A FIRST PRINCIPLES STUDY OF DEFECTS IN A-SI

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ABSTRACT

The structural and electronic properties of vacancies in a fully tetrahedral model of amorphous silicon have been investigated by ab initio calculations. A very rich behavior was observed after the atomic relaxation, from the complete rearrangement of the atoms (self-healing) to the creation of stable vacancies. We have observed that the vacancy internal relaxation volume is negative. After relaxation, the vacancy formation energies were found to be smaller than that of the crystal, and the deep gap levels either disappear or move towards the band edges.

Introduction

Amorphous silicon (a-Si) has been the subject of extensive experimental and theoretical investigations over decades and it is the prototype of disordered covalent semiconductors [1,2]. From the structural point of view, a-Si is considered to have the atoms tetrahedrally coordinated and covalently bonded [1,2]. However, recent experimental [3,4] and theoretical results [5–7] have suggested that vacancy-like defects could be stable and play an important role in the electronic and structural properties of a-Si. These experiments indicate that structural relaxations in a-Si generated by ion bombardment are quite similar to the annealing of point defects in crystalline silicon (c-Si) [3,4]. Up to now, to our knowledge, theoretical studies have been carried out using either empirical potentials [5] or tight binding simulations [6,7].

The aim of this work is to study the electronic and structural properties of vacancies in a-Si using ab initio methods. In particular, we are interested in investigating aspects such as the range of structural relaxation and vacancy annihilation. Furthermore, we would like to determine the differences and similarities between vacancies in a-Si and in c-Si.

Methodology

In order to investigate the effects of isolated vacancies, we adopt the fully tetrahedral continuous network with 216 Si atoms in the simulation supercell generated by the Wooten, Winer and Weaire (WWW) scheme [8]. This supercell is large enough to avoid interactions between the neighboring image defects. This structural model has been tested and its physical properties (Raman spectrum, radial distribution function, vibrational density of states, etc.) are in good agreement with the experimental data [9].

By removing an atom of the WWW structure one generates the vacancy-like defect, consequently creating a dangling bond in each one of the four neighboring atoms. Since in the amorphous material there are nonequivalent sites, we have chosen 10 different atoms with distinct local environments (bond lengths and bond angles) in order to have a representative sampling.

The electronic structure calculations are based on the density functional theory within the local density approximation [10]. The Kohn–Sham orbitals are expanded in a localized basis function of double-zeta-pluspolarization (DZP) quality [11], using the SIESTA code [12]. For each one of the 10 studied cases, the structure with a vacancy was relaxed employing the conjugate gradient method. The norm-conserving pseudopotentials of Troullier–Martins were used in this study [13].

Furthermore, systems were considered fully relaxed when the Hellmann–Feymann forces were smaller than 0.01 eV/Å. The Γ point has been used for the Brillouinzone sampling and the supercell volume was fixed during the calculations.

Results and discussion

The vacancy formation energy (E_F) is defined as $E_F = E_{TOT}^{N-1} - (N-1)/N E_{TOT}^{N}$, where E_{TOT}^{N-1} and E_{TOT}^{N} are the total energies for the calculations with (N - 1 sites) and without (N sites) the vacancy, respectively. This quantity was calculated before and after the atomic relaxation and compared with that of a relaxed vacancy in crystalline Si (3.44 eV). Before relaxation, the vacancy formation energies were typically larger than that of the crystal by approximately 0.5

eV. After relaxation, they always decrease, and in all cases except one the final formation energies are smaller than that of c-Si. The results for four typical sites are described in Table 1. As can be seen, even a negative formation energy (after relaxation) has been observed for one site (V2).

We have also investigated the internal volume of these vacancies using the definition of internal volume as suggested by Kim et al. in reference [6]. As observed for the bulk Si, the internal volume of vacancies in a-Si decreases with the atomic relaxation. It is means that for all sites studied, the nearest-neighboring atoms move towards the vacancy site. These results are in disagreement with tight-binding calculations, where both positive and negative variations of internal volume have been reported [6]. During the structural relaxation only the local environment close to the vacancy has significantly changed. This observation suggests that the relaxations in a-Si are more closely related to point-like defects relaxations rather than global network changes.

Regarding the electronic structure properties, we find that the overall density of states (DOS) for the a-Si with and without a vacancy are rather similar. Obviously, before the structural relaxation, there are deep impurity levels in the gap, related to the four dangling bonds of the neighboring atoms to the vacancy. After relaxation, basically four different cases were observed

Table 1
Physical properties of single vacancies in a-Si WWW model

Vacancy	$E_F^{unrelaxed}$ (eV)	$E_F^{relaxed}$ (eV)	ΔV (Å^3)
V1	4.51	3.34	-17.27
V2	3.34	-0.24	-14.15
V3	3.85	1.88	-21.33
V4	4.60	3.55	-19.11

Table displays: a vacancy label; the formation energies before ($E_F^{unrelaxed}$ and after $E_F^{relaxed}$ the atomic relaxation; the change of the vacancy internal volume ($\Delta V = V_{relax} - V_{unrelaxed}$).

for the behavior of these gap levels: (i) a full vacancy reconstruction with the disappearance of the deep gap states; (ii) a full vacancy reconstruction with the gap states shifted to the bottom of

conduction band; (iii) partial reconstruction (dangling bonds) with the gap states shifted to the top of the valence band; and (iv) stable vacancies, with the gap states shifted both to the top of the valence band and to the bottom of the conduction band.

