Predictive Process Simulation and Ab-initio Calculation of the Physical Volume of Electrons in Silicon

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ABSTRACT

Recently, we have presented the development of a complete predictive simulation capability for the effects of general anisotropic nonuniform stress on dopant diffusion in silicon [M. Laudon, N. N. Carlson, M. P. Masquelier, M. S. Daw, and W. Windl, Appl. Phys. Lett. **78**, 201 (2001)]. As a by-product of these calculations, we calculated a physical volume of 15 Å^3 for electrons in Si from first-principles which is the topic of the present paper. It is argued that the physical electron volume that we have calculated for the silicon solid can be considered to represent a lower boundary for the effective size of semiconductor electrons that needs to be taken into account in quantum transport simulations.

Keywords: semiconductor, stress-mediated diffusion, ab-initio calculations, electron size

1 INTRODUCTION

The silicon-based metal oxide semiconductor field effect transistor (MOSFET) is at the heart of today's semiconductor industry. Because the switching speed of a MOSFET increases linearly with shrinking dimensions, the semiconductor industry has constantly improved computer performance by scaling a more or less unchanged device geometry. Despite the successful history of device miniaturization, scaling is reaching the physical limits of traditional device materials. With the reduction of gate lengths and the use of more exotic materials such as metal gates, to date negligible effects such as dopant deactivation or the influence of stress on diffusion become more important in determining the final dopant profile and subsequent device performance.

Recently, we have presented the development of a complete predictive simulation capability for the effects of general anisotropic nonuniform stress on dopant diffusion in silicon [1]. We derived the macroscopic-diffusion equation from microscopic-transition state theory, calculated the microscopic parameters from first principles, and predicted the feature-scale stress based on stress measurements in the relevant materials as a function of temperature. We used the developed methodology, implemented in a continuum solver, to investigate a titanium nitride (TiN) metal gate system.

As a by-product of these calculations, we calculated a physical volume for electrons in Si from first-principles, which is the topic of the present paper.

2 MULTISCALE MODELING

Simulation of front-end processing is becoming an increasingly critical cost and time-saving component of integrated-circuit technology development, provided it is accurate enough. In addition, today's electronics are so small that characterization of their material parameters is in many cases difficult and expensive. Thus, simulation is often the only effective tool for exploring the lateral and vertical doping profiles of a modern device at the level of detail required for optimization.

Process simulation is being performed more and more by multiscale modeling, using a hierarchy of tools. Ab initio and molecular-dynamics codes generate insight into the physics of mobility and reactions of atoms in the silicon lattice. This information then serves as input into higher-level modeling such as kinetic-lattice Monte Carlo codes (to establish critical mechanisms where they are not obvious) and traditional continuum codes, which are used for production runs.

Such predictive and physical modeling is an extremely important asset for advanced semiconductor development. As an example, Motorola has aggressively built a predictive-modeling group in the past few years, resulting in highly predictive tools such as MD-based implant simulation with the REED (Rare Event Enhanced Domain) MD code [2] or ab initio-based diffusion simulation [1], [3], [4]. In the following section, we summarize a multiscale methodology that simulates diffusion under the previously mentioned metal gate systems, which is strongly influenced by stress effects and therefore needs a combination of mechanical and traditional process-modeling tools.

3 FORMATION VOLUME TENSORS AND ELECTRON VOLUME

Isotropic diffusivities of defects and impurities are usually expressed within an Arrhenius form, derived from harmonic transition-state theory, $D = D_0 \exp\left[-E_0/(kT)\right]$. Under stress, both the diffusion prefactor, D_0, and the

activation energy, E_0, can change according to the applied stress. If the stress is anisotropic, the isotropic diffusion behavior, which is usually observed in cubic crystals like silicon, is disturbed and a fully anisotropic diffusion tensor needs to be employed. In a recent paper, [5] the stress dependence of diffusivities in general crystal lattices for fully anisotropic stress has been derived and applied to boron diffusion in silicon [1].

