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Intrinsic defects and their influence on the chemical and optical properties of TiO_{2-x} films

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ABSTRACT

In this work, TiO_2 films produced by rf sputtering of a TiO_2 target, in argon and argon-oxygen plasmas were studied. The oxygen content in the feed gas was varied in a range of 3% – 20%. The chemical composition and structure of films were characterized by Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction. Important information about the intrinsic defects of the films and their effects on the optical properties as well as a scheme of the energy band structure of the films could be derived from a combined use of optical spectroscopy and XPS.

Keywords: TiO_2 films, optical properties, electronic properties, defects, sputtering

PACS: 68.55.ag; 68.55.Ln; 78.20.-e; 78.20.Ci; 78.40.-q; 81.05.Gc; 81.15.Cd

I- Introduction

Titanium oxide is an important material widely applied to many fields such as water electrolysis and photocatalysis [1,2], photovoltaics where it is employed as the active part of the cells for solar energy conversion [3] and transparent conductive oxides for the production of transparent electrodes equivalent to those of indium tin oxide (ITO) [4-6]. The latter enters the structure of new generation solar cells, organic light emitting devices (OLEDs) and flat panel displays; replacing ITO by a cheaper and more abundant TiO_2 will lower the cost of devices. When doped with rare earth, TiO_2 can be used to increase the silicon-based solar cell efficiency by modifying the solar radiation, through the conversion of high energy photons to other photons with a lower energy, more useful for silicon absorption [7,8].

A common feature unifies all these application fields, which is linked to the defects in TiO_2 structure which strongly determine its electronic, electrical, optical properties and photo-activity. A great amount of work, mainly theoretical, has been done to investigate the nature, the energetics, the chemistry, the creation, the relaxation and the role of the defects states in

titania's band gap [9-14]. These studies treated the crystalline phases, bulk rutile or anatase, of TiO_2 , but very few works have been reported on defect peculiarities in titanium oxide films. In this work, a joint study was conducted to determine the relevant optical, electronic and defect properties of thin TiO_{2-x} films produced by RF sputtering of a TiO_2 target. Density and stoichiometry of films deposited in various Ar- O_2 mixtures and plasma conditions were derived from x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS). The different phases of TiO_2 were determined using X-ray diffraction (XRD). The films reflectance spectra have been measured in the visible range. The optical indices and energy gap of the material have been extracted; their interpretation allowed to define an energy band scheme and the gap states.

II- Experimental details

II.1 The sample preparation

A series of films has been prepared by RF sputtering under a self-bias voltage at cathode and at a 2 Pa pressure. A TiO_2 disk with 10 cm diameter from Goodfellow was used as target. The samples were at floating potential and were not externally heated. The sputtering gas was oxygen-containing argon. Various conditions of process were applied and are summarized in Table 1: oxygen content in argon varied from 0 to 20 vol. % and self-bias voltages at the target were -550 V and -750V; films are consequently labeled.

Films were deposited onto n-doped silicon (100) and 1mm thick glass substrates; their mechanical thicknesses have been determined with a stylus profilometer and serve as starting data in the optical constants calculations. The measured film thicknesses are given in Table 1.

II.2 The sample characterization

a- RBS

The film composition has been determined by RBS, using a 2 MeV Van de Graaff accelerator. The oxygen content was determined with a 5% accuracy, due to the low RBS yield for light elements like oxygen.

b- XPS

Films were analyzed with a Scienta instrument, with $\text{AlK}\alpha$ radiation (1486,6 eV). Both core levels and valence band spectra were acquired. All binding energies are given with respect to Fermi level (E_F).

The chemical composition and oxide stoichiometry of the films surface were derived from XPS analysis by applying Scienta sensitivity factors for the core levels. The position of E_F with respect to the valence band maximum (VBM), and states in the gap below E_F , were determined from analysis of the valence band spectra. A bulk rutile sample from Goodfellow was used as a reference bulk material for the TiO_2 films. No special surface treatment such as ion etching in the analysis apparatus was carried out for rutile or the films. An electron flood gun was used to compensate the accumulation of surface electrostatic charge onto the samples during analysis. Two runs of measurement were made on each film and five on rutile.

c- UV-Visible optical spectrophotometry

Optical reflectance measurements were made on films deposited on glass substrates, with a Jasco V-550 spectrophotometer in the 300–900 nm wavelength range. Calibration has been realized with sapphire, a material whose refractive index is the order of the sample's one, in order to assess the experimental measurement error, which was found as 0.5%. Care was taken to absorb any possible reflected beam from the rear face of sapphire or substrates by a black carbon strip in order to avoid any back-reflected wave. Reflectance spectra R_{exp} were recorded in the visible range, at normal incidence.

d- XRD

The phase structure of the films was determined by using a Seeman-Bohlin (grazing angle configuration) X-ray diffractometer with Cu $K\alpha$ radiation at an incident angle of 3° , in steps of 0.02° .

III- Results and discussion

III.1- Film composition and density from RBS analysis and correlation with deposition rate:

All films can be described as TiO_{2-x} and their composition was obtained by RBS. Table 1 reports the O/Ti atomic ratio given by RBS. The films with the higher O/Ti value are those grown in pure argon plasma, the O/Ti reaches a flat regime when oxygen concentration in the gas is higher than 10%.

The measured film thickness and the number of atoms per cm^2 unit surface allow the calculation of the atomic density of films. For the $F_{10}(1)$ and $F_{20}(1)$ films however, the relative errors of thickness measurement, 13% and 20% respectively, were too high, then we have used the thickness given by the simulations of the optical reflectance and given in Table 1.

Fig.1 shows the atomic density of films: clearly, films $F_0(1)$ and $F_0(2)$ grown in pure argon plasma have the higher density. The decrease in density when adding O_2 to Ar in the feed gas appears more evident for films grown with a -550 V cathode self-bias voltage (group $F_i(1)$, $i=3,10,20$ in Table 1). The lowest value was found for film $F_{20}(1)$, a value $\sim 30\%$ lower than the nominal value of rutile.

The variation of the film density with both the cathode voltage and the oxygen concentration in the gas can be understood by also considering the variation of the film deposition rate. This parameter is plotted in Fig.1(b). As expected, the higher the voltage, the higher the rate. As can also be seen, O_2 introduction resulted in a less efficient sputtering process owing to the fact that the partial pressure of Ar was lowered upon O_2 addition in the gas, which decreased Ar^+ ion density in the plasma too.

Globally, the voltage conditions at the cathode which led to higher deposition rates led also to higher film density. However, as said above, within a film series deposited at a same cathode voltage, film density varied strongly with O_2 concentration in the gas mixture. This result is to be more likely correlated with the energetic conditions at the substrate. The density decrease obtained when O_2 was added can reasonably be explained by a more open structure due to less efficient interaction between the growing film and the most energetic species of the plasma. Plasma-surface interaction through ion bombardment is known to increase surface mobility of the impinging atoms on the substrate or on the growing film surface, leading to film densification.

III.2- Chemical states and film surface stoichiometry from XPS analysis

The XPS analyses regarded all of core levels Ti2p, O1s and valence band spectral regions. Carbon core level spectrum was also acquired. Carbon stems from surface hydrocarbon contaminants, it also serves as a reference to correct the binding energy (BE) shift due to surface electrostatic charging, either under flood electron gun application or without. The C1s spectrum has been set at 285 eV, the same shift has been applied to scale all BE spectra discussed below.

Fig.2 (a) displays the Ti2p core level spectrum related to bulk rutile. It consists of $Ti2p_{3/2}$ and $Ti2p_{1/2}$ contributions located at 458,35 eV and 464,02 eV respectively. The peaks are well-fitted with symmetric gaussian-lorentzians. The $Ti2p_{3/2}$ BE agrees well with published data for Ti^{4+} states in TiO_2 (458,7 eV in [9] and references therein for example).

The corresponding O1s displayed in Fig.3 (a) is dominated by a peak at 529,75 eV, *i.e.* 71.40 eV higher than that of Ti2p_{3/2}. This corresponds well to oxygen O1s BE in titanium oxide [15,16]. This spectrum can be fitted with four peaks: the major one O_I pertaining to O²⁻ ions in titanium oxide and the others at 531,01 eV (O_{II}), 532,01 eV (O_{III}) and 533,06 eV (O_{IV}). The atomic ratio O_I/Ti, deduced from Ti2p_{3/2} and O_I peak areas, is equal to 1,90 (±0,03).

The missing oxygen with respect to the ideal formula of the oxide TiO₂, could be at the origin of the O_{II} contribution. In fact, in many transition metals hydroxylation gives rise to a peak whose energy is close to the O_{II} peak one [17,18], due to metal-OH bond formation. However, O atoms giving rise to O_{II} peak are in a ratio with Ti atoms (O_{II}/Ti) of 0,62 (± 0,01): this is much higher than the oxygen deficiency $x = 0,1$ in the present stoichiometry (TiO_{1,9}) with respect to ideal TiO₂. The O_{II} peak more likely stems also from oxygen bonded to carbon like in C-OH [19], masking any Ti-OH contribution to the present O1s spectrum.

