Nuclear Instruments and Methods in Physics Research B 268 (2010) 365–369

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

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

Elastic behaviour of titanium dioxide films on polyimide substrates studied by in situ tensile testing in a X-ray diffractometer

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ARTICLE INFO

Article history:
Received 30 May 2009
Received in revised form 28 July 2009
Available online 29 September 2009

Keywords:
Atomic Layer Deposition
Titanium oxide
Elastic properties
In situ tensile testing
X-ray diffraction

ABSTRACT

The development of new devices has created needs of precision, conformal at the atomic level deposition of high quality thin film materials. In the last years, Atomic Layer Deposition (ALD) has received much interest as a potential deposition method for advanced thin film structures. ALD presents several advantages: the film is excellently conformal and reproducible; the film thickness depends only on the number of reaction cycles, which makes the thickness control accurate and simple; the film can be deposited onto all kind of substrates. Because of the process slowness, layer thickness is generally less than 100 nm. This makes more difficult to study all characteristics of the coating. Thin layers deposited onto bulk substrates are generally in tensile or compressive stress state, which may significantly affect physical properties and possibly compromise their lifetime. To determine the residual stress it is mandatory to know the elastic constants that may also depend on the microstructure of the layers and thus the deposition process.

In this work, 2D X-ray diffraction (XRD^2) in combination with in situ tensile testing has been applied for the first time to measure elastic properties of TiO_2 anatase films obtained by ALD. Experimental conditions, the tensile stage being installed in a laboratory micro-diffractometer equipped with a 2D image-plate detector, and the information that can be extracted from 2D diffraction patterns will be discussed. Based on these preliminary results, synchrotron radiation beam time has been allocated to study elastic properties of these thin films. The advantages and disadvantages of the proposed laboratory equipment, with respect to the synchrotron beam lines, are discussed.

1. Introduction

In recent years, Atomic Layer Deposition (ALD) technique has been rapidly developed, thanks to its attractive characteristics: ALD is a chemical deposition technique based on sequential self-terminating gas–solid reactions suitable for the synthesis of ultra-thin films with thickness beneath the nanometer [1]. ALD film growth is self-limited and based on surface reactions, which makes achieving atomic scale deposition control possible. While the Chemical Vapour Deposition (CVD) and the Physical Vapour Deposition (PVD) provide that the precursors are pulsed at the same time, ALD reaction is split into two half-reactions, keeping the precursor materials separated during the reaction. ALD permits to deposit many oxides at very low temperature (also down to 100 °C) in comparison with the other chemical deposition techniques, allowing for the deposition on polymeric substrates.

Many metal oxides materials have been deposited by means of ALD. In particular, titanium dioxide (TiO_2) has interesting applications in many research fields owing to its attractive physicochemical properties. Currently TiO_2 thin films are employed in optics, as filters and anti-reflection coatings, in catalysis as photosensitive layers and solar cells, in medicine, as biocompatible coatings for biomaterials, and in electronics. Recently TiO_2 films were also employed successfully as high *k* gate oxide semiconductor manufacturing processes and as constituent of important multi-component oxides for random access memory (ST, BST, PZT).

The deposition of TiO_2 films is currently obtained by ALD through many precursors. The employment of this technique is very attractive in all the applications where high uniformity of the thickness and high density are requested. Titanium tetrachloride ($TiCl_4$) in association with water was widely employed, but the corrosive nature of the reaction by HCl product is considered a drawback [2]. Other precursors, like titanium isopropoxide of the alkoxide group ($Ti(OCH(CH_3)_2)_4$) or tetrakis dimethylamido titanium (TDMAT) ($Ti(N(CH_3)_2)_4$) of the metal amide group were

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doi:10.1016/j.nimb.2009.09.034

tested [3]. TDMAT presents a high reactivity with water also at low temperature and also a higher growth per cycle (GPC) with respect to the isopropoxide. ALD process using TDMAT and water as precursors enables to obtain TiO_2 films with excellent uniformity and sub-nanometric control on thickness [4]. Even if a large number of papers have been devoted to the synthesis and functional properties of films deposited by means of ALD, mechanical properties have not been properly investigated.

X-ray diffraction (XRD) is a well-known non-destructive technique currently used to determine the level of residual stresses in crystalline phases wherein the atomic planes are used as strain gauges: if elastic constants of the material are known or have been experimentally determined, residual stresses can then be calculated in the hypothesis of elastic regime [5]. XRD shows several advantages: it is phase selective, non-destructive, and allows determining both residual stress and microstructure of the diffracting phases.

