

2-3 First-principles study of dopant trap level and concentration in Si(110)/ α -SiO₂ interface

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Abstract—We investigate the dopant trap level and equilibrium concentration of Si(110)/ α -SiO₂ interface with a wide variety of dopants (B, C, N, Br, Cl, F and H). The electronic and atomic properties of intrinsic and extrinsic defects are analyzed using First-principles calculation. It is shown that the average trap levels for hole and electron deepen as the electronegativity of the dopant increases. Also, we applied a simple thermodynamic model to evaluate the equilibrium concentration of active trap as a function of dopant concentration at the interface. From the model it turns out that H and F completely passivate the intrinsic Pb center of Si and reduce the trap concentration, while other elements, especially N, Br and Cl, induces new trap states which amounts to several times more than the pre-existing Pb center.

Keywords—Interface, semiconductor, trap level, doping concentration

I. INTRODUCTION

Si/SiO₂ interface is one of the most investigated system among the semiconductor/oxide interface due to its success in the semiconductor industry. The high degree of perfection achieved in the interface leads the low density of the interface trap, which is directly related to the device reliability.

It is known that the dangling bond of Si atoms at the interface, so called Pb center, acts as a major trap in the Si/SiO₂ system, and the Si/SiO₂ interface shows trap density less than 10¹¹ cm⁻² without external dopants [1]. However, various types of elements can diffuse to the Si/SiO₂ interface during or after the deposition process, which will play a critical role in a variety of physical and chemical properties of the interface. It is noteworthy that the effect of doping can be significantly different even among the elements which belong to the same group. For example, large dose of Cl atoms in the interface is known to worsen the interface integrity and increase the trap density, while F atoms in the interface monotonically decreases the interface trap [2,3]. Even though electronic and atomistic properties of the Si/SiO₂ interface have been extensively studied both experimentally and theoretically [4-6], the effect of extrinsic dopants on the electronic properties of the interface are not explored thoroughly.

Here we calculate the trap level and the concentration of such various defects (B, C, N, Br, Cl, F and H) to address the effect of the dopants in the Si(110)/ α -SiO₂ interface. The average trap level of each dopant is calculated using First-

principles methods. Thermodynamic model which uses formation energy to calculate the equilibrium concentration of dopants based on the reaction energy of trapping and passivation is established and applied to the aforementioned dopants.

II. METHODOLOGY

A. Computational setup

We performed first-principles calculations using the Vienna Ab-initio Simulation package [7]. The generalized-gradient approximation (GGA) was used for the geometry optimization and first-principles molecular dynamics, while the electronic structures were calculated within HSE06 functional [8] to give a better description for the trap level position. The energy cutoff of 400 eV and gamma point sampling were employed. The cell geometry of each structure is fully relaxed with the atomic force less than 0.02 eV/Å.

B. Atomic structure preparation

To generate the crystal-amorphous interface structure, we firstly sprayed 40 formula units of Si and O atoms on the 12 layers of Si(110) surfaces, and applied melt-quench molecular dynamics (MD) simulations to equilibrate the SiO₂ amorphous layers. Firstly, the amorphous portion of interface structure is pre-melted in 5000 K with time step of 4 fs to erase the randomness of initial sprayed structure. After that, melting of 3000 K was applied for 6 ps was carried out to equilibrate the amorphous structure. Finally, the structure was quenched to 300 K within 10 ps. The melting and quenching process were performed with the time step of 3 fs. The melt-quenched atomic structure is fully relaxed before energy and electronic structure calculation.

C. Interface structure selection

Because of the periodic boundary condition, the unit cell of the simulated structure should contain two interfaces. If trap states in those two interfaces have different density or charges, the potential banding which can be problematic in estimating the trap level can occur. In the case of crystalline interface, this can be avoided by creating same trap states in the two interfaces symmetrically, but in the amorphous interface inducing the same trap states in the different interfaces can only be achieved by making a lot of samples. To select the samples in which the internal potential band banding is small, we plotted local-projected density of states (local p-DOS) of

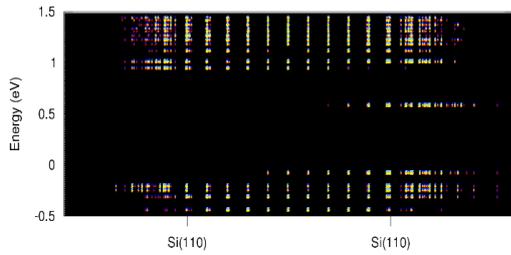


Fig. 1. Local-projected density of states of Si/SiO₂ interface. The energy is plotted with respect to the valence band maximum of the system.