As for the remaining peaks resulting from the spectrum fitting, peak O_{III} and O_{IV}, they have been reported to pertain to either adsorbed molecular H₂O [20, 21] or C-O bondings like O-C-O or O=C-O [19].

Fig.2 (b and c) shows the Ti2p core level spectra related to films F₀(1) and F₁₀(1). With respect to that of rutile, Ti2p_{3/2} BE are slightly up-shifted respectively to 458,83 and 458,80 eV. This shift is also observed in the O1s spectra (Fig. 3 (b and c)). Actually, such a shift towards higher energies were observed for all films. However, the difference between Ti2p_{3/2} and O_I peak BEs remains constant as $71,43 \pm 0.02$ eV and equal to that of rutile: this indicates that the chemical states of Ti and O are the same in these films and in rutile. The BE shift observed in the spectra is only related to a variation of E_F with respect to the core lines, due to band bending caused by a non-zero surface potential during the analysis. Indeed, dealing with semi-conductors materials, band bending is expected in presence of a non-zero surface potential. We verified this effect in the case of rutile. Various spectra were measured under different electron beam energy conditions used for surface charge compensation, which create different sample surface potentials. The latter are reflected in different binding energy shift corrections for misaligned sample and spectrometer Fermi levels. After correction for surface charging, Ti2p and O1s binding energy are given in Table 2; they depend clearly on the energy of the incident electron beam under which the spectra were measured.

The O_I/Ti atomic ratios deduced from Ti2p_{3/2} and O_I peak areas obtained for all films are displayed in Table 1. Contrarily to O/Ti values from RBS analysis, no clear trend is observed in the variation of the O_I/Ti ratio values with the oxygen concentration in the sputtering gas.

As can be seen, all films are under-stoichiometric. As the XPS-derived O_{I}/Ti atomic ratio regards oxygen in Ti-O-Ti bonds only, the observed deviation “x” in these TiO_{2-x} films from the ideal stoichiometry TiO_2 can be due to structural defects as O vacancies, either unhealed or healed by H_2O adsorption giving Ti-OH bonds [22]. Similarly to rutile, the latter cannot be quantified as they are masked by C-O bonds in the O_{II} peak in $O1s$ spectrum. In fact, the O_{II}/Ti atomic ratio is, again as for rutile, in all cases much higher than “x” in these TiO_{2-x} films (Table I).

III.3- Valence band maximum energy

In rutile, Ti atoms are surrounded by six oxygen atoms, forming a distorted octahedron. Due to crystal field, the Ti3d orbitals split into two sets of orbitals, e_g grouping dz^2 and dx^2-y^2 and t_{2g} , grouping d_{xy} , d_{xz} and d_{yz} . Oxygen atoms are surrounded by three Ti atoms in a planar geometry. sp^2 hybridisation of O atoms forms three σ bonds (from p_x , p_y and s orbitals) in the plane and one π bond (from p_z) perpendicularly to the plane. The valence band (VB) spectrum reflects the density of filled states, weighted by the photoemission cross-section. The top of VB of TiO_2 is occupied by $O2p$ non-bonding states. The e_g states of Ti 3d orbitals are bonded in σ orbitals and are located in the lower energy region of the VB, while the t_{2g} states are bonded in π orbitals and lie higher in energy than the σ states, midway between the σ states and the $O2p$ non-bonding states [23]. A VB spectrum is displayed in Fig. 4(a) for $F_{20}(1)$, where the different spectral regions are indicated. For comparison, a fit of the VB spectrum of rutile is also shown in Fig. 4(b). Differences between the two spectra can be observed, in particular in the lowest and in the highest energy sides of the spectra. The assignment of such peaks is given in the following sections.

The valence band maximum energy (VBM) is determined as the zero intensity energy of the low BE region of the spectrum. After a Shirley background subtraction, the VBM energy is found by extrapolating a linear fit of the final spectrum portion to zero-intensity (inset in Fig. 4(a)). The obtained values are reported in Table 2, for the films and the rutile reference. For the latter, only a mean value is given.

III.4- Chemical states above the VBM

The valence band, as described above, did not sign the upper end of the XP spectrum below Fermi level for all the samples. Between VBM and the Fermi level, a low intensity peak can

be measured, as can be seen in Fig. 4(a) and in the inset therein; its position is given in Table 2, together with its area ratio to the $Ti2p_{3/2}$ peak.

Neither rutile nor film $F_0(1)$ spectrum exhibited such a peak, while for all the other films the ratio of this peak to $Ti2p_{3/2}$ peak varied between 3×10^{-4} to 8×10^{-4} . This feature has been reported for under-stoichiometric titanium oxide. It has been assigned to $Ti3d$ states and attributed to oxygen vacancies which result in partially filled $Ti3d$ nonbonding states in the gap [9, 24, 25, 26]. It has been also shown that other defect states like interstitial Ti can give rise to a similar state between the VBM and Fermi level [14].

The area ratio between this gap state peak and $Ti2p_{3/2}$ was calculated and it is shown in Fig. 5(a) in function of the measured O_I/Ti atomic ratio. It appears that the relative quantity of the $Ti3d$ states detected above the VBM doesn't follow the deviation "x" from ideal stoichiometry of the oxide as obtained by XPS, as it should if these states were due to oxygen vacancies. Here, the closer the O_I/Ti ratio value to 2, the higher the $Ti3d/Ti$. In our assumption that the lacking O atoms to form stoichiometric TiO_2 are either O vacancies or O atoms involved in Ti-OH bonds which do not contribute to O_I peak, O vacancies cannot explain the evolution of $Ti3d/Ti$ in Fig. 5(a) as the higher their number, the more intense should be the $Ti3d$ peak. On the contrary, films with more hydroxylated Ti (i. e. lower O_I/Ti ratio value) as a result of O vacancy healing, should give a lower $Ti3d/Ti$ ratio. This can account for the dependence between the O_I/Ti and $Ti3d$ gap states of Fig. 5(a). It is then likely that in regions of the surface sampled by XPS, O vacancies are healed in the form of Ti-OH bonds by dissociation of foreign H_2O molecules from ambient.

A fingerprint of hydroxyl groups bonded to Ti can be found in the VB spectra. Ti-OH bonds give a peak at the bottom of this spectrum, at ~ 11 eV of BE, corresponding to the 3σ orbital of the OH radical [27, 28]. This peak, indicated in Fig.4(a-b), was observed for all the film and rutile spectra. In Fig. 5(b) its relative area with respect to the VB spectrum is plotted in function of the $Ti3d/Ti$ area ratio. The dependence of the Ti 3d sites on the hydroxyl groups number and the healing effect of the latter on the defects is clear.

In contrast with the above XPS analysis which samples the outermost surface layers, RBS gives information about the film composition in its whole volume. Interestingly, the $Ti3d/Ti2p_{3/2}$ area ratio determined by XPS correlates well with the oxide stoichiometry given by RBS. Fig. 5 (c) shows clearly that the highest relative $Ti3d$ states concentrations are obtained for the lowest O/Ti ratio. On one hand, this result would corroborate the attribution of the $Ti3d$ states origin below Fermi level to O vacancies and, on the other hand, the relationship

between Ti3d/Ti and OH3 σ /VB area ratios indicates that the hydroxyl bonds are not confined at the topmost surface layers but are distributed also in the film volume.

III.5- Film structure from XRD analysis

X-ray diffraction analysis for films grown in pure argon plasma showed either a featureless spectrum, indicating an amorphous structure, or a typical peak, though of very weak intensity, of rutile nanoparticles. The spectra obtained with oxygen addition to argon gave both rutile and anatase diffraction patterns, whatever the oxygen concentration in the gas and the cathode voltage. The spectra relative to F₀(1) and F₂₀(1) films are displayed in Fig. 6 (a) and (b) respectively, as representative of the case of Ar and Ar-O₂ plasmas (F₀(2) film appeared amorphous in these analyses, spectrum not shown). The rutile structure is signed by the (110) peak and anatase is by the (101) diffraction peak.

III.6 - Optical properties from reflectance measurements: complex refractive index and optical gap

Possible gap states above the Fermi level due to O vacancies are not detected by XPS. Optical measurements performed on the films under study were of great help in determining both the fundamental gap of the films and the existence of extrinsic gaps due to defect states and to defining a band energy scheme of the films.

III.6.1- Film complex refractive index

A series of five films, F_{0,10,20} (1) and F_{0,20} (2), has been studied. Their reflectance spectra $R_{exp}(\lambda)$ are shown in Fig. 7(a); for clarity, spectra of films F_{0,10,20} (1) are up-shifted respectively by 0.28, 0.6 and 0.65. Here, one intends to simulate the shapes of the various spectra and mainly get the refractive and absorption indices of the films and the energy gap of the material. Transmittance measurements (not reported here) have been performed and have showed that absorption exists to a small extent in our films; reflectance spectra R_{exp} were used in order to extract a thickness “ d ” and the indices in which absorption is taken into account. The thickest films F₀(2) and F₂₀(2) clearly exhibit interferences; then, even if absorption exists, it should remain small but not negligible if one intends to fit calculated and experimental spectra to extract the film complex index $n(\lambda) = \nu(\lambda) + i\kappa(\lambda)$ or its complex dielectric function $\varepsilon(\lambda) = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda)$.

