

### **Abstract**

Thin oxides are used in devices as gate dielectrics. It has been proposed that the current gate oxides be replaced with a high dielectric coefficient oxide, such as  $\text{ZrO}_2$ . In this paper the technique of calculating the equilibrium concentration of point defects by *ab initio* methods will be outlined. As proof of principle, the concentration of various zirconium point defects in silicon will be calculated.

*Ab initio* methods for calculating the  
concentration of point defects in  
semiconductors with application to  
zirconium in silicon.

S P Beckman  
Lawrence Berkeley National Lab  
1 Cyclotron Road Mail Stop 66-332  
Berkeley, CA 94720

November 25, 2002

# 1 Introduction

The metal insulator semiconductor field effect transistor (MOSFET), as shown in figure 1, is extremely important to modern electronic applications. [1] Operation involves imposing a voltage across the gate region,  $v_{gate}$ , that is sufficient to bend the electron bands of the semiconductor in the region near the semiconductor-insulator interface. If  $v_{gate}$  is larger than the threshold voltage,  $v_{th}$ , then the bands bend to the point that the carrier concentration is inverted (the p-type semiconductor becomes n-type) and electrons can flow from the source to the drain.<sup>1</sup> Operation of the gate requires that a critical capacitance exists in the gate oxide so that sufficient charge can build up. The capacitance of plate capacitors is expressed as,  $C = \frac{AK\epsilon_o}{t}$ , where A is plate area,  $\epsilon_o$  is the permittivity of free space, K is the dielectric constant of the insulating material, and t is the thickness of the insulating material.

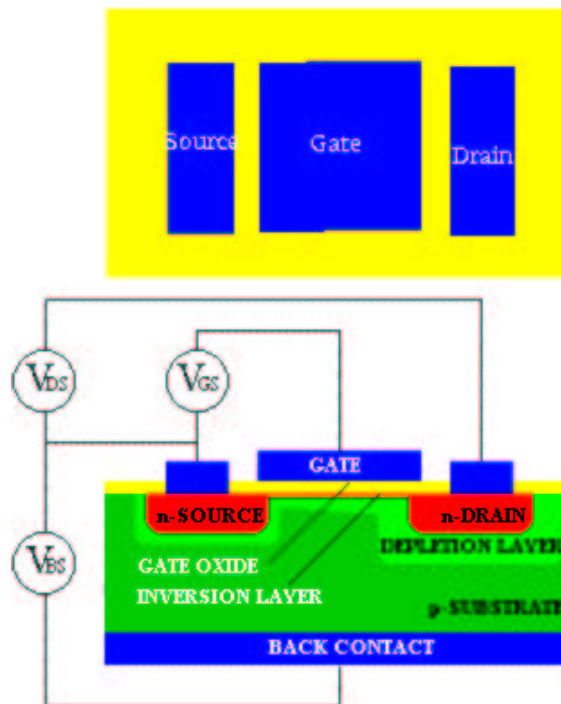


Figure 1: Geometry of MOSFET transistor taken from reference [2].

The drive to miniaturize devices requires a reduction of the area of the gate. To maintain the capacitance while reducing the area requires that the thickness of the oxide be reduced. It has been discovered that once this oxide layer, currently  $\text{SiO}_2$ , becomes thinner than 0.8nm,

---

<sup>1</sup>Current flows from the drain to the source.

the tunnel current through the gate oxide will be sufficient to disrupt operation of MOSFET devices by causing random fluctuations in the  $v_{th}$  value. [3]

It has been proposed to replace the SiO<sub>2</sub> oxide with a higher dielectric material such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>. [4, 5] This would allow the area to be reduced and the capacitance to be maintained without significantly thinning the oxide, thereby avoiding the problem of tunneling. The proposed replacement oxides must have sufficient dielectric coefficient, a low density of defect states at the semiconductor-insulator interface, and be thermally stable. The condition of thermal stability being defined as a low diffusivity of oxide constituents outward and low diffusivity of metal and semiconductor constituents inward, at reasonable temperatures.

