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Application of ion-implantation for improved non-volatile resistive random access memory (ReRAM)

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ABSTRACT

Resistive switching in transition metal oxides is believed to be controlled by the migration of oxygen vacancies and many interesting device structures employ substoichiometric oxide layers as a source of these active defects. However, the growth of thin (~10 nm) oxide/suboxide heterostructures (e.g. HfO_2/HfO_x or Ta_2O_5/TaO_x) is difficult using conventional film deposition techniques. In this study, ion-implantation is shown to provide an alternative means of synthesizing such structures, with results reported for Ta_2O_5/TaO_x heterostructures fabricated by oxygen-implantation of Ta. The electrical properties of the fabricated heterostructures are discussed with reference to the physical structure of the samples determined from transmission electron microscopy and X-ray photoelectron spectroscopy.

1. Introduction

Redox-based resistive switching represents a class of processes by which the resistance of a dielectric thin-film can be electrically switched between low and high resistance states [1]. It is of particular interest for the fabrication of non-volatile resistive random-access-memory (RRAM) where it offers to provide devices with better scalability, lower power consumption, faster switching, longer retention time, and simpler structure than conventional charge-storage technologies [1,2]. Among the broad range of materials that exhibit resistive switching, transition metal oxides (TMOs), including NiO, TiO_2, ZrO_2, Cu_xO, TaO_x, WO_x and HfO_2, are of particular interest due to their simple chemical structure, ease of growth/deposition and excellent resistive-switching characteristics [2].

Bipolar resistive switching in transition metal oxides is believed to be controlled by the migration of oxygen ions, with conductive filaments formed by the accumulation of oxygen vacancies ($V_O^{\bullet\bullet}$) in the form of a substoichiometric oxide (suboxide) [2–8]. In such cases the switching process can be improved by employing an active intermediate electrode [9] (e.g. Ti) to act as an oxygen reservoir or by using oxide/suboxide heterostructures (e.g. Ta_2O_5/TaO_x) in which the conductive filament is formed by oxygen vacancy (ion) migration from the suboxide (oxide) layer to the oxide (suboxide) layer [10]. The latter have shown impressive resistive switching characteristics but the growth of thin (~10 nm) oxide/suboxide heterostructures can be quite challenging, particularly with commonly employed deposition techniques such as atomic layer deposition where the stoichiometry is controlled by chemical adsorption and reactivity, or reactive sputter deposition or chemical vapour deposition, where the stoichiometry is controlled by substrate temperature and gas pressures.

Ion-implantation is particularly well suited to address this issue as it provides a controlled means of adjusting the stoichiometry of thin films, and naturally produces a graded composition profile suited to the fabrication of oxide/suboxide heterostructures. Two basic approaches can be envisaged: one in which a stoichiometric film is fabricated by conventional means and a graded suboxide layer is formed by ion-implantation of the cation species or a dopant [11], and a second where a deposited metallic film is ion-implanted with oxygen ions to form the oxide/suboxide structure [12]. In this study we examine the potential of Ta_2O_5/TaO_x heterostructures fabricated by O-implantation of Ta.

2. Experimental

Fig. 1 summarises the fabrication steps employed to make metal–insulator–metal (MIM) test structures: oxidized silicon wafers (50 nm thick thermal oxide) were coated with a 50 nm Ta layer using sputter deposition. The wafers were then covered with 5 mm-wide masking strips and implanted with 10 keV O^+ ions to

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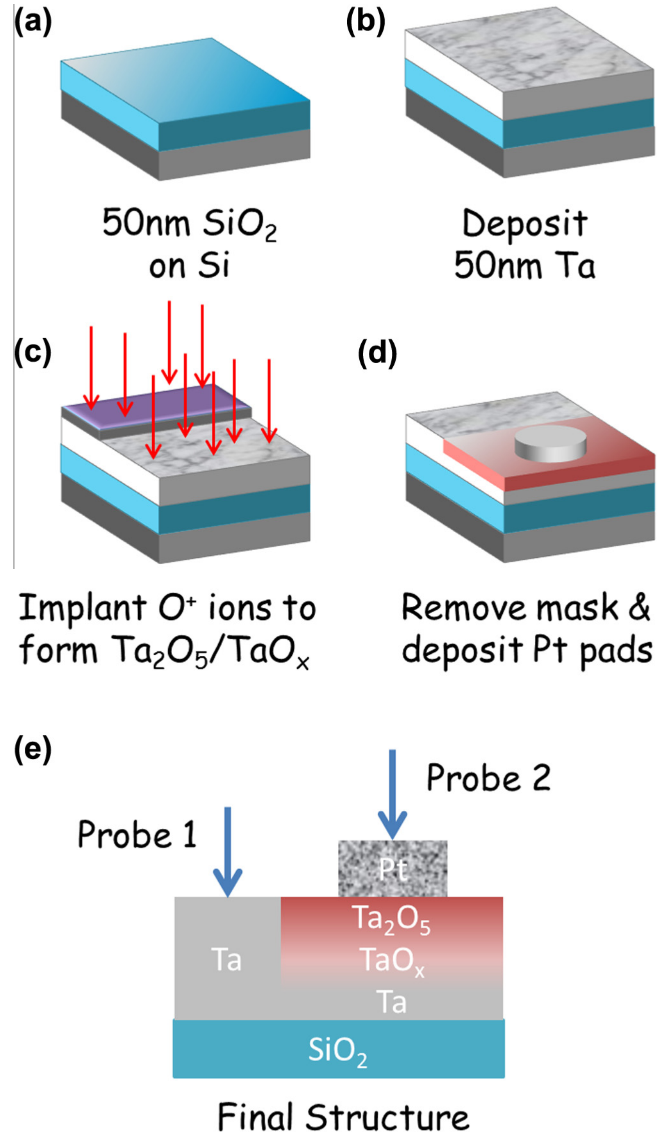

