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Interface and plasma damage analysis of PEALD TaCN deposited on HfO_2 for advanced CMOS studied by angle resolved XPS and *C–V*

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ABSTRACT

Plasma enhanced atomic layer deposition (PEALD) TaCN deposited on HfO_2 was studied by X-ray photoelectron spectroscopy (XPS) to understand the reactions taking place at the interface and connect them with *C–V* electrical characteristics of MOS devices. Moreover, angular resolved XPS (AR-XPS) was used for composition depth profiling of TaCN/HfO_2/SiO_2/Si stacks. Clear oxidation of the metal electrode through Ta—O bonding formation and migration of N in the dielectric with Hf—N are shown. These modifications of chemical bonding give an insight on the electrical results. Low equivalent oxide thicknesses (EOT), as low as 0.89 nm and current leakage improvement by more than 5 decades, are observed for deposition with low plasma power and can be related to HfN content in HfO_2 layer. The increase of plasma power used for TaCN deposition results in densification of the layer and promotes the creation of TaC in TaCN material. However H_2 plasma has an impact on HfO_2 with a reduction and scattering of the measured current leak gain. TaCN/HfO_2 interface is also impacted with further creation of TaO_x, leading to an increase of EOT when plasma power is increased. Based on these findings, reaction mechanisms with the corresponding Gibbs free energy are proposed.

1. Introduction

Advanced 22 nm node devices, based on 3D architecture, such as FinFET, induce new challenges for gate metal deposition. Such technologies require very thin dielectric/metal gate films with good conformity and low current leak. ALD-deposited hafnium oxide is currently used in the advanced CMOS transistors fabrication [1,2] and allows to lower the Equivalent Oxide Thickness (EOT) below a nanometer while maintaining acceptable current leakages. Tantalum-based metal gates have been widely studied as an alternative to the well-known standard Titanium nitride [3]. In particular, Tantalum carbo-nitride alloys (TaCN) can range from TaN to TaC, including TaCN. Tantalum alloys, not only have good thermal stability, chemical inertness and compatibility with current technologies [4], but also have a wide range of possible characteristics; i.e. WF changes from near mid-gap TaN, 4.55 eV [5], to n-type TaC metal 4.2 eV [6,7]. Moreover, tantalum alloys are known to be good chemical etch barriers, which is an asset for integration in current process flows. It also acts as chemical barrier against oxygen diffusion which can limit the regrowth of SiO_2 interfacial layer between dielectric and Si substrate [8]. Thanks to its low roughness and good conformity (plasma enhanced) atomic layer deposition ((PE)ALD), is a good candidate for metal deposition in advanced nodes [9,10]. In a previous study, this deposition technique has been used for TaCN deposition and it has been shown that power of hydrogen plasma has a direct influence on TaCN properties, by modulating the creation of Ta—C bonds [11]. However, the dielectric underneath can be severely affected during the plasma steps of PEALD metal deposition by electrons, excited and hot ionized species from the plasma, such as H^+, NH^+ and other radicals formed by precursor's decomposition [12]. In plasma ambient, ions and electrons are collected by the metal electrode which serves as an antenna [13], a steady-state voltage may appear in the metal due to charge collection and resulting on electrical stress which can affect underlying gate oxide [13–18]. The two main phenomena inducing dioxide degradation are: first the oxide breakdown due to a conduction path formed from the anode to the cathode [15,16], second the weakening of the oxide by charge trapping correlated to the formation of defects in the oxide [17,18].

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Thus, the aim of this work is to first understand the reactions taking place at the metal/high-*k* interface and then evaluate the plasma damages on high-*k* layer, in order to obtain the best TaCN properties with the lowest impact on the HfO_2. First, X-ray photoelectron spectroscopy (XPS) is used to highlight the interactions of TaCN with HfO_2. Then depth composition profile created with angle-resolved XPS (AR-XPS) is used to evaluate reactions at the interface and species (O, N) exchanges between TaCN and HfO_2. Finally electrical characteristics of TaCN/HfO_2/SiO_2/Si are discussed with regards to the metal deposition parameters and chemical environments obtained by XPS analysis.

2. Experimental methods

Material characterizations were carried out on Si (1,0,0) blanket wafers. To measure the variation of EOT simple MOS stacks with TaCN/HfO_2/SiO_2/Si were realized in oxide cavities on p-type silicon substrate (5–10 Ω cm). Both blanket and CMOS wafers were cleaned by an initial HF bath to remove native oxide, followed by a 7 Å chemical oxide formation. This oxide was formed by a wet oxidation and acts as an interfacial oxide layer and nucleation surface for 2 nm thick ALD-deposited HfO_2. HfO_2 was deposited at 350 °C by atomic layer deposition using alternative cycles of H_2O and $HfCl_4$ precursors at 133 Pa. HfO_2 was then annealed under N_2 atmosphere at 650 °C during 2 min for by-products exhaust. To avoid regrowth of SiO_2, HfO_2 deposition was performed within 2 hours after chemical SiO_2 formation. Before metal deposition, a 3 min degasing at 325 °C was performed to allow surface moisture removal from HfO_2 surface. 4 nm TaCN metal was then deposited by PEALD with Tris(diethylamino)(tert-butylimido)tantalum (TBTDET) precursor and H_2 plasma. PEALD deposition principle was already published elsewhere [11]. Finally, to allow electrical measurements on MOS stacks, contact plug based on 5 nm TiN/150 nm W was CVD-deposited at back-end temperatures on top of TaCN.

