Chemical Physics Letters 511 (2011) 367–371

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Annealing of heterogeneous phase TiO_2 films: An X-ray absorption and morphological study

R. Gago [a,*], A. Redondo-Cubero [b], M. Vinnichenko [c], L. Vázquez [a]

[a] Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, E-28049 Madrid, Spain
[b] Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal
[c] Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, PF-510119, D-01314 Dresden, Germany

A R T I C L E I N F O

Article history:
Received 27 May 2011
In final form 22 June 2011
Available online 25 June 2011

A B S T R A C T

Heterogeneous TiO_2 films with nanocrystalline (*nc*-) rutile and amorphous (*a*-) phases were annealed in vacuum up to 450 °C. The structural and morphological changes were studied by *in situ* X-ray absorption and *ex-situ* X-ray diffraction and atomic force microscopy. The annealing process leads to phase and morphological changes depending on the initial phase mixture. Films with dominant *nc*-rutile phase are quite stable whereas in *a*-TiO_2-containing films the *a*-TiO_2 regions crystallize into *nc*-anatase at 300 °C. The latter is attributed to the initial anatase-*like* character of *a*-TiO_2. Interestingly, at 450 °C *nc*-anatase or *nc*-rutile is preferentially promoted for high or low initial *a*-TiO_2 contents, respectively.

1. Introduction

Titanium dioxide (TiO_2) is a polymorphous material whose properties depend strongly on its atomic structure. In thin film form, TiO_2 grows mainly with single or mixed anatase and rutile phases, as well as amorphous (*a*-TiO_2) [1]. Anatase displays efficient photocatalytic activity [2] whereas the higher density and refractive index of rutile make it suitable as protective coating in lenses and optical applications [3]. In addition, mixed-phase TiO_2 may exhibit superior photocatalytic properties than pure single phases [4]. Due to its blood compatibility, *a*-TiO_2 is also used as biomedical coating [5]. Hence, the selective properties displayed by single or mixed-phase TiO_2 films trigger the interest in tuning the desired structure.

The phase of TiO_2 films depends on both the deposition method and preparation conditions. Rutile is the most stable phase while anatase is metastable and only produced at relatively low temperatures [6]. Among the most common deposition methods, reactive sputter deposition [7] in an Ar/O_2 reactive atmosphere has been successfully used to selectively produce TiO_2 films with different structural (mixed) phases [8]. Post-deposition thermal annealing is an additional way to improve and modify the structural properties of *as-grown* films. The anatase to rutile transformation is irreversible and generally occurs at temperatures above 600 °C [9], although it can range between 500 and 1000 °C depending on the initial grain size [10]. It is also generally reported that preferential formation of anatase can be achieved by the crystallization of *a*-TiO_2 upon annealing at moderate temperatures (300–400 °C) [11,12]. The principle for such transformation is attributed to the similar mass densities of *a*-TiO_2 and anatase, which implies lower elastic strain energy for the precipitation of anatase than rutile nuclei [13]. Under this guideline, the key to achieve single-phase anatase is to start with uniform *a*-TiO_2 films.

Up to now, scarce results have been reported on the structure of *a*-TiO_2, mostly due to the problems in characterizing the poorly defined order. The analysis may be even more complicated due to the eventual concurrence of mixed environments. X-ray absorption near edge structure (XANES) [14] is a powerful technique to study complex-systems with amorphous or crystalline nature, since it provides local-order information with atomic site selectivity. In the case of TiO_2, distinct spectral features for each atomic structure can be used for phase identification [15] and quantitation [16]. Due to its local-order character, XANES has been applied to study *a*-TiO_2 in the form of aerogels and nanometer-sized powders [17,18], as well as to analyze highly disordered films [19].

In this work, we address the structural evolution upon annealing of heterogeneous TiO_2 films produced by reactive pulsed magnetron sputtering (RPMS). *As-grown* samples with different mixtures of nanocrystalline (*nc*-) rutile and *a*-TiO_2 phases were grown under different O_2 partial pressures in the Ar/O_2 gas mixture as described in Ref. [20]. *In-situ* XANES, complemented with *ex-situ* grazing-incidence X-ray diffraction (GIXRD), was used to study the phase evolution for the different mixtures. Additionally, atomic force microscopy (AFM) is also presented as a complementary tool to follow the structural evolution with spatial lateral resolution. This has been possible by the image contrast provided on the surface morphology by the different underlying phases on the surface.

* Corresponding author.
E-mail address: rgago@icmm.csic.es (R. Gago).

0009-2614/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2011.06.061

2. Experimental

TiO_2 films with a thickness of ~100 nm were grown on Si(1 0 0) by RPMS. The deposition is based on a plasma discharge between a 3″ Ti circular target acting as a cathode and a grounded anode ring with a distance gap between them of a few mm's. The substrate was also grounded and located facing the Ti target at a distance of ~15 cm. A mid-frequency (100 kHz) pulsed voltage with an overall power of 150 W and a duty cycle (ratio between the pulse duration and the period of the rectangular waveform) of 40% (active time of ~4 μs) was applied to the cathode in order to ignite and maintain the discharge. The base and working pressure were 10^{-4} and 0.3 Pa, respectively. The O_2 content ($[O_2]$) in the reactive Ar/O_2 gas mixture was set at 33%, 50% and 100% by adjusting the individual gas fluxes (partial pressures) with mass flow controllers while keeping the total gas flow (pressure) constant. The growth was performed on unheated substrates although a slight temperature increase (<100 °C) was produced during processing due to the interaction with the plasma.

