Defining the performance of SiO_x ReRAM by engineering oxide microstructure

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***Abstract*—Filamentary resistance switching, or ReRAM, devices based on oxides suffer from device-do-device and cycle-to-cycle variability of electrical characteristics (electroforming voltages, set and reset voltages, resistance levels and cycling endurance). These are largely materials issues related to the microstructure of the switching oxide. Here we outline strategies to engineer the electrical performance of silicon oxide ReRAM by controlling the oxide microstructure at the nanometre scale through approaches including engineered interfaces and ion implantation. We demonstrate control over the distribution of switching voltages, electroforming voltages, and stable multilevel resistance states.**

Keywords—ReRAM; silicon oxide; resistance switching; memristors.

I. Introduction

Oxide-based Resistive Random Access Memory – so-called OxRAM, or oxide-based ReRAM – is a promising technology for future non-volatile semiconductor memory and neuromorphic applications. It has received significant attention over the past decade or more, with many different oxides showing promise as base materials for this exciting technology [1]. Hafnium oxide, tantalum oxide and titanium oxide have received perhaps the most attention while, more recently, silicon oxide (SiO_x, where x may be less than 2) has emerged as particularly interesting [2, 3]. It offers the benefits of a wide band gap oxide – cycling and temperature stability, for example – with intrinsic CMOS compatibility. Nevertheless, there is a perception that all OxRAM technologies, thanks to their inherent stochasticity, suffer from high variability and low yield. Such issues can be overstated, but are related to the physics of field-driven resistance changes in oxides.

At the heart of OxRAM technologies is the control of the resistance states of oxide thin films via the application of an electrical bias. In the case of the materials and devices described here, the applied bias generates nanometre-scale conductive filaments bridging the oxide thin film. Such filaments consist of chains of oxygen vacancies, which form a pathway for electrons to flow through the otherwise insulating oxide. This initial formation of the conductive filament, taking the oxide from its original pristine high resistance state to a low resistance state, is referred to as electroforming. The filament can be ruptured (reset) and regenerated (set) by alternating the polarity of the applied bias in a process that is inherently stochastic. The result is repeatable switching of the resistance state of the oxide (resistance switching). Each time the filament is re-formed it takes a slightly different configuration, and hence the resistance of the filament varies from cycle to cycle.

It should be evident that the source of this stochasticity is the structure of the oxide layer. In the case of crystalline oxides, filaments are nucleated by oxygen vacancies and associated defects seeded by, for example, the addition of a layer of gettering material that induces local disorder at the surface of the oxide. For the devices discussed here, the silicon oxide thin film is amorphous, implying a significant degree of existing short-range and medium-range disorder. Understanding of, and control over, local structure is therefore key to tailor the switching behaviour of the oxide.

Here we report a study of the engineering of the microstructure of amorphous silicon oxide and how this

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affects the electrical properties of SiO_x ReRAM devices. In particular we demonstrate control over electroforming voltage, variability of set and reset voltages, and stability of multiple resistance states through microstructure engineering.

II. Experimental

A. Sample Fabrication

Our test devices consist of metal-insulator-metal (MIM) structures in which the insulating layer is silicon oxide. Devices were fabricated on top of a thermal oxide layer grown onto a single crystal silicon wafer. Bottom electrodes are sputtered molybdenum (280nm thick); top electrodes consist of a 3nm wetting layer of titanium onto which is evaporated a 115nm thick gold layer. Silicon oxide layers were deposited either by reactive sputtering or atomic layer deposition (ALD). Standard photolithographic techniques were used to define square top electrodes of various sizes ranging between 10μm×10μm to 400μm×400μm. Further details of fabrication may be found elsewhere [4].

For the ion implantation experiments, 30nm thick ALD-grown SiO_x films were implanted with argon ions. Ion fluences ranged from 6.9×10^{14} ions/cm^2 to 1.73×10^{16} ions/cm^2. SRIM calculations predicted that the majority of defects generated by the incident ions would be within the SiO_x layer. Argon ions were chosen so as to create localised physical damage to the oxide while avoiding chemical changes or adding metal dopants. ALD was chosen for film growth to ensure high-quality defect-free oxide layers.

