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Room temperature synthesis of HfO$_2$/HfO$_x$ heterostructures by ion-implantation

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Abstract

Implantation of Hf films with oxygen ions is shown to be an effective means of fabricating high-quality HfO$_2$/HfO$_x$ heterostructures at room temperature, with the layer composition and thicknesses determined by the ion energy and fluence. Implantation with 3 keV O$^+$ ions to a fluence of $1 \times 10^{17}$ ions cm$^{-2}$ produces a polycrystalline (monoclinic-) HfO$_2$ layer extending from the surface to a depth of $\sim 12$ nm, and an underlying graded HfO$_x$ layer extending an additional $\sim 7$ nm, while implantation with 6 keV O to a similar fluence produces a near-stoichiometric surface layer of 7 nm thickness and a graded substoichiometric layer extending to depth of $\sim 30$ nm. These structures are shown to be broadly consistent with oxygen range data but more detailed comparison with dynamic Monte Carlo simulations suggests that the near-surface region contains more oxygen than expected from collisional processes alone. The bandgap and dielectric strength of the HfO$_2$ layer produced by 3 keV; $1 \times 10^{17}$ ions cm$^{-2}$ implant is shown to be indistinguishable from those of an amorphous film deposited by atomic layer deposition at 200 °C. The utility of these layers is demonstrated by studying the resistive switching properties of metal-oxide-metal test structures fabricated by depositing a top metal contact on the implanted film. These results demonstrate the suitability of ion-implantation for the synthesis of functional oxide layers at room temperature.

Supplementary material for this article is available online

Keywords: ion-implantation, HfO$_2$, heterostructures, non-volatile memory

(Some figures may appear in colour only in the online journal)

1. Introduction

Oxide films are generally used as passive insulating layers in modern microelectronic devices but are of increasing interest as the active material in a new generation of low-power nanoionic devices [1]. These exploit characteristic resistance changes caused by the drift and diffusion of mobile ions in the oxide layer and are of particular interest for applications such as: resistive random-access memory (ReRAM) as a replacement for non-volatile flash memory; field-programmable gate arrays for reconfigurable electronics; and artificial synapses and neurons for neuromorphic computing nanoionics devices [2]. A wide range of techniques are used to fabricate the functional oxide films, including thermal oxidation, thermal and plasma-enhanced atomic layer deposition (ALD), non-reactive and reactive sputter deposition, and thermal and plasma-enhanced chemical vapor deposition [3–5]. Because nanoionics devices rely on mobile ions and exploit the properties of substoichiometric films, device fabrication is normally limited
to back-end of line processing where processing temperatures are limited to <450 °C. As a consequence there is particular interest in the development of low-temperature oxide synthesis methods [6].

Resistive switching in binary transition-metal oxides is typically mediated by the drift and diffusion of oxygen vacancies created by an initial soft-breakdown (forming) process [7–11]. The forming process can be difficult to control in stoichiometric films due to their low initial vacancy concentration and the large conductivity change during dielectric breakdown. The use of oxide/suboxide heterostructures mitigates the need for vacancy generation and generally leads to improved device performance, reliability and endurance [12, 13]. This can be achieved by direct deposition of oxide/suboxide films using techniques such as reactive sputter deposition, or by employed a reactive metal (e.g. Ti, Hf, Ta) to reduce part of a stoichiometric film [12].

Ion-implantation offers an alternative means of fabricating functional oxide films for resistive switching applications as it provides a controlled means of adjusting the film stoichiometry, and naturally produces a graded composition profile suited to the fabrication of oxide/suboxide heterostructures. It has previously been shown to produce CuOx [14], and TaOx [15–18] films suitable for resistive switching applications. Recent studies have also shown that doping can be used to modify the formation energy of oxygen vacancies and improve resistive switching reliability and uniformity [19–21]. Such doping can be achieved through the co-deposition of the oxide and dopant, but again ion-implantation offers an attractive alternative approach [22, 23].

HfO2 is currently employed as a high-k gate dielectric in CMOS devices and has been shown to exhibit excellent ReRAM characteristics. This study investigates the structure and properties of ion-beam synthesized HfO2/HfOx (oxide/suboxide) heterostructures produced by low-energy oxygen implantation into metallic Hf films. The functionality of the films is verified by testing their resistive switching characteristics.

