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

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Abstract

Physicochemical nature of the change in the effective work function (EWF) of aluminum doped TiN (using TiN/TiAl/TiN laminate structure) was studied by X-ray photoelectron spectroscopy with high kinetic energies (HAXPES). Comparative analysis of Si/SiO₂/HfO₂/TiN-TiAl-TiN and Si/SiO₂/HfO₂/TiN stacks reveals identical composition of the HfO₂/TiN interfaces in both stacks. It was established that EWF decrease for TiN/TiAl/TiN laminate electrode with respect to the “normal” value for TiN is related to redistribution of light N and O atoms in the bulk of TiN/TiAl/TiN instead of frequently supposed Al diffusion and formation of HfAlO_x mixed oxide at HfO₂/TiN interface. Formation of nonstoichiometric TiN_x, metallic Ti and Al, and AlN in the bulk of TiN/TiAl/TiN was revealed by HAXPES.

Introduction

Re-distribution of lightatoms (O, N) is the key factor determiningelectricalproperties ofoxide-based insulators(O vacancies account for resistive switching¹⁻⁶), semiconductors (O vacancies⁷⁻¹⁰ and N vacancies¹¹⁻¹³ determine doping of semiconducting compounds),and conductors(p-type conductionof NiO¹⁴). As one of the factors determining re-distribution of lightatoms (O,N) one can discern chemical interaction of oxides with electrode materials such as TiN. In our previous study¹⁵we noticed that oxygen is re-distributed at interfaces of TiN with oxides leading to the effective work function (EWF) changes about of ≈ 200 meV in magnitude whichcan beusedfor transistor threshold voltage control. According to literature¹⁶⁻²⁰ doping of TiN with Al (using TiN/Al/TiN laminate structures with Al, AlN or TiAl) may further enhance modification of electricalproperties ofoxide-based insulators. In case of HfO₂/TiN-based systems, all of the works¹⁶⁻²⁰ ascribe the effect of EWF lowering to Al diffusion and formation of HfAlO_x mixed oxide at HfO₂/TiN interface. However, this explanation is unlikely to be true since the conduction bands of HfO₂ and HfAlO_x are nearly aligned in energy when is referenced to the same energy levels in Si substrate.²¹ Rather, one should consider modification of the TiN electrode itself, which has not been addressed. In our recently published work²² we preliminarily concerned a question of themechanism ofhuge (in the orderof 1 eV)change ofEWF of TiN/TiAl/TiN laminate electrode relative to reference ALD-TiN on top of oxide insulator (SiO₂ or HfO₂). Changing Nand Obalance inultrathin metallic TiN (2 nm) was revealed but effect of composition of HfO₂/TiN interface is still under question because of its potential distinction in case of reference ALD-TiN and TiN/TiAl/TiN laminate electrode. Research strategy of this study is in-depth nondestructive analysis of composition and chemical bonding by X-ray photoelectron spectroscopy with high kinetic energies (HAXPES) in Si/SiO₂/HfO₂/TiN and

Si/SiO₂/HfO₂/TiN-TiAl-TiN stacks with definitely identical structure of HfO₂/TiN interface. Identity of HfO₂/TiN interfaces is achieved by selective removal of top TiAl/TiN in TiN/TiAl/TiN laminate electrode and subsequent deposition of TiN with the same thickness.

Methods

First, 10 nm thick SiO₂ was grown by thermal oxidation of (100)-oriented 300 mm diam. Si wafers at 900° C. Then 2- or 10- nm thick HfO₂ layer was grown by ALD from HfCl₄ and H₂O precursors at 300° C in ASM Polygon© 300 mm tool, which will be used for HAXPES and electrical measurements, respectively. Next, 2 nm thick TiN layer was deposited by ALD from TiCl₄ and NH₃ at 450° C and annealed in forming gas (10%H₂+90%N₂) at 420 °C and then covered with ALD TiAl of 4 or 15 nm thickness. Finally, the 4 and 15 nm TiAl layer was covered by 2 nm thick TiN cap deposited by ALD or by 15-nm thick protective layer of sputtered W. To get further insight into the mechanism of EWF tuning (to separate effects of TiN/TiAl/TiN bulk composition and formation of HfO₂/TiN interface), in some samples the TiAl film and the top TiN cap were removed by selective etching leaving bottom TiN intact (as controlled by HAXPES) and subsequently capped by protective 6-nm thick TiN layer grown by MOCVD.

