PHYSICAL REVIEW B **79**, 153402 (2009)

Hydrogen adsorption configurations on Ge(001) probed with STM

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(Received 27 January 2009; revised manuscript received 9 March 2009; published 3 April 2009)

The adsorption of hydrogen on Ge(001) has been studied with scanning tunneling microscopy at 77 K. For low doses (100 L) a variety of adsorption structures has been found. We have found two different atomic configurations for the Ge-Ge-H hemihydride and a third configuration that is most likely induced by the dissociative adsorption of molecular hydrogen. The Ge-Ge-H hemihydride is either buckled antiparallel or parallel to the neighboring Ge-Ge dimers. The latter configuration has recently been predicted by M. W. Radny *et al.* [J. Chem. Phys. **128**, 244707 (2008)], but not observed experimentally yet. Due to the presence of phasons some dimer rows appear highly dynamic.

DOI: 10.1103/PhysRevB.79.153402 PACS number(s): 68.43.Fg, 68.47.Fg, 68.37.Ef

I. INTRODUCTION

The adsorption of molecules on the semiconductor group IV (001) surfaces is of great fundamental interest and has a large potential for applications in nanotechnology and molecular electronics. The adsorption of hydrogen on Si(001) is in many ways the prototypical system since hydrogen is the simplest molecule and Si(001) is technologically the most relevant semiconductor surface. Interestingly, much less is known about the adsorption of hydrogen on the closely related Ge(001) surface. Despite the fact that Si(001) and Ge(001) surfaces are commonly regarded as intimately related surfaces, there are also some intrinsic electronic differences between these two surfaces.[1–3]

Si(001) and Ge(001) surfaces both consist of rows of dimers buckled in an antiparallel fashion within a dimer row.[4,5] The adjacent dimer rows can either be in-phase or out-of-phase, leading to $p(2\times2)$ and $c(4\times2)$ reconstructions, respectively. Antiphase defects in the buckling registry of the dimer rows, also known as phasons, usually perform a thermally-activated random walk along the dimer rows with such a high speed that many dimers appear symmetric in standard room-temperature scanning tunneling microscopy images.[6,7]

Since the $\mathrm{Si}(001)/\mathrm{H}_2$ system is studied extensively we first briefly touch upon some relevant results that have been obtained for this system. The dissociative adsorption of molecular hydrogen on Si(001) is thermodynamically favorable, but due to the low-sticking coefficient of molecular hydrogen on Si(001) this process is hindered. There are several possible adsorption configurations for adsorbed molecular hydrogen on Si(001) such as single-dimer, two-dimer, and dihydride structures.[8] It is experimentally and theoretically well established that the two-dimer pathway is the main mechanism for dissociative adsorption of hydrogen on Si(001) surface.[8]

Theoretical studies on the adsorption of molecular and atomic hydrogen on Ge(001) are limited to density-functional theory (DMT) calculations by Okamoto[9] and Radny *et al.*[10] Similar to Si(001) Okamoto[9] found that the two-dimer (inter-dimer) adsorption process on Ge(001) has a lower-reaction barrier as compared to the single-dimer process. In a recent study by Radny *et al.*[10] the attention was focused on the energetically most favorable adsorption configurations and the effect of hydrogen adsorption on the buckling angle of the dimer and its electronic structure as a function of surface-charge accumulation.

So far, experimental techniques like temperature-programmed, collision-induced, and laser-induced desorption,[11–14] high-resolution electron energy loss spectroscopy,[13,15] high-resolution infrared spectroscopy,[16] low-energy electron diffraction,[14,15] and Raman spectroscopy[14] have been used to study the adsorption of atomic hydrogen on Ge(001). The majority of these studies dealt with hydrogen coverages near one complete monolayer. In order to obtain these high hydrogen coverages, molecular hydrogen was decomposed into atomic hydrogen by using a hot *W* filament in the proximity of the Ge sample. Finally, real-space scanning tunnel microscope (STM) studies of atomic hydrogen adsorption on Ge(001) are limited to two reports by Radny *et al.*[10] and Maeng *et al.*[17]