2. Experimental details

Metal–insulator–metal test structures were fabricated on thermally oxidized Si wafers using the steps outlined in figure 1. First, a 50 nm Hf layer was deposited at room temperature over the full area of a wafer by DC sputter deposition from a Hf target (figure 1(a)). This was subsequently masked in selected regions and implanted with 3 keV O+ ions to fluences up to 1 × 1017 ions cm−2 (figure 1(b)). The backside of the wafer was cooled during implantation to maintain the sample near room temperature. Smaller samples were cleaved from the full-wafer for subsequent processing and testing. Half of each sample was maintained in its as-implanted state (hereafter referred to as-implanted) while the other half was subsequently

Figure 1. Schematic showing the test structure fabrication steps: (a) 50 nm Hf layer on thermally oxidized silicon wafer; (b) O implantation of the 50 nm Hf layer with a masking strip; (c) optional ion-implantation with 5 keV Si− ions of different fluences (5 × 1013, 1 × 1014, 5 × 1015, and 1 × 1015 ions cm−2) and (d) final metal–insulator-metal test structure after evaporation of top Pt contact pads.
implanted with 5 keV Si⁺ ions to fluences in the range from $5 \times 10^{13}$ ions cm⁻² to $1 \times 10^{15}$ cm⁻² (hereafter referred to as Si-doped) (figure 1(c)). The implantation masks were then removed to provide access to unimplanted regions of the Hf film that extended beneath the implanted layer (figure 1(d)). A Pt film was finally e-beam evaporated through a shadow mask to define circular top contact pads of 100–250 μm diameters and complete the Pt/HfOₓ/Hf test structures (figure 1(d)). For comparison, similar Pt/Hf/HfO₂/Pt test structures were fabricated from 10 nm thick HfO₂ films deposited by ALD. In this case substrates were held at 200°C during HfO₂ deposition, with the layer grown using alternating pulses of pure tetrakis (dynamethyamido)-hafnium (Hf(NMe₂)₄) and H₂O vapor, with N₂ purged in the reaction chamber between pulses.

As-implanted films were studied by transmission electron microscopy (TEM), glancing incidence x-ray diffraction (GIXRD), electron Rutherford backscattering spectrometry (e-RBS) [24], reflection electron energy loss spectroscopy (REELS) and x-ray photoelectron spectroscopy (XPS). Electrical characterization was performed using a semiconductor parametric analyzer (Agilent B1500A).

3. Results and discussion

3.1. Implantation profiles

Figure 2 shows the oxygen range distributions for 3 keV and 6 keV O⁺ ions implanted into Hf and HfO₂, as calculated by the SRIM code [26]. While this code does not include dynamic effects such as sputtering, diffusion or compositional changes, it can be used to estimate critical range parameters. Specifically, the simulations show that 3 keV oxygen ions implanted into Hf have a mean projected range of 7.8 nm, with 4.5 nm straggling. In comparison, 3 keV oxygen ions implanted into HfO₂ have a mean projected range of 5.9 nm, with straggling of ~3.4 nm, reflecting the reduced ion range in HfO₂ due to its higher atomic density. As the composition of the surface layer is expected to evolve from Hf to HfO₂ during implantation, the actual range parameters will fall between these two extremes and if the profiles were unmodified by sputtering and diffusion this would give a peak O concentration of ~7.4 × 10¹⁷ cm⁻³. Given that the oxygen concentration in HfO₂ is 5.54 × 10²² ions cm⁻³, this would imply a critical fluence for HfO₂ synthesis of ~7.5 × 10¹⁶ O cm⁻². Similar analysis for the 6 keV implants shows that the O range in Hf is ~12 nm with straggling of ~7 nm, and in HfO₂ the range is ~10 nm with straggling of ~6 nm. In this case the critical fluence for oxide synthesis is ~1.4 × 10¹⁷ ions cm⁻². Although simplistic, these estimates are broadly consistent with experimental results which show that for 3 keV O ions implants a fluence of 5 × 10¹⁶ O cm⁻² fails to create a stoichiometric oxide layer (see supplementary information, which is available online at stacks.iop.org/NANO/29/425601/mmedia) while a fluence of 1 × 10¹⁷ ions cm⁻² creates a HfO₂ layer of ~10–12 nm thickness, as discussed below.

3.2. Physical characterization

Figure 3 shows bright-field TEM images of Hf films after implantation with 3 keV O ions to a fluence of $1 \times 10^{17}$ ions cm⁻² (figure 3(a)) and after implantation with 6 keV O ions to a fluence of $1 \times 10^{17}$ ions cm⁻² (figure 3(b)). These show that the lower energy implant produces a well-defined surface layer of ~12 nm thickness, while the higher energy implant produces a thinner surface layer (~7 nm) and an underlying ‘disordered’ layer of ~10 nm thickness. The higher resolution images further show that the near-surface layers are polycrystalline and have a structure consistent with monoclinic HfO₂ (determined from Fourier transform analysis of lattice images). These layer thicknesses are broadly consistent with the ion range data shown in figure 2 but it is interesting that they are polycrystalline, despite the high oxygen implant fluence. This contrasts with the case of O-implanted Ta which has been shown to produce amorphous Ta₂O₅ layers [27, 28].