Because of the elastic constants of thin films may be different from those of corresponding bulk material, it is fundamental to experimentally determine these (mainly the macroscopic Young modulus E) for correctly characterizing the materials. To reach this goal, in situ X-ray stress/strain analysis methods have been developed and applied extensively in the last decade [6–8]: combining an X-ray diffractometer with a tensile tester, it is possible to determine X-ray elastic constants (in particular the Poisson ratio and the Young modulus) of each diffracting phase in a thin film/substrate system [9].

Because of the small amount of matter available to perform XRD measurements (the thickness of thin film can be thinner than 100 nm), these experiments are usually performed at beam lines available at synchrotron facilities. Synchrotron radiation provides many advantages, related also to the possibility of tuning beam wavelength, but, essentially, X-ray intensity is the fundamental characteristic that makes synchrotron radiation crucial for some experiments. However, in recent years, the use of an image-plate detector allows to obtain a significant signal also from small amount of material, with conventional X-ray sources. It has a large dynamical range that makes possible to vary the image exposure without overloading the detector. The use of an image-plate detector allows also evaluating the microstructure of the crystalline phases. To calculate the strain by XRD measurements, it is necessary to collect diffraction peaks for several Ψ angles (Ψ is the angle between the normal to investigated diffracting planes and the normal to the sample surface) for each applied load. Thus, for this kind of experiment, by using point detectors, long data collection times are also required with synchrotron radiation.

The aim of this paper is to present a laboratory experimental configuration to perform mechanical testing of thin films materials. Even if similar experiments were already performed at synchrotron [10], only XRD measurements with conventional punctual detectors have been collected in the past in laboratory. We report the first study of mechanical properties of a TiO_2 thin film, deposited by means of ALD, studied with in situ XRD measurements during an applied load. According to this method, the film was deposited onto a compliant substrate (Kapton HN), which was mechanically strained by a tensile tester. During the in situ tensile test, XRD measurements were performed to evaluate the resulting deformation.

2. Experimental procedure

TiO_2 was deposited by Atomic Layer Deposition (Savannah 100 of the Cambridge Nanotech Inc., MA), using TDMAT (tetrakis(dimethylamido)titanium), Sigma–Aldrich, (Germany) as titanium source and milliQ water as oxygen source. The deposition temperature and pressure were, respectively, 90 °C and 0.5 Torr. TDMAT (99.999%) and H_2O was evaporated from stainless steel reservoirs held, respectively, at 80 °C and at room temperature, and led into the reactor through solenoid valves. Nitrogen was used as a precursor carrier and purge gas. The processing cycle consisted of a TDMAT pulse of 0.1 s, a 10 s of purge time, a 0.1 s pulse of water vapour and 10 s of purge time. The deposition rate was 0.0667 nm per cycle. As-prepared films are amorphous; the sample was then crystallized in oven at 300 °C and in air during 36 h. The physical properties of Kapton HN substrates are not affected by the annealing for temperature below the vitreous transition temperature which appears between 360 and 410 °C.

The XRD^2 images for phase identification and stress analysis were collected by a D/max-RAPID Rigaku micro-diffractometer with CuKα radiation. The use of a two-dimensional detector for stress measurements is now a well-known method [11].

This system is equipped with a cylindrical imaging plate (IP) detector, which can record 2D X-ray diffraction data in angular diffraction ranges from $-45°$ to $160°$ (2θ) horizontally and $\pm45°$ (2θ) vertically with respect to the direct beam position (0°). The irradiated area can be chosen by using collimators of diameters ranging from 800 down to 10 μm. In the experiments, the diameter of the collimator is 300 μm.

