

Vacancy At Si-SiO₂ Interface: Ab-Initio Study

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Abstract— Using density functional theory calculations within the generalized gradient approximation we have examined structure and dynamics of neutral Si vacancies at Si/SiO₂ interface. We show that Si/SiO₂ interface may serve as a limited sink for Si vacancies. Single vacancy and vacancy cluster defects are substantially more stable at c-Si/a-SiO₂ interface compared to the bulk c-Si layers away from interface, mainly due to termination of dangling bonds with bridging O atoms and reduction of interface strain.

Keywords— Si, diffusion vacancy, point defects, SiO₂, interface.

I. INTRODUCTION

In modern MOS fabrication processes large quantities of native defects are introduced in close proximity to the semiconductor surface. With rapid decrease of Metal-Oxide-Semiconductor (MOS) device lateral and vertical dimensions interface and surface reactions and related processes have become dominant for the formation of shallow and abrupt dopant profiles. Understanding of interactions of dopant atoms and point defects with surface films and interfaces is crucial for determining the redistribution of dopants during high temperature treatments. In this paper we will address the structure, bonding, energetics and diffusion of neutral Si vacancies at the vicinity of Si/a-SiO₂ interface as well as mechanism of creation of large vacancy clusters at interface.

II. COMPUTATIONAL DETAILS

We construct a defect-free Si(001)/amorphous SiO₂ (Si/a-SiO₂) (as shown in Fig. 1) structure using continuous random network (CRN) model [1]. This method ensures construction of realistic, fully relaxed c-Si/a-SiO₂ interface. Amorphous SiO₂ layer has structural properties similar to ones observed in the experiment, yielding the average Si-O-Si bond angle, Si-O distance and oxide density consistent with experimental measurements [2]. For calculation of structure and energetics of defects we employ a “large” 4x4x5.26 Si/SiO₂ supercell, whereas defect dynamics was studied on a “small” 2x2x4.26 supercell, where the fractional super-cell size corresponds to the extension into the oxide.

We calculate interstitial defect structures and energies using plane-wave pseudopotential method within the density functional theory [3], as implemented in ab-initio total-energy program VASP[4-7]. The exchange-correlation energy functional is represented using the generalized gradient approximation (GGA) in the Perdew and Wang form. We use a cutoff energy of 300 eV for planewave expansion. For the k-space summation, we use gamma point only for the “large”

supercell and the (2x2x1) Monkhorst-Pack mesh for the “small” supercell.

All atoms are fully relaxed using a conjugate gradient method to minimize the total energy until all residual forces on the atoms are less than 5×10^{-2} eV/Å. We calculate diffusion pathways and barriers under static approximation using the climbing nudged elastic band method [8].

III. RESULTS AND DISCUSSION

For the sake of reference we first calculate neutral vacancy structure and formation inside an inner Si layer of the Si/a-SiO₂ supercell. We found that variation in total energy for a single vacancy created at 5th and 6th Si inner layers to be less than 0.2 and 0.1 eV, correspondingly, with virtually no changes in relaxed vacancy geometry compared to the bulk Si 216 atoms supercell. Herein, we call vacancy at the sixth c-Si sublayer a bulk vacancy.

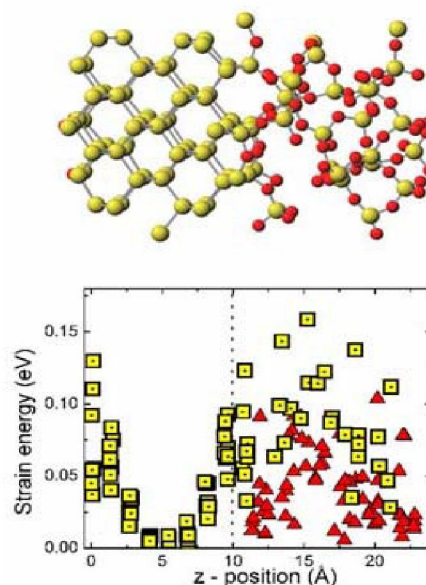


Figure 1. Si/a-SiO₂ interface structure and distribution of strain on atoms in the supercell. Yellow (light grey) and red (dark grey) correspond to Si and O atoms respectively.