Compositional depth profiling of the films was performed by XPS analysis, with results shown in figure (4(a)). These data show a clear difference between the sample implanted with 3 keV O⁺ to a fluence of $1 \times 10^{17}$ ions cm⁻² and other samples, with the former having a clear near-surface layer with O-concentration close to that of stoichiometric HfO₂.
extending from the surface to a depth of ∼12 nm and the others having thin O-rich surface layers that are largely independent of the implant conditions. These results are consistent with the TEM analysis and range data and show that the oxygen concentration saturates at the stoichiometric composition of HfO₂ for the 3 keV; 1 × 10¹⁷ ions cm⁻² implant. This implies that excess oxygen (i.e. that in excess of the concentration required to form stoichiometric HfO₂) is either lost from the sample through redistribution to the surface, or extends the oxide thickness by diffusing to the HfO₂/HfOₓ interface and reacting with Hf. We note that the thin oxygen-rich layers observed for other samples partly reflects the expected ∼3 nm native oxide that forms on Hf metal when exposed to air [29].

GIXRD analysis of the oxide layer produced by the 3 keV; 1 × 10¹⁷ ions cm⁻² implant, shown in figure 4(b), confirms the polycrystalline nature of the film and shows that the dominant phase is monoclinic HfO₂. In contrast, the GIXRD spectrum from an ALD HfO₂ film deposited at 200 °C exhibits a broad peak centered at 2θ values of 32°, consistent with amorphous HfO₂.

To confirm the stoichiometry of the surface layer and assess its electronic structure, implanted films were further characterized by electron Rutherford backscattering spectroscopy (e-RBS) [30] and REELS. Figure 5(a) shows e-RBS spectra of the as-implanted sample for two different scattering geometries: normal incidence (perpendicular in) where elastic scattering includes contributions from the HfO₂ layer and underlying HfOₓ and Hf layers, and rotated by 35° (glancing out) where elastic scattering is dominated by scattering from the HfO₂ layer. The elastic scattering peaks from Hf and O are clearly resolved (the recoil energy transferred from the projectile-electron to the nucleus depends on the atom’s mass), with the O/Hf area ratio being larger for the glancing-out geometry (i.e. the O concentration is larger near the surface). A comparison of the peak ratios and scattering cross-sections

![Figure 3. Bright-field TEM images of (a) sample implanted with 3 keV O ions to a fluence of 1 × 10¹⁷ ions cm⁻², and (b) sample implanted with 6 keV O ions to a fluence of 1 × 10¹⁷ ions cm⁻².](image-url)
The NIST electron elastic-scattering cross-section database \([31-33]\) for the different scattering geometries confirmed the nominal stoichiometry of the surface layer to be HfO\(_2\), with a thickness of \(\sim\)12 nm. Unfortunately, the O peak is not background free and the variation in the background curves for different choices of stoichiometry results in a \(\sim\)10% uncertainty of the O nominal stoichiometry.

Figure 5(b) shows corresponding REELS spectra from the as-implanted HfO\(_x\) sample and an ALD grown HfO\(_2\) film performed with 5 keV electrons. For this energy the elastic scattering peaks from O and Hf cannot be resolved and their energy is taken as zero energy loss. The increase in scattering yield for energy losses greater than \(\sim\)6.0 eV corresponds to elastically scattered electrons that have additionally undergone inelastic scattering, with the onset value corresponding to excitation of electrons across the oxide bandgap \([30, 34-36]\). For HfO\(_2\) layers grown by ALD this gives a bandgap between 5.3 and 5.7 eV, depending on the assumptions made about the functional dependence of the onset \([37]\). For the O-implanted sample the onset is very similar, but there is increased yield at energy losses between 1 and 4 eV. This is attributed to Hf atoms that are not in a 4+ charge state, with the excess intensity arising from excitation of the remaining 5d electron, consistent with the film containing under-coordinated Hf.

3.3. Dynamic profile simulations

To better understand the evolution of the oxide layer during ion implantation as well as the relative contributions of ion-implantation and sputtering to layer formation dynamic Monte Carlo simulations were undertaken using the TriDyn code \([38, 39]\). This code takes account of the changing composition of the sample during implantation and allows for oxygen in excess of the stoichiometric concentration to redistribute to regions of sub-stoichiometry. Results from these simulations are compared with TEM images and XPS profiles in figure 6.