A recent article by Quevedo-Lopez [5] investigated the diffusion of hafnium and zirconium in silicon. The results of the study indicated that Hf does not diffuse well into Si whereas Zr does diffuse under “aggressive” thermal annealing. Some have suggested that the problem of diffusion of Zr in Si can be solved by either the application of a diffusion barrier [6] or by the creation of a Si/SiO<sub>2</sub>/ZrO<sub>2</sub> layered structure. [7]

Although it would be desirable to study the diffusion of these point defect by *ab initio* methods, it is a sufficient first step to investigate the concentration of defect atoms in bulk Si. Insight to the mechanism of and barriers to diffusion can be gained by understanding the point defects that exist under various conditions. In this paper the technique used to study, via *ab initio* methods, the equilibrium concentrations of point defects in elemental and compound semiconductors will be presented. As a proof of principle a sample calculation will be performed to investigate the concentration of zirconium in silicon.

The *Formalism* section of this paper will highlight the technical background necessary to perform the calculations. The *Methods* section will discuss the methods used to study Zr in Si. In the *Results* section, the results from the calculations will be presented.

## 2 Formalism

### 2.1 Thermodynamics

The concentration of a particular point defect in a solid is given by the expression  $[D_j] = Ce^{\frac{-G}{k_B T}}$ .  $G$  is the Gibb’s free energy,  $C$  is a prefactor,  $k_B$  is the Boltzmann constant and  $T$  is the temperature. The Gibbs energy is  $G = E_{form} + S_{form}T$  where  $E_{form}$  is the energy of formation and  $S_{form}$  is the entropy of formation.  $S_{form}$  comes about because of the local strain around a defect and has been shown to be negligible compared to  $E_{form}$ . [8] The prefactor  $C$  is the number of sites

in the volume at which the defect can sit. [1, 9] Upon substitution, the concentration of defects can be rewritten

$$[D_j] = N_{sites} e^{\frac{-E_{form}}{k_B T}} \quad (1)$$

## 2.2 Constitutive Equation

The energy of formation of a defect must be calculated relative to a known reference state. The energy of the atomic constituents in isolated reservoirs is used as the reference state. Below is a detailed demonstration of how to construct a constitutive equation to relate the defect energy to the reference state.

### 2.2.1 Elemental Semiconductors

The constitutive equation for the generation of a vacancy in Si is

$$E_{form} = E_{total} - n^{Si} \mu_{Si} \quad (2)$$

$E_{total}$  is the total energy of the system,  $n^{Si}$  is the number of Si atoms in the system and  $\mu_{Si}$  is the chemical potential of a reference reservoir of crystalline silicon. Equation 2 gives the formation energy by subtracting the reference energy of  $n^{Si}$  Si in a perfect crystal from the total energy of the defect system composed of  $n^{Si}$  Si and a vacancy.

### 2.2.2 Compound Semiconductors

The constitutive equation for compound semiconductors is somewhat different than elemental semiconductors because the reference reservoir is taken as a reservoir of the stoichiometric compound. [8, 9, 10] The chemical potentials of the components of the compound can vary according to environmental considerations. [11] Taking GaAs as an example, the chemical potentials of the components are fixed according to

$$\mu_{GaAs} = \mu_{Ga} + \mu_{As} \quad (3)$$

To calculate the energy of formation of a vacancy on a site in GaAs, the constitutive relation is

$$E_{form} = E_{total} - n^{Ga} \mu_{Ga} - n^{As} \mu_{As} \quad (4)$$

Substituting equation 3 yields

$$E_{form} = E_{total} - n^{Ga} \mu_{Ga} - n^{As} (\mu_{GaAs} - \mu_{Ga}) \quad (5)$$

which can be rearranged to

$$E_{form} = E_{total} - n^{As} \mu_{GaAs} - (n^{Ga} - n^{As}) \mu_{Ga} \quad (6)$$

The energy of formation is given relative to a perfect crystal of GaAs, with  $n^{As}$  GaAs molecules. As mentioned above, the value of  $\mu_{Ga}$  can vary according to environmental conditions and the value of  $\mu_{As}$  will change according to equation 3.

The range of allowed values for  $\mu_{Ga}$  and  $\mu_{As}$  is bracketed by formation of bulk Ga or As metals. When  $\mu_{Ga(bulk)} < \mu_{Ga}$  or  $\mu_{As(bulk)} < \mu_{As}$  then the precipitation of elemental solids is preferred to the formation of GaAs. Because the GaAs of the system is in equilibrium with bulk GaAs, equation 3 can be rewritten.

$$\mu_{Ga} + \mu_{As} = \mu_{GaAs} = \mu_{GaAs(bulk)} = \mu_{Ga(bulk)} + \mu_{As(bulk)} + H_{f GaAs} \quad (7)$$

This relation<sup>2</sup> can be used to give the range for  $\mu_{Ga}$  to satisfy equation 6. One limit is given simply by  $\mu_{Ga} = \mu_{Ga(bulk)}$ . For the other limit the value  $\mu_{As} = \mu_{As(bulk)}$  is substituted into the left hand side of 7 and results in  $\mu_{Ga} = \mu_{Ga} + H_{f GaAs}$ . [10] The allowed range for  $\mu_{Ga}$  is  $(\mu_{Ga(bulk)} + H_{f GaAs}) < \mu_{Ga} < \mu_{Ga(bulk)}$ .

