Mechanisms of TiN effective workfunction tuning at interfaces with HfO₂ and SiO₂

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Abstract

Using combination of electrical measurements and internal photoemission interface barrier characterization the effective workfunction (EWF) changes of nm-thin TiN layer deposited on top of oxide insulators (SiO₂, HfO₂) have been correlated with atomic and chemical composition of the metal/oxide interfaces characterized by photoelectron spectroscopy and X-ray absorption. The major mechanisms of the EWF tuning are shown to be correlated to re-distribution of light N and O atoms. Oxygen scavenging from the underlying changes the TiN EWF by forming Ti oxynitride layer at the interface and introducing charge traps in the near-interface oxide layer. By contrast, significant (≈ 1 eV) reduction of EWF can be achieved by introduction of a thin TiAl getter layer on top of TiN film. The mechanism of this reduction can be traced down to formation of metallic Ti caused by nitrogen scavenging by TiAl as evidenced by AlN formation.

Introduction

Adjustment of transistor threshold voltage V_{th} represents the mainstream approach to reduce power consumption in metal-insulator-semiconductor (MIS) integrated circuits which becomes critically important for a wide spectrum of applications ranging from the cryogenic quantum computer periphery circuitry to wearable electronics. A change in V_{th} is most straightforward realized by a change of the built-in potential related to the effective workfunction (EWF) difference between the semiconductor channel and the top gate electrode of a MIS device. To attain low V_{th} for both n- and p-channel transistors, electrodes with EWF difference of about channel semiconductor bandgap width are required. In the case of Si MIS devices this problem has been solved for decades by using heavily doped polycrystalline Si gate technology. However, transistor size downscaling mandates use of metal-gated devices in which V_{th} tuning can be done by using metals with different EWFs. Technological use of dissimilar metals is not attractive because of additional processing complexity and electromigration issues. It would be far more feasible to use chemically similar gate materials with artificially tuned EWF.

If attempting to tune the EWF, one should consider two factors affecting its value [N. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970)], i. e., the inner chemical potential and the surface (interface) component related to the polarity of chemical bonds at the metal interface and spill of electron density out of metal surface and is also expected to be sensitive to the crystallographic orientation of the metal surface. The latter factor may cause lateral electrostatic potential fluctuations in polycrystalline films used in practical devices [H. F. Dagdour, K. Endo, V. K. De, and K. Banerjee, IEEE Trans. Electron Dev. 57, 2504 (2010)] causing additional carrier scattering in semiconductor channel. Therefore, instead of increasing impact of the interface barrier component, e.g., by introducing an interface dipole, it appears to be worth of exploring possibility of chemical potential tuning which would require change of the metal composition. Though using alloys looks to be the “obvious” choice, limited thermodynamic stability of these electrodes at the interface becomes an issue because different alloy components often have different reactivity. Nevertheless, some conducting compounds from oxide (RuOx) and nitride (TiN, TaN, HfN) families [H. F. W. Dekkers, L. A. Raghuram, T. Schram, N. Horiguchi, J. Appl. Phys. 124, 165307 (2018)] provide good combination of low electrical resistivity and good thermodynamic stability in contacts with oxide insulators. From these metals TiN deserves particular attention since experimental observations indicate that its EWF is highly sensitive to the processing processes [Lima, L. P. B. *et al.* Influence of Al/TiN/SiO₂ structure on MOS capacitor, Schottky diode, and fin field effect transistors devices. *J. Vac. Sci. Technol. B* 31,

0502202 (2013)]. For example, if changing the method of TiN electrode physical vapor deposition (PVD) onto SiO₂ the position of Fermi level can be changed by nearly 1 eV while the impact of crystallographic texture of the film appears to be marginal (see Fig. 7 in [V. V. Afanas'ev, N. Kolomiiets, M. Houssa, A. Stesmans, Phys. Stat. Sol. A 215, 1700865 (2018)]). Though sensitivity of the electrode EWF to the synthesis details is routinely seen as the source of process instability, in the context of EWF tuning it should be considered as an opportunity. Indeed, details of the TiN electrode processing such as SiH₄ soak or vacuum break appear to be useful for the V_{th} adjustment in the nm-scaled Si MIS transistors with HfO₂ gate insulator [L.A. Ragnarsson et al., In: 2014 IEEE VLSI Symp. Tech. Dig., p. 56; L. A. Ragnarsson et al., In: 2016 IEEE VLSI Symp. Tech. Dig.].

While the EWF of atomic layer deposition (ALD)-grown stoichiometric TiN ranges from 4.7 to 4.9 eV, relevant for low V_{th} in p-channel MIS transistor, doping of TiN with low WF metal, e. g., Al results in lower EWF values in the range 4.1 - 4.4 eV [X.-R. Wang, Y.-L. Jiang, Q. Xie, et.al., *Microelectron. Eng.* **88** (2011) 573; A. Veloso, S. A. Chew, Y. Higuchi, et. al. *Jpn. J. Appl. Phys., Part 1*, **52** (2013) 04CA02; L. P. B. Lima, H. F. W. Dekkers, J. G. Lisoni et. al., *J. Appl. Phys.* **115** (2014) 074504; Wang, X.-R. et al. Annealing effect on the metal gate effective work function modulation for the Al/TiN/SiO₂/p-Si structure. *Microelectron. Eng.* **88**, 573 (2011); Hinkle, C. L. et al. Gate-last TiN/HfO₂ band edge effective work functions using low temperature anneals and selective cladding to control interface composition. *Appl. Phys. Lett.* **100**, 153501 (2012); Veloso, A. et al. Effective Work Function Engineering for Aggressively Scaled Planar and Multi-Gate Fin Field-Effect Transistor-Based Devices with High- κ Last Replacement Metal Gate Technology. *Jpn. J. Appl. Phys.* **52**, 04CA02 (2013)]. Another option is provided by exposure of TiN to nitrogen plasma which points towards significant impact of the metal stoichiometry [J. X. Yao, H. X. Yin, Z. H. Wu, J. F. Gao, Q. Z. Zhang, Z. Z. Hou, J. Gu, K. Luo, *ESC J. Solid State Sci. Technol.* **7**, Q152-Q158 (2018); J. X. Yao, Z. H. Wu, H. X. Yin, *ESC J. Solid State Sci. Technol.* **8**, N107-N112 (2019)]. However, there is an additional factor affecting stoichiometry of TiN at interfaces with oxide insulators: the oxygen “scavenging” from the underlying oxide leads to oxidation of the PVD-grown TiN films on SiO₂ and Al₂O₃ [Filatova, E. O., Sakhonenkov, S. S., Konashuk, A. S., Afanas'ev, V. V. Control of TiN Oxidation upon Atomic Layer Deposition of Oxides. *Phys. Chem. Chem. Phys.* **2018**, *20*, 27975–27982; **Inhibition**].

