Effective work-function tuning of $TiN/HfO_2/SiO_2$ gate-stack; a density functional tight binding study

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***Abstract*—In this work, density functional tight binding (DFTB) calculations are used to study the characteristics of full gate stack $TiN/HfO_2/SiO_2/Si$ and possible effective work-function (EWF) tuning options. First, the DFTB parameterization method to produce both electronic and repulsion information for all atom pairs is introduced briefly. Since the simulated gate-stack structure has thousands of atoms, conventional relaxation methods are computationally intensive. Hence a method to relax and passivate the material interfaces is introduced. Next, the impact of aluminum substitution is studied. It is shown that the change in EWF strongly depends on the atom which is substituting Aluminum; e.g. Aluminum substitutions of Hf and Ti show opposite impact on EWF. Finally, the origin of this different behavior is discussed.**

***Index Terms*—Gate stack, density functional tight binding, DFTB, work-function**

I. Introduction

Shrinking transistor dimensions has pushed electronic industry toward transistor structures with better gate control like FinFETs and gate all around (GAA) FETs [1]. The 3D feature of these devices requires very tight control on the height of gate stack. On the other hand, designers need multi-Vth options for target performance. Additionally, reliability, leakage, and process compatibility requirements drastically limit the material choice of gate stack [2, 3, 4]. Taking all these considerations into account, the metal-barrier system of Al and TiN has been matured and optimized for successive generation of high-k/metal gate [2, 3, 5, 6]. To understand EWF engineering of the gate-stacks in atomistic level and under applied bias (e.g. non-equilibrium), density functional tight binding (DFTB) method is one of the best candidates; DFTB has proper transferability for material interfaces and computational efficiency for large structure simulation and allows fine-tuning of material properties like band gap and dielectric constant towards experimental values. Moreover, DFTB is based on LCAO (linear combination of atomic orbitals) and hence suitable for non-equilibrium simulations.

Here, we investigate different configurations for Aluminum dopants and their impact using DFTB. The simulation structure is shown in Fig. 1 including 2000 atoms. Such simulation requires DFTB parameter generation and structure relaxation, explained in first and second sections. The impact of Aluminum dopants on EWF is discussed in the last section.

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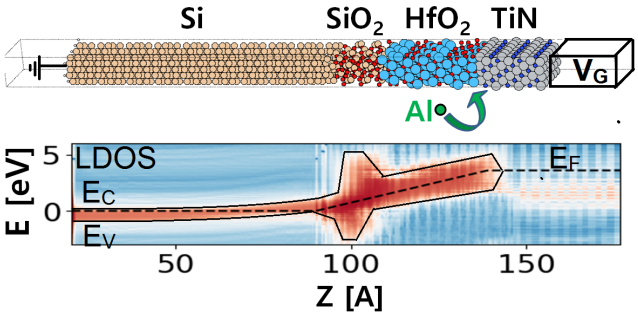

Fig. 1. Atomistic structure of gate stack including about 2000 atoms and corresponding LDOS under applied gate bias.

II. DFTB Parameterization

The computational efficiency of DFTB arises from the fact that all coupling and overlap integrals are pre-calculated and stored in files. Hence, at runtime, program only needs to read the corresponding DFTB file to find the coupling and overlap matrix elements. To produce the Slater-Koster tables, the Kohn-Sham equations should be solved for each atom type. Since, wave-function of single atom can be spatially extended, a confining potential is used usually to truncate the wave-functions. The shape of this confining potential can be used to fine tune the electronic properties toward reference system. We use an in-house DFTB parameterzation tool which takes a set of materials as target environment and tunes the confining potential for each atom such that the resulting DFTB band-structure fits the target bandstructure from experimental results or DFT calculations. To use DFTB for geometry relaxation, one needs to calculate repulsion potential. The repulsion

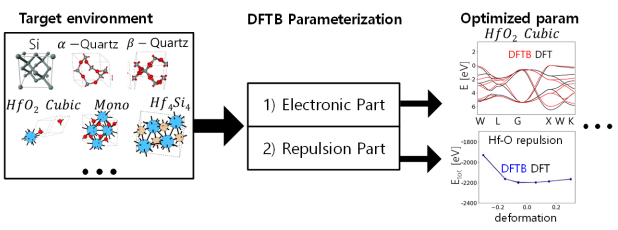

Fig. 2. Parameterization procedure for a target environment.

