ATOMIC TRANSPORT IN SILICON BY FIRST PRINCIPLES DYNAMICAL CALCULATION

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ABSTRACT

The development of the critical path method for atomic motion on a potential energy surface, combined with fictitious-time derivative equations for solving density-functional formalism, is used to find atomic migration pathways and their barrier energies during atomic transport in solids. The calculation method is applied to interstitial migrations in silicon, revealing basic mechanisms for interstitial migration and enabling a full explanation for various aspects of experimental results. It is also extended to the analysis of an elemental dopant migration process in silicon.

I. INTRODUCTION

Atomic transport in solids is an important technological issue, but it also requires a scientific approach for a deeper understanding. Semiconductor crystals are generally stable structures because of their covalent bonds in electronic structures, and neither defects nor break-downs in the crystal structure occurs easily, when they are thermally activated. This is one of the main reasons why semiconductors became the key materials for current device technologies. Atomic diffusion in silicon, however, has now been proved to be far faster than would be expected in a normal crystal structure. Accurate impurity doping into semiconductor structures by ion implantation and subsequent annealing will thus become more difficult as electronic devices are scaled down.

Experimental evidence such as oxidation-enhanced diffusion or oxidation-retarded diffusion has revealed that group III to V dopant diffusion in silicon is mainly attributed to interstitial or vacancy diffusion.[1] Smaller impurities are more likely to diffuse through interstitials because of the smaller spatial occupation than host atoms. In the case of larger impurities, they are more likely to combine with vacancies during diffusion. Interstitials have proven to greatly enhance or retard dopant diffusion in semiconductors, revealing that interstitial migration in semiconductors is far faster than the diffusion of dopant impurities.[2] Using diffusion equations to carry out numerical calculation of dopant diffusion has become a standard means to express dopant diffusions. In this case, the way diffusion coefficients are modeled is a key issue for accurate simulation, since basic mechanisms such as dopant-point defect interaction and point defect migration are wholly included in the diffusion coefficients.

Although many theoretical and experimental efforts have been devoted to clarifying dopant and point-defect migration mechanisms and to model the dopant diffusion coefficients, the basic mechanism of diffusion is still not clear. This is because earlier theoretical works were limited to the realm of static analysis.[3]-[5] In this work, a dynamic calculation based on the first-principles density-function theory has been performed, scarching for the most probable migration path and its migration barrier. Since migration paths and barriers strongly depend on the initial conditions of an atom's location and its vibration energy because of certain temperature, there are infinite paths for interstitial migration. Here, a critical path method is proposed to find the lowest barrier path, because the activation energy for migration is mostly determined by the lowest barrier path. The method is then applied to interstitial and dopant migration in silicon, opening the way for more accurate modeling of dopant diffusion.

II. CALCULATION METHODS

Although numerous models have been proposed to describe atomic interactions in solids, we have

not yet come to a final model which accounts for all the possibilities of silicon structures.[6] The models applicable to crystal or amorphous structures are not always accurate for surface structures. Furthermore, models for interactions between different kinds of atoms are far from reaching consensus even in crystal structures. Those difficulties mainly arise from the method used to determine electronic bond between atoms. We cannot predict the electronic bonding of a covalent structure, unless we carry out electronic state calculations. The only way to do this is to use a first-principles calculation for the system to accurately model the atomic interactions, although such a calculation takes a substantial amount of CPU time. The essential features of the present calculations are that the electronic state calculations converge quickly at each atom motion step, and that atoms move on the well-defined Bom-Oppenheimer potential energy surface.

A. Electronic states

The electronic state calculations are performed using self-consistent pseudo-potential techniques within density-functional formalism in the local-density approximation. Fictitious-time derivatives of electronic wave functions corresponding to the occupied states are integrated as dynamical freedom with fictitious masses, since this is currently the most CPU efficient way to perform electronic states calculations.[7],[8] The equation is as follows,

$$\ddot{\mu\psi_{ik}}(r,t) = -\frac{\delta E}{\delta\psi^*_{ik}(r,t)} + \sum_i \Delta^k_{ij}(t)\psi_{jk}(r,t)$$

where μ , ψ , and E are the fictitious electron mass, the electronic wave function, and the density functional energy function, respectively. The Lagrange multipliers Δ_{ij}^{k} , are determined by orthonormality conditions on the wave functions. In dynamical simulations of atomic motion, the second derivative of the wave function is replaced by a first derivative equation by using a conjugate gradient minimization scheme to reduce CPU time.[9]

The norm-conserving pseudo-potential is employed on the basis of s, p, and d atomic orbitals. The wave functions are expanded by the number of N plane waves. The most computer-intensive work is pushed into fast Fourier transformation (FFT) for wave functions and potentials, which can be fulfilled by N×logN operations. A supercell geometry of 17 atoms including the migrating atom is used in this study. The coordinate axes are along the [110], [110], and [001] directions, respectively.