Electrical characterization of the samples was done after wet-etch patterning of metal electrodes using multifrequency capacitance-voltage (CV) and internal photoemission (IPE) methods aiming at evaluation of processing-induced TiN EWF changes and absolute EWF value, respectively. The IPE spectra were measured in the photon energy (hν) range from 2 to 6.5 eV as described elsewhere²³ with the quantum yield of IPE (Y) defined as the photocurrent normalized

to the incident photon flux. The metal/oxide interface barrier was obtained using linear extrapolation of the Fowler, i.e. $Y^{1/2}$ - $h\nu$, plots to zero yield value.

Chemical characterization of the fabricated stacks was done on un-patterned samples from the same wafers by X-ray photoelectron spectroscopy with high kinetic energies (HAXPES). HAXPES measurements were performed using the HIKE end-station installed at the KMC-1 Beamline at BESSY-II synchrotron light source (Helmholtz-Zentrum Berlin). This experimental setup is equipped with a high-resolution hemispherical electron analyzer optimized for high-energy electrons (VG Scienta R4000). The input of the analyzer is installed at 90° angle to the incident beam, i.e., the electron emission can be detected in the direction along the normal to the sample surface when grazing incidence of the photon beam is realized. The analyzer resolution was set to 0.25 eV while the KMC-1 double-crystal monochromator provided a 0.4 eV bandwidth at 3000 eV and 0.7 eV at 4000 eV. Further details about the experimental setup can be found elsewhere.^{24,25}

To prevent charge accumulation due to X-ray exposure, conducting surface of the samples was grounded by metal clamps connected to a metal sample holder. Photon energy was calibrated by measurement of Au4f_{7/2} line of clean gold (83.95 eV²⁶). The binding energy (BE) scale was referenced to the Fermi energy of TiN. All the photoelectron spectra were normalized to the incident photon flux, the illuminated sample area, and the transmission function of the electron energy analyzer. The fitting was realized using the CASA XPS software package.

Results and discussion

Figure 1. Experimental and decomposed Ti2p (a), N1s (b) and Al2s (c) HAXPES spectra collected from Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) (A) and Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) (B) stacks at the excitation energy of 3000 eV and 5° electron emission angle. Inelastic background is subtracted. The spectra are shifted along the ordinate axis for clarity.

Ti2p and N1s HAXPES spectra of Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) and Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) stacks measured at the same excitation photon energy of 3000 eV and electron emission angle of 5° are shown in Figure 1a,b. Formation and methodology of decomposition of Ti2p and N1s photoelectron spectra was reported in our previous study.¹⁵ Both stacks demonstrate features of titanium nitride (TiN_x) and oxidation species (TiO_x and TiN_xO_y). It should be noted that for Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) stack the ΔE energy splitting between Ti2p_{3/2} and N1s components of TiN_x equals 58.0±0.1 eV, that corresponds to nearly stoichiometric TiN_x with 0.9<x<1.²⁷ Decomposition of N1s spectra of both stacks reveals two peaks at the same binding energies 397.1 eV and 396.4 eV inherent in TiN and TiN_xO_y, respectively.^{15,28–31} Comparison of relative intensity of these peaks points out substantially more pronounced oxidation of TiN layer in Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) stack.

