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Ab initio calculations of a vacancy in a Ge nano-cluster and its passivation with atomic and molecular hydrogen

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Abstract

The mechanism of passivation of germanium vacancies by atomic and molecular hydrogen is investigated at the atomic level by employing ab initio calculations. The deformation provoked by the reconstruction of Ge–Ge dangling bonds is found to propagate in to the network beyond the second neighbors of the vacancy. The structures of the partially passivated vacancies (VH_n , $n = 1, 2, 3$ and 4) are also calculated. For a VH_1 , a 3-center-3-electron structure is found. It is also found that the reconstruction of a Ge–Ge bond in these hydrogen passivated VH_n vacancies is, to a certain extent, controlled by the degree of distortion allowed by the covalent bonds between Ge atoms. The passivation of the vacancy by molecular hydrogen is also studied. The calculations indicate that a VH_3 vacancy cannot be passivated by a H_2 molecule. The energetics calculated for the Ge–Ge bond reconstruction is discussed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Due to the relevance in microelectronics, vacancies and their passivation with hydrogen have been the subject of numerous theoretical [1] and experimental studies, particularly with magnetic resonance techniques [2]. The reports on the subject refer mainly to silicon, whereas germanium vacancies have been much less studied. The understanding of the passivation mechanisms of dangling bonds in elemental amorphous semiconductors is of prime importance for the optimization of their opto-electronic properties, which lead

to improved performances of semiconductor devices. Theoretical calculations on the total energy and the structure of a vacancy in c-Si nano-clusters and its interaction with hydrogen have been reported in recent years [1,3–6]. In particular, the calculation at an atomic scale of the forces between dangling bonds and hydrogen, and the role of atomic relaxation around the vacancy and the reconstruction of near-neighbors' bonds provide useful insights into the problem. These theoretical methods involve substantial computational efforts, but the development of new algorithms and fast computers allows, at present, the calculation of large systems with increasing accuracy. To the present authors' knowledge no ab initio calculations have been reported on Ge vacancies.

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2. Calculations

Ab initio calculations on a model cluster of 35 Ge atoms (Fig. 1) were performed to investigate the mechanism of atomic and molecular hydrogen passivation of a Ge vacancy. The Ge nano-cluster includes the central atom, 4 first neighbors, 12 second neighbors, 12 third neighbors and 6 fourth neighbors, the remaining free bonds at the surface being fulfilled with hydrogen atoms. The calculations were performed using the Gaussian 98 program [7] employing the Hartree–Fock (HF) method [8] and the effective core potential (ECP) split valence basis set CEP-31G [9]. Although the HF/CEP-31G method includes no electron correlation effects, the relative energy of the structures has an accuracy of around 0.2 eV [10]. To the best of our knowledge, our results represent the highest ab initio calculation level applied to a medium size semiconductor nano-cluster.

The full geometry optimization of the nano-cluster resulted in a tetrahedral structure in which the bond length between the central Ge and its first-neighbors is 2.48 Å, a value close to the experimental Ge–Ge bond length found in amorphous Ge (2.46 Å) [11]. This closeness indicates

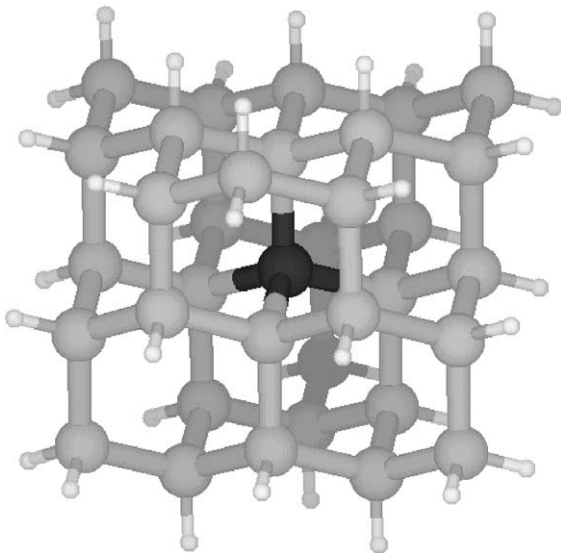


Fig. 1. Model Ge nano-cluster of 35 atoms used for the ab initio calculations. The vacancy is created by removing the central Ge atom, shown in black in the figure.

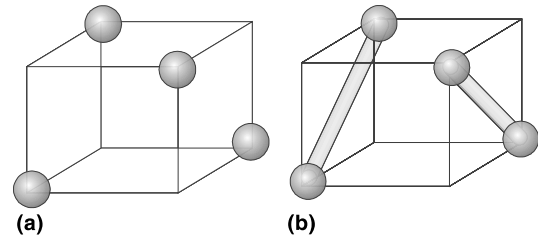


Fig. 2. Representation of (a) the position of the first neighbors in the unrelaxed vacancy created by removing the central Ge atom, and (b) the two reconstructed Ge–Ge bonds resulting from full geometry optimization of the unconstrained cluster.

that the HF/CEP-31G method provides an appropriate description of the electronic structure of an a-Ge nano-cluster. The vacancy (V) was then created by removing the central Ge atom, which is shown in black in Fig. 1. The resulting V structure (Fig. 2(a)) was then used as the starting geometry for subsequent calculations.

