EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

More info at

http://www.esrf.eu/UsersAndScience/UserGuide/ExperimentReports/Preparing_SubmittingYourReportFile

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: Structure determination of niobium oxide in ultrathin films for application as high-k dielectrics**	**Experiment number**: 26-01-853
Beamline: Dubble BM26A	**Date of experiment**: from: 18/09/2009 to: 22/09/2009	**Date of report**: February 2010
Shifts: 12	**Local contact(s)**: Sergey Nikitenko	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

A. Hardy*, M.K. Van Bael

Hasselt University, Institute for Materials Research, Inorganic and physical chemistry

Other experimentalists involved in the measurements:

D. Dewulf*, C. De Dobbelaere*, K. Elen*, A. Riskin*

Hasselt University, Institute for Materials Research, Inorganic and physical chemistry

Report:

Context and motivation

Miniaturization of CMOS (Complementary Metal Oxide Semiconductor) and DRAM (Dynamic Random Access Memory), which for long has driven the advancements dictated by the International Technology Roadmap for Semiconductors (ITRS [1]), no longer suffices, and replacement of the gate or capacitor dielectric by new materials characterized by a high dielectric constant is required [2].
Niobium oxide is a good candidate for this purpose, because of its high permittivity and moderate band gap. As the permittivity is expected to be strongly dependent on the crystallographic phase, it is of great importance that the phase can be well characterized. Currently, experimental and computational results seem to indicate different phases to be characterized by the higher permittivity [3]. Giving experimental evidence is not straightforward based on XRD alone, due to strong peak overlap between the orthorhombic and hexagonal phase [4], due to the structure of the hexagonal phase not being cleared up entirely [3,5], due to the low film thicknesses involved (< 100 nm) and due to the possibility of texture, which results in small numbers of weak diffraction peaks. The uncertainty concerning the structure of the niobium oxide thin films complicates obtaining an in depth understanding of its relation with the dielectric properties. Moreover, interfacial reactions with the SiO_x/Si substrate, leading to intermixing of Si or true silicate formation, will also affect the dielectric properties. Since often amorphous interlayers where the high-k metal ions are intermixed with SiO_x are observed, XRD is not suitable, while FTIR can provide indications but requires confirmation by complementary characterization. EXAFS was chosen as an excellent characterization method to determine the coordination sphere of Nb in Nb_2O_5 present as ultrathin films, to characterize the crystalline and/or amorphous phases, to detect atomic scale intermixing with Si from the substrate through interfacial reactions, finally allowing to relate this structural information with the material's functional, dielectric properties.

Experiments

EXAFS spectra were recorded for different sample sets, allowing the evaluation of different effects, including the anneal temperature, film thickness, and substrate, on the aforementioned structural parameters in thin films. For comparison, commercial niobia powders of orthorombic and monoclinic crystalline phases were measured (Fig. 1). The number of EXAFS scans measured for each sample, ranged from 2 to 10, depending on the sample's concentration (film thickness) and resulting signal intensity. The scans were merged and have been processed using the Athena software[6] in order to achieve background subtraction, normalization and Fourier transformation. XRD patterns as well as GATR-FTIR spectra were recorded of all these samples as well, and complementary characteristics are obtained in this way. Further characterization using Raman spectroscopy and more advanced techniques are planned.

Results

The first focus has been on evaluating the effect of sample thickness and anneal temperature on the EXAFS spectra. The samples have been characterized by XRD, and the result thereof is mentioned in the legend of each figure.

4 samples with different film thicknesses after 600°C anneal, are compared in figure 2a. At this temperature, XRD showed all *but* the ultrathin film to be crystalline or at least contain a crystalline fraction. At 800°C anneal (fig. 2b), different film thicknesses on SiOx/Si substrates are compared. Here, also the ultrathin film remained amorphous according to XRD, while the thicker films were crystallized. The crystallinity was increased compared to the samples prepared at 600°C.

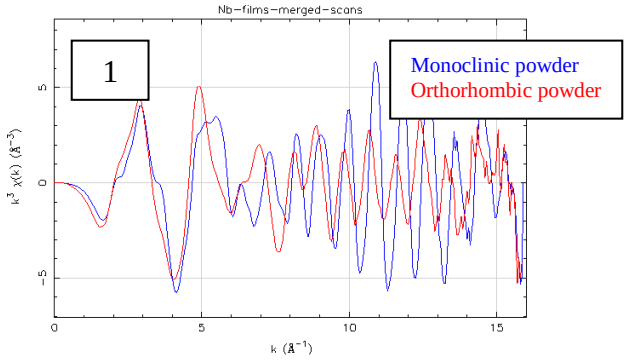

Fig.1. Nb K-edge spectra of the monoclinic and orthorombic Nb_2O_5.

