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Identification of atomic scale mechanisms active in resistance switching devices by atom probe tomography

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14. ABSTRACT This project involved characterization of complex layer structured materials which required new sample preparation procedures for atom probe tomography (APT) measurements. A custom designed sample holder was produced in-house which facilitated in the preparation of APT tips using dual-beam focussed ion beam, which were transferred to APT for measurement without any further modifications to the produced APT tips. Two sets of samples, each having different layer sequences, were investigated using this new apparatus. The first set of experiments were performed on a sample with a HfO surface layer deposited on a Si substrate with Ni forming the intermediate conducting layer. However, this configuration did not result in any successful APT measurement. A second sample with inverted layering sequence was prepared with Cu as the exposed surface layer, which protected the underlying HfO layer deposited over Si substrate. This configuration produced the first successful APT result after several trials. The measurement indicated that Cu does not diffuse along grain boundaries or interfaces into the HfO layer in the as-synthesized electrically unstressed condition. Such a configuration favors in the development of this layered configuration as potential resistance switching devices.					
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Final Report

1. Project title:

Identification of atomic scale mechanisms active in resistance switching devices by atom probe tomography.

Grant No. FA9550-15-1-0176

2. General Overview:

Next generation information storage devices are based on the unique phenomena of resistance switching (RS) that can be activated in Metal-Insulator-Metal (MIM) structures [1]. Such structures are also known as Resistive Random Access Memories (RRAM), wherein, the electrical resistance of the insulating layer can be tuned by applying electrical stresses, facilitating a large amount of data storage [2]. In other words, the insulating properties of the dielectric can be tuned by applying specific electrical fields whereby a high resistive state (“0”) and a low resistive state (“1”) can be achieved for information storage [1]. In recent years, such RRAMs have attracted a lot of attention owing to their simplified structures and superior performance.

3. Objectives:

The primary objectives of the study are the following,

- a. Understanding the atomic scale mechanisms responsible for resistance switching mechanism.
- b. Designing suitable fabrication methods and nano meter scale sampling procedures for the MIM structures and the analysis of the same using advanced atom probe tomography (APT).
- c. Developing appropriate correlative microscopy methodology which would enable in the investigation of internal interfaces such as grain boundaries and multi-layered thin film structures while employing multiple microscopy techniques such as scanning electron microscopy, transmission electron microscopy and APT on the same probe volume.

4. Results:

- a. Multi-layered sample for APT analysis:

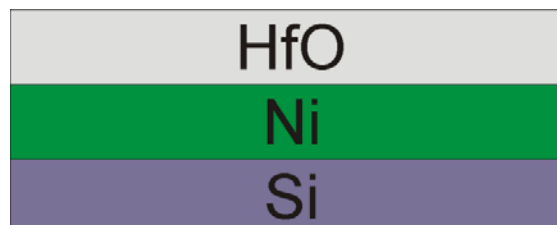


Figure 1. Schematic diagram showing the multi-layer configuration of the sample utilized for Atom Probe Tomography analysis.

The first APT investigations were planned on a thin film, multi-layered sample having the layered configuration as shown in Fig. 1. There were two layers namely, hafnium oxide at the exposed surface followed by an intermediate layer of Ni deposited over Si substrate. Such samples when need to be investigated using APT, they have to be prepared in the form of sharp needles having a diameter of approximately 60-90 nm. Hence, a sample lift-out procedure utilizing a dual-beam (i.e. scanning electron microscope operating together with) focused ion beam (FIB) was developed and employed.

Considering that the first layer of the sample i.e. HfO is a non-conducting material, conventional APT sample preparation using dual beam systems are difficult. Hence, in this case, a thin layer of platinum coating was deposited on the surface of the thin film, in order to both protect the underlying layer configuration as well as to enhance conductivity on the sample for easy operation and handling during sample preparation.

