Atomic Scale Structure of (001) Hydrogen-Induced Platelets in Germanium

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An accurate characterization of the structure of hydrogen-induced platelets is a prerequisite for investigating both hydrogen aggregation and formation of larger defects. On the basis of quantitative high resolution transmission electron microscopy experiments combined with extensive first principles calculations, we present a model for the atomic structure of (001) hydrogen-induced platelets in germanium. It involves broken Ge-Ge bonds in the [001] direction that are dihydride passivated, vacancies, and trapped H_2 molecules, showing that the species involved in platelet formation depend on the habit plane. This model explains all previous experimental observations.

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Defects may modify the structural, mechanical, optical, and electrical properties of materials. Possible defects, either intrinsic or introduced by technological means, are very diverse, ranging from single point defects to extended defects such as dislocation or voids. Besides, the so-called platelets form an important class of extended defects observed in both semiconductors and metals. These two-dimensional structures are formed by the introduction of a high concentration of hydrogen, a chemically active impurity [1–5], but also of rare gases like helium in nuclear environments for instance [6–8]. Platelets are especially important since they are a precursor for forming larger technologically valuable defects. In fact, depending on the conditions, platelets in semiconductors may turn to bubbles, which have been shown to be useful for removing impurities [9], or can evolve in a way leading to layer splitting (for a recent review in silicon see [3]). Obviously, to understand the formation of these larger defects the knowledge of the platelet structure is a prerequisite. It is also fundamental to finely characterize platelets since it could help to unravel the mechanisms leading to point defect aggregation.

The most studied kinds of platelet defects are the hydrogen-induced platelets (HIPs) in semiconductors like silicon or germanium [3,5] (and references therein). However, despite all investigations, the structure of HIPs is still not precisely known. In germanium, for instance, HIPs can lie in two types of habit planes, {111} and {001} [10,11]. As in silicon, their orientation depends on their energy of formation and on the surrounding stress [5] (and references therein). In (001) implanted samples, most of the HIPs are lying in the (001) planes parallel to the surface [10,11]. Raman and infrared (IR) spectroscopies have provided clear evidence that both kinds of HIPs contain Ge-H bonds [12–14]. A fundamental building block of these defects is then expected to be broken Ge-Ge bonds, passivated by hydrogen. However, many issues regarding HIP atomic structure have still to be addressed: monohydride or dihydride passivation and presence or not of vacancies and of H_2 molecules trapped inside the HIPs. The atomic structure of {111} platelets has been studied both experimentally and theoretically [12,13,15]. Proposed models, adapted from similar investigations in silicon [16–19], include a vacancy-free structure, filled with trapped H_2 molecules. However, to our knowledge, no information on the {001} HIP atomic structure in germanium is available. Also, although {001} HIPs have been investigated in silicon, conclusions are controversial. Reboredo, Ferconi, and Pantelides have modeled HIP nucleation from the agglomeration of hydrogenated vacancies [20], in agreement with an early work [21]. But following another approach which consists of studying the energy of infinitely extended HIPs, Martsinovich, Martinez, and Heggie have proposed instead dihydride passivation of Ge dangling bonds, with the presence of H_2 trapped inside the HIPs [22]. Regarding vacancies, differences in formation energy were too small to draw definite conclusions.

Many questions about the atomic structure of HIPs remain thus unanswered, the most challenging ones being whether vacancies are involved or not and how hydrogen interacts with native atoms. This is especially true for (001) HIPs in germanium, for which very little information is available. An argument explaining such a scarcity of results is the size of a platelet, typically a few nanometers, i.e., large enough to be challenging for first principles calculations, while remaining in a scale hardly accessible to experiments. Combining calculations and experiments then appears as an appropriate way to obtain meaningful results. In this Letter, we propose a model for the atomic structure of (001) HIPs in germanium, based on the combination of quantitative high resolution transmission electron microscopy (Q-HRTEM) measurements and first principles results. Our model involves broken Ge-Ge bonds in the [001] direction that are dihydride passivated, vacancies, and trapped H_2 molecules. We also show that the maximum displacement of the core atoms is about 0.6 Å.

