Change Work Function of W by Change Surfaces and Incorporation of Oxygen

Yu-Jen Cheng

Department of Electrical Engineering of National Taiwan University

Chih-I Wu

Advisor

Graduate Institute of Electro-Optical Engineering & Department of Electrical Engineering of National Taiwan University

Abstract

Nowadays, a new technology High-k is introduced to CMOS fabrication technology for smaller and smaller CMOS. We need to use metal gate with High-k to conquer some problems. And we need to change metal's work function in order to align with NMOS and PMOS. We will calculate W in different surfaces and W which surface being oxidized. We will use LDA in our calculation. After that, we found that oxidation can get the work function difference we need in metal gate.

We first make a brief introduction to High-k, and then metal gate. After that, we will introduce to DFT and LDA. Then we will show our calculation and analyze the result. Finally, we will estimate the feasibility using different surfaces and oxidation to change the work function of metal gate, and the accuracy of simulation by LDA.

High-k

When MOS is fabricated smaller and smaller, gate leakage will become a big problem. Gate oxide capacitance can be found as:

$$C = \varepsilon_{ox} A / t$$

Where C is the oxide capacitance, ε_{ox} is the dielectric constant of silicon oxide, A is the area, t is the thickness of gate.

When A becomes smaller, if we want to have the same C, we must use smaller t because A is in the order of length square but t is in the order of length. Smaller t will induce a leakage current due to the tunneling effect. Therefore, we use High-k material instead of silicon oxide to get a larger ε which will give us the same C with a larger t.

Metal gate

Metal gate means that gate in MOS is made by metal. Gate was originally made by metal. Yet nowadays people use highly doped polysilicon instead of metal to reduce cost. Because polysilicon is easier to manufacture and can be manufactured under lower temperature. However, polysilicon has some disadvantages.

1. There is a poly gate depletion effect which will reduce the effective gate voltage.

2. It has much higher resistance than metal.

3. Having poor thermodynamic stability.

4. Easily be oxidized at the interface with gate oxide.

5. Threshold voltage pinning caused by defect at the interface.

Points 4 and 5 are extremely severe in high-k materials, and can be solved by metal gate. Moreover, metal gate can reduce the mobility degradation problem in high-k material by screening the surface optical phonon. So people start to find metals which fit high-k material. High-k with metal gate technology has been used in Intel's 45nm technology node.

Change work function of metal

We want to change the work function of metal to get the work function we need. The goal is we can get two work functions, one fits NMOS which is about 4 eV and one fits PMOS which is about 5 eV. Thus we do not need two different materials so can reduce cost and complexity.

Different surfaces and incorporation of oxygen

There are many ways to change metal's work function. We will research different surfaces of metal and surfaces incorporate with oxygen. We will calculate different work functions of W(211), W(110), W(100), W(111) and oxide coated W(211), W(110). We calculate by Material Studio CASTEP with LDA and we will consider surface reconstruction.

DFT[1][2]

Traditional method in electron structure theories such as Hartree-Fock theory is based on multi-electron wave functions which depend on the 3N spatial coordinates and spin configurations of N electrons. DFT (Density Functional Theory) is an approach that reduces the multi-electron wave functions to electron density which

depends only on three spatial coordinates. Moreover, the correlation of electron motions is included in DFT.

DFT can be calculated by Hohenberg and Kohn Theorem[3]:
The total energy and all observable information of a system are uniquely defined by the ground-state electron density:

$$E[\rho(r)] = \int V(r)\rho(r)dr + F[\rho(r)] \quad \text{---(1)}$$

F[ρ(r)] : Kinetic energy and inter-electron energy. It is the universal function which has not be found, so we use approximation.
V: external potential, that is, Coulomb interaction with the nuclei

LDA[1][2]

We use LDA (Local Density approximation) to calculate energy. LDA is an approximation of F[ρ(r)] used in DFT. LDA was first formulated by Kohn and Sham in 1965[4]. LDA assumes charge density changes slowly and can be approximated uniformly. And surprisingly it can be used in a system when inhomogeneous electron distributions are considered. Therefore, we can use local charge density to approximate all the systems.
The LDA universal function is

$$F[\rho(r)] = E_{KE}[\rho(r)] + E_H[\rho(r)] + E_{XC}[\rho(r)] \quad \text{---(2)}$$

