The electrostatics of Ta_2O_5 in Si-based metal oxide semiconductor devices

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Thin dielectric layers are a prominent route to control the band alignments and effective work function of metal oxide semiconductor (MOS) devices. In this work, the electrostatic effects of thin Ta_2O_5 layers on the band alignments of MOS devices are examined. A detailed analysis of the physical properties of a thick (~6 nm) Ta_2O_5 layer is reported. No significant dipoles at Ta_2O_5-Al_2O_3 and Ta_2O_5-SiO_2 interfaces are found, as well as any significant charges inside Ta_2O_5 layers. When positioned at the interface, Ta_2O_5 is shown to prevent the formation of band offsets between Al_2O_3-SiO_2, resulting in a shift of 1 ± 0.2 eV versus samples without interfacial Ta_2O_5. The relatively large magnitude of this shift in the current experimental configuration compared to previous works may indicate the participation of interface charges in the band offset. The possible use for these effects in devices is discussed. © *2013 American Institute of Physics*.
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I. INTRODUCTION

High-k dielectrics with metal gates (HKMG) were introduced into the microelectronics industry several years ago, following a decade of intensive research on the relationship between the materials and the electrical properties of these materials and their interfaces.[1] Hf-based oxides emerged as the leading high-k dielectric.[2] An important aspect with the usage of HKMG in metal oxide semiconductor (MOS) technology is the position of the metal Fermi level with respect to the semiconductor, which can be described in terms of an effective work function[3] (EWF). The EWF has a critical role in determining the performance of a single device and the entire circuit.[4] Initially, controlling the EWF was attempted by engineering the metal gate by the use of alloys, which was shown to result in several metallurgical and thermal stability challenges.[5–8]

Alternatively, it was shown that thin dielectrics layers, so called capping layers, placed at the metal-dielectric interface, can be useful for controlling the EWF.[9,10] Typically, Al oxide is used for increasing the EWF[11,12] and La oxide[13–16] (and to some extent Gd oxide[17,18]) for decreasing the EWF. It was shown that the position of the capping layers' atoms is important for their functionality,[19,20] and particularly it was shown with different configurations that the contact of Al oxide with SiO_2 is responsible for the EWF increase.[12,21,22] These effects have been further utilized recently for improving metal-semiconductor contacts.[23,24]

In a recent study,[22] we have shown that the formation of a Ta suboxide layer formed at a Ta-Al_2O_3 interface resulted in an EWF increase of 0.4 eV. Following this, in the current work, we studied the effect of deposited thin Ta_2O_5 layers in conjunction with Al_2O_3 on the electrical properties of MOS capacitors.

Despite its relatively large band gap, Al_2O_3 does not have a high enough k value to be used as a gate dielectric for Si MOS devices. However, other than its use as a capping layer, Al_2O_3 is relevant for metal-insulator-metal (MIM) capacitors and for nonvolatile memories.[25] Moreover, Al_2O_3 is an important dielectric for MOS devices based on high-mobility semiconductors such as GaAs,[26] InGaAs,[27,28] and Ge,[29] where it can be used in a bilayer configuration with another dielectric.[30,33] Ta_2O_5 was among the first candidates in the early days of high-k dielectrics.[4,34] However, it was abandoned as the main high-k dielectric for MOS devices, due to insufficient thermal stability and a too small conduction band offset with Si.[1]

In order to understand the role of Ta_2O_5 on the band structure, Al_2O_3-based MOS devices were fabricated with varying positions of thin Ta_2O_5 layers. Since atomic layer deposition (ALD) of Ta_2O_5 is less robust than in the case of Al_2O_3, a physical characterization of ALD-Ta_2O_5 was carried out first.