Fig. 1. Schematic of the procedure employed for test structure fabrication. (a) Silicon substrate with a 50 nm thermal oxide, (b) sputter deposition of a 50 nm Ta layer, (c) ion-implantation of the masked sample with 10 keV Si ions, (d) mask removed and evaporation of top Pt contact pads and (e) final metal–insulator–metal test structure.

fluences in the range 1–5 × 10^{17} O cm^{-2} to produce a graded oxide layer extending from the surface to a depth of around 30 nm. The implants were performed with a Varian VIISta HC tool using an O^+ beam current of 5.8 mA, and with backside wafer cooling to maintain the sample at near room temperature. The masking strips were subsequently removed to provide access to unimplanted regions of the Ta film and to provide electrical contact to the layer beneath the synthesized oxide layer that acts as a bottom contact. Pt contact pads were then deposited onto the O-implanted Ta surface to provide top contacts. This was achieved by electron beam evaporation, with a laser-machined projection mask employed to define arrays of circular pads of diameter 250 μm. The final MIM test structure is depicted in the bottom panel of Fig. 1.

Physical characterisation of samples was undertaken using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), while electrical characterisation was performed using an Agilent B1500A parametric analyser. Electrical measurements included current–voltage (I–V) sweeps and pulsed-mode endurance testing with pulse durations ⩾50 ns. In the latter case, voltage pulses of particular amplitude, polarity and duration were applied to the test structure to induce a change in its resistance state. For this study, negative pulses were applied to the top electrode (probe 2 in Fig. 1) in order to switch the device into a low resistance state (set), while positive voltages were applied to switch it back to a high resistance state (reset). The resistance of the test structure was determined after each switching event by applying a low amplitude (10 mV) voltage ramp to the sample and determining the slope of the resulting current–voltage plot.

3. Results and discussion

3.1. Physical characterisation

Oxygen distributions were simulated as a function of fluence using the TRIDYN code [13] and assuming a saturation stoichiometry of Ta_2O_5. The results are shown in Fig. 2, together with measured oxygen distributions for samples implanted with 1–3 and 5 × 10^{17} O. cm^{-2}, determined from XPS profiling (Fig. 2b). While the overall agreement is reasonable, the simulations appear to overestimate the sputtering rate of the film, and predict that the surface remains substoichiometric for fluences exceeding 3 × 10^{17} O cm^{-2}. In contrast, the XPS data suggests that a thin Ta_2O_5 layer has already formed at this fluence, with a stoichiometric layer extending from the surface to around 16 nm and a graded

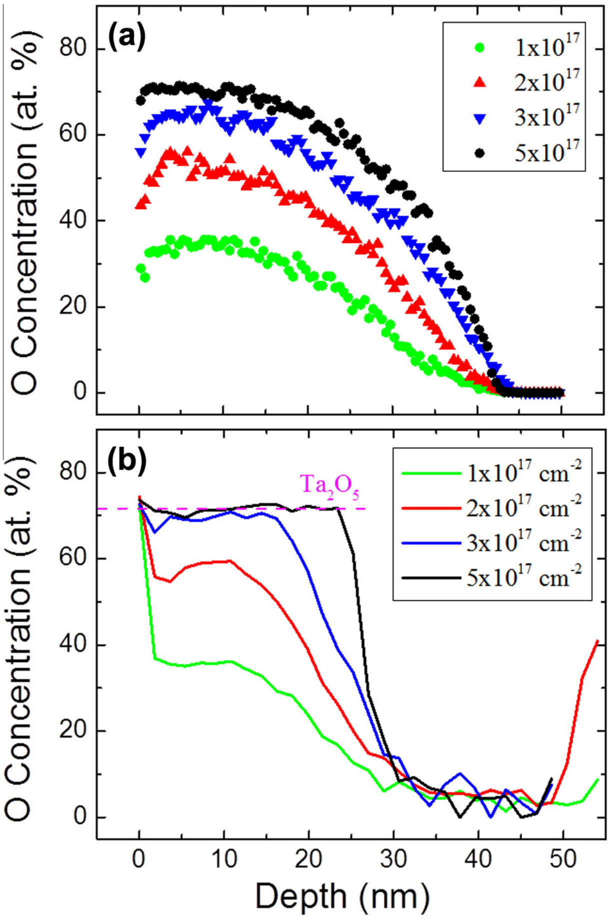

Fig. 2. Implanted oxygen concentration profiles: (a) calculated using the TRIDYN code [13], and (b) measured using X-ray photoelectron spectroscopy depth-profiling.