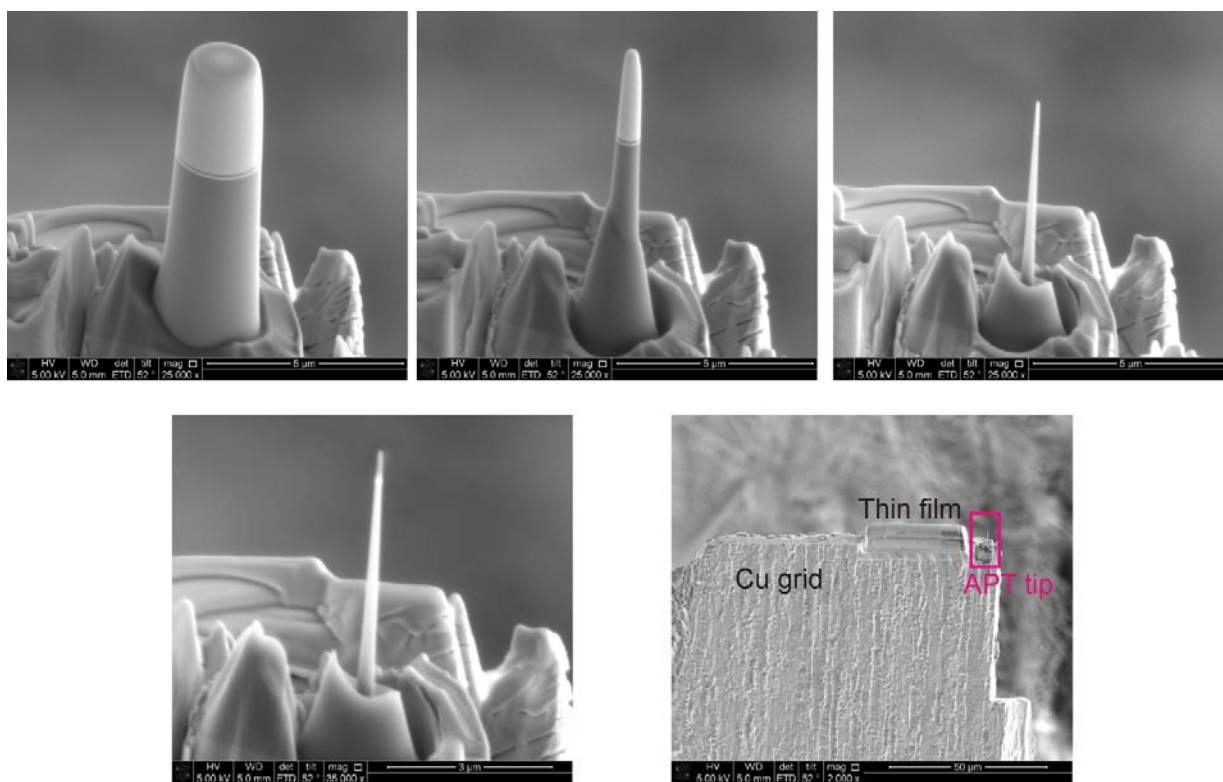


Figure 2 Sequence of annular milling steps involved to produce APT tip from the thin film sample mounted on a commercial Cu grid.

Then, approximately $\sim 25 \mu\text{m}$ length of the sample containing both the layers were lifted-out in a dual-beam FIB and deposited on a commercial Omniprobe Cu grid. APT tip was then prepared at one end of the sample (indicated in red rectangle) that was mounted on the Cu grid (Fig. 2). A series of annular milling steps were employed as shown in Fig. 2 in order to produce a sharp tip (50 nm in diameter) suitable for APT.

b. Development of custom-designed sample holder for correlative microscopy:

Considering that the initial trial involved unconventional method of sample preparation, adequate sample holders had to be developed in order to insert these samples into APT for measurement. Hence, a custom-designed sample holder as shown in Fig. 3 was produced in-house in order to be able to transfer the commercial Cu grid containing the APT tips into the atom probe.

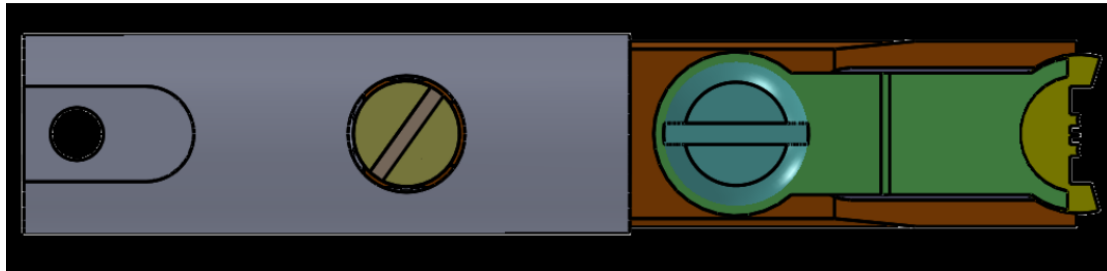


Figure 3. Custom-built sample holder design schematic that can carry the Cu-grid containing APT tip at the edge.