The Ti2p and N1s spectra of Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) stack evidently demonstrate additional peaks besides peaks corresponding to oxidized TiN: N1s peak at 397.6 eV (red color) and Ti2p_{3/2} peak at 453.9 eV (yellow color) can be assigned to formation of AlN phase^{32,33} and metallic Ti,^{34,35} respectively. Analysis of the Al2s spectrum of Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) stack (Figure 1c) performed in our previous study²² revealed four chemical states of Al atoms: Al-O,^{36,37} Al-N,^{38,39} metallic Al⁴⁰ and pristine TiAl.³⁴ It was supposed that TiAl acts as a getter for N- and O-atoms but corresponding Ti2p and N1s spectra should be analyzed here more carefully. It is worth noting that emergence of AlN and pure Ti peaks in N1s and Ti2p spectra shown in Figure 1a,b is accompanied by low binding energy shift of Ti2p of TiN peak by 0.35 eV for Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) stack, that points out a nonstoichiometric composition of TiN_x in this stack with

$0.75 < x < 0.85$.²⁷ All the mentioned regularities prove that TiAl acts as a getter for N- and O-atoms and as a result strong redistribution of nitrogen occurs in the bulk of TiN/TiAl/TiN electrode. Different stoichiometry of TiN_x in the studied stacks can be additionally confirmed by inspection of the top of the valence-band photoemission spectra presented in the inset in Figure 2. According to ref.²⁷ TiN has a metallic conductivity due to free Ti 3d states not involved in covalent bonding with nitrogen, the band near Fermi energy corresponds to these states. The intensity of these band near 1.5 eV is enhanced for Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) stack that is the signature of nonstoichiometric composition of TiN_x .²⁷

Looking at the Al2s and also Ti2p and N1s spectra of Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) stack one can affirm that the total TiAl layer including the Ti-, Al- and the AlN-phases is completely removed since the Al2s spectrum is totally suppressed and pure Ti and AlN signal can no longer be detected in Ti2p and N1s spectra respectively. It is worth emphasizing once again that according to our results MOCVD deposition of TiN after TiAl removal provides nearly stoichiometric TiN_x with $0.9 < x < 1$. Let us turn to analysis of HfO₂/TiN interface in both stacks by inspection of Hf4f spectra, which are shown in Figure 2.

Figure 2. Experimental and decomposed Hf4f HAXPES spectra collected from Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) (A) and Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) (B) stacks at the excitation energy of 3000 eV and the electron emission angle of 5°. Inelastic background is subtracted. The spectra are shifted along the ordinate axis for clarity. Top of the valence-band photoemission spectra of the same stacks are shown in the inset.

Analysis of the decomposed Hf4f spectra reveals the presence of a double peak structure (doublet 1) with spin-orbit splitting of 1.64 eV and the intensity ratio between components as 3 : 4 that agrees with well-known parameters of the Hf 4f peak in HfO₂.⁴¹ The energy position of the Hf4f_{7/2} peak 1 (17.4 eV) of Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) sample correlates well with that of HfO₂ being in contact with TiN deposited by ALD or PVD.^{42–44} As it can be seen O2s and N2s bands overlap the Hf4f spectrum. While O2s overlap is insignificant, the parameters of N2s band (its intensity, energy position and width) were thoroughly controlled based on the intensity of N1s spectra of the samples studied and on experimental N2s spectra of pure TiN (without HfO₂).

