Annealing of heterogeneous phase TiO₂ films: An X-ray absorption and morphological study

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A B S T R A C T

Heterogeneous TiO₂ 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*-TiO₂-containing films the *a*-TiO₂ regions crystallize into *nc*-anatase at 300 °C. The latter is attributed to the initial anatase-like character of *a*-TiO₂. Interestingly, at 450 °C *nc*-anatase or *nc*-rutile is preferentially promoted for high or low initial *a*-TiO₂ contents, respectively.

1. Introduction

Titanium dioxide (TiO₂) is a polymorphous material whose properties depend strongly on its atomic structure. In thin film form, TiO₂ grows mainly with single or mixed anatase and rutile phases, as well as amorphous (*a*-TiO₂) [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 TiO₂ may exhibit superior photocatalytic properties than pure single phases [4]. Due to its blood compatibility, *a*-TiO₂ is also used as biomedical coating [5]. Hence, the selective properties displayed by single or mixed-phase TiO₂ films trigger the interest in tuning the desired structure.

The phase of TiO₂ 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/O₂ reactive atmosphere has been successfully used to selectively produce TiO₂ 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*-TiO₂ upon annealing at moderate temperatures (300–400 °C) [11,12]. The principle for such transformation is attributed to the similar mass densities of *a*-TiO₂ 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*-TiO₂ films.

Up to now, scarce results have been reported on the structure of *a*-TiO₂, 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 TiO₂, 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*-TiO₂ 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 TiO₂ films produced by reactive pulsed magnetron sputtering (RPMS). *As-grown* samples with different mixtures of nanocrystalline (*nc*-) rutile and *a*-TiO₂ phases were grown under different O₂ partial pressures in the Ar/O₂ 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.

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2. Experimental

TiO₂ 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 μ s) 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 O₂ content ([O₂]) in the reactive Ar/O₂ 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 TiO₂ 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 ($\lambda = 1.54056$ 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 Ti2p (left) and O1s (right) XANES spectra for the set of TiO₂ samples before and after annealing at different temper-

atures. 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 Ti2p spectra result from 2p to 3d electronic transitions, showing L₃ (456–462 eV) and L₂ 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 (B₁ and B₂) arise from the Ti second coordination cell [23] and is a clear signature of each polymorph. That is, B₁ (B₂) 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 O1s 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-2p empty states hybridized with Ti-3d (low-energy side) and Ti-4sp (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 TiO₂ phase mixtures as a function of the [O₂] during processing. First, the lineshape resembles that of the rutile polymorph for [O₂] = 100%. In the case of the *as-grown* film with [O₂] = 33%, the spectrum is more similar to that of anatase since the peak intensity of B₁ is higher than in B₂. 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*-TiO₂ although the local-order atomic structure presents anatase-like bonding. This fact can be partially correlated with the similar density normally reported between *a*-TiO₂ and anatase [13]. Finally, for [O₂] = 50% XANES shows a superposition of *a*-TiO₂ 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 [O₂]. Further details about the XANES analysis can be found in Ref. [20].

Figure 1. XANES spectra of RPMS TiO₂ films produced with different [O₂] in the gas mixture before and after different annealing temperatures. The reference spectra for anatase and rutile polymorphs are also included for comparison.

Upon annealing at 150 °C (not shown), which is just slightly higher than the temperature reached during processing, the XANES spectra show no appreciable change with respect to the *as-grown* samples. At higher annealing temperatures (300 and 450 °C), the spectra of the *as-grown* sample grown with $[O_2] = 100\%$ do not display significant changes. This is expected from the clear rutile structure of this sample extracted from the spectra and the stability of such phase. On the contrary, after annealing at 300 °C, the XANES spectra of samples grown with $[O_2] = 33\%$ and 50% show a transition towards (nano)crystalline anatase. This trend is derived from the sharpening of the spectral features (specially, B_1 at the $Ti2p$) and the appearance of anatase-related structure at the high-energy side of the $O1s$ edge. For $[O_2] = 33\%$, clear anatase fingerprints remain upon annealing at 450 °C with additional sharpening of the spectra, indicating further enhancement of the structural order in the anatase phase. On the contrary, after annealing at 450 °C the *as-grown* film with an equal mixture of phases of *a*- TiO_2 and *nc*-rutile ($[O_2] = 50\%$) shows also better ordering but, in this case, with the preferential crystallization of rutile (note the increase in the relative intensity of B_2 and the changes at the high-energy side of the $O1s$). Despite this fact, the anatase contribution is still noticeable. These results point out different structural evolution upon annealing depending on the initial phase mixture.

