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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.

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:** HAXPES to investigate the chemical and electronic properties of advanced metal/high-k stacks	**Experiment number**: SI-1824
Beamline:	**Date of experiment**: from: 17/09/2009 to: 22/09/2009	**Date of report**: 14/02/2011
Shifts:	**Local contact(s): Blanka Detlefs**	*Received at ESRF:*

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1. Results obtained for the OxRRAM devices

Communication of the results was done throught an ESRF spotlight published on the website in May 2010 (http://www.esrf.fr/news/spotlight/spotlight108/spotlight108/**).**

We studied the switching mechanism of resistive memories comparing NiO/Pt full sheet samples in the pristine state (OFF) and after forming (ON). An innovative forming process allowing the creation of a large amount of conductive paths was implemented. Therefore, meaningful comparative HAXPES analyses could be performed on both ON and OFF states in a non destructive way. Photon energies of 2.1, 6.5 and 9.75 keV were chosen to probe the NiO surface, the NiO bulk and the NiO/Pt interface. Measurements were performed with secondary monochromators for a detailed analysis of chemical states with high energy resolution. After forming (ON state), a shift of same magnitude was observed for core levels (Ni2p3/2 and O1s) and valence band spectra toward higher binding energies (see figure 1). This was attributed to Fermi level pinning toward the conduction band due to n-type defects such as electrons trapped at oxygen vacancy sites or delocalized over neighboring Ni^{2+} ions giving rise to metallic nickel defects.

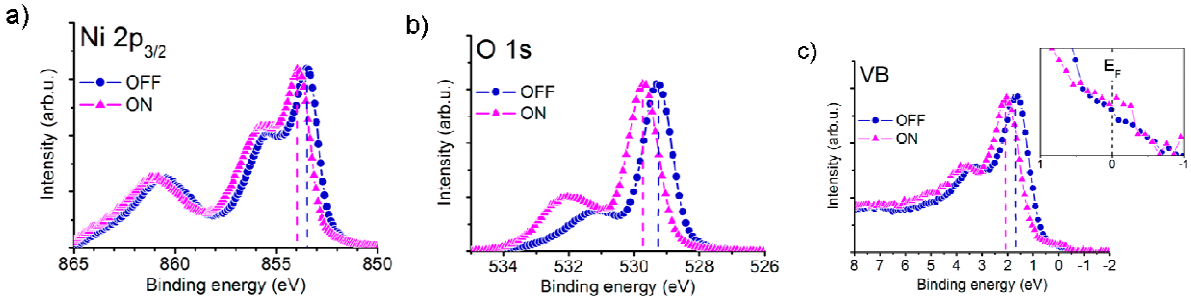

Figure 1: $Ni2p_{3/2}$ (a), O1s (b) core level and valence band (c) photoelectron spectra obtained by HAXPES at 2.1keV.

Our results highlight the role played by defects in the switching mechanism. We suggest oxygen vacancies are created in the NiO conductive state as shown by the core level shifts and band gap states. N-type defects such as oxygen vacancies and metallic nickel could be responsible for the low resistive state of NiO after forming. The non-destructive characterization technique HAXPES was proven a powerful tool for characterizing defects that would otherwise be altered or obscured by destructive characterization techniques. Besides, the link between oxygen defects and resistivity change is established here by direct physicochemical characterization, rather than indirect electrical measurements. This is an important step towards understanding and further development of resistive memories [1,2].

2. Results obtained for the CMOS devices

For sub-32 nm nodes, new materials such as high-k dielectrics and metal gates are integrated together with a thin LaO capping layer to obtain band edge CMOS devices (see figure 2). The aim of the experiment was to investigate the impact of high temperature anneal (1065°, 10s) on the diffusion phenomena across the stack. Indeed, La is expected to diffuse towards the high-k/SiO_2 interface creating a dipole that modifies the band alignment of the structure. Two LaO thicknesses (0.4 and 1 nm) were deposited to evaluate the impact of the La quantity on the dipole strength. Taking advantage from the high photoelectrons escape depths, analyses were performed without removal of the TiN layer, in order to preserve the thin LaO underlying layer. This is a real advantage compared to laboratory XPS.