Further details can be found in the supporting information. Taking into account these constraints on the parameters of N2s band decomposition of the Hf4f spectra reveals the small doublet 2 at the lower binding energy relative to the doublet 1 for both studied stacks. The doublet 2 can be assigned to formation of reduced hafnium due to oxygen scavenging and oxidation of TiN from the underlying HfO₂.⁴² It is worth noting that intensity of the doublet 2 relative to the doublet 1 has nearly the same value for both Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) and Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) stacks: $I_2/I_1=0.14\pm0.01$. This fact points out that removal of TiAl and subsequent MOCVD of 6 nm TiN does not affect the HfO₂/TiN interface. Also it is important to consider energy position of the doublets 1 and 2 for Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) stack: apparently they parallel shifted by 1 eV to the higher binding energy relative to Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) stack. Taking into account exact match of relative intensity of the doublets 1 and 2 and energy separation between its respective components (1.5 eV value) for Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) and Si/SiO₂/HfO₂/TiN (2 nm)-TiN (6 nm) stacks it seems very unlikely that chemical modification of HfO₂ during TiAl removal occurs. On the contrary, the observed energy shift of 1 eV magnitude can be correlated with EWF difference of the same value for the stacks studied as revealed by electrical measurements discussed below. Indeed, since the binding energy *is measured* relative to the Fermi level of grounded metal electrode, in case of its EWF decrease (that is the case for Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) stack) one can expect increase of *the measured* Hf4f binding energy of HfO₂ due to simple shift of zero reference point⁴⁵ (provided that chemical state of Hf atoms do not change).

The variation of EWF of the TiN/TiAl/TiN metal stack as compared to the TiN can easily be observed in electrical measurements as shift of the flatband voltage VFB in CV measurements or

MOS transistor threshold voltage variation.^{17,46} According to the previous qualitative analysis of CV curve behavior. CV curves shown in Figure S1 in the Supporting Information indicate that introduction of TiAl layer on top of 2-nm thin TiN electrode deposited onto SiO₂/HfO₂ insulating stack leads to a ≈ 1 V VFB shift corresponding to the metal EWF lowering as compared to TiN capped by less chemically active metals (TiN, W, Pt). By overlaying the TiN/TiAl/TiN laminate with additional metal layers intermediate VFB values can be achieved. However, direct association of the observed VFB shift with metal EWF change faces well known difficulty due to possible formation of a dipole at the interface between SiO₂ and HfO₂ in the oxide stack. In this connection the analysis of CV curves is extended here to quantitative comparison with IPE zero-field TiN/HfO₂ barrier measurements. The same samples were analyzed by electron internal photoemission (IPE) which allows one to directly measure energy barrier Φ_e between the metal Fermi level and the bottom of the HfO₂ conduction band while being marginally sensitive to the dipole component.⁴⁷

Figure 3. Semilogarithmic spectral plot of the photocurrent quantum yield as measured in Si/SiO₂(10 nm)/HfO₂(10 nm) samples with different top metal electrode stacks comprising of a common 2-nm thick TiN layer with different metals evaporated on top of it (numbers indicate thickness in nm). Spectra are taken at the same bias of -5 Volt applied to the top metal electrode. Vertical arrow labeled $E_g(\text{HfO}_2)$ indicates the spectral onset of the oxide photoconductivity.

The electron IPE yield spectra shown in Figure 3 clearly indicate that deposition of the TiAl getter layer results in ≈ 1 eV shift of the IPE spectral threshold towards lower energy. At the same time, the onset of HfO₂ photoconductivity corresponding to the oxide bandgap remains the same, $E_g(\text{HfO}_2) = 5.6 \pm 0.1$ eV, as shown by vertical arrow in Figure 3. Since the spectral plots of electron IPE are sensitive to the strength of the applied electric field F in HfO₂ due to the image-force interface barrier lowering (the Schottky effect), the IPE measurements were repeated under different bias voltages applied to the capacitors. The spectral thresholds Φ_e were inferred using linear extrapolation of $Y^{1/2} - h\nu$ (Fowler) plots to zero yield (not shown) and then plotted in the $\Phi_e - F^{1/2}$ coordinates (the Schottky plot) as illustrated in Figure 4. In the ideal case, extrapolation to zero field will provide the intrinsic interface barrier value. However, different slopes of the Schottky plots suggest that for the same externally applied bias in the TiN/TiAl/TiN samples the Schottky effect is less pronounced than in the case of electron IPE from electrodes with higher EWF. This may be explained by more efficient filling of electron traps present in ALD-grown HfO₂ in the case of low-EWF TiN/TiAl/TiN laminates which partially “screen” the externally applied electric field. Indeed, the energy distribution of intrinsic electron trap levels in HfO₂ exhibits two peaks centered at ≈ 2 eV and ≈ 3 eV below the HfO₂ CB bottom edge.⁴⁸ As a result, electrons from low-EWF TiN/TiAl/TiN electrodes can fill by far more traps than those from