Here, we will study the adsorption of both molecular and atomic hydrogen on Ge(001) at low hydrogen dosages. High-resolution images recorded at 77 K reveal several hydrogen adsorption geometries. The most abundant one is already well known and well documented, but we also found evidence for another adsorption geometry that has recently been predicted by Radny *et al.*[10]

II. EXPERIMENTAL

Ge samples were cut from 2″×0.5 mm, single side-polished Ge(001) wafers which are slightly *n*-type doped (5–40 Ω cm). Samples were mounted on Mo holders and contact of the samples to any other metal during preparation and experiment was carefully avoided. The Ge(001) samples were cleaned by 800 eV Ar ion sputtering and annealing at 1100 K. After several cleaning cycles the Ge(001) samples were atomically clean and exhibited a well ordered $(2\times1)/c(4\times2)$ domain pattern at room temperature.[4] Subsequently, the Ge(001) sample was exposed at room temperature to hydrogen at a pressure of 10^{-6} Torr for 100 s. The hydrogen pressure was measured with an ion gauge, that was placed in the proximity of the Ge(001) sample. The hot fila-

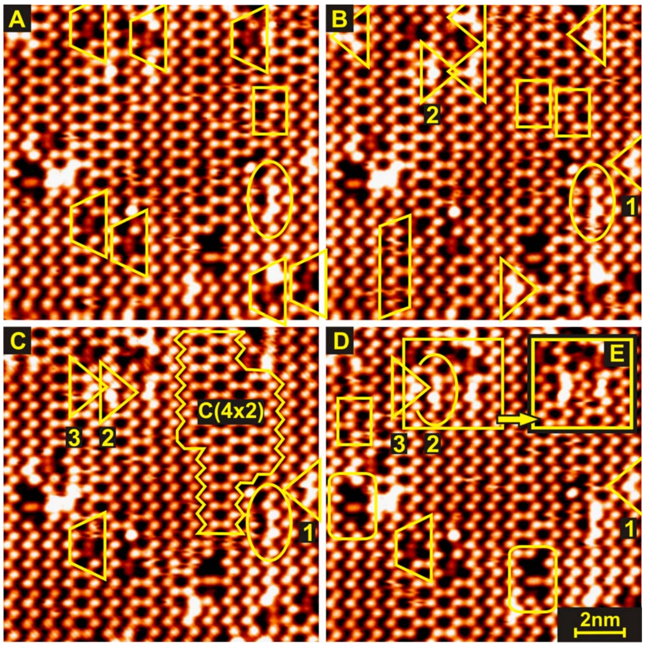

FIG. 1. (Color online) Five successive STM images of a Ge(001) surface—including inset E—recorded at 77 K, after exposure to 100 L hydrogen. Tunnel current 0.5 nA is and sample bias -1.0 V. The time lapse between successive images is 5 min.

ment of the ion gauge decomposes the molecular hydrogen into atomic hydrogen. After pumping away the hydrogen the sample was transferred to the STM chamber and cooled down to 77 K. After a few hours the Ge(001) sample was imaged with STM.

III. RESULTS

Figure 1 shows a series of STM images, recorded at 77 K, of the Ge(001) surface after exposure to 100 Langmuir hydrogen at room temperature. A myriad of features and dynamic processes can be observed in these images.

In Fig. 1(A) the features indicated by trapezoids resemble an antiphase boundary in the buckling registry. The two dim blobs in the middle are most probably dimers that buckled in a parallel direction. However, their buckling angle is much smaller than the buckling angle of their neighbors.

In Fig. 1(C) one can observe a normal diffusing phason at top side of the only outlined trapezoid feature. The trapezoid feature remains unaffected by the diffusing phason [see Fig. 1(D)] and only the adjacent dimer becomes a little fuzzy. We have studied a number of these trapezoid features and all of them were not affected by diffusing phasons throughout the whole experiment. Our data reveals that phasons bounce back when they collide with a trapezoid feature.

