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Characterization of hafnium oxide resistive memory layers deposited on copper by atomic layer deposition

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ABSTRACT

Hafnium oxide-based resistive memory devices have been fabricated on copper bottom electrodes. The HfO_x active layers in these devices were deposited by atomic layer deposition (ALD) at 250 °C with tetrakis(dimethylamido)hafnium(IV) as the metal precursor and an O_2 plasma as the reactant. Depth profiles of the HfO_x by X-ray photoelectron spectroscopy and secondary ion mass spectroscopy revealed a copper concentration on the order of five atomic percent throughout the HfO_x film. In addition to the Cu doped HfO_x, a thin layer (20 nm) of Cu_xO is present at the surface. This surface layer is believed to have formed during the ALD process, and greatly complicates the analysis of the switching mechanism. The resistive memory structures fabricated from the ALD HfO_x exhibited non-polar resistive switching, independent of the top metal electrode (Ni, Pt, Al, Au). Resistive switching current voltage (I–V) curves were analyzed using Schottky emission and ionic hopping models to gain insight into the physical mechanisms underpinning the device behavior. During the forming process it was determined that, at voltages in excess of 2.5 V, an ionic hopping model is in good agreement with the I–V data. The extracted ion hopping distance ~4 Å was within the range of interatomic spacing of HfO_2 during the forming process consistent with ionic motion of Cu^{2+} ions. Lastly the on state I–V data was dominated at larger voltages by Schottky emission with an estimated barrier height of ~0.5 eV and a refractive index of 2.59. The consequence of the Schottky emission analysis indicates the on state resistance to be a product of a $Pt/Cu_2O/Cu$ filament(s)/Cu_2O/Cu structure.

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1. Introduction

NAND Flash has been aggressively scaled in the past two decades, with current technology reduced to less than 20 nm gate lengths [1]. With each generation of devices, memory performance degradation has occurred. Under current technology the read/write endurance has dropped to just 3000 cycles before failure [2]. Continued lithographic scaling of such floating gate style memory will become unfeasible with the continued degradation of endurance and performance. In light of these challenges, a next generation of non-volatile memory is being developed. One promising candidate is based on the reversible resistive switching phenomena present in various transition metal oxides. The resistive switching effect was originally observed in anodic oxides of SiO, Ta_2O_5, Al_2O_3, ZrO_2, and TiO_2 in the 1960s by T. W. Hickmott [3]. It has since evolved into a massive research effort in both commercial and academic arenas; with intended commercialization by Hewlett Packard/Hynix [4], Samsung [5], and Panasonic [6]. Of the possible material combinations that have exhibited resistive switching, HfO_2 is one of the most researched. This is due to the vast knowledge base obtained during the introduction of high-k metal gates in high performance complementary metal–oxide–semiconductor devices. With HfO_2 already so widely used in device fabrication it was natural to explore its resistive switching properties. As such, HfO_2 has been previously studied as the active layer in resistive memory devices by multiple groups. These investigations have demonstrated devices with stable, long-term read/write endurance of 10^9 cycles [7,8], low switching energy [9], and high on/off ratios [10]. The use of Cu as an electrode in resistive memory has been investigated previously, again due to the prevalence of the material in current fabrication strategies. However few groups have explored the combination of HfO_2 and Cu for resistive memory devices. In one study, a Cu layer was inserted between the HfO_x, and was used to intentionally dope the HfO_x [10]. In other studies, Cu was used as a top electrode as a reservoir of metallic ions, which was thought to form conductive filaments during switching [10–18]. The latest work, published by Nagata and Haemori [14], demonstrated in situ hard X-ray photoelectron spectroscopy at various take off angles to observe the chemical and physical structure of the $Cu/HfO_2/Pt$ device under electrical bias.