The holder was designed in such a way that the samples produced following the developed unconventional method can also be utilized for correlative microscopy. Generally, correlative microscopy involves investigation of samples utilizing multiple microscopy techniques such as optical microscope, scanning electron microscope (SEM), transmission electron microscope (TEM) and APT. The main advantage of such a correlative microscopy approach is that the samples are analyzed across all length scales enabling in the investigation of micro and nanostructural details starting from micro-meter down to near-atomic scale. In addition, the different possible modes of operation in each microscope can be utilized for analysis which also includes techniques such as electron back scattered diffraction (EBSD) and electron channeling contrast imaging. In this way, a comprehensive analysis of morphology, crystal structure, local elemental distribution and concentration would be made possible on the same sample i.e. same analysis volume.

c: Optimization in sample preparation:

When following unconventional method of sample preparations such as that shown in Fig. 2, unexpected problems do occur before successful results are obtained. As can be noticed in Fig. 2, the APT tip that was prepared from the $\sim 25 \mu\text{m}$ length of the sample containing both the layers was submerged in the residual thick film on one side. This design of sample preparation was found to be not suitable for successful APT measurement as the APT tip which has to face the local electrode in line for field evaporation could not be positioned. The higher layer thickness of the remaining thin film ensured that the tip is far away in the z-direction in relation to the position of the local electrode. Such positioning of the tip required very high base potential for field evaporation and hence the tip was fractured owing to high stress states. Since, only one sample could be produced at a time by this method, the initial trial was not successful. However, the design and development of the custom built holder was successful as the sample could be

prepared in FIB and measured in APT with successful transfer between them without disturbing the TEM grid.

Hence, the sample preparation procedure was optimized in order to avoid the problem of sample getting submerged (Fig. 4) and also to produce multiple tips from the same lift-out length of the material, so that multiple measurements can be performed resulting in high-throughput.