Figure 1(A) also contains another antiphase boundarylike feature, indicated by a rectangle. The rectangle feature deviates substantially from the trapezoid type since the two middle dimers are as bright as their neighbors. In addition and in contrast to the trapezoid feature, the rectangle features are remarkably dynamic; i.e., they appear, disappear, or jump to neighboring sites from image to image.

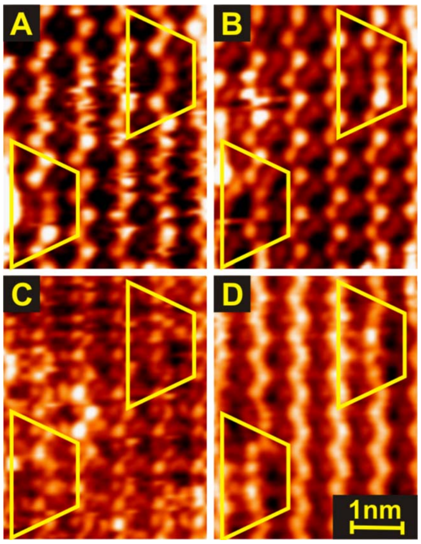

FIG. 2. (Color online) Bias-dependent STM topography images of Ge(001) surface containing two trapezoid features. Sample bias (a) -0.9 V, (b) -0.5 V, (c) -0.2 V, and (d) $+0.8$ V.

Another interesting feature in Fig. 1(A) is outlined by an ellipse. This feature is symmetric around its central atom which appears to be somewhat smaller and less bright than the surrounding atoms. In Fig. 1(B) a phason is approaching the ellipse feature from the lower side. Upon a collision with the phason, the ellipse feature remains intact [Fig. 1(C)].

Figure 1(B) also displays several features indicated by triangles. These triangle features typically consist of three buckled dimers. The middle one is the brightest one, but also the other two dimers are brighter than the normal dimers. The triangle feature labeled by number 1 interacts with a diffusing phason in Fig. 1(C). As can be seen in Fig. 1(D) triangle 1 remains intact. However, this is not the case for triangle 2 [see Fig. 1(B)]. In Fig. 1(C) a phason has passed triangle 2 and triangle 2 has transformed to a configuration as shown in inset E of Fig. 1(D).

Surprisingly Fig. 1(C) shows an example of the birth of a triangle feature. This feature is labeled 3. Note that triangle 3 disappears again in the inset E of Fig. 1(D).

In Fig. 1(C), an isolated $c(4\times2)$ reconstructed domain surrounded by a $p(2\times2)$ reconstructed domain is outlined. Due to the presence of phasons the boundary between the $c(4\times2)$ and $p(2\times2)$ domains is rather dynamic.

In Fig. 1(D) two special features indicated by roundly cornered rectangles are shown. They are stable throughout the whole experiment. This feature consists of three missing dimers: two adjacent missing dimers, then a regular unbuckled dimer, and finally a third missing dimer. These defects are referred as 2+1 type defects and were observed by Niehus *et al.*[18] on Si(001) and later by Gurlu *et al.*[19] on Ge(001).

In order to obtain a better insight in the electronic structure of the trapezoid features, a set of bias dependent topography images have been made, which are shown in Fig. 2. Figure 2(A) is taken at a sample bias of -0.9 V bias (filled states) and shows exclusively the upward buckled atoms of the dimers. The trapezoid feature located at the top of

Fig. 2(A) is in its original configuration, whereas the lower trapezoid feature interacts and transforms upon a collision with a phason into another configuration. The two middle dim dimers stay intact but the lower neighbor dimer has been pushed to an unfavorable buckling configuration. Figure 2(B) shows an image of the same area taken at −0.5 V. The second layer of the substrate becomes more visible at this bias voltage. Moreover, the top trapezoid feature has now transformed to a metastable state, whereas the lower one has returned to its original configuration again. These results again confirm that phasons cannot change or pass the trapezoid features.