II. EXPERIMENTAL

A 4.5 nm layer of SiO_2 was thermally grown on a (100) p-Si wafer (B doped, $\sim 2 \times 10^{15}$ cm^{-3}). ALD of Al_2O_3 and Ta_2O_5 was performed at 300 °C using trimethyl-aluminum (TMA) and pentakis(dimethylamino)-tantalum[31,32] (PDMAT) with H_2O, respectively. The different dielectric stacks are schematically shown in Fig. 1. Capacitors were formed by e-beam evaporation of 40 nm Pt through a shadow mask with a nominal contact area of 2.5×10^{-3} cm^2. The actual area was measured individually for each capacitor using an optical microscope. A back contact was formed by e-beam evaporation of 300 nm of Al. The samples were then annealed at 400 °C for 30 min at 10^{-7} Torr.

Capacitance-voltage (C-V) measurements were done with an HP4284A LCR meter in a light-sealed chamber at 100 KHz. Transmission electron microscopy (TEM) was done using an FEI Technai G^2 T20 microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were done using a Thermo VG Scientific Sigma Probe

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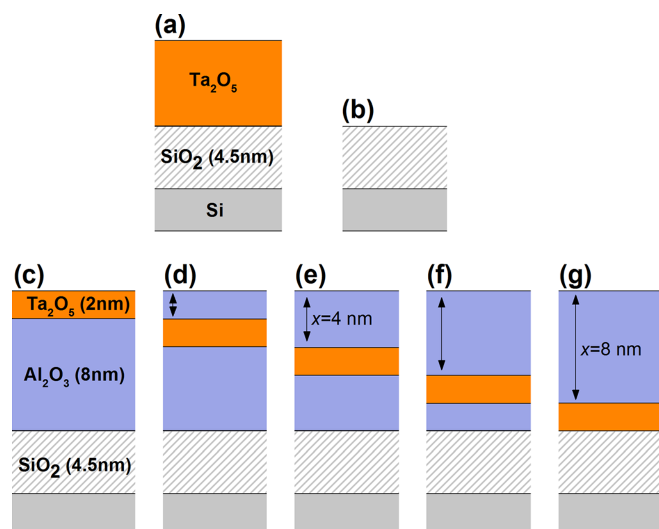


FIG. 1. Schematic cross section of the different samples, (a) thick Ta_2O_5 layer on SiO_2, (b) reference sample with no Ta_2O_5 (c)–(g) varying Ta_2O_5 position in a Al_2O_3 with x = 0,2,4,6, and 8 nm.

using a monochromatic Al Kα (1486.7 eV) as a primary beam and pass energies of 20 and 50 eV for Ta 4f and O 1 s, respectively. The energy scale was aligned by adjusting the C 1 s peak of the adventitious carbon to 284.5 eV.

