EE412 Fall 10: ALD Oxide Nanolaminates Final Report

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Motivation

The main task for this project is to fabricate the metal-insulator-metal (MIM) device structure using the savannah ALD system. Here the insulator is oxide such as HfO2, Al2O3 or HfO2/Al2O3 mixed layers, which is called the nanolaminates. One of the initial goals of this project is to use such MIM device structure for metal oxide resistive random access memory (RRAM). Metal oxide RRAM devices are emerging for future non-volatile memory technology due to its simple structure, fast switching speed, great scalability, and compatibility with current CMOS technology [1]. There are tens of metal oxides has been explored for RRAM application. Here in this project, the materials we plan to explore at the first stage are HfO2 and Al2O3, since they have demonstrated the best memory performance in the literature [2-3]. And the combination of HfOx and Al2O3 together can offer improved switching uniformity probably due to the inter-diffusion of Hf and Al atoms [4]. Before the preliminary results from the HfO2/Al2O3 bi-layer RRAM devices from Cambridge Nanotech at Boston shows very promising device characteristics as shown in Fig. 1. Thus we want to develop our own recipes here at SNF to reproduce the results. On the other hand, the breakdown voltage and initial current leakage information of the fabricated MIM structure in this project can contribute to the knowledge of the oxide quality for the SNF community.

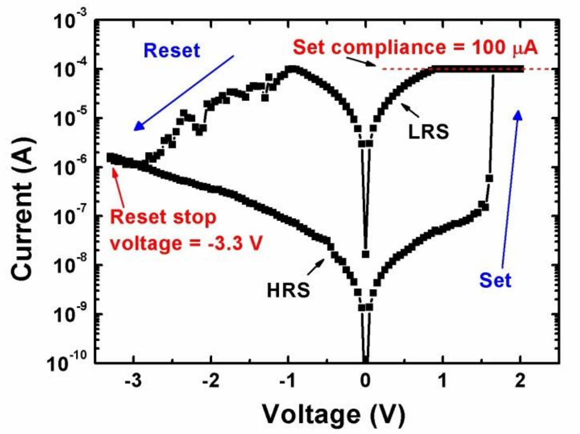

Fig. 1 I-V characteristics of HfO2/Al2O3 bi-layer RRAM devices. The device can set from high resistance state (HRS) to low resistance state (LRS) by a positive voltage sweep, and reset from LRS to HRS by a negative voltage sweep.

Methods

1) Device Fabrication

The MIM device structure process needs three deposition steps (bottom electrode, oxide, top electrode). Because savannah is classified as a semi-clean tool, the bottom electrode materials are limited to TiN grown by savannah or Ti, or Ti grown by gryphon; the top electrode is chosen to be Pt grown by innotec. The lift-off technique will be used for patterning the top electrode and the feature size of the device is 100 um. The fabrication process is sketched as Fig. 2.

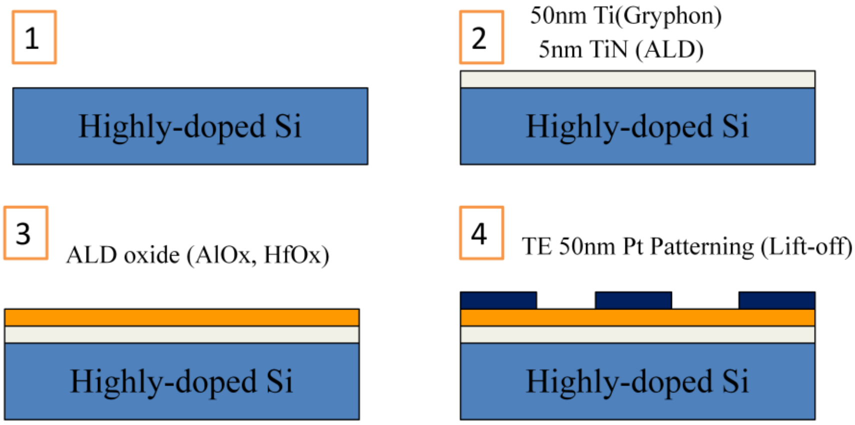

Fig. 2 Process flow for the MIM device structure

2) Measurements

The thickness measurements of the oxide thickness are done by woollam ellipsometry. Because it is very hard to measure the oxide thickness on top of the metal bottom electrode, we use the control sample of which the oxide is deposited on silicon substrate at the same time with the experimental sample. We assume that the oxide thickness is the same for the control sample and the experimental sample. Cautions should be paid here because the actual oxide thickness may not be exactly the same because the nucleation chemistry of the first several cycles of oxide on silicon substrate or on metal substrate may be different. In each control sample, 9 points on the 4 inch wafer is measured to get the statistical information of the thickness.

