Advanced characterization of high-k materials: a nuclear approach

Brijs, B.; Huyghebaert, C.; Nauwelaerts, S.; Caymax, M.; Vandervorst, W.; Nakajima, K.; Kimura, K.; Bergamier, A.; Döllinger, G.; Lennard, W.N.; Terwagne, Guy; Vantomme, A.

Published in:
Nuclear instruments and methods in physics research

Publication date:
2002

Document Version
Peer reviewed version

ELSEVIER

Nuclear Instruments and Methods in Physics Research B 190 (2002) 505–509

NIM B
Beam Interactions with Materials & Atoms

www.elsevier.com/locate/nimb

Advanced characterization of high-k materials: A nuclear approach

B. Brijs [a,*], C. Huyghebaert [a], S. Nauwelaerts [a], M. Caymax [a], W. Vandervorst [a,b], K. Nakajima [c], K. Kimura [c], A. Bergmaier [d], G. Döllinger [d], W.N. Lennard [e], G. Terwagne [f], A. Vantomme [g]

[a] *IMEC, Kapeldreef 75, B-3001 Leuven, Belgium*
[b] *KU Leuven, INSYS, Kard. Mercierlaan 92, B-3001 Leuven, Belgium*
[c] *Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan*
[d] *Physik-Department E12, Technische Universität München, D-85747 Garching, Germany*
[e] *Interface Science Western, Department of Physics and Astromony, The University of Western Ontario, London, Ont., Canada N6A 3K7*
[f] *LARN, Facultés Universitaires Notre-Dame de la Paix, 22 rue Muzet, B-5000 Namur, Belgium*
[g] *KU Leuven, IKS, Celestijnenlaan 200D, B-3001 Leuven, Belgium N6A 3K7*

Abstract

The determination of the composition of thin (1.5–3 nm) high-k layers ZrO_2/Al_2O_3 becomes more and more important in microelectronics. High resolution Rutherford backscattering spectrometry and high resolution elastic recoil detection can achieve depth resolutions down to 1 nm while Rutherford backscattering spectrometry and nuclear reaction analysis are perfectly suited to quantify the zirconium, the oxygen and the aluminum content. The goal of this paper is to investigate the use of nuclear techniques for the characterization of thin high-k materials.

PACS: 68.35.Ct
Keywords: Rutherford backscattering; Elastic recoil detection; Nuclear reaction analysis; High-k; Thin film

1. Introduction

With the downscaling of the electronic devices and the development of new gate materials to replace the thermal SiO_2, the determination of the composition of thin high-k layers (1.5–3 nm) becomes more and more important in microelectronics. In this paper, a study on the characterization of ultra thin high-k films based on nuclear techniques is presented. As the detection limit for the different elements in the high-k layer is never less than 0.1 at.%, conventional Rutherford backscattering (RBS), nuclear reaction analysis (NRA) and elastic recoil detection (ERD) are the perfect tools to quantify the matrix elements in the film. In this paper we focus on high resolution RBS (HRBS) and high resolution elastic recoil detection (HERD) for the true depth profile.

* Corresponding author. Tel.: +32-16-281-306; fax: +32-16-281-507.
E-mail address: brijs@imec.be (B. Brijs).

0168-583X/02/$ - see front matter
PII: S0168-583X(02)00468-8

2. Sample preparation

The metal oxide layers were prepared by means of atomic layer chemical vapor deposition (ALCVD). As metal precursors, we use trimethyl aluminum (TMA) and $ZrCl_4$, and H_2O as O source. The sample of interest was made with 20 cycles of Al_2O_3 and 40 cycles of ZrO_2.

2.1. Quantification

The high-k sample under study consists of a 2 nm ZrO_2 film on top of a 1 nm Al_2O_3 film on a Si substrate.

2.1.1. Nuclear reaction analysis

2.1.1.1. Oxygen. Nuclear reaction analyses for oxygen were performed at the 2.5 MV Van de Graaff facility at the University of Western Ontario using incident deuterons with 0.85 MeV energy to induce the $^{16}O(d,p)^{17}O$ reaction. The silicon charged particle detector was positioned at 140° [1]. The oxygen concentration was quantified by comparison to the yield measured for a 70.7 nm Ta_2O_5 anodic oxide standard, for which the oxygen areal density was known to be 3.90 $(\pm 0.08) \times 10^{17}$ atoms/cm^2. The total oxygen content in this ultra thin $ZrO_2/Al_2O_3/Si$ was 1.9×10^{16} atoms/cm^2.

