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Depth profiling investigation by pARXPS and MEIS of advanced transistor technology gate stack

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The High-k Metal Gate (HKMG) film stack, introduced since 32 nm node of complementary metal oxide semicon-ductor (CMOS) technology, is one major case where composition determination is mandatory. Parallel Angle-Re-solved X-ray Photoelectron Spectroscopy (pARXPS) allows to perform high resolution chemical depth profiling characterization of advanced transistor technology gate stack. By applying the maximum entropy concept to the pARXPS measurements, it is possible to obtain depth profiling information. Although, the capability of this technique has been widely discussed in the past few years, we propose here to validate the pARXPS depth pro-filing technique using Medium Energy Ion Scattering (MEIS), another high resolution chemical depth profiling characterization technique. Comparison between pARXPS and MEIS measurements allowed us to validate the pARXPS depth profiling technique and to determine with accuracy the composition of HKMG HfON/SiON stack from the 14 nm node technology.

1. Introduction

Since the 32 nm node, the High-k Metal Gate (HKMG) film stack has been introduced to replace the SiO_2 gate insulator [1]. For the 14 nm node, the gate oxide stack is composed of a high-κ HfON layer deposited on an interfacial SiON layer. The incorporation of nitrogen into HfO_2 high-k is beneficial to suppress boron penetration, it reduces the leakage current and increases the dielectric constant [2]. The HfON thin layer is deposited on a SiON interfacial layer (IL) to prevent the formation of a bad quality SiO_2 layer between the HfON layer and the channel [3].

The composition determination of nanometer thick multilayers films represents one of the various challenges to face to support the development of advanced technology node. In the case of HKMG films stack, thickness and composition must be precisely controlled to reach the transistor specifications. In a previous work, Parallel Angle-Resolved X-ray Photoelectron Spectroscopy (pARXPS) and Medium Energy Ion Scattering (MEIS), two high resolution chemical depth profiling characterization techniques, have been selected to explore the nature and composition of the HfON/SiON bi-layer [4]. Thanks to pARXPS, chemical profile reconstructions have been conducted and have shown that the nitrogen distribution presented a gradient toward the Si substrate. Nevertheless, the MEIS detection limit for nitrogen was closed to the gate stack nitrogen dose, thus the determination of the nitrogen distribution profile was not achievable with MEIS and the validation of the pARXPS depth profiling technique was not done. Hence, the measurement of similar samples with higher nitrogen dose on both pARXPS and MEIS will be done in this work. The comparison of the different depth profiles obtained with these two depth profiling technique will allow us to validate the nitrogen distribution obtained by pARXPS as well as the chemical profiles obtained on the real HKMG stack in our previous work.

2. Experimental

For this study, two samples were prepared on 300 mm Si(100) wafers: a plasma nitrided SiON film and a plasma nitrided HfON on a SiO_2 IL.

pARXPS measurements were performed using a customized Thermo Fisher Scientific Theta 300 pARXPS. The X-ray source is a monochromatic aluminum anode source at 1486.6 eV. The pARXPS analysis were performed in UHV conditions ($P = 1 \times 10^{-9}$ mbar). The specific lens design and the two-dimensional detector integrated on this tool allows to perform a parallel acquisition of the photoemission signals at eight

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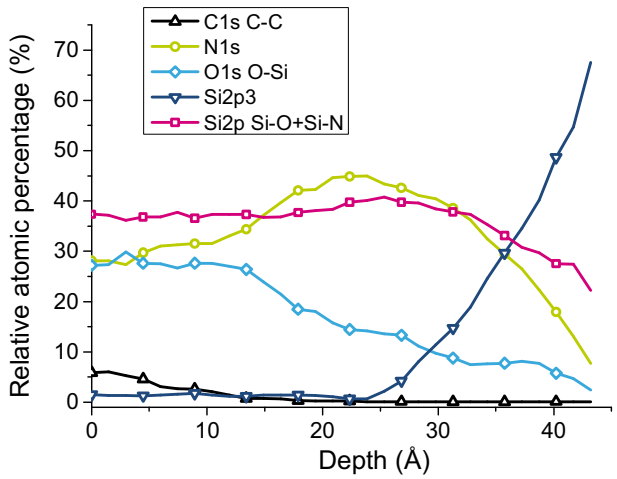

Fig. 1. pARXPS depth chemical profile reconstruction of the highly nitrided SiON sample.