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HIPs were formed by high fluence hydrogen implantation in (001) n-type germanium (for experimental details, see [11]). The HRTEM observations were carried out in the cross-section geometry using a JEOL 3010 microscope (300 kV, LaB_6, 0.19 nm point resolution). A typical example of a HRTEM image of a HIP seen edge on along the [1$\bar{1}$0] crystallographic direction of germanium is shown in Fig. 1(a). A striking feature of this image is the white dumbell-like row, approximately 5 nm long, that is missing at the defect core region. However, simple eye examination of such an experimental image can be misleading and does not allow the determination of the defect core structure. Q-HRTEM was thus carried out by matching images calculated from multislice simulations with the experimental data [23]. To determine conditions under which the experimental image was obtained, defocus and sample thickness ranges were preliminarily determined from a strain free region far from the defect. Input atomistic models for multislice calculations were obtained from atomistic simulations performed with the Tersoff interatomic potential [24], according to the following procedure. Using a large system including 32 000 Ge atoms, rectangular (001) HIP models were built in the center by cutting Ge-Ge [001] bonds for a total length of about 5 nm along [110], thus defining top and bottom inner surfaces of the platelet. Core Ge atoms located at both inner surfaces (all the surface atoms except the edge atoms) were successively shifted along [001] by steps of 0.01 nm, increasing the separation between top and bottom inner surfaces. For each shift, measured by δ, the whole system bar the core atoms is relaxed until atomic forces are negligible. In addition, different defect core structures were considered by removing zero, one, or two germanium layers [25]. Using these atomistic models, the contrast was optimized for a buried defect by fine-tuning of the different parameters: sample thickness, defect thickness and position (step $= 0.8$ nm), defocus (step $= 2$ nm), and δ (step $= 0.01$ nm).

A schematic structure of the defect with two removed germanium layers is shown in Fig. 1(b) together with the corresponding simulated image Fig. 1(c). The intensity profiles along the [001] direction in the middle of the defect for both the experimental and simulated images are compared in Fig. 1(d). As seen, if one layer of germanium atoms is removed [top line (red)], the contrast at the defect core is asymmetric, the intensities of the two peaks on both sides of the defect core being different. On the contrary, when two germanium layers are removed [middle line (blue)], the contrast is symmetric, which is the case when no germanium layer is removed as well (not shown here). As seen, the experimental image exhibits the same contrast symmetry around the core of the defect.

The issue regarding hydrogen passivation was addressed as well. The occurrence of a band at about 2000 cm^{-1} in IR spectroscopy measurements (not shown here) points to the presence of Ge-H bonds. Monohydride and dihydride passivations lead to two different inner surface reconstructions: a (2×1) surface reconstruction is associated with monohydride passivation (each core atom is bonded to a single H), whereas there is no surface reconstruction in the case of dihydride passivation (hydrogen atoms passivate two dangling bonds for each core atom). The (2×1) reconstruction along the [110] direction associated with

