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Pierre-Yves Prodhomme, Fabien Fontaine-Vive, Abram van Der Geest, Philippe Blaise, Jacky Even. Ab initio calculation of effective work functions for a TiN/HfO(2)/SiO(2)/Si transistor stack. Applied Physics Letters, 2011, 99, pp.022101. 10.1063/1.3609869 . hal-00662689

HAL Id: hal-00662689
https://hal.science/hal-00662689

Submitted on 25 Jan 2012

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Citation: Appl. Phys. Lett. **99**, 022101 (2011); doi: 10.1063/1.3609869
View online: http://dx.doi.org/10.1063/1.3609869
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Ab initio calculation of effective work functions for a TiN/HfO_2/SiO_2/Si transistor stack

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(Received 5 February 2011; accepted 21 June 2011; published online 11 July 2011)

Ab initio techniques are used to calculate the effective work function (W_{eff}) of a TiN/HfO_2/SiO_2/Si stack representing a metal-oxide-semiconductor (MOS) transistor gate taking into account first order many body effects. The required band offsets were calculated at each interface varying its composition. Finally, the transitivity of local density approximation (LDA) calculated bulk band lineups were used and completed by many body perturbation theory (MBPT) bulk corrections for the terminating materials (Si and TiN) of the MOS stack. With these corrections the *ab initio* calculations predict a W_{eff} of a TiN metal gate on HfO_2 to be close to 5.0 eV. © *2011 American Institute of Physics*. [doi:10.1063/1.3609869]

Reducing the scale of the metal-oxide-semiconductor (MOS) transistor has led the semiconductor industry to major changes in the MOS stack. First, the SiO_2 oxide has been replaced by a HfO_2 layer on top of a SiO_2 thin film, while TiN is a leading candidate to replace poly-silicon in the gate for the next generation of MOS transistor (22 nm and sub-22 nm). However, the control of the threshold voltage remains one of the major issues. The effective work function (W_{eff}) of a metal in a MOS structure is one of the key properties governing this threshold voltage. The aim of this paper is to construct a milestone for the comparison between an ideal system and available experimental data.

During electrical capacitance-voltage (C-V) measurements, W_{eff} is usually estimated through:

$$W_{\text{eff}} = \phi_{\text{ms}} + \chi(Si) + \zeta(Si). \quad (1)$$

Here, $\chi(Si)$ is the electronic affinity of silicon, $\zeta(Si)$ is the difference between the conduction band and the Fermi energy of doped silicon, and ϕ_{ms} is the difference between the metal Fermi energy and the semiconductor Fermi energy. ϕ_{ms} is extracted from the flat-band voltage through modeling of the defect's charge distribution along the oxide.[1]

The valence band offset (VBO) between the metal and the semiconductor (VBO_{ms}) is related to ϕ_{ms} through $VBO_{ms} + E_g(Si) = \phi_{\text{ms}} + \zeta\ (Si)$, where E_g (Si) (1.1 eV) is the electronic gap of silicon. Combining this relation with Eq. (1) and considering the well-accepted value of $\chi(Si)$ (4.1 eV), the *ab initio* W_{eff} of a given metal can be evaluated through the equation

$$W_{\text{eff}}^{\text{ab initio}} = \text{VBO}_{\text{ms}}^{\text{ab initio}} + \chi(Si) + E_g(Si). \quad (2)$$

Then, one realizes that the *ab initio* quantity of primary importance is VBO_{ms}.

Evaluating the VBO_{ms} from first principles calculations is a challenge. On the one hand, the recent introduction of hafnium oxide requires the accurate treatment of the complex chemistry of the interfaces. On the other hand, in order to reach a sufficient precision on electronic energies (±0.1 eV), one needs to compute the eigenvalues in many body perturbation theory (MBPT). However, this is out of reach for the treatment of a complete MOS stack within the GW approximation (GWA, where G stands for the Green's function and W for the screened potential). Fortunately, the interface's potential drop can be well estimated within the density functional theory (DFT) (Ref. 2) and coupled with the GW eigenvalues for the valence band states calculated only for each bulk material. These eigenvalues are calculated in reference to the electrostatic potential average[3] of each bulk. This reference potential is then aligned with the potential drop at the interface producing the band offset.[2] This technique is generally applicable for a sufficient material thickness (1 to 2 nm thickness for each slab) such that each material approaches a bulk state away from the interface.

