



# Characterization of ultrathin gate dielectrics by grazing X-ray reflectance and VUV spectroscopic ellipsometry on the same instrument

Pierre Boher <sup>\*</sup>, Patrick Evrard, Jean Philippe Piel, Jean Louis Stehle

*SOPRA S.A., 26 Rue Pierre Joigneaux, 92270 Bois Colombes, France*

## Abstract

Precise characterization of high  $k$  gate dielectrics becomes a challenging task due to the very thin thickness (<3–4 nm), which will be needed in the next generation of integrated circuits. Conventional techniques such as spectroscopic ellipsometry (SE) in the UV-visible range becomes difficult to use alone because of the great correlation between thickness and optical indices. To overcome this problem a new versatile instrument integrating SE in the VUV spectral range and grazing X-ray reflectance (GXR) has been developed recently by SOPRA. Both kinds of measurements can be made at the same location on the sample and at the same time. The analysis is made with a common optical model adjusting the layer thickness and the surface and interface roughness on the GXR data and the optical indices and other parameters like surface or interface roughness or inter-diffusion on the SE data. The paper describes some experimental results obtained with this system on  $ZrO_2$ ,  $HfO_2$  and  $La_2O_3$  films. Results are correlated with other experimental techniques in some cases. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

As the semiconductor industry continues to fulfill Moore's law, gate dielectric thickness is one of the most rapidly scaled dimension. The SIA technology roadmap [1] states that sub-0.25  $\mu\text{m}$  process requires equivalent oxide values of less than 50 Å. Some leading edge manufacturers are already pushing 0.18  $\mu\text{m}$  process technologies with

gate oxide thickness in the 30–40 Å range. The roadmap also predicts that gate oxidation technologies must go to the 20 Å range in the coming years for the 0.13  $\mu\text{m}$  process generations. Consequently, chip manufacturers must implement metrology systems that will be effective for statistical process control of ultrathin gate dielectrics. Typically a 10% precision-to-tolerance (P/T) ratio is required for a metrology system to be used in an effective statistical process control. For very thin gate dielectrics, this performance becomes very difficult to achieve with only one single characterization method like spectroscopic ellipsometry (SE) as thickness and optical indices are strongly correlated for all optical characterization methods.

<sup>\*</sup> Corresponding author. Tel.: +33-1 46 49 67 64/1 47 81 09 49; fax: +33-1 42 42 29 34.

*E-mail addresses:* dev@sopra-sa.com, sopra-sa@sopra-sa.com (P. Boher).

In addition, for such very thin layers, the interfaces and the roughness are also non-negligible and consequently must be taken into account in the characterization technique for high reliability.

Nitride/oxide gate dielectrics have already been widely used [2]. In this structure, the reliability at high electric field depends not only on the layer thickness but also on the nitridation level of the  $\text{SiO}_x\text{N}_y$  layer [3–5]. It is then important to characterize precisely the layer thickness and composition of this structure in order to control the process quality. SE is now a well-established non-destructive characterization technique widely used for thin film and multilayer characterization especially in the field of microelectronics. By analyzing the polarization change of light after reflection on the sample surface over a wide spectral range, precise information about physical characteristics of layers can be obtained. Phase change is extremely sensitive to angstroms of gate oxides. Accuracies of 5% can be easily obtained for each layer of a oxide/nitride/oxide structures with total thickness around 150 Å [6]. The thickness of the film  $T$  and its refractive index  $n$  are nevertheless completely correlated for thinner layers, particularly the bottom and top oxide, but the nitride optical thickness  $n \times T$  is very significant. The accuracy of the method is improved when the spectral range is extended in the VUV range because of the layers become generally absorbent. SE becomes also more sensitive to the roughness and surface effects.

The aim of the present study is to demonstrate the potential of a combined system including SE in the VUV spectral range and grazing X-ray reflectance (GXR) techniques. GXR is a technique of choice for measurement of thin film thickness without need of a complex structural model [7,8] as  $n$  is always very closed to 1 and  $k$  negligible at this energy. In the case of multilayers, precise information can also be extracted on the periodicity of the stacks and the interlayer structures [7]. For these high  $k$  films, GXR gives very precisely the layer thickness and some information on the interfaces. SE gives the optical index of the layer and additional information. The same type of approach has been applied independently and recently to  $\text{SiO}_2/\text{Si}$  interfaces [9].

