Adatom diffusion on Ge(111) and the corresponding activation energy barrier

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In this paper, surface diffusion of Ge adatoms on the In-stabilized moderate temperature phase of Ge(111) was studied with a room-temperature scanning tunneling microscope and it has been found that, in addition to diffusion of individual adatoms neighboring to some defects, the majority of the moving adatoms forms strings or closed loops consisting of segments lying along ⟨110⟩ directions. The mean lifetime of Ge adatoms on Ge(111) has been obtained, from which the activation energy barrier has been determined to be 0.83 ± 0.02 eV. This experimental result of this quantity is in excellent agreement with its theoretical value for clean Ge(111) surfaces, thus showing not only that the energy barrier obtained here is a characteristic of clean Ge(111) surfaces, but also that there is no complicated collective motion involved in surface diffusion of Ge adatoms. [S0163-1829(96)03520-5]

I. INTRODUCTION

Although from the annealed Ge(111) surface the ''(111)-8'' low-energy electron diffraction (LEED) pattern was observed a long time ago,[1] only recently the surface reconstruction has been known to be $c(2\times8)$.[2,3] On the basis of the analysis of ''missing'' LEED spots, the $c(2\times8)$ unit cell was predicted to consist of equal (or very similar) (2×2) and $c(2\times4)$ subunits.[3] This prediction was immediately confirmed by scanning tunneling microscopy (STM).[4] More recently, it has been further determined that both the (2×2) and $c(2\times4)$ subunits consist of an adatom and a rest atom.[5–9] Very recently, some quantitative differences between the (2×2) and $c(2\times4)$ subunits have been disclosed both experimentally[10] and theoretically,[11] although in some cases they can be equivalent.[12]

It is known that the $c(2\times8)$ reconstruction transforms to a (1×1) phase at 573 K, i.e., the moderate-temperature (MT) phase,[13–16] and that the MT phase does not have an ideally terminated bulklike structure but still has adatoms and rest atoms,[15] probably forming honeycomb (2×2) domains.[14] At approximately 1050 K, the MT phase transforms to a high-temperature (HT) phase,[17] which has been of much interest.[18–21] It is very likely that this HT transition is of order-order and in the HT phase the adatoms of the original type remain the majority on the surface, although their (2×2) order in the MT phase no longer exists.[19,21]

In view of the great importance of the adatoms and their ordering to clean Ge(111) surfaces at low, moderate, and high temperatures, adatom diffusion on the surfaces has been attracting much attention.[22–25] As a result shift in position of a large number of Ge adatoms along a specific row has been observed with STM (Ref. 22) and, on the basis of *ab initio* molecular dynamics, diffusion of the adatoms is expected to be mostly along the ⟨110⟩ directions with an activation energy barrier of about 0.8 eV.[23] The experimental value, however, has not been reported, so far. On the other hand, by means of a hot STM, diffusion of isolated Pb adatoms on Ge(111) has also been observed and the corresponding activation energy barrier E_D was measured to be 0.54 ± 0.03 eV (Ref. 24), which is in good agreement with the theoretical result of 0.56 eV.[25] The very low effective attempt frequency $(7\times10^5$ Hz) observed in the experiment[24] has been explained in terms of orchestrated exchange (or, complicated collective motion) of many adatoms.[25]

Since very small amounts of group-III metal on Ge(111) can stabilize the MT phase at room temperature,[26–28] in the present paper, we study Ge adatom diffusion on the In-stabilized MT phase of Ge(111) by means of a room-temperature STM.