Comparison of the TriDyn simulations and the XPS profiles shows that simulated profiles fail to reproduce the near-surface oxygen concentrations observed experimentally. This is particularly evident for the 6 keV; \(1 \times 10^{17}\) ions cm\(^{-2}\) implant where the simulation accurately reproduces the deeper implant profile but clearly underestimates the oxygen concentration in the thinner oxygen-rich surface layer. Interestingly this surface layer increases in thickness as the implant fluence increases as evidenced by an increase in the dielectric...
breakdown voltage. It is well known that radiation-enhanced diffusion and chemically-driven diffusion can enhance the transport of implanted ions to a growing compound or alloy layer to make it thicker but this would deplete oxygen at depths beyond the surface layer. The agreement between simulated and measured oxygen profiles for the 6 keV implant (figure 6(b)) suggests that this is not a significant effect in the present case. Attempts to model the excess surface oxygen by increasing the surface binding energies of Hf and/or O (i.e. reducing the sputtering yield) also failed to reproduce the experimental results suggesting that the excess surface oxygen comes from other sources. Possible sources include recoiled implantation of residual oxygen gas in the implant chamber or enhanced oxidation of the surface on exposure to atmosphere [40, 41].

3.4. Electrical properties

The electrical properties of the films were determined by measuring their electroforming and bipolar resistive switching characteristics. The forming process is a one-off operation that is used to create a filamentary conduction path through the insulating layer. It corresponds to soft dielectric breakdown and is a direct measure of the film quality, with more defective or substoichiometric films exhibiting higher leakage currents and lower forming (breakdown) voltages. To avoid permanent damage to the films, a 10 kΩ load resistor was placed in series with the test device and voltage scans were programmed to stop when the current reached a compliance limit of 10 μA. The polarity of the voltage ramp was consistent with that required for a ReRAM set operation; i.e. negative potential applied to the top (Pt) contact to induce oxygen vacancy migration from the deeper suboxide layer at the HfO2/Hf interface towards the Pt layer. Figure 7(a) shows typical forming characteristics of as-implanted samples, as well as for a 10 nm ALD HfO2 film in a structure of the form Pt/Hf/HfO2/Pt. Weibull distributions for the measured forming voltages are summarized in figure 7(b). A mean breakdown voltage of ~4.3 V is measured for the 3 keV; $1 \times 10^{17}$ ions cm$^{-2}$ sample, and 3.8 V for the ALD film. This corresponds
Once formed, devices can be switched from low to high resistance states (RESET) and from high to low resistance states (SET) by applying positive and negative biases, respectively. Figure 8(a) shows typical bipolar resistive switching characteristics of the as-implanted 3 keV; $1 \times 10^{17}$ O cm$^{-2}$ sample for voltage scans over the range from $-1.5$ to 1.5 V. The characteristics are typical of HfO$_2$ devices, with an abrupt SET at $\sim-0.7$ V and a gradual RESET beginning at $\sim+0.7$ V. The resistance distributions of the low (LRS) and high (HRS) resistance states are plotted for 100 consecutive cycles in figure 8(b) and show a resistance window of $\sim10$. The observed spread in $R_{HRS}$ is typical of HfO$_2$ RRAM devices and limits their reliability. Cycle-to-cycle stability and reproducibility of the devices was tested by subjecting the devices to electrical endurance tests in pulse mode using 100 ns pulses with $V_{set} = -1.5$ V, and $V_{reset} = +2.5$ V as shown in figure 8(c). These measurements demonstrate an endurance over $10^6$ RS cycles while maintaining a memory window of $\sim10$. The effect of Si-doping on resistive switching characteristics was also explored as part of this study and shown to improve the switching characteristics (see supplementary information).

4. Conclusions

In conclusion, we have demonstrated ion-beam synthesis of high-quality HfO$_2$/HfO$_x$ heterostructures at room temperature by implanting O$^+$ ions into Hf films. Heterostructures synthesized by implantation with 3 keV O ions to a fluence of $1 \times 10^{17}$ ions cm$^{-2}$ were comprised of a polycrystalline (monoclinic) HfO$_2$ surface layer of $\sim12$ nm thickness and an underlying graded substoichiometric layer of $\sim7$ nm thickness. Samples implanted with 6 keV O ions to a fluence of $1 \times 10^{17}$ ions cm$^{-2}$ were predicted to be substoichiometric but exhibited a thin ($\sim7$ nm) oxygen-rich surface layer that increased in thickness with increasing fluence. In both cases the oxygen content of the near-surface region exceeded that predicted by dynamic Monte Carlo simulations suggesting that this surface layer may result from an additional source of oxygen such as recoil-implanted residual oxygen gas in the implant chamber.

The bandgap and a dielectric strength of the films produced by the 3 keV; $1 \times 10^{17}$ ions cm$^{-2}$ implant was found to be indistinguishable from that of amorphous HfO$_2$ films deposited by ALD at 200 °C. The functionality of these films was demonstrated by measuring the resistive switching characteristics of simple metal–oxide–metal device devices that exploited the underlying Hf film as a bottom electrode and the graded HfO$_x$ interface layer as an oxygen-exchange layer. The switching characteristics, reliability and endurance of these devices were found to be similar to those reported for HfO$_2$ films deposited by ALD at 200 °C. A supplementary study further demonstrated that the resistive switching properties of these films could be improved by Si-doping, consistent with previous reports for ALD films.
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