In this work we explore the mechanisms which make possible change of EWF of metallic TiN electrodes at interfaces with SiO₂ and HfO₂ insulators by varying TiN deposition technique or by introducing additional interlayers. A ≈ 0.3 eV EWF increase is observed if TiN is allowed to “scavenge” oxygen from the underlying oxide insulator. However, introduction of additional

metal getter layer (TiAl) on top of few-nm thin TiN film results in the opposite effect leading to EWF lowering by 0.7-0.8 eV due to consumption of nitrogen from TiN. These observations indicate re-distribution of light anion atoms (N, O) as the common denominator of the EWF changes. From the practical point of view, in both cases the EWF tuning is achieved for annealing temperatures of ≈ 400 °C which makes it compatible with the replacement metal gate and the “back-end-of-the-line” processing.

Experimental methods

In this work we attempted to correlate the observed EWF variations of ≈ 2 nm thin TiN electrodes at interfaces with insulating oxides with changes in their structure and chemical composition on the samples taken from the same wafers. The correlation was traced along three already mentioned lines: 1. Technique of TiN deposition, i.e., PVD vs. ALD; 2) Thermodynamic stability of the underlying oxide layer, i.e., SiO₂ vs. HfO₂; 3) Impact of the capping layer, i.e., the “getter” TiAl layer as compared to less reactive W and Pt overlayers.

First, 10 nm thick SiO₂ was grown by thermal oxidation of (100)-oriented 300 mm diam. Si wafers at 900°C. Then, on some of the oxidized wafers, 2 or 10 nm thick HfO₂ layers were grown by ALD from HfCl₄ and H₂O precursors at 300° C in ASM Polygon© 300 mm tool. Two types of TiN electrodes were deposited either by ALD from TiCl₄ and NH₃ at 450° C or, else, by PVD using stoichiometric TiN target. In the latter case the samples were cleaned prior to the metal deposition by lamp heating at ≈ 370 °C for 15 min to eliminate water and other adsorbates and then cooled down to room temperature in vacuum to grow TiN by PVD on unheated substrate.

To trace the influence of the TiN synthesis route, the electrodes of 8 or 10 nm in thickness were fabricated by ALD or PVD on top of Si/SiO₂ and Si/SiO₂/HfO₂ substrates. The effect TiAl getter layer was studied on 2-nm thick TiN films annealed in forming gas (10% H₂+90% N₂) at 420 °C and covered with PVD TiAl of 4 or 15 nm thickness. To get further insight into the mechanism of EWF tuning, in some samples the TiAl film was removed leaving TiN exposed. To avoid interactions with ambient, the TiN and TiN/TiAl electrodes were capped by PVD-grown 15-nm thick TiN, W, or Pt capping layers which are less chemically active than the TiAl getter. Alternatively, ALD-grown 4-nm thick W capping film (WF₆ and H₂ precursors, 300 °C) was used to reduce the total metal stack thickness. As the final step, second 20 min. anneal at 420 °C in forming gas or in pure H₂ was performed.

Electrical characterization of the MIS samples was done after wet-etch patterning of metal electrodes using capacitance-voltage (CV) and internal photoemission (IPE) methods aiming at evaluation of processing-induced TiN EWF changes and absolute EWF value,

respectively. Though the CV methodology is widely used to characterize the EWF changes, its application of SiO₂/HfO₂ and other insulating stacks can be misleading because of well known dipole layers formation at the interfaces of dissimilar insulators [K.Kita, A. Toriumi, Appl. Phys. Lett. 94, 132902 (2009); S. Guha et al., Appl. Phys. Lett. 90, 092902 (2007); P. D. Kirsch et al., Appl. Phys. Lett. 92, 092901 52008); H. Arimura et al., Appl. Phys. Lett. 96, 132902 52010)]. By contrast, the IPE method is free from this ambiguity since it allows one to directly measure the electron energy barrier between the TiN Fermi level and the bottom of the oxide conduction band (CB) [V. V. Afanas'ev, A. Stesmans, L. Pantisano, T. Schram, Appl. Phys. Lett. 86, 232902 (2005); V. V. Afanas'ev, A. Stesmans, L. Pantisano, S. Cimino, C. Adelmann, L. Goux, Y. Y. Chen, J. A. Kittl, D. Wouters, M. Jurczak, Appl. Phys. Lett. 98, 132901 (2011)]. The IPE spectra were measured in the photon energy (hν) range from 2 to 6.5 eV as described elsewhere [V. V. Afanas'ev and A. Stesmans, J. Appl. Phys. 102, 081301 (2007)] with the quantum yield of IPE (Y) was defined as the photocurrent normalized to the incident photon flux. From the experimental Y-hν spectral curves the height of the interface barrier was obtained using linear extrapolation of the Fowler, i.e., Y^{1/2}-hν plots to zero yield value.

Structural and chemical characterization of the fabricated MIS stacks was done on unpatterned samples from the same wafers by combining X-ray photoelectron spectroscopy (XPS), X-ray photoelectron spectroscopy with high kinetic energies (HAXPES), near-edge X-ray absorption fine structure spectroscopy (NEXAFS) and grazing incidence X-ray diffraction (GI-XRD). GI-XRD was realized with Bruker "D8 DISCOVER" system. For the GI-XRD analyses, all scans were performed in the range 2θ = 25–50° using the fixed grazing incidence angle of 0.4° with monochromatized Cu K_α radiation. The 2θ scanning was performed in the plane of incidence.