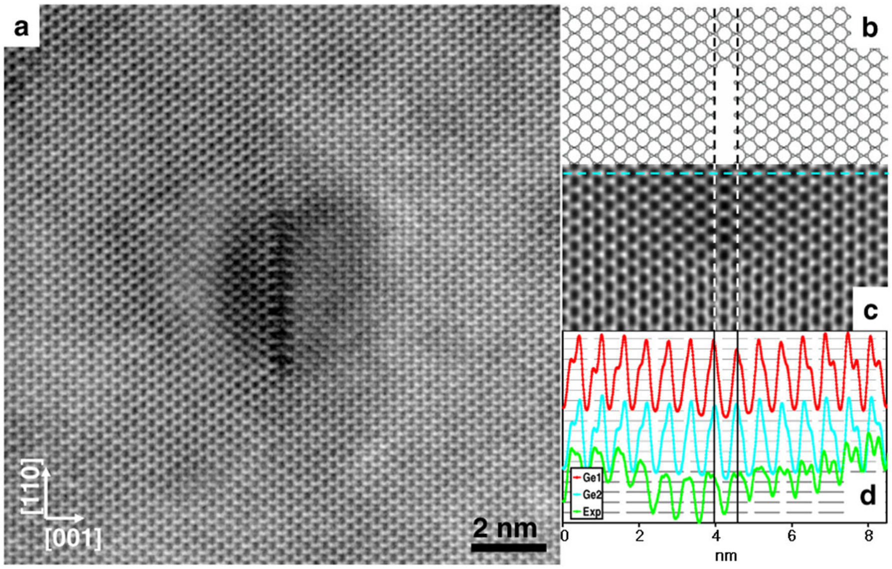

FIG. 1 (color online). (a) HRTEM image of a (001) HIP in germanium. (b) Ball-stick model of a (001) HIP with two removed Ge layers (passivating H atoms are not shown). (c) Corresponding simulated HRTEM contrast (total thickness $= 44.8$ nm, defect thickness $= 8$ nm, defect position $= 22.4$ nm, defocus $= -28$ nm, delta $= 0.6$ Å). (d) Intensity profiles extracted from the simulated images for a defect structure with one removed Ge layer [top line (red)] and two removed Ge layers [middle line (light blue)] and from the experimental image [bottom line (green)]. The latter has been obtained after multivariate statistical filtering of the central part in the HRTEM image shown in (a) for weakening the statistical noise [34,35].

monohydride passivation involves presence of dimers in the HIP inner surfaces. This possibility was ruled out since these dimers give rise to a superstructure of contrast in the simulated images, which is not observed experimentally. Such a result is in agreement with a previous study showing that a dihydride passivation is favored on Ge(001) surfaces [26]. In silicon, dihydride passivation of inner (001) surfaces has been found to be more stable than monohydride [22] as well.

Thus, the conclusion that can be drawn from Q-HRTEM analysis is twofold: Ge atoms in the core of HIPs are dihydride passivated, and no or two germanium layers are missing in the HIPs. We also performed a geometrical phase shift analysis of HRTEM images, which allows a very accurate determination of the strain field around threading defects (for instance, dislocations viewed edge on) [27]. The maximum shift of (001) lattice fringes along [001], related to the atom shift, is found to be 0.7 Å. The relevance of this value is commented on in the following.

These observations were compared to plane waves density functional theory calculations, performed using the Perdew-Burke-Ernzerhof generalized gradient approximation exchange-correlation functional [28], Hartwigsen-Goedecker-Hutter pseudopotentials [29], an energy cutoff of 10 Ha, and a Brillouin zone sampling with 10 irreducible k points. Within these conditions, the Ge lattice parameter is found to be $a_0 = 0.5773$ nm, slightly greater than the experimental value of 0.5658 nm, as expected with generalized gradient approximation calculations. We considered a model with infinite dimensions in the (001) plane of the HIPs, i.e., a single unit periodically repeated, and a large number of (001) planes above and below. Such a configuration is representative of a zone in the center of the real HIP. A primary model is built by cutting bonds between two central (001) planes, each bond being saturated with one hydrogen. Typical cell dimensions are $a_0/\sqrt{2} \times a_0/\sqrt{2} \times 11a_0$, i.e., with 44 (001) layers. Full periodic boundary conditions were used, which allows mimicking of the strength of the material surrounding the platelet, in contrast with previous calculations for which this important point was not included [19,22]. Further calculations with a higher number of (001) planes (58) or higher cutoff (30 Ha) suggested that our results were fully converged. Based on previous results reported for (001) HIPs in silicon and on our Q-HRTEM results, several HIP geometries have been considered. In the HIPs, zero, one, or two Ge layers have been removed, and a variable number of H_2 molecules has been inserted. For the latter, several locations have been tested in each case [30]. After relaxation, all forces being below 2.5×10^{-3} eV/Å, the HIP formation energy ΔE is calculated relatively to a bulk Ge system, computed in the same geometry, plus n times the formation energy of a H_2 interstitial in bulk Ge [31], $2n$ being the number of hydrogens in the HIP configuration.