In this manner, the first order implementation of GWA, called G_0W_0, has been applied to correct the band alignments along III-V heterojunctions. These corrections slightly improved the DFT results in the local density approximation (LDA), which were already in pretty good agreement with experiments.[4,5] Recently, this *ab initio* method has been applied to assess the band alignment at a junction between an oxide (SiO_2, ZrO_2 or HfO_2) and a semiconductor (Si) resulting in a close agreement with experiment unlike the LDA results.[2,6] In this paper, we use the same approach for each interface of a complete TiN/HfO_2/SiO_2/Si stack.

The potential drops at each of the interfaces have been computed within DFT/LDA using the atomic orbital SIESTA software,[7] whereas the GWA computations have been carried out with the plane-waves ABINIT software.[8] To be consistent, identical Troullier-Martins pseudopotentials[9] for each atomic species have been used for Abinit and Siesta and were generated using the Fhi98pp and Atom programs[7,10] in the LDA.[11] Siesta calculations have been performed using a polarized double zeta, Polarized Double-Zeta (DZP) basis with an energy shift of 50 meV and a Meshcutoff of at least 100 Hartrees. A simulated anneal has also been carried out within

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Siesta as an heuristic method to relax the forces for each stack: from 1000 K to 100 K in 1 ps, followed by a conjugated gradient method to reduce the forces to less than 0.07 eV/Å.

All GWA calculations were performed at the G_0W_0 level. The quasiparticles energies were carefully converged with respect to the energy cut-offs, the number of k-points in the Brillouin zone, and the number of bands used to compute the dielectric function and the self-energy. Thus, a numerical accuracy of ± 0.1 eV on the quasiparticles energies was reached. The Plasmon-Pole model proposed by Godby and Needs[12] was used to describe the dynamic dependence of the "screening" function.

Two types of Si/SiO_2 interfaces have each been simulated, one oxygen poor and one oxygen rich. These supercells contained a 22.2 Å long slab of β-cristobalite SiO_2 and a 24.3 Å long slab of diamond Si, both oriented with the (001) plane at the interface. The latter slab was compressed by 3% in the [100] and [010] directions. The simulated LDA value of the VBO_1^{LDA} is +3.0 eV (+2.8 eV) for the oxygen rich (poor) interface using the sign convention, where VBO > 0 when the valence band maximum (VBM) of the material on the left is above the VBM of the material on the right. The G_0W_0 corrections to the VBMs computed for each material are $\delta\epsilon_v^{GW-LDA}(Si) = -0.6$ eV and $\delta\epsilon_v^{GW-LDA}(SiO_2) = -1.9$ eV, which lead to a VBO_1^{GW} of $+4.2 \pm 0.1$ eV. These results are in good agreement with the results published by Shaltaf *et al.*[2] (4.1 eV calculated within GWA starting from Generalized Gradient Approximation (GGA) electronic structures), and a little lower than experimental data ranging from 4.3 eV to 4.5 eV estimated by X-ray photoelectron spectroscopy (XRD).[13,14]

The SiO_2/HfO_2 interface is the second interface of the complete stack (Figure 1) considered here. The HfO_2 slab was simulated in its monoclinic structure with $P2_1/c$ symmetry, which is its stablest phase at ambient pressure and temperature[15,16] with the (001) plane at the interface. The SiO_2 slab was again β-cristobalite and oriented with the (001) plane at the interface. The HfO_2 was stretched by 3.7% in the [100] direction and by 2.1% in the [010] direction to match the 5.23×5.23 Å^2 square interface of the SiO_2, which agrees with the other simulations in literature of SiO_2 in the stack.[2,17] The supercell contained seven HfO_2 layers and ten SiO_2 tetrahedron. At the interface after relaxation, 3 oxygens were each three times coordinated with both Si and Hf. The potential along the stack shown in Figure 1 exhibits a large potential drop of 5.2 eV, which is expected since the electric permittivity and the average valence electronic density are much higher in hafnia than in silica. At the LDA level, the VBO_2^{LDA} is +0.4 eV, which is qualitatively wrong with respect to XPS measurements,[13] i.e., the VBM of SiO_2 is measured below the VBM of HfO_2. Some DFT calculations of the HfO_2/SiO_2 interface at the LDA level have also been performed by Sharia *et al.* showing that the valence band offset is highly dependent on the interface stoichiometry.[17] Using our G_0W_0 correction for SiO_2 (−1.9 eV) and for HfO_2 (−0.5 eV close to the value of Grüning *et al.*[6] of −0.4 eV), the LDA band offset is reversed producing a VBO_2^{GW} of −1.0 eV. This is qualitatively and quantitatively in good agreement with XPS measurements[13] of 1.05 ± 0.1 eV.