high-EWF TiN/metal stacks in which, as can be seen from Figure 4, the Fermi level is ≈ 1 eV deeper in energy. Nevertheless, despite possible trapping effect, the ≈ 1 eV shift of the TiN Fermi caused by TiAl overlayer becomes evident suggesting that the earlier mentioned VFB variations are predominantly caused by the metal EWF change.

Figure 4. Schottky plots of the field-dependent IPE spectral thresholds corresponding to electron excitation in TiN and emission into the CB of HfO₂. Results are shown for samples with different metal stacks labeled in the same way as in Figures 3 and S1. Lines illustrate linear extrapolations to zero average electric field in HfO₂.

Indeed, if comparing changes in VFB and the zero-field electron barrier inferred from the CV and IPE results, respectively, on several samples as illustrated in Figure 5, we came to conclusion that close correspondence exists between the EWF change and the CV curve shift. Another important observation concerns ≈ 2 eV high electron barrier between TiN/TiAl and HfO₂ which is approximately 0.5 eV lower than the barrier at Al/HfO₂ interface.²³ This allows us to

exclude the above mentioned hypothesis ascribing EWF lowering to Al in-diffusion. Rather, this barrier value suggests presence of elemental Ti due to nitrogen scavenging by the deposited TiAl getter layer. This hypothesis would also be consistent with the equivalent oxide thickness reduction observed in scaled $\text{SiO}_2(0.6\text{nm})/\text{HfO}_2(1.8\text{ nm})$ transistor gate stacks when applying the TiAl getter layer to reduce TiN EWF, see Figure 2 in ref.⁴⁶. Scavenging of light atoms (N, O) probably eliminates the partially oxidized TiN interlayer leading to a higher specific capacitance of the oxide stack. Finally, it is worth of mentioning here that wet selective etching of TiAl followed by TiN or W deposition restores the initial TiN barrier height as well as returns the CV curves to the position typical for samples without TiAl in the metal stack. This can be explained by oxidation of Ti in aqueous solution since elemental analysis indicates loss of nitrogen but increase of oxygen content in TiN after etching.

Figure 5. Values of flatband voltage V_{FB} and zero-field electron barrier Φ_e at the TiN/HfO₂ interface as measured on capacitors with different metal stacks labeled in the same way as in Figs. 3 and S1. Lines guide an eye.

Conclusions

Physicochemical nature of the change in EWF of aluminum doped TiN (using TiN/TiAl/TiN laminate structure) was studied using Si/SiO₂/HfO₂/TiN-TiAl-TiN stack and the same one with TiAl and top TiN selectively removed and then subsequently capped by protective 6-nm thick TiN layer. The same composition of the HfO₂/TiN interfaces was revealed by HAXPES for the both stacks while C-V and IPE measurements show the difference in EWF of 1 eV value. EWF decrease for Si/SiO₂/HfO₂/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm) stack with respect to its “normal” value is related to the redistribution of light N and O atoms in the bulk of TiN/TiAl/TiN laminate electrode instead of frequently supposed Al diffusion and formation of a HfAlO_x mixed oxide at the HfO₂/TiN interface. Formation of nonstoichiometric TiN_x, metallic Ti and Al, and AlN in the bulk of TiN/TiAl/TiN is revealed by HAXPES.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Procedure used to separate the Hf4f component from the N2s contribution; capacitance-voltage measurements (PDF)

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Notes

The authors declare no competing financial interests.

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