2.1.1.2. Aluminum. The total amount of aluminum in the high-k material ($ZrO_2/Al_2O_3/Si$) was measured using $^{27}Al(\alpha,p_i)^{30}Si$ $(i = 0, 2)$ nuclear reactions. α-particles were produced with ALTAÏS (Accélérateur Linéaire Tandetron pour l'Analyse et l'Implantation des Solides), the 2 MV tandetron accelerator in Namur. The angle between incident beam and the normal of the sample was 60°. The NRA detector (mylar absorber foil of 36.6 μm, 5.41 msr) was installed at 90° relative to the incident beam. In Table 1, we have reported the energies of the Al peaks, as well the Q-values and the cross-sections of $^{27}Al(\alpha,p_i)^{28}Si$ $(i = 0, 2)$ nuclear reactions as well the Al content.

2.1.2. Rutherford backscattering spectrometry

In order to demonstrate the use of RBS for the characterization of thin ZrO_2/Al_2O_3 films, backscattering as well as forward scattering geometries are used. Conventional RBS with a beam energy of 2 MeV and a scatter angle of 161° was used to determine the content of Zr and Cl in the ZrO_2/Al_2O_3 film. In order to improve the sensitivity of oxygen, a forward scattering mode with a scatter angle of 51° with an exit angle of 6° was used

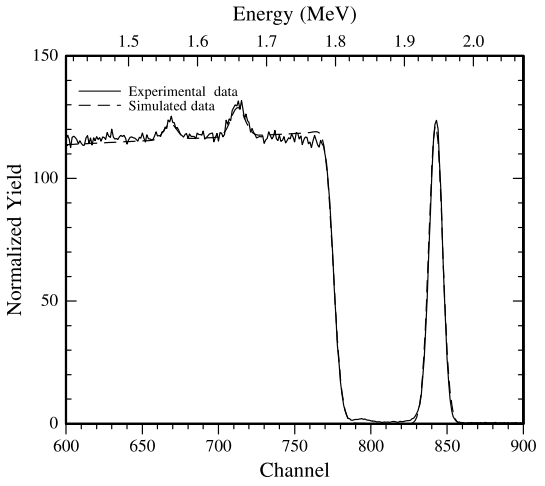

Fig. 1. A forward scattering spectrum of a ZrO2/Al_2O_3/Si (2 nm/1 nm/∞) layer obtained with a 2 MeV He^+ beam. Sample normal is tilted by 45° and the exit angle is 6°. The accumulated He^+ dose was 100 μC.

Table 1
Q-values, calculated energies of protons emitted at 90° and cross-sections for the $^{27}Al(\alpha,p_i)^{30}Si$ reactions

Reaction	Q-value (MeV)	E_p (MeV)	α at 4.958 MeV (mb/sr)	N (atoms/cm^2)
$^{27}Al(\alpha,p_0)^{30}Si$	2.3722	6.148	0.46	4.5×10^{15}
$^{27}Al(\alpha,p_1)^{30}Si$	0.1367	3.862	0.97	4.8×10^{15}
$^{27}Al(\alpha,p_2)^{30}Si$	−1.1260	2.497	0.55	4.0×10^{15}

The energy of the incident particle is 4.958 MeV and the energies of the emitted protons are calculated after the 36.6 μm mylar absorber foil. The last column is the number of Al atoms in the high-k material.

(Fig. 1). The sample was tilted over 45° (normal to beam direction). The oxygen concentration was quantified by comparison to the yield measured for a 10.0 nm SiO_2 oxide standard as well with the corrected cross-section. Both revealed 1.9 and 2.0×10^{16} atoms/cm^2.

2.2. Depth profiling

Achieving a very high depth resolution with RBS/ERD based methods is already a widely investigated topic and the main conclusion from this study reveals that only with a dedicated detector set-up (magnetic sector and position sensitive detector) and optimized beam parameters, a depth resolution of 1 nm can be achieved [2,3].

2.2.1. High resolution rutherford backscattering

High resolution RBS measurements were performed at the Kyoto University using a system described elsewhere [2]. The beam energy was 500 keV, the incident angle was 45° and the exit angle was 5.74°. A typical dose for one HRBS measurement was 10 μC. The energy window of the spectrometer was 25% of the central energy.