For analysis of oxygen movement in samples, samples consisting of metal bottom electrodes with an upper layer of sputtered SiO_x were prepared. Electrical bias was applied to the sample using a grounded and scanned AFM tip with a voltage applied to the bottom electrode. Biased and unbiased samples were analysed using an ION-TOF TOF-SIMS V instrument. Depth profiles were generated by sputtering samples with a 1 keV, 70 nA Cs^+ beam and using a 25 keV Bi^+ analytical ion beam for secondary ion generation. Further details can be found elsewhere [5].

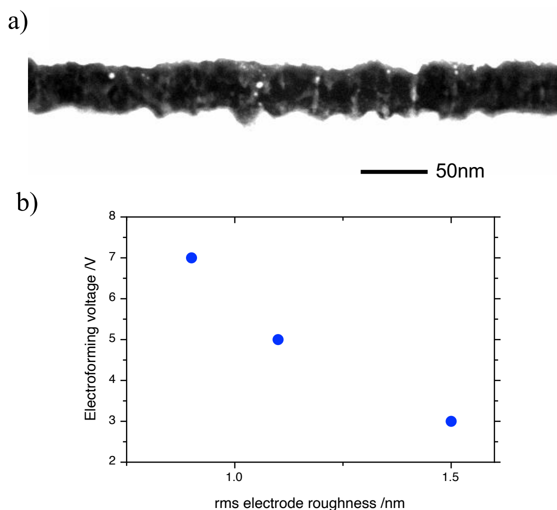

Fig. 1. a) TEM image of a cross-section through an SiOx layer sputtered onto a rough Mo electrode. The contrast has been enhanced to highlight the vertical column edges in the amorphous oxide. b) Dependence of the modulus of the electroforming voltage for samples with different electrode roughnesses.

B. Electrical and Physical Chracterisation

Current-voltage measurements of samples were performed at room temperature in ambient conditions using a Signatone probe station and a Keithley 4200 semiconductor characterisation analyser.

Surface roughness of electrode and oxide layers was measured using Atomic Force Microscopy (AFM). Samples were measured in ambient conditions using a Bruker Dimension Icon AFM.

III. Results & Discussion

We have shown in previous work that the formation of conductive oxygen vacancy filaments in amorphous silicon oxide is driven by the interaction between an applied field and defects within the oxide [6]. Specifically, wide O-Si-O bond angles can trap electrons, lowering the barrier for the breaking of Si-O bonds and enabling the formation of Frenkel pairs (oxygen vacancies and mobile oxygen species). Under electron injection and applied field, percolation pathways of oxygen vacancies can form, ultimately resulting in one or more continuous conductive filaments bridging the oxide. The key to efficient electroforming of such filaments is therefore to ensure the presence of sufficient wide bond angle defects.

We have also previously demonstrated that sputtered SiO_x has a columnar structure [7], which is very often a characteristic of sputtered material [8], in which the edges of the columns have a higher conductivity than the bulk material. This can be attributed to a higher concentration of structural defects at column boundaries. Control over the columnar structure of the oxide should therefore enable control over resistance switching.

A. The Effect of Surface Roughness

Columnar growth during sputtering is a result of shadowing effects during the early stages of material accretion on the substrate surface [8]. Roughening the surface of the bottom electrode of an MIM device prior to the deposition of the oxide layer can emphasise such effects, and hence stimulate a columnar oxide growth mode. Fig. 1a shows a TEM cross-section of an MIM device in which the rough surface of the bottom electrode can be seen to have templated the growth of oxide columns, as shown by the vertical white structures corresponding to column boundaries. Fig. 1b shows the effect on the electroforming voltage of devices of progressively increasing the roughness of the bottom electrode interface by varying the sputtering parameters. AFM topography maps (not shown) confirm an increase in rms surface roughness from 0.9nm to 1.5nm, with a corresponding decrease in electroforming voltage from >6V to around 3V.

COMSOL simulations (not shown) confirmed that field enhancement effects from the rough electrode interface would have a minimal effect on the electrical field within the oxide, and previous work on rough interfaces in hafnium oxide based ReRAM devices by Nandi et al [9] suggested that any such enhancement would be largely screened by charged defects present in the oxide due to electroforming. We therefore hypothesise that the observed reduction in electroforming voltage with increased electrode roughness arises from the presence of more clearly defined column boundaries.

A second result of the change in surface roughness, and hence oxide microstructure, is a reduction in the spread of set and reset voltages, as we have previously reported [10, 11]. Again, we hypothesise that this results from increased localisation of defects – specifically wide O-Si-O bond angles – at column boundaries. By restricting the regions into which oxygen vacancy filaments can form, the cycle-to-cycle variation in filament configuration is reduced.