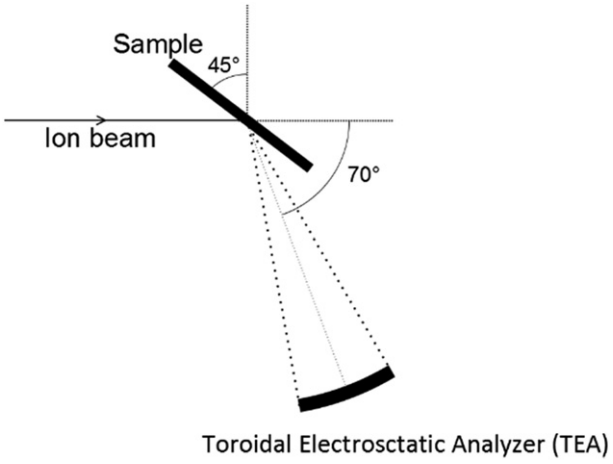

Fig. 3. Schematic representation of the MEIS experimental conditions.

emission angles from 20° to 80° with respect to the sample normal, without any tilt of the sample. Thus, pARXPS can provide depth resolved information about the chemical state of near-surface layers [5–7]. pARXPS can also be used to measure ultra-thin film thickness [8], moreover the angle response obtained with pARXPS leads to a better accuracy and a better reliability.

The MEIS measurements have been realized with a 100 keV He^+ incident ion beam, positioned in a channeling geometry and aligned along the [111] axis of the silicon substrate. The scattered ions were detected along a blocking direction. This geometry increases the sensitivity of the deposited layers by significantly reducing the contribution of the ions scattered from the substrate. This technique has already been validated to provide high depth resolution, quantitative, compositional and structural analysis of high-k nanofilms [9].

3. Results and discussion

The SiON/Si and HfON/SiO_2/Si samples were measured by pARXPS to provide thickness measurements and to perform chemical profile reconstructions to determine the nitrogen distribution. The spectra Si 2p, O 1s, N 1s, Hf 4f and C 1s were recorded at eight different photoemission angles between 23.75° and 76.25°.

The thickness determination by pARXPS is based on the measurement of peak area ratio and on the Beer-Lambert law. For a SiON layer on a Si substrate, the ratio of the Si peak associated to the substrate and the one associated to the SiON layer is given by the following equation:

$$\frac{I_{Si2p\ SiON}}{I_{Si2p\ sub}} = \frac{I^{\infty}_{Si2p\ SiON}}{I^{\infty}_{Si2p\ sub}} \frac{\left(1-\exp\left(-\frac{T}{\lambda_{Si-O,SiON}\cos\theta}\right)\right)}{\exp\left(-\frac{T}{\lambda_{Si,SiON}\cos\theta}\right)}$$

With I^{∞} the peak expected area of a sample of infinite thickness measured under normal XPS conditions, T the SiON thickness, λ the electron attenuation length and θ the photoemission angle. The factors I^{∞} and λ are constant and can be numerically determined [10–12]. Thus, from the Beer-Lambert law and the measurement of the peak area ratio, it is possible to determine the thickness of the SiON layer. In addition, because the pARXPS can provide several measurement points versus angle (eight measurement angles), the thickness measurements are more accurate and reliable. It is also possible to determine the thickness of two layers or more by considering the adapted peak area ratios and by solving the corresponding equation system. For the SiON/Si sample, the SiON thickness was found to be 42 Å and for the HfON/SiO_2/Si sample, the HfON and SiO_2 layer thicknesses were found to be 15.4 Å and 11.5 Å respectively.

