Journal of Non-Crystalline Solids 459 (2017) 75–82

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Growth of crystals in titania-based amorphous gels

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ARTICLE INFO

Article history:
Received 31 October 2016
Received in revised form 22 December 2016
Accepted 3 January 2017
Available online 6 January 2017

Keywords:
Amorphous
Titania
Phase transformation
Orientation growth
HRTEM
Dislocation

ABSTRACT

The growth of crystals in titania-based amorphous gels was characterized using X-ray diffraction and high-resolution transmission electron microscopic methods. Anatase, rutile and SnO_2 crystals can independently precipitate from amorphous gels at lower annealing temperatures through their low-energy surfaces. In the undoped case, the allotropic transformation of anatase to rutile is dominant to form rutile crystals and undergoes rearrangements of the planes $(10\bar{1})_A$ and $(11\bar{2})_A$ to the $(1\bar{1}0)_R$ and $(10\bar{1})_R$, respectively, in which there exist some dislocations. In the Sn-doped case, the rutile crystal changes its formation route, that is, it grows depending on SnO_2 crystals by coherent relationship between $\{110\}_S$ and $\{110\}_R$ and the semi-coherent relationship between $\{110\}_S$ and $\{101\}_R$, in the latter of which the dislocation adjustment is necessary to reduce the mismatch of the planes. The Sn-doping improves the transformations of the amorphous to anatase and further to rutile, inhibits their growth and produces the fine crystals.

1. Introduction

Titania-based powders and films are widely used in fields of photocatalysis and photoelectronic conversion. Generally, titania is present in an amorphous, anatase and rutile structures. The amorphous structure has an incompact network and the highest free energy among the possible titania structures; in contrast, the anatase and rutile crystals have an orthogonal structure. Because of its denser atom arrangement, the rutile has a more compact structure and lower free energy than anatase [1–3]. The sequence of the free-energy yields a spontaneous transformation from amorphous state to anatase and further to rutile with an increase in annealing temperature.

The crystallization procedure of titania crystals always generates significant interest because it has a decisive effect on the microstructure and physicochemical properties of titania products. It has been found that the anatase phase can nucleate in contact regions of amorphous titania particles [4]. The brookite nanoparticles preferentially transform to anatase and further to rutile by means of interfacial nucleation and growth in nanocrystal titania ceramic powders [5]. The rutile phase can nucleate at the amorphous interface between smaller anatase particles through high-temperature annealing, while the martensitic transformation is dominant in larger anatase particles; these phase transformations are controlled by the intrinsic and extrinsic defects. The rutile particle grows in a $[1\bar{2}1]$ direction on the {101} twin plane and is surrounded by the low-energy surfaces [6,7]. The dislocations generated in defect-free nanocrystals induce an imperfect oriented attachment, which occurs typically on high-surface-energy {112} and {001} planes of the anatase nanocrystals [8]. The rutile phase can also nucleate at the anatase {112} twin boundaries by the oriented attachment because the twin interface has a structure similar to that of the rutile [9]. On the other hand, it is believed that the pre-precipitated SnO_2 particles are favorable of the transform to rutile in the TiO_2-SnO_2 nanocomposites through a semi-coherent epitaxial growth manner by providing a crystallographically similar surface, though the direct evidence was not provided [10]. The SnO_2 nanowires can epitaxially grow on a rutile (101) substrate in the [101] direction in case of the Au-catalyzed vapor-liquid-solid route [11]. The SnO_2 thin films can heteroepitaxially grow on the rutile (100) substrate in the pulsed laser deposition route; the high-density dislocations and related planar defects appear in the film at the early growth stage because of the large lattice mismatch and higher point defect condensation [12].

TiO_2-SnO_2 composite nanofilms and porous ceramics are promising sensing materials, which are frequently used to monitor gases and humidity of local environments [13–16]. The nanostructured titania products are generally prepared via sol-gel route. By heating the as-received amorphous gel, the titania crystals and other phases (which depend on doping or composite of the gel) can be obtained; their size, morphology and phase composition are greatly influenced by the crystallization process. However, the direct proofs about the nucleation and grow of titania crystals, the allotropic transformation of anatase to rutile, and the influence of doping or secondary phase on them have not been paid great attentions. The present work is to comparably investigate the details occurring in crystallization process of undoped and Sn-doped amorphous powders, which is significant for accurate controlling of microstructure of the titania-based composites.

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http://dx.doi.org/10.1016/j.jnoncrysol.2017.01.013
0022-3093/

2. Experimental procedures

2.1. Preparations

The analytical reagents of tetrabutyl titanate (≥98.0%), tin chloride ($SnCl_2 \cdot 2H_2O$) (≥98.0%), alcohol (≥70 vol%) and acetic acid (36 vol%) were used as starting materials. First, the tetrabutyl titanate (10 ml) was injected in an alcohol solution (40 ml) with stirring to form a titania sol. Second, the tin chloride (2.21 g) was dissolved into another alcohol solution (20 ml). By mixing the Sn-containing solution with the titania sol using strong stirring, the 25 mol% Sn-doped titania composite sol can be obtained. Third, dilute acetic acid was titrated into the sols until gels were formed. Afterwards, the gels were dried at 100 °C for 24 h. The dried gels were ground and screen-filtered to powders with a granularity range of 74–63 μm (ASTM E11-58T) and repeatedly washed with deionized water under supersonic vibration. The washed powder samples were dried at 100 °C for 24 h and annealed at various temperatures for 2 h in air. The annealed samples were ground and screened to the fine powders, which were used for measurements.