B. Ion Implantation

Structural defects can be introduced into high quality, uniform materials by ion implantation. While previous reported work has focused on ion implantation to modify existing resistance switching behaviour by, for example, reducing electroforming voltages [12, 13, 14], here we use implantation to enable otherwise inert oxides to switch.

Fig. 2a shows current-voltage characteristics for both a pristine ALD-grown SiO_x film, and an ALD-grown film that has been implanted with 6.9×10^{14} argon ions per square cm to induce structural defects. Unimplanted ALD-grown oxides characteristically do not switch, instead breaking down irreversibly at very high fields. Fig. 2b shows the success rate for electroforming devices as a function of implantation dose. Of note is the very low electroforming success rate for the unimplanted sample: 3%. Here we define successful electroforming as a reversible increase in oxide conductance, in contrast to hard breakdown, which is unrecoverable.

Fig. 3a shows twenty set-reset cycles of a device implanted with 1.73×10^{16} argon ions per square cm, highlighting a tight distribution of set and reset voltages and currents in the high and low resistance states. Figure 3b shows seven discrete and stable resistance states obtained in an implanted sample by varying the maximum voltage of the positive reset sweep. We have thus demonstrated that ion implantation is a viable method to both induce and control the switching behaviour of high quality amorphous silicon oxide.

a)

b)

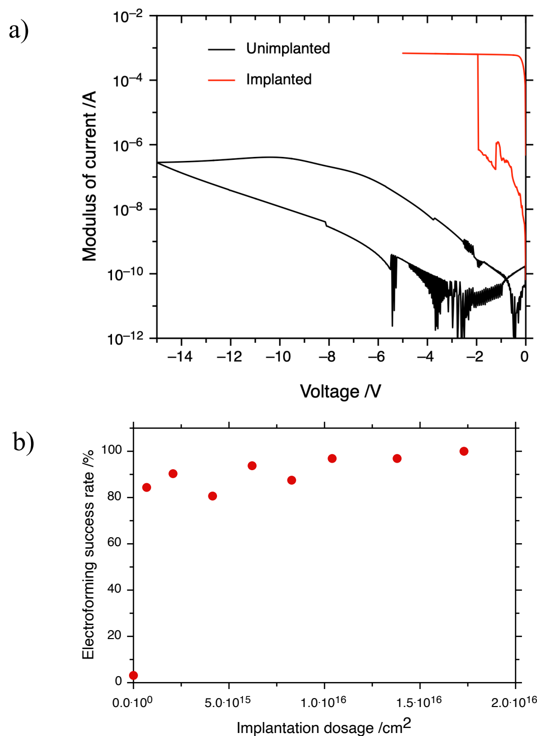

Fig. 2. a) Current/voltage sweeps of an unimplanted ALD-grown oxide (black curve – lower) and an oxide implanted with 6.9×10^{14} cm^{-2} argon ions (red curve-upper). b) Percentage of devices that elecroform successfully as a function of implantation dose. Note the rate for unimplanted samples is 3%.

a)

b)

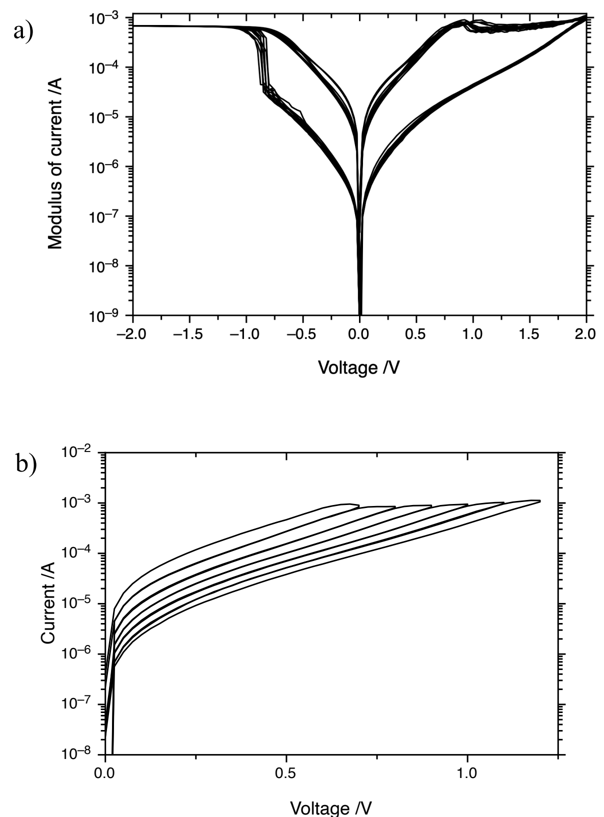

Fig. 3. a) multiple cycles of a sample implanted with 1.73×10^{16} cm^{-2} argon ions. b) Multilevel resistance control of sample implanted with 1.04×10^{16} cm^{-2} argon ions. by varying the stop voltage during reset.