A classical relation [29] gives the theoretical expression of Fresnel reflectance R of a film deposited onto a substrate: $R_{Fresnel} = \rho\rho^*$ where

$$\rho = \frac{\rho_{12} + \rho_{23} e^{2ikd}}{1 + \rho_{12}\rho_{23} e^{2ikd}} \quad (1)$$

k is the wave vector inside the film, ρ_{12} is the vacuum-film reflection coefficient, ρ_{23} that of the film-substrate interface.

A multi-step calculation procedure was applied in order to determine starting data with a good approximation, which consisted in successively using the following models:

- Sellmeier and Wemple-Didomenico (W) [30] models; the latter expresses $\nu(\lambda)$ in the transparency domain of the material but recalling absorption explicitly through a measure of the strength of interband optical transitions (E_d) and the single oscillator energy associated with the maximum of absorption (E_0): $\nu_w^2 = 1 + \frac{E_0 E_d}{E_0^2 - E^2}$
- Forouhi-Bloomer (F-B) model to calculate $\kappa_{F-B}(\lambda)$ [31], which, used with $\nu_w(\lambda)$ previously estimated, served as entry data for reflectance simulation; F-B' model leads to first values of the energy gap E_g : $\kappa_{F-B} = \frac{A'(E - E_g)^2}{E^2 - B'E + C'}$
- Ketteler-Helmholtz model (K-H), based on the complex dielectric function and in which transparency and absorption domains are consistently taken into account. In contrast with what was done in the previous steps, within K-H model the real and imaginary part of the dielectric function are determined simultaneously. d , $\nu_w(\lambda)$, $\kappa_{F-B}(\lambda)$ and E_g determined above served as input data in order to determine $\nu_{K-H}(\lambda)$ and $\kappa_{K-H}(\lambda)$ which were the final values of these calculations.

The substrate index has been determined first (the calculations are given in Appendix A). Each step of the film reflectance simulation is described in more details in appendix B.

Fits between R_{exp} and $R_{Fresnel}$ were performed and, in the following, we give the final results of the calculations. Fig.7(b) shows the agreement that has been obtained by our simulations between R_{exp} and $R_{Fresnel}$ for film F₀(2) and $\nu(\lambda)$ and $\kappa(\lambda)$ are given in Fig. 8 (a) and (b) respectively. What can be noticed is that $\nu(\lambda)$ varies significantly among the various samples. In order to better illustrate this result, the real part $\nu(\lambda)$ of $n(\lambda)$ corresponding to $\lambda = 632,8$ nm (i.e. the He-Ne laser wavelength commonly used for ellipsometry) is plotted in Fig. 9 in function of the atomic ratios O/Ti from RBS (plot a) and O₁/Ti from XPS (plot b). Except for

$F_{10}(1)$ (not represented), all the points are fairly aligned in Fig.9(a) following a decreasing linear function with O/Ti from RBS. By considering the relationship between this ratio and the Ti3d states relative amount (Fig.5(c)) and between the amount of the Ti3d states and OH states (Fig. 5(b)), the effect of hydroxylation on $v(\lambda)$ value become clear. This is also what can be observed in Fig. 9(b): $v(\lambda)$ increases with O_T/Ti from XPS. So, in determining the film refractive index values is the extent to which water interacts with the films. This can be due to the film internal structure itself as a low refractive index is usually related to a low packing density of the film grains or columns. With a high melting point material like titanium oxide (1867°C), films grown at room temperature as the present ones are more likely of a columnar structure [32]. The surface area of the columns can affect strongly the refractive index values [33]. On the other hand, for these films, crystallisation can also be a factor of the higher values of refractive index of the films grown in presence of oxygen [34, 35]: XRD analysis revealed an amorphous state or weak crystallinity of the films deposited in a pure Ar plasma while a stronger crystallinity (though at nanoscale) was observed in all films grown in Ar-O₂ plasma, as shown in Fig. 6. Correspondingly, the $v(632,8 \text{ nm})$ values of $F_0(1)$ and $F_0(2)$ are lower than those of $F_{20}(1)$ and $F_{20}(2)$. The variations of the refractive index of the present films appear to be determined by both crystallinity and packing density which, in turn, determines the hydroxylation extent.

Finally, the imaginary part $\kappa(\lambda)$ of $n(\lambda)$ has been used to determine the optical band gap of the films, this is discussed in the next section.

III.6.2 - Film optical gap from $\kappa_{K-H}(\lambda)$ and gap states:

The optical band gap can be determined from the absorption coefficient $\alpha = 4\pi\kappa/\lambda$. Tauc model [36] describes α in the high absorbance region of the wavelength range as:

$$\alpha E = A (E - E_g)^\gamma \quad (2)$$

where E is the incident photon energy, E_g is the energy gap, A a constant independent of E and γ has four possible numeric values: 1/2, 2, 3, 3/2. Generally an *ad hoc* assumption is made of a kind of transition (direct allowed when $\gamma=1/2$, indirect allowed when $\gamma =2$, indirect forbidden for $\gamma =3$ and direct forbidden for $\gamma =3/2$) and the $(\alpha E)^{1/\gamma}$ versus E curve is fitted with a linear function.

$(\alpha E)^{1/2}=A(E-E_g)$ and $(\alpha E)^2=A(E-E_g)$ were plotted versus E in order to derive a direct and indirect allowed gap, which values are reported in Table 3. As it can be seen, the values for the direct allowed transitions are higher than for bulk TiO₂ which direct allowed gap can be of

3,3 – 3,4 eV [37]. This can be related to amorphicity or to a quantum size effect due to a nano-crystallinity in the film structure.

On the contrary, the E_g energy values corresponding to an indirect allowed transition resulted lower (between 2,04 and 2,93) than what reported in literature for titanium oxide (3,02 – 3,19 eV respectively) [37]. This light absorption is unlikely to pertain to the *intrinsic* band structure of the films, but rather to absorption by intrinsic defects. In order to check the existence of such a transition mode, no *a priori* assumption was made for the γ value in Eq. 2, rather the αE versus E curve is fitted following:

$$\text{Ln}(\alpha E) = \text{Ln}A + \gamma \text{Ln}(E-E_g) \quad (3)$$

The E_g value as well as γ value are obtained as curve fit results. In the inset of Fig. 8(b) such a curve fit is shown for film F₂₀(1) for photon energies $\geq 3,5$ eV. The fit results regarding E_g and γ are summarized in Table 3 for all the films. This method allowed to identify the dominant transition mode in the photon energy range under study. In the case of F₁₀(1), $\gamma = 0,66$ indicating rather a direct allowed transition and confirming that for $E \geq 3,5$ eV, the intrinsic gap is direct. For all other films, we can see that γ is close to 2. No value of γ representative of a forbidden direct or indirect transition resulted from the fit following Eq. 3. So, only the allowed transitions are likely to occur. All the energies fall in the visible range. For F₁₀(1), a second gap value of 2,69 eV could be found by fitting $\text{Ln}(\alpha E)$ following Eq. 3 for $E < 3,5$ eV, far from the fundamental gap energy region.

Light absorption in the visible can, in fact, be due to lattice defects which create energy levels within the gap of titanium oxide: defects in the oxygen sub-lattice related to O vacancies and those related to Ti^{n+} ($n=3$ or/and 2) ions. Although literature is abundant for the electronic structure of titanium oxide, many recent papers recognize that there still exists insufficient information on the optical properties of point defects. In a review made by Kuznetsov and Serpone [38], the absorption bands in the visible spectral region are reported to be associated to O vacancies, which act as F-type color centers in a range of 2,93- 2 eV. In this case, light absorption can originate from transitions between the defect-induced energy levels inside the gap and the Ti3d levels in the conduction band (CB). Let's recall that there are three types of the F-type centers: doubly-ionized and optically silent O vacancies (the so-called F^{++} centers), O vacancy with one trapped electron (F^+ -center) and with two trapped electrons (F-center). In turn, Chen *et al.* attributed an absorption energy of 1,78 eV for transitions between a F^+ -center and CB, and one of 0,87 eV for transition involving a F-center and 0,20 eV for a F^{++} -center [39].

For our films, the *extrinsic* absorption energy values found so far fall in the interval 2,60 – 2,78 eV as it can be seen in Table 3, corresponding to wavelengths between 446 – 470 nm. Such a set of values could be F- and F⁺- centers related to O vacancies [40], although no unambiguous identification can be made.

Moreover, at variance with the other films, the film F₁₀(1) shows an increase of $\kappa(\lambda)$ beyond ~850 nm (below ~1,45 eV). The trend of $\kappa(\lambda)$ in this region clearly indicates absorption in the near infra-red which could be associated with Ti³⁺-related centers (Ti³⁺ in substitutional or interstitial sites) [38, 40].

III.7- Electronic band structure scheme:

In order to define a band structure of the various films of this study, optical results were used in conjunction with XPS analysis of the valence band. In Fig. 10, a schematic representation of the band structure is given, which shows the VBM energy, the conduction band minimum (CBM) and the gap states, all referred to the Ti2p_{3/2} BE. This reference level of energy was chosen in order to get rid of band bending effects due to surface states.

