

X-ray Photoelectron Spectroscopy Study of the Physical Chemistry of the TiN/Hf_{0.5}Zr_{0.5}O₂ Interface

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Abstract

The physical chemistry of the interface between a TiN electrode and a ferroelectric Hf_{0.5}Zr_{0.5}O₂ thin film was studied using X-ray photoelectron spectroscopy (XPS). Oxidation of the electrode surface is due to contact with air while a 0.8 nm TiO_xN_y layer is formed at the interface with HZO. Hf reduction is caused by oxygen scavenging by the top electrode. The oxygen vacancy (V_O) concentration near the top interface is 1.25%. Increasing the crystallization annealing temperature decreases the Schottky barrier height for electrons. Finally, increasing the top electrode thickness results in higher V_O concentration.

1. Introduction

The discovery of the ferroelectricity in silicon-doped hafnium oxide offered the solution for the integration and scalability of ferroelectric-based devices allowing a CMOS compatible 3D deposition [1]. This has initiated strong research efforts on different doped hafnium oxide materials [2]. The single phase, solid solution of Hf_{1-x}Zr_xO₂ (HZO) appears to be the most promising material for device integration thanks to its low crystallization temperature, fully compatible with the back end of the line technology. The electrode/ferroelectric interface and the post—metallization crystallization temperature appear to play a key role in device performance. There have been several studies of the interface between the TiN electrode and HZO [3,4] but no clear and quantitative identification of the physical chemistry and accumulation of defective charges has been provided. X-ray photoelectron spectroscopy (XPS) is a powerful tool to investigate buried interface chemistry and has been used to characterize oxygen scavenging [5] and to evaluate the bands line-ups [6,7].

2. Experiment

The samples are planar, metal-ferroelectric-metal (MFM) capacitor structures deposited on p-type doped Si/SiO₂/TiN substrate. The bottom TiN electrode is 9 nm thick. 10 nm thick Hf_{0.5}Zr_{0.5}O₂ was grown by ALD at 300°C. 2 nm thick TiN top electrode was then deposited by sputtering at room temperature. The electrode continuity was checked by conducting tip atomic force microscopy and photoemission electron microscopy. After the top electrode deposition, the sample was annealed for 20s at 600°C in nitrogen atmosphere to

stabilize the orthorhombic phase. Two samples were crystallized at 800°C (20s) and 1000°C (1s) after the top electrode deposition. The XPS measurements were conducted using a monochromatic Al K α source (1486.7 eV) with an energy resolution of 0.3 eV. The take-off angle relative to the sample surface was varied in order to tune the probing depth between ~2 and 5 nm. Fitting of the core level spectra was performed using the Casa XPS software and backgrounds were of the Shirley type. The peaks were modeled using a convolution of Lorentzian (30%) and Gaussian (70%) functions. Ultraviolet photoelectron spectroscopy (UPS) was carried out using a He I source to measure the sample work function. For the electrode thickness study, the top electrode was thinned by Ar⁺ sputtering. Electrode lift-off was made by standard cleaning 1 (SC1) followed by a HF treatment.

3. Results

Interface chemistry

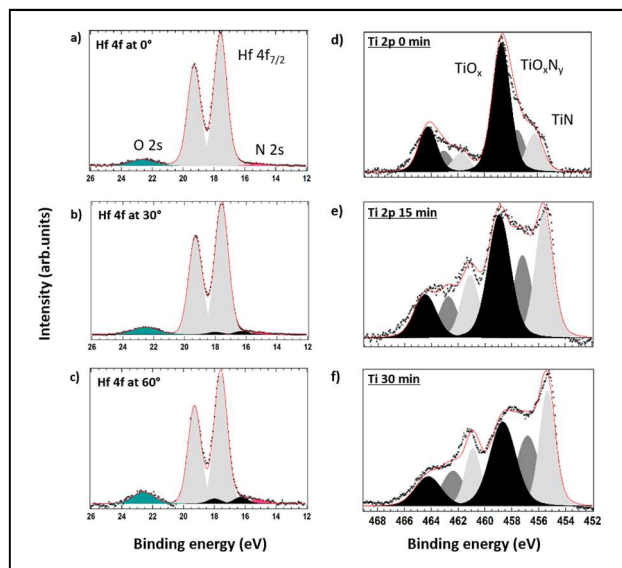


Fig. 1 (a) Hf 4f core level acquired with the 2 nm TiN top electrode sample at normal emission (b) at 30° (c) and at 60° emission angle. Ti 2p core level before (d) and after Ar⁺ sputtering at 0.5 kV primary energy for (e) 15min and (f) 30min, all at normal emission.