## 2. Experimental details

### 2.1. Grazing X-ray reflection

In the X-ray wavelength range, the optical indices of all the materials are always very near one. In spite of this, a small index contrast between layers and substrate produces interference fringes. The position of these interference fringes obtained versus angle for fixed wavelength gives directly the thickness of the layers without any need of model. The grazing geometry and the short wavelength make the measurement very sensitive to roughness. The amplitude of the interference fringes depends directly on the index contrast between silicon substrate and the layer itself. This contrast is very small for  $\text{SiO}_2$ , higher for  $\text{Si}_3\text{N}_4$  and large for high  $Z$  compounds like  $\text{ZrO}_2$ ,  $\text{La}_2\text{O}_3$  or  $\text{HfO}_2$ . This technique is then especially suited for new high  $k$  material characterization.

A GXR setup has been developed at Sopra to be mounted as an option on the spectroscopic ellipsometers. One general view of the system is reported in Fig. 1. In addition to the ellipsometer arms, a X-ray setup is mounted on the same high precision  $\theta$ ,  $2\theta$  variable angle goniometer. It includes a ceramic fine focus X-ray tube (copper K- $\alpha$  line at 1.54 Å) cooled with water. A computer controlled stabilized high voltage supply is used at 40 kV, 30 mA. All safety relative to X-rays has been included. The beam is defined perpendicular to sample surface using Soller slits located just after the X-ray tube. The beam divergence is limited by interchangeable slits (or a parabolic multilayer mirror as option). A curved graphite crystal is used to select the wavelength of the X-ray beam after reflection on the sample surface. A standard sample holder is manually adjustable on three axes. The sample dimension can be up to 200 mm diameter and 25 mm thickness. The detection is made using a NaI scintillator with beryllium window and a photo multiplier tube in photon counting mode as for the standard GESP5 instrument. The dynamic range of the instrument can be extended to more than  $10^6$  using automatic Ni attenuators and optimized integration time. The system is computer controlled with a user-friendly software under Microsoft Windows

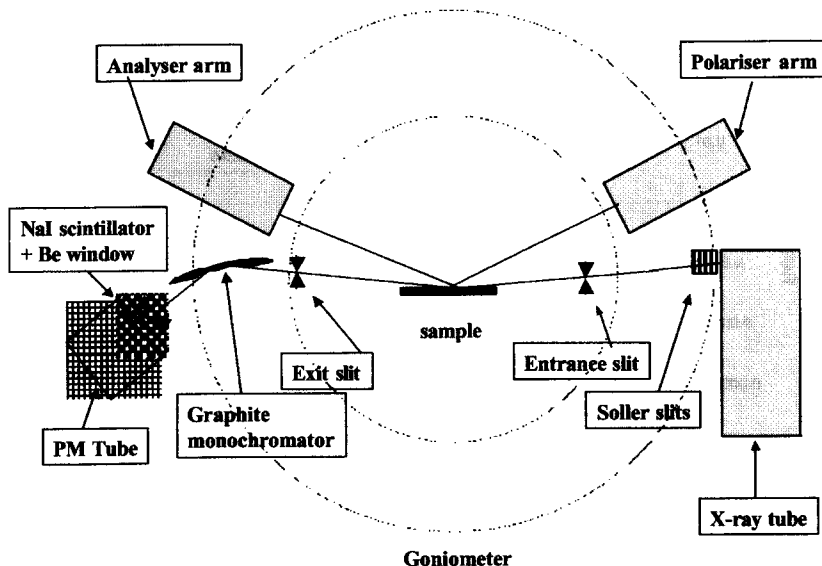


Fig. 1. Schematic diagram of the GXR system as an option of a spectroscopic ellipsometer.

NT environment. Standard X-ray diffraction measurement can also be made with the same optical setup. This system is described in details with some examples of application in Ref. [10].