II. EXPERIMENT

The experiment, carried out in a UHV system consisted of a sample preparation chamber and a main chamber where the STM, LEED, and AES (Auger electron spectroscopy) were installed. The homemade STM has been reported before[29] and is capable of giving atom-resolved images from clean Au(001) and Au(111) surfaces.[30] The constant-current mode was used throughout the STM work. The bias was applied to the sample and the tip was grounded. The tip was made out of tungsten wire with electrochemical etching. The sample with a size of $7 \times 7 \times 0.5$ mm^3 was cut from a Sb-doped Ge(111) wafer (18–20 Ω cm) and was used in a previous work of In/Ge(111) interfaces.[31] Before any In deposition, after several cycles of Ar^+ bombardment (5×10^{-5} Torr, 600 V, 1.5 h) and annealing (800 °C, 15 min), a clean and well-ordered Ge(111)-$c(2\times8)$ surface was obtained, as verified by its sharp LEED patterns and the very small AES signals of O and N, i.e., the O(503 eV)/Ge(47 eV) and N(379 eV)/Ge(47 eV) ratios being below 3×10^{-4}. At the end of the In/Ge(111) work, however, even after the same cleaning and annealing cycles, only the typical LEED patterns of the MT phase,[14] were observed, rather than the $c(2\times8)$ patterns, indicating that the surface had a structure of the In-stabilized MT phase,[26–28,32] although the In coverage was below the detecting level of AES, i.e., lower than 0.05 ML. We study the surface diffusion of adatoms on this surface in the present work.

To find out which adatoms among hundreds or more had moved between two consecutive STM images of a same area, we subtract the latter from the former and get the re-

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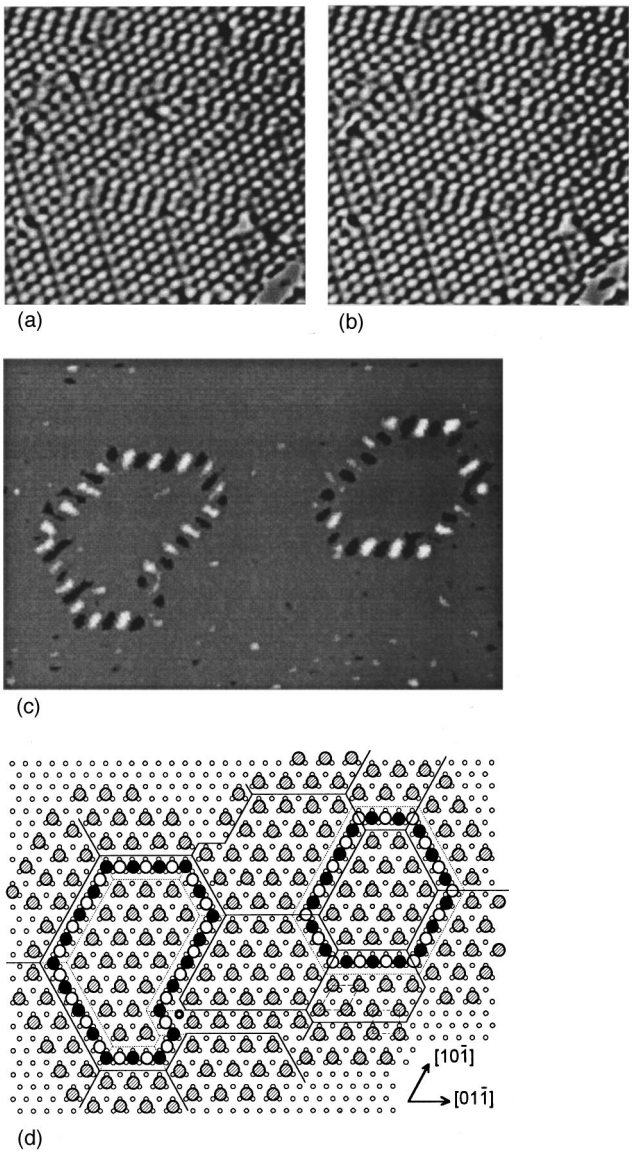

FIG. 1. (a) STM image (144 × 144 Å^2, 1.5 V, 1 nA) collected from the In-stabilized moderate-temperature phase of Ge(111). (b) Same as (a), 6 min later collected at exactly the same place (after drift correction). (c) Difference image of (a) and (b), obtained by subtracting (b) from (a), showing shifts of tens of the adatoms forming two closed loops. (d) Schematic drawing of (c), showing the details relevant to the adatom shifts, as well as the resultant breathing fluctuation of the domains surrounded by the shifted adatoms. Small and large circles represent the first layer atoms and adatoms, respectively. Among the large circles, the shaded, open, and filled ones represent the adatoms appearing in both (a) and (b), in (a) only, and in (b) only, respectively. Solid lines represent the new domain walls, while the dotted the old ones.