Based on the results obtained at the different angles, pARXPS technique can provide key chemical profile information by applying the maximum entropy concept, as described in ref. [13,14]. Fig. 1 shows

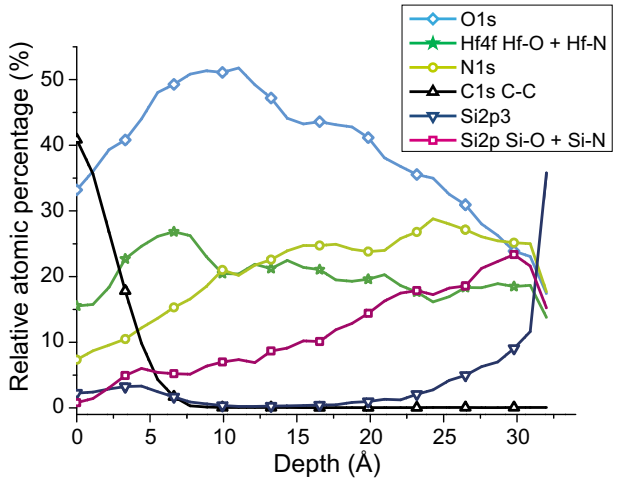

Fig. 2. pARXPS depth chemical profile reconstruction of the highly nitrided HfON/SiO_2/Si sample.

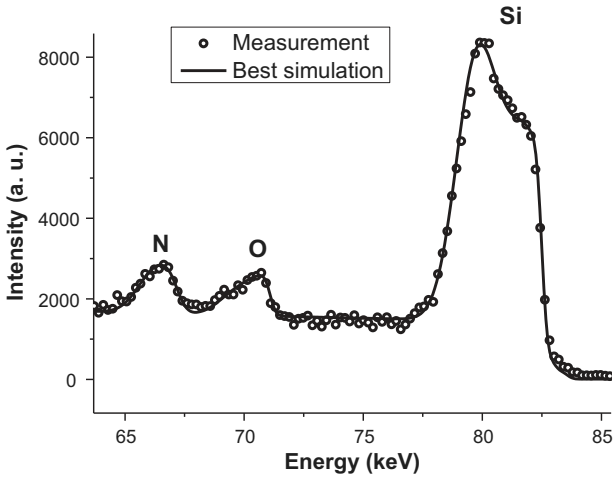

Fig. 4. MEIS measured spectra and simulation of the highly nitrided SiON sample.

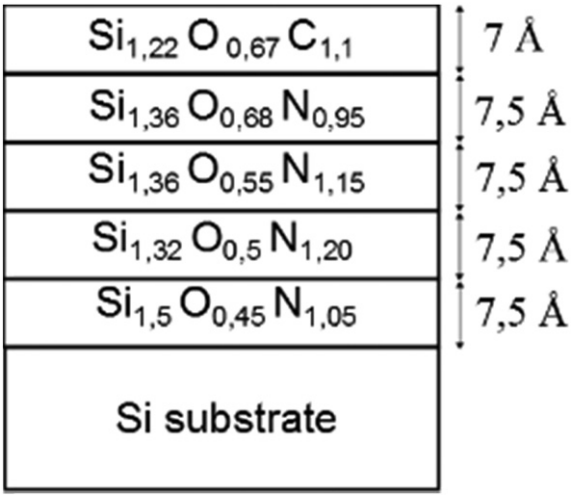

Fig. 5. MEIS simulated stack of the highly nitrided SiON sample.

