperature of 200 °C, and the response decreases with increasing annealing temperature owing to the sintering of nanoparticles. Zakrzewska and Radecka [10] prepared TiO_2–SnO_2 system for H_2 sensing and photodegradation of organic components; AFM image indicates that the grain size of titania and SnO_2 is of the order of 10–50 nm for the films produced by RF sputtering on silica substrates, which depends on the chemical composition and substrate temperature. Lee and Hwang [11] studied the effect of substrates on the oxygen gas sensing properties of SnO_2–TiO_2 thin films with mean SnO_2/TiO_2 granularity of 56–77 nm for Corning glass 1737 and 44–67 nm for SiO_2/Si substrate. It was found that the oxygen sensitivity of the film deposited on Corning glass 1737 substrate is significantly lower than that of the film grown on SiO_2/Si substrates. Gusmano et al. [12] found that the titania thin film prepared by the sol–gel route has a rapid response to the humidity but a much higher electric resistance at lower humidity. Faia et al. [13] prepared a titania thick film humidity sensor, obtaining anatase crystals with a granularity of larger than 1μm when sintered at 800 °C for 2 h. Biju and Jain [14] noticed that, the sol–gel derived TiO_2–ZrO_2 multilayer films with an anatase phase possess the best humidity sensing properties due to their higher water adsorption capacity. Traversa et al. [15] observed that 10 at.% K^+-doped TiO_2 sintered at 300 °C for 30 min presents the best humidity sensitivity, however the activity decreases with the increase of sintering temperature. Yoshimura et al. [16] found that the humidity sensitivity of TiO_2–SnO_2 films is much better than that of pure TiO_2. Tai et al. [17,18] confirmed that the resistance of TiO_2–SnO_2 films linearly decreases with the increase of SnO_2 content and the nanostructured TiO_2–SnO_2 film possesses the highest sensitivity. Sousa [19] noticed that TiO_2 and (Ti, Sn)O_2-based polycrystalline shows a non-linear electricity–voltage response at low voltages. Shi et al. [20,21] studied the phase transformation behaviors of TiO_2–SnO_2 gels, it was found that the transformation temperatures of gel to anatase and anatase to rutile present the trend of first decrease and then increase with the increase of Sn^{2+} content, and the Sn^{2+}-doping depresses the growth of anatase and rutile crystals. When sintered at 600 °C for 2 h, the granularity is reduced from 70 nm to less than 30 nm for anatase crystals and from 140 nm to less than 40 nm for rutile.

As mentioned above, the TiO_2–SnO_2 porous ceramic and film have better sensing properties than that of pure titania. Rare earths are good candidates for modifying the sintering process and improving the properties of functional ceramics owing to their special physicochemical activities. Therefore, the present work aims to investigate the phase transformation behaviors of La^{3+}/Ce^{3+}-doped TiO_2–SnO_2 gels, as well as the variations of crystal granularity and phase composition with sintering temperature and rare earth contents, hoping to further improve sintering procedure and decrease the granularity of anatase and rutile crystals.

2. Experimental procedures

2.1. Preparation of samples

The sol-gel method was adopted to prepare La^{3+}/Ce^{3+}-doped TiO_2–SnO_2 gels. Chemical reagents of tetrabutyl titanate (⩾98.0%), $SnCl_2{\cdot}2H_2O$ (⩾98.0%), $Ce(NO_3)_3 \cdot 6H_2O$ (⩾99.0%), $La(NO_3)_3 \cdot 6H_2O$ (⩾99.0%), absolute alcohol (⩾99.7%), HCl (36%) and ammonia (27%) were used as precursory materials. First, Tetrabutyl titanate was poured into strongly stirring absolute alcohol with a volume ratio of 1:5(±0.2); 1(±0.2) vol.% of HCl was added into the solution to insure tetrabutyl titanate to be sufficiently hydrolyzed into sols. Then, $SnCl_2 \cdot 2H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were respectively dissolved into other absolute alcohol solutions with mass ratio of 1:5(±0.1). These solutions were mixed with the previous sol and continuously stirred to obtain seven composite sols. The nominal compositions of samples are shown in Table 1. The composite sols were titrated with ammonia solution until the gels are formed. The gels were dried at 80(±2) °C for 24 h and ground for 3 h through ball-milling for use.

The ground dried gels were conducted to analyze the crystallization process. The powder samples for phase analysis were prepared as follows. The ground dried gels were molded into green bodies through half-dry compression by 70 ± 2 MPa, which were then heated to different temperatures (with errors of ±2 °C) at a constant rate of 5 °C/min, soaking for 2 h in air. The sintered products were ground and screened into powders with a granularity range of 74–63 μm (ASTM E11-58T).

2.2. Measurements

A differential thermal analyzer (DTA) (DTG-50/50 H, Shimadzu, Japan) was adopted to examine the crystallization process of dried gels, using α-Al_2O_3 powder as the reference, in air and at a heating rate of 10 °C/min. The accuracy of measurement is ±1 μV. An X-ray diffractometer (XRD) (D8 Advance, Bruker, Germany), with copper Kα radiation, 40 kV, 120 mA and at a scanning speed of 4/min, was employed to inspect the phase compositions. The accuracy of measurement is ±0.0001° and the minimum step is 0.0001 degree. The relative content (χ) of rutile crystal was calculated by using following formula [22]

$$x = \frac{1}{1 + 0.8\frac{I_A}{I_R}}, \tag{1}$$

where I_A and I_R respectively are the diffraction peak intensity of anatase (101) and rutile (110).

The granularity (D) of both crystals was calculated by using Scherrer formula [23]

$$D = \frac{0.89\lambda}{B\cos\theta}, \tag{2}$$

Table 1
Nominal compositions of La^{3+}/Ce^{3+}-doped TiO_2–SnO_2 samples, wt%

Samples	TiO_2	SnO_2	La_2O_3	CeO_2
ST			0	0
5L			0.5 (±0.05)	/
8L			0.8 (±0.05)	/
11L	80 (±1)	20 (±1)	1.1 (±0.05)	/
5C			/	0.5 (±0.05)
8C			/	0.8 (±0.05)
11C			/	1.1 (±0.05)