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Structural impact of chromium incorporation in *as-grown* and flash-lamp-annealed sputter deposited titanium oxide films

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ABSTRACT

We address the impact of chromium (Cr) incorporation (<15 at.%) in the structure of titanium dioxide (TiO_2:Cr) films for *as-grown* and after *flash-lamp-annealing* (FLA) states. Samples were produced by DC magnetron sputtering on either unheated or heated (400 °C) substrates. Complementary medium- and local-order information was extracted by X-ray diffraction and absorption near-edge structure, respectively. TiO_2:Cr grown on unheated substrates are amorphous with the major contribution from Cr^{3+} and progressive formation of Cr^{6+} with Cr. On heated substrates, anatase phase is dominant for low Cr levels ($\leq$7 at.%) and the structure evolves with Cr towards a disordered mixed-oxide with rutile structure. By tuning the FLA energy density, customized (single or mixed) phase formation is achieved from (initially amorphous) Cr-free TiO_2. For amorphous TiO_2:Cr with low Cr ($\leq$7 at.%), FLA induces a short-range rutile structure but structural ordering is not observed at higher Cr levels. Nonetheless, FLA annihilates Cr^{6+} sites and promotes Cr^{4+}, which is associated to the mixed-oxide rutile. FLA also improves the pristine structure of anatase TiO_2:Cr grown on heated substrates. These results provide relevant information about the atomic structure of mixed oxides and the use of FLA for the synthesis of band-gap engineered TiO_2-based materials.

1. Introduction

Titania or titanium dioxide (TiO_2) is a functional wide band-gap semiconductor with variable electrical and optical properties which can be tuned intrinsically by the atomic structure (pure or mixed anatase/rutile phases and/or native defects) or, extrinsically, through doping with impurities [1]. One of the most interesting properties of TiO_2 relies on its photoactivity, which has been exploited in many applications such as photocatalysis, hydrogen production, pigments or solar cells [2]. However, TiO_2 photoactivity is limited to the ultraviolet (UV) region of the solar spectrum due to the relatively large band-gap of the different polymorphs (>3 eV) and, therefore, many efforts have been focused on band-gap narrowing of TiO_2 to achieve visible-light (VISL) response [2].

The most common approach to narrow the bandgap of TiO_2 is via doping [2]. Non-metal (anion) doping has been extensively studied to achieve narrow-gap TiO_2, especially for the particular case of nitrogen (N) doped TiO_2 [3]. However, the effective optical absorption of N-doped TiO_2 does not seem to be related to band-gap narrowing but, rather, to the formation of intragap localized states [4]. Moreover, another obstacle is related to the low thermodynamic solubility at substitutional sites [3] and, hence, the dopants excess would promote (undesirable) interstitial positions. This situation does not only compromise the effectiveness of band-gap narrowing but also provide recombination centres that are responsible for the loss of photogenerated electron-hole pairs [5]. Metal (cation) doping represents another alternative to increase VISL absorption (and it does so significantly) but it introduces severe structural distortions in the host matrix that result in a large number of defects acting as carrier recombination centres [3]. Among the most relevant cation dopants in TiO_2, Cr (TiO_2:Cr) has been widely studied due to the improved catalytic properties [6,7]

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but also for the eventual induced magnetic properties [8].

The introduction of large structural distortions in the host matrix can be normally overcome by processing or post-processing thermal treatments at moderate temperatures (~500 °C) [6]. Additionally, one could achieve further dopant activation or the enhancement of a desired structural phase. In this case, sub-second non-equilibrium thermal processing poses a great interest for practical applications as it may increase throughput and allow non-contact treatments (e.g., floating glass). Among such methods, millisecond-range and energetic heat pulses by flash-lamp annealing (FLA) [8] would allow a more precise treatment where only the near surface region is annealed and rapidly cooled. Therefore, one could actively control dopant diffusion and activation by tuning the annealing time.

In this work, we address the impact of Cr in TiO_2:Cr films and evaluate the structural evolution after *post-deposition* FLA. The aim of FLA is to promote phase formation and, eventually, do so in a customized way (selective anatase/rutile single or mixed phase structures). In particular, we pay special interest in enhancing Cr-containing anatase TiO_2 due to its implications in VISL photoactivity. For phase identification, the bonding structure around host and dopant sites is studied in detail by X-ray absorption near-edge structure (XANES) [9]. XANES provides short-range information of electronic states with elemental selectivity [10], making it suitable to study complex multielemental systems with either amorphous or crystalline structure. Particularly, XANES has been widely used to study TiO_2-based materials since it provides clear distinct spectral fingerprints of each polymorph and, hence, can be used for univocal phase identification [11] and even quantification [12]. XANES studies of TiO_2:Cr are relatively sparse, mostly probing with hard X-rays to extract the Ti and Cr K-edges [8,13–15]. Also, there is a lack of systematic XANES reports comprising a complete analysis of the three elemental edges or covering a broad range of compositions. Previously, we have used soft X-rays XANES to identify the spectral features related to different phases in *as-grown* and annealed TiO_2 [16,17] and, more recently, for chromium oxide films [18]. Here, the obtained results provide a framework for understanding the atomic structure of mixed oxides and the development of new scalable methods for the synthesis of band-gap engineered TiO_2–based materials.