### 2.3 Complex Defect: defect atoms and charged defects

The addition of defect atoms can complicate the constitutive equation. Mention of the defect atom must be included in the reference state. For example, to place a single defect atom, say Zr, on a silicon lattice site, equation 2 must be modified to include a term  $-1\mu_{Zr}$ . The allowed range for  $\mu_{Zr}$  can be determined by a method similar to that demonstrated in section 2.2.2. The allowed range for Zr is bracketed by the formation of metallic Zr and the stoichiometric compound ZrSi<sub>2</sub>. So  $\mu_{Zr}$  is bracketed by  $(\mu_{Zr(bulk)} + H_{f ZrSi_2} < \mu_{Zr} < \mu_{Zr(bulk)})$ . In the case that the defect atom is sitting in a compound semiconductor, AB, the compounds A<sub>x</sub>Zr<sub>y</sub>, B<sub>x</sub>Zr<sub>y</sub>, and A<sub>x</sub>B<sub>y</sub>Zr<sub>z</sub> must be compared to determine which phase brackets the allowed value for  $\mu_{Zr}$ .

Charging of the defect is simulated by adding or subtracting electrons from the supercell. The addition or removal of electrons is accounted for by adding or subtracting the energy of electrons from a reservoir of free electron gas. The chemical potential of a free electron gas is the fermi energy of the gas. The value of  $E_{fermi}$  is not an independent variable. The value is solved from the atomic system configuration. It is noteworthy that a higher dopant concentration, such as Zr donors, means a higher  $E_{fermi}$  and thereby a higher energy of formation of dopant atoms, and therefore a lower dopant concentration. This

---

<sup>2</sup>Unlike reference [10], in this paper the heat of formation is added to the constituents instead of subtracted. This is done because the author chooses to define exothermic reactions, such as GaAs and ZrSi<sub>2</sub> (below), as having a negative heat of formation.

negative feedback loop has the consequence that the concentration of dopant defects is *less* sensitive to uncertainties in the formation energy calculations. [11, 9]

The addition of charged defects complicates not only the constitutive equation but also the *ab initio* calculations themselves. Most modern day *ab initio* type calculations are based on pseudopotential-density functional theory methods. [12, 13] The construction is based on a momentum space formalism and the exchange-correlation energy is approximated by the local density approximation. [14] Within these methods it is known that there are two terms in the momentum space formalism that mandate charge neutrality. In addition the local density approximation also requires a charge neutral cell. Van de Walle explains in reference [15] the modifications to modern *ab initio* software necessary to accurately calculate energies of charged supercells. The details will not be presented here.

### 3 Method

As proof of principle a few sample calculations will be performed to approximate the concentration of Zr point defects in Si.

The total energies are computed using the ultrasoft pseudopotential formalism embodied in the Vienna *Ab-Initio* Simulation Package (VASP). [16, 17] The atoms will be allowed to relax into a minimum energy configuration using a conjugate gradient method. The changes discussed in reference [15] to allow for the calculation of charged defects are non-trivial considering the time limitations for this project. Only neutral defects will be examined.

It will be assumed that the ultrasoft pseudopotentials [18] provided by VASP are sufficiently accurate for the atomic configurations in the system. Periodic boundary conditions are employed and a basis of 64 Si atoms will be used in the calculation. It will be assumed that a 64 atom basis will be sufficient in size to isolate the point defects through the periodic boundaries. [15] Sampling of k-space will be performed by a Monkhorst-Pack scheme [19] and it will be assumed that a mesh of 2x2x2 k-points will be sufficient to accurately determine the energy of the system. [15] For a more definitive calculation, these conditions can not be assumed but must be determined by convergence tests.