The sample was mounted on a commercially available Deben tensile module with a 20 N force sensor. The testing module was inserted in the Rigaku micro-diffractometer (see Fig. 1) inclined by an angle α equal to 45° with respect to the vertical. In the same figure, the diffractometer (D) and the sample (S) reference systems are reported considering a recently proposed general approach [12]. In this configuration, with the sample holder tilted at 45°, the angles Ψ and ϕ, which are usually considered to define the diffraction vector q direction, are given by the following equations:

$$\psi = ar\cos\left(\frac{\sin\theta\sin\omega}{\sqrt{2}} + \frac{\cos\theta\sin\chi}{\sqrt{2}} + \frac{\cos\theta\cos\omega\cos\chi}{\sqrt{2}}\right) \quad (1)$$

$$\phi = ar\cos\left(\frac{\sin\theta\cos\omega - \sin\omega\cos\theta\cos\chi}{\sin\psi}\right) \quad (2)$$

Considering the curvature of the image-plate, the χ angle, defining the rotation on the diffraction cone, can be related to the β angle along the Debye ring (see Fig. 2) by the following relation:

$$\beta = \left(\sqrt{tg^2(2\theta) - tg^2 k}\right)\frac{1}{k}\cos k \quad (3)$$

where $k = arctg(tg(2\theta)\cos\chi)$.

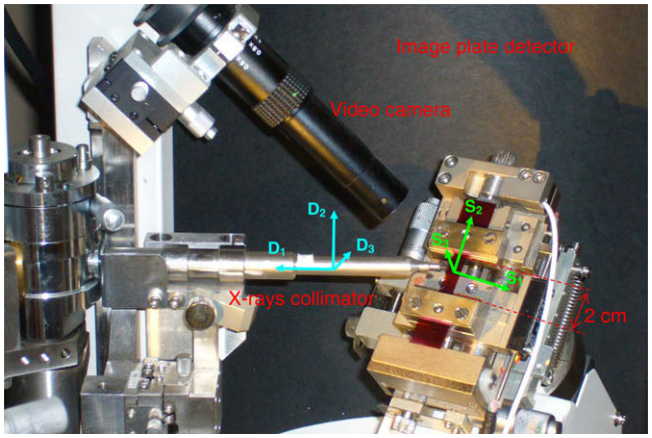

Fig. 1. D/max RAPID apparatus, with the Deben testing module inserted at the centre of the diffractometer. The diffractometer (D) and the sample (S) reference systems are also reported.

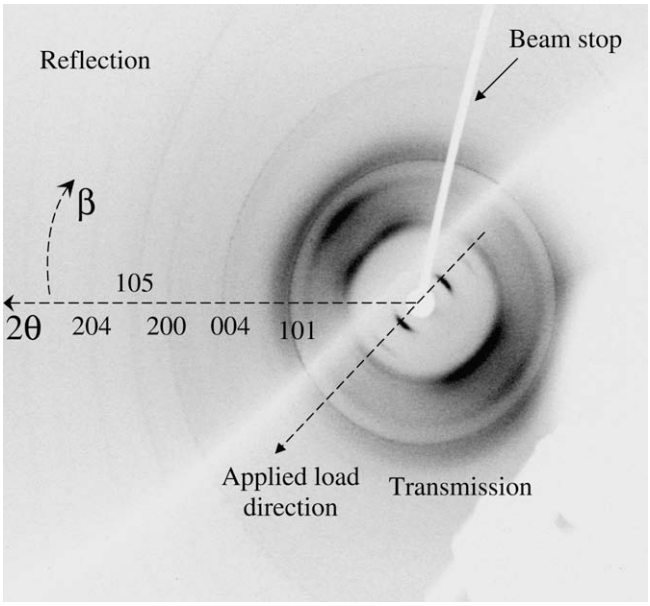

Fig. 2. XRD^2 image collected for sample in the unloaded state. The diffraction peaks identification of anatase is reported. 2θ and β angles, which give the direction of integration on the XRD^2 image, are also shown. The white area that is inclined by an angle of 45° in the 2D image is due to the sample positioning in the diffractometer. Sample shadow separates transmitted and reflected diffracted intensities.

By fixing the ω angle value to 10° for incident X-rays, we can calculate from the β angle along the Debye ring the corresponding Ψ angle. Thus, the 2θ, obtained from the integration of a specific area of the Debye ring, gives the distance d_{hkl} in the corresponding direction and allow the application of d-sin$^2\Psi$ technique for stress calculation [11,12].

The thin film/substrate composite system is submitted to an uni-axial tensile load, and the resulting lattice strains are measured by XRD.

Sample drift may affect strain measurements accuracy; this effect occurs mainly at low applied strain during the set-up of the dogbone sample. For this reason, only measurements with an applied load higher than 5 N were considered for this first experiment (5.6 and 7.1 N) [10].

