STM tip-induced creation and annihilation of small Ge clusters and missing dimer vacancies on Ge(001)

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We have observed the appearance and disappearance of small Ge clusters and missing dimer vacancies on Ge(001) during scanning with a scanning tunneling microscope (STM) under standard tunneling conditions at room temperature. We claim that these processes are induced by the STM tip. Moreover, we emphasize that the observed features depend on the usage of different *W* tips, even if prepared following the same procedure and using the same tunneling conditions, suggesting a critical influence of the tip shape. [S0163-1829(98)03603-0]

With the advent of the scanning tunneling microscope (STM), it has become possible to study surfaces in real space with atomic resolution. The STM technique allows the observation of individual surface defects such as, e.g., kinks, steps, and vacancies.[1–6] Despite the fact that the tunneling conditions are in most cases quite severe (typically tunneling currents are in the sub-nA range, and the sample bias is in the volt range) several experimental papers have shown or, at least, assumed that the influence of the STM tip is negligible. There are several interactions between tip and substrate, e.g., electron-current-induced or electric-field-induced effects and for very small tip-substrate distance even direct contact and chemical interactions, which can modify the surface morphology on an atomic level. Recently, the dramatic influence that the tip of a STM can have on the atomic motion of Ag on Ag(110) and the displacement of monatomic steps of Ag(110) has been demonstrated by Li, Berndt, and Schneider.[7] For semiconductor surfaces like Si and Ge most energetic parameters such as, atomic diffusion barrier and kink detachment barriers are usually much higher than on metals. Therefore, it seems very likely that the perturbative effect of the STM tip in the case of semiconductor surfaces is much less pronounced. In this Brief Report, however, we show that the STM tip can also have a dramatic influence on the semiconductor group-IV Ge(001) surface. Under standard tunneling conditions of 1 nA, and a negative sample bias of 1.5–2-V, Ge ad-dimers and small Ge clusters are removed from the substrate and missing dimer vacancies are created or annihilated on Ge(001) at room temperature. We will argue that these surface modification processes are induced by the STM tip.

The experiments are performed in an ultrahigh-vacuum system with a base pressure of 1×10^{-10} torr that contains an Omicron STM and an ion gun. STM tips are made from electrochemically etched (2-ML NaOH) *W* wires. After etching, the *W* tips are introduced into the vacuum system. The *W* tips were bombarded with Ar^+ ions of 800 eV for 10 min before they were used to image the Ge(001) surface. Occasionally we applied sample biases of ±5 V in order to improve the resolution. The Ge(001) samples are cleaned by cycles of sputtering with Ar^+ ions, and annealing at temperatures 1000–1100 K. Ge ad-dimers and small Ge clusters are created by low dose ion bombardment with 800-eV Ar^+ ions and subsequent annealing at 350–500 K.

STM images of Si or Ge surfaces represent these surfaces at a freezing-in temperature between 500 and 800 K. A striking observation in filled-state STM images of (001) surfaces is the presence of randomly distributed dark spots. The concentration of these dark spots is typically about 0.5–1 % on the Si(001) and typically 0.1% or less on the Ge(001) surface. A STM image, taken at constant current, maps out the contour of constant surface charge density, and as such, the dark areas in Figs. 1 and 2 do, in principle, not have to correspond to a missing dimer vacancy or missing dimer vacancy complex. The dark areas may also represent a dimer or dimer complex that has recessed into the surface.[8] Recently, however, Wang, Arias, and Joannopoulos[9] performed *ab initio* total-energy calculations in order to determine the properties of several missing dimer vacancy and dimer interstitial complexes of the Si(001) surface. These calculations have revealed that the missing dimer vacancy model is a much more probable model than the dimer interstitial model proposed by Ihara *et al.*[8] The formation energy of missing dimer vacancies in different local arrangements on Si(001) varies from 0.14 to 0.22 eV per dimer. Wang, Arias, and Joannopoulos identified two mechanisms that contribute to the low formation energy and stability of missing dimer vacancies: first, the need to eliminate dangling bonds in the lower layer and, second, the tendency to relief surface strain energy. Provided that the *barrier* for formation of missing dimer vacancies is not too high, the electric-field strength in