3.2. Ex-situ grazing-incidence X-ray diffraction (GIXRD)

Figure 2 shows the GIXRD diffractograms of TiO_2 samples grown with different $[O_2]$ before (lower curve) and after annealing at 450 °C (upper curve). In all the cases, *as-grown* samples do not yield detectable peaks, indicating an 'X-ray amorphous' character or short-range structural order (e.g. very fine grains). The analysis of thicker samples grown under the same conditions (see Ref. [20])

Figure 2. GIXRD for TiO_2 films produced by RPMS with different $[O_2]$ before and after annealing at 450 °C. The reflections from rutile (■) and anatase (□) polymorphs are also indicated.

reveals that rutile reflections appear for $[O_2] > 50\%$, yielding a grain size of few nm's. In line with XANES, these results point out the promotion of rutile with $[O_2]$ and the larger disorder of the anatase-like (*a*- TiO_2) phase with respect to *nc*-rutile. After annealing, the sample grown with $[O_2] = 100\%$ still does not show any pattern, which implies no detectable crystalline improvement of the initial *nc*-rutile (remaining with a grain size of a few nm's). On the contrary, the *as-grown* film with a dominant contribution from *a*- TiO_2 ($[O_2] = 33\%$) shows the appearance of *nc*-anatase upon annealing. Although the signal to noise ratio is rather low, the crystal size can be estimated from the peak width to be around 20 nm (much higher than the *nc*-rutile grains). In line with XANES, the formation of *nc*-anatase also appears in the sample grown with $[O_2] = 50\%$ but, in this case, the anatase signal is reduced. Therefore, the higher content of *a*- TiO_2 phase in the *as-grown* samples the higher the content of *nc*-anatase formed upon annealing.

3.3. Ex-situ atomic force microscopy (AFM)

Figure 3a–c show AFM images of the *as-grown* RPMS TiO_2 films under different $[O_2]$. There is a progressive surface roughening with $[O_2]$ due to the emergence of hollow and rough structures (imaged as darker areas) over a rather flat surface. The depth of these depressions ranges between 5 and 8 nm with a broad distribution of lateral sizes (up to 400 nm in width). As reported previously [20], the distinct topography of flat and hollow regions in the images originates from different underlying structural phases. On the one hand, hollow features present an internal nano-granular morphology associated to *nc*-rutile domains. On the other hand, flat and featureless regions correspond to *a*- TiO_2 . Therefore, the surface morphology can be used to image the phase mixtures derived by XANES with a dominant *nc*-rutile (*a*- TiO_2) contribution

Figure 3. AFM $4 \times 4 \mu m^2$ images of RPMS TiO_2 films grown with $[O_2] = 33\%$ (a, d), 50% (b, e) and 100% (c, f) before (left) and after annealing at 450 °C (right).

for high (low) $[O_2]$. Such surface morphology is interpreted as the competition of lateral and vertical growth rates between rutile domains and the surrounding α - TiO_2 [20].

The morphological and structural correlation displayed by the RPMS TiO_2 films allows us to follow the structural evolution upon annealing with spatial lateral resolution. Figure 3d–f shows the surface morphology after annealing at 450 °C. First, in line with XANES and GIXRD, there is no significant change for a complete surface coverage with nc -rutile (see Figure 3c and f). In contrast, initially flat α - TiO_2 regions in Figure 3a display interesting changes (see Figure 3d) due to the formation of prominent features (brighter lines) which are connected to the crystallization of nc -anatase. It seems that anatase crystallization is limited by the available α - TiO_2 since these features follow paths that clearly avoid the nc -rutile domains. These topographical structures induce a slight increase in the surface roughness upon annealing (from 0.9 to 1.1 nm) and also indicate that some material expansion takes place. Note that such broad features cannot be related to grain boundaries since the crystal size of nc -anatase is much smaller (in the order of a few tens of nm's). Therefore, they are probably related to the emergence of strain upon crystallization. Likewise, a more detailed inspection reveals differences in the rims of nc -rutile hollow regions before and after the annealing, the latter displaying steeper (more defined) edges. This can be seen in the 3D images of typical hollow morphologies of Figure 4a and b extracted from Figure 3a and d, respectively. This trend is more evident in the corresponding line profiles shown in Figure 4c, where the steeper edges are indi-