Si/SiO₂ interfaces (Fig. 1). The example structure in Fig. 1 has one deep trap states (around 0.6 eV from valence band maximum) on the right interface, which leads slight band banding in the Si bulk region. By checking the local p-DOS of each structure, we analyzed only the cases where the same number of traps exist at each interfaces and the potential banding is not too significant.

III. RESULT AND DISCUSSION

We generated 20 Si(110)/*a*-SiO₂ interface structures using the aforementioned melt-quench procedure and select 10 samples which show small band banding by plotting local p-DOS. We added a dopant at each interface region and performed atomic relaxation. Five random positions at the interface region were chosen for each dopant, which means 360 structures (doped structures with B, C, N, Br, Cl, F and H with 10 samples and 5 random positions, plus 10 pristine structures) were generated. A representative structure for this ensemble is shown in Fig. 2(a). Most of the Si atoms positioned in the interface are almost passivated with O atoms, and the change of the density of the *a*-SiO₂ layer after the cell optimization was less than 5 %.

The density of states (DOS) for the interface structure with and without dopants are presented in Fig. 2(b) and Fig. 2(c), respectively. The inset of Fig. 2(c) shows the representative atomic configuration of Cl-doped case. It should be mentioned that in the most of the cases (except N) the trap states are mostly originated from Si dangling bond, so called Pb center. This means that the dopant generates a trap state by breaking Si-Si bond and passivate one of the Si atom, rather than by forming the localized orbital of itself.

In Fig. 3, the calculated trap levels of intrinsic Pb center and each dopant are plotted with respect to the electronegativity of the dopant elements. It is clear that both

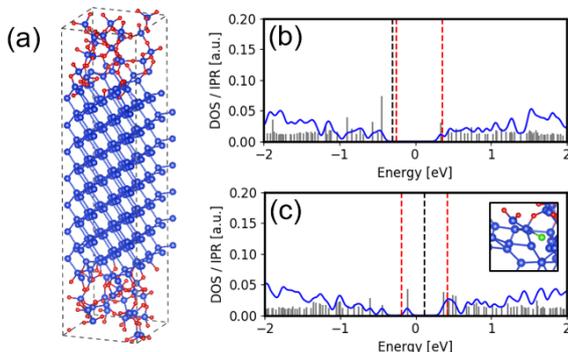


Fig. 2. (a) Atomistic structure of Si(110)/*a*-SiO₂ interface. Blue and red circles represent Si and O atoms, respectively. The DOS of (b) clean interface without traps and (c) interface with trap states.

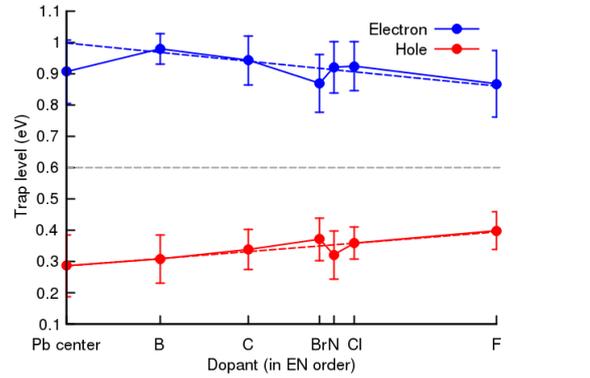


Fig. 3. Averaged trap levels of Si Pb center and extrinsic dopants.

electron and hole trap levels deepen as the electronegativity of the dopant increases. The dependency of trap levels on the electronegativity can be explained by the orbital hybridization between dopants and the Si dangling bond, and the local potential from dopant atoms exerted to the Pb center.

