DOI 10.5162/IMCS2012/2.4.1

Mesoporous TiO_2 Sensitive Films for Love Wave Humidity Detection: Origins of Stress Release Induced by Sorption

Laurianne Blanc[1], Angelique Tetelin[1], Cédric Boissière[2], Corinne Dejous[1], Dominique Rebière[1]
[1] Université de Bordeaux, Laboratoire IMS, Bordeaux, France,
angelique.tetelin@ims-bordeaux.fr
[2] Université Pierre et Marie Curie, Laboratoire LCMCP, Paris, France

Abstract:

Mesoporous titania-coated acoustic humidity sensors show strongly non-linear responses at high exposure, not fully explained by water condensation. Three possible sources of stresses that alter the film mechanical behavior have been considered in this work: increased swelling, unreleased sol-gel stress, and capillary contraction. If the latter is linked to the film porous nature and cannot be avoided, the two other are mainly side effects of the specific fabrication process developed for the deposition of mesoporous oxides on quartz piezoelectric substrates: partial crystallization and a large pore size distribution.

Key words: Love wave sensors, Humidity sensors, Mesoporous titania sensitive film, Thin film characterization.

Introduction

Mesoporous oxides are attractive to design mass-sensitive sensors with increased sensitivities thanks to large specific surface areas (typically over 100 $m^2.cm^{-3}$), and wide structuring and functionalizing possibilities [1]. They are defined as porous oxides whose pore diameter is in the 2–50 nm range. More specifically, Love wave sensors have been developed for highly sensitive volatile organic compounds detection, with mesoporous silica (SiO_2) and mesoporous titania (TiO_2) coatings, fabricated through the evaporation-induced-self-assembly (EISA) technique [2,3].

Mesoporous TiO_2 thin films (100-120 nm) were previously considered as sensitive coatings for humidity detection, and because their shear modulus was not a constant parameter, the usual wave propagation models did not fit experiments [4]. A dedicated experimental set-up was then developed for the characterization of the film shear modulus under humidity exposure, based on the combination of environmental ellipsometric porosimetry (EEP, [5]) with a Love wave platform operated at 117 MHz and a dedicated numerical model for data recovery [4]. Previous work showed that water sorption has a strong influence on the "apparent" shear modulus of the sensitive film filled with vapour, measurable from a macro-scale point of view for the whole "sorbed vapour – mesoporous oxide" matrix [4].

In this work, we discuss new insights on possible explanations of the physical phenomena induced by sorption from a nano-scale point of view. The experimental setup combining EEP with the Love wave device and corresponding modelling are described after a few details on the acoustic platform and on the deposited film to characterize. Then the study of the recorded shear modulus, thickness and pore size distribution leads to three possible explanations for the mechanical behavior of the considered film: capillary contraction, swelling and remaining sol-gel stress.

Experimental Setup: Love Waves and Environmental Ellipsometric Porosimetry

Mesoporous titania films were prepared through the EISA process with block copolymer F127 structuring agent (amphiphilic $(PEO)_{100}$-$(PPO)_{70}$-$(PEO)_{100}$) [1]. This process enables to control the structural properties of the film, such as the porosity and the pore size. The titania precursor solution contained 20.66 g ethanol, 1.45 g of acid water (pH 2M/36), 0.56 g of F127 and 3.347 g of a solution containing a ratio of one $TiCl_4$ molecule for five ethanol molecules.

The film to characterize was deposited on the acoustic path of a Love wave device, represented in Fig. 1. It consists in a 500 μm AT-cut quartz piezoelectric substrate, on which Titanium-Gold interdigital transducers (IDT) were deposited as 44 split finger pairs with a 40 μm periodicity (or wavelength λ).

DOI 10.5162/IMCS2012/2.4.1

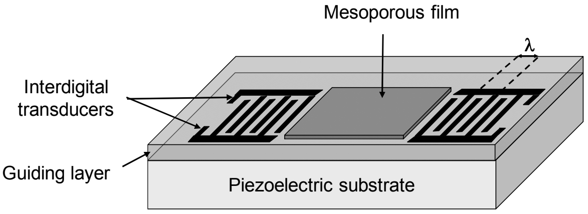

Fig. 1. Love wave platform.