The case (i) above (V1 in Fig. 1) is related to sites where all atoms became tetrahedrally bonded after the structural relaxation, as can be seen in Fig. 1(a). The DOS curves (obtained from the calculated eigenvalues with a Gaussian line broadening of 0.01 eV inside, and 0.1 eV outside, the gap region) clearly show that this vacancy, with a negative formation energy and full lattice reconstruction (self-healing), does not present any gap states. The bond lengths between atoms near to the vacancy site become smaller than the average bond length obtained for the a-Si (2.347 Å). In summary, this case can be considered as a full annihilation of the vacancy after the atomic relaxation.

Now we turn to a situation (V4 in Fig. 2) where all atoms remain tri-coordinated after the relaxation. Nevertheless, the DOS (see Fig. 2(b)) shows that the

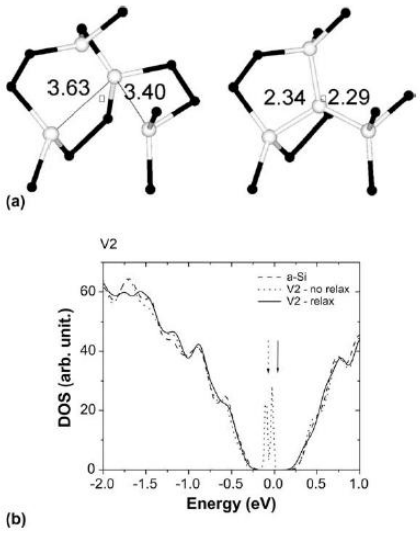

Fig. 1. Structural and electronic properties of vacancy V2 (see Table 1). (a) Local structures of the unrelaxed vacancy (left) and after the atomic relaxation (right). The large white (small black) spheres represent the first (second) nearest neighbors of vacancy site (square). Distances between atoms are in _A. (b) Electronic density of states (DOS) near the gap region. The presented DOS are the a-Si without the vacancy (dashed line), a-Si with the vacancy, before (dotted line) and after (full line) the atomic relaxation. Arrows represent the Fermi level for each

curve.

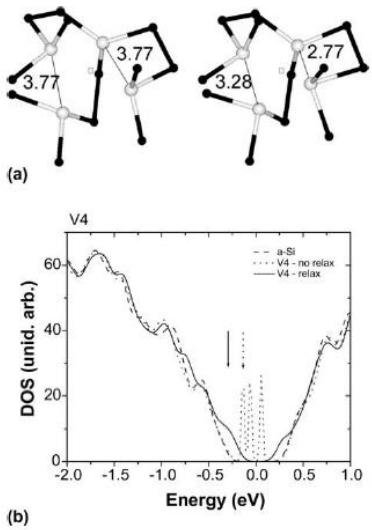

Fig. 2. Structural and electronic properties of vacancy V4 (see Table 1). Same legend as 1.

deep levels in the gap are shifted to the top of the valence band and to the bottom of the conduction band. The bond lengths and the angular distortions are higher than the average in a-Si. From Table 1, we also observe that the vacancy formation energy in this case is higher than that for a vacancy in crystalline Si. This V4 case also suggests that only a geometrical and topological analysis can lead to incorrect conclusions regarding the interaction between vacancy neighbor atoms in a-Si. A 'stable' vacancy from a topological point of view, with all the atoms around the vacancy site tri-coordinated (which would, in principle, result in four possible dangling bonds), does not present energetically deep gap levels, but only tail states appearing close to the band edges. This electronic structure result suggests that atoms close to the vacancy site can be (weakly) bonded.

Conclusion

In summary, we have presented first principles calculation of single vacancies in a-Si. Our results indicate that the structural relaxations are basically related to point-like defects, with significant atomic changes occurring only in the local environment close to the vacancy site. Moreover, for all sites studied, the variation of the interval volume was negative (decrease in

volume). After relaxation, in some cases we observed a vacancy annihilation (self-healing). This could either lead to a full disappearance of gap states or to their dislocation towards the band edges. We have also concluded that there can be stable configurations where the atoms remain tri-coordinated. However, even in these cases the original deep gap states tend to move towards the band edges. This indicates that, in order to fully understand the behavior of vacancies in a-Si, the knowledge of structural properties is not enough, and an electronic structure study is necessary.

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