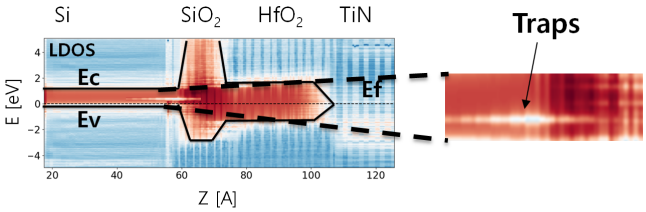

Fig. 3. Appearance of interface trap states without the passivation-relaxation procedure in Fig. 4.

potential is optimized such that the total energy curves for different deformations of materials in environment match the reference values.

The target environment is composed of bulk materials which include atom pairs in different configurations: Al, AlN, Al_2O_3, Hf (hcp), HfO_2 (monoclinic and cubic) Si, SiO_2 (alpha and beta), Ti, TiN, HfN, HfSi, Si_3N_4.

A. Poisson-DFTB Method

Usually DFTB II is used for self-consistent DFTB calculations [7]. However, the boundary conditions for gate contact cannot be applied in DFTB II. To overcome this problem, DFTB I method is solved self-consistently with Poisson equation. It is easy to prove that in the case of Neumann boundary condition, these two methods are equivalent.

$$(H_0 + V^M S)\psi = ES\psi \tag{1}$$

$$\nabla^2 V = \frac{\rho}{\epsilon_0} \tag{2}$$

Notice that H_0 and S are constructed using the Slater-Koster tables obtained from DFTB parameterization. V^M is a matrix obtained from potential V with matrix elements $V^M_{i,j} = 0.5(V_i + V_j)$ where V_i is potential at atom i. Moreover, since all valence electrons are considered in this method, the polarization is induced by electron transfer and hence ϵ_0 is used for everywhere.

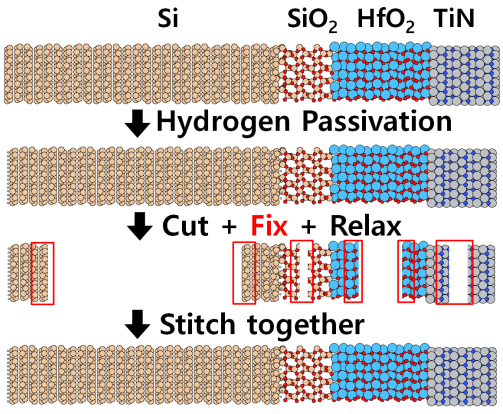

Fig. 4. Steps of efficient passivation-relaxation procedure.

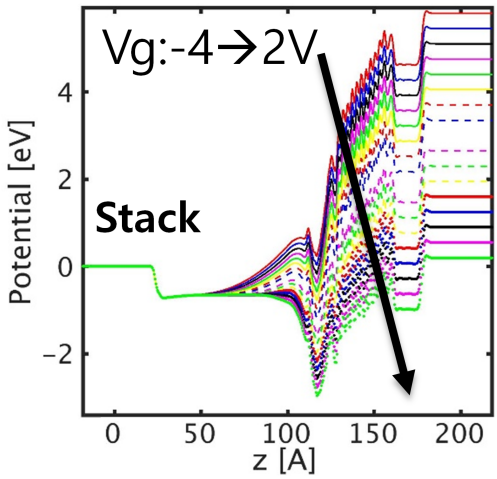

Fig. 5. Potential profiles for gate voltage sweep. The difference between potential of gate stack with Aluminium dopants and without them.