It can be seen that in the films the band edges move with respect to that of rutile, there is a recession of the VBM, probably due to the disappearance of states at the top of the band in relation with the oxygen deficiency. As for the intermediate states inside the gap, two extreme cases can be assumed concerning their positioning on the energy scale: the transitions occur between the VBM and the color center level (Fig.10(a)) or between the center level and the CBM (Fig. 10(b)). The first case would place the defect related level above the Ti3d states while, in the second one, it would be between the Ti3d states and the VBM. The latter case is unlikely because no significant peak was observed in that region of the films XP spectra. Besides, in Fig. 10(a), the energy difference δ between the color center level and CBM is reported. The values are close to those of Chen *et al* [39] for F-color center absorption in rutile, i.e. O vacancies with two trapped electrons.

IV- Summary

In this study, TiO_{2-x} films were deposited by RF sputtering in Ar-O₂ mixtures at room temperature. Emphasis was put on the structural and optical properties of the films in order to define a method based on a combined use of x-ray photoelectron and optical reflectance spectroscopies. The intrinsic defects were also studied in conjunction with RBS analysis and a scheme of the energy band structure of the films was proposed.

In order to quantify optical behaviour, the experimental reflectance spectra were fitted within the frame of a multi-step procedure using different models. This approach was necessary to rigorously derive the film optical constants for a spectral region where absorbance cannot be totally neglected in spite of a high transparency.

The following conclusions were drawn from this study:

- (1) All the films were oxygen-deficient and adding oxygen to the sputtering gas was found to further increase the deviation from a full stoichiometry.
- (2) The reduced oxide state in the films induced states related to O-vacancies between the VBM and the Fermi level which were strongly correlated with hydroxylation.
- (3) Hydroxylation did not appear confined to the surface layers but concerns the film volume as well and had an effect on the refractive index.
- (3) O-vacancies made band edges recede, due to energy states disappearance from the top of the VB.
- (4) Intermediate bands inside the fundamental gap were likely due to the F-centers.

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Appendix A: Index of the substrate

The rear face of the substrate being blackened, its reflectance is expressed by

$R_s = \left(\frac{n_s - 1}{n_s + 1} \right)^2$ and does not show interference fringes. The substrate index $n_s(\lambda)$ is involved in

the relations that express the reflectance of the film deposited onto its substrate and it must be known prior to the interpretation of optical spectra of TiO₂ films. $n_s(\lambda)$ has been developed in

series $n_s^2 = a_0 + \frac{a_1}{\lambda} + \frac{a_2}{\lambda^2} + \frac{a_3}{\lambda^3} + \frac{a_4}{\lambda^4}$ and limited to the fourth order in λ , no gain being added

with higher orders. From R_s , one extracts $n_s(\lambda)$. The a_i 's are determined by a least square procedure which gave $a_0 = 2,248$, $a_1 = -16,7nm$, $a_2 = 41617nm^2$, $a_3 = -5518400nm^3$ and $a_4 = -43112nm^4$.

Appendix B: Film optical parameters calculations from reflectance spectra

B.1 First step: calculation of $v(\lambda)$

Absorption is neglected; a Sellmeier model of bulk TiO₂ index $n(\lambda)$, valid for $\lambda > 430$ nm [41], gives

$$n^2(\lambda) = a' + \frac{b' \lambda^2}{\lambda^2 - c'} + \frac{d' \lambda^2}{\lambda^2 - e'} \quad (4)$$

This allows to obtain an order of magnitude of $n(\lambda)$ by a simple mean.

In the transparency domain and within Wemple-Didomenico model (W) [30], the real part v_w^2 of $n(\lambda)$ can be transformed as

$$v_w^2(\lambda) = 1 + \frac{\lambda_{0W}}{\lambda_{DW}} \frac{\lambda^2}{\lambda^2 - \lambda_{0W}^2} \quad (5)$$

The authors give $E_d = 25,7$ eV which corresponds to $\lambda_{DW} \approx 48,11$ nm and $E_0 = 5,24$ eV corresponds to $\lambda_{0W} \approx 236$ nm, then $\frac{\lambda_{0W}}{\lambda_{DW}} = 4,0548$. For TiO₂, Eq.5 is valid for $\lambda > \lambda_{gap}$.

Remark that, for $\lambda = 550$ nm, $c' \approx 22,44$ and $\frac{d' \lambda^2}{\lambda^2 - e'} \approx 0,0026$; then Eq.5 is formally

equivalent to Eq.4 if one neglects the third term in the latter and let $a' \approx 1$, $b' \approx \frac{\lambda_{0W}}{\lambda_{DW}}$ and

$$c' \approx \lambda_{0W}^2.$$

The "optical" thickness d has been determined for each film. Actually, Wemple's model describes the properties of the "red part" of TiO₂ optical spectrum. An agreement between calculated and experimental spectra that reproduces their general shape while fitting the "red peak" is obtained with the values given in Table 1. These thicknesses will be used whatever the model for absorption.

B.2 Second step: calculation of $\kappa_{F-B}(\lambda)$

As derived from W simulations, an absorption band exists at $\lambda_{0W} \approx 236$ nm. Sellmeier and W models assume that the absorption band would be far enough for its influence to be negligible. In the various simulations of R_{exp} , we found that one could not consider that this was the case. Actually, λ_{0W} is close to the wavelength range under study and is responsible for the difficulties encountered along the index solving procedure. This absorption band has been taken into account with F-B [31] formalism given in Section III.6.1. Once the extinction

coefficient $\kappa_{F-B}(\lambda)$ is introduced in $n(\lambda)$, Eq. 5 must be slightly modified, since the numerical values of $v(\lambda)$ that have led to $v_w(\lambda)$ were obtained assuming that $\kappa(\lambda) = 0$. More generally, Eq. 5 writes

$$v_w^2 \approx A + \Delta \frac{\lambda^2}{\lambda^2 - \lambda_0^2} \quad (6)$$

The magnitude of A remains small compared to that of the second term, and so does its influence in the simulations. Using $\kappa_{F-B}(\lambda)$ expression and Eq. 6, and entry data $A \approx 1$,

$$\Delta = \frac{\lambda_0}{\lambda_D} \approx 4,9, \text{ the simulation gives } \kappa_{F-B}(\lambda) \text{ that realize the best fit between } R_{exp} \text{ and } R_{Fresnel}.$$

In R_{exp} simulations, λ_0 is found to influence the position of extrema in the blue part of spectra; for our series of samples, the best fit occurs when the mean value $\langle \lambda_0 \rangle \approx 231,8 \pm 3,0$ nm, very close to $\lambda_{0w} \approx 236nm$ already published [30].

B.3 Application of the Ketteler-Helmholtz model

A set of thicknesses, indices and energy gaps has been estimated through the previous simulations. They serve as entry data for Ketteler-Helmholtz model, in which the real and imaginary part of the dielectric function are determined simultaneously, in contrast with what was done in the previous steps.

The absorption band recognized before is unique in the range under study; the real and imaginary parts of the complex dielectric function $\varepsilon(\lambda)$ of TiO_2 are recalled in Eq. 7 and 8.

$$\varepsilon_{1-K-H} = 1 + \frac{\Delta \lambda^2 (\lambda^2 - \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^2 + (\lambda \lambda_0 \Gamma)^2} = v^2_{K-H}(\lambda) - \kappa^2_{K-H}(\lambda) \quad (7)$$

and

$$\varepsilon_{2-K-H} = \frac{\Delta \lambda^3 \lambda_0 \Gamma}{(\lambda^2 - \lambda_0^2)^2 + (\lambda \lambda_0 \Gamma)^2} = 2 v(\lambda) \kappa(\lambda) \quad (8)$$

$$\text{where } \Delta = \left[\frac{\omega_p}{2\pi c} \right]^2 \lambda_0^2 = \varphi \lambda_0^2 \text{ and } \Gamma = \left[\frac{1}{2\pi c \tau} \right] \lambda_0 = \beta \lambda_0$$

Approximate values of a few parameters that enter K-H's relations have been determined according to the following arguments.

- We assume that far from the absorption band, *i.e.* in the red part of spectra, all models should give more or less the same results. When $\Gamma \lambda \lambda_0 \ll \lambda^2 - \lambda_0^2$ and simultaneously $\varepsilon_2 \ll \varepsilon_1 - 1$, K-H reduces to Sellmeier or Wemple's relations. This implies that one can write

$\varepsilon_{1-K-H} \approx \nu_w^2$ and get approximate input values of Δ , λ_0 and Γ . A first run uses Eq. 7 and 8, simulates R_{exp} and gives an approximation of $\varepsilon_{1-K-H}(\lambda)$ and $\varepsilon_{2-K-H}(\lambda)$. A first value of λ_{0-K-H} comes then from $\varepsilon_1 - 1 = 0$.

