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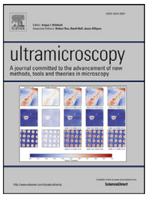

Laboratory based X-ray photoemission core-level spectromicroscopy of resistive oxide memories

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ABSTRACT

HfO_2-based resistive oxide memories are studied by core-level spectromicroscopy using a laboratory-based X-ray photoelectron emission microscope (XPEEM). After forming, the top electrode is thinned to about 1 nm for the XPEEM analysis, making the buried electrode/HfO_2 interface accessible whilst preserving it from contamination. The results are obtained in the true photoemission channel mode from individual memory cells ($5 \times 5\,\mu m$) excited by low-flux laboratory X-rays, in contrast to most studies employing the X-ray absorption channel using potentially harmful bright synchrotron X-rays. Analysis of the local Hf 4f, O 1s and Ti 2p core level spectra yields valuable information on the chemistry of the forming process in a single device, and in particular the central role of oxygen vacancies thanks to the spectromicroscopic approach.

1. Introduction

Oxide resistive random access memories (OxRRAMs) are promising candidates in the search for fast, low power memory devices for cache, system and storage applications [1]. Hafnium based OxRRAMs take a special place, because they can be readily integrated into existing semiconductor technology [2]. However, the chemistry of the resistive switching mechanism still needs better understanding to bring the technology to mass production readiness levels [3].

Investigations of the chemistry of the forming and switching processes point to filamentary conduction and cation reduction near the interface with the electrode. While X-ray photoemission spectroscopy (XPS) provides high chemical selectivity, including for buried layers underneath a thin top electrode, the probed area, defined by the beam spot sizes typically in the range of 0.1–1 mm, limits its use for near-technology devices, as filaments are often well below the micrometer scale [4,5]. Furthermore, typical XPS sensitivity is about 1% making such area-averaged analysis of nanometric filaments challenging. By reducing the analyzed area in photoemission to a single device, the filament to surrounding oxide ratio is significantly enhanced and the chemical sensitivity increased.

Photoelectron emission microscopy with hemispherical energy analyzers provides the simultaneous lateral and energetic resolution necessary to investigate the chemistry of single OxRRAM devices. However, a major obstacle is that the overall transmission of the PEEM optics and energy analyzer is rather low [6]. Furthermore, when using a laboratory X-ray source such as Al $K\alpha$, the photoionization cross-section for many core levels is weak compared to that possible when using soft X-ray energy typical of synchrotron light sources. Nevertheless, in this paper we show that a highly stable laboratory XPEEM setup can compensate to some extent by much longer acquisition times than those usually used at synchrotron sources, additionally avoiding any possible sample modification by the use of a low-flux X-ray source.

The availability of such highly stable laboratory based XPEEM is also of considerable interest when allied with complementary characterization techniques such as scanning Auger nanoprobes (SAM), scanning electron microscopy (SEM), conductive atomic force microscopy (C-AFM), Ar^+ sputtering and gas cluster ion beam milling. The lateral resolution in core level spectroscopic imaging of about 0.5 μm [7] is sufficient to select single devices of several μm size, ensuring that measured chemical changes can be directly related to the area in which the switching occurs, rather than to spurious edge effects or changes in background signal inevitably

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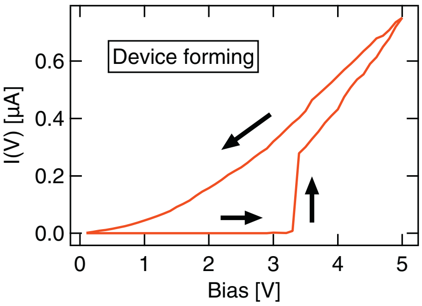

Fig. 1. C-AFM curve of the forming process with 5 V bias and 1 mA compliance current.

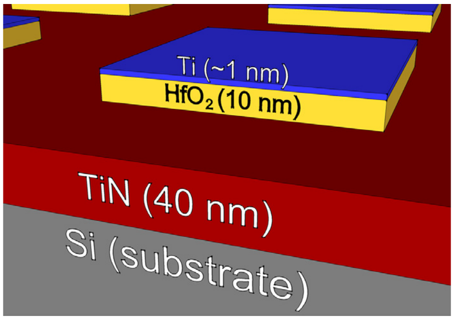

Fig. 2. Sketch of sample geometry after thinning procedure.

present in XPS area-averaged over several devices and the intervening oxide regions. Besides, it was shown previously that a high energy resolution can be maintained at the highest level (< 0.5 eV) [7] even at a good lateral resolution, which is of prime importance for getting direct chemical fingerprinting from individual devices.

In this paper, we report on threshold, Hf 4f, O 1s and Ti 2p core-level XPEEM microscpectroscopic analysis of the forming process in individual resistive memory devices, i.e. the changes between the virgin and low resistance state (VS and LRS) of thin film devices of near-technological size.