ρ is the local density at r, E_{KE} is electron kinetic energy, E_H is the Hartree electrostatic energy, E_{XC} is the total exchange correlation energy.
Hartree electrostatic energy E_H is

$$E_H[\rho(r)] = \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|}drdr' \quad \text{--(3)}$$

And we have the total exchange correlation energy E_{xc} to be

$$E_{XC}[\rho(r)] = \int \rho(r)\varepsilon_{XC}(r)dr \quad \text{---(4)}$$

ε_{XC} is the local exchange correlation energy function of ρ (calculated per particle).
If we constraint the system to be an N electrons system, we will have

$$\int \rho(r)dr = N \quad \text{--(5)}$$

We substitute E_H in (3) into F[ρ(r)] in (2), and then substitute F[ρ(r)] into DFT equation(1), we can get

$$\int \delta\rho(r)\left\{ \frac{\delta E_{KE}[\rho]}{\delta\rho(r)} + V(r) + \int \frac{\rho(r')}{|r-r'|}dr' + \frac{\delta E_{XC}}{\delta\rho(r)} - \mu \right\}dr \quad \text{----------------------------(6)}$$

where μ is the Lagrangian multiplier equivalent to the chemical potential

Consider wave function theory, we will have:

$$\rho(r) = \sum_{\lambda=1}^{N} |\psi_\lambda(r)|^2 \quad \text{--(7)}$$

So the kinetic energy will be

$$E_{KE}[\rho(r)] = -\frac{1}{2} \sum_{\lambda=1}^{N} \int \psi_\lambda^*(r) \nabla^2 \psi_\lambda(r) dr \quad \text{--(8)}$$

Finally, solving the following Schrödinger equation for ψ_λ will get the solution of (6)

$$\left\{ -\frac{1}{2}\nabla^2 + V(r) + \int \frac{\rho(r')}{|r-r'|} dr' + \frac{\delta E_{XC}}{\delta\rho(r)} \right\} \psi_\lambda(r) = \varepsilon_\lambda \psi_\lambda(r) \quad \text{---------------------------(9)}$$

Where ε_λ is the energy eigenvalue of the λ th state.

We thus can solve wavefunction ψ_λ.

We can see from the theory that LDA is especially suitable for large uniformly distributed system which does not affected by edge discontinuity. So we can use LDA to calculate metal surface.
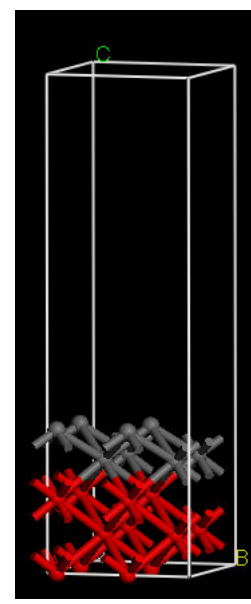
Calculation and Results