The TiN/HfO_2 interface is the final interface of the stack. Constructing this interface requires a specific procedure because of the large lattice mismatch. First, a slab of 6 layers of monoclinic HfO_2 surrounded by vacuum oriented in the direction perpendicular to the (001) plane containing three unit cells in the [100] direction and one unit cell in the [010] direction was generated. During molecular dynamic simulations, several TiN layers were successively added to the surface. We found that the positions of the interfacial

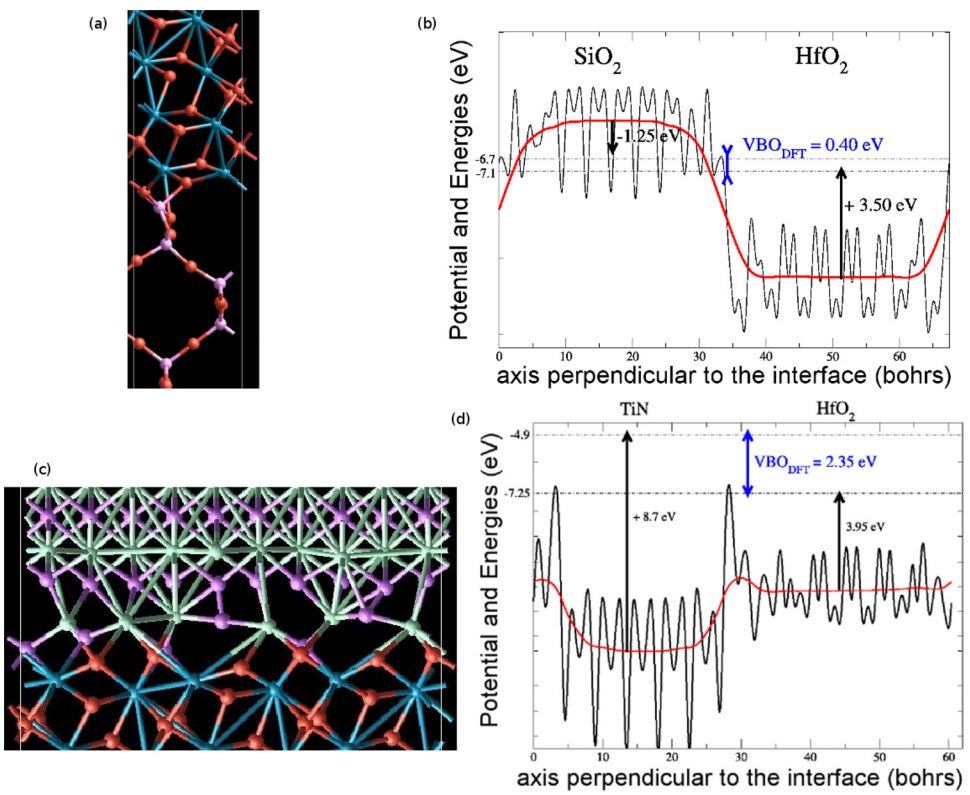

FIG. 1. (Color online) O rich SiO_2/HfO_2 interface (a) and nitridized TiN/HfO_2 interface (c): N in purple, Ti in turquoise, Hf in blue, Si in pink, and O in red. Potential projected along the HfO_2/SiO_2 (b) and the TiN/HfO_2 (d) superlattices (black line) and smoothed by a double convolution (red line). The black arrows indicate the shifts of the eigenenergies with respect to the averaged potential in the bulk. The blue arrow indicates the VBO^{LDA}.

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TABLE I. Valence band (VBO) and conduction band (CBO) offsets with the resulting effective work function. The sign of the band offset is positive when the VBM of the material on the left is above the VBM of the material on the right.