2. Experiment

The samples were made in the Silicon Technology Platform of CEA-LETI (Grenoble, France). The TiN(20 nm)/Ti(10 nm)/HfO_2(10 nm)/TiN(40 nm) heterostructure was grown on the Si substrate by physical vapor (for the TiN and Ti electrode layers) and atomic layer (for the HfO_2 resistive oxide) deposition. (5×5) µm^2 top electrodes were patterned into a grid with 5 µm device spacing. The devices were individually electroformed by Conducting tip Atomic Force Microscopy (C-AFM) with a compliance current of 1 mA (Fig. 1). However, the low resistance state of all devices only registered 800 µA at the 5 V maximum bias. The devices had, on average, a resistance of $R_{VS} = 465$ MΩ in the VS and $R_{LRS} = 6.5$ kΩ in the LRS, resulting in a resistance ratio of about 71,500. The third, near linear branch is the ramping down of the current with bias in the LRS.

In order to perform XPEEM measurements of the HfO_2 layer, we thinned the top electrode after C-AFM forming using first Ar^+ sputtering (21 min., Ar^+ ion energy of 2 keV, ion current on sample of 2 µA in a 4 mm^2 target area) and then Gas Cluster Ion Beam (GCIB) milling (10 min at 15 keV, 13 nA, 4 mm^2). Clusters of 2500 Ar atoms were used, giving an average energy per atom of 6 eV [8,9]. This procedure was used to minimize possible cascade damage in the HfO_2 which could result from using high energy Ar^+ ions to thin the electrode down to 1 nm [10]. The milling conditions were determined by previous calibration samples. A sketch of the final sample structure before XPEEM analysis is shown in Fig. 2.

Scanning Auger electron spectroscopy in a 25 µm field of view using a 30 nm electron beam and 10 keV primary energy was used to analyze the composition of the sample after all XPEEM experiments had been carried out. An SEM image obtained in the Auger system in Fig. 3 shows the OxRRAM devices on the sample surface. Two areas were analyzed, marked by the blue (on a device) and red (outside the devices) circles. The corresponding Auger spectra are presented in Fig. 4. The lower (red) Auger spectrum shows that the thinning procedure completely removed the exposed HfO_2 layer between the devices, leaving only Ti and N of the bottom electrode in the Auger spectrum. The signal from the devices shows a contribution of Hf and O Auger electrons from the resistive oxide, in addition to the Ti Auger electrons from the 1 nm top electrode. In the latter case, the signature of the combined Ti and N peaks confirm that the Ti signal comes from the residual TiN top electrode whereas between devices it is due to the exposed

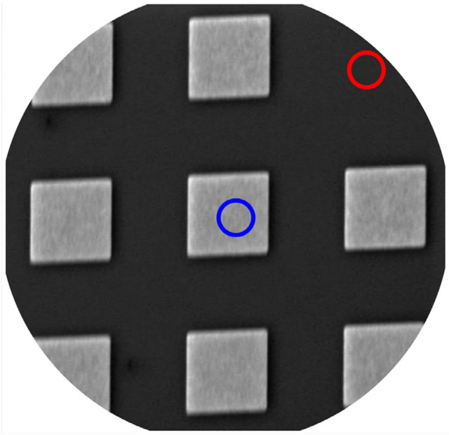

Fig. 3. SEM image showing nano-Auger measuring spots as blue and red circles. The measurement areas were 30 nm in the center of the circles; devices are (5×5) µm^2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

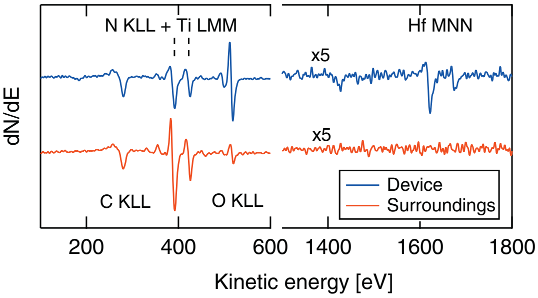

Fig. 4. Nano-Auger spectra after thinning of the top electrodes from the devices and surrounding material and XPEEM experiments.

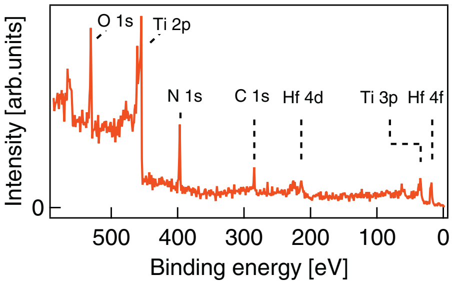

Fig. 5. XPS survey scan after transfer to the XPEEM.

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