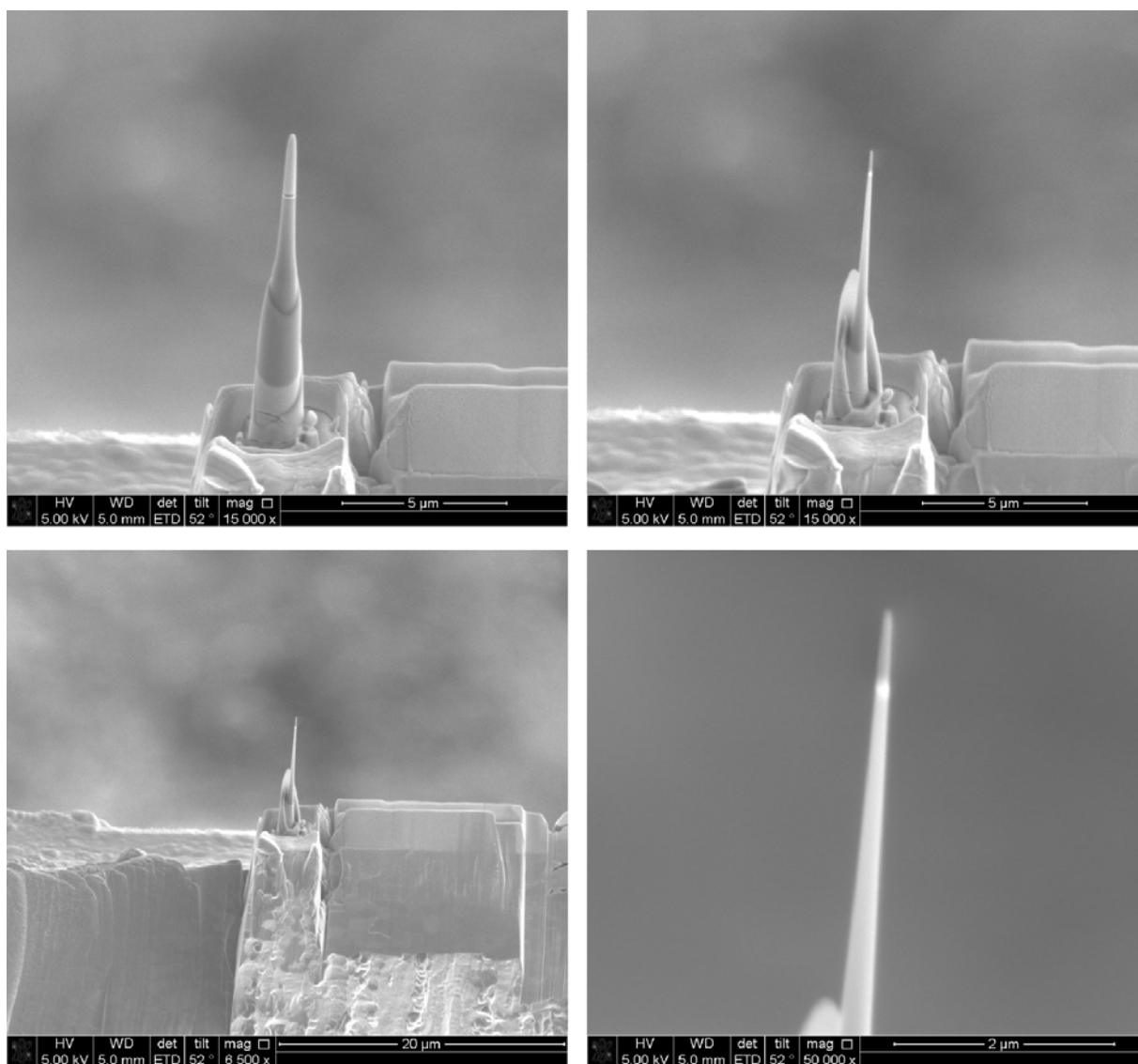


Figure 4. Optimized free-standing APT tip with no shoulders on either side.

Even with the optimized method of sample preparation, the samples did not survive in APT possibly because of weak connection to the base of the TEM grid or that the thin film stacking sequence was not appropriate as the first layer of the exposed surface namely, HfO being non-conductive would have increased the stress on the sample due to charge accumulation leading to sample fracture.

Hence a modification in the layer stacking sequence was attempted in order to further investigate these materials. Accordingly a new set of samples was prepared with the following sequence as illustrated in Fig. 5.



Figure 5. Schematic diagram showing the multi-layer configuration of the sample prepared for Atom Probe Tomography analysis

The sample with modified layer sequence was then used to prepare APT tips in order to investigate the elemental distribution across the interfaces and also within each layer. The SEM image of the APT tip with well-defined positioning of layers is shown in Fig. 6.