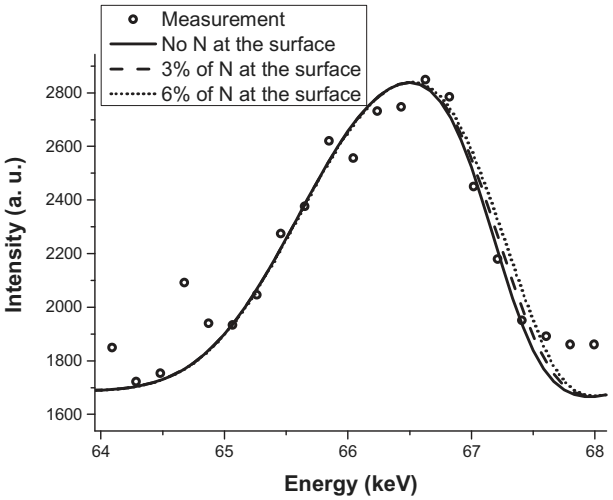

Fig. 7. MEIS nitrogen measured spectra and simulations with different nitrogen surface distributions.

the chemical profile reconstruction of the SiON/Si sample, directly obtained with this technique, without applying any constrain or predefined models on the calculations. Only the six first angles have been used (from 23.75° to 61.25°) to obtain the chemical profile reconstruction, the elastic scattering phenomenon becoming predominant over 60° [15] and deteriorating the measurement validity. The N 1s distribution has been obtained by considering the total area under the nitrogen peak.

On this figure, the relative atomic percentages of the different elements are plotted as a function of depth (0 represents the surface of the sample). Nitrogen distribution first increases with the depth and then decreases, while the oxygen percentage constantly decreases with depth. We can notice that the oxygen variation (from 28% to 5% at 40 Å) is stronger than the nitrogen variation (between 28% and 45% at 25 Å). The silicon distribution associated to the SiON layer is constant with the depth.

Same technique is applied to characterize $HfON/SiO_2/Si$ stack to obtain the chemical profile reconstruction of this sample. Fig. 2 shows the relative atomic percentages of the different elements of $HfON/SiO_2/Si$ as a function of the depth. The total areas under the N 1s peak and the O 1s peak have been taken into account to obtain the chemical profile reconstruction. Thus the contributions of the N—Hf bonds and the N—Si bonds have been merged to represent only the nitrogen atoms, as well as the O—Hf bonds and the O—Si bonds to represent only the oxygen atoms.

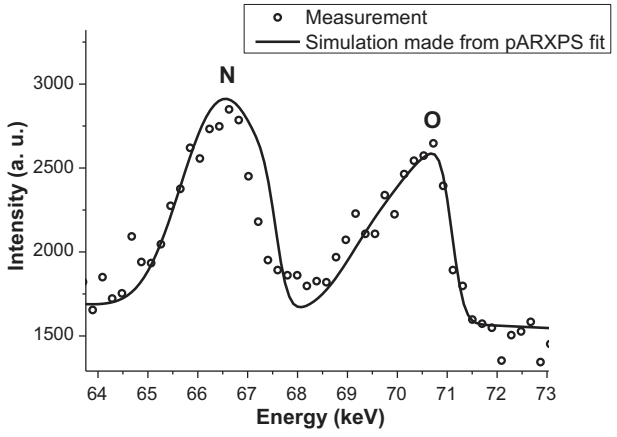

Fig. 6. MEIS measured spectra and simulation based on the pARXPS results of the highly nitrided SiON sample.

The nitrogen seems to show a gradient toward the substrate, thus the SiO_2 layer has been nitrided and contains more nitrogen than the top HfON layer. Additionally, the nitrogen atomic percentage increases with the depth, while in meantime we observe a decrease of the oxygen atomic percentage.

To confirm the results obtained by pARXPS measurement and maximum entropy calculations, MEIS measurements have been performed. The thickness of the different layers and the stoichiometry of the material have also been determined thanks to MEIS. These measurements were realized with a grazing angle detection, in order to distend the MEIS peaks and to be more accurate with the peak modelling. A channeling geometry was used to reduce the substrate contribution. The Fig. 3 shows schematically the MEIS measuring system geometry.

MEIS scattering energy spectrum of the SiON sample and the best simulation of this sample are shown in Fig. 4. The simulated MEIS spectra is obtained after setting the different elements, their stoichiometry, the layer's thickness and the layers' density. The best simulation is thus obtained by adjusting the different parameters to fit the different MEIS peaks.