Fig. 2 shows an example of the observed HRBS spectrum for $ZrO_2/Al_2O_3/Si(001)$. The arrows show the energies of the He ions elastically scattered by Zr, Si, Al and O atoms. The thickness of the Al_2O_3 layer was estimated through simulations

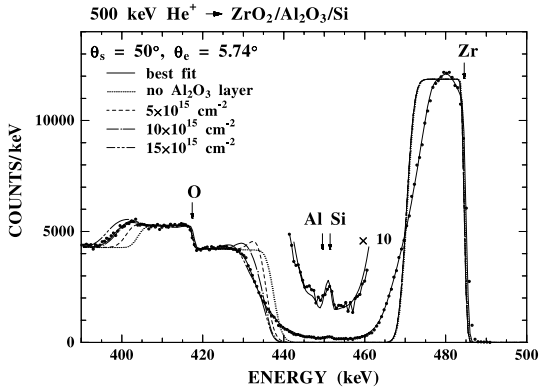

Fig. 2. Experimental and simulated data obtained with HRBS of a $ZrO_2/Al_2O_3/Si$ (2 nm/1 nm/∞) layer.

of HRBS spectra. In the simulation, the stopping power given by Ziegler [4] and the semi-empirical formula for energy loss straggling given by Lindhard et al. [5] were employed, and the reduction of the cross-section due to screening effects was included. Comparing the observed HRBS spectrum with the simulation in detail, the trailing edge of the Zr peak and the leading edge of the Al(Si) signal are broader than those of the simulated spectrum. This is attributed to the non-full coverage of the Al_2O_3 layer. The observed oxygen trailing edge agrees with the simulated result very well, indicating that the thickness of the oxide layer is rather uniform. It should be noted that there is a small peak at 451 keV, which corresponds to surface Si. This indicates that Si atoms also diffuse into the ZrO_2 layer through the Al_2O_3 layer.

The best-fit simulation result is shown by a solid curve in Fig. 2. The contents of the elements derived by integrating the profiles are 6.5×10^{15}, 4.3×10^{15} and 1.9×10^{16} cm^{-2} for Zr, Al and O, respectively, and in good agreement with the sample estimation discussed above.

2.2.2. High resolution elastic recoil analysis

High resolution ERD analysis was performed at the Munich tandem accelerator and its Q3D magnetic spectrograph [5,6]. With the present scattering conditions, i.e. 40 MeV ^{197}Au for oxygen analysis 170 MeV I for Al analysis, a scattering angle of 15° and a large solid angle of detection (7.5 msr), sensitivity of around 10^{13} atoms/cm^2 for oxygen and can be expected. The 5+ (6+) charge state of the oxygen recoil ions, being the most prominent charge state of the recoil ions, were analyzed.

Quantification was done using a low resolution $\Delta E - E$ or TOF-E measurement [7] at a scattering angle of 38°, which was simultaneously performed beside the magnetic analysis. Total integrated values for the different elements were as follows, oxygen ($1.98 \pm 0.04 \times 10^{16}$ atoms/cm^2), zirconium ($6.1 \pm 0.2 \times 10^{15}$ atoms/cm^2), aluminum ($3.5 \pm 0.02 \times 10^{15}$ atoms/cm^2) and some hydrogen ($5.4 \pm 0.1 \times 10^{15}$ atoms/cm^2). In Fig. 3 we notice that the Al profile is situated inside the oxygen distribution. Both, the slope of the oxygen profile at the surface

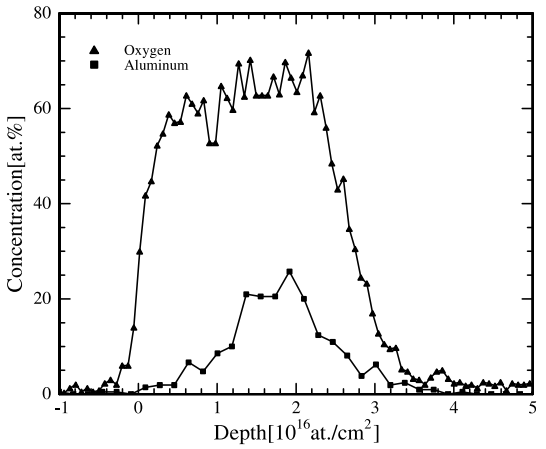

Fig. 3. HERD spectra of a $ZrO_2/Al_2O_3/Si$ (2 nm/1 nm/∞) layer. Only the aluminum and oxygen are drawn.

and that at the interface are significantly wider than the experimental resolution. The interfacial width may be influenced by island grow of the Al.

