EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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 via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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.

<table>
<tr><td> </td><td>Experiment title:
HAXPES and GIXRD characterization of Hafnium Zirconium Oxide ferroelectric thin films deposited on single-layer, CVD-grown graphene.</td><td>Experiment number:
HC-5179</td></tr>
<tr><td>Beamline:
BM25</td><td>Date of experiment:
from: 4th July to: 10th July</td><td rowspan="2">Date of report:
15/07/2023
Received at ESRF:</td></tr>
<tr><td>Shifts:
18</td><td>Local contact(s):
Juan Rubio Zuazo</td></tr>
<tr><td colspan="3">Names and affiliations of applicants (* indicates experimentalists):
Iciar Arnay*, Adrián Gudín*, Paolo Perna, Julio Camarero
IMDEA Nanoscience institure, C/Faraday 9 28049 Madrid, Spain
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Report:

Proposal summary and main objectives: The aim of the proposal was to characterize, by means of hard x-ray photoelectron spectroscopy (HAXPES) and complementary grazing incidence x-ray diffraction (GIXRD), the structural and electronic modifications in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) ferroelectric films deposited on graphene (gr)/ferromagnet (FM)/ heavy metal (HM) stacks using different seed layers (SLs) before and after electrical cycling. HZO shows a poor nucleation on bare graphene, so that an in-situ or ex-situ deposited interlayer is neccesary in order to nucleate a conformal film. Our previous results indicated that under certain conditions fatigue appears during electrical cycling, most likely due to HZO/interlayer oxygen exchange. The use of hard x-ray is mandatory in order to access the buried HZO/interlayer interface, and to obtain information about the Hf oxidation state and interlayer modification.

Experiment results: For this experiment we were granted 18 shifts of beam time. Samples consisted of HZO/SL/gr/Co/Pt/Al_2O_3(0001) stacks prepared in several stages. SL (Ta or Pt)/Gr/Co/Pt stacks were prepared at IMDEA Nanociencia (Madrid, Spain) by combination of different physical and chemical vapor deposition techniques following a previously optimized protocol [1]. HZO deposition and sample processing was performed at NamLab (Dresden, Germany). HZO films were grown by atomic layer deposition (ALD) as described in reference [2]. Devices were design according to beamline specifications and optimal ferroelectric layer behavior. The mask consisted of an array of devices measuring 50 x 100 μm^2 with a separation of 200 µm. TiN contacts were deposited for electrical measurements and then etched away for HAXPES measurements. Initially, we intended to characterize HZO devices with different number of electrical cycling, in order to study possible modifications of the HZO layer during electrical measurements. However, when starting the measurements, the intensity coming from the device was too weak compared to the background originating from the Pt layer underneath, which was particularly critical due to the proximity between the Pt and Hf core energy levels. A copper tape mask was placed around the devices in order to optimize signal/background ratio but still this was not enough to measure each device individually with enough intensity and resolution to obtain information about the Hf oxidation state.

Nevertheless, we performed HAXPES measurements on ensembles of devices (including cycled and uncycled devices) for samples prepared using different seed layers (SLs): Pt (0.5 nm) and Ta (0.5 and 2 nm). A beam energy of 10 keV was used and Hf 3d, Ta 3d and O1s edges were characterized. Taking advantage of the versatily of the BM25 beamline, we additionally performed x-ray absorption spectroscopy (XAS) measurements in the Hf L_3 edge, to complement HAXPES data. Also, we performed fully characterization of HZO references films deposited on Si, including HAXPES, GIXRD and XAS.

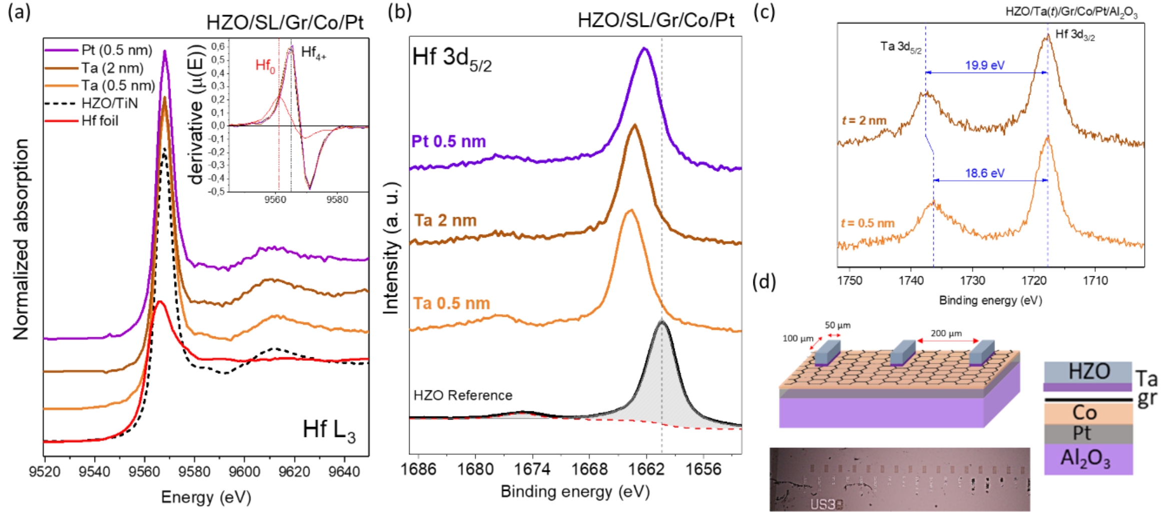

Figure 1: (a) XAS measurements on the Hf L_3 edge and (b) HAXPES spectra at the Hf $3d_{5/2}$ core level for HZO samples prepared with different seed layers.(c) HAXPES measurements around Ta $3d_{5/2}$ and Hf $3d_{3/2}$ core levels for samples prepared with different Ta thicknesses. (d) Schematic view of the devices and sample stack as well as microscope image of one of the samples measured during the experiment.