Fig. 2: scheme of the high-k/metal gate

HAXPES measurements were performed at two photon energies: 3.81 and 7.95 eV. High energy resolution (300 meV) was reached thanks to a beam spectral width optimized with a post monochromator. In these conditions, we were able to perform high-resolution analysis of the in-depth La-related chemical states [3]. Binding energies are given relative to the Fermi level measured with a clean gold surface. In order to take into account the decay of the beam intensity during acquisition, all spectra were normalized to the secondary electron background at low binding energies, which is assumed to be directly proportional to the photon flux.

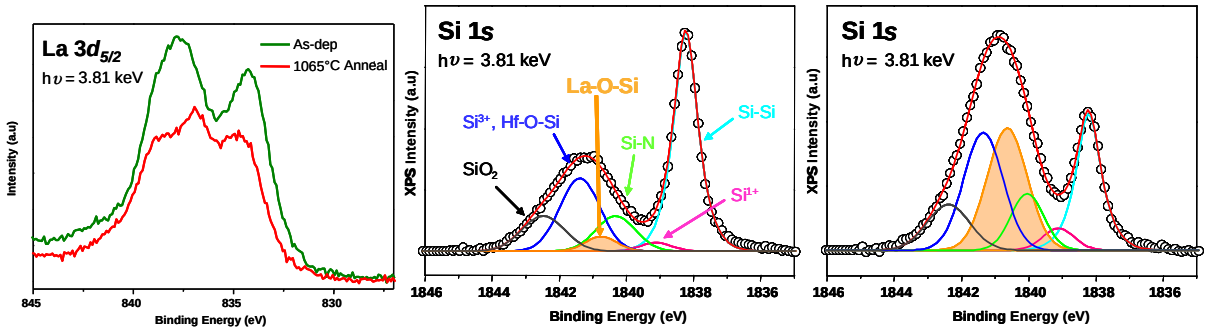

Figure 3: HAXPES spectra of gate stacks with 1 nm of LaO_x capping layer. Left: La $3d_{5/2}$ core-level of as-deposited and annealed samples. The Si 1*s* core-level spectra obtained for as-deposited (middle) and annealed sample (right).

Figure 3 shows the La $3d_{5/2}$ core-level spectra for the as-deposited and annealed samples with 1 nm of LaO_x capping. Upon annealing, a decrease of the La $3d_{5/2}$ intensity is observed, which suggests the diffusion of lanthanum towards the bottom interfaces in the gate stack. In addition, the line shape (known to be extremely sensitive to the La first nearest neighbours) drastically changes: this indicates an evolution of the La-related chemical states upon annealing.

The Si 1*s* core level was used to further investigate the interfacial chemistry of the buried interfaces. Figure 3 also shows the Si 1s spectra obtained for both as-deposited and annealed samples with 1 nm of LaO_x capping layer, respectively. A detailed decomposition of the spectra was made based on the analysis of the reference spectra (samples without LaO_x capping layer, not shown), and previous work to identify Si sub-oxides and nitrided states. Four components are identified and characterized by their chemical shift relative to the bulk silicon Si^0 located at 1838.2 eV: i) Si^{1+} (1839.1 eV), ii) Si-N (1840.3 eV), iii) Si^{3+} in Hf silicate oxinitride (1841.4 eV) and iv) Si^{4+} in SiO_2 (at 1842.5 eV). After insertion of La into the gate stacks, an additional component appears at an energy shift of ~ 2.6 eV relative to the bulk Si^0. This new component is ascribed to La-O-Si bonds and exhibits a clear enhancement after annealing, thus indicating the formation of La silicate as a result of La diffusion inside the high-k and interfacial layers.

[1] ESRF Spotlight n° 108 entitled “Innovative resistive memories studied by hard X-ray photoelectron spectroscopy (HAXPES)”, 31/05/2010.
[2] P. Calka, E. Martinez, D. Lafond, S. Minoret, B. Detlefs, J. Roy, J. Zegenhagen, C. Guedj, “Origin of resistivity change in NiO thin films studied by hard X-ray photoelectron spectroscopy”, submitted to J. of Appl. Phys.
[3] R. Boujamaa, N. Rochat, R. Pantel, E. Martinez, O. Renault, B. Detlefs, J. Zegenhagen, V. Loup, F. Martin, S. Baudot, M. Gros-Jean, F. Bertin, C. Dubourdieu, to be submitted to J. of Appl. Phys.