## 2.2. Spectroscopic ellipsometer

One of the main drawbacks of SE, is the necessity to use optical models to extract physical parameters. For most of the situations when the optical indices of all the materials are known and when layer thickness is large enough to avoid correlation with the refractive index, SE is a very powerful method now routinely used especially in the microelectronics field. Nevertheless, in the case of very thin quasi transparent layers like for high  $k$  gate dielectrics, the thickness and optical index are completely correlated and cannot be extracted separately even if the measurement is extended in the VUV spectral range. Moreover, the importance of the interface and surface roughness or inter diffusion becomes critical to build an accurate structural model for these samples. These parameters are extracted by GXR measurements. Then SE is applied and optical indices of the high  $k$  gate dielectrics are extracted.

The measurements have been made in the VUV down to 140 nm using the purged UV (PUV) ellipsometer developed by Sopra recently [11]. In contrast with the standard ellipsometers, the double monochromator is included in the polarizer arm just after the deuterium lamp. This mounting ensures an optimized stray light rejection with a minimized beam path. The light beam goes through a  $\text{MgF}_2$  Rochon polarizer mounted on a stepper motor. The reflected beam passes through another Rochon analyzer and is detected by a photo multiplier in photon counting mode. The two arms are mounted on the same goniometer as for GXR. The angle of incidence can be changed automatically in the range  $7\text{--}90^\circ$ . The system works in rotating analyzer mode to avoid parasitic polarization due to the monochromator. Polarization sensitivity of the detector is calibrated in straight line. The spectral range is 140–700 nm. The entire system is installed inside a glove box with continuous  $\text{H}_2\text{O}$  and  $\text{O}_2$  purification. Residual  $\text{H}_2\text{O}$  and  $\text{O}_2$  are measured continuously. They are in the parts per million range during normal working conditions.

For both techniques, the experimental data are fitted adjusting automatically the parameters of a

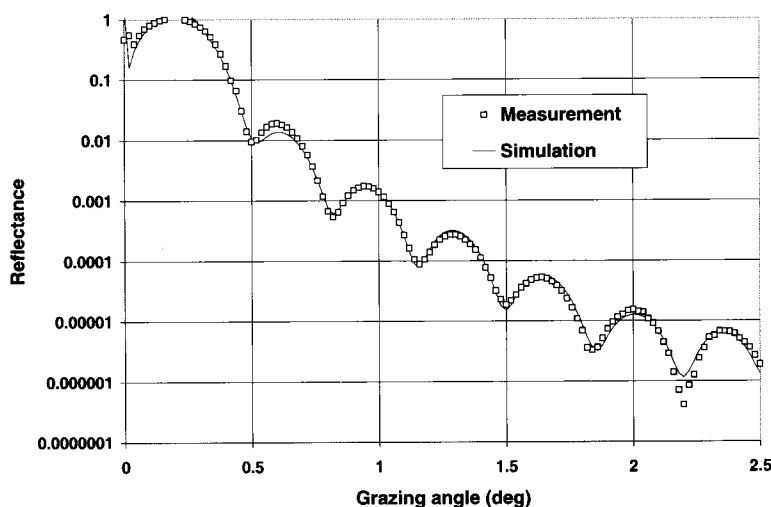


Fig. 2. Experimental and simulated GXR spectra of sample 2 of Table 1.

common multilayer model. Standard numerical algorithms such as Levenberg Marquard or Simplex are used to adjust automatically the model on the experiment. Thickness and roughness are fitted on the GXR data. Optical indices are deduced from SE data.

### 3. Experimental results

To scale gate thickness below the 1.5 nm equivalent oxide thickness range, a dielectric with large dielectric constant ( $k > 20$ ) is needed. Different candidates are already in study like  $\text{HfO}_2$ ,  $\text{La}_2\text{O}_3$  or  $\text{ZrO}_2$ . However, this kind of metal oxides introduces a lot of new problems including metal diffusion into the substrate, silicide formation and thermal stability. Hereafter, we present some results on these three type of materials.

#### 3.1. $\text{ZrO}_2$ gate dielectrics

Three  $\text{ZrO}_2$  layers deposited on silicon substrate by reactive sputtering using a Zr target and  $\text{Ar} + \text{O}_2$  gas mixture have been measured. The first sample is measured just after deposition without thermal treatment. The second one has been annealed at 700 °C during 60 s after deposition.

These two samples have a thickness of about 12 nm. A third sample is thinner around 3 nm.