Plasma power influence was studied at different conditions: low, middle and high plasma power, respectively named PEALD-LP, PEALD and PEALD-HP, all other deposition parameters were kept constant. To allow complete understanding of chemical interactions, samples with SiO_2/Si only, HfO_2/SiO_2/Si and TaCN/SiO_2/Si were also prepared on blanket wafers.

Physical vapor deposition (PVD) TiN and ion beam deposition (IBD) TaN metals were also deposited on HfO_2 as references for electrical measurements.

XPS measurements were performed with a Theta 300 XPS tool from Thermo Scientific. A high resolution monochromatic Al Kα X-ray source (1486.6 eV photons) was used with pass energy of 100 eV and a resolution of 0.1 eV. No carbon nor oxide removal was performed on the samples before XPS characterization, thus due to oxidation and atmospheric contamination high levels of C and O were observed at the extreme surface of the samples. Carbon C1s, located at 285 eV [19] was used to remove any possible shift in the binding energy due to sample charging. Observation of Ta, Hf, Si, C, N, and O chemical environments were extracted from the Ta4f, Hf4f, Si2p, C1s, N1s and O1s core level energy regions, respectively. Using a numerical procedure, spectral fitting was performed to extract the peak contributions in the acquired energy regions. Individual line shapes were simulated with a combination of Lorentzian and Gaussian functions using Advantage software from Thermo Fisher Scientific. The background subtraction was performed using a Shirley function calculated from a numerical iterative method. AR-XPS measurements used the same parameters as XPS, with the simultaneous acquisition of eight angles, in the range 23–76°, without physical tilt of the sample, which allows the formation of an accurate depth resolved profile. Based on intensity evolution of the Ta4f, Hf4f and Si2p different features, it is possible to build a depth composition profile of the sample. As a result of this analysis the variation of intensity (in arbitrary unit) is plotted through the depth of the sample. It is noteworthy that only the variation of composition should be taken into account: the higher intensity of an element cannot be interpreted as a higher concentration of this element in the sample.

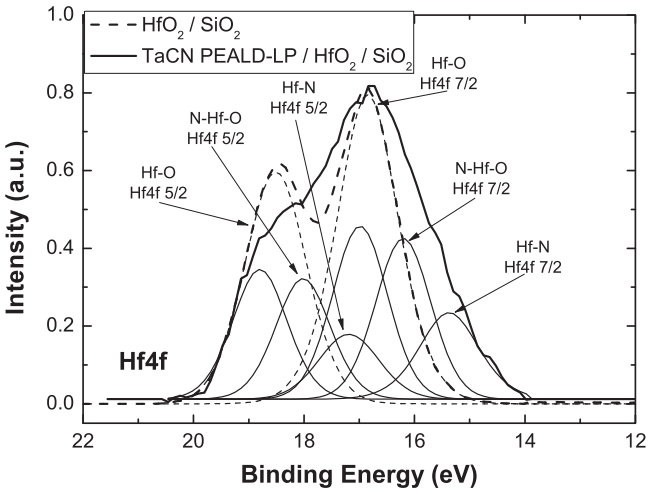

Fig. 1. XPS Hf4f spectra of HfO_2/SiO_2/Si and PEALD-LP TaCN/HfO_2/SiO_2/Si.

XPS spectra fitting were done using the following constraints: a shift in bonding energy of $\Delta E = 1.71$ eV, with an area ratio of 0.75, was used between $Hf4f_{5/2}$ and $Hf4f_{7/2}$ [19]. Similarly a shift in energy of $\Delta E = 1.91$ eV was taken used for $Ta4f_{5/2}$ and $Ta4f_{7/2}$ doublets separation, with also an area ratio of 0.75. To help with reading the graphs only $4f_{7/2}$ components are displayed on the figures.

Thanks to the identical Si2p line shapes obtained with SiO_2/Si, HfO_2/SiO_2/Si and TaCN/SiO_2/Si (not shown here), Si can be considered as not interacting with the HfO_2 and TaCN materials. Thus Hf4f and Ta4f peaks from HfO_2/SiO_2/Si and TaCN/SiO_2/Si samples are used as individual references for TaCN/HfO_2/SiO_2/Si stack peaks fitting and interpretation.

3. Results

3.1. Chemical interactions

XPS Hf4f spectra of HfO_2 before and after TaCN low plasma power deposition are presented in Fig. 1. Fitting of HfO_2/SiO_2 reference can be achieved using only one doublet, standing for Hf—O environment and located at 16.8 eV. Deposition of TaCN PEALD-LP on top of HfO_2 is leading to the creation of new chemical environments in Hf4f region. Hence, TaCN PEALD-LP/HfO_2/SiO_2/Si spectrum is noticeably broadened, thus indicating at least two additional bonding environments. The first one, adjusted at 15.3 eV is attributed to the creation of Hf—N bonds [19] in HfO_2 layer. The second environment doublet at 16.2 eV corresponds to the presence of O—Hf—N-like bonds. From O—Hf—N peak it is not possible to discern if N is placed as a first or second neighbour of the Hf.

Due to the similar electronegativities of Hf and Ta resulting in the overlapping of both Hf—O and Ta—O environments, it is not possible to resolve the O1s spectrum, therefore O1s region is not presented in this article.

To complete the understanding of TaCN interactions with HfO_2, Ta4f spectra from TaCN low power deposited on HfO_2/SiO_2/Si and on SiO_2/Si are now compared in Fig. 2a. Although the same TaCN deposition is achieved, Ta4f spectra are different when deposited on both dielectrics and three modifications are noticed: (i) the first one concerns Ta—O bonding environment, located at 26.2 eV.