We first calculated W(211) with 3x2 surface, 8 layers and W(211) with 2x2 surface, 5 layers. We found out that the results are very close (about 1% difference) and also close to the reference[5]. Because larger scale is time consuming so we use 2x2 surface, 5 layers to do other calculations. The structures are as following:
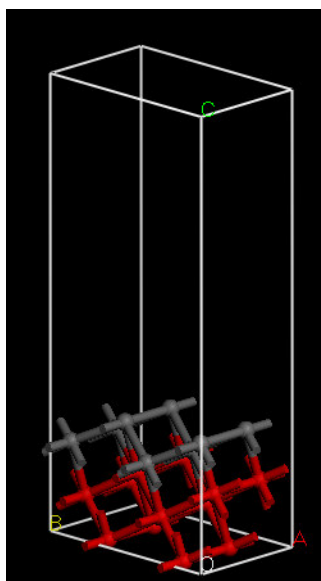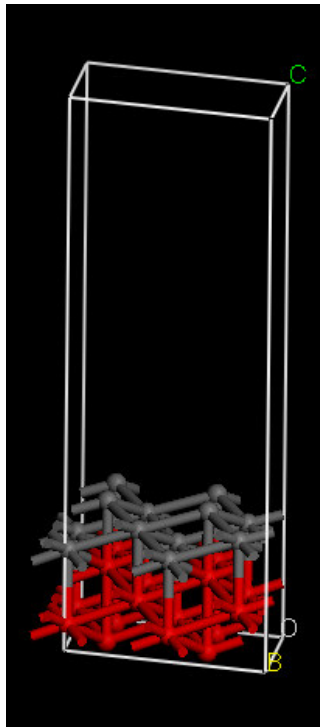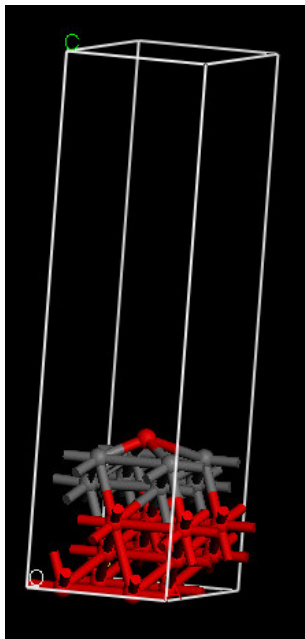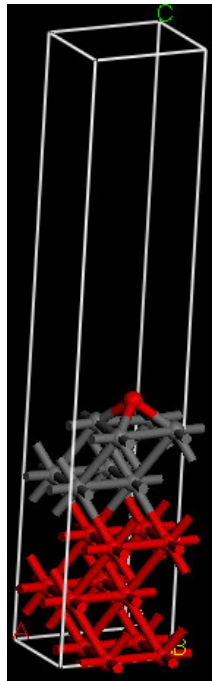

W(211)   W(110)   W(100)
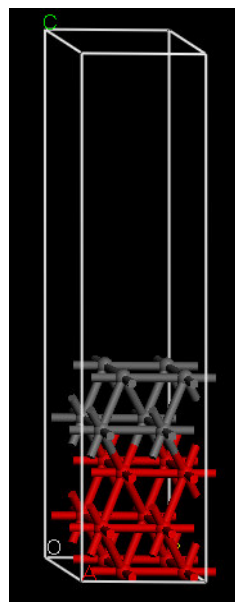
Vacuum levels are set to about 10 angstroms. The gray ones are the atoms which can be slightly moved to get geometrical optimization. The red ones are the atoms which we do not let them move. Doing so is because we simplify the geometric optimization calculation by just considering the atoms near the surface, which will cause surface reconstruction.
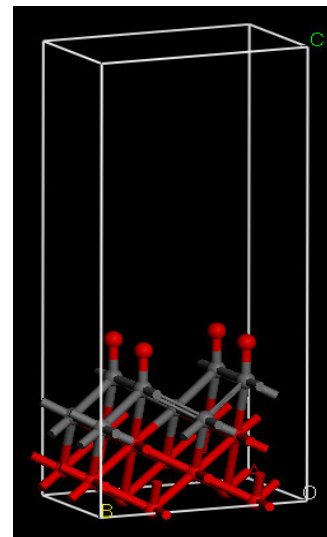
W(111)

We also calculated surface oxidation of W(211) and W(110). We calculated 25% O on W surface and 100% O on W surface separately.
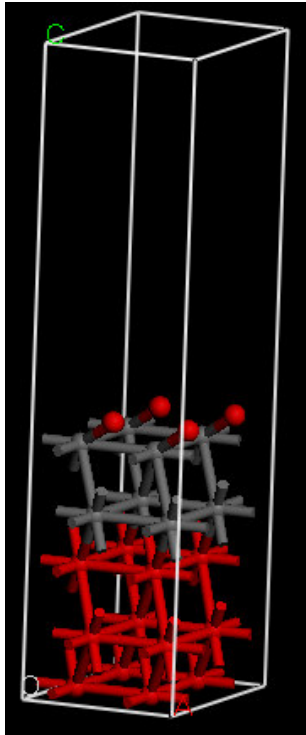

