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# Angle resolved X-ray photoemission spectroscopy double layer model for *in situ* characterization of metal organic chemical vapour deposition nanometric films

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**Abstract**

*In situ* Angle Resolved X-ray Photoemission Spectroscopy (ARXPS) characterizations of $TiO_2$ thin films grown on silicon by Metal Organic Chemical Vapour Deposition were performed in order to get information on interfacial reactions at the first stages of the growth, one of the aims being to understand the influence of deposition conditions. Thickness measurements were also carried out from ARXPS analyses. As the real structure of the films was shown to be a double layer system such as $TiO_2/SiO_2/Si$, an ARXPS model of thickness and surface coverage determination was applied to each layer independently. However, the application of this model to very thin films underestimates the surface coverage of the interfacial layer. A "Double Layer" model taking into account the attenuation of the silicon oxide and substrate signals by the external layer was also developed.


*Keywords:* ARXPS; Thickness measurement; Interface; Thin film; MOCVD; $TiO_2$

## 1. Introduction

From technological and commercial considerations, thin films deposition by Metal Organic Chemical Vapour Deposition (MOCVD) is of great and increasing interest. However, few works have been performed to clarify growth mechanism of this deposition process (for instance, see [1–3]), partly due to the difficulty of achieving *in situ* characterizations in reactive gas environment. Electron spectroscopies, such as Angle Resolved X-ray Photoemission Spectroscopy (ARXPS), are powerful methods to investigate *in situ* and non-destructively the film/substrate interface at the first stages of the growth. Then the challenge of coupling ultra high vacuum chambers devoted to surface analyses techniques (XPS, ARXPS, Auger Electron Spectroscopy, Low Energy Electron Diffraction) to a MOCVD reactor was taken up by building an original experimental set-up.

The modification of the MOCVD process parameters directly affects the deposition rate, and the thickness of the deposited films as a consequence. Thus the determination of the film thickness, which can be done from *in situ* ARXPS analyses, is key point to the understanding of MOCVD growth mechanism. More or less complex ARXPS calculation models of film thickness were developed in the last decades [4–7]. To avoid problems related to absolute quantification, the use of intensity ratios of the XPS lines was preferred in this study. Fadley's model [8], which gives also the surface coverage of the substrate after film deposition, was chosen as a starting point. In this paper, we will apply this model to samples of different thicknesses. Its development towards a double layer model is presented in order to take into account the real structure of the $TiO_2/Si$ films grown by MOCVD, that is to say the presence of an interlayer.

## 2. Experimental

Titanium dioxide thin films were deposited by MOCVD with Titanium TetraIsoPropoxide (TTIP), $Ti(OCH(CH_3)_2)_4$, used as both titanium and oxygen precursor. Silicon wafers, (100) oriented n-type, were used as substrates and *ex situ* cleaned for native oxide removal by following the method described

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elsewhere [9]. The deposition rate was modified by changing growth conditions: the first deposit (d) was obtained at a working pressure of $5.10^{-3}$ Pa and a deposition time of 60 min, a thinner one (d′) being deposited at 2 Pa during 135 min. Both growths were performed at 675 °C.

*In situ* ARXPS analyses were performed using a VG Microtech CLAM 4 MCD analyser system. Experiments were carried out with a non-monochromatised Al $K_\alpha$ radiation with emission angles varying from 0 to 85° with respect to the surface. Spectra of the transitions used for thickness determination, Si 2p and Ti 2p, were recorded at a pass energy of 20 eV and with an analyser slit of 1 mm. Gaussian–Lorentzian (70–30) lineshapes and Shirley background subtraction were used for peak area measurements. The Ti 2p line was recorded including the $2p_{3/2}$ and $2p_{1/2}$ components. The Si 2p line was decomposed according to the procedure described in a previous work [10]. After deposition, it exhibits two components: one corresponding to the substrate ($Si^0$) at 99.3 eV, which is the only one present before deposition showing the efficiency of the native oxide removal, and a second one, called $Si_{ox}$, at a higher binding energy corresponding to silicon oxide.