NEXAFS and HAXPES measurements were performed at the BESSY II synchrotron light source at the Helmholtz-Zentrum Berlin. The HAXPES experiments were performed using the HIKE station at the KMC-1 Beamline. 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 is detected in the direction along the normal to the sample surface and grazing incidence of the photon beam. 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 in elsewhere [Gorgoi, M.; Svensson, S.; Schäfers, F.; Öhrwall, G.; Mertin, M.; Bressler, P.; Karis, O.; Siegbahn, H.; Sandell, A.; Rensmo, H.; et al. The High Kinetic Energy Photoelectron Spectroscopy Facility at BESSY Progress and First Results. Nucl. Instrum. Methods Phys. Res., Sect. A 2009, 601, 48–53; Schaefer, F.;

Mertin, M.; Gorgoi, M. KMC-1: A HighResolution and High Flux Soft X-Ray Beamline at BESSY. *Rev. Sci.Instrum.* 2007, 78, 123102].

The NEXAFS measurements were carried out at the Reflectometer station at Optics Beamline [Schäfers, F.; Sokolov, A. The At-Wavelength Metrology Facility at BESSY-II. *J. Large-Scale Res. Facil.* 2016, 2, A50]. The spectra were obtained by monitoring the total electron yield found by measuring the total photoemission current from the sample at an incident angle of 45° using s-polarized synchrotron radiation. The GaAs diodes were used as X-ray detectors with a Keithley 6400 electrometer as a current meter. The absolute energy calibration was attained by measuring of the reference absorption edges of titanium and iron radiation filters in the first and higher orders of diffraction. The estimated energy resolution was better than $E/\Delta E = 3000$ with the absolute accuracy of the energy scale of about 0.1 eV.

The XPS measurements were conducted at the NanoXPS station at the Kurchatov synchrotron light source of the Kurchatov Institute. The station is equipped with PHOIBOS HSA3500 150-mm hemispherical photoelectron energy analyzer at 45 degree of angle to the incident synchrotron radiation beam. The monochromator of the beamline ensures the working photons energy range from 25 to 1500 eV with energy resolution better than 0.4 eV. Further details about the experimental setup can also be found elsewhere [<http://kcsni.nrcki.ru/pages/main/sync/beamlines/nanopes/index.shtml>].

To prevent charge accumulation due to X-ray exposure, the samples were mounted on sampleholders by metal clamps. Photon energy was calibrated by measurement of $\text{Au}4f_{7/2}$ line of clean gold (83.95 eV [M. G. Helander, M. T. Greiner, Z. B. Wang and Z. H. Lu, Note: Binding energy scale calibration of electron spectrometers for photoelectron spectroscopy using a single sample, *Rev. Sci. Instrum.*, 2011, 82, 096107]). The binding energy (BE) scale was referenced to the $\text{W}4f_{7/2}$ BE of metallic W^0 with reference value 31.34 ± 0.06 eV [Powell, C. J. (2012). Recommended Auger parameters for 42 elemental solids. *Journal of Electron Spectroscopy and Related Phenomena*, 185(1-2), 1-3]. All the photoelectron spectra were normalized to the incident photon flux, the illuminated sample area, and transmission function of the electron energy analyzer. The fitting was realized using a CASA XPS software package.

Results and discussion

EFW variations from CV and IPE measurements

As the first step, we isolated the TiN processing factors which have impact on the EFW of TiN electrode which will later be analyzed by atomic-sensitive methods to reveal the nature of the changes in the TiN/insulator electronic structure. First, it has been noticed that PVD

deposition of TiN on SiO₂ reproducibly leads to ≈ 0.3 eV higher energy barrier for electrons, close to 4.1-4.2 eV, than the ALD deposition method. The EWF of PVD TiN on SiO₂ is in this case close to 5 eV which is similar to the previously reported values [V. V. Afanas'ev, A. Stesmans, L. Pantisano, T. Schram, Appl. Phys. Lett. 86, 232902 (2005)]. This is to be compared to ≈ 4.7 eV EWF typically found for ALD TiN in good agreement with the values for ALD TiN found in the literature. Among the possible causes of this difference are different composition of the TiN films, different crystallographic texture or, else, sputtering-induced damage of the oxide surface layer. We shall address the compositional and structural differences between PVD and ALD grown TiN films later in this work.

Furthermore, if comparing TiN layers deposited on top of SiO₂/HfO₂ stack, the onset of electron IPE shows unexpected shift when HfO₂ thickness decreases from 10 nm (nearly “bulk” HfO₂) to ≈ 2 nm film (44 H₂O/HfCl₄ cycles): As one can see from the spectral plots of electron IPE yield shown in Fig. 1, the spectral onset of IPE from the ALD-grown TiN into “thick” HfO₂ layer is shifted towards lower photon energy by ≈ 1 eV as compared to SiO₂ which approximately corresponds to the energy difference in the CB bottom edge position between these oxides [V. V. Afanas'ev and A. Stesmans, J. Appl. Phys. 102, 081301 (2007)]. Surprisingly, reduction of HfO₂ thickness to ≈ 2 nm results in ≈ 0.5 eV shift of the spectra in opposite direction indicating electron IPE to occur into the CB of SiO₂ while transitions into CB of HfO₂ become unobservable. The latter effect suggests that the thin HfO₂ layer is significantly modified upon TiN deposition. Indeed, the onset of intrinsic photoconductivity of HfO₂ at $E_g(\text{HfO}_2) \approx 5.5$ eV clearly seen for the 10-nm thick HfO₂ film (cf. vertical arrow in Fig. 1) is not visible in the spectral plot of the 2 nm layer. In the presence of 2-nm HfO₂ on top of SiO₂ insulator the EWFs of the TiN electrodes, both ALD- and PVD-grown, becomes larger than 5 eV suggesting formation of additional dipole at the interface due to trapping of electrons in the oxide interlayer. These observations prompted us to analyze the compositional and structural changes at the HfO₂/TiN interface which will be addressed in the next section.