Ab-initio calculations within the harmonic Vineyard approach have shown that the diffusion prefactor D_0 changes under typical stress values by not more then a few tens of percent. [6] However, the changes observed for the activation energy can easily change the overall diffusivity by several orders of magnitude. Therefore, the pressure dependence of the prefactor is usually neglected, whereas the stress-dependence of the activation energy in the form $E(p) = E_0 + pV_c$ (in the isotropic case) is considered.

Thus, V_c determines the stress dependence of the activation energy. In the anisotropic case, the scalar volume changes to a volume tensor [5]. It can be calculated from the volume difference between the system at the saddle point configuration and at the minimum-energy valley configuration, where the lattice of both has been minimized at constant pressure zero [5], [7].

Since the potentially different symmetries of saddle point and valley configuration make the "real" calculation in the fully anisotropic case a messy task, a separation of the overall diffusivity in a part depending solely on the valley configuration and one depending solely on the saddle point is highly desirable. In order to achieve this, "creation" volumes were recently introduced, which are calculated by the tensor of volume difference of the system at the valley or saddle point, respectively, and a perfect silicon cell, where the lattice of both has been minimized at constant pressure zero. [5], [7]

Many defects and impurities in Si prefer a charged over a neutral state. A substitutional B atom, e.g., likes to attract an electron from somewhere within the silicon crystal and have it help to satisfy the four bonds it has to form with its silicon neighbors, which would be a hard task with the three valence electrons a boron atom comes naturally with. This extra charge, however, makes the defect or impurity susceptible to interactions with the local potential or, equivalently, dependent on the Fermi level it experiences. This Fermi-level dependence can be considerable and in general cannot be neglected for diffusion [3]. Thus, if one wants to calculate a correct creation volume for a defect in silicon, it needs to be calculated for the correctly charged species like, e.g., the BI^+ boron-interstitial pair in the case of boron diffusion. [3]

In our work on stress-mediate diffusion, a problem arose when the calculated volumes for cells with different charge (i.e., number of electrons), but otherwise identical atomic arrangement were found to be significantly different. As we will show, the volume difference was nearly perfectly linear with the difference in the number of electrons if large enough cells ($\geq$ 64 atoms) were employed. Therefore, we consider it to represent a "physical volume" of electrons in silicon, since for every electron taken out of the system, the overall volume decreases by the same amount.

A change of cell volume with charge has been reported before [8], but we could not find work where its meaning or origin has been discussed. In case this difference is real and not an artifact of the calculation, the question needs to be addressed if the reference silicon system would as well need to carry charge or not, since the choice of its charge changes the overall result significantly. Therefore, we will report in the following our calculations of the physical electron volume, an attempt of a preliminary interpretation, and relate it to other observed or predicted aspects of the size of an electron.

4 AB-INITIO CALCULATIONS

Our calculations have been performed within the generalized-gradient approximation (GGA) using the ab-initio total-energy molecular dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut für Materialphysik of the Universität Wien [9]. Ultrasoft pseudopotentials [10] with a default "medium" cut-off energy (150 eV in the case of plain silicon) and k-point meshes equivalent to 2^3 in a 216-atom supercell have been used for non-constant pressure calculations. Wherever constant pressure calculations were employed, the cutoff energy has been raised to the "high" setting (180 eV in the case of silicon). For calculations with non-neutral electron number, VASP adds a compensating homogeneous background charge to the system.

5 AB-INITIO RESULTS

For a given cell size, we have found the volume change with varying charge state to be the same within a few percent error, no matter if the Si cell in question had a defect or dopant in it or not and independent of the type of the defect. In the following, we discuss our results for the simplest system possible, perfect silicon supercells.