W(211) + 25% O on surface

W(110)+ 25% O on surface

W(211)+100% O on surface

Vacuum levels are set to about 10 angstroms. The gray ones are W atoms which can be slightly moved to get geometric optimization, and the red ones in the bottom are W atoms which we do not let them move. The red ones on the top are O atoms which can be moved to get geometric optimization. We initially put O atoms randomly and the geometrical optimization calculation processes will align O atoms to the place which will have the lowest energy.

W(110)+100% O
on surface

Our results are as following:

type	work function(eV)		
	our simulation	experimental[5]	
		reference	Error
W(211)	4.68	4.76	-1.7%
W(110)	5.11	5.25	-2.7%
W(100)	4.46	4.65	-4.1%
W(111)	4.33	4.47	-3.1%
W(211)+25% O on surface	4.94	N/A	N/A
W(110)+25% O on surface	5.48	N/A	N/A
W(211)+100% O on surface	7.37	N/A	N/A
W(110)+100% O on surface	6.28	N/A	N/A
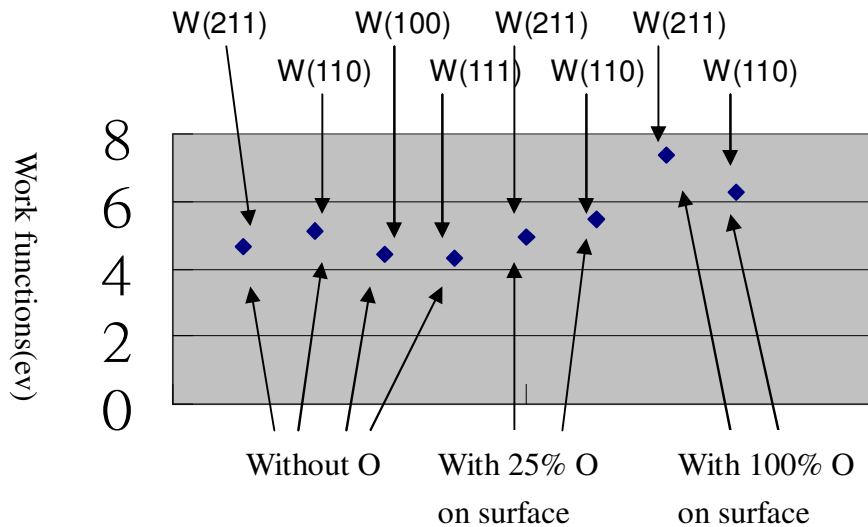
Conclusion

We found out that different surfaces of W(211), W(110), W(100) and W(111) have maximum difference of work functions to less than 0.8 eV. The highest one is W(110) which is larger than 5 eV. Other surfaces have work functions about 4.5 eV. This difference is not enough to coordinate with NMOS and PMOS simultaneously which need about 1 eV difference. Yet the differences are in the reasonable scale, so we may find some surfaces have enough difference in other materials.

We get about 0.3 eV higher work function by put 25% O on W surface. If we choose W(110) with 25% O on surface and W(100) without O, the work function difference is enough to coordinate with NMOS and PMOS separately. However, it is not so suit for the NMOS and PMOS in absolute value. By similar argument, we predict that putting Al on W surface may get a lower work function, and may have the right work function we need. The differences are about 1-2.5eV when we put 100% O on W surface. After incorporation of oxygen, the work function will increase significantly with more oxygen on the surface because W will go from metal to insulator(WO_x) which will lead to higher work function. Yet the work functions of the 100% O ones are not so meaningful because they behave like insulator.

We showed that we can change the work function of metal by incorporation with oxygen and may be used in metal gate technology. The results without incorporation of oxygen are less than 4.1% difference to experimental value, which are surprisingly accurate. This means LDA is a powerful tool in metal work function calculation. We can do LDA simulation before experiment to save time and resources.

References:

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