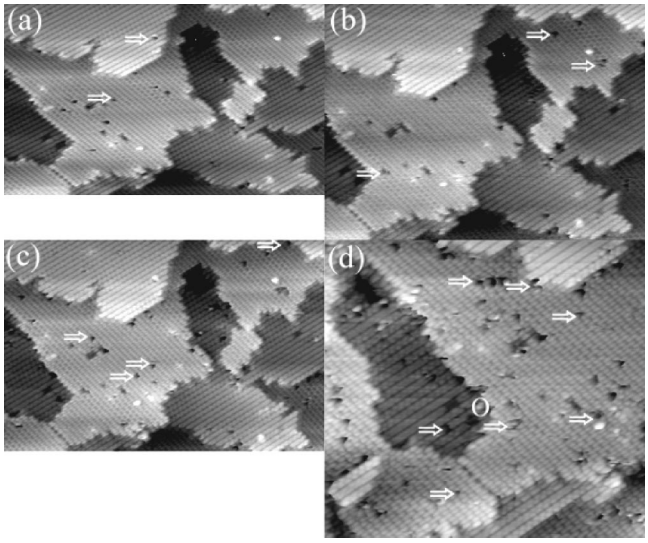

FIG. 1. Four subsequent images of Ge(001) taken at room temperature. The tunneling current is 1 nA, and the sample bias is -2 V. (a)–(c) 400×300 Å^2 and (d) 220×260 Å. ($\Rightarrow$) refers to a missing dimer vacancy that annihilates [image (a)] or to a newly created missing dimer vacancy [images (b)–(d)] and (o) to an appeared cluster, probably a Ge ad-dimer in image (d).

the tunneling region is in most cases sufficiently strong to allow the creation of a missing dimer vacancy on Si(001). An observation in favor of the missing dimer vacancy model on Ge(001) is that high-resolution line scans across the missing dimer vacancy complexes shows depths of the order of the monatomic step height, i.e., 1.4 Å, indicating that indeed at the location of the defect a dimer (or dimers) are absent in the top layer of Ge(001).

In Fig. 1 four subsequent images of a Ge(001) surface are displayed. In Figs. 1(b)–1(c) a number of missing dimer vacancies are created or annihilated. Some of the newly created or annihilated missing dimer vacancies in Fig. 1 are labeled by $\Rightarrow$. For reasons of clarity, we have only labeled some missing dimer vacancies that are *annihilated* in Fig. 1(a), and only labeled some *newly created* missing dimer vacancies in Figs. 1(b)–1(d). Close examination of Fig. 1 reveals that the number of created missing dimer vacancies exceeds the number of missing dimer vacancies that are annihilated. In Fig. 1(d), an STM image is shown, taken with the same tip and under exactly the same tunneling conditions apart from a smaller step size in the x and y range the step interval in the x and y directions of Figs. 1(a)–1(c) is 2 and 1 Å in Fig. 1(d)]. The most noticeable difference between Figs. 1(a) and 1(c) on one hand, and Fig. 1(d) on the other hand is the dramatic increase in the density of newly created missing dimer vacancies. The experimental observation that longer scanning times results in more missing dimer vacancies strongly supports the idea that these vacancies are induced by the STM tip, and that tip-assisted diffusion plays a minor role. Moreover, a closer observation of the location where missing dimer vacancies are created reveals that most of the defects have a particular triangularlike shape, suggesting that the dimer is pulled out by the tip during scanning (the triangular shape may be explained in the following way: the substrate dimer rows make an angle of about 45° with the scan direction, combined with the fact that the missing dimer vacancy is probably created in a single scan line). Remarkably, the resolution does not change after this process, which left us to conclude that the outermost apex of the tip remains unaltered. It seems as if the dimer (or dimers) which was removed from the Ge(001) surface was picked up by the tip, but does not reside at the apex of the W tip. Probably this dimer has diffused to an energetically more favorable position,[10] or is dragged along by the tip. The observation that some missing dimer vacancies are annihilated suggest that at least some of the dimers which have been attached to the tip during scanning can detach again, and fill an existing missing dimer vacancy position. This scenario is basically the scenario as proposed by Li, Berndt, and Schneider.[7] These authors argued that in their case diffusing atoms might condense at the STM tip. In Fig. 1(d), another cluster, probably a Ge ad-dimer, appears in the label ''o''. Interestingly, some W tips give rise to the annihilation and creation of missing dimer vacancies and small Ge clusters, whereas others do not. This might also explain why, on metal surfaces such as Cu, Au, and Ag, contradicting experimental observations with respect to the tip-surface interactions have been reported.[7,11–13]