Figure 1 summarizes the experimental results obtained during the experiment in HZO/SL/gr/Co/Pt stacks. XAS measurements in the x-ray absorption near edge structure (XANES) region of the Hf L_3 edge (fig. 3a) indicate identical features between the reference and the HZO films prepared on gr-based stacks, without significant differences between samples. Nevertheless, HAXPES measurements (fig. 3b) indicate significant shifting of the Hf $3d_{5/2}$ core level spectra depending on the SL chosen. Although this could be related to oxygen stochiometry in the HZO film, lack of correlation with XANES spectra points to a different origin. This behaviour has been related in previous works with the potential built up across a dielectric contact in HZO films, which is dependent in the interlayer chosen [3]. However, the most relevant conclusion results from the analysis of the Ta $3d_{5/2}$ core level spectra (fig. 3c). For samples with 2 nm Ta SL, where fatigue is more pronounced, Ta $3d_{5/2}$ is shifted more than 1 eV to higher binding energies with respect to Hf $3d_{3/2}$, compared to the sample with 0.5 nm Ta SL. This is related to a higher oxygen concentration in the Ta interlayer [4], which is consistent with oxygen transfer from HZO to Ta. Due to the local formation of oxygen vacancies in the HZO layer, this does not translate to a shifting of the Hf 3d core level, but a slight broadening is observed together with the shifting of Ta core level.

Relation with the previous work: The motivation of the experiment was to unravel the relation between the choose of the seed layer and the observation of different electrical behavior in HZO films. Electrical measurementes in HZO/SL/gr/Co/Pt stacks show that for SL=Ta, increasing the interlayer thickness resulted in remanence loss (fatigue after cycling), while for SL=Pt, the ferroelectric response is maintained even for thicker interlayers (fig. 2). These behaviors can be explained due to oxygen exchange at the Ta/HZO interface, reducing polarization with electrical cycling. This is also consistent with the fact that remanence loss only occurs when increasing Ta thickness and not Pt thickness, as inert Pt prevents oxygen scavenging at the bottom HZO interface. Although we weren´t able to characterize each device individually, The average response of the devices after different sequences of electrical cycling show a clear dependence as a function of the Ta thickness. Samples prepared with thicker Ta SL show an increase of the oxygen concentration in the Ta layer, with a broadening of Hf core level, which is fully consistent with oxygen exchange at the HZO/Ta interface.

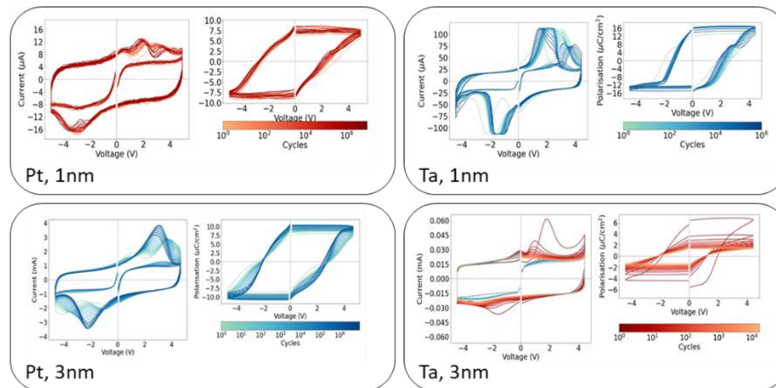

Figure 2: Electric characterization of HZO films deposited on Gr/Co/HM stacks using different interlayers. Partially adapted from [1].

Performing further HAXPES measurements at the individual devices as initially planned, by upgrading the mask design so peak/background intensity is improved, would provide information about the intermediate stages during the cycling processing. Fully understanding of the exchange process in the HZO/SL interface is fundamental for the design of voltage-controlled spintronic devices. Moreover, comparing structural and electronic properties of HZO films deposited on inert and reactive ILs, with observable differences in their electrical switching properties, should further contribute knowledge on the topic of oxygen vacancies in HZO, their role in ferroelectric switching and how electrodes can be optimized for different technological applications.

References

[1] F. Ajejas, et al. CS Appl. Mater. Interfaces 2020, 12, 3, 4088–4096; F. Ajejas, et al. Nano letters 2018, 18, 5364–5372; A. Anadón, et al., APL Materials 2021 9, 061113,
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[3] Y. A. Matweyev et al. Thin solid films 2014, 563, 20-23
[4] M. Kazar Mendes et al. 2018, *Sci Rep* 8, 17919