A. Interface Vacancy

To create the interface vacancy we remove a Si atom from the interface Si-O-Si bridge and relax the configuration (Fig. 2 a)). Upon structure relaxation all atoms in the interface vacancy structure become fully coordinated. As a result, the interface vacancy structure does not have any dangling bonds at all and is expected to be much more energetically stable compared to vacancies in inner Si layers. The interface vacancy structure is examined at eighteen different locations. The most and least stable states are respectively 1.9 eV more and 0.8 eV less stable than the bulk vacancy, with the average energy reduction of about 1.0 eV. Vacancy stabilization at the interface is facilitated by rearrangement of interface O atoms and formation of strong Si-O bonds with vacancy neighbors. The above stabilization strongly depends on the a-SiO₂ network topology near the interface vacancy site. At elevated temperatures formation of the interface vacancy may introduce topology changes in amorphous oxide network, leading to farther stabilization. In addition, the vacancy may migrate along the interface to more energetically favorable location.

B. Sub-interface Vacancy

At the first two Si layers under the interface we find the vacancy formation energy to be reduced by 0.9 eV to 1.3 eV. As can be seen from the Fig. 1, removal of one atom from the Si layer provides immediate strain relief for the vacancy's nearest neighbors located in the first few atomic layers around interface. Furthermore, upon the vacancy structure relaxation additional reduction of strain in the second and third nearest neighbor shells occurs. We therefore suggest that one of the major sources of vacancy stabilization at Si layers is the strain-assisted pairing and the immediate strain relief. Indeed, relaxed vacancy structures at the second and third sublayers show significant inward relaxation compared to the bulk. For vacancy at third sublayer the most significant stabilization is observed for vacancies created directly under the Si-O-Si bridge, where vacancies on average are 1.2 eV more stable compared to the bulk vacancies.

We carefully examine the influence of the interface on the electronic structure of the sub-interface and interface vacancy. In unrelaxed vacancy structure one of the vacancy-induced defect levels is created inside the valence band manifold and the one triply degenerate level inside the band gap. The band gap level is unstable with respect to distortion due to the orbital degeneracy. As vacancy structure relaxes, Jahn-Teller (JT) distortion lowers the symmetry and partially remove degeneracy of the triplet, splitting it into two levels in the band gap. This pairing will sweep defect states from the band gap. The effect of pairing close to interface is well reflected in the vacancy DOS and should be distinguished from the pure strain relief effect discussed earlier.

Besides pure effect of strain assisted pairing we should also take into account possible interaction between vacancy states and the states close in energy that are induced by distorted Si bonds near the interface as well as by interface sub-oxidized Si atoms. Although it is difficult to distinguish between this resonance effect and strain-assisted pairing, we can gain some insight by comparing vacancy stabilization under Si/a-SiO₂ with Si/c-SiO₂ interface. Both interfaces have comparable

oxidation-induced strain. However, the interface states Si/a-SiO₂ inherently have broader spectrum compared to the Si/c-SiO₂. Thus coupling of the interface-induced states with vacancy defect states is more feasible in case of Si/a-SiO₂. This may explain why we observe much smaller vacancy stabilization of 0.6 eV under Si/c-SiO₂.

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C. Vacancy Clustering at Si/a-SiO₂ Interface

We check interface di-vacancy (DV) configurations at several interface locations. For DV construction we remove two Si atoms from an interface Si-O-Si bridge and rearrange remaining unpaired O atoms such that the four-fold coordination of all remaining atoms in the supercell is recovered (Fig. 2 b)). For all tested configurations pairing of two single vacancies into a DV leads to an additional energy reduction per vacancy ranging from 0.2 eV to 0.8 eV. The most stable interface DV is 1.8 eV more stable compared to a DV at 5th and 6th c-Si sublayers of the Si/a-SiO₂ supercell.

As widely known, cluster formation energy per vacancy decreases with cluster size. Contrary to above, adding another vacancy to an interface DV does not lead to considerable increase in stabilization per vacancy. Advantages of dangling bonds removal are achieved at the expense of increased strain energy. The later imposes an upper limit on the number of vacancies that can be accommodated at the interface. The Si/a-SiO₂ interface can absorb up to a monolayer (7×10^{14} /cm²) of vacancies without undergoing step or void formation.