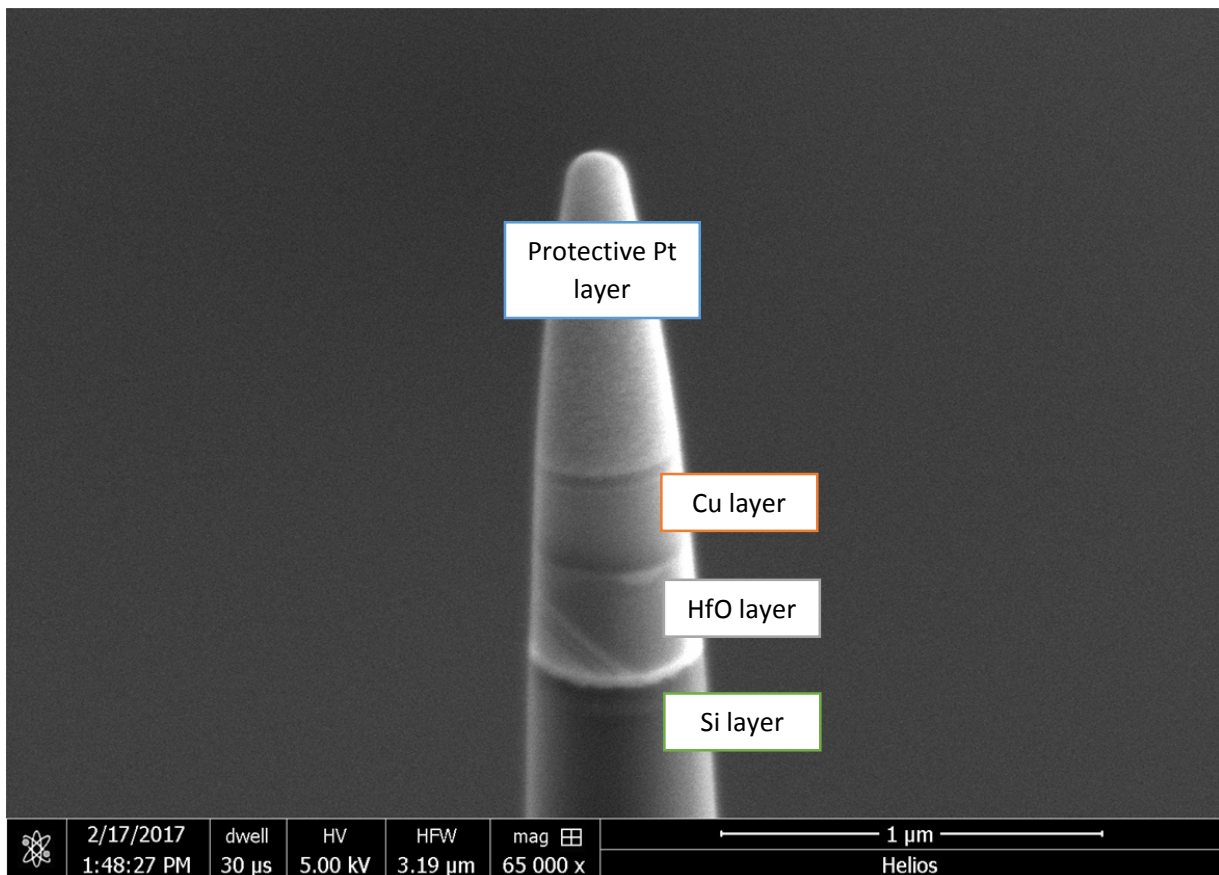


Figure 6. SEM image displaying the inverted layer sequence of the thin film sample.

Multiple APT tips per prepared using the sample shown in Fig. 6. After several trails, one successful APT measurement was finally obtained with the overall (Fig. 7) concentration of 26.70 at.% Cu, 46.90 at.% O and 26.40 at.% Hf within the analyzed volume of $90 \times 90 \times 44 \text{ nm}^3$.

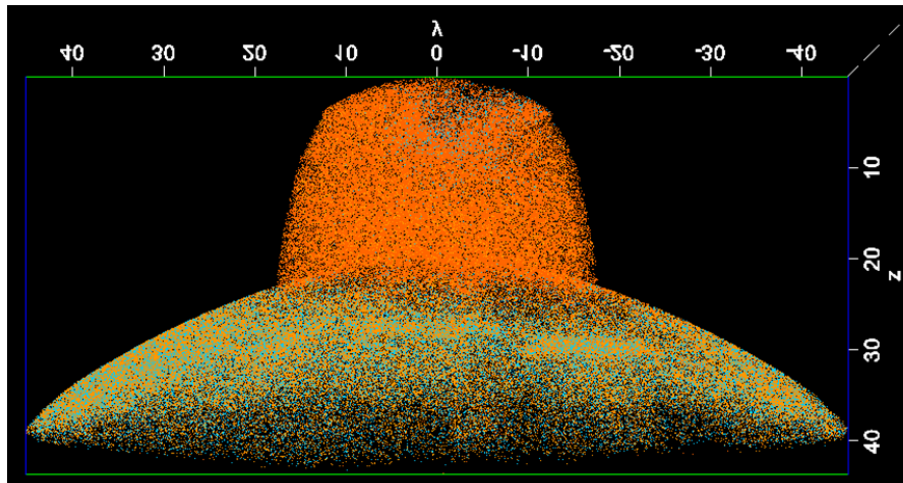


Figure 7. Overall elemental distribution in the measured APT volume of $90 \times 90 \times 44 \text{ nm}^3$.