The IDT aperture is 39*λ*, and the acoustic path between both transducers is 164*λ* for a center-to-center length of 210*λ*. A 4.5 µm dense silicon dioxide guiding layer was then deposited through plasma-enhanced-chemical-vapor-deposition. The love wave “device” becomes the Love wave “platform” when it is inserted in the feedback loop of a radiofrequency oscillator, for frequency shift measurements from a synchronous frequency close to 117 MHz. More details on the electronic circuit are available in [3].

The deposition process of the mesoporous thin film, compatible with the Love wave platform, is presented in details in [2]. The film was deposited by spin- or dip-coating while masking the transducers. The thermal cure process was designed in order not to be harmful to the piezoelectric substrate. The considered films showed porosities close to 25%, and ellipsoidal-shaped pores with an average pore size of 5.5 nm × 7.5 nm, determined through EEP.

The experimental set-up combining EEP with the Love wave platform for the shear modulus assessment is represented in Fig. 2. The EEP system comprises a spectroscopic ellipsometer (SOPRA Co.) and a pressure controlled chamber. Tests were carried out under an air flow of adjustable relative humidity (RH) level at 18°C, exposing the device to full adsorption-desorption cycles. The computers record the thickness and the refractive index provided by the EEP system on the one hand, and the frequency shifts provided by the oscillator circuit on the other hand.

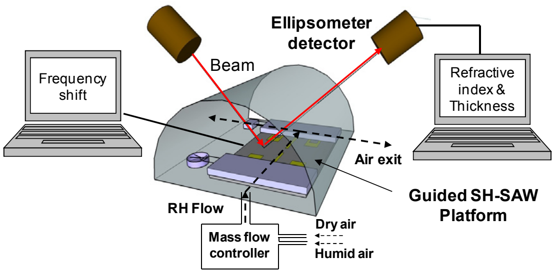

Fig. 2. Experimental setup combining EEP (environmental ellipsometric porosimetry) with the Love wave platform.

Model for the shear modulus extraction

The numerical model implemented for the extraction of the shear modulus from the experimental frequency shifts is described in details in [4]. Frequency shifts are directly linked to phase velocity shifts that are modeled using the transfer matrix method [6], which solves the propagation equations in the considered multilayered structure. A simplex curve fitting procedure then computes the shear modulus value (C_{44}) for which the model fits experiments.

The modeling approach is represented in Fig. 3. EEP provides the Love wave platform with the thickness, the porosity, and the sorbed water volume. The density of the film filled with vapor is calculated from the measured sorbed water volumes with a simple effective medium approximation [4].

Capillary Contraction

During adsorption, the strong re-increasing of the shear modulus in the condensation zone (shown in Fig. 4) suggests a contraction. The film is supposed to shrink because of the capillary forces induced by the water films growing on the surface of the pores and pulling on the pore walls, due to the strong affinity of water for itself (Fig. 5). The shear modulus variations are not linear because the pores have different sizes within the film (Fig. 6) and thus do not undergo capillary condensation at the same time: the smallest pores are filled first.

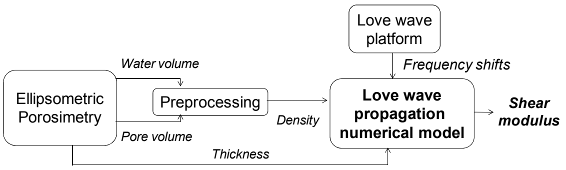

Fig. 3. Modelling approach.

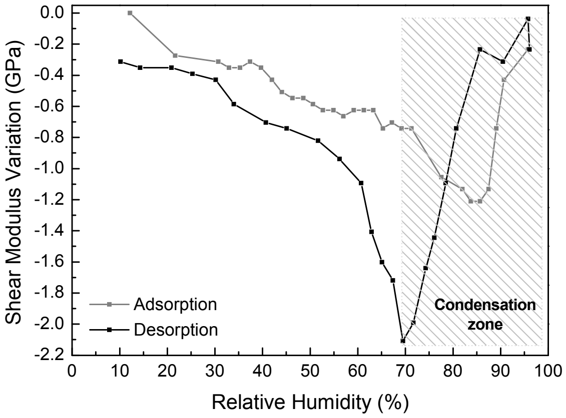

Fig. 4. Shear modulus variation of the TiO_2 thin film versus the relative humidity level at 18°C [4].