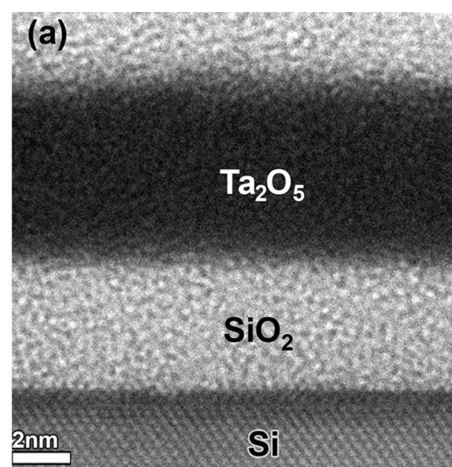
III. RESULTS AND DISCUSSION

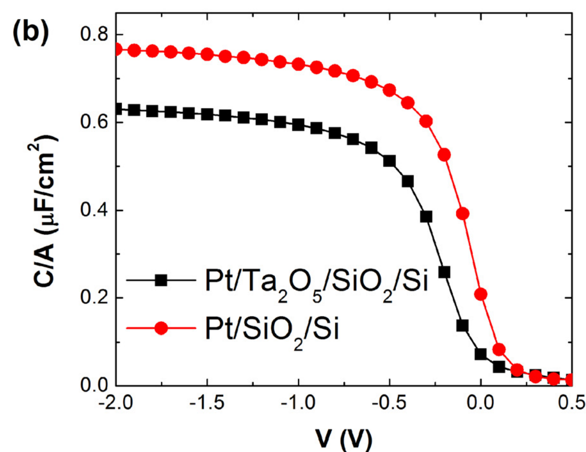
A. Ta_2O_5 characterization

Ta_2O_5 deposition is not reported as extensively as that of Al_2O_3 in the literature and is more sensitive to process conditions due to lower precursor vapor pressure and reactivity. Therefore, the physical properties of a "thick" Ta_2O_5 layer were investigated prior to its application as a thin dielectric. A cross section TEM micrograph (Fig. 2(a)) shows a uniform and dense layer. A thickness of 4.5 ± 0.4 nm and 6.1 ± 0.7 nm for SiO_2 and Ta_2O_5, respectively, is obtained from Fig. 2(a), with the latter used for calibrating the thickness in the deposition of the subsequent samples.

Capacitance-voltage curves of the Ta_2O_5 are compared to those of the same device without the Ta_2O_5 layer (Fig. 2(b)). Leakage currents measured on sample b (with the smallest effective oxide thickness, EOT) were found to be below 10^{-7} A/cm^2 in the voltage range of Fig. 2(b). The Ta_2O_5 contribution to the capacitance, $C_{Ta_2O_5}$, can be calculated by ${C_{Ta_2O_5}}^{-1} = {C_{(a)}}^{-1} - {C_{(b)}}^{-1}$, with $C_{(a)}$, $C_{(b)}$ being the capacitance of samples a and b (Fig. 1) taken at accumulation (Fig. 2(b)). Using $C_{Ta_2O_5}$ and the measured Ta_2O_5 thickness (Fig. 2(a)), a dielectric constant of 22.3 ± 2.5 is calculated, with the error stemming from the uncertainty of the Ta_2O_5 thickness measurement. This value is in agreement with the earlier reports.[1,34] The use of a bottom SiO_2 layer and the reference sample circumvents the deposition of the dielectric directly on Si, which usually forms a silicate interface layer (e.g., Refs. 32 and 35) that complicates the analysis and can lead to significant errors.

The Ta 4f XPS spectrum of the Ta_2O_5 layer shown in Fig. 2(c) displays a single doublet corresponding to fully oxidized Ta. No other components can be observed in the lower





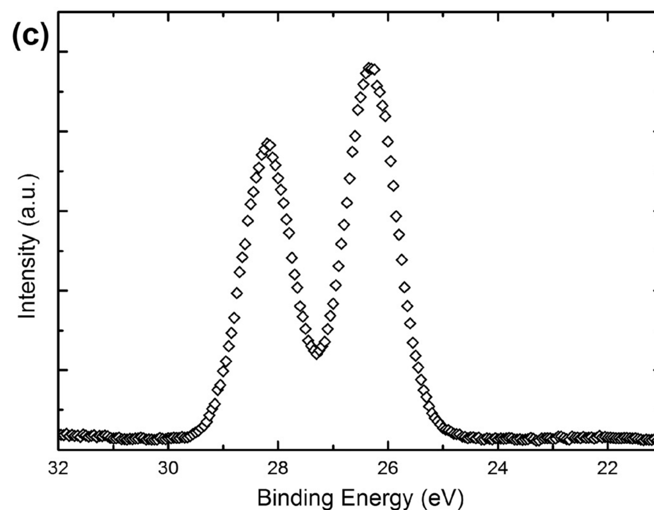


FIG. 2. (a) Cross section TEM micrograph of a 6.1 nm Ta_2O_5/4.5 nm SiO_2/Si stack. (b) Capacitance-voltage curves compared to a reference sample without Ta_2O_5. The lines connect the data points for clarity. (c) Ta 4f XPS spectrum.

binding energies[22,36] indicating that up to the detection limit of XPS, the deposited layer is fully oxidized. It should be noted that the carbon content is not evaluated in this work due to the difficulties associated with quantifying carbon by XPS. A survey XPS scan reveals a 25 ∼ 30% surface concentration of carbon which is typical of samples exposed to the atmosphere and cannot be used for actual quantification.