Figure 1. Semi-logarithmic plot of spectral dependence of quantum yield of electron IPE from ALD-TiN metal electrode into 10-nm thick SiO₂ layer (■), insulator stack consisting of 10 nm SiO₂ and 10 nm HfO₂ (▲) or 10-nm thick SiO₂ with ~2-nm thick (44 ALD cycles) HfO₂ layer on top (●). The average strength of electric field in the insulators is 1.7-2.0 MV/cm with the gate electrode biased negatively. The vertical arrow indicates the onset of intrinsic PhotoConductivity(PC) in HfO₂, $E_g = 5.6$ eV; Horizontal arrow shows direction of the spectral threshold shift at SiO₂/TiN interface caused by introduction of 2-nm thin HfO₂ interlayer.

Finally, when examining the samples with PVD-grown TiAl getter layer on top of 2-nm thin ALD TiN electrodes several remarkable effects were encountered. First, while the presence of TiAl is found to reduce the EWF values of 2-nm TiN on HfO₂ by ≈ 1 eV as compared to the same TiN electrodes protected by a 15-nm thick W, Pt, or TiN capping layer as illustrated by CV curves shown in Fig. 2 for Si/SiO₂(10 nm)/HfO₂(10 nm)/TiN(2 nm) capacitors with different metal capping layers on top of TiN. Second, removal of TiAl by wet etching followed by W deposition (samples D07, D09) returns the CV curves to the position close to that in the control TiN/W or TiN/Pt stacks. This reversibility of the TiAl effect suggests that the EWF lowering is caused by compositional changes in the TiN electrode rather by a dipole associated with the oxide layer.

Figure 2. 100 kHz capacitance-voltage traces taken on p-Si/SiO₂(10 nm)/HfO₂(10 nm)/ALD-TiN(2 nm) capacitors with different metal capping layers on top of 2-nm thin ALD-TiN. Numbers give thicknesses of the capping metal stacks in nm or in ALD cycles (for 13 c ALD W). In samples D07, D09TiAlgetter layer was removed by wet etching followed by deposition of W capping layer (13 cycles ALD + 15 nm PVD).

More insight into the mechanism of the EWF lowering is provided by IPE experiments on HfO₂/TiN(2 nm)/TiAl(15 nm) and HfO₂/TiN(2 nm)/W(15 nm) interfaces. As can be seen from the Fowler plots shown in Fig. 3 which illustrate determination of energy barrier between the metal Fermi level and the oxide CB bottom edge, deposition of the TiAl film results in a ≈ 1 eV interface barrier lowering. The resulting barrier height of $\Phi_e = 2$ eV is ≈ 0.5 eV lower than the barrier height at the HfO₂/Al interface [V. V. Afanas'ev and A. Stesmans, *J. Appl. Phys.* 102, 081301 (2007)]. This result indicates that frequently invoked hypothesis associating the TiN EWF lowering with Al doping effect is not reflecting the experimentally observed EWF value. Rather, the presence of elemental Ti due to nitrogen scavenging from TiN by the getter layer might explain this behavior. This possibility will further be explored using electron spectroscopy methods.

Figure 3. Fowler plots of electron IPE quantum yield illustrating determination of the spectral thresholds by linear extrapolation to zero yield value (lines). Results are shown for the Si MIS capacitors with SiO₂(10 nm)/HfO₂(10 nm) insulating stack and top ALD-TiN(2 nm) electrode with 15 nm thick W (open symbols) and TiAl (filled symbols) PVD-grown overlayers. The measurements are conducted when applying the indicated bias to the top metal electrode.

XRD studies

GI-XRD angular scan results obtained on TiN/HfO₂/SiO₂/Si stacks prepared by deposition of TiN using two methods are shown in Fig. 4. As follows from these results, the PVD-TiN film shows a preferential growth in the (200) orientation while the ALD (450° C)-TiN contains crystallites of two different orientations. Similar behavior was also reported earlier [Husain 2006]. Joint analysis of the angular position and shape of the (200) diffraction peak indicates the similar grain size in both types of the deposited TiN films. At the same time the absence of the (111) diffraction peak in the spectrum of the PVD-TiN suggests better ordering with (200) preferential orientation in the PVD-film.

Figure 4. Measured (grey lines) and smoothed (red and blue lines) GI-XRD curves from TiN films deposited by ALD (1) and PVD (2) methods in TiN/HfO₂/SiO₂/Si stacks. Reference positions of (111) and (200) TiN diffraction peaks are shown by dashed lines.

HAXPES study

Traditionally the sample probing depth in any photoemission experiment is associated with the inelastic mean free path (IMFP, λ_i), which is defined as the average distance that an electron with a given kinetic energy travels between successive inelastic collisions. In HAXPES a large value of λ_i provides in-depth analysis of layered system, which was realized in the current studies. All the measurements were carried out at excitation energy of 3000 eV or 4000 eV. The choice of such excitation energy provides analysis of the complex multi-layered structure as a whole with a total thickness of not less than 15 nm. For example, inelastic mean free path λ_i (IMFP) calculated by means of TPP-2M formula [S. Tanuma, C. J. Powell and D. R. Penn, Calculation of electron inelastic mean free paths (IMFPs) VII. Reliability of the TPP-2M IMFP predictive equation, *Surf. Interface Anal.*, 2003, **35**, 268–275] for HfO₂ and TiN amounts to 3.5 nm and 4.1 nm for Hf 4f and N 1s photoelectrons excited by photons of energy 3000 eV, respectively. The maximum probing depth can be defined as $(3\lambda_i \cos\theta)$, which corresponds to $\approx$ 95% of the total signal intensity to be formed within the layer of this thickness. The analysis of Si 2s line measured at different angles using excitation energy of 3000 eV reveals a distinct signal from the Si substrate at the emission angle 5°. Therefore, the selected excitation energy allowed us to study the whole sample depth.