Each sample has been measured by grazing X-ray reflection. An example of such a measurement is reported in Fig. 2 in the case of sample 2. The model used for the regression includes only a  $\text{ZrO}_2$  layer on top of a substrate and the thickness and the top surface roughness of the layer are adjusted. The best adjustment is also reported in Fig. 2 and the results of the regression are summarized in Table 1. The accuracy on the thickness is very good (less than 0.1 nm) due to the occur-

Table 1  
Summarized results obtained by GXR and SE on  $\text{ZrO}_2$  films on silicon

Sample number	Structure	GXR	SE
Sample 1	Roughness (nm)	$0.34 \pm 0.008$	
	Top $\text{ZrO}_2$ (nm)	$10.94 \pm 0.06$	
	Bottom $\text{SiO}_2$ (nm)		$4.70 \pm 0.18$
Sample 2	Roughness (nm)	$0.35 \pm 0.009$	
	Top $\text{ZrO}_2$ (nm)	$12.28 \pm 0.08$	
	Bottom $\text{SiO}_2$ (nm)		$4.19 \pm 0.27$
Sample 3	Roughness (nm)	$0.35 \pm 0.004$	
	Top $\text{ZrO}_2$ (nm)	$2.58 \pm 0.01$	
	Bottom $\text{SiO}_2$ (nm)		$2.67 \pm 0.05$

rence of numerous interference fringes in the explored angular range. These interference fringes are very well defined due to the high index difference between  $\text{ZrO}_2$  and silicon in the X-ray range. When the layer thickness is further reduced, the number of interference fringes becomes smaller. Nevertheless, the same kind of approach can be applied and gives the same parameters also with a good accuracy as reported in Table 1.

The analysis of the SE results has been made using the thickness values determined by GXR. A simple model with a  $\text{ZrO}_2$  layer on top of a silicon substrate does not work properly when we adjust only the optical indices of the layer. To get an acceptable agreement between the experiment and the simulation it is necessary to include a bottom interface layer (assumed with the optical index of  $\text{SiO}_2$ ) in addition to  $\text{ZrO}_2$  layer. This layer does not produce a sensitive effect on the GXR measurement due to the very low contrast between  $\text{SiO}_2$  and silicon in the X-ray range. During the regression, the interface layer thickness is adjusted with the optical indices of the  $\text{ZrO}_2$  layer applying a dispersion law model (Cauchy law with different Lorentz oscillators). The optical indices of the  $\text{ZrO}_2$  layer is then extracted at the same time. Results are summarized in Table 1. Our structural

analysis is confirmed by transmission electron microscopy. As shown in Fig. 3, a thick interface with much lower density is clearly visible between the silicon substrate and the  $\text{ZrO}_2$  layer.

### 3.2. $\text{HfO}_2$ gate dielectrics

One sample with a layer thickness around 13 nm has been measured by GXR (cf. Fig. 4) and VUV SE (cf. Fig. 5). The GXR spectrum presents fewer interference fringes than the corresponding measurement on the  $\text{ZrO}_2$  layer discussed previously (cf. Fig. 2), in spite of a similar layer thickness. The index contrast predicted for this type of layer is slightly higher than for  $\text{ZrO}_2$ . Then the amplitude of the interference fringes should be higher in Fig. 4 than in Fig. 2. This is in fact the case just after the total reflection threshold but the amplitude of the fringes is dumped for the  $\text{HfO}_2$  sample when the grazing angle is higher than  $1^\circ$ . This effect is not detected for  $\text{ZrO}_2$  samples. It is due to the occurrence of large surface roughness that we have simulated including a surface layer 0.9 nm thick on top of the  $\text{HfO}_2$  layer and a Debye–Waller factor of 0.7 nm on the interface (cf. Fig. 4). The surface roughness is then substantially higher for  $\text{HfO}_2$  films than for  $\text{ZrO}_2$  films. The SE data have been analyzed using the model deduced from GXR data. The thickness of the  $\text{HfO}_2$  film and of the top surface film have been fixed and the optical indices of the layer have been adjusted using a dispersion law model including a Cauchy law and three Lorentz peaks. The best adjustment using this model is also reported in Fig. 5. The deduced optical indices are reported in Fig. 6. The film becomes absorbent above 6 eV (below 200 nm), demonstrating the interest to use VUV spectral range for this kind of sample. It is also, in our knowledge, the first determination of optical indices for  $\text{HfO}_2$  in the VUV range. On the other hand,  $\text{HfO}_2$  is used commonly for optical coatings and its refractive index is well known in the visible range [12]. If we compare to our determination, the refractive index of our gate dielectric is slightly lower than expected (1.9 instead of 2 for  $n$  at 450 nm). This is probably due to the very thin layer thickness of the film which results in a lower density.