In Fig. 2(C) which is taken at a bias voltage of −0.2 V, the dimer rows and trapezoidlike features are not visible anymore. Finally, in Fig. 2(D) an empty-state image recorded at +0.8 V bias is displayed. Note that in the empty state images the bright spots of the dimers appear on the opposite side of the dimers as compared to the filled-state images. The latter also holds for the trapezoidlike features.

IV. DISCUSSION

The bright triangle features shown in Fig. 1 are already well known and correspond to the adsorption of a single hydrogen atom. It is predicted by DFT calculations that the Ge atom, at which the hydrogen atom has adsorbed, relaxes toward the surface.[10] Consequently, its counter atom buckles upwards which appears as the bright spot at the middle of the triangle feature. In this case an additional electron has been transferred from the bulk to the upper atom of the hydrogen-adsorbed dimer. This makes the dangling bond of the up atom of the dimer completely filled. This configuration is referred as HH1-N_e+1 by Radny *et al.*[10]

The ellipse feature matches very well to the other adsorption geometry, HH1-N_e, that has been put forward in Ref. 10. The main difference with the HH1-N_e+1 geometry is that the hydrogenated atom now buckles upward. In this case the dangling bond of the other atom of the dimer becomes empty because its unpaired electron is delocalized on the surface.

Intuitively one would expect that the antiparallel buckled configuration (HH1-N_e+1) has a lower energy than the parallel one (HH1-N_e) since it minimizes the surface strain more effectively. However, because the total number of electrons in these configurations is different, they cannot be compared directly.[10]

The fact that we observe the coexistence of both adsorption geometries makes it very likely that the energy difference between them is quite small. However, we cannot rule out the possibility that a defect or an impurity atom near the hydrogen adsorption site stabilizes the HH1-N_e-adsorption geometry.

The existence of antiphase boundaries on Ge(001) dimer rows, also known as phasons, has been predicted theoretically but because of their high diffusion speed, so far no real-space observation has been reported for them. The only indirect evidence for their existence is the appearance of fuzzy dimers in some parts of the images [see, e.g., the parallelogram in Fig. 1(B)].

In order to study the dynamics of these rapidly diffusing phasons we have locked the STM on top of a dimer and recorded the current as a function of the time in the open feedback loop configuration. Figure 3 shows such a current time trace. The current jumps back and forth between its set point of 0.5 nA and a much higher value of about 2–3 nA. We anticipate that these higher current values correspond to the passages of a phason.

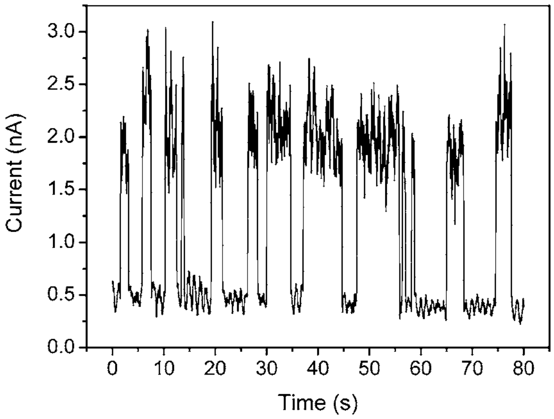

FIG. 3. Open-loop current time trace recorded on a fuzzy appearing dimer row [see parallelogram in Fig. 1(B)]. The STM tip was placed above one of the atoms of a dimer of a dynamic dimer row. Each jump in the current time trace is due to the passage of a phason. The set point current is 0.5 nA, and the sample bias is −1.0 V.

The rectangle features shown in Figs. 1(A)–1(C) can be considered as temporarily immobile phasons. It is most likely that these phasons are temporarily pinned by a (sub)surface defect, interstitial atom, or dopant atom.