The changes in the bonding structure of TiO_2 films upon annealing were studied with elemental sensitivity to O and Ti sites by soft X-rays XANES in the total electron yield mode. Sequential measurements after 60 min annealing steps at increasing temperatures (*as-grown*, 150, 300, and 450 °C) were performed *in situ* under ultra-high-vacuum conditions. The microstructure of the *as-grown* films and after annealing at 450 °C was further examined by GIXRD using a D5000 (BRUKER AXS) diffractometer under Cu-K_α radiation (λ = 1.54056 Å). The data were collected within the scattering angle range, 2θ, of 20–70° at an incidence angle of 1° (the latter to minimize the signal from the single-crystal substrate). Further, the surface morphology of the films before and after annealing was imaged by AFM with a Nanoscope IIIa (Veeco) using silicon cantilevers in tapping mode.

3. Results

3.1. In-situ X-ray absorption near-edge structure (XANES)

Figure 1 shows Ti*2p* (left) and O*1s* (right) XANES spectra for the set of TiO_2 samples before and after annealing at different temperatures. In order to interpret the data, the reference spectra for rutile and anatase polymorphs (taken from Ref. [21]) are also displayed. Although rutile and anatase present a similar coordination cell (in each case, an octahedron with different degrees of slight distortion), they show distinct lineshape that can be used as fingerprint of each bonding environment [15]. On the one hand, XANES Ti*2p* spectra result from *2p* to *3d* electronic transitions, showing L_3 (456–462 eV) and L_2 edges (462–468 eV) due to spin–orbit splitting of the Ti-*2p* core-level into $2p_{3/2}$ and $2p_{1/2}$ [21,22]. These levels are further split into t_{2g} (A and C peaks) and e_g (B and D peaks) states due to the crystal-field interaction [15]. The double peak structure of feature B (B_1 and B_2) arise from the Ti second coordination cell [23] and is a clear signature of each polymorph. That is, B_1 (B_2) is more intense in the case of anatase (rutile). Moreover, the energy separation between C and D is ~0.1 eV larger and C is more intense in the case of rutile than in anatase. On the other hand, XANES O*1s* spectra show a double-peak structure (E and F) with an energy difference close to the t_{2g} and e_g states and a broad band on the high-energy side between 537 and 550 eV. These features are related to O-2*p* empty states hybridized with Ti-3*d* (low-energy side) and Ti-4*sp* (high-energy side) bands [22]. In this case, the relative intensity of E and F peaks and the lineshape of the high energy side of the spectra can be used to identify rutile or anatase environments.

XANES of *as-grown* films reveals different TiO_2 phase mixtures as a function of the $[O_2]$ during processing. First, the lineshape resembles that of the rutile polymorph for $[O_2]$ = 100%. In the case of the *as-grown* film with $[O_2]$ = 33%, the spectrum is more similar to that of anatase since the peak intensity of B_1 is higher than in B_2. However, the spectrum presents broader features with respect to the crystalline polymorph that indicates the presence of structural disorder (amorphization) [19]. Hence, this film can be cataloged as *a*-TiO_2 although the local-order atomic structure presents anatase-*like* bonding. This fact can be partially correlated with the similar density normally reported between *a*-TiO_2 and anatase [13]. Finally, for $[O_2]$ = 50% XANES shows a superposition of *a*-TiO_2 and rutile environments, which indicates an equivalent mixture of both phases. Therefore, the analysis shows the formation of different phase mixtures with a promotion of the rutile contribution with $[O_2]$. Further details about the XANES analysis can be found in Ref. [20].

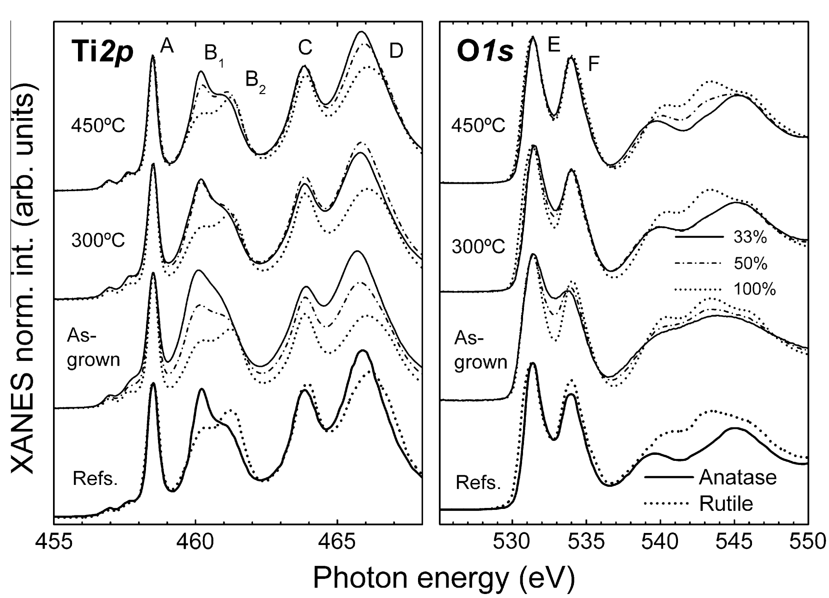

Figure 1. XANES spectra of RPMS TiO_2 films produced with different $[O_2]$ in the gas mixture before and after different annealing temperatures. The reference spectra for anatase and rutile polymorphs are also included for comparison.