ALD-TiN/HfO₂/SiO₂/Si structure

Since introduction of HfO_2 as a high-k dielectric, TiN has been used as a gate metal electrode due to its thermodynamic stability with HfO_2 . However, physical and electrical properties of TiN films are highly sensitive to film composition; furthermore, variation of TiN properties have been reported for different deposition processes [Lima, L. P. B. *et al.* Influence of Al/TiN/ SiO_2 structure on MOS capacitor, Schottky diode, and fin field effect transistors devices. *J. Vac. Sci. Technol. B* **31**, 0502202 (2013)]. This "flexibility" of TiN makes it the perfect candidate for EWF tuning aiming at multi- V_{th} application. Let us first clarify the impact of the HfO_2 layer introduced between TiN and SiO_2 layers to the formation of the metal/oxide interface (its composition and extension) affecting the effective work function of metal electrode. To understand this impact, we will analyze ALD-TiN/ SiO_2 /Si stack with/without thin HfO_2 layer inserted at the metal/oxide interface.

Figure 5. Experimental Ti2p (a) and N1s (b) XPS spectra collected from ALD-TiN/ SiO_2 /Si (red color) and ALD-TiN/ HfO_2 / SiO_2 /Si (black color) stacks at the excitation energy of 3000 eV and the electron emission angle of 5°.

Figure 6. Experimental and decomposed Si2s XPS spectra collected from ALD-TiN/HfO₂/SiO₂/Si (a) and ALD-TiN/SiO₂/Si (b) stacks at the excitation energy of 3000 eV and the electron emission angle of 5° with linear background subtracted.

Figure 5 compares the Ti2p and N1s photoelectron spectra of ALD-TiN/SiO₂/Si and ALD-TiN/HfO₂/SiO₂/Si stacks measured at the same excitation photon energy of 3000 eV and electron emission angle of 5°. Formation of Ti2p and N1s photoelectron spectra was reported in our previous study [sci. rep.]. Analysis of Ti2p spectra did not reveal major differences; nevertheless, N1s spectra (Fig. 5b) indicate loss of nitrogen in the case of TiN deposited onto HfO₂ which might suggest stronger oxidation of the TiN at the interface with HfO₂ layer than at the interface with SiO₂. As can be seen from the Fig. 5b, the main N1s emission band consists of two major peaks which can be assigned to TiN phase (the peak *a*) and to the TiN_xO_y phase observed at the lower binding energy (the peak *b*) [Sci. Rep., 29–33 from sci.rep]. The presence of the peak *b* suggests significant oxidation of the electrode material [Sci. Rep.]. One can see that the intensity ratio of the peaks stemming from the TiN and TiN_xO_y phases depends on the presence/absence of HfO₂ layer: The relative intensity of the TiN signal with respect to the peak from TiN_xO_y phase is larger in the spectrum of ALD-TiN/SiO₂/Si (without HfO₂ layer).

Let's now turn to the Si2s band analysis. Experimental and decomposed Si2s XPS spectra from the ALD-TiN/SiO₂/Si structure without/with HfO₂ layer collected at the excitation energy of 3000 eV and the electron emission angle of 5° with linear background subtracted are shown in Fig. 6. The spectra can be decomposed to the known signals corresponding to different oxidation states of Si atoms which are related to both the substrate (Si⁰) and the stoichiometric SiO₂ phase (Si⁴⁺). In addition, the components originating from the intermediate oxidation states of silicon are also present in the spectra indicating formation of oxygen deficient oxide layer due to oxygen scavenging by TiN from the initially stoichiometric thermally-grown SiO₂. According to angular dependence of Si2s spectra the peak area percent contribution of O-deficient SiO_x increases with increasing the emission angle (decreasing the probing depth) while the contributions from the Si substrate and stoichiometric SiO₂ layer become smaller. This behavior confirms formation of a thin SiO_x layer at the TiN/SiO₂ and HfO₂/SiO₂ interfaces. Comparison of the peak area percent contribution of the O-deficient SiO_x (SiO_x contribution is taken as a sum of Si¹⁺, Si²⁺ and Si³⁺ components) shown in table 1 shows almost the same amount of SiO_x in the TiN/SiO₂ stacks with/without HfO₂ interlayer. Nevertheless, as already noted when analysing Ti2p and N1s spectra, a stronger oxidation of the TiN appears to occur at the interface with HfO₂ layer. As a result, one can conclude that there is the scavenging of oxygen by TiN from SiO₂ to form oxynitride TiN_xO_y in both cases (TiN/SiO₂ and TiN/HfO₂/SiO₂). However, if in the first

case the TiN directly scavenges some oxygen from SiO₂, in the second one the HfO₂ layer adds some extra oxygen to that amount as evidenced by enhanced oxynitride signal in TiN/HfO₂/SiO₂/Si.

TiN (10 nm ALD 450°C)/SiO ₂ (10 nm)/Si			
Emission angle; deg	Area %		
	Si	SiO _x	SiO ₂
5	17.5	38	44.5
25	14.7	43.9	41.4
TiN (10 nm ALD 450°C)/HfO ₂ (2 nm)/SiO ₂ (10 nm)/Si			
Emission angle; deg	Area %		
	Si	SiO _x	SiO ₂
5	18.8	36.8	44.4
25	16.9	40.1	43
TiN (10 nm PVD 370°C)/HfO ₂ (2 nm)/SiO ₂ (10 nm)/Si			
Emission angle; deg	Area %		
	Si	SiO _x	SiO ₂
5	15.1	55.5	29.4
25	10.7	63.4	25.9

Table 1. Peak area percent contribution of Si (substrate), SiO_x and SiO₂ states in Si2s spectra measured at 5° and 25° emission angles. Si and SiO₂ contributions correspond to Si⁰ and Si⁴⁺ components respectively, SiO_x contribution is taken as a sum of Si¹⁺, Si²⁺ and Si³⁺ components. Uncertainty is ±0.5% and is associated with the uncertainty of the spectra decomposition.