However, one should be cautious about regarding the rectangle features as genuine phasons. We noticed that for almost all rectangle features there is a small dim protrusion exactly in the middle of the feature as highlighted in Fig. 4(A). This leaves the possibility that a rapidly diffusing phason just passed the STM tip during imaging of the structure under study. As outlined in the Figs. 4(B)–4(D), this will alter the buckling registry of the neighboring dimers as well, leaving the impression that the rectangle feature is an immobile phason.

In contrast to the rectangle features, the trapezoid ones do not exhibit any dynamics. Even an encounter with a phason does not alter their geometry. This observation, along with the fact that the two dim atoms are identical, suggests that we are dealing with two hydrogen atoms adsorbed at neighboring sites. The latter is in accordance with the dissociative adsorption of hydrogen molecules via the two-dimer pathway.

The two middle dimers of a trapezoid feature are much dimmer than the dimers of a single hydrogen atom adsorption site, i.e., triangle feature. The trapezoid feature looks very similar to DFT simulated filled-state STM images for the adsorption of hydrogen on Si(001) dimers.[20] In this case both middle dimers reside in the HH1 configuration. In this case the hydrogen atoms have adsorbed on the downward buckled atom. But the dangling bonds of their upward buckled counter atoms are now filled with one electron each.[20]

The fact that we have not found any evidence for the dissociative adsorption of molecular hydrogen via the one

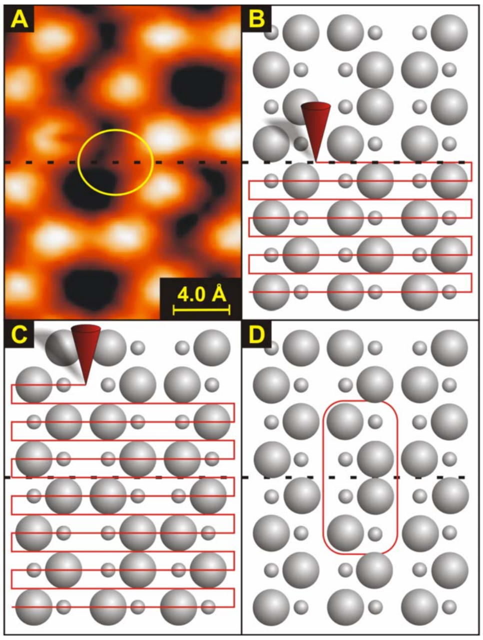

FIG. 4. (Color online) The rectangle features can be an artifact generated by the fast movement of a phason under the STM tip. (a) STM image of a rectangular feature. The protrusion in the middle of rectangle feature is marked by a circle. The latter might be due to a change of the buckling configuration when the tip is scanned along the dashed line. (b) shows the STM tip [the red (dark gray) cone] scanning across a dimer row. A phason presents at the upper half of the graph. Immediately after the tip passes the middle of the dashed line, the phason moves downward and changes the phase of the dimer row as shown (c). (d) shows the final result as imaged by STM. The image suggests the presence of an immobile phason.

dimer pathway is consistent with DFT calculations for Ge(001).[9] Similar results have been reported for Si(001).[21]

Figure 2 gives valuable information on the electronic structure of the trapezoid features. In the STM image taken at -0.9 V bias [Fig. 2(A)] the most obvious features are the individual upward buckled atoms of the dimers. This shows that at this bias voltage the tunneling electrons mainly come from the π dangling bonds of the Ge dimers. Lowering the sample bias to -0.5 V enhances the electronic features of the lower lying layer, while the dimer row related features are getting more blurred. By lowering the absolute value of the bias voltage the dimer rows and trapezoid features become even more invisible for both polarities. As can be seen in Fig. 2(C), at -0.2 V there is no specific signature of the hydrogen adsorption sites. At low negative sample biases, electrons mainly tunnel from the back bonds of the dimers to empty states of the tip.[1] As is obvious from the image Fig. 2(C) the adsorption of hydrogen hardly affects the electronic structure of these back bonds.