Let us notice that XRD synchrotron experiments were also collected very recently on the same TiO_2 samples at Diffabs beamline (Soleil, France). The results and discussion related to the elastic behaviour and the residual stress state of TiO_2 samples, treated for different times at 300 °C, are under investigation and will be reported in forthcoming paper [14].

3. Results and discussion

Fig. 2 displays a typical XRD^2 image of the TiO_2 film. This diffraction pattern was collected on sample before applying loads. We can clearly see all the Debye rings, belonging to the anatase phase [15]. Large diffused halos near the centre of the image are due to the Kapton substrate, partially crystalline. The white area that is inclined by an angle of 45° in the 2D image is due to the sample positioning. Sample shadow separates transmitted and reflected diffracted intensities: the signal, collected in the lower part of the image corresponds to the transmission mode while the signal in the higher part of the figure is related to reflection mode. This experiment, combining both reflection and transmission conditions, is called reflection–transmission mode, as one part of the signal is also studied in transmission [10]; this was possible thanks to low thickness of studied films and the X-ray transparency of the Kapton substrate.

Fig. 2 shows that the intensity distribution along diffraction rings attributed to the anatase phase is almost constant (excluding the white area, due to the sample shadow), indicating that the film is polycrystalline with no preferred crystallographic orientation (isotropic texture). This was confirmed by omega-scans performed on the same samples at Synchrotron Soleil, France. For each applied load, the 2D image was collected similar to the one shown in Fig. 2.

Integrating the intensities of 2D images along the rings allows to obtain 2θ conventional XRD patterns that can be analysed by powder diffraction analysis software. For example, XRD 1D pattern can be obtained by integrating the entire image over 360°. In this manner, an XRD pattern, where microstructural informations are mediated in all scattered directions, is obtained: for example preferred orientation effects can be overcome [16]. To evaluate the strain due to an external load applied along one direction, the integration of 2D image must be performed at different β angles (see Fig. 2). When the sample is stress-free, the peak position along one single Debye ring is the same whatever the β angle is. On the contrary, if the peak position is dependent of β direction, the presence of strain is then detected and can be measured. Indeed, a distortion of a Debye ring can be associated to a different deformation of a single crystallographic plane, considering differently Ψ-oriented grains. In the case of an applied load (along one direction) strain values can be calculated from the difference between the deformed shapes of Debye rings, with respect to the reference shape (unloaded state). As a result, lateral strain values may be positive in some directions (e.g. along the tensile axis) and negative in the others (e.g. in the direction perpendicular to the loading axis). In order to study the Debye rings deformation produced by a stress, a new approach (DRAST) was recently proposed [13]. In summary, the d_Ψ values obtained from the analysis of XRD integrated patterns can be directly used in the d-sin$^2\Psi$ plot to calculate the stress with the classical method. For the unloaded sample, a slight deformation of the (1 0 1) Debye ring was found, due to the presence of residual stress. However, only the applied stress is important for the analysis of elastic behaviour of the thin film: elastic modulus is not influenced by the presence of eventual residual stress.

Fig. 3 shows the strain calculated from the (1 0 1) peak position shift, by the application of the DRAST method for two applied loads. XRD and, more generally, all diffraction methods, measure strain by considering the change in the d-spacing in a crystalline sample, with respect to an "un-strained" state. The most common difficulty in the strain measurement refers to the incertitude in the knowledge of the strain-free d-spacing reference, the so called d_0 spacing. Because thin film structure can depend on the deposition technique, this parameter is generally not known. In the present case, thanks to the synchrotron study of several TiO_2 samples deposited by ALD and treated at 300 °C for different times [14], results indicate that the lattice parameter values of anatase are close to those of bulk. The first interesting result that we can see in Fig. 3 is that a large sin$^2\Psi$ region (from 0 to 1) is available with only a single XRD^2 measurement. This is very important because, even if synchrotron XRD experiments can be realised with high intensity radiation, if only punctual detectors are available, very often the maximum sin$^2\Psi$ values can only reach 0.8 (or less). The second interesting result is that, performing an integration in 2θ direction, at some selected β angles (then for specific Ψ-oriented planes), the operator can decide the numbers of Ψ angles for the d calculation: during the measurement all Debye rings are collected in different directions, then it is possible to decide (and eventually change), during the data elaboration, the number of directions (β) along those to perform 2θ integrations. This is a very important improvement, with respect to punctual measurement. In the present case, for example, a large numbers of d values have been evaluated in the reflection part of the pattern, because of the higher intensities.