The Hf 4f core level spectrum from the sample annealed

at 600°C acquired at normal emission is shown in Fig. 1a. The spectrum is dominated by the spin-orbit split doublet corresponding to Hf^{4+} with $4f_{7/2}$ binding energy (BE) = 17.58 eV. The spectral component with the lower BE belongs to the N 2s core level line, while the component at higher BE is attributed to the O 2s emission. Changing the emission angle to 30° and 60° (Fig. 1b,c), thus increasing the interface sensitivity, an additional component is observed at BE = 16.23 eV. This signal confirms partial reduction to Hf^{3+} near the top interface. Oxygen vacancies (V_O) are the most likely source of electrons to reduce the interfacial Hf. We estimate the density of free electrons from the ratio of Hf^{3+} with respect to the total Hf intensity. Assuming that one V_O releases two electrons, the V_O concentration, x , in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_{2(1-x)}$ at the top interface was calculated as 1.25%.

The Ti 2p spectrum before sputtering (Fig. 1d) is fitted with three components. The first, located at the lowest binding energy (455.8 eV) is due to the metallic TiN. The additional components at 457.3 and 458.8 eV point to the formation of TiO_xN_y and TiO_x phases, respectively. The spectra acquired after the sputtering for 15 and 30 min are shown in Figs. 1b and c. First, the etching leads to a decrease of the intensity of the TiO_x peak relative to the TiN, confirming that the TiO_x phase is present at the electrode surface. The TiO_xN_y component, like the metallic TiN, increases in intensity relative to the TiO_x with sputtering. This suggests that the TiO_xN_y is at the interface with the HZO and that there is little or no TiO_xN_y at the surface of the electrode.

Interface band line-up

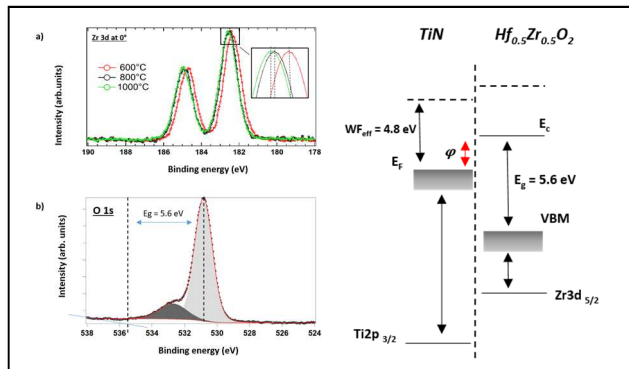


Fig. 2 (a) Zr 3d core level acquired at normal emission with the three annealing temperatures (b) O 1s spectrum acquired from the bare HZO at normal emission. Schematic diagram of the band offset at the TiN/ $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ top interface.

To investigate the effect of temperature on the electronic structure, we measured the band offset following the methodology of Kraut et al [8] at the TiN/HZO interface for three annealing temperatures. The energy positions of the core level emission lines of the interface materials (TiN and HZO) were established on reference samples: a 9 nm TiN layer as a reference for the position of the Ti 2p line and the HZO thin film after SC1 and HF lift-off for the Zr 3d line.

The valence band maximum (VBM) of HZO is determined

using UPS by linear extrapolation of the leading edge to the energy axis. The energy between a core level and the VBM is constant in the absence of chemical change. The shift in the Zr 3d core level can thus be used to determine the valence band offset (VBO) as a function of temperature. The band gap was obtained using the O 1s core level (~5.6 eV) leading to conduction band offsets (CBO) of 2.05, 1.87 and 1.83 eV for the samples annealed at 600, 800 and 1000°C, respectively.

Oxygen scavenging

The as-fabricated capacitor shows a hysteresis loop asymmetric toward negative bias. Electron trapping (positively charged V_O are more likely) leads to domain pinning (screening of the positive polarization charges). The asymmetry of these defective mobile charges causes the internal field. The V_O concentration near the top interface is the same (1.25%) for the three annealing temperatures but the conduction band offsets varied. We suggest that this may be due to V_O profiles across the whole film, not just at the top interface, modifying the internal field.

Finally, we have evaluated the effect of top electrode thickness on oxygen scavenging. The electrodes were thinned in order to observe a similar photoemission intensity as the 2 nm electrode. Increasing electrode thickness leads to an increase of the V_O concentration near the top interface from 1.25% (2 nm TiN) to 6.2% for the 9 nm electrode.

4. Conclusions

We have established reliable protocols for analysis of the physical chemistry of the TiN/HZO interface using XPS. A 0.8 nm TiO_xN_y layer forms and partial reduction of Hf occurs at the TiN/HZO interface. Oxygen scavenging is enhanced by increased top electrode thickness whereas post-metallization annealing modifies the conduction band offset.

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