Electrical measurements to characterize the breakdown voltage and initial leakage current of the fabricated MIM devices are done by Agilent 4156C using cascade probe station. 25 cells at different locations of the wafer are tested to get the statistical information. Oxide breakdown occurs when the current density through the oxide becomes high enough to cause thermal run-away. MIM two-terminal voltage is ramped up to 10V and extract voltage node at sudden substantial current jump. Initial leakage current before the oxide breakdown is extracted at 1V. From the breakdown voltage and initial leakage current, we can know the oxide quality, dense degree, etc.

Results:

Al2O3 and HfO2 was deposited by savannah both at standard temperature (200C) for different cycles and at different temperatures for the same cycles (100cycles). Thickness measurement data for Al2O3 and HfO2 are shown in fig. 3 and fig 4 respectively.

From the curve fitting of fig. 3a, we can see that the deposition rate of Al2O3 is approximately 1A/cycle and the native oxide thickness on silicon substrate is approximately 13.7A. From fig. 3b, we can see that Al2O3 deposition rate are approximately the same at different growth temperatures, ranging from 100C to 250C.

From the curve fitting of fig. 4a, we can see that the deposition rate of HfO2 is approximately 0.9A/cycle and the native oxide thickness on silicon substrate is approximately 12.5A. From fig. 4b, we can see that HfOx deposition rate decreases from 1.3A/cycle to 0.6A/cycle as increasing growth temperature from 100C to 250C, assuming the native oxide is approximately 10A, the deposition rate.

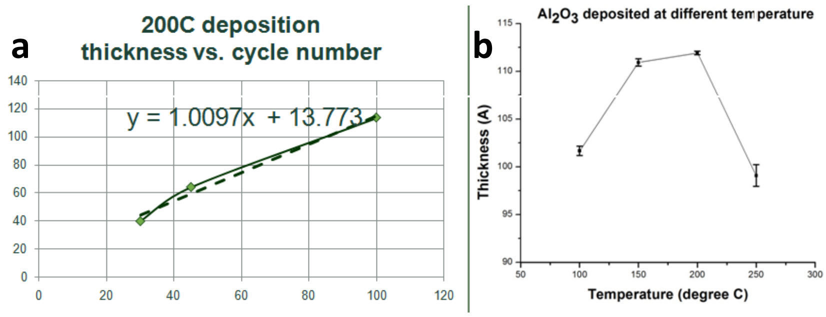

Fig. 3 a. Al2O3 deposited using standard recipe for 30 to 100 cycles. b. Al2O3 deposited for 100 cycles at 100C to 250 C.

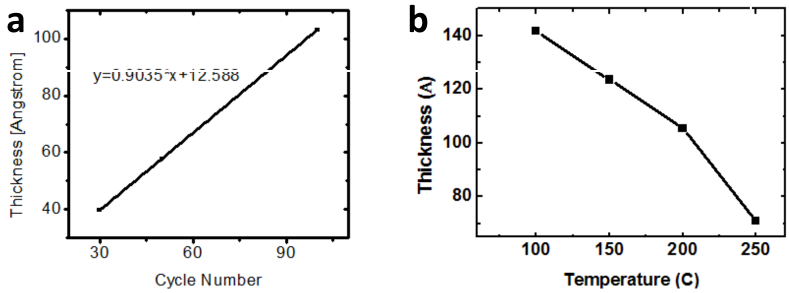

Fig. 4 a. HfOx deposited using standard recipe for 30 to 100 cycles. b. HfOx deposited for 100 cycles at 100C to 250 C.