Analysis of the decomposed Hf4f spectrum from the ALD-TiN/HfO₂/SiO₂/Si sample shown in Fig. 7 reveals the presence of a double peak structure (peak 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 [T. Ting-Ting, L. Zheng-Tang, L. Wen-Ting and Z. Wen-Hua, Chemical Structure of HfO₂/Si Interface with Angle-Resolved Synchrotron Radiation Photoemission Spectroscopy, Chin. Phys. Lett., 2008, 25, 3750–3752; V. Sammelselg, R. Rammula, J. Aarik, A. Kikas, K. Kooser and T. Kašmire, XPS and AFM investigation of hafnium dioxide thin films prepared by atomic layer deposition on silicon, J. Electron Spectrosc. Relat. Phenom., 2007, 156–158, 150–154; D. Barreca, A. Milanov, R. A. Fischer, A. Devi and E. Tondello, Hafnium oxide thin film grown by ALD: An XPS study, Surf. Sci. Spectra, 2007, 14, 34–40]. Furthermore, we observe additional doublet 2a at lower BE (fig. 7a) as well as the overlapping N2s and O2s components of the spectrum which mandate extra attention to confirm the reality of the formation of additional peaks in the Hf4f spectra. Therefore, below we describe a procedure used to separate the Hf4f component from the N2s contribution. Parameters (peak area, FWHM and

energy position) of the N2s component were estimated by using two independent methods. First, we analyzed our experimental N2s spectra of the TiN layer without hafnium contribution reported previously in [sci. rep.]. 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 N2s 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 found by the second method. According to formula for photoelectron peak intensity [TiO₂ STAM], we normalized integral area of N1s band to all energy and orbital dependent factors:

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

where λ is the inelastic mean free path estimated by TPP-2M formula [Tanuma], d is the nominal thickness of TiN layer, σ is photoionization cross-section [Trzhask...], $T(KE_{\text{orbital}})$ is the analyzer transmission function for KE_{orbital} kinetic energy. As a result, we obtained the energy position and FWHM of N2s component in the decomposed Hf4f spectra in the ranges 16.5 ± 0.2 eV and 3.8 ± 0.3 eV, respectively. The area of N2s components was calculated from the integral intensity of N1s band using the intensity ratio coefficient of 0.055 ± 0.003 .

The joint analysis of Hf4f and N1s spectra allows one to assign the additional doublet 2 to formation of HfN_x phase. This suggests that the HfO₂ interlayer layer not only allows oxygen diffusion from SiO₂ to TiN but, also, it acts like a "scavenger" for N from the TiN leading to formation of some amount of HfN_x.

TiN/HfO₂/SiO₂/Si structure as affected by the TiN synthesis method

Figure 7. Experimental and decomposed Hf4f XPS spectra collected from ALD-TiN/HfO₂/SiO₂/Si (a) and PVD-TiN/HfO₂/SiO₂/Si (b) stacks at the excitation energy of 3000 eV and the electron emission angle of 5°. Ratio of peak areas of doublets 2 and 1 is shown in the inset in panel (b). Inelastic background is subtracted.

Now let us consider the spectra collected from TiN/HfO₂/SiO₂/Si stacks with TiN layer fabricated by ALD or PVD methods. The Ti2p and N1s photoelectron spectra acquired from the ALD- and PVD-TiN/HfO₂/SiO₂/Si stacks at different electron emission angles are shown in Fig. 8. It should be added that there is a pronounced angular dependence of the difference in the shapes of the Ti2p and N1s spectra between the ALD- and PVD-TiN/HfO₂/SiO₂/Si stacks. Worth noting is that the Ti2p as well as N1s spectra collected at 5°, which correspond to the maximum probing depth, vary significantly. As the electron emission angle increases (probing depth decreases) up to 50°, the differences decrease significantly: the Ti 2p spectra practically do not differ and the N1s spectra become as similar to each other as possible. This observation indicates that the differences observed in the spectra collected at 5° reflect the structural dissimilarity between the interfaces of ALD/PVD TiN and HfO₂ while the surfaces of ALD-TiN and PVD-TiN appear to be oxidized by the ambient to the same extent. Worth noticing that difference in Ti2p spectra is mostly manifested by change in the intensity of the shoulder *b*, which has been previously assigned to the formation of TiNO_x [Sci. Rep., +]. The maximum intensity of the shoulder *b* is encountered in the PVD-TiN/HfO₂/SiO₂/Si stack.

Though the spectra reflecting the surface structure of the ALD- and PVD-TiN electrodes are found to be similar we additionally analyzed the same materials in stacks with the surface of TiN capped with 4-nm thin ALD W film. Being covered by a thin W layer the surface of TiN electrode is protected from the oxidation during subsequent exposure to air. In these studies, we used the excitation energy of 1000 eV, which corresponds to a smaller probing depth thus excluding contribution from the bottom interface. As expected, no differences in the shape of the Ti2p and N1s photoelectron spectra between the stacks with two favors of TiN were found.

Finally, the Ti2p and N1s spectra of both ALD- and PVD-grown stacks were decomposed to conduct detailed chemical analysis. Since the energy separation between Ti2p_{3/2} and N1s photoelectron lines $\Delta E(\text{Ti}2p_{3/2}, \text{N}1s)$ represents specific property of TiN which reflects its stoichiometry [Portel], we compared this parameter for ALD and PVD-TiN. It was found that the energy splitting $\Delta E(\text{Ti}2p_{3/2}, \text{N}1s)$ in the measured spectra approaches the same value of 58.0 eV. This means that the electrodes have the similar composition close to the nearly stoichiometric TiN. Therefore, we conclude that dissimilarity between the spectra measured at 5° is caused by stronger oxidation of the PVD-grown TiN at the interface with HfO₂.

Figure 8. Ti2p (a) and N1s (b) XPS spectra collected from ALD-TiN/HfO₂/SiO₂/Si (black) and PVD-TiN/HfO₂/SiO₂/Si (blue) stacks at the excitation energy of 3000 eV and different electron emission angles (5°, 40° and 50°). The spectra are vertically shifted for visibility.