By increasing the bias to $+0.8$ V, the dimer rows become again visible. At this sample bias, electronic states are smeared out along the dimer row direction, but rather localized in a direction perpendicular to the dimer row direction. At $+0.8$ V the hydrogen adsorption sites become visible as well. They have more or less the same brightness as the other atoms, but their electronic states are localized in both orthogonal directions.

V. CONCLUSION

In summary, we have studied the adsorption of hydrogen on Ge(001) with scanning tunneling microscopy at 77 K and found a number of hydrogen-induced adsorption features as well as mobile and immobile appearing antiphase boundaries. We have found evidence for a hydrogen adsorption geometry that has recently been predicted by DFT calculations.

ACKNOWLEDGMENTS

This work is financially supported by NanoNed, the nanotechnology network of the Netherlands.

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[1] M. W. Radny, G. A. Shah, S. R. Schofield, P. V. Smith, and N. J. Curson, Phys. Rev. Lett. **100**, 246807 (2008).
[2] O. Gurlu, H. J. W. Zandvliet, and B. Poelsema, Phys. Rev. Lett. **93**, 066101 (2004).
[3] E. Landemark, R. I. G. Uhrberg, P. Kruger, and J. Pollmann, Surf. Sci. Lett. **236**, L359 (1990).
[4] H. J. W. Zandvliet, Phys. Rep. **388**, 1 (2003).
[5] H. J. W. Zandvliet, Rev. Mod. Phys. **72**, 593 (2000).
[6] T. Sato, M. Iwatsuki, and H. Tochihara, J. Electron Microsc. **48**, 1 (1999).
[7] A. van Houselt, R. van Gastel, B. Poelsema, and H. J. W. Zandvliet, Phys. Rev. Lett. **97**, 266104 (2006).
[8] M. Dürr and U. Höfer, Surf. Sci. Rep. **61**, 465 (2006).
[9] Y. Okamoto, J. Phys. Chem. B **106**, 570 (2002).
[10] M. W. Radny, G. A. Shah, P. V. Smith, S. R. Schofield, and N. J. Curson, J. Chem. Phys. **128**, 244707 (2008).
[11] S. Shimokawa, A. Namiki, M. N. Gamo, and T. Ando, J. Chem. Phys. **113**, 6916 (2000).
[12] L. B. Lewis, J. Segall, and K. C. Janda, J. Chem. Phys. **102**, 7222 (1995).
[13] L. Surnev and M. Tikhov, Surf. Sci. **138**, 40 (1984).
[14] G. Underwood, L. Keller Ballast, and A. Campion, Surf. Sci. **602**, 2055 (2008).
[15] L. Papagno, X. Y. Shen, J. Anderson, G. Schirripa Spagnolo, and G. J. Lapeyre, Phys. Rev. B **34**, 7188 (1986).
[16] Y. J. Chabal, Surf. Sci. **168**, 594 (1986).
[17] J. Y. Maeng, J. Y. Lee, Y. E. Cho, S. Kim, and S. K. Jo, Appl. Phys. Lett. **81**, 3555 (2002).
[18] H. Niehus, U. K. Köhler, M. Copel, and J. E. Demuth, J. Microsc. **152**, 735 (1988).
[19] O. Gurlu, H. J. W. Zandvliet, B. Poelsema, S. Dag, and S. Ciraci, Phys. Rev. B **70**, 085312 (2004).
[20] M. W. Radny, P. V. Smith, T. C. G. Reusch, O. Warschkow, N. A. Marks, H. F. Wilson, S. R. Schofield, N. J. Curson, D. R. McKenzie, and M. Y. Simmons, Phys. Rev. B **76**, 155302 (2007).
[21] M. Durr, Z. Hu, A. Biedermann, U. Hofer, and T. F. Heinz, Phys. Rev. Lett. **88**, 046104 (2002).