sulting difference image. If we see a row or a string of white spots separated by the same number of black spots in the difference image, then we know that those adatoms in the first image that were at the sites of the white spots had shifted to their neighboring black spot sites before they were imaged in the second image. Shown in Fig. 1 are two typical consecutive STM images obtained from the In-stabilized MT phase of the sample, along with the difference image of them. Actually, because of the small but noticeable variation of the tip shape, as well as the limited lateral resolution of the images, the white and black spots in difference images can only roughly disclose where those moving adatoms were in the first and second images, respectively. To be sure, we need to check the two images from which the difference image was obtained.

III. RESULTS AND DISCUSSIONS

From the difference image shown in Fig. 1, we see clearly that tens of adatoms forming two closed loops shifted their position at some time after they were imaged in the first image, but before the second. The schematic drawing in Fig. 1 shows the precise locations of those moving adatoms. It shows that both loops consisted of several segments of adatom rows in $\langle 110 \rangle$ directions and both surrounded a (2×2) domain, and that the domain surrounded by the right loop shrank, because of the adatom shiftings, while the one on the left expanded. Actually, this type of domain wall movement, i.e., breathing, was expected to happen in the MT phase,[14] but had never been observed before (to ourknowledge).

Another type of domain wall movement, i.e., meandering, was also expected to happen in the MT phase[14] and has also, to our knowledge, been observed only here from the In-stabilized MT phase (Fig. 2). In this case, we see again that only adatoms on the walls shifted and, as a result, some domains shrank and some expanded, and that all the shifts were along the $\langle 110 \rangle$ directions.

Figure 3 shows a case which, in many senses, is different from the above cases. First, comparing Fig. 3(a) with 3(c), we see that a string of 11 adatoms shifted towards the defect pointed out by the white arrow in (a), and as a result the defect was moved (step by step along the string, as will be discussed later) to the end of the string as pointed out by the white arrow in (c). This means that here, we know the direction of the shifts, but not in the above two cases. Second, we see that the adatom string penetrated the (2×2) domain at the lower-right corner of Fig. 3(a), rather than along walls as in the above two cases. Third, comparing these images, we can see the step-by-step shifting processes of the adatoms along the string. Roughly speaking, between (a) and (b), the first six adatoms of the string shifted, while the last five shifted between (b) and (c). Finally, looking at (b) more carefully, we can even find out when the sixth and seventh adatom shifted. At the moment pointed out by the white arrow in (b), the sixth adatom, after being partly imaged, shifted to its new site and was imaged there again, meanwhile the seventh adatom also shifted its position only 2–3 sec before it was completely imaged in this image. The eighth adatom stayed at its old position until it was imaged completely, at least 5 sec after the seventh adatom shifted away (according to the scanning rate used for this image, it took about 10 sec to completely image an atom). On the basis of the above discussion, we know that the adatoms must shift along the strings or loops one after another.

As for the motivation of the shifts, tip triggering should be ruled out first as in most cases the adatoms shifted, while the tip was not scanning over them. It is then very likely that the shifts that we observed here were thermally activated single hops. If this is true, then we should be able to know

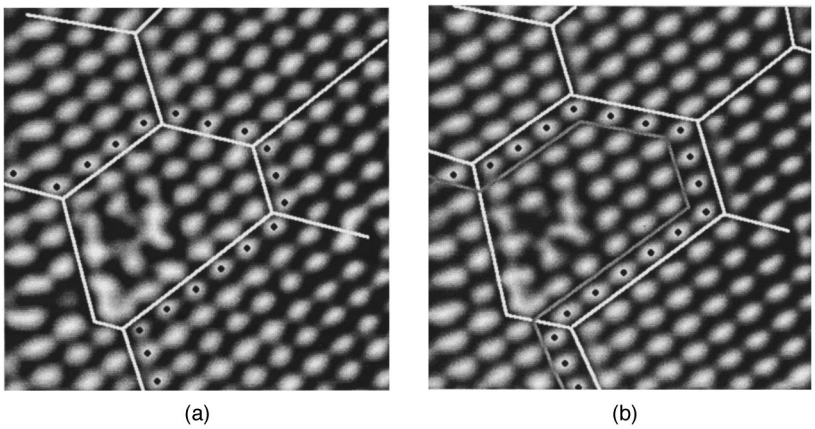

FIG. 2. Two consecutive STM images (80 $\times$ 80 Å^2, 1.5 V, 1 nA) collected from the In-stabilized moderate-temperature phase of Ge(111), showing domain wall meandering caused by adatom shifts along walls. The adatoms carrying a black dot represent those shifted between the two images. White (gray) lines represent the new (old) domain walls.