- The end of the whole process described above comes from a few remarks:

From the previous run, the numerical ratio $\frac{\varepsilon_1 - 1}{\varepsilon_2}$ can be drawn; it gives a rather linear

behaviour (not shown) as a function of λ , that is expressed by $\frac{\varepsilon_1 - 1}{\varepsilon_2} \approx u\lambda + v$. At this stage,

one gets a new value of $\lambda_{0-K-H} \approx -\frac{u}{v}$ from a full K-H treatment, although not yet the most

accurate one. In the last run of the simulation, we use the theoretical ratio

$\frac{\varepsilon_1 - 1}{\varepsilon_2} = \beta^{-1} \frac{\lambda^2 - \lambda_{0-K-H}^2}{\lambda \lambda_{0-K-H}}$ of Eq.7 / Eq.8, and β^{-1} is expanded as a polynomial function of

λ . The fit is improved especially in the spectral zone [300-400] nm where absorption is important.

Fits for all films have led to the absorption band located at a λ_0 with a mean value $\langle \lambda_{0-K-H} \rangle = (238,2 \pm 3,1)$ nm.

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Table 1: Plasma conditions (voltage at the cathode and O₂ concentration in Ar-O₂ gas), film thicknesses (geometrical and derived from optical calculations), oxide stoichiometry from RBS analysis, O_I/Ti and O_{II}/Ti atomic ratios from XPS analysis

Films	F ₀ (1)	F ₃ (1)	F ₁₀ (1)	F ₂₀ (1)
Cathode self-bias (V)	-550	-550	-550	-550
[O ₂] in Ar- O ₂ gas	0 %	3%	10 %	20 %
Films	F ₀ (2)	F ₃ (2)	F ₁₀ (2)	F ₂₀ (2)
Cathode self-bias (V)	-750	-750	-750	-750
O ₂ in Ar- O ₂ gas	0 %	3%	10 %	20 %
Films	F ₀ (1)	F ₃ (1)	F ₁₀ (1)	F ₂₀ (1)
Thickness (nm)	82 (± 4)	46 (± 10)	39(± 5)	40(±8)
Thickness from reflectance (nm)	58	-	64	89
Oxide stoichiometry by RBS	TiO1, 95	-	TiO1, 80	TiO1, 80
O _I /Ti atomic ratio by XPS (based on O _I /Ti2p _{3/2} peak area ratio)	1,88	1,91	1,89	1,95
O _{II} /Ti atomic ratio by XPS (based on O _{II} /Ti2p _{3/2} peak area ratio)	0,23	0,34	0,28	0,22
Films	F ₀ (2)	F ₃ (2)	F ₁₀ (2)	F ₂₀ (2)
Thickness (nm)	294 (±8)	142(±8)	123(±7)	150(±5)
Thickness from reflectance (nm)	230,5	-	-	140
Composition from RBS	TiO1, 90	-	TiO1, 85	TiO1, 85
O _I /Ti atomic ratio by XPS (based on O _I /Ti2p _{3/2} peak area ratio)	1,90	1,93	1,89	1,93
O _{II} /Ti atomic ratio (based on O _{II} /Ti2p _{3/2} peak area ratio)	0,19	0,39	0,27	0,25

Table 2: Corrected binding energy (BE) of Ti2p_{3/2} and O1s peaks for rutile in function of the analysis conditions (flood gun energy) and for the films; corrected Ti3d peak BE and Ti3d/Ti2p_{3/2} peak area ratio

	Electron gun energy (eV)	BE shift correction (eV)	Ti2p _{3/2} BE (eV)	O1s BE (eV)	VBM (eV)	Ti3d peak BE (eV)	Ti3d/Ti2p _{3/2} area ratio
Rutile	0,5	-3,4	458,35	529,75		Not detected	0
	2	-3,03	458,04	529,47			
	3	0,37	458,32	529,67	1,69		
	3,5	1,23	457,86	529,26	±0,19		
	5	4,53	458,60	529,9			
F ₀ (1)	5	0,75	458,83	530,27	2,81	Not detected	0
F ₃ (1)	0	- 1,18	458,86	530,26	2,79	0,94	5,89E-4
F ₁₀ (1)	5	0,67	458,80	530,25	2,86	1,15	3,046E-4
F ₂₀ (1)	5	0,7	458,85	530,33	2,95	1,09	8,13E-4
F ₀ (2)	5	0,32	458,85	530,36	2,91	1,15	4,23E-4
F ₃ (2)	0	- 1,1	458,72	530,07	2,29	1,29	8,94E-4
F ₁₀ (2)	5	0,8	458,96	530,2	2,56	1,29	4,26E-4
F ₂₀ (2)	5	4,85	458,78	529,99	2,60	1,22	7,08E-4

Table 3 : Optical absorption energies and dominant transition mode

Films	Indirect allowed gap (eV)	Direct allowed gap (eV)	γ from $\text{Ln}(\alpha E) = \text{LnA} +$ $\gamma \text{Ln}(E-E_g)$	Gap from $\text{Ln}(\alpha E) = \text{LnA} +$ $\gamma \text{Ln}(E-E_g)$	Dominant transition mode
F ₀ (1)	2,6	3,61	2,01	2,76	Indirect allowed
F ₁₀ (1)	2,04	3,47	0,66 0,53*	3,16 2,69 *	Direct allowed
F ₂₀ (1)	2,93	3,68	2,02	2,68	Indirect allowed
F ₀ (2)	2,78	3,61	2,00	3,08	Indirect allowed
F ₂₀ (2)	2,64	3,65	1,94	2,51	Indirect allowed

* in λ range $< 3,5$ eV

Figure captions

Figure 1: (a) Film atomic density from RBS analysis and (b) deposition rate, in function of O₂ concentration in the gas, for cathode voltage -550V and -750V.

Figure 2: XPS Ti2p spectra for (a) rutile and (b) films F₀ (1) and (c) F₁₀ (1)

Figure 3: XPS O1s spectra for (a) rutile and (b) films F₀ (1) and (c) F₁₀ (1)

Figure 4: Typical XPS VB spectrum and fitting results for (a) F₂₀ (2) and (b) rutile

Figure 5: (a) Ti3d/Ti2p area ratio versus oxide stoichiometry from XPS analysis (O_T/Ti ratio)
(b) OH 3σ / VB area ratio versus Ti3d/Ti area ratio
(c) Ti3d/Ti2p area ratio versus oxide stoichiometry from RBS analysis (O/Ti)

Figure 6: XRD patterns of F₀ (1) and F₂₀ (1) films

Figure 7: (a) Reflectance R_{exp} of TiO₂ films deposited onto glass substrate
(the corresponding thicknesses, as measured by profilometry, are indicated)
(b) Fit between R_{exp} and $R_{Fresnel}$ for sample F₀(2)

Figure 8: (a) real part of the complex refractive index $\nu_{K-H}(\lambda)$ for the TiO₂ films
(b) imaginary part of the complex refractive index $\kappa_{K-H}(\lambda)$ for the TiO₂ films.
Inset: Tauc model fit of Ln(αE) curve for F₂₀ (1). α is in cm⁻¹

Figure 9: (a) real part of the complex refractive index, $\nu_{K-H}(\lambda)$, versus RBS O/Ti ratio
(b) imaginary part of the complex refractive index, $\kappa_{K-H}(\lambda)$ versus XPS O_T/Ti ratio. The values corresponds to $\lambda = 632.8$ nm

Figure 10: Band energy scheme for rutile and the TiO_{2-x} films with transitions from VB to the F-type color center level (a) and from the F-type center to CB (b).