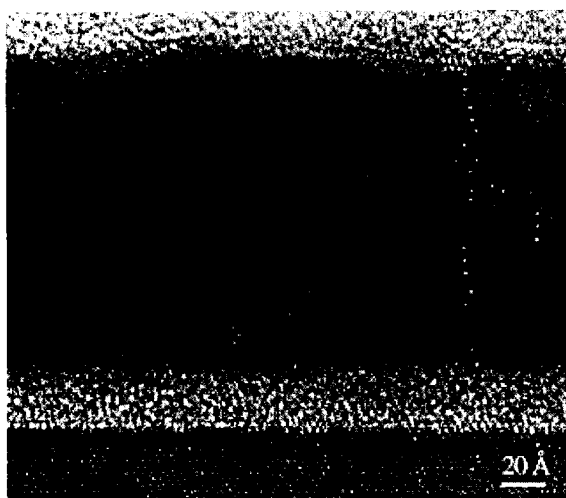


Fig. 3. Transmission electron microscopy on sample 2 of Table 1.

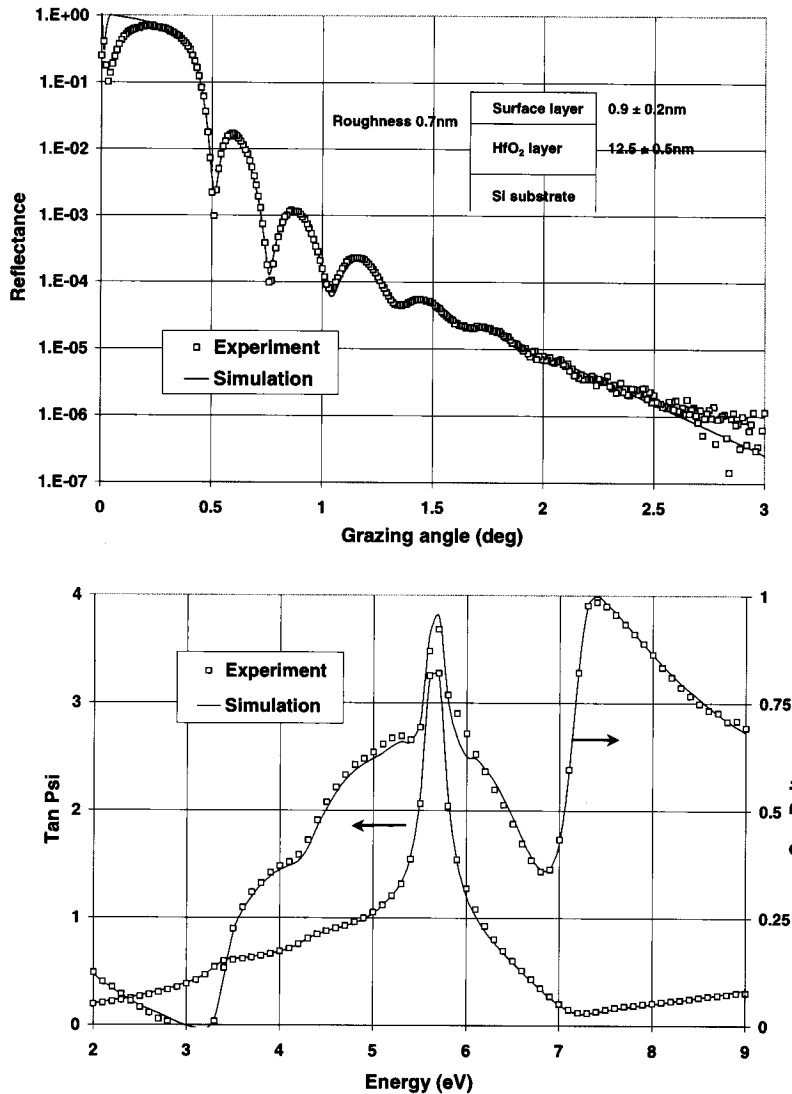


Fig. 4. GXR on one HfO<sub>2</sub> layer on silicon.