The constitutive relation used for Zr neutral substitutional and interstitial defects are given in 8 and 9 and the range for  $\mu_{Zr}$  is given in 10

$$E_{form\ sub} = E_{total} - 63\mu_{Si} - 1\mu_{Zr} \quad (8)$$

$$E_{form\ inter} = E_{total} - 64\mu_{Si} - 1\mu_{Zr} \quad (9)$$

$$(\mu_{Zr\ (bulk)} + H_{f\ ZrSi_2}) < \mu_{Zr} < \mu_{Zr\ (bulk)} \quad (10)$$

## 4 Results

In the table below are listed the parameters used in the calculation and the results.

Parameter	Value	Source
$a_{cubic}$	$5.387(10^{-10})\text{m}$	calculated
$\mu_{Si}$	$-5.971 \text{ eV/atom}$	calculated
$\mu_{Zr (bulk)}$	$-9.362 \text{ eV/atom}$	calculated
$H_f_{ZrSi_2}$	$-12.7 \text{ kcal/mol} = -0.551 \text{ eV/molecule}$	reference [20]
$N_{substitution}$	$8/a^3 = 5.12(10^{22})\text{cm}^{-3}$	
$N_{tetrahedral}$	$4/a^3 = 2.56(10^{22})\text{cm}^{-3}$	
$N_{octahedral}$	$3/a^3 = 1.92(10^{22})\text{cm}^{-3}$	
$E_{total sub}$	$-382.684\text{eV}$	calculated
$E_{total tet}$	$-389.894\text{eV}$	calculated
$E_{total oct}$	$-389.896\text{eV}$	calculated
$E_{f sub}$	$-6.51 - \mu_{Zr}$	
$E_{f tet}$	$-7.75 - \mu_{Zr}$	
$E_{f oct}$	$-7.752 - \mu_{Zr}$	

The energy to form a substitutional Zr point defects is approximately 2.8eV and the energy to form interstitial defects is 1.6eV. The error of energies calculated by VASP is on the order of  $1(10^{-2})$ . Ignoring the possible error introduced by the assumptions, one can approximate the error of these  $E_f$  energies to be 0.6eV.

These results are of a believable magnitude although one may expect slightly higher  $E_f$  values. Maroudas and Brown calculated, via EAM potential, the energy of formation for silicon vacancy, self-substitution, and self-interstitial<sub>tet</sub> defects to be 2.66eV, 3.09eV, and 4.84eV respectively. [21] Within the present context there is insufficient information to explain why the calculated energy of formation for Zr substitutional defects is lower than Maroudas's energy of formation for vacancies. A more detailed investigation should yield clues to determining if there is a failure in one of the assumptions from section 3 or if this discrepancy in results is indicative of the shortcomings of EAM methods.

From the results above the equilibrium concentrations of Zr point defects are plotted in figures 2. From the Arrhenius plot, it is apparent that in the Zr rich limit ( $\mu_{Zr} = \mu_{Zr (bulk)}$ ) the concentration of defects is slightly higher. At low temperatures the number of interstitial defects dominates the overall number of Zr defects, but this difference in concentration decreases with increasing temperature. A cross-over in concentration occurs at around 5000K, a temperature much higher than the melting point of silicon. It is therefore expected that for all temperatures the concentration of Zr interstitials will be greater than that of substitutional Zr.