B. Atomic motion

The important issue in understanding the basic mechanism of diffusion is the elemental migration process in crystal structures. The molecular dynamics technique is usually employed to simulate atomic motion in liquids or solids, where certain initial structure conditions are the starting point. At high temperatures, however, thermal lattice vibrations cause a variety of atom migration pathways. Molecular dynamics cannot predict the lowest energy path within a finite CPU time. The most probable migration process among the infinite paths corresponding to the various initial conditions will have the lowest activation energy. The most probable process with the lowest activation energy can be found by pushing the atom up the valley through the saddle configuration on the potential energy surface from a stable configuration and pushing down on the potential energy surface, while moving the remaining atoms into the lowest



Fig. 1. Atom motion scheme on potential energy surface to find a minimum energy barrier. The atom is moved by ΔR toward the final location and is added corrective motion δR .

energy configuration at each time step. The path through the saddle configuration corresponds to the critical path for diffusion in the system. Once the final configuration of the diffusion process is determined, the atom responsible for the minimum barrier migration process is found by pushing up the valley on the potential energy surface before passing through the saddle point, and moved over the lowest energy ridge on the potential energy surface, as shown in Fig. 1.

The potential energy surface for the migrating atom can be derived by integrating the Hellmann-Feynman force given by

$$F = -\sum_{k,i} \langle \psi_{ki} | \frac{\partial V_{ps}}{\partial R} | \psi_{ki} \rangle$$

where V_{ps} and R are pseudo-potentials for the atom and its coordinates, respectively. When the atom climbs up the valley on the potential energy surface, the direction of the force acting on the atom is exactly opposite to the direction of motion. Therefore, the atom moves one step ΔR toward the final location, and then a corrective motion δR , perpendicular to the original motion ΔR , is added in proportion to the Hellmann-Feynman force. This procedure puts a slight constraint on the atomic motion, forcing the atom to avoid higher potential hills and to inevitably move into the valley on the potential energy surface.

III. ELEMENTAL PROCESS

A. Interstitial migration

In this section, typical examples of atomic transport as applications for the present calculation method are presented. Among the species of migrating atoms, knowledge of the point-defect migration mechanism is a basic starting-point in the understanding of dopant migration behavior, because dopant diffusion is enhanced or retarded by the presence of interstitials or vacancies. Since vacancy diffusion is simple, the present method is first applied to interstitial migration. Recent experimental results for extrinsic conditions indicate that the interstitial diffusion rate is extremely high, about ten orders higher than that of self-diffusion in intrinsic conditions.[1] This inevitably leads to the assumption that interstitialcy or interstitial mechanisms may dominate interstitial diffusion in silicon, given that if it has to to account for general silicon migration characteristics at high temperatures. However, interstitial migration has been observed even at cryogenic temperatures in irradiated silicon.[10] Here, by carrying out a dynamic simulation for interstitials, the basic mechanisms of atomic transport have been revealed.



Fig. 2. Atom trajectory for interstitial migration from Si^0 hexagonal configuration by interstitial mechanism.



Fig. 3. Atom trajectory for interstitial migration from Si^{2+} tetrahedral configuration by interstitial mechanism.

The migration was investigated by shifting from one stable configuration to another configuration; the pathway and the activation energy needed for interstitialcy as well as for interstitial and selfdiffusion mechanisms were considered. Before the migration process was begun, stable configurations involving an interstitial were searched by staring from several highly symmetrical configurations for Si^0 and Si^{2+} , which were proved to be the lowest energy states for n-type and p-type silicon, respectively, because of the negative U system.[3] This process revealed stable hexagonal, split, and bond-centered configurations for Si^0 and tetrahedral, split, and bond-centered configurations for Si^{2+} . The elemental migration processes were then investigated, starting from these initial stable configurations. Totalenergy density-functional calculations were performed for Si^0 and Si^{2+} at each time step.

Migration by interstitialcy mechanism occurs as a point defect modulated structure transport as a soliton. A plausible structure for intermediate states will be an energetically stable configuration. Although the stable structures found in this study, such as split and bond-centered configurations for both Si^0 and Si^{2+} , are examined as intermediate stable configurations, the structures are found to become unstable during migration even along a critical path and to relax into more stable structures.

The remaining mechanism for an atom interchanging migration is the interstitial mechanism. Interstitial migration occurs when an energetically activated interstitial kicks out a lattice site atom into an adjacent interstitial site. The plausible initial stable structures for the elemental processes in this mechanism are a hexagonal configuration for Si^0 and a tetrahedral configuration for Si^{2+} . Figure 2 shows a typical interstitial migration process from the hexagonal site for Si^0 , passing through a critical path. The interstitial on the left side is moved toward one of the four adjacent lattice sites located at the center of the system, and is stabilized at the lattice site after pushing away the lattice atom. The atom initially located at the center of the system turns into an interstitial migration of Si^0 thus ends in the same structure as the initial one. The energy barrier for this transition is 1.2 eV, a reasonable value to account for the experimental results ranging from 1 eV to a little above 2 eV. The Si^{2+} interstitial migration by interstitial mechanism was also found to occur with a relatively high energy of 2.4 eV as shown in Fig. 3. The interstitial on the left side also kicks out the adjacent lattice atom and is stabilized at the lattice site.