Let us analyze the Hf4f photoelectron spectra of TiN /HfO₂/SiO₂/Si stacks shown Fig.7. The spectra for stacks with differently synthesized TiN are similar in the number of essential features and their energy positions of the component peaks but differ by the intensity of the main lines: The intensity of the additional doublet 2 appears to be much larger in the stack with PVD-TiN electrode. This would correspond to the more intensive “scavenging” of nitrogen from the PVD-TiN electrode, which correlates with more extended oxidation of this electrode as discussed above. Moreover, analysis of the angular dependence of the ratio of areas of doublets 2 and 1, shown in the insets in panels *a* and *b* reveals its increase for higher electron emission angles. It is worth reminding here that in the ALD-TiN a trace of HfN_x is detected. Therefore, we can conclude that method of the synthesis of TiN electrode impacts to the composition of the interlayer TiN/HfO₂ layer: PVD method promotes more intense oxidation of the electrode with formation of TiN_xO_y accompanied by the intensive “scavenging” for N from TiN with formation of HfN_x. The higher degree of TiN oxidation may explain the observed EWF increase in the PVD layers while “nitridation” of HfO₂ may cause incorporation of additional charge traps in the near-interface oxide layer.

ALD-TiN/HfO₂/SiO₂/Si and TiN/TiAl/TiN/HfO₂/SiO₂/Si

Figure9. Experimental and decomposed Al2s HAXPES spectra ofW/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm)/HfO₂/SiO₂ /Si stack with background subtracted measured at the excitation energy of 1 keV and normal emission (a) and at the excitation energy of 4 keV and the electron emission angle of 5° (b). (c) Angular dependence of the peak area percent contribution of different chemical states designated in panels (a) and (b). (d) Depth sensitivity function $P(x)$ (see comments in the text) for different measurement conditions, the nominal thicknesses of layers in the TiN/TiAl/TiNstack with W cap are shown by colored rectangles.

Al2s HAXPES spectra of W/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm)/HfO₂/SiO₂ /Si stack measured at the excitation energies of 1 keV and 4 keV are shown in Fig. 9 a,b. The protective 4-nm thick W cap was *in situ* Ar⁺-ion sputtered in order to increase the Al2s signal intensity (this is most important for studies at the excitation energy of 1 keV). Thickness of the remaining W cap was about 2 nm as estimated based on the sputtering rate. According to depth sensitivity function $P(x)$ calculation (Fig. 9d), the spectrum measured at the excitation energy of 1 keV corresponds to photoemission from the very surface of the TiN/TiAl/TiNstacked electrode without contribution from the interface with HfO₂, whereas the measurement at the excitation energy of 4

keV provides bulk-sensitive spectra. Function $P(x)$ is defined by Eq. (2) and describes attenuation of photoelectron signal from depth x due to inelastic scattering in the matter over depth x . n is a number of layer, 1 corresponds to the surface layer:

$$P(x) = \prod_{i=1}^{n-1} e^{-\frac{d_i}{\lambda_i \cos(\theta)}} * e^{-\frac{x}{\lambda_n \cos(\theta)}}, \quad \sum_{i=1}^{n-1} d_i \leq x < \sum_{i=1}^n d_i. \quad (2)$$

Decomposition of Al2s HAXPES spectra reveals the presence of Al atoms in four chemical states. According to literature, Al₂O₃ is characterized by an Al2s peak at 119.2 eV binding energy (BE) [Sygellou, Бухтияров] while a somewhat higher BE of 120.6 eV corresponds to the natural aluminum oxide [Olefjord]. Fig. 9a and Fig. 9b illustrate contributions of the Al2s peaks at 120.5 eV and 119.8 eV, as measured in the surface-sensitive and bulk-sensitive XPS modes, respectively. Taking into account the BE values and more pronounced Al-O peak in the spectrum measured at the excitation energy of 4 keV one can conclude that the surface of TiN/TiAl/TiN electrode contains scanty amount of oxidized aluminum probably due to residual oxygen during the stack fabrication; However, more significant oxidation due to oxygen scavenging from hafnium and silicon oxides is seen to occur at the TiN/HfO₂ interface.

Al2s spectra also exhibit two “metallic” peaks at 117.8 eV and 117.2 eV, which can be assigned to pure Al and TiAl, respectively [Olefjord, Geng 2000]. FWHM of Al and TiAl peaks correlates well with Al2s natural line width [Campbell] convoluted with instrumental broadening. If taking into account this instrumental FWHM increase, it was possible to decompose the experimental Al2s spectra using only two “metallic” Al2s peaks. Surface of TiN/TiAl/TiN composite electrode demonstrates the presence of the synthesized TiAl with some contribution of pure Al (probably due to Al diffusion to the surface). However, in the “bulk” of the TiN/TiAl/TiN stack pure Al is present in by far higher concentration while the TiAl component is suppressed that correlates with more pronounced oxidation due to oxygen scavenging from the underlying Hf and Si oxides. According to literature [Maurice 2007, Geng 2007, Seal 2000, Dettenwanger 1998], oxidation of TiAl leads to segregation of Al and Ti accompanied with selective Al oxidation at initial stages. In addition, both Al2s spectra in Fig. 9a,b demonstrate an intense peak at 118.6 eV related to formation of Al-N bonds [Esaka 1999, Krause 2013] that can be considered as indication of N scavenging or, else, Al diffusion into top and bottom TiN layers.

Figure 10. Experimental and decomposed Ti2p (a) and Hf4f (b) XPS spectra of 1 – ALD-TiN/HfO₂/SiO₂/Si and 3 – TiN (2 nm)-TiAl (4 nm)-TiN (2 nm)/HfO₂/SiO₂/Si measured at the excitation energy of 4000 eV (with W cap) and 3000 eV (without W cap), respectively, and the electron emission angle of 5°. Inelastic background is subtracted; the spectra 1 are vertically shifted for clarity.