3. Discussion

An ultra thin high-k layer ZrO_2/Al_2O_3 has been quantified with a variety of nuclear techniques (NRA, RBS and ERD). Basically NRA can provide essentially background-free detection of light elements (O and Al) while RBS can provide background-free detection of heavy elements (Cl and Zr). Moreover, high energy/heavy ion ERD is the only technique which can provide background-free detection of light and heavy elements. Since the NRA cross-section as well as the RBS cross-section are a varying function of energy and angular distribution, it is still a good practice to verify the obtained results with reference samples (SiO_2, Ta_2O_3). Table 2 summarizes the obtained results. HERD, and to some extent HRBS are the only techniques which can quantify the layer completely, but a combination of RBS/NRA leads to the same results. With respect to depth profiling, only HRBS and HERD have shown an intrinsically high depth resolution around or below the nm-level. Due to the high cross-sections in the used geometry, HRBS can profile the ZrO_2 layer very well. Moreover, HRBS can locate some interdiffusion of Si at the surface of the ZrO_2 layer. The interface is very broad and is composed of aluminum, zirconium and oxygen. The latter is not unexpected since the Al_2O_3 layer is mainly composed of 50% islands filled up with ZrO_2. The aluminum profile obtained with HERD peaks at the interface. This spectrum is basically free from deconvolution and simulation problems and very reliable [8]. Both profiles are in rather good agreement, but taken into account that the coverage of the Al_2O_3 layer is in the order of 50% for the first 20 cycles, there seems to be a small overestimation with HRBS and a small underestimation with HERD, but both techniques point less than 40%. The latter is also suggested by the oxygen profile obtained with HERD. For a perfect Al_2O_3 layer, the oxygen yield should be 6% less than for the ZrO_2 layer, the HERD oxygen profile reveals a slightly increase of oxygen.

Table 2
Arial densities of Zr, Cl, Al, O and H obtained with RBS, ERD and NRA

	RBS	HRBS	HERD	NRA
Zr	6×10^{15}	6.5×10^{15}	6.1×10^{15}	
Cl		2.5×10^{14}		
Al		4.3×10^{15}	3.5×10^{15}	4×10^{15}
O	2×10^{16}	1.9×10^{16}	1.98×10^{16}	1.9×10^{16}
H			5.4×10^{15}	

With respect to the interface structure between ZrO_2 and Al_2O_3, both techniques indicate at the interface a mixture of a ZrO_2/Al_2O_3.

4. Conclusions

The characterization of ultra thin high-k materials is a challenging task. For a rapid, quantitative measurement of Zr, O, Cl and Al, RBS in combination with NRA is the obvious choice. Depth profiling is only possible with RBS/ERD. The recent developments of magnetic spectrometers (HRBS) demonstrate that they deliver accurate depth profiles and can be applied in a routine manner for process development. HERD combines both a good quantification and an absolute profile of all elements. Despite the fact that HERD

is more time consuming, it provides an excellent support for the validation of HRBS profiles.

Acknowledgements

K. Kimura and K. Nakajima are grateful to the members of the Quantum Science and Engineering Center at Kyoto University for the use of the Van de Graaff accelerator. They are supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology. The support of the Beschleunigerlaboratorium der Universität München und der Technischen Universität München is kindly acknowledged. This project is supported by the Fund for Scientific Research Flanders (Belgium) FWO42/476. C. Huyghebaert is indebted to the Belgian IWT for financial support.

References

[1] W.N. Lennard, G.R. Massoumi, I.V. Mitchell, H.T. Tang, D.F. Mitchell, J.A. Bardwell, Nucl. Instr. and Meth. B 85 (1994) 42.
[2] K. Kimura, K. Ohshima, M. Mannami, Appl. Phys. Lett. 64 (1994) 2232.
[3] G. Döllinger, C.M. Frey, A. Bergmaier, T. Faestermann, Nucl. Instr. and Meth. B 136–138 (1998) 603.
[4] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, Pergamon Press, New York, 1985.
[5] J. Lindhard, M. Scharff, K. dan Viedensk, Selsk. Mat. Fys. Medd. 28 (1954).
[6] G. Döllinger, T. Faestermann, P. Maier-Komor, Nucl. Instr. and Meth. B 79 (1992) 422.
[7] A. Bergmaier, G. Döllinger, C.M. Frey, Nucl. Instr. and Meth. B 136–138 (1998) 638.
[8] B. Brijs, J. Deleu, T. Conard, H. De Witte, W. Vandervorst, K. Nakajima, K. Kimura, I. Genchev, A. Bergmaier, L. Goergens, P. Neumaier, G. Döllinger, M. Dobeli, Nucl. Instr. and Meth. B 161–163 (2000) 429.