Breakdown voltage measurement data for Al2O3 and HfOx are shown in fig. 5 and fig 6 respectively. Leakage current measurement data for Al2O3 and HfOx are shown in fig. 7 and fig 8 respectively. Breakdown voltages of are approximately proportional to the oxide thickness. And leakage currents of Al2O3 and HfOx decrease with increasing oxide thickness. Fig. 5b and 7b show that the oxide quality of Al2O3 deposited by savannah are similar at 150C, 200C and 250C, but the oxide quality of Al2O3 deposited at 100C is lower considering breakdown voltage and leakage current. However, the HfOx quality at different temperatures are not very clear from fig 6b and 8b because the thickness of HfOx varies from 100C to 250C. Hence, we deposited HfOx at different temperatures for different cycles and targeting at similar thickness(10±0.5nm). We can conclude from fig. 9 that the oxide quality of HfOx grown at low temperatures (100C, 150C), is not good probably due to the loose structure.

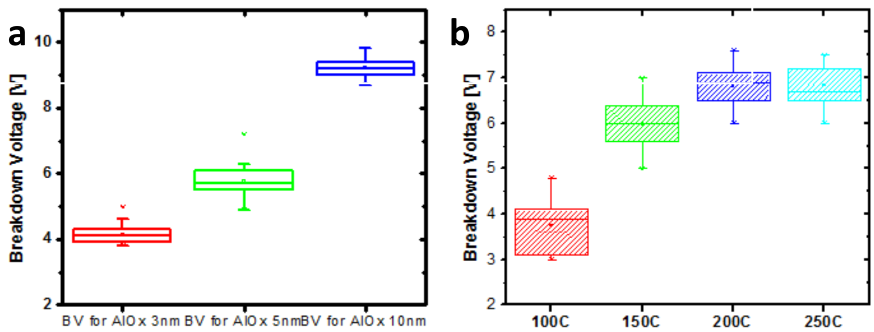

Fig. 5 a. Breakdown voltage of Al2O3 deposited using standard recipe for 30 to 100 cycles. b. Breakdown voltage of Al2O3 deposited for 100 cycles at 100C to 250 C.

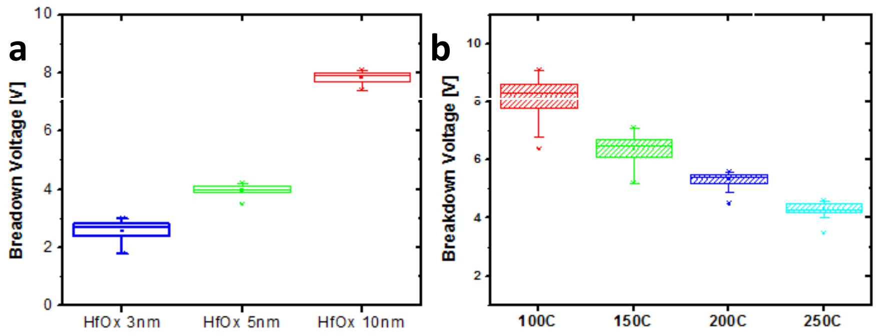

Fig. 6 a. Breakdown voltage of HfOx deposited using standard recipe for 30 to 100 cycles. b. Breakdown voltage of HfOx deposited for 100 cycles at 100C to 250 C.

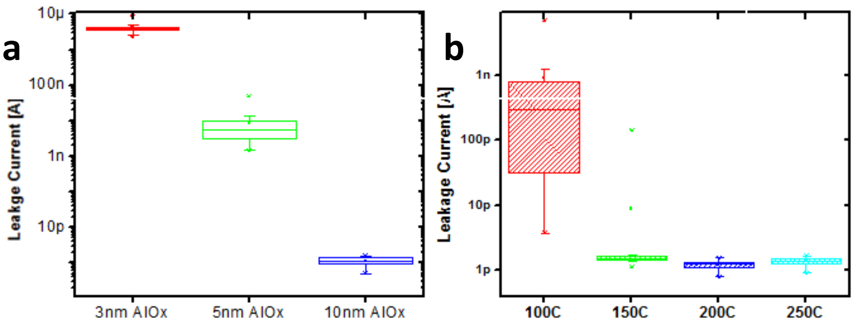

Fig. 7 a. Leakage current of Al2O3 deposited using standard recipe for 30 to 100 cycles. b. Leakage current of Al2O3 deposited for 100 cycles at 100C to 250 C.