2.2. Measurements

The phase composition of the powders was analyzed by an X-ray diffractometer (D/MAX-2500/PC, Rigaku) using copper Kα radiation, 40 kV, 200 mA and at a scanning speed of 1°/min. To obtain the size and lattice constants of crystals of the samples annealed at different temperatures, the diffraction peaks of low-index planes were carefully examined three times to calculate their averages [17]. The morphology of the powders was characterized using a high-resolution transmission electron microscope (FEI, Tecnai G2 F20 S-Twin), at 200 kV and with a lattice resolution of 0.102 nm. The powders for TEM analysis were ultrasonically treated for 15 min by mixing them with absolute alcohol and were then dispersed on a holey carbon copper grid. The selected electronic area diffraction (SEAD) and inverse fast Fourier transform (IFFT) were used to identify phases and structures of the crystals.

3. Results and discussion

3.1. Phase compositions of the titania gels annealed at different temperatures (XRD)

The undoped gel maintains the amorphous state up to 300 °C. The distinct anatase peaks (PDF# 21-1272, a = 0.3785 nm, $\boldsymbol{c}$ = 0.9513 nm) appear at 400 °C and remain up to 700 °C. The rutile peaks (110) (PDF# 21-1276, $a = 0.4593$ nm, $c = 0.2959$ nm) were identified at 600 °C and above in the undoped samples (Fig. 1(a)). In contrast, a very weak SnO_2 peak (110) (PDF# 77-0449, $a = 0.4742$ nm, $c = 0.3190$ nm) can be identified in the Sn-doped sample annealed at 200 °C (Fig. 1(b)). The weak peaks of anatase (101) and rutile (110) simultaneously appear at 300 °C, which are lower than those (400 °C and 600 °C) of the undoped sample, indicating that Sn-doping decreases the transformation temperatures of the amorphous to anatase and further to rutile. The peaks of rutile at (110) are asymmetric even heated to 700 °C, which are attributed to overlapping of the peaks of rutile and SnO_2. This indicates that the Sn-doped products are composted of SnO_2, anatase and rutile phases that depend on the annealing temperatures.

Moreover, the peak height of the anatase phase is rapidly decreased when the annealing temperature is higher than 600 °C, which indicates that there is an allotropic transformation of the anatase to rutile. In contrast, the anatase peaks in the Sn-doped samples are lower and wider and are not greatly reduced when increasing the annealing temperature from 300 °C to 500 °C, while the rutile peak is greatly increased in this temperature range. This indicates that the Sn-doping inhibits the transformation of the amorphous to anatase and promotes the transformation of rutile; the rutile forms in a different way rather than in the allotropic transformation.

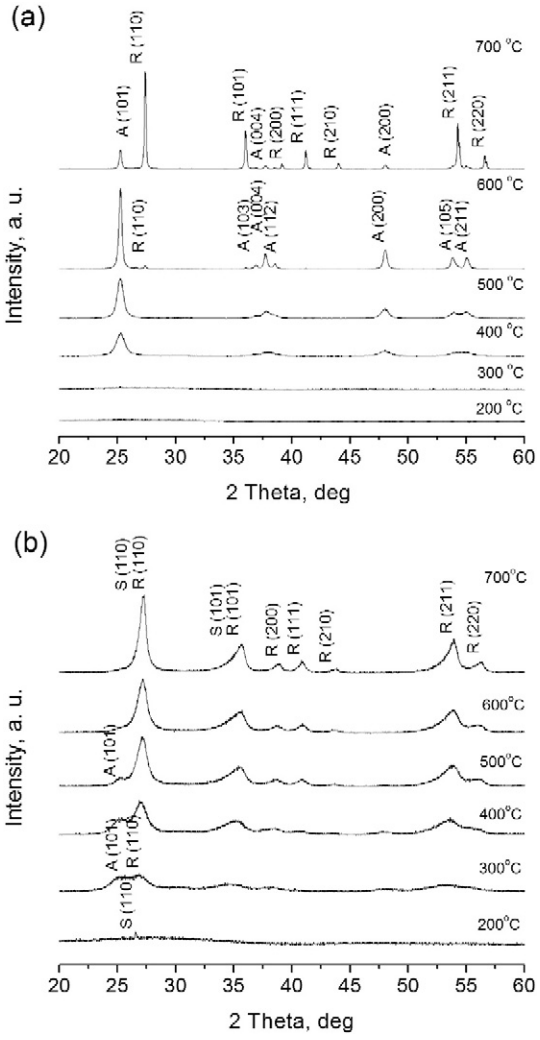

Fig. 1. XRD patterns of titania gels annealed at different temperatures for 2 h, (a) undoped; (b) Sn-doped.

This is because, before the anatase starts to crystallize, Sn ions must discharge out of the amorphous by solid diffusion due to that the solubility of Sn ions in anatase is much lower than that in amorphous. The

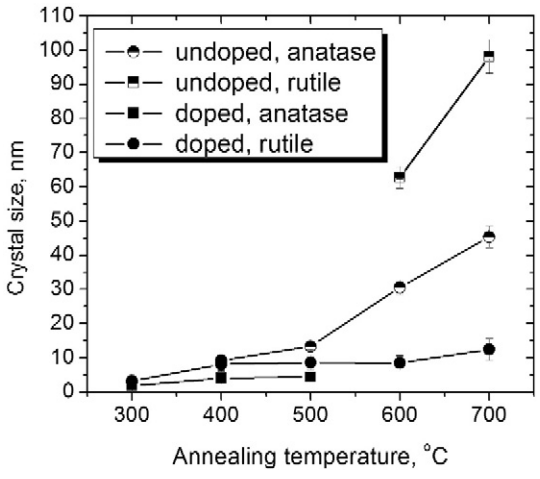

Fig. 2. Variation of crystal size of TiO_2 with annealing temperature.