Fig. 10a shows experimental and decomposed Ti2p spectra of W/ALD-TiN/HfO₂/SiO₂/Si and W/TiN (2 nm)-TiAl (4 nm)-TiN (2 nm)/HfO₂/SiO₂/Si stacks measured at the excitation energy of 4 keV and the electron emission angle of 5°. Decomposition of spectrum of the ALD-TiN reveals the presence of the pure TiN phase and the Ti oxynitride phase formed due to oxygen scavenging by TiN. Analysis of the spectrum of TiN/TiAl/TiN stacked electrode also points towards formation of TiN and Ti oxynitride phases but, in addition, the Ti2p_{3/2} peak at 454.2 eV can also be traced. This peak can be attributed to formation of pure titanium [Geng 2000, Seal 2000] that correlates with analysis of Al2s spectra, though some contribution of TiAl phase can't be excluded. We did not introduce a separate peak for TiAl phase because of its close energy position with that of pure titanium [Geng 2000, Seal 2000].

Fig. 10b demonstrates Hf4f XPS spectra of ALD-TiN/HfO₂/SiO₂/Si and TiN (2 nm)-TiAl (4 nm)-TiN (2 nm)/HfO₂/SiO₂/Si stacks measured at the excitation energy of 3 keV. Noteworthy that doublet 1* for the stack with TiN/TiAl/TiN electrode is shifted by 1 eV to the higher BE's relative to that in the stack without TiAl. We can suggest two pertinent reasons of this energy shift. First, since the BE is *measured* relative Fermi level of grounded metal electrode, in case of its EWF decrease one can expect increase of *measured* Hf4f BE of HfO₂ due to simple shift of zero reference point [Lebedinski 2007] (provided that chemical state of Hf atoms do not change). Though the inferred 1 eV value of the *measured* Hf4f BE shift is quite large it appears to be consistent with the conclusions drawn from the CV (Fig. 2) and IPE measurements (Fig. 3). The feasibility of this explanation is supported by CV and IPE results indicating that introduction of

the TiAl layer significantly reduces EWF in thin TiN layers deposited on SiO₂, i.e., this effect is associated with re-distribution of N atoms in the metal stack itself.

The second possible reason invokes some chemical modification of the HfO₂ layer below TiN/TiAl stack. According to literature [Cho 2004, Kaichev 2011, Cho 2004 nitrogen], the increase of Hf4f BE relative to that of HfO₂ is associated with formation of HfAlO mixed oxide. Indeed, incorporation of more covalent Al oxide (relative Hf oxide) leads to increase of Hf oxide ionicity, i.e., to the increase of Hf4f BE in HfAlO relative HfO₂. This is general phenomenological rule for BE's evolution in mixed oxides [Guittet 2001]. Thus we can assert that HfAlO mixed oxide is formed in TiN/TiAl/TiN stack and a possible reason of this is Al diffusion into HfO₂ layer during the synthesis and annealing: oxidation of the TiAl layer caused by oxygen scavenging from HfO₂ and SiO₂ may lead to segregation of pure Al promoting migration of Al into underlying HfO₂.

NK- NEXAFS spectra

Figure 11. NK-absorption spectra of 1 – ALD-TiN/HfO₂/SiO₂/Si, 2 – PVD-TiN /HfO₂ /SiO₂/Si and 3 – TiN (2 nm)-TiAl (4 nm)-TiN (2 nm)/HfO₂ /SiO₂ /Si stacks. The spectra were obtained by monitoring the total electron yield by measuring drain current from the sample at the incident angle of 45° using s-polarized synchrotron radiation. All the spectra were normalized to the continuum jump after subtraction of linear background extrapolated from the energy region below the corresponding absorption onset. For the sake of comparison the reference model spectra of cubic TiN [Gago 2013] and cubic AlN [Endrino 2011] are also shown.

NK-absorption spectra of ALD-TiN/HfO₂/SiO₂/Si (stack 1), PVD-TiN /HfO₂ /SiO₂/Si (stack 2) and TiN (2 nm)-TiAl (4 nm)-TiN (2 nm)/HfO₂ /SiO₂ /Si (stack 3) stacks are shown in Fig. 11 together with the reference spectra of cubic TiN [Gago 2013] and cubic AlN [Endrino 2011]. The spectra of TiN exhibit four features *a-b* and *c-d* related to N1s electron transitions

into unoccupied N 2p–Ti 3d and N 2p–Ti 4sp states. The spectra of ALD-TiN and PVD-TiN stacks agree well with those of c-TiN except that apparent intensity of feature **b** is enhanced for PVD-TiN indicating the presence of molecular N₂ [Esaka, sci-rep]. The latter represents a signature of enhanced oxidation of PVD-TiN relative to ALD-TiN that supports the above presented analysis of the HAXPES spectra. The NK-absorption spectrum of the stack with TiN/TiAl/TiN electrode exhibits the same features **a-b** and **c-d** but its shape differs significantly from that of ALD and PVD-TiN: The absorption between the features **b** and **c** is enhanced. It is plausible to associate this effect with formation of AlN phase: The NK absorption band of AlN is energetically positioned between the features **b** and **c** in the spectrum of TiN. In its turn, this result agrees with the above analysis of Al 2s XPS spectra.

Conclusions

Correlative analysis of EWF changes and structural features of nm-thin TiN electrodes on top of oxide insulators (SiO₂, HfO₂) suggests that the major mechanisms allowing for the EWF tuning are associated with re-distribution of light element atoms (N, O) between the components of the stack. Scavenging of oxygen is found for both oxides but appears to be more pronounced in the case of PVD-TiN as compared to the ALD-grown material of the same composition. Oxidation of the PVD TiN at the interface can be correlated with the ≈ 0.3 EWF increase. At the same time, loss of oxygen may lead to significant modification of thin (≈ 2 nm) HfO₂ interlayer between SiO₂ and TiN resulting in charge trapping and the corresponding interface barrier enhancement. On the other hand, the EWF can be significantly (≈ 1 eV) reduced by introduction of a thin TiAl getter layer on top of TiN film. The mechanism of this reduction can be traced down to formation of metallic Ti caused by nitrogen scavenging by TiAl as evidenced by AlN formation. In both cases the EWF tuning is achieved for processing temperatures of ≈ 400 °C which makes it compatible with the replacement metal gate and the “back-end-of-the-line” device technology.

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