For our work, we are particularly interested in the role of copper doping in HfO_2 films and reservoirs of Cu at the electrodes. In this effort, we investigated the material properties of HfO_2 deposited by atomic

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layer deposition directly onto Cu substrates. Physical and chemical analysis of the as-deposited film was performed, and the conduction behavior of the atomic layer deposition (ALD) HfO_2 on Cu films was analyzed, in an attempt to understand the physical mechanism of resistive switching in these devices.

2. Experimental procedure

A starting substrate of SiO_2/SiN was fabricated on 300 mm silicon wafers using standard chemical vapor deposition techniques. Atop the substrate, Cu/Ta/TaN were deposited by physical vapor deposition, acting as the electroplating seed, adhesion layer, and diffusion barrier, respectively. To create the bottom electrode, 1 μm of electrochemically deposited (ECD) Cu was deposited on the Cu seed layer. Chemical mechanical planarization (CMP) was then used to level and polish the ECD Cu. The deposition of HfO_x layer was carried out by ALD, with a chuck temperature of 250 °C and a chamber pressure of 25.33 Pa. Tetrakis (dimethylamido)hafnium(IV), known as TDMAH, was used as the metal–organic precursor and a 300 W RF O_2 remote plasma as the reactant. The target thickness of HfO_2 was 50 nm, which required 603 ALD cycles and 6.23 h of deposition time, at a deposition rate of 0.08 nm/cycle or 0.133 nm/min.

Following ALD, micron scale devices were fabricated by depositing metal by electron beam evaporation through a metal shadow mask. The top electrodes (Pt, Ni, Al, Au) were deposited with thicknesses of 75–100 nm and resulted in a top electrode geometry of 120 × 120 μm square.

Atomic force microscopy (AFM) was performed using a Veeco Dimension 3100 AFM (Billerica, MA, USA) in tapping mode. Silicon Tap300Al-G from Budget Sensors (Sofia, Bulgaria) were used to probe the surface of the sample with a force constant of 40 N/m and a tip radius <10 nm. Scans were performed on 1–10 μm^2 areas with 512 pixels per line to collect height information and analyzed using Digital Instruments NanoScope image analysis software version 6.14R1. First order image flattening was performed when analyzing scan offline.

X-ray diffraction (XRD) measurements were made with a Bruker D8 Diffractometer (Billerica, MA, USA) equipped with a sealed copper X-ray source (40 kV, 40 mA) and a graded parabolic mirror at the X-ray source. The diffractometer was operated in a parallel-beam geometry with Soller slits in both incident and diffracted beam paths. A fixed angle of incidence of 0.5° was used for all scans with a detector step size of 0.05°/step and a count time of 10 s/step, while scanning the detector from 10–90° for all scans.

X-ray photoelectron spectroscopy (XPS) surface characterization and sputter depth profiling of the as-deposited HfO_x structure were performed using a ThermoFisher Thetaprobe equipped with a hemispherical analyzer and a monochromated Al Kα X-ray source (1486.6 eV) operated at a 100 W/400 μm spot mode for area-averaged analyses. Sputter depth profiling was accomplished using an argon ion gun operated at 2.5 keV with a sample current of ~1.4 μA, yielding a sputter rate of 4 nm/min for SiO_2. In addition, a completed device structure was depth profiled with secondary ion mass spectroscopy (SIMS). Depth profiles were acquired using an IonTof V time-of-flight SIMS system. The sputtering beam was 2 keV Cs at 45° incidence and the pulsed analysis beam was 25 keV Bi+ at 45°. Negative secondary ions were collected from a 30 × 30 μm area. The primary beam pulse time yielded a mass resolution of 7000–8000, allowing full separation of interfering masses.

High resolution cross-sectional transmission electron microscopy (HR-XTEM) of completed devices was performed on a 200 kV Jeol 2010 TEM. Cross sectional lamella were formed and thinned in a FEI NanoSEM 600 SEM/FIB. Electron energy loss TEM images were taken using a Gatan imaging system.