cated by the arrows. Therefore, expansion of the crystallized region does alter the outer part of the hollow structures. This is also consistent with the statistical fact that upon annealing the number of smaller hollow structures (<50 nm in width) is considerably reduced, as extracted from the size histogram of hollow structures shown in Figure 4d. This histogram also reveals a slight increase in size of the larger hollow structures although this change does not have a significant impact on the rutile surface coverage (~10%). Therefore, it can be stated that rutile promotion is not appreciable, which is in agreement with the fact that rutile signal was negligible in the XANES spectra (Figure 1).

The surface morphology of the sample produced with $[O_2] = 50\%$ also shows the preferential formation of nc -anatase from the initial α - TiO_2 (flat) regions (Figure 3b and d), although the changes are partially masked by the higher content of nc -rutile. In this case, the size increase of hollow regions is more evident and do have an impact in the nc -rutile surface coverage since it increases from 25% to 40%. Accordingly, XANES of this sample after annealing revealed the formation of nc -anatase in this sample at 300 °C but a posterior promotion of nc -rutile at 450 °C.

4. Discussion

The above results related to the evolution of different TiO_2 phase mixtures with annealing temperature can be analyzed in terms of a competition between the thermodynamically most stable phase at each temperature and crystallization of the existing structure. Thanks to the image contrast provided by the underlying structural phases, the morphological analysis yields lateral-resolved analysis of the local regions where the structural changes take place. In this way, the crystallization of nc -anatase from the initial α - TiO_2 regions is clearly shown, in agreement with the results of Nakamura et al. [11]. By means of XANES, we can additionally point out that the preferential formation of anatase upon annealing of α - TiO_2 may originate from a pre-existing anatase-like local-order structure in the *as-grown* α - TiO_2 . This result complements the results of Nakamura et al. [13] where this transformation is explained by the similar mass densities of anatase and α - TiO_2 and, hence, the lower strain energy required with respect to rutile precipitation.

It is also noteworthy that the anatase formation upon annealing of α - TiO_2 is normally reported above 400 °C [12] whereas in our case it is already observed at 300 °C. This slight difference could be explained by limitations of conventional GIXRD analysis for phase identification in such disordered systems or/and by the limited amount of α - TiO_2 in the *as-grown* films. In fact, Nakamura et al. [11] also reported an annealing temperature of 300 °C for anatase formation although, in order to attain so low temperatures, they had to produce very uniform α - TiO_2 films.

The relevance of the starting conditions before annealing can also be highlighted from the present analysis. For example, nc -rutile-rich films are quite stable upon annealing. On the contrary, α - TiO_2 -containing films evolve towards nc -anatase and nc -rutile phase mixtures by the transformation of initial α - TiO_2 regions into nc -anatase. This transformation takes place at ~300 °C but a further annealing step at 450 °C results in the preferential promotion of either nc -anatase or nc -rutile phases for low and high nc -rutile contents in the initial film, respectively. This result is remarkable since the anatase to rutile phase transformation is not expected to occur at such low temperatures and it shows that crystallization is somehow driven by the phase composition. In this way, *as-grown* films can be designed to tune the desired phase mixture by post-annealing at different temperatures. This finding is relevant for practical applications due to the superior photocatalytic activity of mixed- with respect to single-phase TiO_2 materials [4].

Figure 4. 3D image ($400 \times 400 \text{ nm}^2$) of typical hollow structures before (a) and after (b) annealing obtained from Figure 3a and d, respectively, together with the corresponding line profiles (c). (d) Size histograms of hollow structures obtained from the AFM images before and after the annealing process from Figure 3a and d, respectively.

5. Conclusion

In conclusion, heterogeneous TiO₂ films grown on unheated substrates by RPMS have been annealed in vacuum up to 450 °C. The structural evolution of different phase mixtures has been assessed by means of XANES, GIXRD and AFM. It is found that *nc*-rutile-rich films are quite stable upon annealing whereas partial contents of *a*-TiO₂ evolve towards *nc*-anatase at 300 °C. The preferential growth of anatase from *a*-TiO₂ is attributed to a pre-existing anatase-like character. Further annealing up to 450 °C results in the preferential formation of *nc*-anatase or *nc*-rutile depending on the *as-grown* phase mixture.

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