The simulation represented on the Fig. 4 was obtained by considering a 37 Å over layer. The thickness obtained by MEIS is thus really closed to the one obtained by pARXPS. Fig. 5 shows in details the stack used in this simulation. Because of the weak signal intensity of the nitrogen and the oxygen peaks, the simulation was made by considering, at the starting point, the nitrogen and the oxygen pARXPS chemical profile distributions and was then improved to fit the best the MEIS nitrogen and the oxygen peaks by adjusting the simulation.

In this model, the oxygen stoichiometry decreases with the depth. Nitrogen exhibits a surface depletion, indeed the first layer does not contain nitrogen, then its stoichiometry increases slightly and finally decreases in the depth. If we convert the nitrogen stoichiometry into atomic relative percentage for the four layers that contain nitrogen, we notice a variation from 31.8% to 39.7%, which is close to the variation that we observe with pARXPS (from 28% to 45%). We can also notice that the first layer contains carbon atoms. These atoms come from the atmospheric surface contamination (typically air-break). Regarding

Table 1
χ^2 MEIS values for the three different nitrogen surface distribution simulations.

Simulation	χ^2_N value
With no nitrogen at the surface	81.5
With 3% of nitrogen at the surface	86.7
With 6% of nitrogen at the surface	99.1

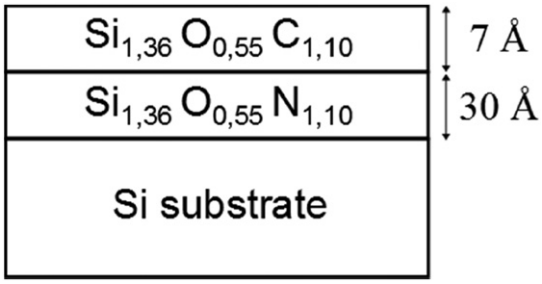

Fig. 8. MEIS simulated stack of the highly nitrided SiON sample with constant nitrogen, oxygen and silicon compositions.

silicon in the SiON layer, it is rather stable, which is also consistent with the pARXPS results.

As seen previously, pARXPS chemical profile reconstruction does exhibit a surface nitrogen depletion but not as strong as the one observed with the MEIS results. Hence, to compare the MEIS results with the pARXPS chemical profile reconstruction, a MEIS simulation elaborated from the pARXPS results has been realized and compared to the measured MEIS spectra. The Fig. 6 presents this simulation:

In order to get a more quantitative comparison between the simulated MEIS spectra and the measured ones, we introduce a χ [2] parameter. This parameter is an indicator of goodness of fit. Here, it is the Pearson's chi-squared parameter that is used. The calculation of this parameter uses the sum of differences between the measurement and the simulation:

$$\chi_j^2 = \sum_{i=1}^{N} \frac{(M_{j,i} - F_{j,i})2}{F_{j,i}}$$

with χ_j the chi parameter associated to the j^{th} peak, $M_{j,i}$ the value of the j^{th} measured peak at the i^{th} point and $F_{j,i}$ the value of the j^{th} fitted peak at the i^{th} point. As defined here, two assumptions are made: the first one is that the different MEIS peaks are independent and do not have any influence on the other peaks' shape, and the second one is that the measurement uncertainty for every point is the same. Taking into account the measurement uncertainty would be more accurate, nevertheless we cannot access this information. For the oxygen peak, the χ_O^2 value obtained for the simulation elaborated from the pARXPS is 103, while the χ_O^2 for the oxygen best simulation is 95. This two values are really closed, thus the oxygen gradient is similar for the two characterization techniques. Nevertheless, the nitrogen peak is not as well fitted. Indeed, the simulated peak is larger than the experimental peak. The χ_N^2 value obtained with this simulation is 313.4, which is much larger than the 81.5 χ_N^2 value of the nitrogen best fitted peak. This simulation confirms that we don't see nitrogen at the surface of the sample by MEIS, contrary to pARXPS results. This can be explained if one considers the method of chemical profile reconstructions used by pARXPS. As said earlier, the two more grazing angles (68.75° and 76.25°) are not taken into account to prevent the elastic scattering phenomenon to deteriorate the profile reconstructions. Nevertheless, these two angles are the ones which are the most sensible to the surface. Thus, removing these two angles can cause a loose of information at the extreme surface, which can explain the fact that we are not sensible to this nitrogen surface decrease. Hence, the results obtained by MEIS are not incompatible with the pARXPS profile reconstruction. The MEIS appears here to be more extreme surface sensitive.