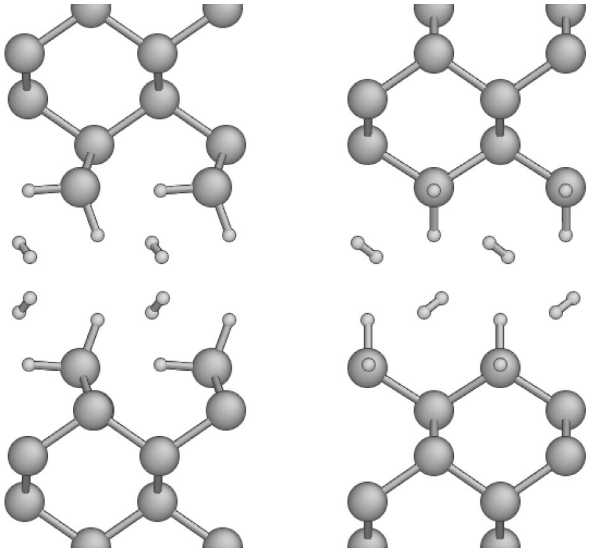

FIG. 2. Hydrogenated vacancy-based (001) HIP structure, with two germanium layers removed and two trapped H_2 molecules, along two perpendicular orientations (Ge, large spheres; H, small spheres). The structure has been repeated for clarity.

First, in almost all cases and especially for low energy configurations, the as-built symmetric dihydride structures were found to transform spontaneously into a canted structure (Fig. 2), as observed for silicon [22,32]. Moreover, we found that the position of H_2 molecules in HIPs is not a predominant factor, with involved energy differences of the order of 10 meV. Therefore in the following, we will not make any distinction between these positions. The energy of the different HIP geometries calculated and the corresponding displacement of the core atoms along the [001] direction (δ) are shown in Table I. As seen, except for the vacancy-free structure (no Ge layer removed), the insertion of one H_2 molecule, or even better two, significantly lowers the formation energy of the HIPs, as observed for (111) HIPs in germanium [13] and for both types of HIPs in silicon [19,22].

Furthermore, for a fixed number of H_2, the more stable HIP configurations are obtained with two removed Ge layers. An example of a low energy configuration, i.e., a vacancy-based structure with two removed Ge layers and containing two H_2 molecules, is shown in Fig. 2. These results are in full agreement with our Q-HRTEM analysis

TABLE I. Energy difference ΔE (in eV) as defined in the text and displacement of the core atoms δ (in Å), as a function of the numbers of removed Ge rows and of inserted H_2 molecules.

		Number of removed Ge rows		
Number of H_2		0	1	2
0	ΔE	−0.21	−0.96	−0.97
	δ	0.10	0.37	0.25
1	ΔE	0.56	−1.58	−1.83
	δ	0.73	0.82	0.50
2	ΔE	0.29	−2.28	−2.66
	δ	1.54	1.12	0.64

and confirm that two layers of germanium atoms are indeed missing in the experimental image. This vacancy-based model is in line with a recent IR spectroscopy study [14]. In the most recent model proposed for such a defect in silicon [22], it was concluded that two structures, one involving and the other one not involving vacancies, may coexist, due to small energy differences. However, in these calculations, the cell size was not fixed so that the strength of the material surrounding the HIPs was not taken into account. We believe that this limitation might be responsible for the discrepancy observed in our study.

Finally, as reported in Table I, the displacement of the core atoms in the lowest energy structure is found to be 0.64 Å. This value is close to the value derived from the geometrical phase shift analysis performed on our image. It has however to be noted that the geometrical phase shift analysis, although well established and valuable on threading defects, has still to be assessed for buried defects. Preliminary investigations tend to prove that this method has to be used with great care as the HRTEM contrast of buried defects is very sensitive to the defect position and thickness notably.

In this Letter, by combining experimental observations and simulations we propose a model for the atomic structure of (001) HIPs in germanium that may be generalized to elemental semiconductors. In contrast to the {111} HIPs [12,13,15–19,33] , the formation of (001) HIPs requires the agglomeration of vacancies. The role of hydrogen is twofold: dihydride passivation of the HIP internal surfaces and formation of trapped H_2 molecules inside the HIPs. This model explains all previous experimental observations.

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