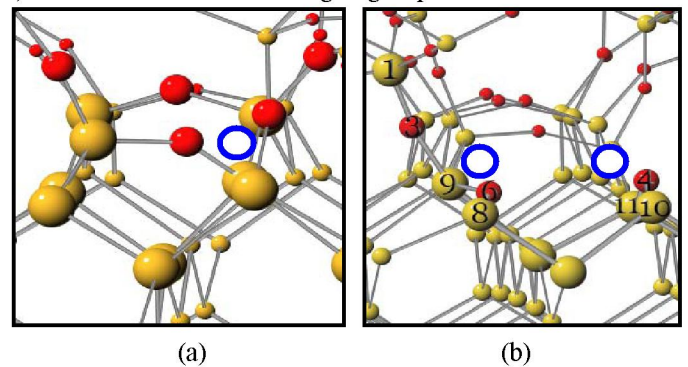
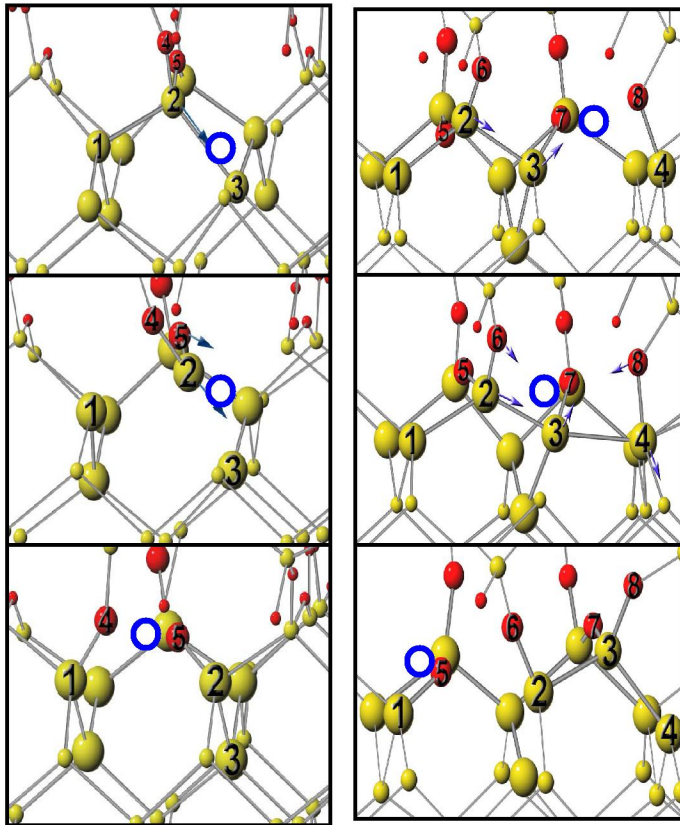


Figure 2. a) relaxed interface vacancy structure b) relaxed interface di-vacancy structure. Positions of the removed Si atoms are shown by dark blue circles. Note that the coordination of all atoms is restored.



(a)

(b)

Figure 3. Vacancy migration pathway: a) from bulk layer to the interface b) along the interface. Frame sequence is top to bottom, with saddle point illustrated at middle. Direction of atom displacements is shown by blue arrows. Yellow (light grey) and red (dark grey) correspond to Si and O atoms respectively.

D. Vacancy Dynamics at Si/a-SiO₂ Interface

To identify a possible mechanism of a single vacancy formation at Si/a-SiO₂ interface, we calculate the migration pathway of a vacancy to the interface from a c-Si sublayer (Fig.3 a)). We test four different locations and find the range of migration barriers from 0.1 eV to 1.3 eV, with the average migration barrier of 0.8 eV. The return barrier is found to be at least 0.5 eV higher since as a surface vacancy is generally more stable compared to the subsurface one. The wide range of migration barriers and the higher return barrier suggest that

the interface might be an effective sink for vacancies even at low temperatures.

We also calculate the energy barrier and the pathway for vacancy migration along interface (Fig.3 b)). Migration barriers for pathways between the chosen three pairs of neighboring interface vacancies are found to be 0.4-0.8 eV. Thus at a sufficiently high temperature an interface vacancy can migrate along the Si-O-Si row before either it is trapped at the low energy location or combined with another vacancy in the same row forming a more stable DV defect.

IV. CONCLUSION

In summary, we found that vacancy formation energy at interface is reduced up to 1.9 eV, and even larger stabilization possible for interface vacancy clusters. We attribute this stabilization to the two factors: i) strain relief c-Si sub-layers under Si/a-SiO₂ interface, and ii) strain-assisted pairing between vacancy neighbors and the effect change of periodicity and a chemical composition of the system on the electronic states associated with a vacancy. We found that a vacancy can migrate easily from bulk Si layers to the interface. Clustering can further reduce vacancy formation at interface. We may conclude that Si/a-SiO₂ interface may serve as a (limited) sink for neutral vacancies.

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