Table 2
χ^2 MEIS values of the nitrogen and oxygen atoms for the simulations with and without gradient.

Simulation	χ_N^2value	χ_O^2value
Without gradient	76.6	129
With gradient	81.5	95

In order to validate the depletion of nitrogen at the surface, we compare three simulations: the one obtained in Fig. 5 (without nitrogen at the surface), together with two similar simulations with respectively 3% and 6% of nitrogen at the surface. This comparison is represented in Fig. 7 where we focalized on nitrogen information.

The χ_N^2 values obtained for the three simulations are detailed in Table 1:

The simulation without nitrogen at the surface best fits the experimental points but the χ_N^2 value of the simulation with 3% of nitrogen at the surface is close to the one without surface nitrogen simulation. This MEIS measurement allows us to conclude that we have a depletion of nitrogen at the extreme surface, and that its atomic relative percentage does not exceed 3%.

In order to evidence the nitrogen gradient obtained by MEIS, two different simulations of the SiON/Si stack have also been compared: the first one with a nitrogen and oxygen gradient as presented in Fig. 5, and the second one with a constant nitrogen and oxygen composition along the depth as detailed just below (Fig. 8):

The Fig. 9 presents these two simulations:

The χ^2 values obtained for these two simulations are detailed in Table 2:

If we consider the nitrogen peak, the difference between the two simulations is not very significant. The simulation with no gradient

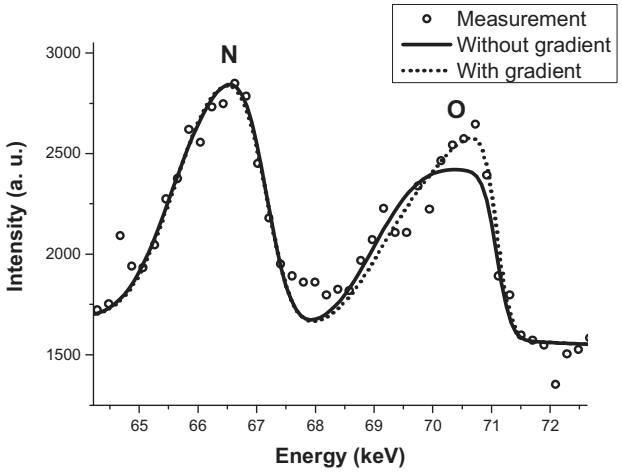

Fig. 9. MEIS measured spectra and simulations with and without gradient along the depth.

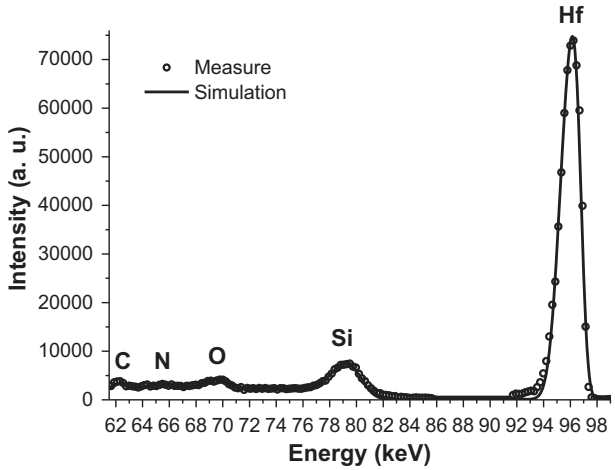

Fig. 10. MEIS measured spectra and simulation of the highly nitrided HfON/SiO_2/Si sample.