Given the agreement of the physical properties to previous reports, it is concluded that no abnormalities in the C content exist in the samples.

The O 1 s XPS spectrum shown in Fig. 3 is fitted using a Shirley-type background, and peak parameters of 1.56 eV full width at half-maximum, and 12% Lorenzian-Gaussian ratio. The major component ("Peak1") is attributed to O-Ta bonding states, while the minor components ("Peak2", "Peak3") can be attributed to small O-Si signal coming from the bottom SiO_2 layer and/or to surface contamination oxygen bonds.

The method used by Miyazaki *et al.*[37,38] is applied for the extraction of the band gap of Ta_2O_5 by measuring the distance between the O-Ta component to the onset of the plasmon losses signal. The latter is obtained by the intersection of the linear fit of the plasmon losses slope with the background.[39,40] This procedure results in a band gap value of 4.5 ± 0.2 eV, in agreement with the reported values of 4.4–4.65 eV (Refs. 1 and 38). Changes in the parameters of the peak fitting do not change the position of the major peak by more than 0.05 eV, which is much smaller than the estimated error in the band gap, attributed mostly to the plasmon-background intersection.

B. Ta_2O_5 in Al_2O_3-MOS devices

After asserting that the physical properties of Ta_2O_5 are well within the expected parameters, it is incorporated as a thin layer in Al_2O_3-based MOS capacitors by the preparation of the set of samples described in Fig. 1. A cross section TEM micrographs (Fig. 4) of a representative sample (corresponding to that of Fig. 1(g)) show that even for a Ta_2O_5 as thin as ∼2 nm, it is continuous. In order to understand the electrostatic role of the Ta_2O_5 layer, a series of samples were produced in which the distance of the layer from the metal-dielectric interface, denoted x in Fig. 1, is varied from the top interface (x = 0 nm, Fig. 1(c)) to the bottom interface (x = 8 nm, Fig. 1(g)). It is expected that if Ta_2O_5 contains any significant charges, the flatband voltage (V_{FB}) of the

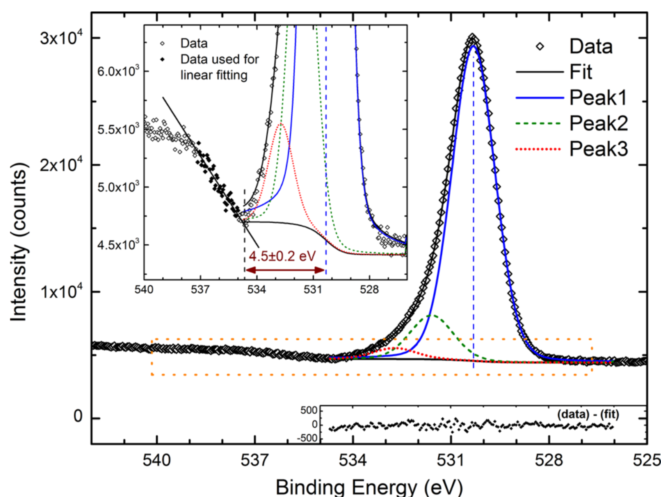


FIG. 3. O 1s XPS spectrum and its EELS tail; inset showing an enlargement of the dashed rectangle with the details of band gap extraction, bottom bar showing the fitting error.