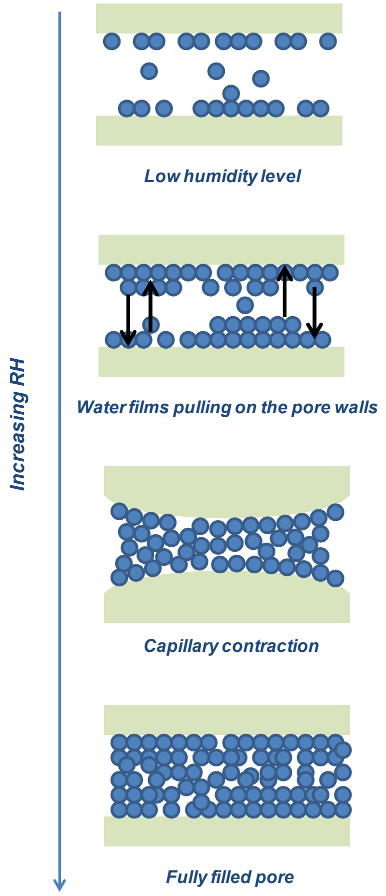

Fig. 5. Capillary contraction phenomenon.

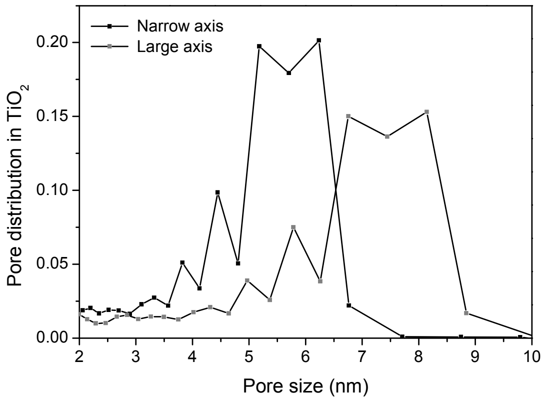

Fig. 6. Pore size distribution in the considered TiO_2 mesoporous film [4].

The differences between adsorption and desorption are explained by the “ink-bottle” shape of the ellipsoidal pores, the “bottleneck”-shaped openings delay the release of water.

However, capillary contraction should not be considered as the sole mechanical phenomenon occurring in the film, as it is only visible on the thickness variations induced by sorption as an inflection point in the course of the swelling process, when capillary condensation occurs (Fig. 7).

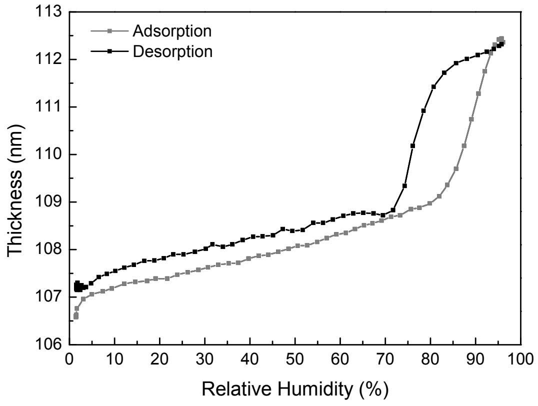

Fig. 7. Thickness variations of the TiO_2 thin film versus the relative humidity level (provided by EEP alone) [4].

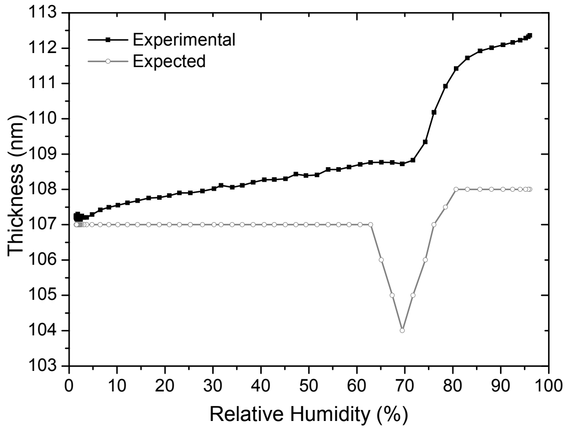

Fig. 8. Thickness variations of the TiO_2 thin film versus the relative humidity level - experimental and theoretical for a fully crystallized film.

Swelling and Sol-Gel Stress

For low RH levels, it was quite expected that the film should expand as a result of the filling of the smallest pores first, but afterwards the film continuously expands as the RH level increases, and does not fit the expected pattern suggested by the shear modulus variations, that is, a constant up to the capillary condensation threshold followed by capillary contraction and then stress release, as represented on Fig. 8. Capillary contraction seems to be shadowed, on the one hand, by overall condensation (a water multilayer grows on the surface of the film); and on the other hand by the presence of grain boundaries in the mesoporous matrix, which swell during sorption.