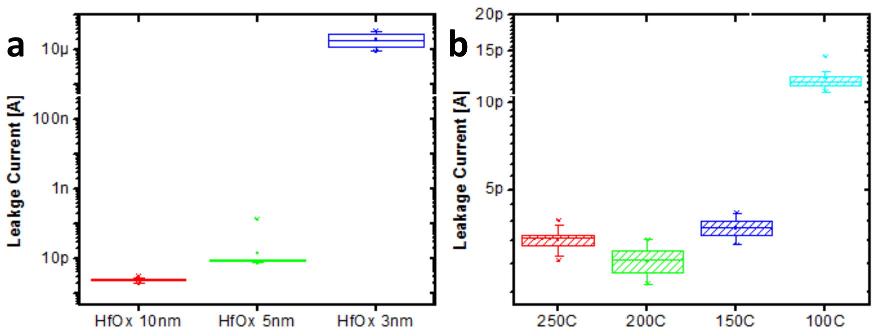

Fig. 8 a. Leakage current of HfOx deposited using standard recipe for 30 to 100 cycles. b. Leakage current of HfOx deposited for 100 cycles at 100C to 250 C.

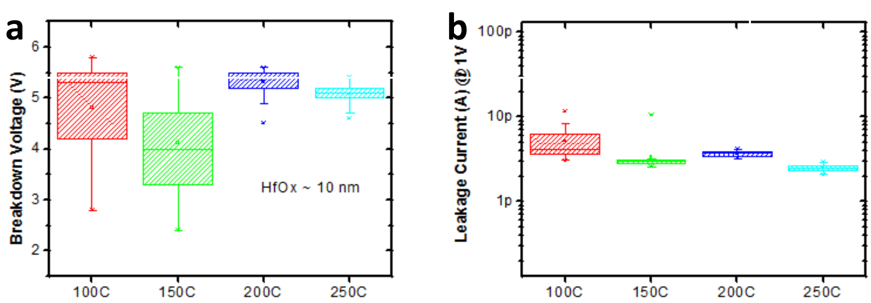

Fig. 9 a Breakdown voltage of HfOx deposited at 100C to 250 C to similar thickness (10±0.5nm). b Leakage current of HfOx deposited at 100C to 250 C to similar thickness (10±0.5nm).

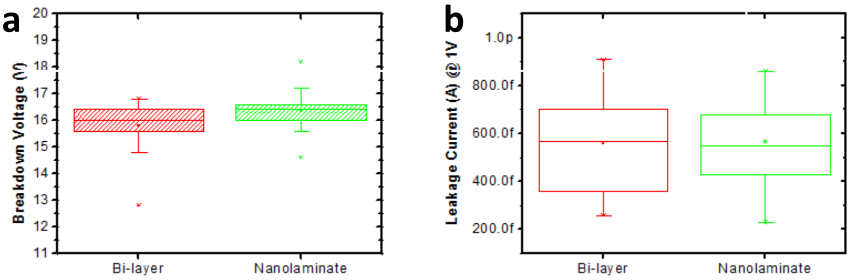

Fig. 10 a. Breakdown voltage of bi-layer oxide and nanolaminate oxide. b Leakage current of bi-layer oxide and nanolaminate oxide.

We also compared the electrical properties of bi-layer oxide structure and nanolaminate structure. Fig 10 shows that their breakdown voltage and leakage current are similar. Bi-layer oxides consist of 100 cycles Al2O3 deposition (~10nm) and 100 cycles HfOx deposition (~10nm) on top. Nanolaminate structure means Al2O3 and HfOx are deposited alternately for totally 200 cycles. Because of the self-limiting nature of the sequential precursors, the nanolaminate structure is built up with one layer of Al2O3 and one layer of HfOx. We did not observe significant difference of the bi-layer and nanolaminate samples in terms of breakdown voltage and leakage current.

Conclusion:

1. Both Al2O3 and HfO2 has a deposition rate around 1 A per cycle at 200 degree C for the standard recipe.
2. Al2O3 has a very large deposition temperature window, from 100 degree C to 250 degree C, the deposition rate is almost constant. But the deposition rate for HfO2 is very sensitive to deposition temperature.
3. Typically the breakdown voltage for both Al2O3 and HfO2 linearly decreases with the oxide thickness, and the initial leakage current exponentially increases with the oxide thickness. Generally, with thickness less than 5 nm, the oxide is not longer a good insulator.
4. Low temperature deposited HfO2 has a faster deposition rate more than 1 A per cycle, whose quality is not so good due to the loose density, thus not recommended for insulator.

References

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