Analysis of the process in more detail reveals the relatively low energy of 1.2 eV needed for kicking out a lattice atom, compared with the point defect creation energy of 5 eV. The total valence charge densities at the initial stage and at the atom interchanging stage during interstitial migration of Si^0 corresponding to Fig. 2 are shown in Figs. 4 and 5. The valence charge density is shown on the three planes formed by slicing the interstitial and its adjacent atoms perpendicularly to the coordinate axes.



Fig. 4. Valence charge density on the (001), (110) and (110) planes involving the interstitial and its adjacent atoms at the initial stage by Si^{0} interstitial mechanism.



Fig. 5. Valence charge density on the (001), (110) and (110) planes involving the interstitial and its adjacent atoms at the atom exchanging stage by Si^0 interstitial mechanism.

The charge density at the initial stage shown in Fig. 4 indicates that the valence electron of a hexagonal interstitial is loosely bonded to the two pairs consisting of four adjacent lattice atoms, while adjacent atoms are tightly bonded to their nearestneighbor lattice atoms. As the transition proceeds, as shown in Fig. 5, atomic bonds are found to be remade successively from the location of the original lattice atom to the interstitial so as not to increase energy too much during the atom interchanging migration process. This will be the reason why atom interchanging migrations occur with low barrier energies in covalent bond system.

The self-diffusion process is also found to occur with a relatively low energy barriers, a finding also attributed to the successive bond remaking processes for migration procedures through bonds, while other types of self-diffusion occur as the interstitial atoms loosely bond to adjacent sites during the migration procedure. These results suggest



Fig. 6. Atom trajectory for boron migration from lattice boron and Si^0 hexagonal configuration by interstitial mechanism.

that interstitial diffusion occurs not only as a result of the interstitial mechanism but also through the self-diffusion mechanism, that is somewhat surprising, considering the prior assumption. It does not, however, contradict with the experimental results. The small diffusion coefficient for self-diffusion must be mostly determined by the defect generation rate.

B. Dopant migration

To examine the extent of applicability, the present calculation is extended to boron diffusion in silicon, which is mostly dominated by the interstitial mechanism. Since the atomic radius of boron is very small compared with silicon, the incorporation of boron into crystal structures induces a large relaxation on neighboring lattice sites, and a cluster sometimes forms with adjacent interstitial atoms. To free the calculation from such difficulties, a typical example, shown in Fig 6 is calculated with an interstitial on a hexagonal site and a B^- atom on a lattice site as the initial condition. The Si^0 interstitial on the left side was moved up to the boron lattice site, while other atoms are relaxed into stable sites. The boron is pushed up above the interstitial atom. The final structure is a deformed split configuration formed by the silicon and boron atoms, indicating that a more complicated migration is possible than in the interstitial case.

Although present applications are limited to interstitial migrations and a typical boron migration in silicon, this method will also be applicable to various other aspects of atomic transport. By continuing those efforts to find accurate migration energies for each atomic species, it will become easy to understand the basic mechanism of atom transport more deeply, and we will be able to construct more accurate models for atomic diffusion simulations.

V. SUMMARY

This paper is devoted to an efficient way of searching for atom migration pathways and activation energies. The first-principles dynamical calculation is achieved by combining a fast solution for the total-energy density-function based on fictitious-time derivative equations for wave functions with a critical path method for atomic migration on potential energy surfaces. The present calculation has enabled us to find the critical path for atom migration corresponding to the lowest energy-barrier pathway.

As a practical search for a critical path in the diffusion process, the total-energy density-function

calculation clarified silicon interstitial migration mechanisms involving paths and barrier energies in a rigorous way. The calculation for Si^0 and Si^{2+} interstitials revealed several stable configurations. Interstitial diffusion occurs mainly as a combination of interstitial and self-diffusion mechanisms when the migration starts from stable hexagonal and tetrahedral configurations. The calculated migration energies ranging from 1.2 eV to slightly above 2 eV agreeing with various experimental results ranging from 1 to slightly above 2 eV obtained so far. Migrations with relatively low energy barriers are attributed to a process of successive bond remaking, while in some cases self-diffusion occurs as with interstitial atom loosely bonding to adjacent sites during the migration process.

This study has also shown that the method is applicable to dopant migration, including boron diffusion in silicon. By extending this method to the various migration of atoms in solids, we will be able to understand the basic mechanism of elemental migration and to obtain rigorous barrier energies, opening the way for the development of more accurate models for large scale atomic diffusion simulations.

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