B. Relaxation Method

The simulated gate structure contains about 2000 atoms. Relaxation of complete structure is computationally intensive. Here, a method is developed to relax structures efficiently without losing too much accuracy. The method is based on the fact that the chemical bonds and forces are local in nature. Hence, far from the interfaces, atoms do not distort significantly. Without correct passivation and relaxation, the interface states appears and may affect the results. Such issue is shown in Fig. 3 which results in screening electric field. The interface states study is important, but out of scope of this work. The procedure is shown in Fig. 4 and has following steps: 1) Initial structure is generated such that the strain is in acceptable range, 2) dangling bonds at interface are passivated with Hydrogen atoms, 3) Atoms far from interfaces are removed, boundary atoms are fixed and the rest are relaxed using DFTB or DFT, 4) stitch back all together.

C. Results

Fig. 5 shows the potential profile for different gate voltages of the gate stack without Al atoms. The depletion and inversion regimes are clear from the depth of electric field penetration into the silicon channel. To investigate the impact of Al dopants, we replace Hf or Ti atoms at the HfO_2/TiN interface with Aluminum atoms and repeat the procedure to relax the structure. The relaxed structure is simulated under same gate bias conditions.

The potential and charge outputs of Al substitution of Hf atoms are shown in Fig. 6. Notice that the potential difference between gate stack with and without Al atoms are shown, hence there is no atomic level variation of potential. The induced dipole due to Al substitution of Hf atoms moves the band diagram in silicon towards p-type. Moreover, increasing the concentration of Al dopants results into linear increase of induced dipole.

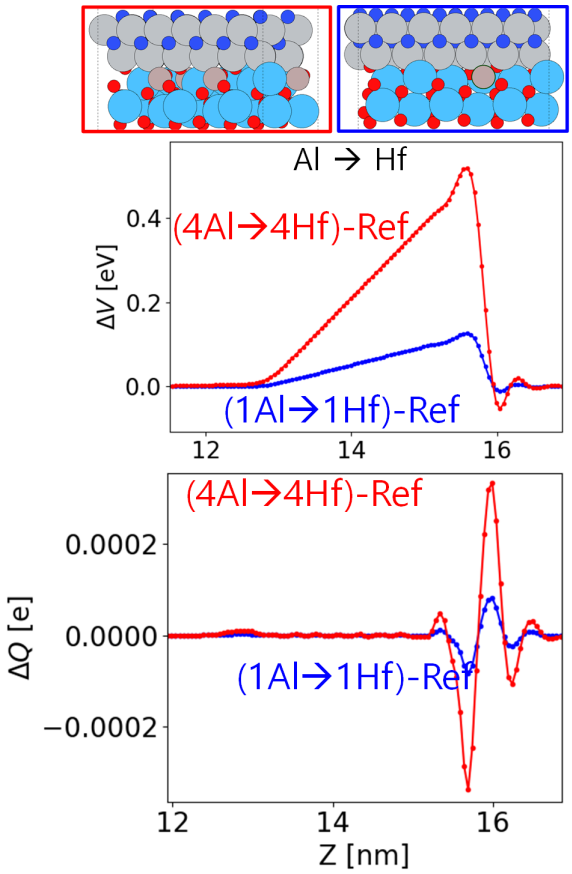

Fig. 6. The potential and charge outputs of Al substitution of Hf atoms. Potential of gate stack with 4 and 1 Al replacement is compared to the one without any Al atom.