	Si/SiO_2			HfO_2/TiN			
Interfaces	O rich	O poor	SiO_2/HfO_2	Nitridized	Oxidized	Si/TiN	W_{eff} (TiN)
VBO(LDA)	+3.0	+2.8	+0.4	−2.4	−2.5	[+0.7, +1.0]	[5.9, 6.2]
VBO(G_0W_0)	+4.3	+4.1	−1.0	−3.3	−3.4	[−0.3, 0.0]	[4.9, 5.2]
CBO(G_0W_0)	−3.2	−3.4	+1.6	+2.7	+2.6	[+0.8, +1.1]	

atoms from TiN were influenced by the underlying HfO_2 slab arranging themselves in almost the same structure as the oxide (at ± 0.3 Å of the atom sites). Thanks to this observation, when we constructed our TiN/HfO_2 stack model, the Ti atoms at the interface were placed in the sites of the hafnium and the nitrogens in the oxygen sites. The stack was finalized by adding a face-centered-cubic TiN slab oriented with the (111) surface plane on top of the interfacial TiN layer, which minimizes the mismatch between the slabs. Indeed, it has been pointed out experimentally that the (111) growth direction lowers the film strain.[18,19] In our case, the TiN is 1.8% stretched out in the $[1\bar{1}0]$ direction and 0.5% compressed in the $[11\bar{2}]$ direction and contained 6 TiN layers expanded by 1% in the [111] direction in order to keep the average electronic density of the TiN bulk. Two types of interfaces were computed: one "nitridized" with oxygen sites of HfO_2 substituted by N at the interface (Figure 1), the second "oxidized," with six O replacing the six N at the interface. The VBO_3^{LDA} obtained for these two interfaces are −2.4 eV (Figure 1) and −2.5 eV, respectively. Previous DFT calculations have been done on TiN/HfO_2 stacks but cannot be compared with ours since they were computed in the generalized gradient approximation.[20] The quasiparticle correction to the LDA Fermi energy of TiN was calculated to be $\delta\epsilon_v^{GW-LDA}(TiN) = +0.4$ eV.

The valence band alignments along the whole stack at the LDA and G_0W_0 levels where

$$VBO_{ms} = VBO_1 + VBO_2 + VBO_3 \quad (3)$$

are depicted in Table I. Also included in Table I are the conduction band alignments calculated by using our G_0W_0 band gaps for Si (1.1 eV), SiO_2 (8.6 eV), and HfO_2 (6.0 eV). The VBO_{ms}^{LDA} ranges between −1.0 eV and −0.7 eV depending on the chemistry of the interfaces which would correspond to a work function of between 6.2 eV and 5.9 eV. This is in qualitative disagreement with the experimental W_{eff} which is usually equal to or below 5 eV. It is worthy of note that in order to calculate the VBO between the two materials on the extremities of the stack one only needs to compute the GW energies for the top and the bottom slabs because for the intermediate slabs the corrections vanish yielding,

$$VBO_{ms}^{GW} = VBO_{ms}^{LDA} + \delta\epsilon_v^{GW-LDA}(Si) + \delta\epsilon_v^{GW-LDA}(TiN). \quad (4)$$

VBO_{ms}^{GW} ranges from 0.0 eV to 0.3 eV depending on the chemistry of the interfaces, and one finally obtains an *ab initio* W_{eff} evaluated in the MBPT framework ranging from 5.2 eV to 4.9 eV (i.e., P+ in jargon of the semiconductors industry). The W_{eff} for (111) oriented TiN is in agreement with those measured during cold growth process which mostly does not modify the TiN stoichiometry.[1,21] We also point out that the GW corrections applied with a coherent methodology are mandatory in order to obtain qualitatively correct results for the evaluations of VBOs and W_{eff} in a MOS stack.

We think that our results can be used to adjust the parameters of the model used to simulate the whole MOS device. Second, by comparing our "ideal" model system (no defects and a perfect stoichiometry) with the dispersion of the experimental values (from 4.2 to 4.9 eV) assessed by C-V measurements,[1,22] we think that our values can be used as a reference to study the impact of the fine chemistry in such a gate stack. Finally, in this paper, we show that the W_{eff} is an accessible and reliable *ab initio* quantity and that this type of calculation is promising to help the understanding of the W_{eff} for nanodevices in microelectronics.

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