It can be seen that the layers had very different evaporation fields leading to an abrupt increase in layer thickness upon reaching the HfO layer. Also, multiple ions fraction was significantly high and the Hf ions were mainly detected in the form of HfO and HfO₂. Also, the non-conductivity of HfO layer resulted in the failure of the APT tip within a short period of measurement into the HfO layer. The individual elemental distribution of Cu, Hf, HfO₂ and O are shown in Fig. 8.

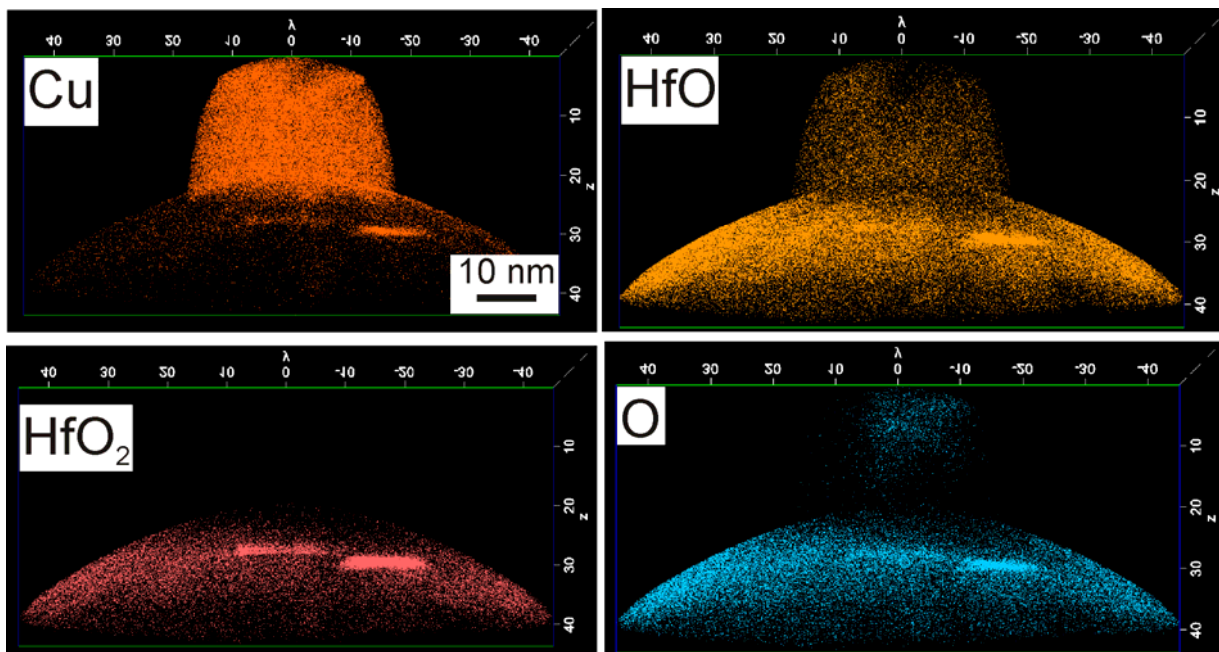


Figure 8. Three dimensional elemental distributions of Cu, Hf, HfO₂ and O.

Further, a 1D concentration profile was plotted normal to the interface using a 5 nm diameter cylindrical region of interest as shown in Fig. 9. It is obvious that there is almost no Cu in the interior of the HfO layer, suggesting that Cu has not diffused into the insulating HfO layer. This observation indicates that the synthesized material can become an ideal platform for developing resistance switching devices. During the application of electrical stresses, it is plausible that some Cu atoms can diffuse along the grain boundaries and interface region of the HfO layer thereby changing the electrical resistance locally facilitating in information storage.