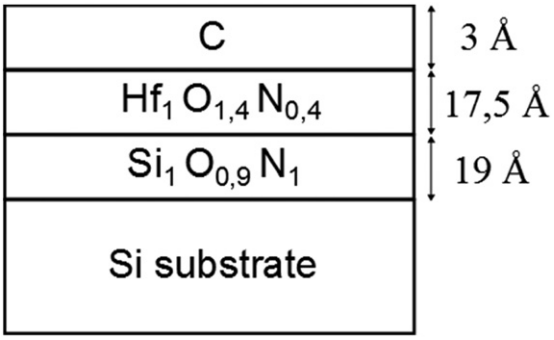

Fig. 11. MEIS simulated stack of the highly nitrided HfON/SiO_2/Si sample.

seems to be better, within the measurement dispersion, but it is hard to conclude on the best one. Moreover, since the nitrogen is a light atom, the MEIS sensitivity for this atom is weaker compare to a heavier atom. Hence, for this sample we cannot discriminate a soft gradient from a constant nitrogen composition. Nevertheless, it is clear that nitrogen does not present a strong gradient. Conversely, from the oxygen peak, we can clearly assert that oxygen presents a gradient. Indeed the simulation without gradient does not fit at all the experimental points and the χ^2_O values are very different. The MEIS results suggest that the oxygen stoichiometry decreases from 0.68 to 0.45 toward the interface with the Si substrate, which corresponds to a variation of 23% to 15% in relative atomic percentage. This result is coherent with pARXPS, indeed the relative atomic percentage of oxygen decreases from 28% to 5% at 40 Å, according to the chemical profile reconstruction.

Thus, MEIS results seem to confirm the different atomic distributions obtained by pARXPS

The HfON/SiO_2/Si sample has also been measured by MEIS using the same conditions. The spectra obtain by MEIS for this sample and the best simulation are shown in Fig. 10

The simulation developed to fit the experimental results was found by considering a 17.5 Å thick HfON overlayer and a 19 Å interfacial SiON interlayer. These values are not consistent with the pARXPS thickness measurement. Nevertheless, pARXPS thickness measurement technique seems to be more reliable since this measurement relies on a peak area ratio while for MEIS we can only access the thickness * density product, thus the thickness measurement depends on density values used in the simulation. The Fig. 11 details the simulated stack:

In this simulation we can notice that SiON layer is more nitrided than HfON, and conversely the oxygen stoichiometry is weaker in the SiON compare to the HfON. This results are consistent with the one obtained by pARXPS.

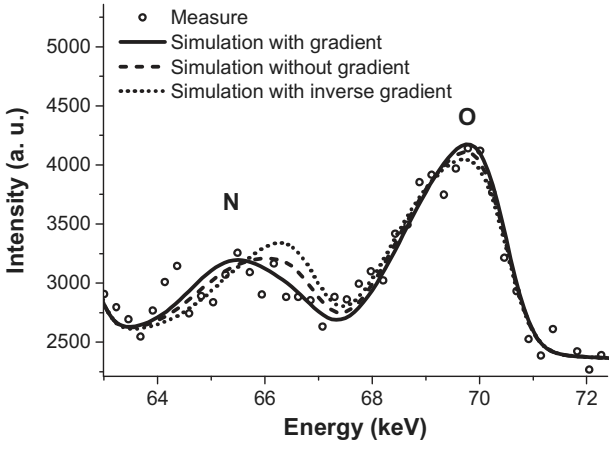

Fig. 12. MEIS measured spectra and simulations of the HfON/SiO_2/Si sample with different nitrogen gradients.

Table 3
χ^2 MEIS values of the different nitrogen distribution simulations in the HfON/SiO_2/Si sample.