### 3.3. La<sub>2</sub>O<sub>3</sub> gate dielectrics

La<sub>2</sub>O<sub>3</sub> is not intensively studied as gate dielectric. Potentially its physical properties are very attractive but the material is difficult to deposit in good condition. We have measured one quite thick layer deposited by magnetron sputtering of a La<sub>2</sub>O<sub>3</sub> target on silicon substrate. The thickness is measured

precisely by GXR at 52.5 nm and a quite high surface roughness is also detected (1.2 nm). The sample is also measured by VUV SE at different angles of incidence (cf. Fig. 7). Then the optical indices are extracted point by point, adjusting the  $n$  and  $k$  values at each wavelength to fit the curve versus incidence angle. The result is reported in Fig. 6 where we can see that the dispersion curve of La<sub>2</sub>O<sub>3</sub>

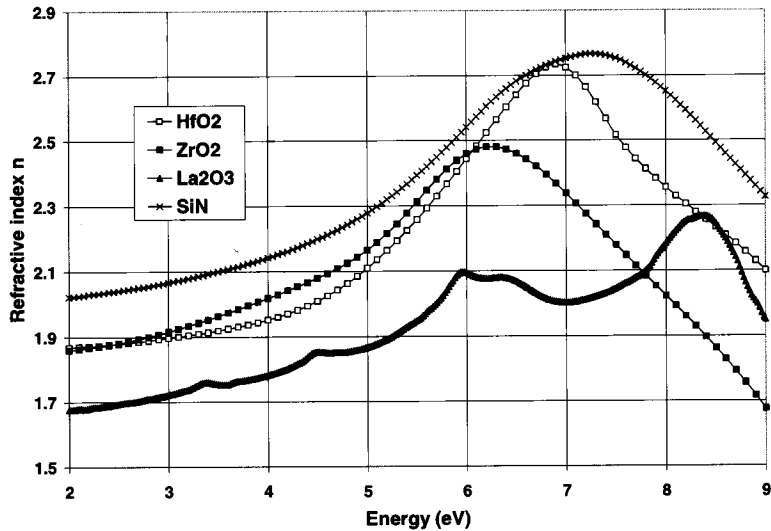


Fig. 5. VUV SE on the same  $\text{HfO}_2$  layer as for Fig. 4.

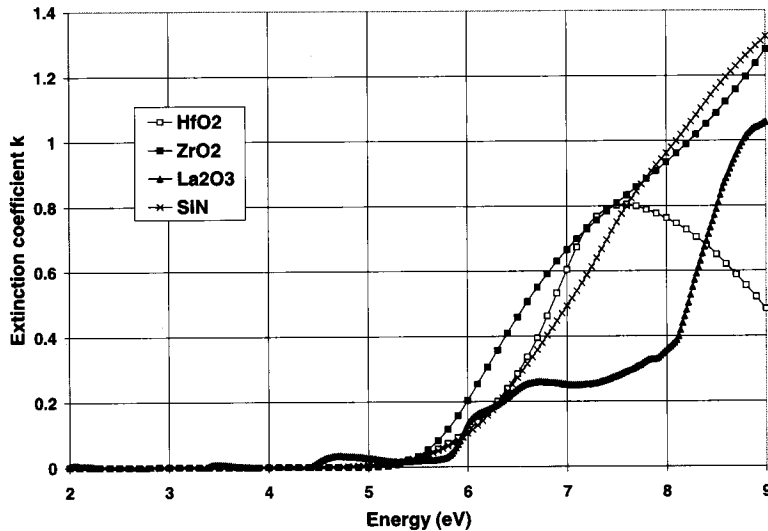


Fig. 6. Optical indices extracted from VUV SE.

presents different well-defined optical transitions at 3.3, 4.5, 6, 6.6 and 8 eV. This is characteristic of a well ordered material with probably a high degree of crystallization. It should be also an explanation to the important top surface roughness. Further investigation is needed to clarify this first analysis.

#### 4. Conclusion

We have presented a new metrology system combining SE and GXR on the same setup. This system has been applied to the characterization on high  $k$  gate dielectrics which is one of the more