Figure 1 shows the volume of 64-atom silicon supercells with a changing number of electrons. $\Delta N = 0$ in the figure corresponds to a neutral system, which has $64 \times 4 = 256$ valence electrons, and the dots represent the *ab-initio* results. We find the cell volume to depend nearly perfectly linearly on the electron number. A quadratic fit determines the slope of the curve and the deviation from linearity, where the linear coefficient gives the change in system volume when adding or subtracting electrons and hence represents the physical electron volume. From the least-squares result in the

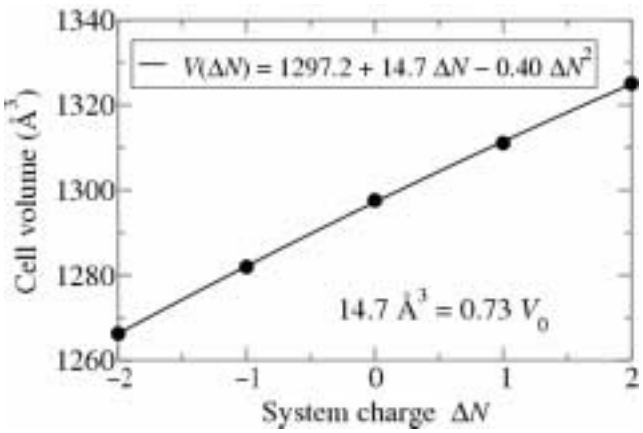

Figure 1: Volume of a sixty-four-atom silicon cell with varying number of electrons (dots). $\Delta N = 0$ corresponds to a neutral system with $64 \times 4 = 256$ valence electrons. The solid line is a quadratic fit to the calculated points with parameters as shown in the boxed equation (in Å^3).

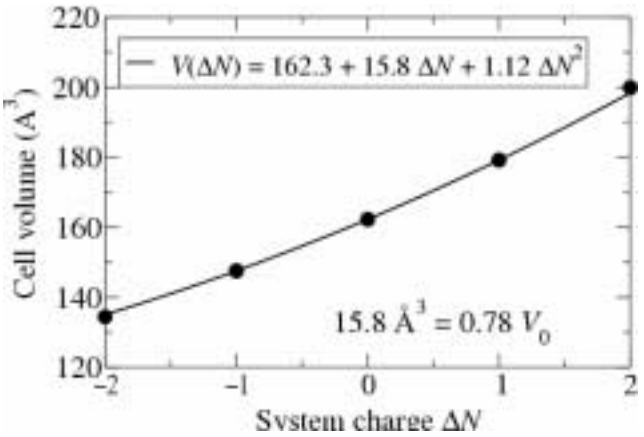

Figure 2: Volume of an eight-atom silicon cell with varying number of electrons (dots). $\Delta N = 0$ corresponds to a neutral system with $8 \times 4 = 32$ valence electrons. The solid line is a quadratic fit to the calculated points with parameters as shown in the boxed equation (in Å^3).

figure, it can be seen that we fit the physical volume of an electron in this system to be 14.7 Å^3.

This result is surprising, since it means that the physical electron volume is approximately three quarters of the volume V_0 of a complete Si atom in the solid.

Benchmark calculations for other cell sizes give similar results. Even for very small system sizes like eight-atom cells, where the addition or removal of one atom changes the (periodic) system considerably, we still find a reasonably small deviation from linearity and a very similar physical electron volume of 15.8 Å^3. These results are shown in Fig. 2. Overall, we find a consistent physical electron volume of $V_e \simeq 15$ Å^3.

6 DISCUSSION

A set of relations between the different thermodynamic variables can be derived from the Second Law of thermodynamics known as the Maxwell relations. One of these equations relates the change of the system volume V with particle number N to the change in chemical potential μ with pressure p,

$$\frac{\partial V}{\partial N} = \frac{\partial \mu}{\partial p}. \qquad (1)$$

Equating the chemical potential to the Fermi level of the system and writing its pressure dependence in linear form, Eq. (1) gives a new meaning to our physical electron volume, since it also determines the pressure dependence of the Fermi energy E_F,

$$E_F(p) = E_F(0) + V_e p. \qquad (2)$$

This second interpretation of the physical electron volume gives a convenient method to examine if our result is real: First of all, a calculation of the pressure dependence of valence and conduction band for *neutral* perfect Si without possible charge artifacts, where the Fermi level is exactly at mid gap, examines the consistency of the calculations. Secondly, measurements for the change in the band gap with pressure exist for a number of semiconductors, a quantity that is usually known as deformation potential [11]. Although the optical measurements of deformation potentials measure them relative – for a transition between bands – and not absolute, which is what we would need to determine the physical electron volume, the results are excellently suited to benchmark the quality of the theory.