Incomplete crystallization should also explain the continuous film swelling through the presence of grain boundaries. The original fabrication process of mesoporous films required high temperature gradients that could have damaged the considered acoustic platform. It had to be modified to a longer cure process with lower temperatures [2], which has two major consequences: the film is probably not fully crystallized and the pore size distribution span is larger than expected (Fig. 6) [7]. Before crystallization, the amorphous film is strongly stressed by the substrate, and this stress is usually released through full crystallization. Incomplete crystallization is thus responsible for an additional remaining “sol-gel stress” perpendicular to the substrate. Moreover, the large thermal expansion coefficient of the quartz substrate tends to delay film crystallization [8].

Conclusion

The mechanical stress induced by humidity sorption in mesoporous titania sensitive films has been studied thanks to a Love wave platform operated at 117 MHz and environmental ellipsometric porosimetry, through the measurement of the shear modulus, the thickness and the pore size distribution of the film. The results were presented for 100 nm thin mesoporous titanium dioxide films with 25% porosity. Three possible sources of stresses have been considered: capillary contraction, swelling induced by porous filling, and remaining sol-gel stress. Capillary contraction is due to the nature of the porous film whereas swelling is a consequence of the specific fabrication technique for mesoporous oxides on quartz piezoelectric substrates. The alteration of the cure process induces a larger pore size distribution and the presence of grain boundaries. Remaining sol-gel stress is caused by partial crystallization, that is, from the process as well. Improvements could thus come from modifying the fabrication process or upgrading numerical models for data recovery. Moreover, thoroughly controlling crystallization and pore size may lead to better overall linearity or enhanced linearity in specific humidity ranges for some specific applications.

References

[1] C. Sanchez, C. Boissiere, D. Grosso, C. Laberty, L. Nicole, Design, synthesis and properties of inorganic and hybrid thin films having periodically organized nanoporosity, *Chemistry of Materials* 20, 682–737 (2008) ; doi : 10.1021/cm702100t

[2] G. Tortissier, L. Blanc, A. Tetelin, C. Zimmermann, J-L. Lachaud, C. Boissière, C. Sanchez, C. Dejous, D. Rebière, Mesoporous coated films on Love wave acoustic devices for gas detection, *Sensor Letters* 7, 1-5 (2009) ; doi : 10.1166/sl.2009.1185.

[3] L. Blanc, A. Tetelin, C. Boissière, G. Tortissier, J-L. Lachaud, C. Dejous, D. Rebière, Mesostructured TiO_2 and SiO_2 as high specific surface area coatings for Love wave gas sensors, *Sensor Letters* 9, 1-4 (2011); doi: 10.1166/sl.2011.1611

[4] A. Tetelin, L. Blanc, G. Tortissier, C. Boissière, C. Dejous, D. Rebière, Guided SH-SAW Characterization of Elasticity Variations of Mesoporous TiO_2 Sensitive Films during Humidity Sorption, *Proc. of 2010 IEEE Sensors Conference, Waikoloa* HI (USA), Nov. 1-4 2010, 2136-2140; doi: 978-1-4244-8168-2/10

[5] C. Boissiere, D. Grosso, S. Lepoutre, L. Nicole, A. Brunet Bruneau, C. Sanchez, Porosity and mechanical properties of mesoporous thin films assessed by environmental ellipsometric porosimetry, *Langmuir* 21, 12362–12371 (2005); doi: 10.1021/la050981z

[6] E. L. Adler, Matrix methods applied to acoustic waves in multilayers, *IEEE Trans. UFFC* 37, 485–490 (1990)

[7] E. Lancelle-Beltran, P. Prené, C. Boscher, P. Belleville, P. Buvat, S. Lambert, F. Guillet, C. Boissière, D. Grosso, C. Sanchez, Nanostructured hybrid solar cells based on self-assembled mesoporous titania thin films, *Chemistry of Materials* 18, 6152-6156 (2006); doi: 10.1021/cm060925z

[8] J. D. Bass, D. Grosso, C. Boissière, C. Sanchez, Pyrolysis, Crystallization, and Sintering of Mesostructured Titania Thin Films Assessed by in Situ Thermal Ellipsometry, *Journal of the American Chemical Society* 130, 7882-7897 (2008); doi: 10.1021/ja078140