Figure 1

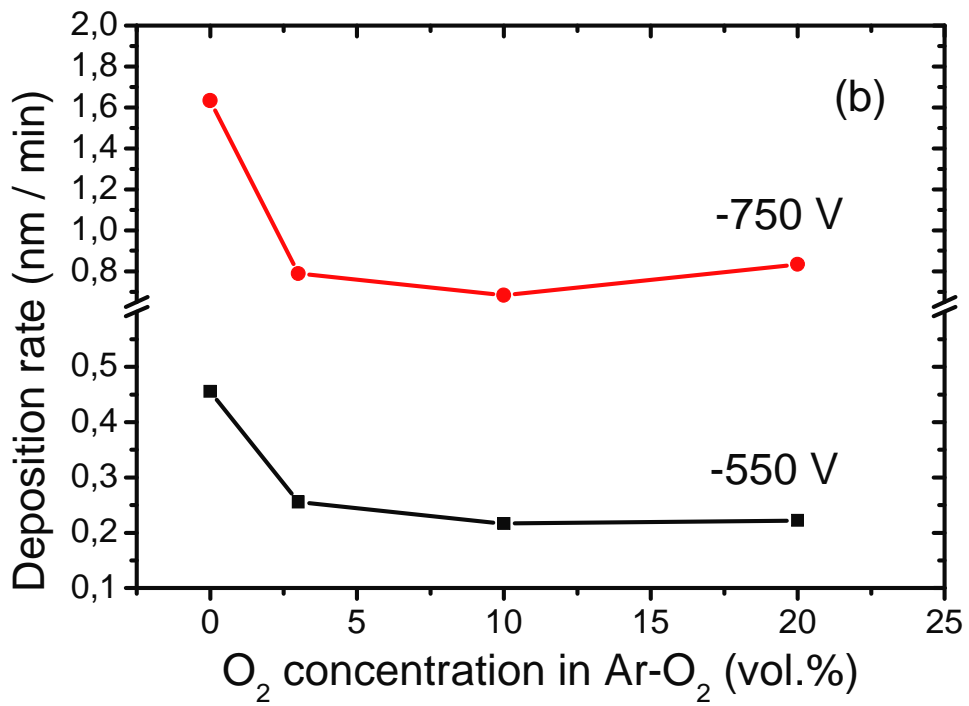
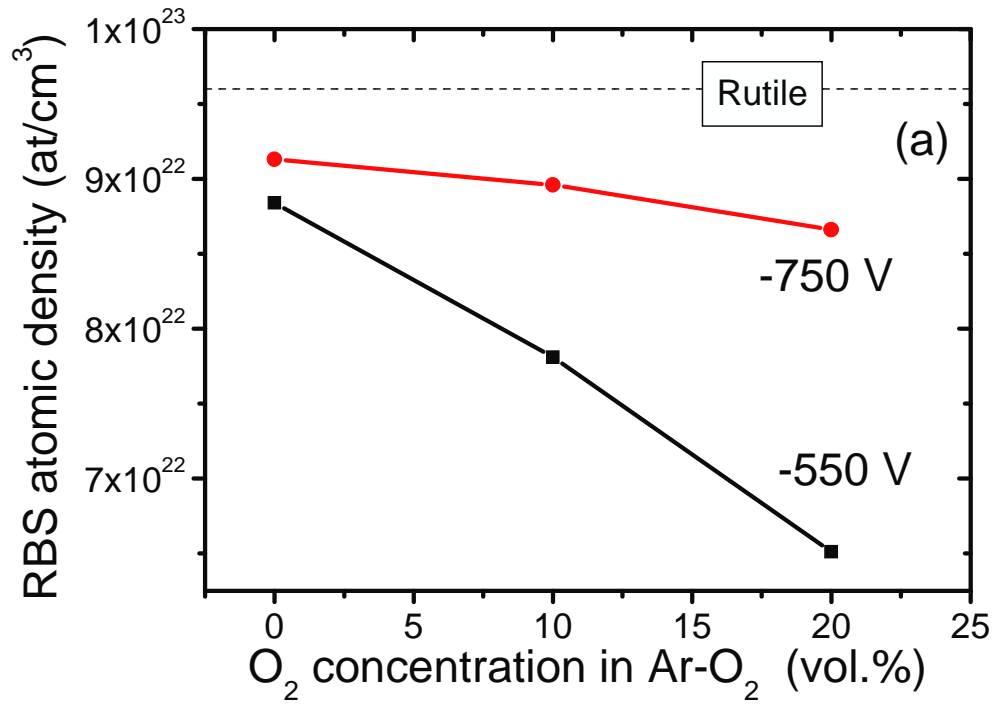