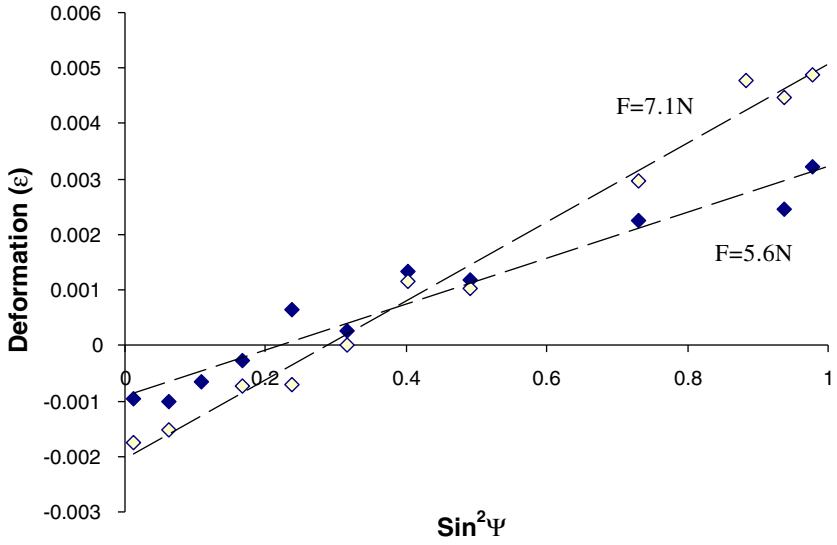

Fig. 3. $\ln(1/\sin\theta_{101})$–$\sin^2\Psi$ values calculated for the 1 0 1 peak by the application of the DRAST method [13] for two applied load states.

In Fig. 2 we can see, that, as expected, the deformation increases with $\sin^2\Psi$, i.e. (1 0 1) planes perpendicular to the direction of the applied load present a greater *d*-spacing value (dilatation), while the planes parallel to the applied load present a smaller *d*-spacing value (compression). It is very important to highlight that we have access to maximum deformation because we are considering planes in two orthogonal directions, i.e. planes that show maximum and minimum *d*-spacing values. This facilitates the measurements of applied deformation, because the largest differences in the (1 0 1) planes distance can be investigated. On the contrary, considering the same measurements performed at synchrotron beamline in the reflexion geometry, the maximum deformation cannot be detected [14] because of the restricted availability of the $\sin^2\Psi$ up to only 0.8 (and moreoften 0.6). The ratio between the maximum strain values, corresponding to the directions parallel and perpendicular to the tensile axis, allowed calculating, for any applied load, a Poisson ratio of about 0.3, very close to that of bulk.

Thanks to the availability of several Ψ angles, either compressive or tensile strains were measured, and, from the fit of curves in Fig. 3, it is possible to calculate the deformation corresponding to planes perpendicular to the applied loads ($\Psi = 90°$). The values obtained when extrapolating ε for $\Psi = 90°$ correspond to experimental results, indicating great reliability of the obtained data. These values are plotted in Fig. 4, where the applied loads axis are reported as a function of the deformations along the applied load direction. In the unloaded state, a residual strain in compression was found in the film. The points show a linear trend indicating that the mechanical testing corresponds to the elastic regime. To model elastic properties of the film, we have to remember that there is a difference between the macroscopic strain ("mechanical strain") and a lattice strain, that depends on intergranular interactions: the last one can be determined by XRD peak shift, while the overall stress is determined by the load cell. To extract the relationship between in-grain strains and mechanical stresses (macrostress), it is necessary to know the average elastic behaviour of the crystals, which results from averaging the elastic properties over the volume under study, where elastic grain interaction occurs [17]. The mechanical behaviour of a polycrystalline thin film is determined by the distribution of the crystallite orientations within the thin film and the grain interaction. If the orientations are randomly distributed, the thin film is quasi-isotropic, i.e., the