3. Discussion

The full geometry optimization of the completely relaxed nano-cluster containing a vacancy (V_{F-r}) induces, as expected, the reconstruction of two Ge–Ge bonds. This bond reconstruction causes a considerable deformation of the cluster structure. Its total volume shrinks from 1050 to 1031 Å³ and the distance between the Ge atoms in the reconstructed bonds shortens from 4.06 Å (V) to 2.65 Å (V_{F-r}). In an extended Ge crystal, however, the rigidity of the network would prevent such a drastic deformation. To evaluate the influence of network relaxation on the Ge–Ge bond reconstruction, calculations were performed constraining the Ge atoms surrounding the vacancy. If only the first neighbors (1) are allowed to relax (V_{r1}) while keeping all the other atoms frozen, a small distortion happens: the Ge–Ge bonds between the first and second neighbors stretch from 2.46 to 2.55 Å and bond reconstruction is prevented by the rigidity of the remaining network. The two Ge atoms cannot reconstruct a bond and stay 3.94 Å apart. Hence, the bond relaxation beyond first neighbors is necessary for the reconstruction to occur. Now, if the second neighbors (2) are also allowed to relax

Table 1
Bond lengths and electronic energies of a H-free and a H-passivated germanium vacancy in a 35 Ge atom nano-cluster

Structure	Ge–H bond length (Å)	(Reconst.) Ge–Ge length (Å)	Electronic energy (hartrees)	Relative energy (eV)
V	–	4.06 (no)	–146.89878	0
V _{r1}	–	3.94 (no)	–146.90812	–0.29
V _{r2}	–	2.90 (yes)	–146.97090	–2.28
V _{F-r}	–	2.65 (yes)	–147.02952	–4.13
(VH ₁) _{F-r}	1.53	2.60 (yes)	–147.61348	0
(VH ₁) _{F-r(3c3e)}	1.53	4.57 (no)	–147.62282	–0.25
(VH ₁) _{r1}	1.52	3.94 (no)	–147.60688	+0.43
(VH ₂) _{F-r}	1.53	2.60 (yes)	–148.20681	0
(VH ₂) _{r1}	1.50	3.74 (no)	–148.13115	+2.06
(VH ₃) _{F-r}	1.53	–	–148.78424	0
(VH ₃) _{r1}	1.50	–	–148.77021	+0.38
(VH ₄) _{F-r}	1.53	–	–149.36832	0
(VH ₄) _{r1}	1.50	–	–149.34948	+0.51

The second column indicates when Ge bond reconstruction occurs and its respective bond length. The relative energies are given, except for the (V) structure, with respect to the energy of the fully relaxed structure. The subscript following H indicates the number of H atoms in the vacancy. The subscripts r1 and r2 indicate the relaxation of first-neighbors and of first- and second neighbors, respectively.

(V_{r2}), Ge–Ge bond reconstruction occurs with a length of 2.90 Å. The energy involved in the reconstruction process (Table 1) correlates clearly with the degree of relaxation: the further the relaxation propagates, the shorter the reconstructed Ge–Ge bond length, and the lower the energy. The present data represent the first ab initio study of the propagation of the deformation caused by a Ge–Ge bond reconstruction.

The passivation of the Ge vacancy with atomic hydrogen was then investigated starting from the original structure (V). Depending on the input geometry, the introduction of one hydrogen atom (VH₁) leads to two different structures: *one* having one Ge–H bond, a Ge–Ge reconstructed bond and a dangling bond, and *another* having a Ge–H bond and an interesting 3-center-3-electron bond (VH₁)_{F-r(3c3e)}, Fig. 3(a). Both structures have close energies within the accuracy of the calculation. The (VH₁)_{F-r(3c3e)} structure is similar to that found by Roberson and Estreicher [1] on a positively charged silicon vacancy {VH₁}⁺. The neutral VH₁ silicon vacancy, however, does not display a 3-center-3-electron bond.