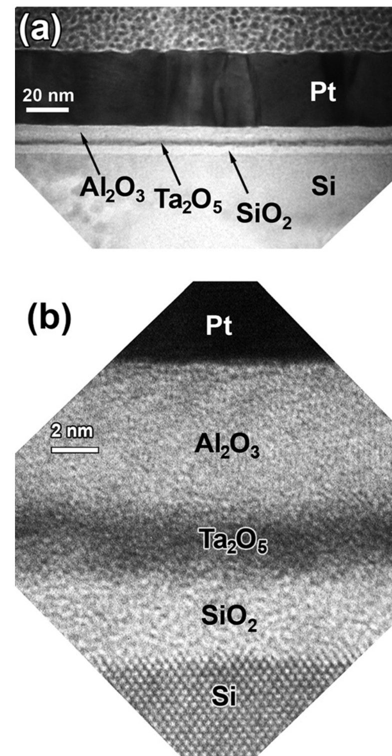


FIG. 4. Cross-section TEM micrograph of a $x = 8$ nm sample (Fig. 1(g)) at a low (a) and high (b) magnifications.

capacitors will change linearly with x.[41] Alternatively, if dipoles are formed at Ta_2O_5-Al_2O_3 interfaces, they will cancel each other on both sides of the Ta_2O_5 layer for all samples except x = 0 and 8 nm.

The C-V characteristics of the Ta_2O_5-Al_2O_3 samples show well-behaved curves with a consistent accumulation capacitance (Fig. 5(a)). Interestingly, the V_{FB} values of all the samples are quite close (Fig. 5(b)), with the exception of the sample where the Ta_2O_5 layer is positioned at the Al_2O_3-SiO_2 interface (x = 8 nm, Fig. 1(g)).

The constant value of V_{FB} for x = 0–6 nm rules out the existence of Ta_2O_5 (bulk or surface) charges that have any significance in terms of the C-V behavior of MOS devices. This is consistent with the behavior observed in Fig. 2(b). Next, dipoles at the Ta_2O_5-Al_2O_3 interface are considered; in the x = 2–6 nm samples such dipoles would cancel each other from both sides of the Ta_2O_5 layer, having no net effect. However, no deviation of the C-V behavior occurs at the x = 0 nm sample, where there is only one Ta_2O_5-Al_2O_3 interface, indicating that no significant dipoles exist between these two materials. To complement and support this conclusion, we note that no significant differences are observed in (a) the V_{FB} of Pt/Ta_2O_5 versus Pt/SiO_2 (Fig. 2(b)) and (b) in the band alignment at Pt/Al_2O_3 interfaces versus Pt/SiO_2 (Ref. 22).

Examining the sample with x = 8 nm, we note that it consists of a Ta_2O_5-SiO_2 interface that shows no significant dipole (Fig. 2(b)), and an Al_2O_3-Ta_2O_5 interface that shows no dipole as well, as discussed in the previous paragraph. This means that the only electrostatic contribution of Ta_2O_5 at the Al_2O_3-SiO_2 interface is by creating a separation between Al_2O_3 and SiO_2. Indeed, it is known that an