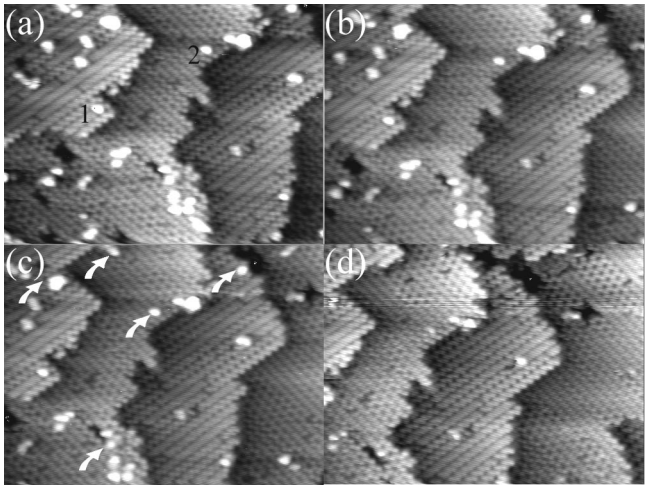

FIG. 2. Four subsequent images of Ge(001) taken at room temperature. The tunneling current is 1 nA, the sample bias is -2 V, and the scan size is 250×200 Å^2. The Ge clusters are created by low dose ion bombardment with Ar^+ ions at room temperature followed by subsequent annealing at 450 K. ($\Rightarrow$) refers to a Ge cluster or Ge ad-dimer that disappears. The cluster, probably a Ge ad-dimer, labeled ($\Rightarrow$) in the middle of image (c), converts to a weaker and smaller white spot in image (d). In image (a), Ge ad-dimers with dimer bonds aligned along and perpendicular to the substrate dimer bonds, are labeled 1 and 2, respectively.

It still seems very remarkable that some W tips do give rise to surface modifications, whereas others do not influence the surface morphology at all. The presence of small amounts of H_2 in the background pressure cannot explain our observations for the following reason: although the Ge(001) surface is almost inert for H_2, it might be possible that H_2 dissociates by the W-STM tip, and then subsequently reacts with the Ge(001) surface. At room temperature, however, the reaction of Ge(001) with atomic hydrogen results in the Ge(001)-2×1:H monohydride phase, e.g., the dimer bond is still intact.[13–16] Moreover, we did not find any evidence of bright ball-like features in the filled-state images character-

istic of atomic hydrogen adsorbed on the unpaired dangling bonds of the surface atoms.[17] Even intentional exposure of the Ge(001) to a molecular hydrogen pressure of 10^{-7} torr during scanning with the STM tip does not alter our observations. Therefore, we rule out the possibility that the presence of H_2 results the creation of additional missing dimer vacancies during scanning in our specific case.

In Fig. 2 four subsequent images of Ge(001) are shown. The small white blobs which are elongated along or perpendicular to the substrate dimer rows are Ge ad-dimers. Several, somewhat larger, white blobs are probably clusters containing three or more Ge adatoms. The time lapse between the images is about 1 min, the tunneling current is 1 nA, and the sample bias is -2 V. Remarkably there are no differences between Figs. 2(a) and 2(c), whereas in Fig. 2(d) the Ge ad-dimers or clusters labeled $\rightarrow$ have suddenly disappeared.[18] Notice also the slight increase in resolution of Fig. 2(d) compared to Figs. 2(a)–2(c).

Most of the smaller white blobs are Ge ad-dimers that reside on top of the substrate dimer rows. Some of these dimers are oriented along the substrate dimer bond [e.g., the dimer labeled 1 in Fig. 2(a)], whereas others are oriented perpendicular to the substrate dimer bond [e.g., the dimer labeled 2 in Fig. 2(a)]. Since the on-top residing Ge ad-dimers are not observed to make even one single hop to a nearest-neighbor lattice site [apart from the removal of the Ge ad-dimers in Fig. 2(d)], a lower limit on the barrier to diffusion can be made. The maximum observation time is $\sim$1000 s. Assuming a preexponential factor of 10^{13} s^{-1},[19] the barrier to diffusion is at least 0.9 eV. On the closely related Si(001) surface, the diffusion barrier for Si ad-dimers is 1 eV.[19] Interestingly, these Si ad-dimers on Si(001) rotate on a time scale of seconds (minutes) at room temperature.[20] Despite the fact that both Ge ad-dimers positions, i.e., dimer bonds aligned along or perpendicular to the substrate dimer rows, on Ge(001) are found, we have found no rotation event at room temperature. This is an interesting result because most energetic barriers, such as kink detachment and nearest-neighbor interaction energies between dimers, are found to be somewhat lower as compared to the corresponding barriers on the closely related Si(001) surface.

In summary, under standard tunneling conditions the STM tip can create and annihilate small Ge clusters and missing dimer vacancies on Ge(001). Whether or not these processes occur during the scanning process (under standard tunneling conditions) depends crucially on the STM tip. These experimental findings *stress* the need to critically examine STM data, even in the case of relatively stable semiconductor surfaces.

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