Electrical contact was made on a Cascade M150 wafer probe station utilizing a two probe configuration. To contact the bottom Cu electrode, a small section of the sample was rubbed with an abrasive to remove the blanket HfO_2 layer and allow for probing of the underlying Cu. Switching characteristics and conduction analysis were investigated using sweep based current voltage (I–V) measurements on an Agilent B1500A semiconductor parameter analyzer.

3. Results and discussion

Post-deposition metrology was used to characterize the ALD HfO_2/Cu material system before top electrodes were fabricated. Atomic force microscopy (AFM) was used to characterize the surface morphology and roughness of the HfO_2 films. Fig. 1 shows 10 μm and 1 μm square tapping mode AFM scans of the surface of a 50 nm thick HfO_2 film. The surface appears rough with height differentials of 25 nm observed. An average root mean square roughness of ~4 nm was calculated utilizing the 10 × 10 μm scan. This is comparable to the surface roughness of blanket CMP Cu substrates (data not shown).

X-ray diffraction was utilized to obtain crystallographic information about the as-deposited HfO_2. X-ray diffraction analysis (Fig. 2) showed no observable HfO_2 peaks. Instead the XRD peaks primarily pertain to the underlying copper substrate. The presence of strong Cu_2O peaks is peculiar; a thin layer of benzenetriazole was used as a corrosion inhibiter post-Cu CMP. The absence of any crystalline peaks from HfO_2 indicates an amorphous structure or regions of nanocrystallinity. The observed Cu_2O peaks, however, raise significant questions about the as-deposited film composition and structure.

XPS was employed to investigate the composition of the film as a function of depth (Fig. 3). An unexpected Cu and O surface layer is present in the profile indicated by a rise in Cu and O, peaking at Cu:O of 1:1.54, which after surface sputtering, dropped to 1:0.65. These data corroborate the XRD findings shown in Fig. 2, in which only Cu_2O (and Cu) peaks are present in the 2θ scans. The surface Cu_xO layer was removed after 250 s of sputtering, with a rise in Hf concentration into the bulk of the oxide film. The measured ratio of O to Hf results in a substoichiometric oxide of HfO_{2-x} where $x \approx 0.9$. There was also a 5% atomic concentration of Cu contained within the bulk HfO_x film. Dissolved Cu present within the HfO_x has been reported previously by Yang et al. [10]. However, the work by the Majumder et al. [19] has shown that ALD HfO_2 can be used as a Cu diffusion barrier. Their work suggests that Cu has a limited solubility in HfO_2 and is thermally robust to a temperature of 600 °C for 5 min.

In this work, however, we have observed self-doping of HfO_{2-x} with a similar high doping concentration to that of Yang et al. [10], which occurs in our ALD process unintentionally. We hypothesize that the high platen heat during deposition (~250 °C) combined with the layer by layer cycle process of 6.23 h allowed the Cu to sufficiently diffuse through the half reaction layers during the course of the deposition. After removing the sample from the ALD chamber the surface Cu layer then oxidized in the ambient air atmosphere. We will explore the validity of this hypothesis later in the discussion.

Although the presence of Cu_2O on the topmost layer of the HfO_x film and the Cu doping was unexpected, we fabricated the top electrodes and subsequently investigated the structure of a completed Pt/HfO_x/Cu resistive memory device (RMD). For our investigation, we depth profiled using SIMS, since it afforded enhanced depth resolution, smaller analysis area, and greater trace elemental sensitivity compared to XPS. Fig. 4 shows the results from a SIMS depth profile analysis of a Pt/HfO_x/Cu device structure. This device was profiled "as-fabricated" and, therefore, was not influenced by any electrical bias before analysis. At the uppermost interface (Pt/HfO_x), the Cu signal peaks, along with O, indicate the presence of the Cu_xO layer, similar to the observation by XPS. The thickness of the Cu_xO was estimated at less than 20 nm (via profilometry of the etch crater post SIMS depth profile). The accuracy of the thickness measurement from SIMS is limited by the differential sputtering rates of the materials in the metal–insulator–metal (MIM) device structure. After the peak concentration of Cu at the

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