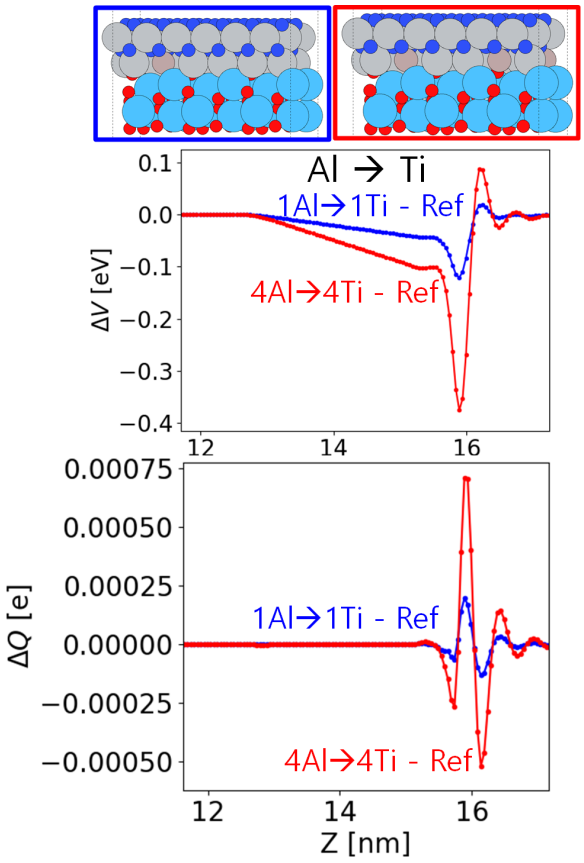

Fig. 7. The potential and charge outputs of Al substitution of Ti atoms. Potential of gate stack with 4 and 1 Al replacement is compared to the one without any Al atom.

Fig. 7 shows the results for Al substitution of Ti atoms at the TiN/HfO_2 interface. Although Ti and Hf are from the same group in periodic table, the Al substitution with these two atoms results to a very different behavior. Al substitution of Ti atoms moves the band diagram in Silicon toward n-type. The origin of this behavior is explained in the next section. Another difference between Hf and Ti atom is that in the latter case, the increase of Al concentration results into a sublinear increase of dipole. Additionally, the magnitude of dipole for Ti substitution is smaller.

Fig. 8 depicts the polarization field as a function of number of dopant atoms within the super-cell. The linear dependence of polarization field on Al substitution of Hf is clear. The main question is that despite the fact that Ti and Hf are from the same group in periodic table, the Al substitution with these two atoms results into a very different behavior. To answer these questions qualitatively, we doped super-cells of HfN and TiN with Al and investigate their work-function change.

The main question which Fig. 8 arises is that what is the cause for difference in Al substitution of Ti and Hf; is this difference related to atom properties (i.e. electronegativity) or material itself. To answer these questions, we have Al doped super cell super cell of TiN and HfO_2. Fig. 9 shows the energy resolved density of states for TiN and HfO_2. Adding Al dopants to these materials results into 2 effects: 1) Reducing the number of valence electrons since Al has one valence electron less than Ti and Hf. 2) Reducing and shifting the density of states. These two effects are competing against each

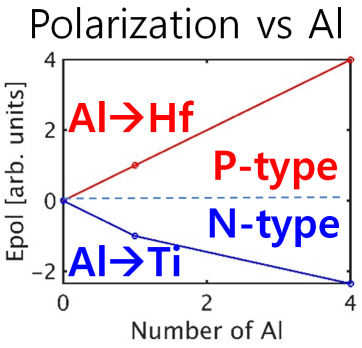

Fig. 8. The polarization electric of field as a function of number of Al substitutions of Ti and Hf atoms at TiN/HfO_2 interface.