2. Material and methods

2.1. Sample preparation

TiO_2:Cr films were grown on Si(100) substrates by DC reactive magnetron co-sputtering from 3″ Ti and Cr targets (99.99% purity). The cathodes were located at a distance of ~15 cm from the grounded substrates both with their axis at a relative angle of 30° with respect to the substrate normal. The base and working pressure were 10^{-4} and 0.3 Pa, respectively. The processing gas was a mixture of Ar (99.9995% purity grade) and O_2 (99.9995% purity grade) with a ratio 5/1 adjusted with individual mass flow controllers. For plasma generation, a DC signal with a power of 150 W was applied to the Ti cathode whereas the power at the Cr cathode, W_{Cr}, was varied from 0 to 50 W to produce films with different Cr contents. The depositions were carried out for 2 h on either unheated or heated substrates. In the latter case, a substrate temperature, T_s, of 400 °C was employed to promote crystal nucleation and growth.

Post-deposition FLA was performed for 3 or 20 ms at a continuous flow of N_2 (99.999 purity). The overall energy density was varied between 50 and 110 J/cm^2. This corresponds to a maximum surface temperature in the range of 600–1100 °C. Further details about the FLA system can be found in Ref. [19]. The heating and cooling rate of the oxide layer during millisecond FLA is in the range of 100 K/ms and 200 K/s, respectively.

2.2. Sample characterization

The composition of the layers was determined by Rutherford backscattering spectrometry (RBS). The measurements were performed with the 5 MV Cockroft-Walton tandetron at the *Centro de Microanálisis de Materiales* (CMAM) in Madrid (Spain) and the 2 MV Van-de-Graaff accelerator of the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) in Dresden (Germany) using 2.3 and 1.8 MeV He^+ probing beams, respectively. The beam impinged at normal-incidence with respect to the sample surface and the backscattered ions were detected with a silicon detector at a scattering angle of 165 and 170°, respectively. The RBS spectra were simulated with the SIMNRA code [20] to extract a quantitative analysis. The films thickness and optical properties were extracted from spectroscopic ellipsometry (SE) with a GES-5E (SOPRA©) device within the 1.5–5 eV spectral range. For data fitting, a Tauc-Lorentz (TL) model was considered since it can describe the dielectric function of amorphous or nanocrystalline semiconductors and dielectrics [21].

The microstructure of the samples was examined by glancing-angle XRD measurements using a D5000 (BRUKER AXS) diffractometer with Cu-K_α radiation ($\lambda = 1.5418$ Å). The data was collected at an incidence angle, ω, of 0.5° within the scattering range, 2θ, between 20 and 80°. Complementary, the local bonding structure with element sensitivity was studied by XANES with soft X-rays. The measurements were carried out at the dipole beamline PM4 using the SURICAT endstation at the synchrotron facility BESSY-II of Helmholtz-Zentrum Berlin (HZB), Germany. The data were acquired in the total electron yield (TEY) mode by recording the current drained to ground with the sample normal positioned parallel to the X-ray beam. The TEY intensity from the samples was normalized to the yield recorded simultaneously from a gold-covered grid located upstream the X-ray path.

3. Results and discussion

3.1. Thickness, composition and optical properties of as-grown films

Fig. 1(a) shows the experimental (dots) and fitted (solid lines) RBS spectra of *as-grown* TiO_2:Cr samples on unheated substrates at $W_{Cr} = 0$, 20 and 40 W. The regions corresponding to the different elements are labelled for identification and the individual contributions to the fitted spectra from Ti and Cr are also included (dotted lines). For the film constituents (O, Ti and Cr), the maximum energy of backscattered projectiles is given by the kinematic factor of the collision and corresponds to scattering events occurring at the surface. This energy increases with the atomic number of the scattering center. Events (counts) at lower energy correspond to collisions deeper from the surface since part of the projectile energy is lost in the way in and out through the sample. Note that due to the similar mass of Ti and Cr atoms there is a partial overlap of the corresponding signals. Nevertheless, Ti and Cr concentrations could be extracted reliably using SIMNRA simulations as shown in Fig. 1(a). The yield for each element is proportional to the convolution of its areal density and corresponding Rutherford cross-section (which is proportional to the square of the atomic number). Clearly, the Cr content in the films rises with W_{Cr} as the relative Ti/Cr atomic flux is reduced. There is also a broadening of the regions corresponding to the film elements since the deposited thickness also increases with the higher flux of Cr atoms. Note that the thickness increase also causes a shift in the onset of the Si substrate signal to lower energies (deeper regions).

Fig. 1(b) shows the quantitative compositional analysis for the