The inclusion of two H atoms into the vacancy (Fig. 3(b)) induces the formation of two Ge–H

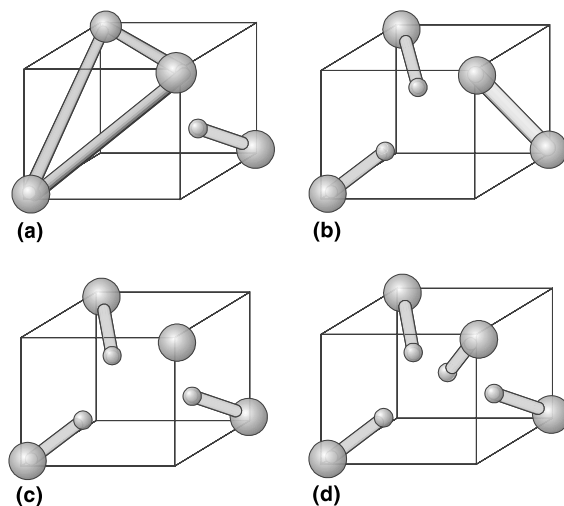


Fig. 3. Schematic representation of the calculated structures for vacancies containing: (a) one Ge–H bond and a 3-center-3-electron Ge–Ge–Ge bond (VH₁)_{F-r(3c3e)}, (b) two Ge–H bonds and a reconstructed Ge–Ge bond (VH₂)_{F-r}, (c) three Ge–H bonds and a dangling bond (VH₃)_{F-r}, and (d) four Ge–H bonds (VH₄)_{F-r}.

bonds and a 2.60 Å long reconstructed Ge–Ge bond. When three H atoms are added, three Ge–H bonds are formed and one dangling bond remains unfilled (Fig. 3(c)). Finally, when four H

atoms are added, four Ge–H bonds are formed, and the vacancy is now completely passivated (Fig. 3(d)). The hydrogens of the Ge–H bonds repel themselves, and this steric effect makes the Ge–Hs to move away from the vacancy. As a consequence, the Ge–Ge bonds between the first and second neighbors shrink from 2.48 to 2.46 Å. The Ge–H bond length in $(\text{VH}_n)_{\text{F-r}}$ structures is always 1.53 Å.

As expected, when the reconstruction of a Ge–Ge bond occurs, the Ge atoms move asymmetrically towards the center of the vacancy, which causes an asymmetric stretching of the Ge–Ge bonds between first and second neighbors. The three bonds between first and second neighbors, which were originally 2.48 Å long, become 2.49 Å (two bonds) and 2.52 Å (the remaining bond) after reconstruction.

To evaluate the extension of the deformation caused by hydrogenation and the reconstruction of a Ge–Ge bond, the energy of the (VH_1) and (VH_2) structures was also minimized allowing the relaxation of the first neighbors only $(\text{VH}_1)_{\text{r1}}$ and $(\text{VH}_2)_{\text{r1}}$. As for the H-free vacancy, no Ge–Ge bond reconstruction occurs under these conditions. A distortion beyond the first neighbors is *also* needed for a Ge–Ge bond reconstruction to occur in a H-passivated Ge vacancy. It is important to note at this point that the constrained structures shorten the Ge–H bond to 1.50 Å, a consequence of the repulsion between the Hs of the passivated bonds and also of the non-optimal position of the second neighbors in the constrained structure.

The passivation of the Ge vacancy with molecular hydrogen was also studied using ab initio methods. When a H_2 molecule is introduced into a Ge vacancy containing four dangling bonds, the H–H bond breaks spontaneously and two Ge–H bonds and a reconstructed Ge–Ge are formed. The calculations indicate therefore that no H_2 molecule can survive inside a Ge vacancy with four dangling bonds. Another interesting result is observed when a H_2 molecule is introduced into a partially passivated vacancy. For a VH_1 vacancy, H_2 dissociates without any energy barrier and two additional Ge–H bonds are formed. However, for a VH_2 vacancy, two structures are formed: (i) when the VH_2 vacancy has already a reconstructed Ge–Ge bond, the molecule stays intact inside the vacancy; (ii) when

the VH_2 vacancy has two dangling bonds, then H_2 dissociates to form a VH_4 vacancy. The latter structure is energetically favored by near 2.30 eV, but its spontaneous formation is hampered by an energy barrier corresponding to the breaking of the H–H and Ge–Ge bonds. When H_2 is introduced into a VH_3 vacancy, the molecule does not dissociate to form a VH_4 structure and a free hydrogen atom. This trend is also observed when a free H atom is introduced in to a VH_4 vacancy: the free H captures a hydrogen from a Ge–H bond to form a H_2 molecule inside a VH_3 vacancy.

4. Conclusions

The HF/CEP-31G ab initio calculations applied to a model Ge nano-cluster of 35 atoms have proven to be a useful tool to study the structures and energetics of constrained, unconstrained, H-free and passivated Ge vacancies. The energy involved in the mechanisms of bond reconstruction and the passivation by atomic and molecular hydrogen are reported for different levels of atomic relaxation around the defect. Most of the results on the ab initio level for Ge vacancies mirror those reported for an Si vacancy performed at a lower level of theory [1]. However, some important differences appear, particularly for the conditions under which bond reconstruction occurs. In germanium, the reconstruction of Ge bonds in a H-free and in a partially passivated vacancy occurs only when the first- and second-neighbors are allowed to relax.

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