Simulation	χ^2_N value
With gradient	9.6
With no gradient	11.1
With inverse gradient	18.8

To analyze the nitrogen profile in the HfON/SiO_2 stack we compared three different simulations: a first one with an increasing nitrogen gradient toward the Si substrate (simulation represented Fig. 9), a second one with a decreasing nitrogen gradient toward the Si substrate (a nitrogen stoichiometry of 1 in the HfON layer and 0.4 in the SiON layer) and a third one with a constant nitrogen distribution in the stack (0.7 in the two layers). The Fig. 12 presents these three simulations:

To evaluate the best nitrogen peak fit among the three simulations, the associated χ^2_N values have been calculated and visible in Table 3:

Even if the experimental points of the nitrogen peak are scattered, the simulation with the increasing nitrogen gradient toward the substrate is clearly the one that fit the best the experimental points. Thus, this measurement allows us to say that we have more nitrogen in the SiON layer compare to the HfON layer, which is consistent with a nitrogen gradient that increases toward the substrate. The MEIS measurement validates here the nitrogen profile obtained by pARXPS. Nevertheless, for this sample, the MEIS sensitivity does not allow access to the nitrogen profile inside the HfON layer nor in the SiON layer.

4. Conclusions

Thanks to the angle information and by applying the maximum entropy concept, pARXPS can provide chemical profile reconstruction. A comparison between pARXPS and MEIS allowed us to validate the pARXPS chemical profile reconstruction obtained on the materials used to compose the HKMG stack of the 14 nm FDSOI technology. Indeed, the nitrogen and the oxygen distributions in the two nitrided SiON/Si and HfON/SiO_2/Si reference samples were found to be coherent regarding the two profiling techniques.

To conclude, this work allowed us validate the pARXPS profile reconstruction obtained on the real HKMG stack in our previous work [4].

Acknowledgment

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References

[1] ITRS, Roadmap for Semiconductors - Process Integration, Devices, and Structures, 2013.
[2] H.J. Cho, C.S. Kang, K. Onishi, S. Gopalan, R. Nieh, R. Choi, S. Krishnan, J.C. Lee, IEEE Electron Device Lett. 23 (2002) 249–251.
[3] M. Cho, J. Park, H.B. Park, C.S. Hwang, J. Jeong, K.S. Hyun, Appl. Phys. Lett. 81 (2002) 334.
[4] L. Fauquier, et al., Surf. Interface Anal. (2016) (Published online in Wiley Online Library).
[5] B. Pelissier, A. Beaurain, R. Gassilloud, J.P. Barnes, F. Martin, O. Joubert, Microelectron. Eng. 85 (2008) 1882–1887.
[6] M. Py, J.P. Barnes, R. Boujamaa, M. Gros-Jean, K. Nakajima, K. Kimura, C. Roukoss, B. Pelissier, N. Gambacorti, J. Vac, Sci. Technol. (2011) B 29, 032208.
[7] T. Conard, W. Vandervorst, A. Bergmaier, K. Kimura, J. Vac. Sci. Technol. A 30 (3) (2012).
[8] D.F. Mitchell, K.B. Clark, J.A. Bardwell, W.N. Lennard, G.R. Massoumi, I.V. Mitchell, Surf. Interface Anal. 21 (1994) 44–50.
[9] M.A. Reading, J.A. Van Den Berg, P.C. Zalm, D.G. Armour, P. Bailey, T.C.Q. Noakes, A. Parisini, T. Conard, S. De, J. Vac, Sci. Technol. 28 (1) (2010) (1071-1023).
[10] P.J. Cumpson, M.P. Seah, Surf. Interface Anal. 25 (1997) 430–446.
[11] S. Tanuma, C.J. Powell, D.R. Penn, Surf. Interface Anal. 11 (1988) 577–589.
[12] M.F. Hochella Jr., A.H. Carim, Surf. Sci. 197 (3) (1988) L260–L268.
[13] Application Note 31014, Angle Resolved XPS, Thermo Fisher Scientific Inc., 2008
[14] A.K. Livesey, G.C. Smith, J. Electron Spectrosc. Relat. Phenom. 67 (1994) 439–461.
[15] C.J. Powell, W.S.M. Werner, W. Smekal, Surf. Interface Anal. 43 (2011) 1046–1056.