Figure 2

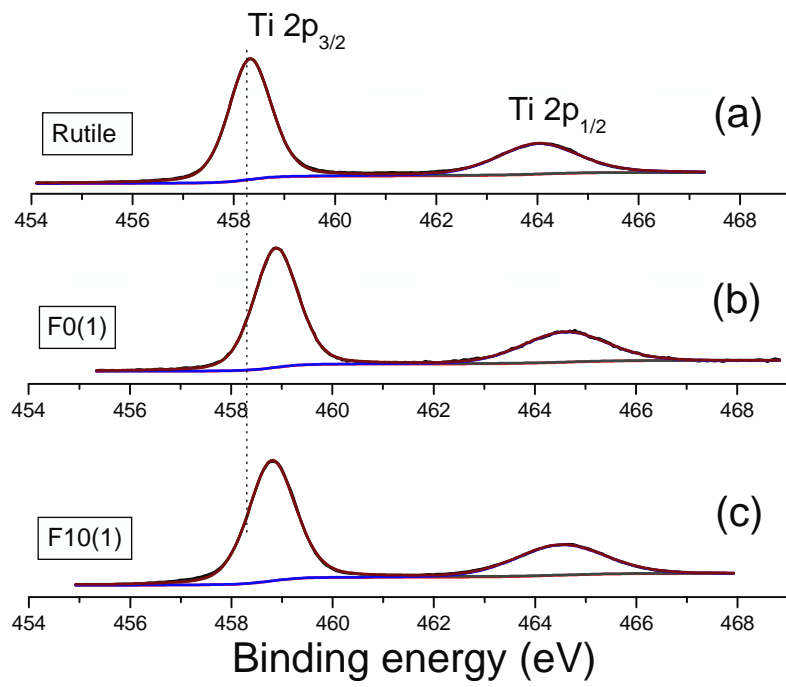


Figure 3

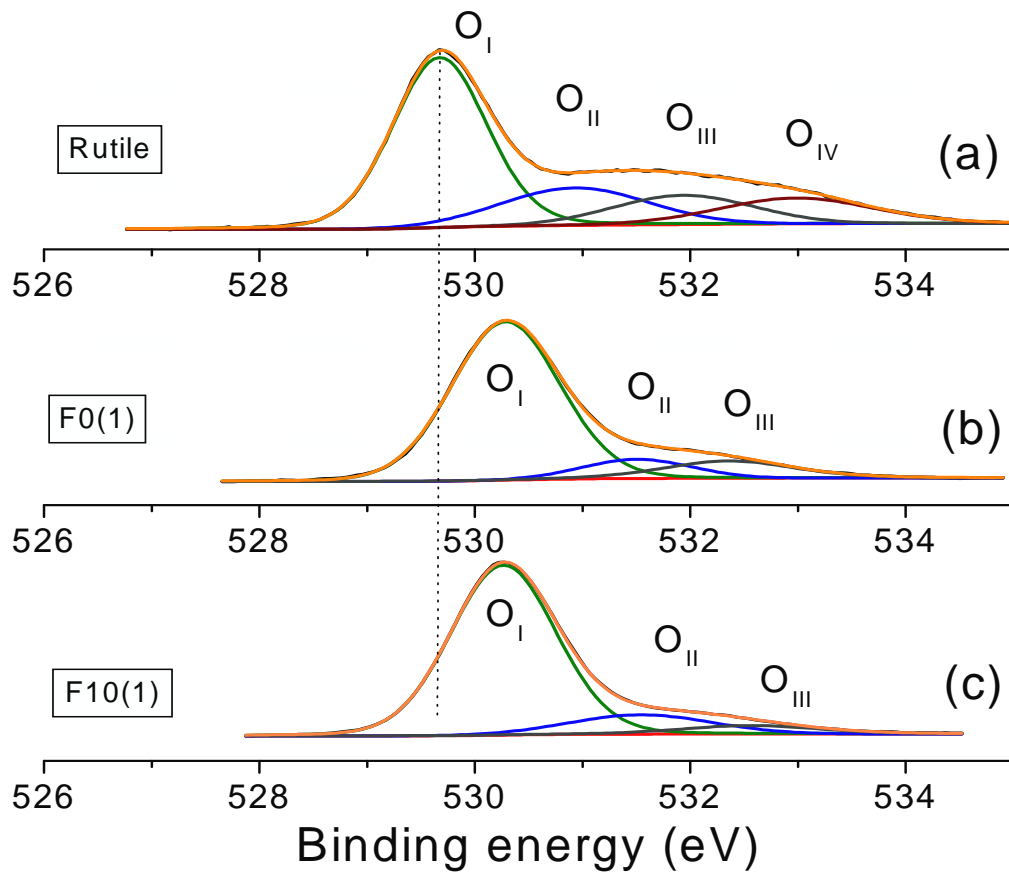


Figure 4

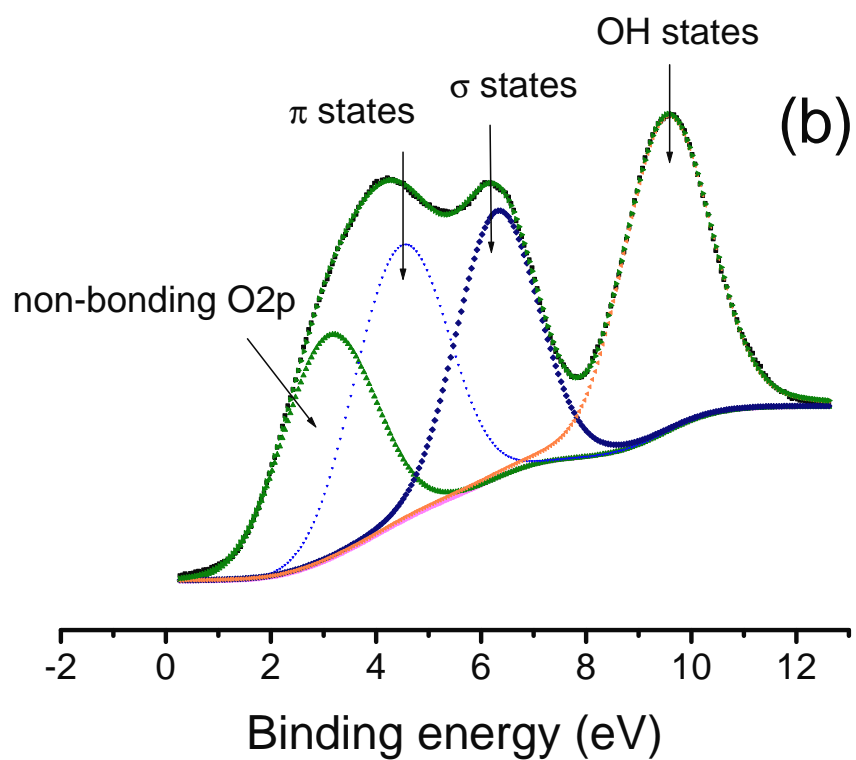
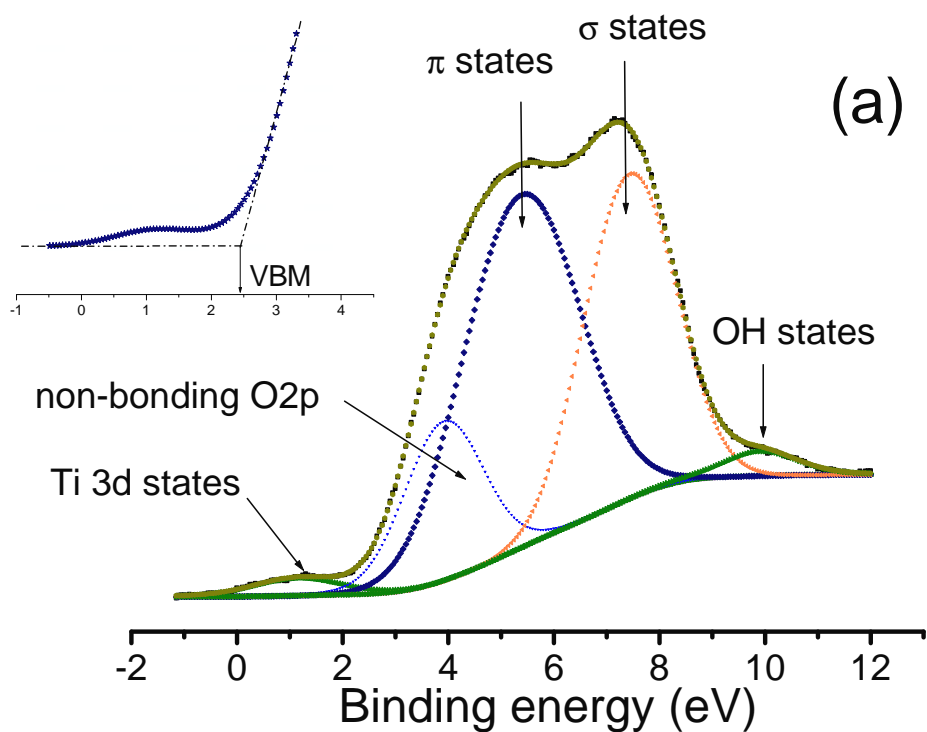
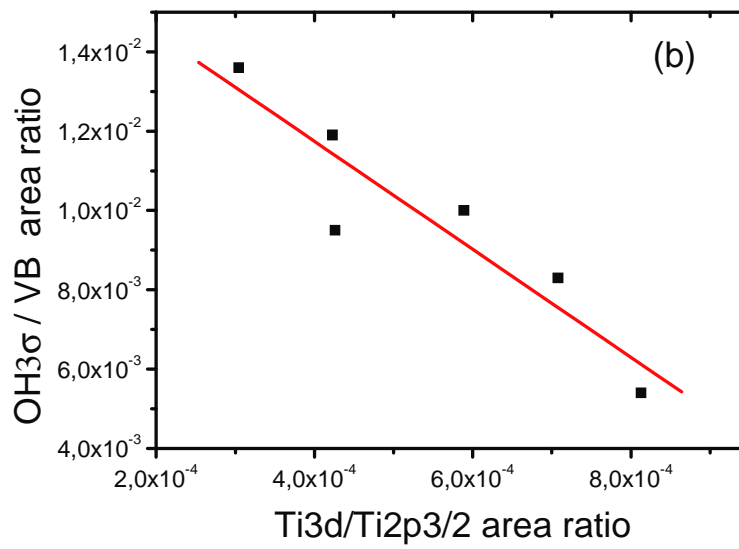
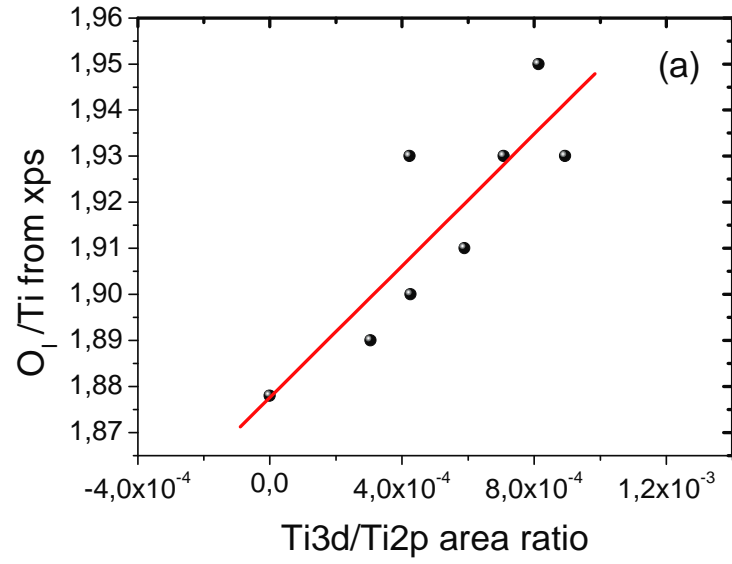