C. Oxygen Mobility

Resistance switching in oxides is fundamentally a redox process [15]; hence, control of oxygen movement can be expected to contribute to device behaviour. We have shown previously that extreme biasing of devices in vacuum results in oxygen emission, and in such cases it can be difficult to set devices once reset [6]. We therefore studied the ability of oxygen to move across oxide-electrode interfaces and device-environment interfaces, and how this is affected by oxide microstructure.

Fig. 4 shows a series of SEM images of the surfaces of three samples with different microstructure, as revealed by their very different surface structure and roughness. For each sample we determined by SIMS analysis the change in relative oxygen concentration within the oxide as a function of distance from the top interface as a result of electrical bias. These results are shown in the left-hand side of the figure, and indicate a complex picture of oxygen movement as a function of microstructure. In the case of the roughest, most porous, oxide, applying a negative bias to the top of the oxide very clearly drives oxygen into the sample, as would be expected. Similarly, the smoothest, least porous, sample takes up very little, if any, oxygen from the environment under negative bias. However, the third sample, which has roughness and porosity lying between the other two, shows more complex behaviour. While there is a large increase in relative oxygen concentration close to the sample surface, and a smaller enhancement beyond a depth of 1.5nm, the region between 0.5

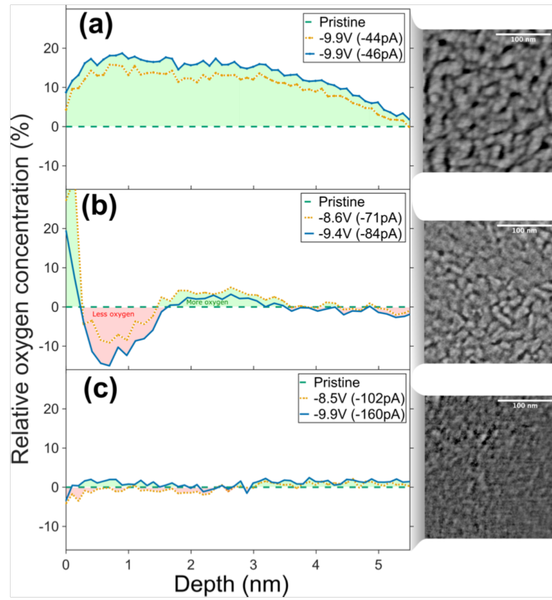

Fig. 4. Plots of changes in relative oxygen concentration after electrical biasing of samples with high (a), medium (b) and low (c) surface roughness, as illustrated by the corresponding SEM micrographs (RHS). All oxygen concentrations are relative to those in the pristine, unbiased, layers, and depth is depth into the oxide from the upper interface. Boas voltages and currents are specified, and two measuerments per sample are presented.

Samples consist of SiOx layers depostied on metal electrodes: (a) molybdenum; (b): titanium; (c): platinum. Figure taken from [5] and reproduced under the CC-BY licence.

and 1.5nm into the sample is depleted of oxygen. While we have no definitive explanation, we hypothesise that self-limiting oxidation of the sample just sub-surface forms a region that blocks the ingress of oxygen from the environment while allowing oxygen already within the layer to migrate deeper under negative bias. Further work is needed to test this hypothesis.

IV. Conclusions

We have demonstrated that oxide microstructure is a determining factor governing resistance switching behaviour in amorphous silicon oxide ReRAM devices. Modulating the surface roughness of electrodes onto which switching oxides are sputtered helps define defect-rich regions around column boundaries that promote the formation of conductive oxygen vacancy filaments. Equally, ion implantation with noble gas ions can induce precursor structural defects that enable otherwise inert oxides to switch.

A complex picture is emerging of oxygen movement in amorphous SiO_x ReRAM devices. Here we have shown that, while oxide microstructure undoubtedly has a role to play, more work is needed to understand the complexity of the situation.

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