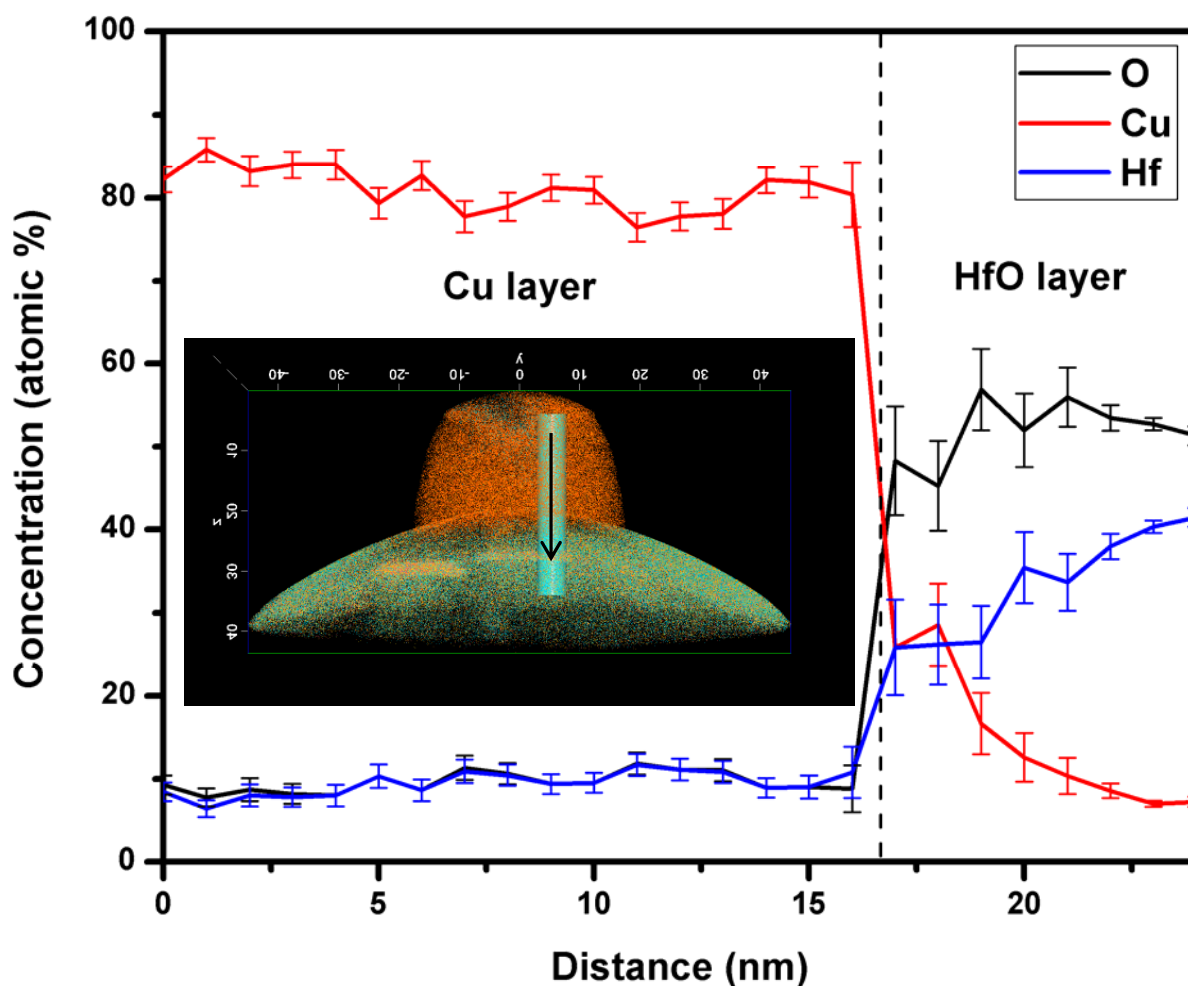


Figure 9. 1D concentration profile obtained along the cylindrical region of interest positioned normal to the interface of Cu and HfO as shown in the inset.

5. Conclusions:

Even though the project had limited success, a lot of technical advances have been made towards characterizing non-conductive samples using a state of art atom probe tomography. Below are some of the key outcomes of this project,

1. A novel methodology of APT sample preparation using commercially available Cu TEM grids has been introduced.
2. A custom made correlative microscopy holder capable of carrying APT tips prepared on commercial Cu TEM grids has been developed. Further modifications, would enable in utilizing this set-up as a robust tool for correlative microscopy studies.
3. Extensive laser parameter optimization studies have been performed in order to successfully measure multi-layer samples consisting of non-conductive oxides suitable for resistive switching.

6. References:

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2. Akinaga, H. and H. Shima, Resistive Random Access Memory (ReRAM) Based on Metal Oxides. *Proceedings of the Ieee*, 2010. 98(12): p. 2237-2251.