The first results of the study of the $TiO_2$/Si interface reaction during MOCVD growth by *in situ* ARXPS presented in a former paper have concluded to the formation of an interfacial silicon oxide layer in addition to the $TiO_2$ expected one [10]. Consequently the system that should be considered is $TiO_2$/$SiO_2$/Si, as explained in Fig. 1. At first, the determination of the film total thickness was achieved by calculation of the thickness $t$ and surface coverage $\gamma$ of each layer using Fadley's model (Eq. (1)) [8]. This model considers a single overlayer A on a substrate B. The evolution of the experimental ratio $I_A/I_B$ of the overlayer A line intensity to that of substrate B, as a function of the emission angle $\Theta$, is fitted with the function $R(\Theta)$ taking into account some fixed parameters: the inelastic electron mean free path (IMFP) of photoelectrons of the transition $i$ through the layer $j$ ($\lambda_i^j$), which was obtained from the QUASES-IMFP calculation software based on the Tanuma, Powell and Penn formula [11], the photoionisation cross-section of transition $i$ ($\sigma_i$) [12], the theoretical concentration of each element $i$ in the corresponding bulk material $j$ ($C_i^j$).

$$R(\theta) = K\frac{\gamma\left(1-\exp\left(-\frac{t}{\lambda_A^A\cos\theta}\right)\right)}{(1-\gamma)+\gamma\exp\left(-\frac{t}{\lambda_B^A\cos\theta}\right)},\ \text{where } K=\frac{\sigma_A\lambda_A^A C_A^A}{\sigma_B\lambda_B^B C_B^B} \quad (1)$$

For the external $TiO_2$ layer thickness determination, the interfacial layer of $SiO_2$ should be considered as the substrate.


Fig. 1. Scheme of the structure of the film grown on a silicon substrate by MOCVD using Titanium TetraIsoPropoxide as precursor of $TiO_2$ from previous work [10]. The thickness $t_i$ and the surface coverage $\gamma_i$ of each layer $i$ are determined from ARXPS measurements.

Table 1
Values of the parameters of Eq. (1) used to determinate the thickness and surface coverage of the $TiO_2$ and $SiO_2$ layers of the $TiO_2$/$SiO_2$/Si system grown by MOCVD: the photoionisation cross-section of transition $i$ ($\sigma_i$) [12], the theoretical concentration of each element $i$ in the corresponding bulk material $j$ ($C_i^j$) and the inelastic electron mean free path (IMFP) of photoelectrons of the transition $i$ through the layer $j$ ($\lambda_i^j$) [11]

| Overlayer/substrate | Transitions | $\sigma_i$ | $C_i^j$ | $\lambda_i^i$ (nm) | $\lambda_i^j$ (nm) |
|---|---|---|---|---|---|
| $TiO_2$/$SiO_2$ | Ti 2p | 0.1069 | 1/3 | 2.126 | / |
| | $Si_{ox}$ 2p | 0.011 | 1/3 | 3.746 | 2.673 |
| $SiO_2$/Si | $Si_{ox}$ 2p | 0.011 | 1/3 | 3.746 | / |
| | $Si^0$ 2p | 0.011 | 1 | 3.090 | 3.754 |

The experimental ratio of intensities $I_{Ti2p}/I_{Siox2p}$ was fitted by Eq. (1) using parameters values detailed in Table 1. Identically, the ratio $I_{Siox2p}/I^0_{Si2p}$ was fitted by Eq. (1) and the appropriate parameters (Table 1) to obtain the thickness of the silicon oxide interfacial layer. The error on thickness and surface coverage determination was estimated for each experimental data fitting.

## 3. Results

The method described above was applied for the thickness determination of the deposit d. The results, presented in a former paper [10], are mentioned in Fig. 2 to allow the following discussion. The surface coverages $\gamma_i$ were close to one corresponding to a perfect wetting of the substrate by the film, as expected from the MOCVD process. The total thickness of the film calculated by adding the two intermediate thicknesses was 11.7±1.2 nm, which was in good agreement with the thickness determined by High Resolution Transmission Electron Microscopy (HRTEM): 11.8±0.4 nm [10]. The model applied for the determination of the film thickness was also validated, in spite of

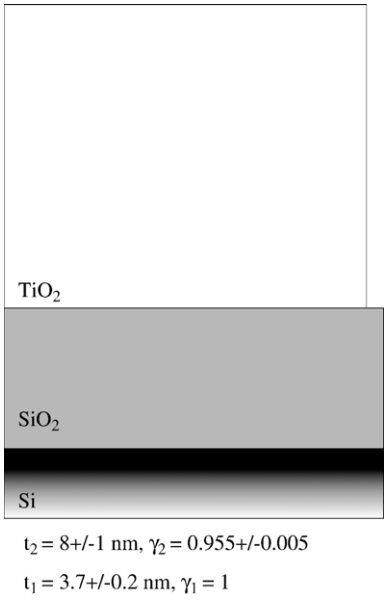


Fig. 2. Scheme of the structure of the deposit d grown by MOCVD on a silicon substrate. The thickness $t_i$ and the surface coverage $\gamma_i$ of each layer $i$ (1 for $SiO_2$, 2 for $TiO_2$ respectively) determined from ARXPS measurements are mentioned.