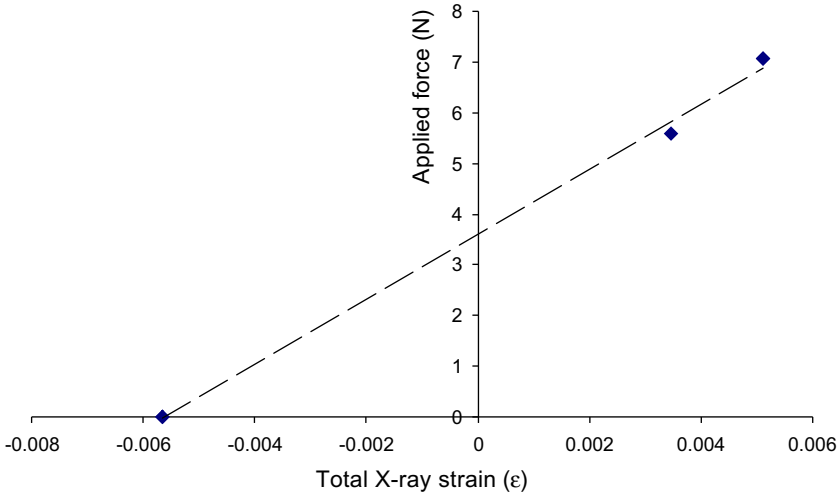

Fig. 4. Evolution of the applied load as a function of the applied strain.

average mechanical properties of the mechanically macroscopically isotropic thin film are the same along all directions. Then, XRD strain measurements, during applied load, may be performed following only one diffraction peak. Moreover it should be better to evaluate the response of several crystallographic planes, to verify this. 2D detectors allow collecting simultaneously all Bragg peaks, but unfortunately, because of the great contribution of the substrate, in the present experiment it was very difficult to obtain satisfactory fits of the reflections at higher angles than 25°. We are currently working for modellization of the sample system to extract information about elastic modulus of the film. Because of the thermal annealing, the elastic modulus of Kapton may be changed, with respect to tabulated one. Indeed, a first calculation shows that a lower young modulus of Kapton must be considered for getting a reasonable young modulus value for the film. We planned to measure this value for different annealing times by using an optical system for following in situ the evolution of strain during loading. Finally, deposition of TiO_2 by ALD is done on both substrate surfaces; this must be considered in the mechanical modelling of the system.

4. Conclusions

Based on the XRD^2 data, an alternative X-ray diffraction method is proposed for mechanical properties measurement of thin films with a laboratory instrument. The mentioned technique can implement the evaluation of the mechanical properties within short time, as only one measurement and the analysis of single Debye ring are needed, for each applied load. The main advantages of this method are:

- very fast measurement because only one X-ray diffraction pattern recording is needed, for each applied load;
- a large $\sin^2\Psi$ region is accessible with only one single measurement;
- very good resolution in the d calculation, as a function of different Ψ can be obtained;
- the sample and the beam are fixed during the measurement, thus the statistical errors introduced by rotations of diffractometer mechanical components are absent.

The use of a micro-beam allows to study in detail elastic properties of materials, with not planar surfaces or samples with complex geometries.

Despite all the above mentioned advantages, this method shows one main disadvantage, with respect to synchrotron analysis: diffraction rings show weak intensities, then only low angle diffraction peaks may be detected, making possible to study only some crystallographic directions. As most crystalline materials are heterogeneous from the mechanical point of view, X-rays strain measurements should be carried out for several diffracting planes, i.e. for different Bragg peaks, to obtain reliable results. In addition, for better precision of stress measurement, Debye ring with higher 2θ would improve the analysis for getting higher accuracy in peak position calculation.

However, the proposed laboratory method is very interesting and seems to produce reliable results. The obtained strains correspond to those extracted, for the same sample and the same loading conditions, at synchrotron beamlines [14].

Some improvements of the proposed experiments will be (1) to correct the sample alignment after any loading; (2) to use a standard powder (stress-free) to verify, for any 2D image collection, the sample and/or instrument misalignments; (3) the coupling of XRD measurements with optical deformation measurements to monitor the total strain (elastic and plastic); (4) the use of a soft substrate, possibly without any contribution in XRD pattern.

Moreover, the introduction of new accessories, as for example poly-capillary, to increase the intensity of incident radiation, may drastically reduce the difference in the diffracting signal between synchrotron and laboratory X-ray sources.

A more comprehensive study about residual stress of anatase thin films obtained through ALD technique after thermal annealing at 300 °C for several hours (performed with Synchrotron radiation) will be discussed in more detail in another work [14].

Acknowledgements

This work was partially supported by Soleil Synchrotron: proposal number 20080450 February 2009 and by Galileo project 2008 under contract PHC-17602YC (France).

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