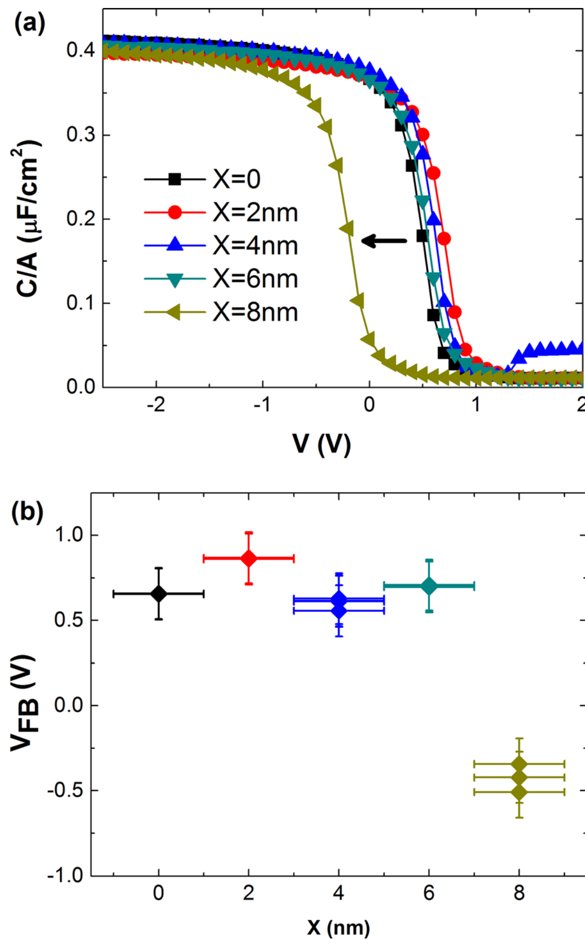


FIG. 5. (a) Capacitance-voltage curves of the Ta_2O_5-Al_2O_3 system and (b) the effect of the position of a Ta_2O_5 layer (x) on the flatband voltage.

Al_2O_3-SiO_2 contact increases the EWF (and V_{FB}), and we have previously reported an increase of 0.4 eV,[12,22,42] in agreement with other reports of 0.2 ~ 0.7 eV.[20,43–45] By contrast, in the current work, the contribution of the Al_2O_3-SiO_2 interface is 1 ± 0.2 eV (Fig. 5(b)). The principal difference between the current work and the literature is the larger EOT between the Al_2O_3-SiO_2 interface and the top metal, which is ~4 nm in the current work versus ~2 nm in previous reports.[22,42] According to the Poisson equation,[41] the potential shift caused by Al_2O_3-SiO_2 interface charges will have a distance (between the metal and the Al_2O_3-SiO_2 interface) dependence. If this V_{FB} shift indeed depends on the EOT of the Al_2O_3 layer, it could imply that charges at the Al_2O_3-SiO_2 interface may play a role in the shift, as argued before.[45]

These results may seem to contradict those obtained with Ta(TaO_x)-Al_2O_3 interfaces, where a TaO_x layer was formed and shown to cause a surface dipole attributed to Ta-O bonds.[22] However, the previous case is different from the Ta_2O_5-Al_2O_3 system in several aspects. The TaO_x layer was formed by a reaction between Al_2O_3 and Ta, resulting in a different metal-dielectric interface compared to the case of metal deposited on the dielectric in the current work. Moreover, the TaO_x layer was found to contain almost no fully oxidized Ta_2O_5 (mostly suboxide components), meaning that the chemical state of the interface layer is different. Therefore, the structure and chemistry differences between TaO_x and Ta_2O_5 explain the difference in the electrical behavior.

IV. CONCLUSIONS

Ta_2O_5 can be grown by ALD to form thin and uniform layers having a high dielectric constant. Although not suitable as a single layer high-k dielectric,[1] the electrostatic inertness of thin Ta_2O_5 layers demonstrated in this work can be harnessed to several purposes. First, a thin Ta_2O_5 layer can be used to reduce and thereby control the dipole at Al_2O_3-SiO_2 interfaces. Moreover, the high dielectric constant of Ta_2O_5 allows flexibility in use, with a small EOT increase (~0.18 nm per 1 nm of physical thickness).

Al_2O_3 is emerging as the leading dielectric for the challenging surface passivation of high channel mobility MOS devices, but its relatively low dielectric constant compromises its scalability. The results of this work suggest a combination of Al_2O_3 and Ta_2O_5 as a possible route for this area as well.

The low conduction band offsets of Ta_2O_5 can be turned into an advantage when used as a charge trapping layer in non-volatile memories (NVMs).[46] Our results can further be applied for band structure engineering in such devices, keeping in mind that Al_2O_3 is a useful blocking layer in NVMs.[25]

In summary, the properties of Ta_2O_5 films were studied electrically, structurally, and chemically. A systematic variation of the position of thin Ta_2O_5 layers inside Al_2O_3-based MOS devices has excluded the existence of significant charges inside the layer and dipoles at the Al_2O_3-Ta_2O_5 interface. Furthermore, it was shown that thin Ta_2O_5 can prevent the formation of the band offset that is known to exist at Al_2O_3-SiO_2 interfaces. The results further indicate the possibility that this offset may be partially caused by interface charges.

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