the activation energy barrier if we can measure the mean lifetime τ. According to what we discussed earlier, we know that the last four adatoms of the 11-adatom string in Fig. 3(b), i.e., the eighth to eleventh adatom, did not shift until 15 sec after the seventh adatom shifted. This corresponds to a $\tau \geqslant 3.8$ sec. Similarly, in Fig. 1 all 21 adatoms on the left loop took less than 306 sec to accomplish their shifts, corresponding to a $\tau \leqslant 14.6$ sec, while in Fig. 2, the string of 19 adatoms accomplished their shifts within 285 sec, corresponding to a $\tau \leqslant 15$ sec. As for thermally activated hops, there is $\tau = \nu^{-1}\exp(E_D/K_BT)$, where ν is the attempt frequency, as usual, taken to be about the Debye frequency, $\approx 10^{13}$ sec^{-1}, and $T = 300$ K as the experiment was carried out at room temperature, we obtain $E_D = 0.83 \pm 0.02$ eV or 0.81 eV $\leqslant E_D \leqslant$ 0.85 eV as 3.8 sec $\leqslant \tau \leqslant$ 14.6 sec. This value is in excellent agreement with the very recent theoretical result of 0.8 eV obtained with *ab initio* molecular dynamics,[23] as the mean lifetime of an adatom staying at H_3 sites compared with that for T_4 sites is negligibly small.[23]

So far, we have shown that both the directions ($\langle 110 \rangle$) and the activation energy barrier (0.83 eV) of the adatom shifts on the In-stabilized MT phase are in good agreement with those obtained with *ab initio* molecular dynamics for clean Ge(111) surfaces. This fact indicates that our results, though obtained from the In-stabilized MT phase, reflect the intrinsic characteristic of Ge adatoms on clean Ge(111) surfaces. In other words, in our case, the activation energy barrier is not reduced by the existence of a small number of In atoms, while, in a recent report, it was concluded that the energy barrier was reduced by the addition of a small number of Pb atoms to a Ge(111) surface.[22] Our results also indicate that there is no complicated collective motion (or orches-