Figure 5



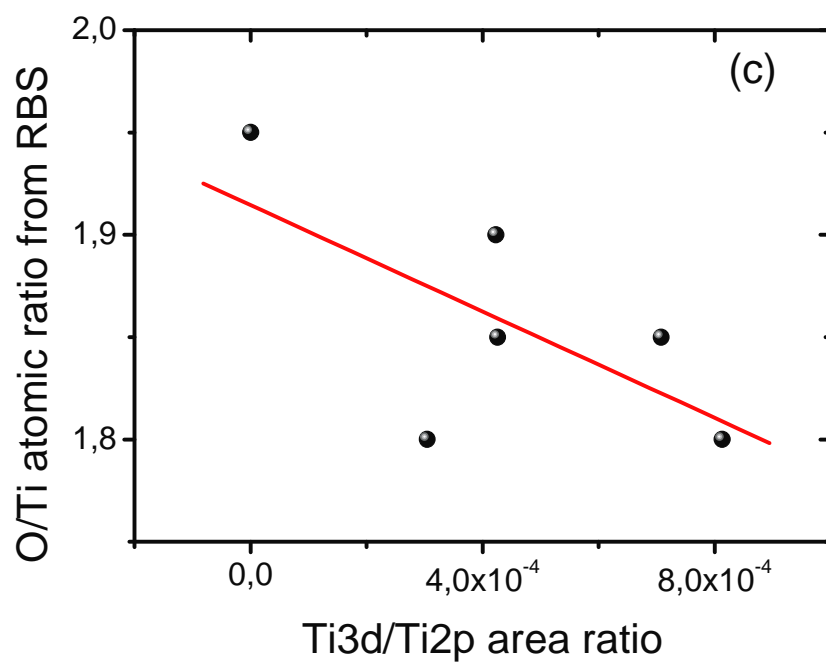


Figure 6

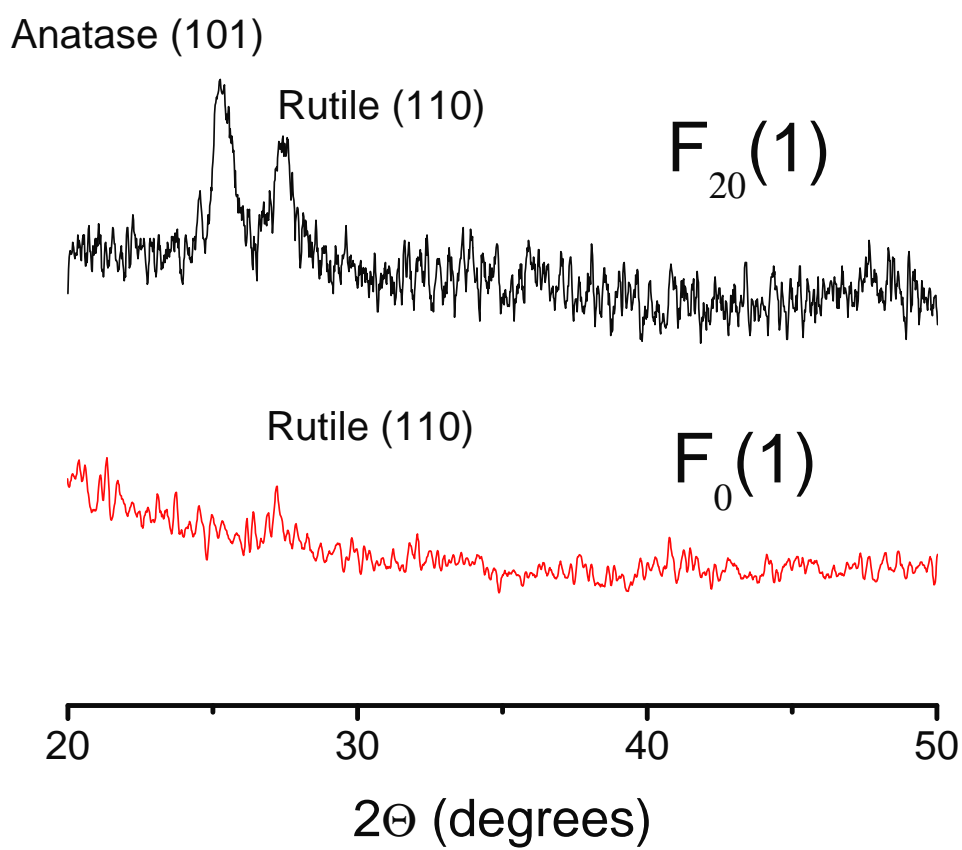


Figure 7

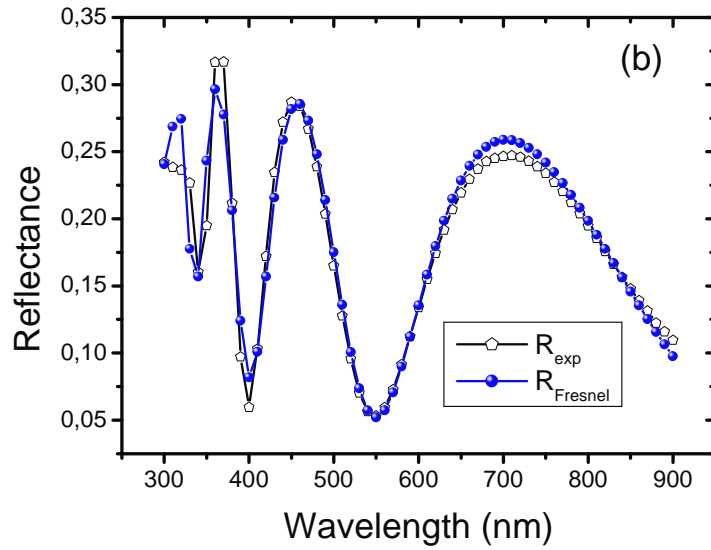
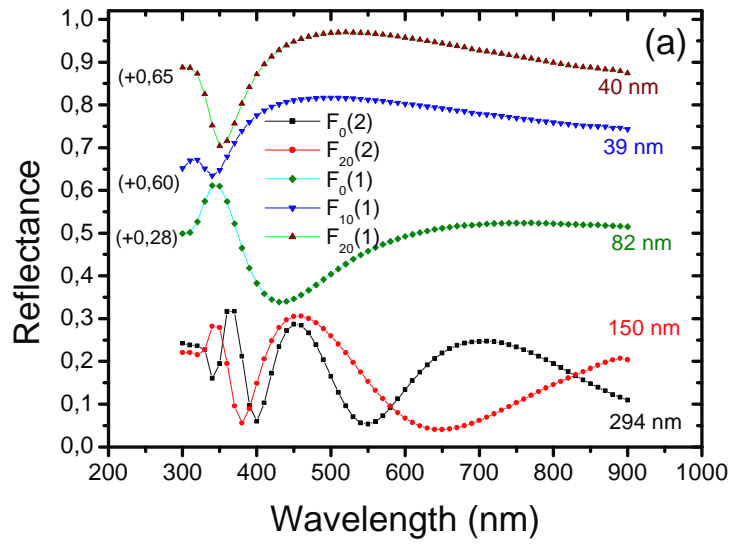


Figure 8

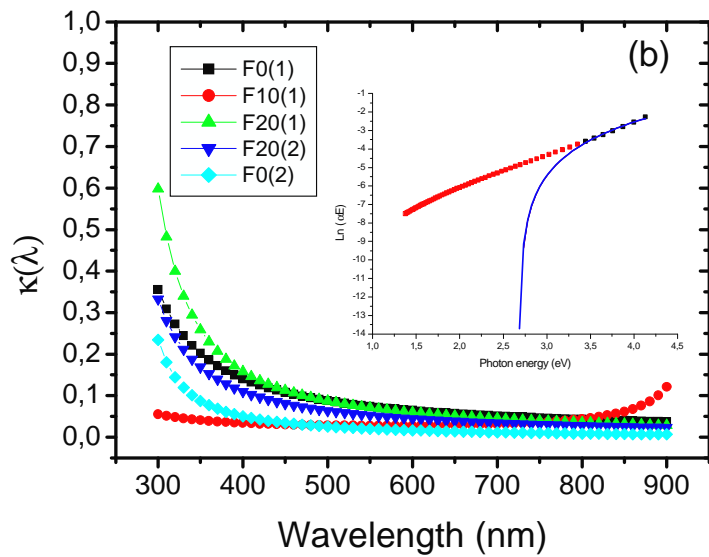
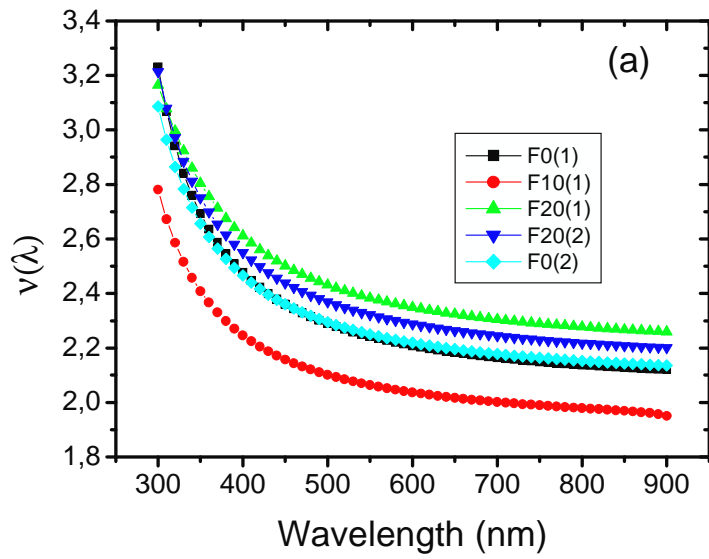


Figure 9

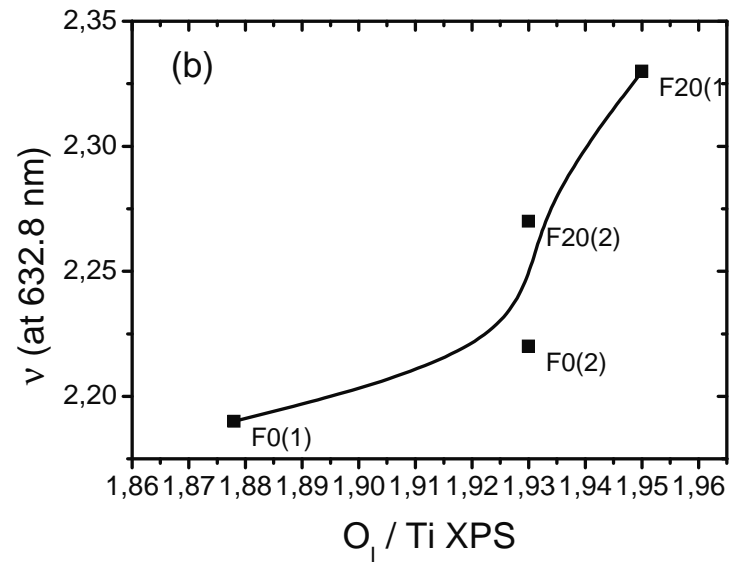
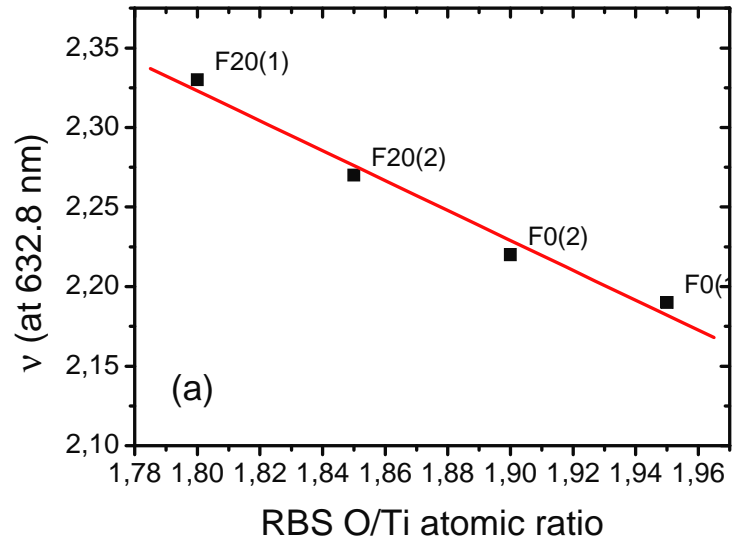


Figure 10