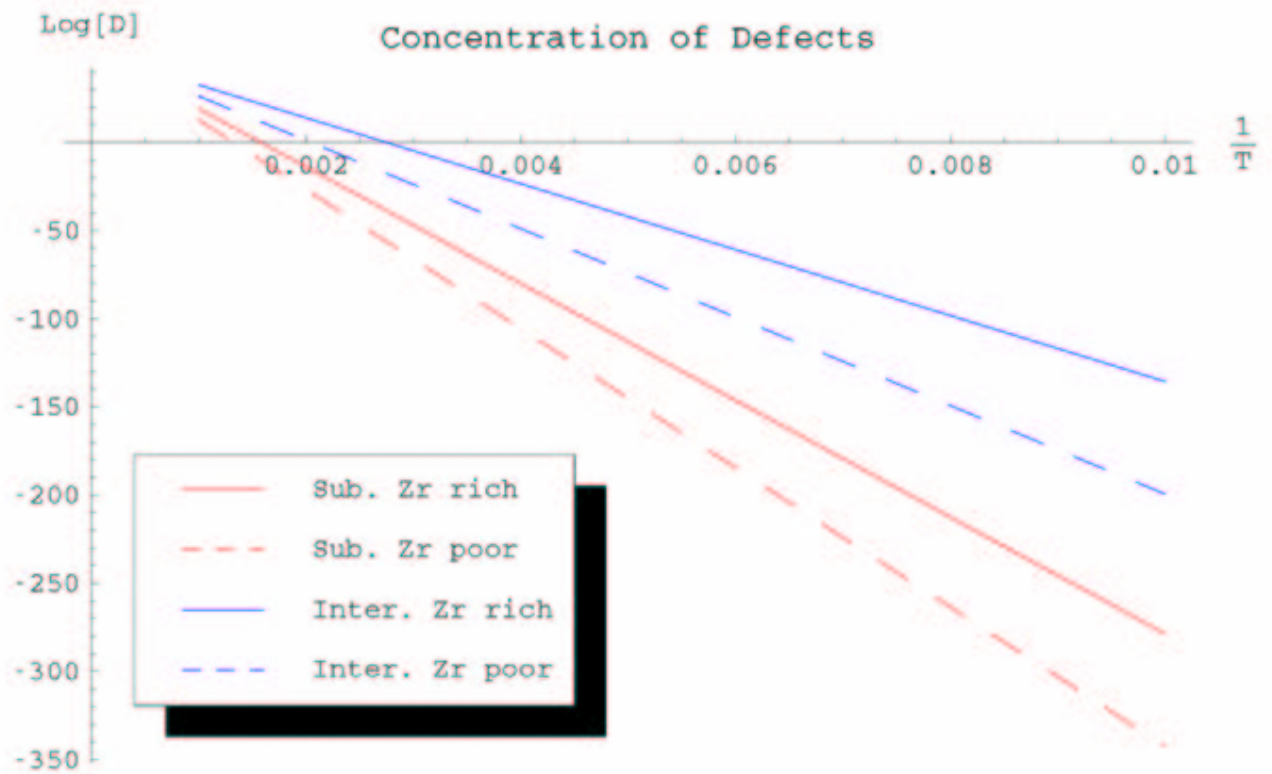


Figure 2: The concentration of zirconium substitutional and interstitial defects in silicon as a function of temperature for Zr rich and Zr poor environments.

## References

- [1] E. E. Haller, Reading Materials for: MSE223 Semiconductor Materials (2002).
- [2] B. V. Zeghbroeck, Principles of Semiconductor Devices, <http://ece-www.colorado.edu/~bart/book/book/>, 2002.
- [3] M. Koh *et al.*, IEEE Transactions on Electron Devices **48**, 259 (2001).
- [4] K. Cho, Computational Materials Science **23**, 43 (2002).
- [5] M. A. Quevedo-Lopez *et al.*, Journal of Applied Physics **92**, 3540 (2002).
- [6] C. H. Lee *et al.*, in *International Electron Devices Meeting 2000.*, IEEE (IEDM, Piscataway, NJ, USA, 2000).
- [7] C. M. Perkins *et al.*, Applied Physics Letters **81**, 1417 (2002).
- [8] D. B. Laks, C. G. V. de Walle, G. F. Neumark, and S. T. Pantelides, Physical Review Letters **66**, 648 (1991).
- [9] C. G. V. de Walle, D. B. Laks, G. F. Neumark, and S. T. Pantelides, Physical Review B **47**, 9425 (1993).
- [10] G.-X. Qian, R. M. Martin, and D. J. Chadi, Physical Review B **38**, 7649 (1988).
- [11] S. B. Zhang and J. E. Northrup, Physical Review Letters **67**, 2339 (1991).
- [12] D. R. Hamann, M. Schlüter, and C. Chiang, Physical Review Letters **43**, 1494 (1979).
- [13] W. Kohn and L. J. Sham, Physical Review **140**, A1133 (1965).
- [14] J. Ihm, A. Zunger, and M. L. Cohen, Journal of Physics C: Solid State Physics **12**, 4409 (1979).
- [15] C. G. V. de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, Physical Review B **39**, 10791 (1989).
- [16] G. Kress and J. Fürthmüller, Physical Review B **54**, 11169 (1996).
- [17] G. Kress and J. Fürthmüller, Computational Material Science **6**, 15 (1996).
- [18] G. Kresse and J. Hafner, Journal of Physics: Condensed Matter **6**, 8245 (1994).

- [19] H. J. Monkhorst and J. D. Pack, *Physical Review B* **13**, 5188 (1976).
- [20] T. Yamauchi *et al.*, *Journal of Applied Physics* **69**, 7050 (1991).
- [21] D. Maroudas and R. A. Brown, *Physical Review B* **47**, 15562 (1993).