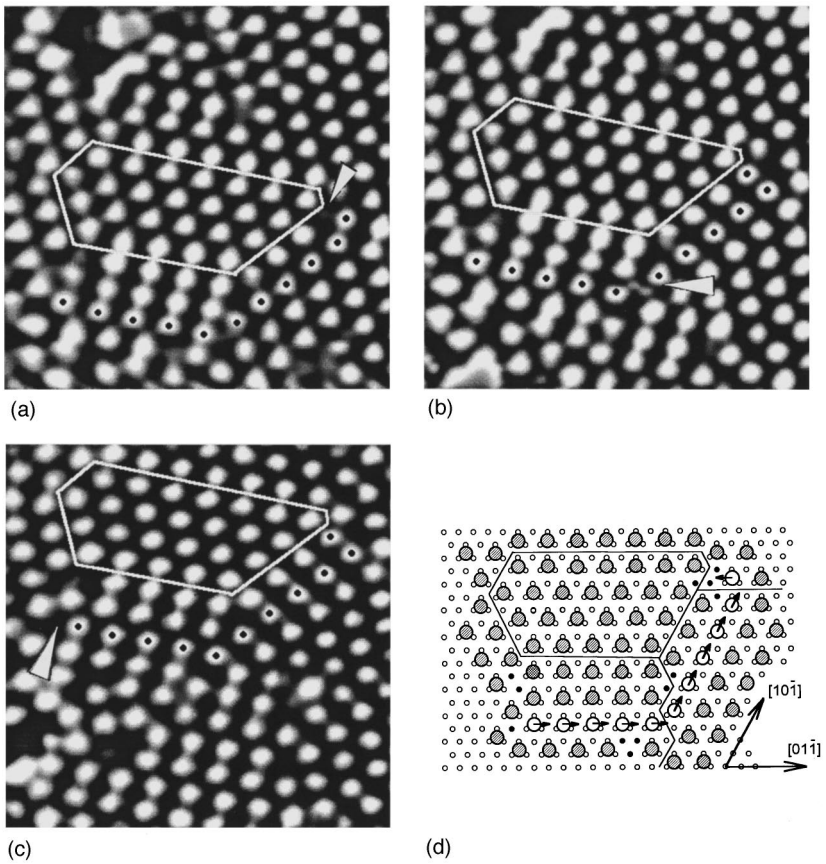

FIG. 3. (a)–(c) Three consecutive STM images (80 $\times$ 80 Å^2, 2.5 V, 1 nA) collected from the In-stabilized moderate-temperature phase of Ge(111), showing step by step the crossing-domain shifts of a string of 11 adatoms. The white lines and black dots have the same meaning as in Fig. 2. Note that, as a result of shifts of the adatoms on the string, the defect that the gray arrow points to was moving from image to image. (d) Schematic drawing of part of image (a), with small and large circles representing first layer atoms and adatoms, respectively. The vector shifts of the 11 adatoms that shifted (large open circles) are represented by short arrows. Two 2×2 domains at the center and lower right are enclosed with thin lines.

trated exchange) involved in the adatom shifts, as otherwise the same mean lifetime would imply a much lower activation energy barrier.[25] This is also different from diffusion of single Pb adatoms on Ge(111),[24] where they are expected to diffuse through sequential hoppings of a large number of adatoms (including Ge adatoms), i.e., orchestrated exchange.[25]

We have not found any clue that explains why the adatoms forming a long string shift in one direction, rather than hopping back and forth even if there is a defect at one end of the string. However, if, somehow, there is a small asymmetry in the energy barrier, say, in one direction, it is 0.80 eV, while in the opposite direction, it is 0.86 eV, then the mean lifetimes would have a difference of one order of magnitude. This might be responsible for the unidirectional shifting of the adatoms. It should also be pointed out that such adatom shifts were almost not observed from our clean and well-ordered $c(2\times8)$ sample surfaces or, at least, much less often as in the case of the In-stabilized MT phase, in agreement with previous observations.[6,22] This difference is likely due to the fact that the $c(2\times 8)$ reconstruction has a lower total energy than that of the MT phase, rather than from any difference of the adatoms.

Now we understand why Feenstra *et al.*[16] did not see the (2×2)-domain-and-wall structure[32] of the MT phase, but disordered surface areas or ''premelting in two dimensions'' when they were directly observing the 573 K phase transition of the Ge(111) surface, as an energy barrier of 0.83 eV corresponds to a mean lifetime of only 1.6 μs at 573 K, while their scanning speed was only 1000 Å /s,[16] which is too slow to image the individual fast-shifting adatoms in the MT phase.

IV. SUMMARY

Surface diffusion of Ge adatoms on the In-stabilized moderate-temperature phase of Ge(111) was studied with a room temperature STM and it has been found that, in addition to diffusion of individual adatoms neighboring to some defects, the majority of the moving adatoms forms strings or closed loops consisting of segments lying along ⟨100⟩ directions. The closed-loop diffusions always appear at the walls of the (2×2) domains and result in breathing fluctuation of domain sizes. The strings may, however, happen either at walls or crossing domains, resulting in meandering of domain walls. The lower and upper limits of the mean lifetime of the adatoms have been obtained from the scanning speeds to be 3.8 sec and 14.6 sec, respectively, corresponding to a range of the activation energy barrier of 0.81 eV–0.85 eV. To our knowledge, this is the first experimental result of this quantity and is in excellent agreement with its theoretical value for clean Ge(111) surfaces. This fact shows not only that the energy barrier obtained here is a characteristic of clean Ge(111) surfaces, but also that there is no complicated collective motion involved in the surface diffusion of Ge adatoms.

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