Analysis of Oxygen and Nitrogen Redistribution at Interfaces of HfO2 with Laminate TiN/TiAl/TiN Electrodes

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Supporting information for publication

Procedure used to separate the Hf4f component from the N 2s contribution

Parameters (peak area, FWHM and energy position) of the N 2s component were estimated by using two independent methods. First, we analyzed our experimental N 2s spectra of the TiN layer without hafnium contribution reported previously in ref.1 Energy position and FWHM were estimated to be respectively 16.5±0.2 eV and 3.8±0.3 eV for 3 keV photon energy. Area of N 2s band was compared to the integral area of N1s band and a proportionality coefficient was found to be 0.055±0.003. This experimentally determined intensity ratio is in good agreement with theoretically estimated value of 0.054 found by the second method. According to formula for photoelectron peak intensity,2 we normalized integral area of N1s band to all energy and orbital dependent factors:

\[ I_{N2s} = \frac{\lambda_{N2s} \left( 1-e^{-\frac{d}{\lambda_{N2s, TiN} \cos(\theta)}} \right) \sigma_{N2s} T(KE_{N2s})}{\lambda_{N1s} \left( 1-e^{-\frac{d}{\lambda_{N1s, TiN} \cos(\theta)}} \right) \sigma_{N1s} T(KE_{N1s})} I_{N1s} \]  

(1)

where \( \lambda_{x, TiN} \) is the inelastic mean free path of an x photoelectron in TiN layer estimated by TPP-2M formula,3 d is the nominal thickness of TiN layer, \( \sigma \) is photoionization cross-section,4 T(KE_{orbital}) is the analyzer transmission function for KE_{orbital} kinetic energy. As a result, we obtained the energy position and FWHM of N 2s component in the decomposed Hf 4f spectra in...
the ranges 16.5±0.2 eV and 3.8±0.3 eV, respectively. The area of N 2s components was calculated from the integral intensity of N 1s band using the intensity ratio coefficient of 0.055±0.003.

**Capacitance-voltage measurements**

Capacitance-voltage (CV) measurements (published in ref.5) were done on p-Si/SiO$_2$(10 nm)/HfO$_2$(10 nm)/metal capacitors with the top metal electrode comprising of 2-nm thick TiN layer capped with different metal films. As illustrated in Figure S1, comparison between samples with TiN/TiAl/TiN – based stacks (D03, D05, D08) reveals a ≈1 V CV curve shift towards negative voltages as compared to TiN (D04) or TiN capped with W(D06) or Pt (D02). In sample D09 the deposited TiAl getter layer was removed by wet etching followed by deposition of the W capping layer (13 cycles ALD from WF$_6$ and H$_2$ precursors at 300 °C followed by PVD of 15 nm film). This processing is seen to “return” the CV curve to the position close to that for the pure TiN and TiN/W electrodes. As the final step, second 20 min. anneal at 420 °C in forming gas or in pure H$_2$ was performed.
Figure S1. 100 kHz CV curves measured on planar p-Si/SiO$_2$(10 nm)/HfO$_2$(10 nm)/metal capacitors with the top metal electrode comprising of 2-nm thick TiN layer capped with different metal films. Numbers indicate thickness of metal layers in nm.

References