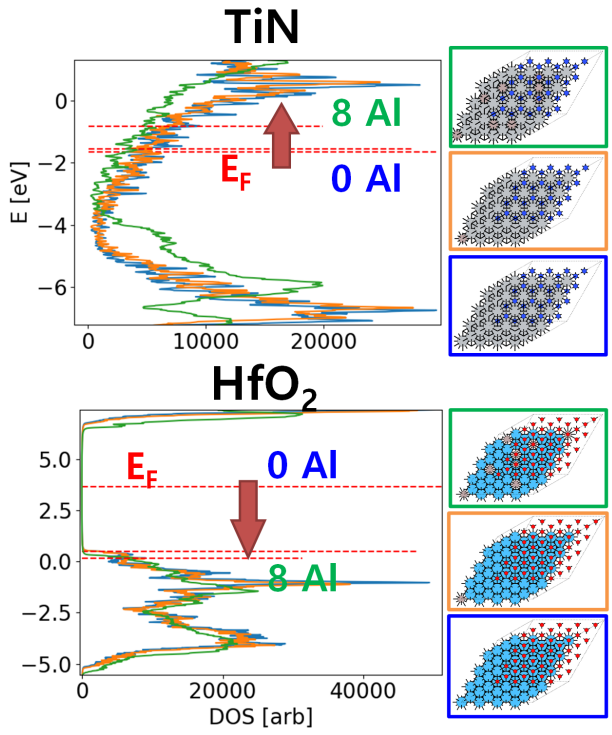

Fig. 9. Energy resolved density of states of TiN and HfO_2 for different amount of Al doping.

other. If DOS does not change significantly, then the reduced number of electrons push material toward p-type. However, if the shift in DOS is significant, then material becomes more n-type.

To make sure if the origin is material related or atom related, we have also doped HfN and TiO_2. Interestingly, Al doping of both HfN and TiN shifts work-function toward n-type, whereas Al doping of HfO_2 and TiO_2 makes work-function p-type. It is apparent that the origin of shift in work-function is more related to material. For metals, such as TiN and HfN, the shift in DOS is much more significant than the reduced number of electrons. Hence, work-function of the metal and Aluminium matters most. However, in the oxides, the change in DOS is negligible and the change in number of electrons determines the shift in work-function.

D. Conclusion

In summary, a computationally efficient approach to study gate stack engineering at atomistic level is proposed. The density functional tight binding (DFTB) parameters for the full gate stack TiN/HfO_2/SiO_2/Si are obtained from an in-house tool based on band structure and total energies of reference systems (Al, AlN, Al_2O_3, Hf (hcp), HfO_2 (monoclinic and cubic) Si, SiO_2 (alpha and beta), Ti, TiN, HfN, HfSi, Si_3N_4). Moreover, an efficient method to relax and passivate the material interfaces is introduced. Using this infrastructure, the impact of aluminum substitution of Ti and Hf atoms at TiN/HfO2 interface and the origin of its difference is studied.

REFERENCES

[1] M. Salmani-Jelodar et al., "Design Guidelines for Sub-12 nm Nanowire MOSFETs," in IEEE Transactions on Nanotechnology, vol. 14, no. 2, pp. 210-213, March 2015. doi: 10.1109/TNANO.2015.2395441

[2] A. Veloso et al., "Process control and integration options of RMG technology for aggressively scaled device," in Proc. Symp. VLSI Tech. Dig., pp. 33-34. 2012.

[3] A. Veloso et al., "Effective Work Function Engineering for Aggressively Scaled Planar and Multi-Gate Fin Field-Effect Transistor-Based Devices with High-k Last Replacement Metal Gate Technology," Jpn. J. Appl. Phys., Park 1 52, 04CA02, 2013.

[4] M. Salmani-Jelodar et al., "Optimum high-k oxide for the best performance of ultra-scaled double-gate MOSFETs" IEEE Transactions on Nanotechnology, vol. 15, no. 6, pp. 904-910, Nov. 2016. doi: 10.1109/TNANO.2016.2583411

[5] Chen, Y. W., et al. "Effective Work Function Modulation by Aluminum Ion Implantation on Hf-Based High-k/Metal Gate pMOSFET." IEEE EDL 31.11 (2010): 1290-1292.

[6] Singanamalla, R., et al. "Effective Work-Function Modulation by Aluminum-Ion Implantation for Metal-Gate Technology (Poly-Si/TiN/SiO_2)." IEEE EDL 28.12 (2007)

[7] Elstner, Marcus, et al. "Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties." PRB 58.11 (1998): 7260.