The trap concentration, which means the concentration of defect states that can act as a carrier trap, can differ from the concentration of the dopants at the interface. Here we applied simple thermodynamic model which relates the trap concentration and dopant concentration at the interface by using calculated formation energy and counting the active sites for the dopant:

$$p_{n+1} = p_n + C_{add} * \frac{D - p_n}{(N - t_n + D - p_n)} * \exp\left(-\frac{E_p}{kT}\right) \quad (1)$$

$$t_{n+1} = t_n + C_{add} * \frac{N - t_n}{(N - t_n + D - p_n)} * \exp\left(-\frac{E_t}{kT}\right)$$

where p_n and t_n are the number of passivated and induced trap site at n th step, respectively, and C_{add} is the amount of added dopant. D is the number of Pb center in the pristine interface and N is the number of Si-Si bonds. E_p and E_t are the reaction energy for passivation and trapping. By iterating (1) with small value of C_{add} , the concentration of dopant at the interface (nC_{add}), the number of induced traps and passivated sites, and hence the number of non-passivated traps can be calculated. The total trap concentration of interface is the sum of induced traps and the non-passivated traps. from dopant atoms exerted to the Pb center.

In Fig. 4 is the calculated equilibrium trap concentration with respect to the dopant concentration at the interface. It is shown that H and F completely passivate the intrinsic Pb centers and decrease the trap concentration, while B and C have small variation with the dopant concentration. For the other elements, N, Br and Cl, the concentration of newly induced trap states amounts to several times the intrinsic Pb center concentration with the considered doping range. In the

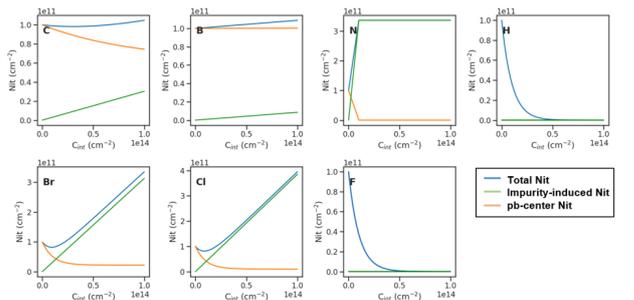


Fig. 4. Interface trap concentration as a function of dopant concentration at the interface.

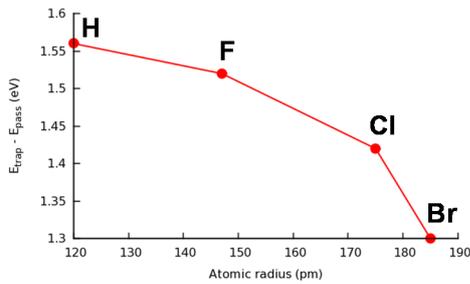


Fig. 5. The average coordination number and the difference in the reaction energy of trapping and passivation.

case of halogen atoms or H, this tendency can mostly be explained with the size of the dopants, as the bigger dopants induces structural strain which ease the formation of the trap states, while small dopants such as F and H induces no such strain and rather prefer the passivation of the existing trap sites. To illustrate this point more clearly, we plotted the difference between reaction energy of trapping and passivation versus atomic radius of halogen atoms and H in Fig. 5. In the figure, the difference in the energy decreases as the dopant size increases, which means the formation of trap site is more dominant in the case of big dopants, while passivation prevails in the interfaces with small dopants. This size effects can also exist in the case of non-halogen atoms such as C, B, and N, but we find that the relation between the atomic characteristic and the reaction energy are more complex due to the covalent character of those atoms.

IV. CONCLUSION

In conclusion, we calculated the dopant trap level and equilibrium concentration for wide range of dopants in

Si(110)/ α -SiO₂. It is found that the average trap level of the interface approaches to midgap as the electronegativity of the dopant atom increases. We also calculated the active trap concentration as a function of dopant concentration, and it is shown that H and F completely passivate the intrinsic trap center of Si/SiO₂ interface, while N, Br and Cl induces new trap states which can worsen the device performance..

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