Figure 3 shows valence and conduction band edge for an 8-atom Si supercell as a function of pressure. The cell size has been equilibrated for each pressure value in a constant-pressure minimization, and the band structure values have been determined for the relaxed system. The valence band maximum is at the Γ point of the Si Brillouin zone, and the conduction band minimum lies along the (100) direction of the Brillouin zone of the primitive cell. Since this is a perfect intrinsic Si system, the Fermi energy or chemical potential is determined as the midpoint between valence and conduction band edge.

A linear fit of the calculated values of the Fermi energy as a function of pressure finds V_e from Eq. (2) to be 14.9 Å^3, in excellent agreement with our previous value, which was obtained from the charged-cell volumes.

The experimental value for the hydrostatic deformation potential of the silicon band gap is -14 meV/GPa [12]. Fitting the difference between calculated valence and conduction band edge in Fig. 3, we find a theoretical value for the corresponding deformation potential of -17 meV/GPa, in good agreement (20%) with experiment. Earlier work by Alouani and Wills found for

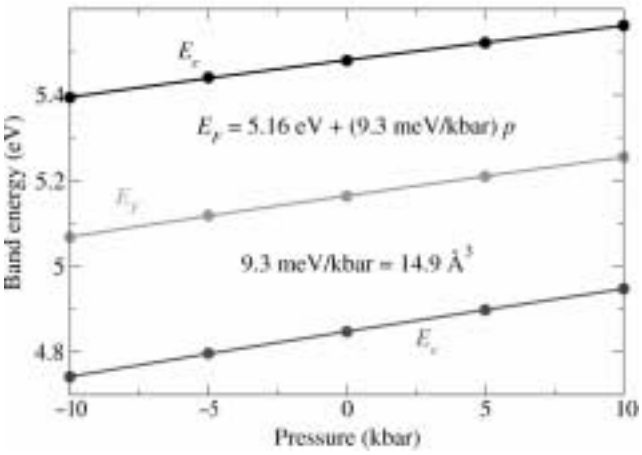

Figure 3: Fermi level (E_F), valence (E_v) and conduction (E_c) band edge energies of a 8-atom Si supercell, structurally minimized at different pressures in constant-pressure ab-initio relaxations. Dots are calculation results, lines are linear fits.

the pressure dependence of the direct gaps in Ge and GaAs an agreement between density-functional calculation and experiment within 4% and 9%, respectively [13]. Therefore, we estimate that the error in our calculated physical electron volume should not exceed 20%, or 3 Å^3, leaving its size in close proximity to the size of the Si atom in the solid state.

7 CONCLUSIONS

Many different sizes have been attributed to the electron in the past, dependent on its environment and the specific question to be addressed. Particle collision experiments put an upper limit of 10^{-17} m on the size of the free electron [14].

While free electrons are tiny as compared to atoms, their interaction with the other particles lets them influence the size of a solid strongly. This can be seen, e.g., from the ionic radius of silicon, which is 0.44 Å for a 4+ charged ion as compared to a covalent radius of 1.17 Å for a neutral Si atom. The absence of the four valence electrons lets the volume per atom collapse to about 5% of the original volume, which assigns a much larger physical volume (defined in the above sense, i.e., volume change of the solid when removing one electron from the system) to the single electron. At the current state of our discussions, we would sort our physical electron volume into this class.

For quantum transport simulations, the important question is at what dimensions electrons will start to display signs of confinement effects, which give rise to quantum corrections to a classical treatment of transport [15]. Recently, the effective size of the electron has been suggested to be given by λ_F/π for a two-dimensional electron gas, where λ_F is the Fermi wave length, or by $\sqrt{3}/8\lambda_D$ in a three-dimensional non-degenerate semiconductor, where λ_D is the thermal De Broglie wavelength [16]. From this approach, an electron size of about 50 Å has been estimated, which comes close to the physical size that we have calculated in the present work. Therefore, we speculate that our physical electron volume for the silicon solid is at least similar to the effective size that needs to be considered in quantum simulations and at a minimum represents the lower boundary for the value of the effective size.

8 ACKNOWLEDGMENTS

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