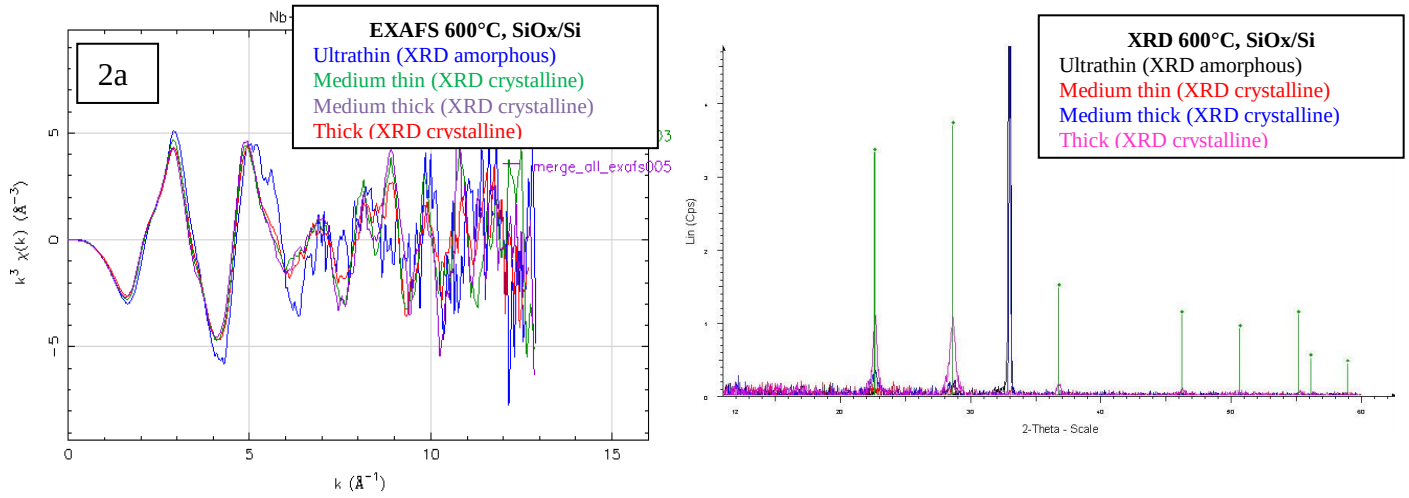

Fig. 2a. Nb K-edge experimental scan of Nb films with different thicknesses deposited on a SiOx/Si substrate at 600°C and accompanying XRD patterns (reference pattern in green for hexagonal Nb_2O_5 JCPDS 28-317)

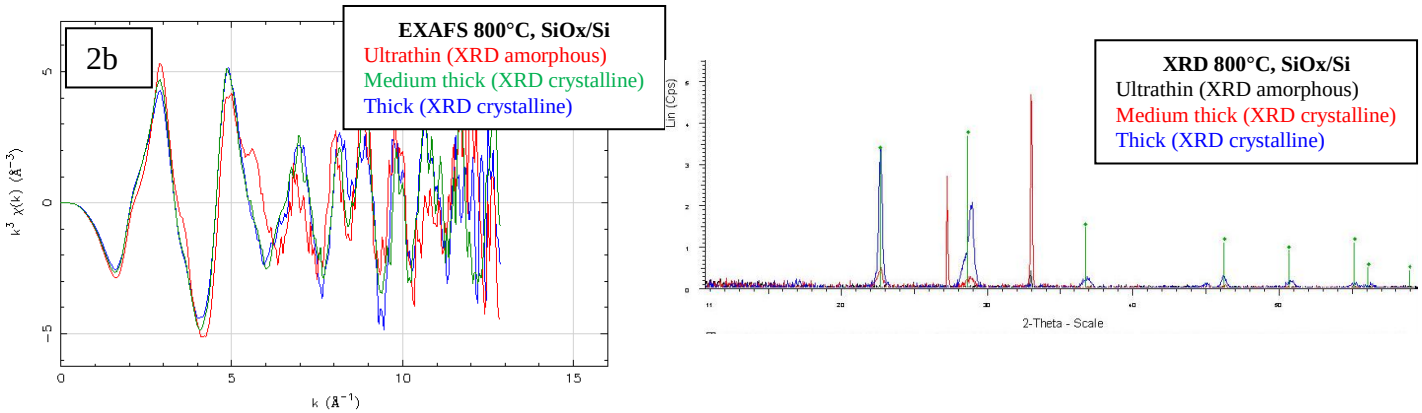

Fig.2b. Nb K-edge experimental scan of Nb films deposited on a SiOx/Si substrate at 800°C and accompanying XRD (reference pattern in green for hexagonal Nb_2O_5 JCPDS 28-317). Substrate peaks are observed in the XRD pattern of the medium thick sample.

These spectra can be compared to the powder samples as well, which were identified by XRD to consist of monoclinic and orthorhombic phase niobia respectively.
The comparison of the experimental EXAFS spectra of the samples at 600°C (Fig. 2a) and 800°C (Fig. 2b) with eachother show similarities except for the ultrathin film. For example, the spectra between 5-6 A^{-1} show a splitting of the oscillation, which is not observed in the Nb_2O_5 reference spectra. By further comparison of the EXAFS spectra of the reference powders with those of the thin film samples, it appears that there is a stronger resemblance up to 6 A^{-1} between the orthorhombic powder and the signature observed for the crystalline films, in accordance with XRD.
However, as there is currently no reference available of the hexagonal phase, it will only be possible to conclude on the presence of orthorhombic or hexagonal niobia after fitting the structural model of the hexagonal and orthorhombic phase with Artemis and verifying the best agreement. This, together with the verification of Si intermixing with the niobia layer will be the focus of further processing and interpretation steps in this work. Finally, the effect of the substrate upon which the films are deposited will be evaluated.

References

1 http://www.itrs.net/.
2 J. Robertson, Reports on Progress in Physics **69,** 327-396 (2006).
3 S. Clima, G. Pourtois, A. Hardy, S. Van Elshocht, M. K. Van Bael, S. De Gendt, D. J. Wouters, M. Heyns, and J. A. Kittl, Journal of The Electrochemical Society **1557,** G20-G25 (2009).
4 JCPDS, Powder diffraction file of inorganic phases, Joint Committee on Powder Diffraction Standards, Swarthmore**,** Powder diffraction file of inorganic phases, Joint Committee on Powder Diffraction Standards, Swarthmore (1997).
5 A. Fukumoto and K. Miwa, Physical Review B **55,** 11155-11160 (1997).
6 B. Ravel and M. Newville, Journal of synchrotron radiation **12,** 537-541 (2005).